Nanoparticles of Scandium Oxide, Zirconium Oxide and Hafnium Oxide in Alcoholic Medium, used for High Index Optical Coatings at 351nm

Thesis submitted to the University of Surrey for the Degree of Doctor of Philosophy in Chemistry

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Abstract

Sc$_2$O$_3$, HfO$_2$ and ZrO$_2$ colloidal nanoparticles have been synthesised by sol-gel chemistry from organometallic precursor in alcoholic medium. Hafnia and zirconia particles were spherical and less than 5nm in diameter. Scandia particles were lozenge shaped platelets of 70 $\times$ 40 $\times$ 8nm in dimension. Sol stability was analysed by viscosity measurement. Particle morphologies were characterised by TEM, XRD and SAXS analyses. Scandia, hafnia and zirconia xerogels were obtained by solvent evaporation at room temperature and pressure. Bulk materials had structures, thermal stabilities and compositions deduced by XRD, TGA-DSC, EDX, N$_2$-BET adsorption-desorption and FTIR spectrometry. Elementary analyses were undertaken to study the mechanisms of synthesis. Present and potential applications of the so formed xerogel materials are discussed. Optical coatings to be used at 351nm were produced on fused silica substrates by dip coating from stable scandia hafnia and zirconia sols. Coatings containing organic impurities were purified via chemical or thermal treatment, or solvent extraction. The optical properties (absorption, scattering, reflection, transmission, refractive index), compositions, homogeneity and surface topologies of these thin films were obtained by UV transmission, photothermal deflection at 520nm, XPS and AFM investigations. Resistance to laser radiation at 351nm was also measured for xerogel coatings of quarter wavelength thick. These coatings exhibited high refractive indices, good structural homogeneity and good resistance to laser damage. Future uses of such coatings are considered.
Acknowledgement

Abstract

Introduction and aims of the work

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Introduction and aims of the work

The Inertial Confinement Fusion (ICF) programme is focused on the goal of demonstrating thermonuclear fusion ignition and energy gains in the laboratory. The potential application of high-power Nd-YAG lasers to initiate this fusion reaction, has stimulated the study and the development of new materials resistant to laser radiation at $\lambda=1056\text{nm}$ or its harmonics at $\lambda=528$, $351$ or $264\text{nm}$ [1,2]. Amongst the optical devices to be used in such a system [3,4,5], the present project focuses on high index materials applied to highly reflective transport mirrors. These are composed of stacked pairs of low and high refractive index coatings deposited on fused silica substrates.

In the present work, high-reflective mirrors were to be used at $351\text{nm}$ (e.g. $3\omega$), in other word in the near-UV region. Materials to be used at such a wavelength must not absorb this radiation. Ideally, they must be highly transparent at the laser emission, and must be thermally and chemically stable. Most of all, they must not undergo dramatic structural and optical damage upon radiation absorption. This absorption occurs by electronic transition (i.e. promotion of an electron from the fundamental level to the conductive level of the material band structure). If the material has a band gap (i.e. $E_g=$ energy difference between the fundamental and the conductive levels (given in eV)) greater than the energy of the incident photon, no electronic transition occurs and the material is transparent to this latter. The band gap and UV cut-off of a material (i.e. $\lambda_{\text{cut-off}}=$ wavelength at which the material starts to absorb (given in nm)) are linked through the relation $E_g=hc/\lambda_{\text{cut-off}}$, where $h$ is the Planck's constant and $c$ the light speed. As a result, a material to be used at $3\omega$ must have an UV cut-off below 350nm (i.e. equivalent to $E_g$ above $3.55\text{eV}$). However, the presence of impurities or structural defects in the material can induce local absorption. The presence of these defects leads to the formation of an intermediate energetic level that favours the jump of electrons between the fundamental and the conduction levels. Such local absorption can be centres of damage initiation. Hence, a highly transparent coating to $3\omega$ lasers must be made of a highly pure and defect-free material with a wide band gap. Several metal
oxides and non-oxides have already been investigated as UV optical coatings, namely SiO$_2$, MgF$_2$, TiO$_2$, ZrO$_2$, Ta$_2$O$_5$, HfO$_2$, Y$_2$O$_3$, Sc$_2$O$_3$, ZnF$_3$ and LaF$_3$ [3,9].

The titania-silica system (i.e. TiO$_2$-SiO$_2$) is commonly used in optical devices [6]. Silica offers a low refractive index (i.e. 1.2<\(n\)<1.54), an appreciable UV transparency (i.e. \(\lambda_{\text{cut-off}}<200\text{nm}\)), and a good laser resistance above 250nm. Unfortunately, and despite its high index of refraction (i.e. 2.2<\(n\)<2.7), the UV cut-off of titania (i.e. \(\lambda_{\text{cut-off}}>330\text{nm}\)) is too high and prevents its use in UV optics. So far the ZrO$_2$ and SiO$_2$ system seems to possess the best characteristics for use at low wavelength [7]. However, investigations into the design of even better materials remain under way.

In order to give the best transmission, each layer must be built up to an optical thickness of a quarter wavelength of the laser emission radiation (i.e. \(H=\lambda/4\)). The optical thickness (\(H\)) is linked to the refractive index (\(n\)) and the physical thickness (\(h\)) by the equation \(H=hn\). As a result, reflective and anti-reflective coatings to be used at 3\(\omega\) need to be between 80 and 40nm thick. The intensity of a radiation passing through a material is submitted to four phenomena: absorption, transmission, reflection and scattering. The best coatings have optical properties in the absence of absorption and scattering. Knowing that these effects are created by structural defects, impurities and low surface homogeneity, it is important to control the thickness (\(H\)), the purity and the roughness of the coating during the deposition process.

Depending on their role in the laser, optical devices are made of one or several coatings. Anti-reflective coatings are generally composed of a layer of low refractive index material deposited on a substrate of higher refractive index. However, they can also be made with several deposited layers, with the top-layer always being of low refractive index. On the other hand, high reflectivity is obtained if the top layer is made of the high refractive index material. Amongst the optical devices that are to be used in such systems, the development of high reflective mirrors is, without a doubt, one of the most challenging. Their processing requires the deposition of alternate low and high refractive index materials on a fused silica substrate. The reflectivity coefficient of the mirror increases with the number of pairs stacked on top of each other, and also when
the difference of both material refractive indices increases. As a result, in order to achieve a reflectance of more than 99%, it is not unusual to have to reach more than 10 pairs with the common ZrO2-SiO2 system. A lower number of pairs is then required if the difference in refractive indices is higher. On the other hand, two materials of highly different refractive indices usually present very different thermal expansion coefficients due to different structures and natures. These can induce interfacial stresses often expressed by coating peeling. Hence when processing such optical devices several different limiting factors make compromises necessary but also difficult to find.

Optical thin films can be prepared by physical vapour or chemical vacuum deposition methods (i.e. PVD and CVD). Other techniques exist and amongst them the dip-coating liquid deposition method offers advantages in terms of stability of layers, low investment and easy processing. Sols that can be used for thin film production by liquid deposition techniques can be synthesised by sol-gel chemistry. This chemistry also has advantages in terms of coating purity, homogeneity, low temperature of formation, and control of nanotechnology. The availability of highly pure precursors, that can be indefinitely purified, allows for a very clean coating chemistry. It is also a gentle chemistry, because it usually does not require very strong conditions and can take place in solution. Once understood, changing one of its parameters can lead to gels of different properties as a result of a modification in the formation mechanism of nanoparticles. The density of a xerogel can be increased by annealing it at high temperature but lower than this of the bulk material. In addition, the nanometric size of the particles allows for the combination of compositions that can not be made by conventional means. Differences in precursor reactivities, phase separation or devitrification prevent a homogeneous mixing by classical methods. One of the most important advantages of sol-gel chemistry is the simpler process of thin films and fibres. There is no loss of material. However, the cost of precursors tends to limit the use of the sol gel process to applications that require high quality materials in small quantities. Furthermore, sol-gel chemistry can produce aggregate materials of controlled average particle size, surface area, porosity and therefore refractive indices. As a result, in addition to the application in optics, such a chemistry opens new prospects in a variety
of coating applications and areas (e.g. highly porous ceramics for catalysis, coatings for sensors, etc...) [8].

The aims of the present project were to prepare ZrO$_2$, HfO$_2$ and Sc$_2$O$_3$ by sol-gel methods and from the sols to produce (by dip-coating) thin films that could be applied in optical devices for Nd-YAG 3m lasers. In order to satisfy the coating property requirements, the following conditions were to be fulfilled.

- $n$ higher than that of the fused silica substrate (i.e. $n > 1.474$)
- UV cut-off $\lambda_{\text{cut-off}} < 250$nm
- good purity and no morphological changes upon heating
- stable sols involving particles small enough and homogeneous enough
- using alcoholic solvents (suitable for liquid deposition methods)
- the coatings were then to be crack-free and not undergo structural changes and inter-penetration between layers or induced interfacial stresses
- non-reactive with CO$_2$, O$_2$ and H$_2$O in the atmosphere

References

Chapter I

FUNDAMENTALS OF SOL-GEL CHEMISTRY
Chapter I  
Fundamentals of Sol-Gel Chemistry  

I-1  The Chemistry of Metal Oxides

Metallic oxides have been of technological and industrial interest for a long time because of their broad range of properties (e.g. electric, magnetic, optical...). Also their general characteristics (e.g. mechanical resistance, thermal stability and chemical inertia) make them highly interesting materials. Nowadays, in many applications, silica (SiO₂) is one of the most common ceramics used. This is due to its low price, good optical properties, hardness, chemical resistance and its electrical and thermal insulator properties. However, a wide range of other ceramics; which are more expensive and more complicated to process, are used for more specific applications. Ferromagnetic ferrite-spinel iron oxide (γ-Fe₂O₃) is highly suitable as information storage and transmission material. Some oxides with variable electronic mobility (such as vanadium oxide V₂O₅) are used as semi-conductors, or supra-conductors in the case of Yba₂Cu₃O₇. Oxides of perovskite structure (BaTiO₃, PbZrTiO₃,) with dielectric or ferroelectric properties are widely used as components for electronic devices.

Over the last few decades, there has been an increasing interest in nanomaterials due to their specific properties defined by particles of nanometric sizes. Small particles can be more easily incorporated in host materials, therefore processing of hybrid or combined composites can be greatly enhanced. The high ratio “surface area / volume” characterising these nanomaterials leads to very interesting applications in catalysis. The dispersion-suspension of nanoparticles in various solvents allows the processing of thin layers and coatings for anti-reflective protection, dielectric films and high reflective mirrors. They require a good control of the thin film physical thicknesses.

Micro- and nano-particles of oxides are processed using a variety of techniques. The most common consists of dividing up massive bulk materials by electrical or thermal erosion (e.g. laser ablation) or by physical bombardment of ions or atoms (e.g. etching). Another method consists of condensing ions or molecules by polymerisation. In solution, the precipitation or coprecipitation of ions is already widely used in thin powder industries for the production of catalyst supports and ceramics. However, condensation of molecular species and reactivity of elements in solution are often quite
disparate. The chemistry of sol-gel offers considerable possibilities of chemical manipulation leading to new solid phases of very different structures, morphologies and compositions. It is a mild-chemistry, usually taking place at room temperature or in hydrothermal conditions. The sol-gel technique allows for the production of metastable phases and then the control of the material texture (e.g. porosity, surface area, particle size and degree of shrinkage). In contrast, the classical processes of material production take place at high temperature and do not offer such flexibility.

However, the control allowed by the sol-gel chemistry requires thorough understanding of the formation process of colloidal particles. The phenomenon is complicated. The structural and chemical mechanisms involve several possibilities of simultaneous and successive reactions. Also, experimental conditions considerably influence these mechanisms (e.g. nature and concentration of the precursors, nature of solvent, pH, concentration, and temperature, ageing time, nature of the counter-ion, and nature and concentration of the catalyst). The formation of the solid phase is a result of an inorganic polycondensation process involving hydrolysis of metallic ions and condensation of the hydroxides. The formation of sol, gel, flocculate and aggregate depends on the repulsive and attractive forces applied between the particles in the solution. These different forces are governed by the physico-chemical conditions of the system and it is possible to control these phenomena by adjusting the experimental conditions. The process is now described in detail.

I-2 The Partial Charge Distribution Model

Bjerrum first studied the hydrolysis of metal cations at the beginning of the 20th century. However, the formation of condensed species by addition of hydroxyl groups to cations is now well known [1]. The model of partial charge distribution, proposed below, is used to predict the chemical reactivity of precursor complexes and thus basic mechanisms of the sol-gel chemistry.
If two neutral atoms combine, the covalent effects (e.g. changes of the atom sizes and forms in the combined complex) lead to a variation of the initial electronegativity and hardness (i.e. $\chi_a$ and $\eta_a$) of the atoms. The local electronic potential on each neutral atom $i$ is given by $(\chi_{ai} + \Delta\chi)$. Because of electronic transfers due to the bond formation, partial charges of the atoms induce an electrostatic potential influencing the local electronic potential. This electrostatic potential contains a term $(\eta_{ai} + \Delta\eta)$ $\delta_i$, resulting from the presence of the charge $\delta_i$ on the atom $i$, and a term $\Sigma(\delta_j/R_{ij})$ induced by the charges $\delta_j$ carried by the atoms $j$ at distances $R_{ij}$. The following equation gives the electronegativity of the combined atoms.

$$\chi_i = (\chi_{ai} + \Delta\chi) + (\eta_{ai} + \Delta\eta) \delta_i + \Sigma_{j=1}^{n}(\delta_j/R_{ij})$$

As $\Delta\chi$ and $\Delta\eta$ are unknown, the following equations are set.

$$\chi^* = \chi_a + \Delta\chi \quad \text{and} \quad \eta^* = \eta_a + \Delta\eta$$

In these relations, $\chi^*$ are electronegativities of the Mulliken type, which take into account the average environment of the atoms. The use of Mulliken electronegativities requires the knowledge of the atom valence states. The use of the Pauling scale is adequate only for small and simple molecules [2]. Therefore, electronegativities of Allred and Rochow, easily calculable for any element, are used from this point [3].

$\chi$ and $\eta$ are linked together and as the hardness is proportional to the inverse of a distance, choosing the electronegativity scale of Allred and Rochow (i.e. $\chi \propto Z_{\text{eff}}/r^2$) allows the setting of the following relation,

$$\eta^* = k (\chi^*)^{1/2}$$

where $k$ is a constant that depends on the electronegativity scale ($k=1.36$ on the Allred and Rochow scale) [3].
I-2-1 Electronegativity Equalisation

When two atoms combine, a partial electron transfer occurs and each atom acquires a partial positive or negative charge $\delta_i$, which linearly affects the electronegativity $\chi_i$ of the atom. The more electronegative atom gains a negative partial charge and its electronegativity decreases. The less electronegative atom gains a positive partial charge and its electronegativity increases. At equilibrium, the transfers stop when the atom electronegativities reach the same mean $\chi$. The intensity of transfer depends on the hardness of the atoms involved. This can be applied to more complex molecules where the electronegativity of each atom has the same value as the mean electronegativity of the molecule $\chi$, at equilibrium. $\chi$ is correlated to the partial charges of each atom. As a result, knowing the mean electronegativity allows the determination of these charges.

I-2-2 Determination of the Mean Electronegativity $\chi$

If perturbations, induced on the atom $i$ by the presence of the atoms $j$ in the environment, are neglected in comparison to the perturbation induced by the partial charge $\delta_i$ on this atom, one can write for a specific atom $i$.

$$\chi_i = \chi_i^* + \eta_i^* \delta_i \quad \text{with} \quad \eta_i^* = k (\chi_i^*)^{1/2}$$

According to the principle of electronegativity equalisation, the charge transfer should stop when the electronegativity of all constituent atoms becomes equal to the mean electronegativity $\chi$ (i.e. $\chi = \chi_i = \chi_i^* + \eta_i^* \delta_i$). Therefore, the partial charge carried by the atom $i$ is given by

$$\delta_i = (\chi - \chi_i^*) / \eta_i^* \quad \text{or} \quad \delta_i = \sigma_i^* (\chi - \chi_i^*)$$

where $\sigma_i^*$ corresponds to the inverse of the hardness (the softness).
Knowing that the sum of the partial charges, carried by each of the atoms involved in the molecular complex, equals the charge \( z \) of the complex (i.e. \( \Sigma_i \delta_i = \chi \)), we can write

\[
\chi = \left[ \Sigma_i \sqrt{\chi^*} \cdot 1.36 \right] / \left[ \Sigma_i (1/ \sqrt{\chi^*}) \right].
\]

As a result, \( \chi \) can be calculated for any molecule from the stoichiometry, the global charge \( z \) and the electronegativity of each constituent atom. Then \( \delta_i \) can easily be calculated.

The Partial Charge model can be applied to both inorganic and organic metal precursors, however some limitations do arise:

- In its present form, the partial charge model does not take into account the real structures of the chemical species.
- Resonance effects and \( \pi \) overlapping are not included.
- It is difficult to account for coordination variations that occur during the chemical process.

Nevertheless, this model can be applied to describe the chemical reactions involved in the sol-gel process and provides a useful guide for understanding the inorganic polymerisation reactions.

1-2-3 Determination of Coordination Number

In order to predict the hydrolysis and condensation mechanisms, it is also very useful to know the coordination number of the metallic atom. According to the rule of radius ratio from Pauling [4], the maximum coordination number associated with an atom depends on the atomic radii of the atoms engaged in the coordination. The geometric requirements for close packing of spheres of different sizes can be expressed simply in terms of the radius ratio \( \rho = R_s/R_l \), where \( R_s \) and \( R_l \) correspond to the radii of the smaller and the larger ions respectively. If \( \rho < 0.414 \) the coordination number is 4; if \( 0.41 < \rho < 0.73 \) the coordination number is 6; if \( \rho > 0.73 \) the coordination number is 8 or
over. Depending on the circumstances, a complex associated with $p \approx 4$ can be tetrahedral or octahedral. The maximum coordination possible of 9 is very rarely met.

### I-3 The Sol-Gel Transition

The sol-gel process is a chemical synthesis of condensed colloidal compounds in solution (e.g. salts, hydroxides, oxides or oxyhydroxides), that undergoes a sol-gel transition. The sol-gel transition is characterised by the formation of chemical and physical bonds between particles in solution. The viscosity of the solution increases upon ageing until a three-dimensional network of infinite molecular weight (i.e. the gel) is formed. The sol-gel process is used to produce glass and ceramics either amorphous or of crystalline structure depending on the nature of the compound and the heat treatment. Two processes can be described.

- The *powder process* refers to any process that involves the formation of colloidal discrete particles. The sol-gel transition occurs upon aggregation and condensation in solution of the discrete particles.

- The *powder-free* process refers to any process that does not involve the condensation or aggregation of discrete particles, but the direct polycondensation of the molecular species leading to a porous preform of glass or ceramic in the desired geometry (e.g. fibre, film or three-dimensional bulk)[5].

The first step to the synthesis of gels is the preparation of the precursor solution. The initial compound (e.g. salt or organometallic complex) is first dissolved in an appropriate solvent. Hydrolysis of metal atoms takes place when OH$^-$ groups from water or hydroxide-salt are added or created in the solution. Then the condensation between hydrated species occurs through the powder or the powder-free process. The sol formed through the powder process is then composed of suspended particles ideally of homogeneous size. The particles can be of various shapes, compositions, sizes and stability depending on the experimental conditions. Upon ageing, the sol viscosity increases due to the formation of bridges and bonds between particles. If the
concentration is high enough, the condensation finally leads to a compact gel. The sol-gel powder process is briefly summarised in Figure 1-1.

![Diagram of the sol-gel powder process](image)

**Figure 1-1: The sol-gel powder process**

The sol-gel transition occurs after a certain ageing time ($t_g$) and is usually expressed by the following equation [6].

$$t_g = \left( \frac{C_0}{k f (f^2 - 2f)} \right)^{1/4}$$

where $C_0$ is the precursor concentration, $k$ is the rate constant of bimolecular condensation and $f$ the functionality of the precursor. $f$ corresponds to the number of ligands surrounding the metal atom that can be potentially substituted by OH$^-$. These parameters can be varied in order to adjust the rates of the reactions and then optimise the sol-gel process. Increasing the concentration always leads to a fast gelation. Increasing $f$ by addition of hydroxyl groups or by acid catalysis also diminishes the sol stability. This relation is empirical and is verified only between a certain range of conditions. Stable translucent gels are often obtained when hydrolysis and condensation
rates are slow (i.e. long gelation time). Table I-1 gives the types of products obtained with the different relative rates of hydrolysis-condensation [2].

Table I-1: Effect of the hydrolysis-condensation rates on the structure of the final compound.

<table>
<thead>
<tr>
<th>Hydrolysis rate</th>
<th>Condensation rate</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>slow</td>
<td>slow</td>
<td>Colloids/sol</td>
</tr>
<tr>
<td>fast</td>
<td>slow</td>
<td>Polymeric gel</td>
</tr>
<tr>
<td>fast</td>
<td>fast</td>
<td>Colloidal gel or gelatinous precipitate</td>
</tr>
<tr>
<td>slow</td>
<td>fast</td>
<td>Controlled precipitation</td>
</tr>
</tbody>
</table>

The transition can be reversible or irreversible. If the particles undergo physical bonds between one another, the gel structure can be broken by convection-disaggregation (e.g. by mechanically stirring or increasing the temperature). The sol state is then re-established. On the other hand, if chemical bonds such as oxygen bridges link the particles in the network, the process is then irreversible and the gel cannot be destabilised.

New technologies often require the processing of nanomaterials made of several metal oxides. These materials can be amorphous or crystalline and could involve treatment such as doping or annealing. Multi-component solutions, sols and gels can be prepared by mixing appropriate precursors of the various desired metal oxides. In order to avoid inhomogeneities due to the reactivity differences existing between the different precursors (rate of hydrolysis and condensation), partial prehydrolysis of the less reactive precursors takes place before the more reactive ones are introduced into the system. The process is generally not so simple and often requires several steps depending on the nature and stability of the oxides to combine [7-9].

Hybrid organic-inorganic compounds (e.g. ormosils, polycerams, etc) are nowadays some of the most investigated materials. Many applications require the processing of such materials and sol-gel chemistry offers a unique approach to their synthesis due to lower temperatures involved. The sol-gel processing of organically modified silicates
(e.g. vinyl or phenyl silicates as waveguide materials [10], MPEOU SiO₂-TiO₂ as optoelectronic coatings [11]) represent one of the most promising and interesting research areas for new materials. One could also mention the process of high-density optical coatings of ZrO₂-PVP [12], alkyl amine or isocyanate functionalised Si(ΟEt)₃ [13].

I-4 The Sol-Gel Chemistry of Transition-Metal Oxides in Aqueous Media

Water is the least expensive solvent in which most transition metal salts are soluble. Furthermore it contains hydroxyl groups (generated from H₂O ionic dissociation). These characteristics make it one of the most appropriate mediums for sol-gel chemistry.

I-4-1 Mechanisms of Hydrolysis

The solvation of transition metal cations M²⁺ by water molecules is characterized by the formation of a partially covalent bond. A partial electronic charge-transfer occurs between the filled 3a₁ bonding orbital of the water molecule to the empty d orbital of the metallic cation. The positive charges, carried by the hydrogen atoms, increase and thus the water ligand becomes more acidic. The transformation involved is summarized in the following equilibrium (1).

\[ [M-OH_2]^{2+} \leftrightarrow [M-OH]^{(x-1)+} + H^+ \leftrightarrow [M=O]^{(x-2)+} + 2H^+ \] (1)

Three kinds of ligands can be considered in aqueous medium: aquo (OH₂), hydroxo (OH) and oxo (O). If N is the coordination number of M²⁺, the species present in the solution are \([MO_NH_{2N-h}]^{(x-r)+}\), where r is the molar ratio of hydrolysis. Depending on r, the complex can be aquo, aquo-hydroxo, hydroxo, hydroxo-oxo or oxo. The “charge-pH” diagram, shown in Figure I-2 gives the nature of the precursor as a function of the cation charge (z) and the pH of the solution.
Applying the partial charge model, one can show that the number of protons removed by direct hydrolysis depends on the charge \( z \), the coordination number \( N \) and the electronegativity \( \chi^* \) of the metal. These last two parameters depend directly on the size of the cation.

**I-4-2 Mechanisms of Condensation**

Depending on the coordination number of the metal atom, condensation reactions can occur through either a substitution or an addition mechanism.

If the preferred coordination is already fulfilled in the molecular precursor, condensation occurs via substitution reaction between an entering group and a leaving group. This reaction expressed in equation (2) shows that the coordination number remains unchanged.

\[
M-\text{OR} + M-\text{OR}' \rightarrow M-\text{OR-M} + \text{OR'}
\]  

(2)
However, the substitution can be decomposed in two steps: the elimination of the leaving group (OR') followed by the addition of the entering group (MOR). As a result the reaction is not concerted and follows a $\text{SN}_1$ mechanism.

If the number of ligands is less than the maximum coordination number, the addition reaction displayed in equation (3) is then possible. The entering group aims at fulfilling the coordination sphere of the metal.

$$\text{M-OR + M-OR'} \rightarrow \text{M-OR-M-OR'} \quad (3)$$

If the precursor is an oxo complex, O is a very poor leaving group (i.e. very good nucleophile), the preferred coordination is not fulfilled and condensation occurs only by addition. If the precursor is an aquo complex, where H$_2$O ligands have a slightly positive partial charge (i.e. poor nucleophile but good leaving group), no entering group is present in the medium and condensation cannot occur. If the precursor contains good leaving hydroxo groups (i.e. oxo-hydroxo or hydroxo-aquo complexes), the condensation takes place readily by substitution. As a result, the condensation to oligomers, polymers, sols, gels or precipitate compounds requires the presence of leaving hydroxo groups in the coordination sphere. Adjusting the pH of the solution can control the ratio of such hydroxo groups surrounding the metal atom. The condensation can occur through different mechanisms as described now.

*The condensation via olation* leads to the formation of hydroxo bridges, and occurs by nucleophilic substitution from hydroxo-aquo precursors. The following equations describe the mechanisms (4, 5 and 6).

$$\text{M-O}^{\delta+} \text{H} + \text{M}^{\delta+}\text{-OH}_2^{\delta+} \rightarrow \text{M-OH-M} + \text{H}_2\text{O} \quad \text{mechanism }_{2(\text{OH})_1} \quad (4)$$

$$\text{M}_2\text{O}^{\delta+} \text{H} + \text{M}^{\delta+}\text{-OH}_2^{\delta+} \rightarrow \text{M}_2\text{OH-M} + \text{H}_2\text{O} \quad \text{mechanism }_{3(\text{OH})_1} \quad (5)$$

$$\text{H}_2^{\delta+}\text{-M}^{\delta+}\text{-O}^{\delta+} \text{H} + \text{HO}^{\delta+}\text{-M}^{\delta+}\text{-OH}_2^{\delta+} \rightarrow \text{M}^{(\text{OH})_2\delta+} \text{M} + \text{H}_2\text{O} \quad \text{mechanism }_{2(\text{OH})_2} (6)$$
These mechanisms are characterised by $x(OH)_y$ where $x$ is the number of electropositive atoms M linked by hydroxo bridges, and $y$ is the number of bridges between these $x$ atoms. As oxygen cannot form more than four covalent bonds, $x$ maximum is 3. The kinetic of olation depends strongly on the lability of the $M^{-}\text{OH}_2$ bond; thus the charge, size, electronegativity and the electronic configuration of $M$ influence the rate of the reaction. However, partial charges $\delta(OH)$ and $\delta(M)$ increase upon condensation due to the decreasing of the OH group nucleophilic characteristics and the dehydration process. Condensation carries on as long as the leaving groups and the electropositive atoms, contained in condensed intermediates, carry suitable electric partial charges. The condensation is usually total when the precursor is electrically neutral and leads to colloidal particles. On the other hand, cationic precursor complexes form soluble polycations (molecular complexes) with limited degrees of condensation [14].

The formation of a gel rather than a precipitate is difficult to control and depends on several parameters. These are listed below.

- pH (a pH gradient takes place during the reaction)
- concentrations of catalysts, precursors, and agents
- the addition mode and the speed of agitation may have to be controlled
- order of mixing the reagents has a critical importance on the result
- temperature

All these parameters must be taken into account because nucleation and growth mainly involve olation reactions that are diffusion-controlled processes. As a result, colloidal gels are not very stable when prepared in a pure form. Metals that give stable hydroxo bridges lead to well-defined hydroxides. Metals that do not form stable hydroxo bridges lead to hydrated amorphous gelatinous precipitates when a base is added to the aquo precursor. These precipitates lose water continuously through oxolation reactions that finally lead to oxides.

*Condensation via oxolation* leads to the formation of oxo bridges ($M$-$O$-$M$) between two metal cations, and occurs when no aquo ligands are coordinated to the metal atom. Therefore this reaction concerns elements with a high formal charge (i.e. $z \geq 4$). If the
coordination is not fully saturated, the process follows a nucleophilic addition through which edge or face bridges are easily formed (see equation (7) and (8)).

Edge bridge formation by mechanism $2(O)_2$

$$M=O + M=O \rightarrow M\{O\}M$$  \hspace{1cm} (7)

Face bridge formation by mechanism $2(O)_3$

$$M=O + M=O \rightarrow M\{O-M\}$$  \hspace{1cm} (8)

If the coordination is fully saturated, the process follows a nucleophilic substitution decomposed in two steps. The addition of $M-OH$ to $M-OH$ leads to an unstable $2(OH)_1$ bridge that can be catalysed by bases. This is followed by the departure of a water molecule that can be catalysed by acids (i.e. proton transfer). This explains why oxolation occurs over a wide range of pH. The limiting rate can be either the proton transfer or the elimination of the leaving group. Of the different types of bridges that can be formed via oxolation (see equations 9 to 11), $2(O)_1$ is the most common one.

$$M-OH + HO-M \rightarrow M-O-M + H_2O$$  \hspace{1cm} (9)

$$\begin{array}{c}
\text{M} \\
\text{OH} \\
\text{M}
\end{array} + \begin{array}{c}
\text{HO-M} \\
\text{M}
\end{array} \rightarrow \begin{array}{c}
\text{O-M} \\
\text{M}
\end{array} + H_2O$$  \hspace{1cm} (10)

$$\begin{array}{c}
\text{M} \\
\text{OH} \\
\text{M}
\end{array} + \begin{array}{c}
\text{HO-M} \\
\text{M}
\end{array} \rightarrow \begin{array}{c}
\text{O-M} \\
\text{M}
\end{array} + H_2O$$  \hspace{1cm} (11)

As for the reaction of polycation olation, the condensation of anionic and neutral complex precursors via pure oxolation leads to condensed species with limited degrees
of condensation. The oxolation usually stops because all hydroxo ligands have reacted and there are no more leaving groups on the growing polymer.

I-4-3 Influence of the Counter Ion

The role of the counterion present in the solution cannot be neglected. For example, anions can be strongly coordinated to the metal and consequently affect the particle morphology and the colloid stability. Particles can exhibit spherical, rod-like, star-like or cubic shapes. Anions can block specific sites of condensation on the intermediate polymers preventing homogeneous polymerisation and leading to anisotropic particles. Particles of WO$_3$ and MoO$_3$ can be obtained with different shapes depending on the counterion [15]. Also, the hydrolysis-condensation of yttrium nitrate through an exchange-resin colon leads to platelets of Y$_2$O$_3$ [16]. Nevertheless it is very difficult to predict their morphology. Organic agents of modification can be added to the system to control the size and the shape of the particles. Iron oxide particles have been synthesised under disc form using a chelating agent [17].

I-5 The Sol-Gel Chemistry of Transition Metal Oxides in Organic Media

Metal alkoxides M(OR)$_n$ are known for almost all transition-metal elements and are used as precursors for sol-gel chemistry. The number and stability of metal alkoxides decrease from left to right in the periodic table, the soft d$^n$ late transition metal alkoxides tend to oligomerise, then they become insoluble polymeric species difficult to study. The alcoholate ligand is a hard $\pi$-donor, and therefore it stabilises the highest oxidation state of the metal. Transition metal-alkoxides can be prepared following the methods [2] usually consisting of dissolving and refluxing the metal salt (e.g. chloride or nitrate) in the parent alcohol. Synthesis of organometallic complexes of rare metals and lanthanide have also been investigated recently [18,19].
The sol-gel chemistry of silicon alkoxides has been extensively studied [5,20,21], and colloidal Al₂O₃ is now also commonly used for optical coatings [22,23]. Unfortunately there is a lack of data concerning the hydrolysis-condensation of transition-metal organo-metallic, but the most commonly referenced are TiO₂ [24] and ZrO₂ [25]. The high electronegativity of transition metal elements leads to high electrophilic characters and high oxidation states. Also, their ability to have several coordination numbers allows for coordination expansion by solvation or alcoxo-bridging. As a result, transition metal alkoxides are much more reactive and must be handled with care in absence of moisture. They readily form precipitate rather than gel when water is added.

### I-5-1 Mechanisms of Hydrolysis

Highly electron-donor organic ligands make the metal prone to nucleophilic attacks. Therefore metal alkoxides react strongly with water and form hydroxides or hydrous oxides. A three-step mechanism for hydrolysis has been proposed and is shown in the following equations (1) to (3).

1. \[ \text{H}_2\text{O} + \text{M}-\text{OR} \rightarrow \text{H}_2\text{O}::\text{M}-\text{OR} \]  
   \[ \text{(1)} \]

2. \[ \text{H}_2\text{O}::\text{M}-\text{OR} \leftrightarrow \text{HO-}\text{M-::OHR} \]  
   \[ \text{(2)} \]

3. \[ \text{HO-}\text{M-::OHR} \rightarrow \text{M-}\text{OH} + \text{ROH} \]  
   \[ \text{(3)} \]

The first step is a nucleophilic addition of water on the positively charged metal atom increasing its coordination number by one. The second step is an equilibrium involving proton transfer between hydroxo and alkoxo groups. The third step is the loss of the better leaving group, which is the most positively charged specie in the intermediate state. The whole process follows a nucleophilic substitution reaction of SN₂ type. The thermodynamics are governed by the charge distribution and are favoured when \( \delta(O)_{\text{entering}} < 0 \) and \( \delta(M) > 0 \) (i.e. the metal has a strong electrophilic character and the entering molecule has a strong nucleophilic character) and when \( \delta(HOR) > 0 \) (i.e. the
nucleofugal character of the leaving molecule is high). The rate of the nucleophilic substitution depends on the following parameters:

- The coordination unsaturation (i.e. difference between the maximum coordination number in the oxide state and the oxidation state \((N-z)\)) is high. The increasing of \((N-z)\) induces the decreasing of the activation energy of the substitution reaction leading to a faster exchange.

- The proton ability to transfer from the entering group to the leaving group; the more acidic is the H\(^+\), the lower is the activation energy.

Condensation can occur as soon as the alkoxide is hydrolysed. Depending on the experimental conditions, a competition between three reactions takes place.

I-5-2    **Mechanisms of Condensation**

The *alcoxolation reaction* follows the same mechanism as the hydrolysis, except that MO is the entering group. The thermodynamic is governed by the same parameters. The *oxolation reaction* is also governed by the same mechanism, except that the leaving group is a molecule of water.

\[
\begin{align*}
\text{MOH} + \text{MOR} & \rightarrow \text{M-O-M} + \text{ROH} \\
\text{MOH} + \text{MOH} & \rightarrow \text{M-O-M} + \text{H}_2\text{O} \\
\text{M-OH} + \text{M} \rightarrow \text{OH} & \rightarrow \text{M-OH-M} + \text{ROH} \\
\text{M-OH} + \text{M} \rightarrow \text{OH}_2 & \rightarrow \text{M-OH-M} + \text{H}_2\text{O}
\end{align*}
\]

*The olation reactions* occur when the full coordination is not satisfied (i.e. \(N-z\neq 0\)). Hydroxo bridging groups can be formed by elimination of a solvent molecule or a water molecule depending on the water concentration in the solution. The thermodynamic is governed by the charge distribution. The reaction rate is usually fast because no proton transfer is involved. The reaction is favoured when \(\delta(O)_{\text{entering}} \ll 0\) and \(\delta(M) \gg 0\).
The formation and nature of the oxide network formed depend on the relative intensity of reactions (4) (5) (6) and (7) in the whole process. The contribution of each reaction is controlled by the experimental conditions that have to be carefully adjusted in order to produce sols or gels with particles of suitable characteristics.

I-5-3 Ligand Exchange Reactions

Exchange reactions are governed by the same rules as hydrolysis (SN₂), and therefore follow the same mechanisms. The nucleophilic attack takes place first increasing the coordination number of the transition metal atom. Then, the proton transfer occurs from the entering group to the leaving one. The charge distribution shows that the more protonated ligand is the better leaving group.

Exchange with Alcohol

Metal alkoxides react with a variety of alcohol to set up the following equilibrium (8).

\[ M(OR)_x + xR'OH \leftrightarrow M(OR)_{x-x}(OR')_x + xROH \] (8)

The interchange rate increases when the steric hindrances induced by the alkoxo groups decrease. Transition metal alkoxides lead to faster exchanges than silicon alkoxides. This can be explained by their full coordination number, usually not satisfied.

Exchange with Chelating Agents

In general, ethanoic acid is used as an acid catalyst in sol-gel reactions increasing the rate of hydrolysis by favouring the proton transfer. In the case of silica, the acid is added to decrease the gelation time. However, in certain cases such as the formation of ZrO₂ [26], TiO₂ [5] or HfO₂ [27], the addition of ethanoic acid to a solution of these metal alkoxides leads to the formation of stable metal alkoxo-acylates. The main goal of this complexation is to increase the gelation time. This can be attributed to the stabilisation ability of the acetate ligand. An exothermic reaction takes place when ethanoic acid is added to Ti(OR)₄ and the coordination number of Ti increases. Acetate groups are bonded to titanium atoms and behave as bidendate ligands that are chelating or bridging...
metal atoms. β-diketonate such as pentanedionate [28] and tetramethyl heptanedionate [29], are very good chelating ligands due to their enolic form containing a reactive hydroxyl group which reacts readily with metal alkoxides [5]. Therefore, acetylacetone has often been used in sol-gel chemistry as a stabilising agent.

### I-5-4 Influence of the Metal Atom

We have seen transition metal alkoxides react strongly with water due to their high electropositive partial charge induced on the metal. The following Table I-2 shows that partial charges carried by transition metals are much more positive than for silicium in alkoxide complexes. This explains why they are so unstable toward hydrolysis.

**Table I-2:** Partial charges carried by transition metal atoms in alkoxide form compared to the silicium partial charges in Si(OEt)₄ [2].

<table>
<thead>
<tr>
<th>Alkoxides</th>
<th>Zr(OEt)₄</th>
<th>Ti(OEt)₄</th>
<th>Nb(OEt)₅</th>
<th>Ta(OEt)₅</th>
<th>W(OEt)₆</th>
<th>Si(OEt)₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ(M)</td>
<td>+0.65</td>
<td>+0.63</td>
<td>+0.53</td>
<td>+0.49</td>
<td>+0.43</td>
<td>+0.32</td>
</tr>
</tbody>
</table>

The fact that transition metals, as organometallic complexes, do not satisfy the full coordination number existing in their oxide states allows their coordination expansion by solvation or hydration. Thus, the hydrolysis of these precursors is faster than the hydrolysis of fully coordinated species such as tetraethoxysilane. After the exchange of the first ligand by a hydroxo group, previous studies have shown that the condensation occurs preferably by alcoxolation rather than oxolation. This is due to the more positive charge carried by (HOR) compared to the charge of (H₂O) as leaving groups. Alcoxolation of transition metal alkoxides leads to well-defined oxo-alkoxide compounds with the maximum coordination number always satisfied. They can be isolated as single crystals. We have also seen that the rate of hydrolysis increases when the difference between the maximum coordination number and the oxidation-state increases. Hence, because of their different and variable electronic configurations, the nature of the metal plays a very important role in the reactivity of the relative alkoxides.
1-5-5 Nature of the Organic Ligand

In alkoxide, the partial charge distribution between atoms depends on the alkyl group. M-OR bonds are more or less polar. The rate of hydrolysis decreases when the size of the alkyl group increases. The presence of many H atoms in the ligand slightly decreases the negative charge carried by the bonding O, but sufficiently decreases the positive charge of the metal atom. This effect leads to a less nucleofugal character of the ROH as leaving group. Moreover, $\alpha$(H) decreases when the size of R increases diminishing the acid characteristic. We have shown that the hydrolysis rate increases with the rate of the proton exchange. Therefore, the presence of many H on the alkyl group also prevents a fast proton exchange. As a result, organometallic complexes containing ligands with high ratios of H are less reactive toward hydrolysis than complexes containing ligands with poor ratios of H. In addition, the decreasing of the hydrolysis-condensation rate with the size of the ligands can be explained by steric hindrance. A bigger ligand is less nucleofugal than a small one due to geometric encombrements. In some cases, charge distribution and steric hindrance can not alone explain the hydrolysis kinetics, and some inductive effects of the alkyl chain must be taken into account.

These general phenomena work the same way for each type of ligand. Some organic ligands can increase the stability of the organo-metallic compound such as acetate, acetyl acetone or tetramethyl heptanedionate. The nature of the ligand also strongly affects the condensation reaction. Hence oxide particles morphology and composition depend on the size and the nature of the ligand. Generally, transition metal alkoxides with large R groups lead to small polymers.

1-5-6 Precursor Concentration

Dilution can help to separate hydrolysis from condensation process. This effect is enhanced when acid catalysis and high hydrolytic ratio are used. High concentrated sols often lead to precipitation. Another aim of diluting is to prevent growth by aggregation. The molecular complexity represents the oligomerisation degree of the precursor. For a
transition-metal alkoxide, the oxidation state is generally smaller than the normal coordination number \( N \). As a result the full coordination is not satisfied in monomers and metal atoms tend to use their vacant d orbitals to accept oxygen lone pairs of electrons from nucleophilic ligands. Oligomerisation occurs by alcolation, increasing the coordination number of the metal by 1 through the mechanism proposed in equation (9):

\[
2 \text{M-OR} \rightarrow \text{M} \left\langle \begin{array}{c} \text{M} \\ \text{OR} \end{array} \right. \]

The molecular complexity increases with the size of the metal atom (see Table I-3).

**Table I-3: Molecular complexity of common transition metal ethoxides [2].**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ti(OEt)(_4)</th>
<th>Zr(OEt)(_4)</th>
<th>Hf(OEt)(_4)</th>
<th>Th(OEt)(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent radii (nm)</td>
<td>0.132</td>
<td>0.145</td>
<td>0.144</td>
<td>0.155</td>
</tr>
<tr>
<td>Molecular complexity</td>
<td>2.9</td>
<td>3.6</td>
<td>3.6</td>
<td>6</td>
</tr>
</tbody>
</table>

Alkoxides should adopt the smallest possible structural unit consistent with all atoms attaining their higher coordination number. The molecular complexity also depends on the nature of the alkoxy group. It decreases with the increasing branching and bulkiness of the OR group because of steric hindrance effects. The molecular complexity is usually estimated from molecular weight measurements in solution or by mass spectroscopy.

### I-5.7 Nature of the Solvent

The sol is an intermediate state between the solution and the gel that can be stable or unstable. In the powder process, the particles are pushed apart by electrostatic, chemical or Van der Waals effects of the solvent encombrement. If interactions between particles are greater than the interaction between particles and solvent molecules, precipitation occurs by aggregation. Metal alkoxides are often dissolved in their parent organic solvents before performing hydrolysis. As a general rule, dilution should lead to lower
association and, in certain cases, the use of polar solvents even leads to dissociation of the oligomers and solvation of the monomers. As a result, metal alkoxides can behave as Lewis acids and react with Lewis bases leading to solvate formation. Therefore, the solvent nature can change the molecular structure of the precursor. Alkoxide bridges appear to be more stable towards hydrolysis than solvate bonds. Starting from a given alkoxide, different molecular complexities can be obtained depending on the solvent nature. Thus, different hydrolysis rates are also expected that can lead to different oxide structures. For each case, the molecular complexity can be related to the hydrolysis ratio \( r \). The structure of the molecular precursor is not supposed to change upon hydrolysis and condensation occurs between polymerised species.

**I-5-8 Water Content**

The hydrolysis ratio can be defined as follows:

\[
 r = \frac{[\text{H}_2\text{O}]}{[\text{M(OR)}_2]} 
\]

A mathematical relation can be established between the average condensation degree \((n)\) and the hydrolysis ratio \((r)\), where \((a)\) is a constant that has to be experimentally determined.

\[
\frac{1}{n} = \frac{1}{a} - \frac{1}{r}
\]

This relation can be used to predict the hydrolysis ratio needed to obtain a certain oxide structure from a given oligomer precursor. Generally:

- If \( r < 1 \), condensation is mainly governed by alcoxolation and alcolation. Under such conditions, as long as no excess water is present, gelation and precipitation cannot occur (alcolation is possible only if \( N-z \neq 0 \)).
- If \( 1 < r < 2 \), competition between oxolation and alcoxolation may occur in this domain, depending on \( r \). The partial charge on the protonated group ORR is generally positive thermodynamically favouring the alcoxolation. Upon further hydrolysis, the partial charge of the OR group \( \delta(O) \) becomes more and more positive preventing an easy proton transfer. Therefore, total hydrolysis may not be completed, and condensation via oxolation becomes highly competitive.
Also, for transition metal alkoxides, olation could occur preferentially because 
\( \delta(OH) << 0, \delta(M) >> 0 \) and \( N-z >> 0 \).
- If \( r > z \), cross-linked polymers are formed under gel or precipitate forms, preferably via olation, expressed by the rapidity of the hydrolysis-condensation.

I-5-9 **Catalysts**

Another way to control the hydrolysis and condensation rates is to control the protonic transfer by addition of acid or base. Addition of protons usually increases the reaction rates by proton transfer catalysis. However, in presence of certain acids such as ethanoic acid, secondary reactions can occur. A nucleophilic substitution between the ligand and the acetate takes place in solution. The chelating and stabilising effect of the acetate will considerably slow down the reaction. Using \( \text{NH}_3 \) as catalyst, the hydrolysis is activated due to a nucleophilic activation of the metal atom via the formation of \( \text{M-O}^- + \text{NH}_4^+ \). Strongly cross-linked polymers are expected to form, resulting in gels or precipitates if olation is favoured.

I-5-10 **Temperature**

Increasing the temperature generally activates the hydrolysis and condensation reactions. As a result the sol-gel transition can be accelerated for precursors of poor reactivity by increasing the temperature. It is commonly called thermohydrolysis. On the other hand, decreasing the temperature slows down hydrolysis of high reactive precursors.

I-5-11 **Agents of Chemical Modification**

In order to improve the control of the sol-gel process, extra components can be added to the solution. These are agents of stabilisation, of drying control or coating control. Most of the time they are nucleophilic molecules \( \text{HOR} \) leading to ligand exchange. Addition or substitution reactions lead to new molecular precursors reacting differently with respect to hydrolysis and condensation. The enthalpy changes while the entropy
changes occur when the coordination number increases. Both effects lead to a modification of the reactions together with a differentiation of the ligand reactivities for hydrolysis and condensation. The reactivity of the $\text{M(ORMOX)}_z$ is very difficult to establish from parent alkoxides. Molecular modifications have a strong effect on the structure of a material by changing rates of hydrolysis and condensation. Brinker et al have explained in details the stabilizing effect of ACAC and acetate groupments on the reactivity of $\text{Ti(Opr)}_4$ toward hydrolysis-condensation, and their influences on the final structures [30].

I-5-12 Phenomenon of Aggregation

A colloidal system has a tendency to become unstable and aggregates spontaneously. Aggregates are often described by the concept of fractal geometry; and small angle X-ray scattering or neutron scattering techniques (i.e. SAXS and SANS) are used to measure the particle morphologies in solution. For transition metals, two possibilities must be considered. The first is the formation of isotropic aggregates due to non-preferred orientation of the particles while collision (usually found for spherical isotropic particles). The second is the formation of anisotropic aggregates due to collisions of particles under a particular orientation. This occurs usually with anisotropic particles such as rod-like or plate-like, and leads to sols and gels that exhibit specific properties such as chemical intercalation, birefringence, etc.

The stability of a sol requires some repulsive forces applied between particles in order to create an energetic shield limiting their approach. These forces can result from existence of electrostatic charges at the surface of the particles. The stability can also be maintained by adsorption of molecules at the surface assuming the steric hindrance effect between particles. Because of the high interfacial surface between solid and solution, a slight variation in a parameter such as $pH$ and concentration can lead to the destabilisation of the system.

When a particle approaches another, the overlapping of diffusion layers leads to the increasing of the potential between the two surfaces. As a result, the density of counter
ions increases in this area. The decreasing of the distance between the particles leads to
the creation of an osmotic pressure effect tending to separate them. A simultaneous
variation of the particle charges by protonation or deprotonation of the surface groups
occurs. Aggregation, floculation or precipitation of colloids can be observed when
contact between particles is achieved (i.e. distance of separation \( d=0 \)), assuming a
cancellation of their mutual charges. Aggregations are kinetics phenomena that are
governed by the diffusion of the particles, the viscosity of the solution, the relaxation
time of the surface groups, and the Van der Waals interactions.

Van der Waals interactions are due to variations of molecular dipolar interactions within
a certain medium. The total potential energy of the interaction is given by the sum of
attractive and repulsive interactions [31]. Flocculation and aggregation can be predicted
by the stability ratio \( W \) (i.e. \( W \) is the ratio of the number of collision between particles
per time unit to the effective collisions leading to aggregation) given by the following
equation.

\[
W = \int_{2a}^{\infty} x^{-2} \exp\left[\frac{V(x)}{kT}\right] dx
\]

Where \( V(x) \) is the total potential energy of the interaction at the distance \( x=D+2a \)
between two spherical particles of radius \( a \). \( W \) is simplified for \( V(x) \) maximal \( V_m \) as:

\[
W = \frac{1}{2} k a \exp(V_m/kT)
\]

If \( V(x) \) does not have a maximal, \( W=1 \) and the rate of flocculation is only limited by the
particles diffusion.

I-6 Types of Gel

Once produced, the gel consists in an oxide skeleton containing solvent molecules
trapped in pores that has to be removed by a solvent evaporation process. Sols and gels
can be dried into films, fibres or bulk shapes. This latter is called a monolith and,
contrary to the two first shapes, presents problems during the drying process. The major problems of making bulk samples are the large volume involved and the frequent cracking of the pieces. This arises when the surface energy at solid liquid interfaces is lower than the surface energy at solid vapour interfaces. In wet regions, the gel contracts to lower the solid liquid surface area. When the gas phase enters the gel in its dry regions, the solvent molecules tend to cover the solid vapour interface. Meanwhile, in order to lower the solid vapour surface area, dry regions tend to contract [32]. At first, the shrinkage process is slow when there is a high concentration of water in the gel characterised by the presence of an excess of water in the capillaries. The shrinkage process increases upon drying as the hydroxyl groups at the surface of the particles get closer and closer forming hydrogen bonds eventually condensing to hydroxo or oxo bridges. The various types of dried gels are now defined [33].

I-6-1 Aerogel

These sort of gels are produced via a drying method consisting of removing the liquid phase of a sol under hyper-critical conditions obtained in an autoclave. Aerogels are processed by increasing the pressure and the temperature above the critical point to bypass the liquid vapour interface and then to vent out the vapour leaving a network of about 95% porosity. Pores can then be closed by firing.

I-6-2 Xerogel

Natural evaporation of the solvent and water at normal pressure and room temperature leads to xerogels. While the liquid evaporates the gel structure collapses on itself. Large stresses develop when the liquid is removed from capillaries leading to shrinkage. First, the drying is slow to permit the gel itself to become stronger by further polymerisation. Subsequently, the sample may be heated to lower the solvent viscosity. If the temperature is raised too high too soon, the solvent escapes too rapidly causing cracks in the gel network. The interest in xerogels, despite long drying time, is that they are denser and simpler to prepare.
I-6-3 **Sonogel**

The sol or gel is first ultrasonically treated before being dried in an autoclave or under atmospheric pressure.

I-F-4 **Cryogel**

The method of obtaining cryogels consists of drying aqueous hydrogels in a freeze-drying apparatus by subliming the water at a pressure below the triple point so only ice and water vapour are present. Drying time may exceed 24h. Gels obtained in this way exist as a finely divided porous powder.

I-F-5 **Additional Gels**

A number of methods have been developed to produce hybrid materials that are composed of both organic and inorganic phases. Precursors to these hybrid gels are usually organometallic compounds containing alkoxide ligands (i.e. metal oxygen bonds) or alkyl groups (i.e. metal carbon bonds). These gels are called ceramers or ormosils and contain organic bridges forming a cross-linked network [12,13]

Monolithic bulks, films, and fibres can be prepared by sol-gel chemistry. Solutions selected for thin films are typically those with fast gelling and rapid drying. The solution for fibres must show gradual increases in viscosity rather than abrupt increases. The solution for monoliths must have an excessive amount of water in order to insure that the shrinkage between particles is sufficient enough to increase the strength of the gel.

I-7 **Types of Ceramic Preforms**

Monoliths are usually difficult to produce because of the cracking occurring during the drying process. As a result, the most common ceramic performs obtained from sol-gel
chemistry are thin films or coatings. These are performed by spin-coating [34], dip-coating [30], meniscus-coating [35] and more recently by spray-coating [36].

I-7-1 Fibres

Fibres are one of the most common applications of sol-gel chemistry and especially optical fibres used for information transfer. The direct drawing of the fibre from the solution requires the controlled hydrolysis of the metal alkoxides and the gradual increase of the solution viscosity upon time. Also, dispersion of colloidal particles in an aqueous or non-aqueous medium mixed with a binder allows the processing of fibres by extrusion. These fibres can then be coated with ceramics of different refractive indices in order to obtain optical fibres.

I-7-2 Films and Coatings

Films and coatings are generally produced by dipping the substrates in sols. A meniscus develops at the contact of the liquid and the substrate. As the substrate is withdrawn, the meniscus creates a thin layer of sol at the surface of the substrate. Then the film gels and dries forming a layer of ceramic of thickness depending on the viscosity, the surface tension and the speed of withdrawal. The film thickness generally increases with the sol viscosity and the rate of dipping. As a result, it is possible to control the layer thickness as long as the evolution of viscosity with time is known. When the substrate is flexible, as it is the case with fibres, a continuous process can be designed. In order to prepare single-side coated devices, the spin-coating method is more appropriate. In this case, the substrate is fixed on a spinner rotating between a few and a few thousands revolutions per minute. While spinning, the solution is dripped at the centre of the substrate. The rotation allows for the solution to spread on the surface forming a homogeneous layer of sol that gels and dries. The thickness increases with the solution viscosity but inversely decreases with the spin rate. Another methods of preparing thin ceramic films are meniscus-coating and spray-coatings. These methods are quite new and still at the experimental stage, therefore not commonly used. Thermal treatments of coatings are
commonly used as densification process. Coating processes will be further developed later in chapter V.

I-7.3 Monoliths

The sol-gel formation of three-dimensional ceramics with none of the dimension being thin is problematic. The sol is usually poured into a mould and left to gel and dry in order to obtain the monolith of the mould shape. The monolith dimension depends on the drying method and is often smaller than the mould. The real problem encountered during the process occurs via the drying step and is characterised by the formation of cracks. The solvent is removed from the interconnected pores of the oxide network by natural evaporation, which leads to xerogel, or in hyper-critical conditions leading to aerogel. Aerogel usually are less dense, more porous, of the mould dimension and stress-free. On the other hand, the xerogel is less porous, denser and requires a significant time to age in order to prevent the formation of cracks. Cracks due to residual stresses within the xerogel could be avoided by using low surface-tension solvents or by trying to obtain large and homogeneous pores. Monoliths can be densified by thermal treatment. The rate should be fast enough to provide shrinkage and slow enough to allow elimination of gases before trapping the latter in isolated pores.

I-8 Techniques of Characterisation

Several classical and specific methods can be applied for the characterisation of sol-gel systems along the multitude of stages involved in the processing.

I-8-1 Sols

In the most common powder process case, at the early stage, sols are composed of discrete colloidal particles in suspension in aqueous or organic media. The average size and the shape of these particles give very important information on the mechanism of formation and on the structure of the future gels. For spherical particles, dynamic light scattering (DLS) analysis allows the determination of their diameter. Electronic
microscopy (TEM-SEM see Annexe A-1) reveals the particle morphology. However, if one or more of the particle dimensions are smaller than the resolution of the above techniques, the use of small angle X-ray (see Annexe A-3) or neutron scattering analysis (SAXS or SANS) is required to fully characterise the particle shapes. Nowadays, these techniques are commonly used to investigate smaller and smaller particles with specific morphologies. However, the interpretation of small angle scattering results requires the fitting of models. Thus, the system must be well understood for the results to be interpreted [16].

During the sol-gel transition, particles condense one to another and the evolution is usually followed by viscosity measurement (see Annexe A-13). The understanding and control of the transition is important because the density and network structure of the final material mostly depend on the viscosity.

I-8-2 Gels

The characterisation of the ground bulk material obtained after drying can be done with several classical techniques. H\textsuperscript{+} and $^{13}$C nuclear magnetic resonance (NMR), Fourier transform infra red spectroscopy (FTIR, see Annexe A-4), and residual gas analysis (RGA) are usually used to determine the nature of the organic phase retained in the material network. Raman spectroscopy, solid $^{17}$O-NMR, thermogravimetric analysis (TGA, see Annexe A-5), X-ray diffraction (XRD, see Annexes A-6 and A-7), and X-ray photoelectron spectroscopy (XPS, see Annex A-11) give information about nature, thermal evolution, phase separation [37], and crystallinity of the material. Porosity, surface area, and pore sizes can be deduced from mercury porosimetry and N\textsubscript{2}-BET adsorption-desorption isotherms (see Annex A-9), or from SANS investigated in the Porod region [38,39].

I-8-3 Coatings

The characterisation of thin films requires the use of surface analysis methods. XPS (see Annexe A-11), EXAFS, and secondary ion mass spectroscopy (SIMS) give the nature
of the surfaces, interfaces and a depth profile [40] in terms of bond characterisation. Atomic force microscopy (AFM, see Annexe A-10) can picture the disposition of particles on the surface. The physical thickness of the coating can be measured from scratch test or electron microscopy on cut samples. Optical thickness and refractive index are deduced from UV transmission (see Annexe A-8 and part VI-2-3). Optical characteristics are measured with an UV-spectrometer in terms of transmittance and reflectance. Absorbance and scattering factors have to be deduced from thermal deflection mapping analysis (see Annex A-12) [41,42].

Other methods can be applied to obtain specific characteristics of sols, coatings and gels. Not all of them could have been used and only techniques described in Annexes A were undertaken for the present work.

Reference

144.


[37] F. Babonneau, 9th International Workshop on Glasses, Ceramics, Hybrids and Nanocomposites from Gels, (September 1997), (Sheffield, UK), Abstract A4(I), p8.


[40] N. Bazin, D. Spriggs and J. E. Andrew, 9th International Workshop on Glasses, Ceramics, Hybrids and Nanocomposites from Gels, (September 1997), (Sheffield, UK), Abstract GP17, p211.


Chapter II

THE SOL-GEL CHEMISTRY OF SCANDIA
II-1 Scandium Oxide

II-1-1 Interesting Properties

Scandium is the lightest of the d-block elements, but is not extensively used because of its high price and low annual world production due to its rarity (i.e. 200kg [1]). Consequently, scandium is the only light element (atomic number 21, outer electron configuration 4s² 3d¹) not in common use. Scandium exists in only one oxidation-state (i.e. Sc³⁺O₃). Its oxide has a cubic structure (a = 0.9845nm) that becomes monoclinic after calcination at 1273K and 13GPa [2,3].

Scandia possesses a high melting point (i.e. 2753K), a high bulk refractive index (n=1.91) and a high band gap (5.7eV corresponding to an UV cut-off of 215nm). These properties make it a good alternative to hafnia [4] or zirconia [5,6] as a high index material to be used at low λ. Recent works have shown that UV high-reflective mirrors, made by vacuum deposition of stacked pairs of high and low refractive index materials, were of higher resistance to laser damage when scandia is the high index stack component than with any presently available alternative [7-9]. We have seen that liquid deposition methods were interesting to produce optical coatings. Therefore, synthesis of scandia particles by sol-gel suspended in an alcoholic medium (precursor to liquid deposited films to be used in UV high-reflective mirrors) was investigated and is now presented.

II-1-2 General Chemistry

Despite its place in the Periodic Table, the chemistry of scandium is closer to that of yttrium and the rare-earths [10]. The chemistry of its oxide is closer to that of Al₂O₃ than to Ln₂O₃ (where Ln corresponds to a Lanthanide). Despite the common association of scandium with yttrium and lanthanum of group III of the Periodic Table, it is rarely found in significant concentrations in rare-earth element deposits. Nor is it commonly associated in nature with aluminium. The extraction of scandium from its raw materials
involves its dissolution with either HCl or H$_2$SO$_4$ acids, before purification by solvent extraction or by ion exchange resin.

Scandium sol-gel chemistry has not been well-developed previously and scandia has only be considered for specific applications (e.g. as a dopant in garnet lasers [11], a component in composite electronic devices [12,13], or in optical coatings [7,14]). Organo scandium compounds are suitable precursors to the sol-gel formation of scandia. Because of the high reactivity of scandium$^{III}$ towards hydroxyl groups, ligands are usually very heavy alkoxides (e.g. OC$_6$H$_2$Me-4-tBut$_2$-2,6) [15], or highly chelating agents such as tetramethyl heptanedionate (TMHD) [16], acetyl acetate (ACAC) [17], or acetate which stabilise the hexacoordinate scandium (see section II-2-1).

The synthesis of organo-scandium precursors from ScCl$_3$ takes usually place in the parent organic medium with dried ammonia catalyst [18]. Sc$^{III}$ salts are often very hygroscopic and undergo fast hydrolysis leading to Sc(OH)$_3$ precipitate when in contact with water. Therefore these compounds must be handled in an anhydrous environment. Scandium chloride is very soluble in alcohol (i.e. 37.5% w/w in ethanol and 25.5% w/w in butan-1-ol at 298K). The addition of dried ammonia to a butanolic solution of scandium chloride leads to the substitution of Cl$^{-}$ by the butoxide group (and also to the co-precipitation of insoluble NH$_4$Cl). However, the incomplete transformation of scandium salt to its alkoxide is due to the formation of unwanted scandium hydroxide and amine ions. Anhydrous ScCl$_3$ reacts with ammonia to give products containing between 5 and 8 NH$_3$/Sc [3]. The formation of these different hydrated, aminated, and combined scandium complexes is very difficult to prevent in the synthesis of the organometallic precursors. However, the presence of an excess of chelating groups such as acetate, $\beta$-pentanedionate (ACAC) in a solution of Sc$^{III}$ leads to the formation of very stable complexes of scandium that may be used as precursors for sol-gel chemistry.

_Sol-gel chemistry_ involves two main reactions (i.e. hydrolysis and polycondensation) governed by a SN$_2$ mechanism and have a complexity that varies with the conditions, the nature of the precursors, the solvent, and the catalyst. As described in Chapter I, the reaction _thermodynamics_ are governed by the partial charge distribution between the
central atom and the O of the leaving group (i.e. $\delta(\text{Sc})$ and $\delta(\text{O})$). The reaction rate increases if $\delta(\text{Sc})$ increases. In this chapter, it will be seen that because of the good doublet and $\pi$-electron donor characters of ACAC and acetate ligands stabilising the complexes, nucleophilic attack and ligand departure do not occur readily. The sizes of these big organic groups create steric hindrance effects that also slow down the reaction kinetics. However, it is shown later that starting from such organo scandium precursors allows for the separation of the different steps, leading to a better control on the mechanism of the particle formation.

II-1-3 Fields of Application

Scandia is already used in several applications. We can find it as a stabiliser for zirconia and as a densification agent in silicon nitride. Its presence in mixed nickel-copper oxides leads to materials that are NO$_2$ sensitive. Catalytic applications have been studied in terms of N$_2$O decomposition, propan-2-ol decomposition, CO$_2$ reduction and CO oxidation. Thin layers of scandium oxide can be processed by CVD or liquid deposition methods. Such coatings are used as optical or optoelectronic devices. More precisely, scandium can be used in the following applications:

The addition of 6 to 10 mol% of scandium oxide to zirconium oxide allows the stabilisation of the cubic ZrO$_2$, and causes the formation of oxygen ion vacancies within the network. Between 1073 and 1273 K the increase in oxygen-ion conductivity of the solid electrolyte has led to the development of oxygen sensors [1]. The stabilisation of zirconia with yttria or ytterbia is also used for the same purpose, but the combination with scandia gave the best conductivity. Sc$_2$Cu$_2$O$_3$ formed by mechanical-thermal process at 1273 K, from a mixture of Sc$_2$O$_3$ / NiO / CuO, has a better NO$_2$ adsorption capacity than the material without scandia [19]. The sensor material is composed of four different phases (i.e. Ni$_{0.8}$Cu$_{0.2}$O, Sc$_2$Cu$_2$O$_3$, CuO and Sc$_2$O$_3$) and its electrical resistance varies with the amount of NO$_2$ adsorbed.

Stabilisation of zirconia with 4.5 mol% of scandia leads to a tetragonal structure that exhibits good properties as a thermal barrier in gas turbines and diesel engines [1].
Recently sol-gel prepared scandia-yttria stabilised zirconia compounds, fired at 1173K, have been produced with superior properties than the monostabilised ZrO$_2$·Y$_2$O$_3$ [20].

The presence of scandium oxide in silicon nitride (i.e. Si$_3$N$_4$) leads to a densification of the structure. At high-temperature, these combinations give materials that show mechanical properties superior to silicon nitride system densified with other oxides. They also exhibit high resistance to oxidation [1]. The excellent high-temperature deformational resistance is attributed to the formation of a refractive phase (Sc$_2$Si$_2$O$_7$) at thin grain boundaries or to the impossibility of formation of quaternary metal silicon nitrides that can expand upon oxidation and cause cracking [21]. The material is produced via a sintered reaction of the mixed pre-ground components.

So far, because of its price, the catalytic potential of scandia has not been extensively studied. However production methods of porous scandia gels via precipitation with ammonium hydroxide [22], or sodium hydroxide [23], in aqueous medium have been described. The N$_2$-BET surface-areas measured on these materials were between 6 and 100 m$^2$·g$^{-1}$. The study of dehydration and dehydrogenation of propan-2-ol in propylene and acetone has shown that scandia has to be considered as a catalyst easily developing a preponderance of dehydration over dehydrogenation activity. The investigation of adsorption of CO and CO$_2$ on a Sc$_2$O$_3$ surface has led to the study of adsorbed (CO)$_2^{2+}$. The thermal stability and reactivity of these species have been explained and a mechanism to the oxidation of CO has been proposed [24,25].

To use laser diodes as superluminescent LEDs or amplifiers, it is necessary to coat their faces with anti-reflective films. A single $\lambda/4$ coating for InGaAsP and AlGaAs LEDs requires a refractive index ($n$) in the vicinity of 1.8. These conditions can be achieved by vacuum depositing a thin layer of scandia followed by a controlled densification [26].

Lead scandium tantalate (PST) is an insulating electroceramic that crystallises in a perovskite structure (ABO$_3$). It is a candidate for pyroelectric imaging and new dielectric devices (e.g. capacitors). Order-disorder behaviour on the B-site cation in the (i.e. Sc and Ta sites) can be manipulated by thermal treatment to modify the dielectric
response of the thin layer. The material is produced via a multi-step sol-gel method [12,13]. P-type oxide-halide high-temperature superconductor, containing scandium oxide \((\text{Ba}_2\text{Sc}_2\text{O}_5\text{F})\), have been prepared by high temperature sintering of well-ground mixtures of appropriate molar ratios of initial components [26].

The increasing interest in high power lasers radiating at low wavelengths has required the design of optics coated with materials of high band gap. The high refractive index \((n)\) of scandia in addition to its high band gap makes it a good material for this purpose. Vacuum deposition methods have been used to produce highly reflective coatings on fused silica substrates [6,14,27]. Such coatings have been shown to have good laser damage resistance. Further investigations are on the way to ameliorate the optical and mechanical characteristics shown.

II-2 Sol-Gel Processing of Lozenge-Shaped Nanoparticles

Different sol-gel routes to scandia suspensions have been investigated here and colloidal particles of scandium oxide have been produced in organic solvents and analysed as sols, bulk materials and coatings. The present part describes the synthesis of lozenge shaped particles of scandia in methoxyethanol from a scandium acetylacetonate precursor. These colloidal particles are homogeneous and stable. The sols and xerogels produced via this method are also fully characterised. No sol-gel route to the formation of stable scandia colloidal nanoparticles in organic medium was found in literature. The present work could be the first method ever investigated to produce such particles.

II-2-1 Introduction on Scandium Acetylacetonate (ACAC)

\(\text{Sc}^{\text{III}}\) is hexa-coordinated in its highest oxidation state [3]. The presence of three pentandionate ligands fulfils its coordination sphere by forming strong bidendate bonds that stabilise the complex. Hexa-coordination is confirmed by the rule of radius ratio from Pauling [28] described in part I-2-3 (\(\text{Sc}^{\text{III}}\) surrounded by O ligands led to \(\varphi=0.53\)). ACAC molecules contain two carbonate groups with two electron doublets and two \(\pi\)
electrons each. When combined with scandium ion, a carbonate group shares a π-electron with one of the empty orbital of Sc$^{\text{III}}$ (4s or 3d) forming a covalent bond. A dative bond is also created with an electron from the O 2s or 2p doublet of the second carbonate group with another empty orbital of Sc$^{\text{III}}$. Therefore complexion occurs via the formation of aromatic plane structures composed of one scandium, three carbon and two oxygen atoms (see Figure II-1). The aromatic character of the system is given by the plane hexagonal structure and the presence of delocalised electrons allowing conjugation between atoms. As a result, Sc(ACAC)$_3$ is highly stabilised by chelation.

\[
\begin{array}{c}
\text{Sc} \\
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\end{array}
\]

*Figure II-1: Structure of the Sc$^{3+}$ complex with acetylacetonate.*

The nature of this aromatic chelation is clearly shown in FTIR by the presence of both stretching vibration of C=O and C=C at 1585 and 1525cm$^{-1}$ [29] (see Figure II-2). The exchange of the pentandionate groups involves SN$_2$ or SN$_1$ mechanisms. The SN$_2$ reaction is favoured if the coordination number of the central atom is not complete and the SN$_1$ reaction is favoured if the leaving group is labile [30,31]. ACAC is a poor leaving group, and Sc$^{\text{III}}$ combined with it is already hexacoordinated. As a result neither SN$_1$ nor SN$_2$ are greatly favoured and it will be shown later that the removal of these ACAC ligands is the limiting factor. Hydrolysis-condensation of this precursor to scandia is thus difficult and requires strong conditions or high temperatures and long periods of refluxing-ageing. Sc(ACAC)$_3$ precursor has also a low solubility in the most common alcohol (see Table II-1) leading to even less soluble compounds when partially condensed into oligomers.
Sc$^{III}$ has a small atomic radius (0.074nm) [3] and chelation by the relatively heavy pentanedionate ligands induces high steric hindrance. Therefore it is expected to be in solution in a monomeric form [30]. The partial charge distribution carried by Sc$^{III}$ and the bonding O (i.e. $\delta$(Sc) and $\delta$(O)) could no be calculated, as described in part I-2, because of the presence of dative bonds. When dissolved in alcohol, Sc(ACAC)$_3$ is yellow due to the combined effects of ACAC ligands and solvating alcoloholate groups on the electronic environment of Sc$^{III}$, suggesting that such scandium are in complex form rather than dissociated.

![FTIR transmission spectrum of Sc(ACAC)$_3$.](image)

**Figure II-2: FTIR transmission spectrum of Sc(ACAC)$_3$.**

**Table II-1: Solubility of Sc(ACAC)$_3$ in alcohol at 300K and solvent boiling point.**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Solubility at 300K (mol dm$^{-3}$)</th>
<th>Solubility at boiling point (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.035</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.095</td>
<td>0.4</td>
</tr>
<tr>
<td>Methoxyethanol (MOE)</td>
<td>0.075</td>
<td>&gt; 0.2</td>
</tr>
</tbody>
</table>

Usually, the addition of stabilising ACAC to a highly reactive metal system allows control of the sol-gel steps. ACAC removal is difficult and requires a high amount of water and even then, the total removal of these chelating groups is almost never
achieved. Sc(ACAC)$_3$ or scandium III 2,4-pentanedionate or scandium acetylacetonate (source see Annexe B-19) exhibited the FTIR spectrum shown in Figure II-2. This precursor was not further purified.

### II-2-2 Experimental Synthesis of Lozenge Scandia Particles

Platelet-lozenge shaped particles of ScO$_x$(OH)$_y$(ACAC)$_z$ were produced from Sc(ACAC)$_3$ in anhydrous MOE via the procedure detailed below. The precursor was dissolved in MOE in which a methoxyethanoic solution containing a ratio of H$_2$O to Sc$^{III}$ of $r=4$ (i.e. $pH=7.5$) was slowly added. MOE is very hygroscopic and absorbed water is often enough to initiate hydrolysis. Before being aged for 2 weeks, the solution was refluxed until its yellow colour, corresponding to solvated Sc(ACAC)$_3$, converted to a light bluish colour corresponding to a fine colloidal suspensions (i.e. refluxing time: 5h). The sol (containing 25mmol Sc.dm$^{-3}$) was centrifuged to remove the larger aggregates. The final colloidal sol was then stable and only developed a flocculate after ageing for 4 months. A transparent gel could be obtained from this sol via very slow evaporation to remove between 60 and 80% of the solvent at room temperature and pressure.

### II-2-3 Viscosity of Scandia Sols

As described in Annexe A-13, the stability of a sol can be followed from the variation of its viscosity upon time. As shown in chapter I, an increase in viscosity denotes the beginning of the sol-gel transition due to formation of links between particles. The reference liquid was chosen to be propan-1-ol ($\eta_{298K}=1.94$cps). Because of the low concentration in particle (i.e. $C_{5c}=0.025$M), the density difference measured between pure MOE and the Sc$_2$O$_3$ sol was negligible. Therefore the scandia sol density was taken to be constant and equal to that of MOE at 298K. Table II-2 shows the evolution of viscosity with time of a 0.025M sol produced via the route described above and kept in a sealed flask at 298K. Two capillaries of different sizes were used: size 1 corresponds to the capillary of smaller diameter and size 2 to the larger one in Table II-2.
Table II-2: Viscosity of pure propan-1-ol and MOE solvents, and of a 0.03M Sc$_2$O$_3$ sol at 298K during ageing.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Age (days)</th>
<th>Capillary size</th>
<th>Passing Time (min-s)</th>
<th>Viscosity η (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-PrOH</td>
<td>-</td>
<td>1</td>
<td>15'-28''</td>
<td>1.94</td>
</tr>
<tr>
<td>n-PrOH</td>
<td>-</td>
<td>2</td>
<td>4'-25''</td>
<td>1.94</td>
</tr>
<tr>
<td>MOE</td>
<td>-</td>
<td>1</td>
<td>10'-36''</td>
<td>1.33</td>
</tr>
<tr>
<td>MOE</td>
<td>-</td>
<td>2</td>
<td>3'-05''</td>
<td>1.35</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>1</td>
<td>1</td>
<td>12'-25''</td>
<td>1.56</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>1</td>
<td>2</td>
<td>3'-32''</td>
<td>1.55</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>40</td>
<td>1</td>
<td>12'-22''</td>
<td>1.56</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>40</td>
<td>2</td>
<td>3'-31''</td>
<td>1.54</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>98</td>
<td>1</td>
<td>12'-21''</td>
<td>1.56</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>98</td>
<td>2</td>
<td>3'-33''</td>
<td>1.55</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>123</td>
<td>1</td>
<td>15'-13''</td>
<td>1.91</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>123</td>
<td>2</td>
<td>4'-19''</td>
<td>1.89</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>145</td>
<td>1</td>
<td>15'-20''</td>
<td>1.92</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ sol</td>
<td>145</td>
<td>2</td>
<td>4'-19''</td>
<td>1.89</td>
</tr>
</tbody>
</table>

The viscosity of scandia sol remained visibly unchanged after 40 and 98 days ageing but increased from 1.55 to 1.90cp between 98 and 123 days ageing. The viscosity measured at 123 days corresponded to a few days before a clear phase appeared at the top of the sol that corresponded to the beginning of the flocculation. The flocculate phase needed several more weeks to settle and the viscosity, measured on the stirred aliquot, did not change during this period.

II-2-4 Characterisation of scandia particles by TEM

Principles of TEM analysis techniques are described in Annexe A-1 and A-2. After deposition on carbon-coated copper grids, the composition of the particles were obtained by X-ray probe analysis (Jeol 2000fx TEM) and showed the characteristic energy
spectrum of a compound containing scandium. The average size was established by assessing the dimension of 50 particles randomly chosen on the TEM picture shown in Figure II-4.

*Figure II-3:* X-ray energy dispersed spectrum obtained from colloidal scandia particles, (Energy source: Cu Kα). 4.05KeV corresponds to Sc L_{2,3}.

*Figure II-4:* TEM micrograph of scandia lozenge-shaped platelets, (×125 000; 1cm=80nm); with an enlargement (×300 000; 1cm=33nm).
These platelets clearly exhibit a lozenge shape with a width of 40±3nm and a length of 70±5nm. Figure II-5 represents a TEM image of these scandia particles shadowed with gold at a 60° incident angle. The thickness \( T \) of the particles was deduced to be less than 10nm. The real thickness was difficult to deduce because of the already small size of the particles and their possible stacking one on another.

![TEM micrograph of scandia lozenge-shaped platelets shadowed with gold at a 60° angle (x300 000; 1cm=33nm).](image)

**II-2-5 Characterisation of scandia particles by SAXS**

In order to complete the characterisation of the scandia particle morphology, small angle X-ray scattering was performed on the colloidal particles within the MOE solution and data were collected in a Kratky camera (Cu K\( \alpha \) radiation). The principle of SAXS and the method applied is explained in Annexe A-3.
Scattering results were analysed in terms of disoriented and widely separated particles or clusters. Interpretation of the SAXS investigation of scandia particles required to plot $\log(I)$ versus $\log(q)$, $\ln(q^*q^*I)$ versus $(q^*q)$ and $\ln(I)$ versus $(q^*q)$ (see Figures II-6, II-7 and II-8), where (I) represents the scattered intensity and the scattering vector is expressed by $(q)$ given in (Å$^{-1}$). No modification was observed when the sol concentration in Sc$^{\text{III}}$ increased from 0.025 to 0.05M by slow solvent evaporation, suggesting that the present results obtained with this range of concentration were consistent. More concentrated sols could not be analysed because of induced particle destabilisation characterised by aggregation and flocculation.

![Figure II-6: log(I) versus log(q) plot.](image)

In Figure II-6, the variable slope denoted the anisotropic morphology of the scandia particles (non-spherical). At lower $q$ ($\log(q)<-1.5$), a gradient of about $-2$ was found for the tangent which corresponded to disc, platelet or lamellar shaped particles (two dimensions greater than the third one). A gradient of $-1$ would have corresponded to rod-like particles (one dimension greater than the others). To be more precise, the gradient of $-2$ can be verified from $\log(q)=-1.6$ (i.e. $q^*q<0.0006\text{Å}^{-2}$). Therefore, the Guinier $\ln(I.q^2)$ versus $q^2$ plot (see Figure II-7) corresponded to platelet particles only for $q^*q<0.0006\text{Å}^{-2}$. The gradient of the best fitted line for this region was found to be $g=550$. The model corresponding to platelet particles gives the average thickness $(T)$ of the particles through the relation $T=(12*\tau)^{1/2}$ [32,33]. Thus, for scandia platelet particles $T\approx 80\text{Å}$, the thickness was evaluated to be about $8\text{nm}$.
Scandia particles were not spherical but the following interpretation led to the approximate average dimension of the particles deduced from the distortion dimension induced around the particles when irradiated by X-ray at a small angle. For spherical particles, the maximum mean radius of gyration ($R_g$) can be calculated from the Guinier sphere plot ($\ln(I)$ versus $q^2$) shown in Figure II-8 (see Annexe A-3). $R_g$ maximum is deduced from the gradient ($g$) of the tangent at lower values of $q$ as $R_g=(3g)^{1/2}$. In Figure II-8, the gradient at lower $q$ was determined to be $g=8400$, hence the particles had a maximum mean $R_g$ of 16nm. $R_g$ is not a dimension but rather related to particular dimensions, depending upon the particle shape. For platelet particles (model) with a $R_g$ of 16nm, Livage et al described their $Y_2O_3$ platelet particles of about 100nm wide [34].
In agreement with the TEM evidence (see Figure II-4), scandia particles were several tens of nanometres large and less than 10nm thick.

Results obtained from TEM and SAXS investigations on scandia sol produced in methoxyethanol suggested that the particles were effectively platelets and of lozenge shape in suspension. These lozenge-shaped platelet particles were not formed during drying process, but were formed in the solution and remained stable in suspension. The SAXS investigation of the particle thickness (i.e. 8nm) does confirm the thickness deduced from TEM of shadowed particles (i.e. <10nm). However, the presence of organic species, in addition to the low particle concentration and the only one small dimension of platelet particles, might have contributed to the difficulty of interpreting the results.

II-2-6 Characterisation of scandia xerogels by FTIR

The principle of FTIR spectrophotometry is briefly developed in Annexe A-4. Scandia xerogels, formed from the platelet particles, were obtained by solvent evaporation at room temperature in a fume-cupboard and then vacuum-dried at 373K for several hours. Samples were analysed using FTIR spectroscopy (Nicolet, Magma-IR550) in the form of KBr discs containing 5% xerogels and pressed 10min at 10^6Pa.

The main FTIR absorption bands recorded for the precursor, intermediates and final compounds are listed in Table II-3 with their corresponding modes of vibration. These were attributed from the reference data obtained from literature [31,36]. Unlisted absorption bands were attributed to additional vibrations from organic species. V S, S, M and W are used to denote very strong, strong, medium and weak vibrations. The absorption from 1620 to 1650cm\(^{-1}\) corresponds to the bending vibration of water molecules. Stretching of free carbonate groups is at 1710 - 1750 cm\(^{-1}\). Transmission FTIR spectra of Sc(ACAC)\(_3\) reference, scandia based platelet particles dried at 373K, heated at 773K and 973K are displayed in Figure II-9.
Table II-3: Characteristic FTIR bands recorded for prepared \( \text{Sc(ACAC)}_3 \), and \( \text{Sc(OCOCH}_3)_3 \), commercial \( \text{Sc}_2\text{O}_3 \), and reported for \( \text{Sc(OH)}_3 \) and \( \text{ScOOH} \) [31,36].

<table>
<thead>
<tr>
<th>Bands (cm(^{-1}))</th>
<th>Attribution</th>
<th>( \text{Sc(ACAC)}_3 )</th>
<th>( \text{Sc(C}_2\text{H}_4\text{O}_2)_3 )</th>
<th>( \text{Sc(OH)}_3 )</th>
<th>( \text{ScOOH} )</th>
<th>( \text{Sc}_2\text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>( \nu(\text{OH}) ) stretching of ( \text{ScOH} )</td>
<td>-</td>
<td>-</td>
<td>S</td>
<td>V S</td>
<td>V S</td>
</tr>
<tr>
<td>610</td>
<td>( \nu(\text{OH}) ) stretching of ( \text{ScOH} )</td>
<td>-</td>
<td>-</td>
<td>W</td>
<td>M</td>
<td>-</td>
</tr>
<tr>
<td>633</td>
<td>( \nu(\text{Sc-O}) ) stretching</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>S sharp</td>
</tr>
<tr>
<td>640</td>
<td>( \nu(\text{Sc-O})\text{COCH}_3 ) stretching</td>
<td>-</td>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>660</td>
<td>( \text{Sc-ACAC} ) stretching</td>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>(( \text{Sc(ACAC)}_3 )) deformation</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>930</td>
<td>ACAC or ( \delta(\text{OH}) ) bending</td>
<td>S</td>
<td>-</td>
<td>S</td>
<td>W</td>
<td>-</td>
</tr>
<tr>
<td>1025</td>
<td>( \nu(\text{Sc-OC}) ) stretching</td>
<td>V S</td>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1275</td>
<td>( \nu(\text{C-O}) ) stretching</td>
<td>S</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1350-1460</td>
<td>( \delta(\text{C-H}) ) bending</td>
<td>V S</td>
<td>V S</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1450</td>
<td>( \nu(\text{CO}_2^-) ) symmetric</td>
<td>-</td>
<td>V S</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1525</td>
<td>( \nu(\text{C=C}) ) from ( \text{ScO(C=C)} )</td>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1550</td>
<td>( \nu(\text{CO}_2^-) ) antisymmetric</td>
<td>-</td>
<td>V S</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1585</td>
<td>( \nu(\text{C=O}) ) Chelating ( \text{Sc}^{\text{III}} )</td>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1620-1650</td>
<td>( \delta(\text{H}_2\text{O}) ) bending</td>
<td>-</td>
<td>-</td>
<td>M</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1710-1750</td>
<td>( \nu(\text{C=O}) ) free carbonate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2900-3000</td>
<td>( \nu(\text{C-H}) ) stretching</td>
<td>W</td>
<td>W</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3250</td>
<td>( \nu(\text{OH})(\text{H}_2\text{O}) ) stretching</td>
<td>-</td>
<td>-</td>
<td>V S</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3400</td>
<td>( \nu(\text{OH})(\text{H}_2\text{O}) ) stretching</td>
<td>-</td>
<td>-</td>
<td>W</td>
<td>S broad</td>
<td>-</td>
</tr>
</tbody>
</table>

\( \text{Sc(ACAC)}_3 \) exhibited a \( \nu(\text{C=O}) \) band at 1585 cm\(^{-1}\) and a \( \nu(\text{C=C}) \) band at 1525 cm\(^{-1}\) characteristic of diketonate bidendate chelation. The \( \nu(\text{Sc-O}) \) band at 660 cm\(^{-1}\) was also present. After partial hydrolysis-condensation, the characteristic bands of \( \text{ScO(OH)} \) were present (i.e. \( \nu(\text{OH}) \) at 3400 cm\(^{-1}\), \( \nu(\text{O-H}) \) at 469 and 610 cm\(^{-1}\)) in addition to the \( \nu(\text{ScACAC}) \) monodendate stretching at 1582 cm\(^{-1}\). Absorption at 1710 cm\(^{-1}\) corresponded to the \( \nu(\text{C=O}) \) stretching of non-bonding carbonyl groups.
Figure II-9: FTIR spectra of Sc(ACAC)$_3$ precursor, scandia based xerogel vacuum drying at 373K, heating at 773K and heating at 973K.

A sharp absorption band at 633 cm$^{-1}$, corresponding to $\nu$(Sc-O) from Sc$_2$O$_3$, was visible after heating above 773K, and was accompanied by low intense absorption at 1400-1700 cm$^{-1}$ assigned to carbonate residues. Thus, controlled thermohydrolysis of Sc(ACAC)$_3$ in MOE led to successful partial condensation and formation of platelets particles composed of monodendate Sc-ACAC, Sc-O-Sc, and Sc-OH units.

II-2-7 Characterisation of Scandia Xerogel by TGA-DSC

Characterisation of finely ground scandia xerogels by TGA in air and DSC in N$_2$ and air were carried out with a DuPont 2000 apparatus. The theory of this technique is described in Annexe A-5. The TGA profile on Figure II-10 suggested that, after vacuum-drying at 373K, scandia xerogel contained 27% w/w ACAC that could be thermally decomposed at 750K without significant polymorphic transformation. This weight loss suggested that the vacuum-dried compound had the formula ScO$_x$(OH)$_y$(ACAC)$_{0.27}$ (where $2x+y=2.73$).
Endotherms were seen in DSC at 350K and may have been related to desorption of water. Exotherms at 600 -800K under air suggested that oxidation-decomposition of ACAC ligands was then occurring.

![TGA-DSC plots obtained with a scandia xerogel predried at 373K: (TGA in air (a), DSC in air (b), DSC in N$_2$ (c)).](image)

**Figure II-10:** TGA-DSC plots obtained with a scandia xerogel predried at 373K: (TGA in air (a), DSC in air (b), DSC in N$_2$ (c)).

Such thermal analysis confirmed the results of elementary analysis, presented in II-2-10 (where the same xerogel was analysed to be ScO$_{0.55}$(OH)$_{1.66}$(ACAC)$_{0.25}$).

**II-2-8 Characterisation of Scandia Xerogels by XRD**

XRD was applied to finely ground samples of pure scandia xerogels using a PW1710 equipment with the following conditions: Source anode = Cu K$_\alpha_1$ (i.e. $\lambda$=0.1541nm), counting time = 10s and step size = 0.05° between $2\theta$ = 3° and between $2\theta$ = 60°. The technique is detailed in Annexe A-6. X-ray diffraction patterns are given in Figure II-11 (for xerogels dried at 373K, and heated at 523, 693, 773, and 973K).
Figure II-11: XRD patterns obtained for scandia xerogels pre-dried at 373K (a), and heated at 533K (b), 773K (c), 973K (d). (e) corresponds to commercial Sc$_2$O$_3$ reference.

Diffraction patterns for the scandia xerogel finely ground and dried at 373K exhibited no peak, suggesting that the particles were amorphous despite their lozenge morphology. Low intensity diffraction peaks started to appear after heating at 533K. Xerogels heated at 773K and above for 1h exhibited diffraction peaks that could all be attributed to inter-planar distances in cubic scandia with the correct relative intensities, but with a decreased broadening when heated at 973K. As a result, scandia-based lozenge-shaped particles were amorphous because of their nanometric size but had condensed with a preferred orientation. Their crystallinity increased with ACAC decomposition. The relative intensities of the diffraction peaks are given in Table II-4. Intensities of the highest peak and the background are also reported. Peaks for commercial Sc$_2$O$_3$ and heated xerogels corresponded to cubic scandia data reported in literature [38].
Table II-4: Relative intensities, d spacing and Miller indices attribution of diffraction peaks obtained for commercial Sc₂O₃ and scandia xerogels heated at 373K, 533K, 773K and 973K.

<table>
<thead>
<tr>
<th>d(hkl) (nm)</th>
<th>Miller indices (h, k, l)</th>
<th>Relative intensities I/Iₘₐₓ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sc₂O₃ ref</td>
</tr>
<tr>
<td>0.4020</td>
<td>211</td>
<td>30</td>
</tr>
<tr>
<td>0.2844</td>
<td>222</td>
<td>100</td>
</tr>
<tr>
<td>0.2464</td>
<td>400</td>
<td>25</td>
</tr>
<tr>
<td>0.2324</td>
<td>411</td>
<td>10</td>
</tr>
<tr>
<td>0.2099</td>
<td>332</td>
<td>30</td>
</tr>
<tr>
<td>0.1931</td>
<td>510</td>
<td>20</td>
</tr>
<tr>
<td>0.1790</td>
<td>521</td>
<td>10</td>
</tr>
<tr>
<td>0.1742</td>
<td>440</td>
<td>80</td>
</tr>
<tr>
<td>0.1598</td>
<td>611</td>
<td>15</td>
</tr>
<tr>
<td>Highest intensity (cps)</td>
<td></td>
<td>130</td>
</tr>
<tr>
<td>Background intensity (cps)</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

Figure II-12: TEM micrograph of scandium-based lozenge-shaped platelet particles after heating at 773K for 5h (x300 000; 1cm = 33nm).

In Figure II-12 the TEM image shows particles that have been heated at 773K and then dispersed in ethanol. These particles have retained their flat lozenge morphology during
the decomposition of organics at 773K. This observation and the XRD investigation confirmed that recrystallisation to cubic scandia occurred gradually without changing the initial lozenge morphology of scandia particles. In theory, for non-spherical particles (e.g. rod-like or platelet particles), XRD patterns can show preferred orientations in terms of comparing intensities of diffraction peaks. Unfortunately too many factors interact with planar diffraction, and calculation of the particle dimensions from peak widths (as described in Annexe A-7) do not lead to accurate and exploitable results. In the present scandia xerogel case, the four main cubic scandia peaks, (corresponding to the Miller indices 211, 222, 332, 440) appearing at 573K, showed broad diffraction, suggesting that the particles had small average size. On the other hand, a more accurate analysis of the scandia particle morphology has been obtained by TEM and SAXS for particles in their primary MOE solution (see part II-2-5).

II-2-9 Characterisation of Scandia Xerogel by N₂-BET

N₂ adsorption-desorption at 77K was investigated for scandia xerogels pre-heated at 773K for 1h. It was performed on a (0.200g) sample with a Micromeritics ASAP 2010 apparatus after outgassing in situ at 573K.

![N₂-adsorption-desorption isotherm at 77.5K for a scandia xerogel pre-heated at 773K for 1h.](image)
Data were analysed by application of BET theory (see Annexe A-9). The N₂ adsorption-desorption isotherm obtained is shown in Figure II-13. It was of type-IV with a capillary condensation hysteresis loop, suggesting that the scandia xerogel heated at 773K was mesoporous. The total BET surface area was estimated in Figure II-14 to be 129.7 m²/g, while the Langmuir surface to area plot in Figure II-15 gave 181.8 m²/g. In this latter method, surface area measurement assumes that adsorption is limited to a monolayer (see Annexe A-9).

\[ \frac{I}{(V_a p_0(p-1))} \]

\[ p/p_0 \]

Figure II-14: BET plot obtained for a scandia xerogel pre-heated at 773K for 1h.

\[ \frac{p}{(V_m p_0)} \]

\[ p/p_0 \]

Figure II-15: Langmuir plot obtained for a scandia xerogel pre-heated 1h at 773K.
The desorption cumulative pore volume of pores was estimated at 0.14 cm$^3$/g and the desorption average pore diameter was given to be 3.6nm. The pore volume distribution is given in Figure II-16 in terms of pore volume (cm$^3$/g) versus pore diameter (nm).

![Graph of desorption cumulative pore volume](image)

*Figure II-16: Desorption (dV/dD) pore volume distribution obtained for a scandia xerogel pre-heated at 773K for 1h.*

The pore volume of 0.14cm$^3$/g suggested that the particles organised themselves into a dense structure. Also, bulk sample presented an interesting high surface area. Therefore this scandia xerogel could make a good material to be used for optical and catalysis applications.

**II-2-10 Influence of Refluxing Time and Water Content on the Scandia Particle Composition. Measured by Elemental Analysis.**

The influence of longer refluxing (thermohydrolysis) times and higher water contents on the particle composition was now investigated. This also was to give an idea of the relative importance of different mechanisms involved in the particle formation (i.e. exchange and condensation). Only reactions (1), (2) and (3) below were considered to occur in the sol-gel processing:
**Chapter II The Sol-Gel Chemistry of Scandia**

\[
\text{Sc(ACAC)}_3 + r \text{H}_2\text{O} \rightarrow \text{Sc(ACAC)}_{(3-r)}(\text{OH})_r + r \text{HACAC} \quad (1)
\]

Exchange (hydrolysis)

\[
=\text{Sc(OH)} + (\text{OH})\text{Sc}= \rightarrow =\text{Sc(OH)}_2\text{Sc}=
\]

Condensation by olation (formation of \(2(\text{OH})_2\) bridges)

\[
=\text{Sc(OH)} + (\text{OH})\text{Sc}= \rightarrow =\text{Sc-O-Sc}= +\text{H}_2\text{O} \quad (3)
\]

Condensation by oxolation (formation of \(2(\text{O})_1\) bridge)

Reaction (1) is an exchange reaction (i.e. nucleophilic substitution mechanism concerted or non concerted) that is favour at high temperature and when the concentration of water is high. Reaction (2) occurs when the coordination sphere of the scandium trivalent ion is not fulfilled to its maximum coordination number of 6. It is a concerted substitution reaction that follows the \(\text{SN}_2\) mechanism. Reaction (3) can take place as soon as \text{Sc(ACAC)}_3 is hydrolysed. This later is in competition with reaction (2). Therefore (3) is favour when the coordination sphere of \text{Sc}^{\text{III}} is completed.

The following scandia sol samples (i.e. from A to M) were prepared via the experimental procedure described in section II-2-2. Water ratio to \text{Sc}^{\text{III}} (r) and reflux time (t) were varied in the ranges \(2<r<50\) and \(10\text{min}<t<7\text{h}\). Sols were then (i) left a few days to allow the solvent to totally evaporate and (ii) were vacuum-dried at \(398\text{K}\) for \(12\text{h}\) to remove the remaining adsorbed water and solvent.

Elementary analysis was performed at around \(2000\text{K}\) by a CE440 Elemental analyser from Leeman Labs INC on these xerogel samples twice. At this temperature, xerogels were expected to transform into pure \text{Sc}_2\text{O}_3 and every C and H atoms released were expected to be detected by the analyser. Assuming the particles have the formula \(\text{ScO}_x(\text{OH})_y(\text{ACAC})_z\) (see TGA and FTIR investigation), one can deduce \(x, y\) and \(z\) from the mean weight percentages of C \((v)\) and H \((u)\) atoms found in each sample. These are listed in Table II-5 and errors of \(\pm 0.06\) for \(x\), \(\pm 0.12\) for \(y\) and \(\pm 0.02\) for \(z\) were thought to be relevant.
Table II-5: Conditions of formation and compositions deduced for scandia-based particles.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ratio of water: (r)</th>
<th>Refluxing time t (h-min)</th>
<th>C (%/w): (v)</th>
<th>H (%/w): (u)</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50</td>
<td>0h-15’</td>
<td>17.45</td>
<td>3.78</td>
<td>0.29</td>
<td>2.08</td>
<td>0.35</td>
</tr>
<tr>
<td>B</td>
<td>50</td>
<td>0h-30’</td>
<td>13.66</td>
<td>3.35</td>
<td>0.42</td>
<td>1.91</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>0h-58’</td>
<td>12.55</td>
<td>3.14</td>
<td>0.51</td>
<td>1.76</td>
<td>0.22</td>
</tr>
<tr>
<td>D</td>
<td>50</td>
<td>4h-06’</td>
<td>8.49</td>
<td>2.70</td>
<td>0.61</td>
<td>1.65</td>
<td>0.14</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>0h-10’</td>
<td>38.93</td>
<td>5.24</td>
<td>0.16</td>
<td>1.39</td>
<td>1.29</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>0h-45’</td>
<td>15.13</td>
<td>3.34</td>
<td>0.50</td>
<td>1.73</td>
<td>0.28</td>
</tr>
<tr>
<td>G</td>
<td>20</td>
<td>3h-10’</td>
<td>11.18</td>
<td>2.88</td>
<td>0.62</td>
<td>1.58</td>
<td>0.19</td>
</tr>
<tr>
<td>H</td>
<td>20</td>
<td>7h-00’</td>
<td>7.50</td>
<td>2.28</td>
<td>0.80</td>
<td>1.28</td>
<td>0.11</td>
</tr>
<tr>
<td>I</td>
<td>4</td>
<td>0h-30’</td>
<td>24.06</td>
<td>3.95</td>
<td>0.50</td>
<td>1.48</td>
<td>0.52</td>
</tr>
<tr>
<td>J</td>
<td>4</td>
<td>1h-26’</td>
<td>14.93</td>
<td>3.27</td>
<td>0.54</td>
<td>1.66</td>
<td>0.27</td>
</tr>
<tr>
<td>K</td>
<td>4</td>
<td>4h-53’</td>
<td>13.90</td>
<td>3.18</td>
<td>0.55</td>
<td>1.66</td>
<td>0.25</td>
</tr>
<tr>
<td>L</td>
<td>4</td>
<td>8h-53’</td>
<td>5.97</td>
<td>1.97</td>
<td>0.90</td>
<td>1.11</td>
<td>0.09</td>
</tr>
<tr>
<td>M</td>
<td>2</td>
<td>20h-00’</td>
<td>19.15</td>
<td>3.55</td>
<td>0.55</td>
<td>1.54</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Figures II-17, II-18 and II-19 show the evolution with refluxing time of calculated x, y and z values at different level of water addition. At time t=0, x=0, y=0 and z=3.

For a water ratio r=50 (see Figure II-17), the appearance of the colloidal particles started after 15min refluxing. The number of ACAC coordinating Sc\textsuperscript{III} (z) decreased very rapidly until the value of 0.35 and then continued to decrease but at a much slower rate until 0.25. After the same period, the number of hydroxy group coordinating Sc\textsuperscript{III} (y) was deduced to reach 2.08 suggesting that the first 2.65 ACAC groups were easily exchanged by OH\textsuperscript{-} via reaction (1). Oxo group contents (x) increased rapidly with the loss of hydroxy groups (due to the olation-condensation of hydroxo intermediates (3)). After 60min reflux, stabilisation of x, y and z started to appear while large aggregates started to precipitate. Rates of exchange and condensation decreased as a result of the particle growth.
Figure II-17: Evolution of $x$, $y$ and $z$ with refluxing time for $r=50$.

Figure II-18: Evolution of $x$, $y$ and $z$ with refluxing time for $r=20$.

Figure II-19: Evolution of $x$, $y$ and $z$ with refluxing time for $r=4$. 
For such a high ratio \((r)\) of water, the hydrolysis and condensation process were fast and difficult to control and separate.

When a water ratio \(r=20\) was used (see Figure II-18), appearance of particles was noticed after refluxing for 45 min, and flocculation occurred after prolonging the thermohydrolysis to 3 h. The exchange of ACAC ligands by hydroxy groups (reaction (1)) was still the first reaction to take place. However, the rate was slower than previously with \(r=20\), although 2.75 ACAC were exchanged after 45 min refluxing. Also, at 45 min, \(y\) value was maximum (1.73). In the same earlier period, \(x\) increased rapidly before its progression slowed down. This suggests that condensation by oxolation (reaction (3)) occurred as soon as the hydrolysis took place. After 45 min \(y\) decreased due to the disappearance of OH groups via oxolation. Therefore, as expected with a lower water concentration, the reaction rates were slower than with \(r=50\) but still too fast to allow a good control on the mechanism steps.

At \(r=4\) (see Figure II-19), same comments as with \(r=20\) could be made, except that hydrolysis-condensation rates were slower. Particles started to appear after 90 min refluxing and flocculation occurred after 9 h. The maximum number of OH groups coordinating Sc\(^{III}\) \((y)\) was measured to be \(y=1.75\) after about 3 h refluxing.

One can notice that for each \(r\) value, \(z\) decreased very rapidly up to a value of 0.25 and then decreased more slowly. Also, as soon as water was added to the solutions, the hydroxy ratio \((y)\) were deduced to be high and the oxo ratio \((x)\) increased instantly to values close to 0.5. These observations suggested that hydrolysis (reaction (1)) took place as soon as water was introduced into the systems. Then, condensation by olation (reaction (3)) occurred as soon as OH groups were in the coordination sphere of Sc\(^{III}\). Condensation by olation (reaction (2)) could not be followed here, but it was supposed to occur throughout the process when intermediates with non-fulfilled coordination number were formed \((N<6)\). After \(y\) had reached its maximum, condensation still occurred between species in solution but with a faster rate for lower water contents. No large particles (offering less reactive surfaces) were formed for lower \(r\) values. On the other hand, decreasing the water content led to the slowing down of hydrolysis and
condensation reactions allowing a better control on the particle stability. TEM analysis of the particles taken between their times of appearance and flocculation showed the characteristic lozenge-platelet shape (see Figure II-3). However, the use of a low ratio of water (i.e. \( r=4 \)) led to particles with a lower content of ACAC and OH and a higher content of oxo bridges suggesting higher level of condensation. The presence of OH groups may be related to hydroxy bridges (Sc-OH-Sc) formed by olation (reaction (2)) throughout the process. The remaining ACAC ligands were not chelating Sc\(^{\text{III}}\) any more (see FTIR investigation). Rather they were bound at the particle surfaces as shown in the model proposed in the following part.

### II-3 Discussion and Proposed Mechanism of Formation of Scandia Lozenge Particles

The advantage of using MOE as a medium lies in its solvating properties due to its high dipole moment (i.e. \( d=2.36\text{D} \)), in addition to its high refluxing temperature (i.e. 398K). The activation energy of the substitution decreases when increasing the temperature due to thermal energy brought to the system. Therefore the high temperature (allowed by the MOE high boiling point) was required to break the highly stable aromatic rings formed by the chelation of Sc\(^{\text{III}}\) with ACAC. By breaking the chelation, the coordination number of the scandium ion decreased from 6 to 5 allowing for the attack of an entering group (e.g. OH\(^{-} \)). The first step of the sol-gel process (hydrolysis-substitution) could then occur.

Scandia sols produced at \( r=4 \) and \( t=5\text{h} \) were stable for more than three months. No gelation was observed as long as the solvent was not evaporated. FTIR suggested that the ACAC ligands were not totally removed and were bound to the scandium as unidentate groups. Elementary analysis and TGA/DSC suggested that the final particles were best represented as ScO\(_{0.55}\)(OH)\(_{1.66}\)(ACAC)\(_{0.25}\). ACAC thermal decomposition (which was exothermic in air) started at 650K and finished at 770K [17].

Scandium is hexa-coordinate, and the three pentandionate ligands fulfil its coordination sphere thereby stabilising the complex. Hydrolysis occurs via concerted or non-concerted SN mechanisms, after the opening of the ACAC ring, via attack of an hydroxy group and
departure of the ACAC (see equation (1)). The removal of ACAC ligands is the limiting step, but is favoured by thermohydrolysis at the refluxing temperature of MOE. One could believe that pre-condensation occurs by olation, because of the uncompleted coordination sphere of the first intermediate Sc(OH)(ACAC)$_2$. The stability of the remaining ACAC bound to Sc$^{III}$ leads to an anisotropic condensation process. This polymerisation process occurs via olation and oxolation. Olation between Sc(OH)(ACAC)$_2$ is favourable in one direction leading to chains (see equation (2) and (3)). Then oxolation in the second direction occurs between chains, because of the full coordination existing in these intermediates (see equation (4)). Thin platelet particles of scandium oxy-hydroxy-ACAC are thus formed. Afterward the growth of the particles occurs by olation at the ends of the chains or by oxolation on their middle. The pentanedionate ligands are proposed to be bound to the apex of the octahedral units on each face of the platelets, blocking these sites and slowing down the potential condensation on the platelet faces. Elementary analysis has shown that condensation by oxolation and olation occurs simultaneously as soon as Sc(ACAC)$_3$ is hydrolysed. The relative rates of these reactions (and the steric hindrance created by the presence of the ACAC in addition to its poor leaving properties) lead to the formation of lozenge platelets. Therefore the mechanism of formation of these scandia based particles is proposed below and in Figure II-20.

\[
\text{Sc(ACAC)}_3 + \text{OH}^+ \cdot \text{H} + \Delta \rightarrow \text{Sc(OH)(ACAC)}_2 + \text{ACACH}
\]

(1)

\[
2\text{Sc(OH)(ACAC)}_2 \rightarrow (\text{ACAC})_2\text{Sc(OH)}_2\text{Sc(ACAC)}_2 - (\text{H}_2\text{O}) \rightarrow \text{Sc}_2(\text{OH})_3(\text{ACAC})_3 + \text{ACACH}
\]

(2)

\[
\text{Sc}_2(\text{OH})_3(\text{ACAC})_3 + (n-2)[\text{Sc(OH)(ACAC)}_2 ] + (n-3)\text{H}_2\text{O} \rightarrow \text{Sc}_n(\text{OH})_{2n-2}(\text{ACAC})_{n+2} + (n-3)\text{ACACH}
\]

(3)

\[
r[\text{Sc}_n(\text{OH})_{2n-2}(\text{ACAC})_{n+2} ] \rightarrow \text{ScO}_x(\text{OH})_y(\text{ACAC})_z \text{ (platelets form) + H}_2\text{O}
\]

(4)

where $x=0.55$, $y=1.66$ and $z=0.25$ at $r=4$ $t=5h$. 

\[
\text{Sc(OH)(ACAC)}_2 + \text{ACACH} \rightarrow \text{ScO}_x(\text{OH})_y(\text{ACAC})_z + \text{ACACH}
\]

(5)
The bulk material obtained by vacuum evaporation at 350K is XRD amorphous. Treatment at 773K does not change the morphology of the platelets, suggesting that the xerogel is thermally stable. However, the crystallinity of the particles increased gradually with thermal treatment. The recrystallisation of ScOOH to cubic Sc$_2$O$_3$ occurs at 673 - 873K (as recorded from Sc(OH)$_3$ formed in aqueous medium [35,36,23]). In the present case, the transformation from ScO$_{0.55}$(OH)$_{1.66}$(ACAC)$_{0.25}$ to cubic Sc$_2$O$_3$ is progressive and the morphology of the particles is lost if thermally treated at 973K.

Figure II-20: Proposed mechanism for the formation of scandia as lozenge-shaped platelet particles. Circular arcs represent chelating ACAC. Monodendate ACAC are represented by straight lines bound to the apex of the octagonal units.
The high surface area (i.e. 128-182 m²/g) suggests that sol-gel scandia could be interesting in a catalytic sense. Its dense xerogel could find application as high index optical coating.

Similar lozenge shapes have been produced by sol-gel polycondensation to Y₂O₃ [34] and by thermohydrolysis of chelated oxy-hydroxy-iron precursors [38]. The condensation with preferred orientation of precursor and intermediates led to the present scandia sol particles of flat lozenge shape. These plate-shaped particles may organise themselves in a preferred horizontal orientation on a surface upon deposition.

II-4 Sol-Gel Processing of Sc₂O₃ (extension of the chemical investigation)

In order to understand the chemistry of scandium ACAC and to manage the synthesis of scandia particles, investigations were undertaken with different conditions. These were acid, base and neutrally-catalysed routes and are now briefly described.

II-4-1 Acid Catalysis

The final oxide must exhibit a high UV transparency at 351 nm. Common inorganic acids such as HCl or H₂NO₃ were unsuitable because of their UV absorption. Therefore the use of ethanoic acid (i.e. CH₃COOH, with its π-π* electronic transition at λₘₐₓ=210 nm and absorption coefficient ε=40 mol⁻¹.dm³.cm⁻¹) as a proton source for the hydrolysis-condensation catalysis was investigated.

Generally the use of acid increases the rate of the hydrolysis by favouring proton exchange. H⁺ attack the oxygen bridging the organic ligand with the metal. This addition increases the partial charge of the bonding O, increasing the lability of the ligand. However, in the present case, acetate ions were formed after dissociation of ethanoic acid and reacted directly with the Sc^{III} to form scandium-acetate chelating
bonds. This substitution could be deduced from the characteristic FTIR metal-acetate absorption bands. The absorption at 1450 cm\(^{-1}\) corresponds to \(\nu(CO_2^-)\) symmetric stretching while the absorption at 1550 cm\(^{-1}\) corresponds to \(\nu(CO_2^-)\) antisymmetric vibration (see Table II-3). The energy difference \(\Delta \nu\) of 100 cm\(^{-1}\) did not permit the author to determine if the acetate was actually chelating one scandium atom or bridging two. The mechanisms for the acid catalysis are as proposed below.

\[
\text{CH}_3\text{COOH} + \text{ROH} \rightarrow \text{CH}_3\text{COOR} + \text{H}_2\text{O} \quad \text{esterification (1)}
\]

\[
\begin{align*}
\text{CH}_3\text{COOH} & \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \\
\text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{H}^+
\end{align*} \quad \text{dissociation (2) and (2')}
\]

\[
\text{Sc(ACAC)}_3 + x\text{CH}_3\text{COOH} + y\text{H}_2\text{O} \rightarrow \text{Sc(ACAC)}_{(3-x-y)}(\text{OCOCH}_3)_x(\text{OH})_y + (x+y)\text{H}^+ \\
+ (x+y)\text{ACAC}^- \quad \text{Hydrolysis and substitution by acetate (3)}
\]

Ethanoic acid not only catalysed the hydrolysis rate of the scandium ACAC precursor, but also acted as a chelating agent. This chelation enhanced the stability of the hydroxy intermediate quenching further potential hydrolysis. \(x\) and \(y\) depended on the relative amount and ratio of acid and water added in the system. The condensation mechanism is given by the following reaction (4).

\[
2\text{Sc(ACAC)}_{(3-x-y)}(\text{OCOCH}_3)_x(\text{OH})_y \rightarrow \text{Sc}_2(\text{OH})_2(\text{ACAC})_{2(3-x-y)}(\text{OCOCH}_3)_{2x}(\text{OH})_{2(y-1)} \quad \text{Condensation by olation (4)}
\]

Hydrolysis of the precursor is thought to produce a penta-coordinated complex. Olation was then the most favourable condensation process, because of the uncompleted coordination of the central Sc\(^{\text{III}}\) ion and because of low ligand lability (i.e. \(\delta(O)<0\)). Oligomers of low molecular complexity were supposedly formed through these mechanisms. In addition to the high stabilisation of these oligomers by the acetate and ACAC ligands, they often presented low solubility in alcohol. As a result, the
polycondensation to scandium oxihydroxide colloidal sols suitable for optical coatings could not be reached.

Figure II-21: TEM micrograph of scandium-based particles containing acetate and ACAC ligands. These were obtained in methanol with the following conditions: Conc. $Sc^{III}=0.1M$, Conc. $H_2O=1M$, Conc. $EtCO_2H=0.3M$, aged for 8 days, ($\times50000;1\text{cm}=200\text{nm}$).

Figure II-22: TEM micrograph of scandium-based particles containing acetate and ACAC. These were obtained in methoxyethanol with the following conditions: Conc. $Sc^{III}=0.075M$, Conc. $H_2O=0.15M$, Conc. $EtCO_2H=0.375M$, aged for 1 day, ($\times50000;1\text{cm}=200\text{nm}$).
Interesting particle shapes were obtained by anisotropic condensation in presence of ethanoic acid in other alcoholic solvents (precipitates) (see Figures II-21 and II-22). Controlled hydrolysis of Sc(ACAC)$_3$ catalysed by ethanoic acid in methanol led to formation of a scandium hydroxy-acetyl-acetylacetonate compounds in a flat lozenge shape. The plane structure of the scandium based solid-phases shown in TEM micrographs suggested that the polycondensation of the precursors is favoured and organised in two directions. $a$ corresponds to the ratio of ethanoic acid to Sc$^{III}$. 

II-4-2  Base Catalysis

It has seen in chapter I that, generally, basic conditions produce strong nucleophilic species via deprotonation (e.g. OH$^-$, RO$^-$ and MO$^-$). Therefore nucleophilic attacks of OH$^-$ and MO$^-$ are favourable and results in increasing the rate of hydrolysis and condensation relatively. Furthermore, the attack of such strong nucleophiles on the metal can favour the departure of a generally poor leaving group by SN$_2$. Usually fast hydrolysis and fast condensation, created by basic condition, often lead to precipitates

Figure II-23: TEM micrograph of scandium-based particles. These were obtained in methanol with the following conditions: Conc. Sc$^{III}$=0.1M, Conc. $H_2O$=1M, Conc. $NH_3$=0.5M, aged for 2days, ($\times$100 000; 1cm=100nm).
FTIR spectra of NH$_3$ catalysed precipitates showed the characteristic absorption bands of ScOOH. In addition, the characteristic bands of acetylacetonate ligands chelating Sc$_{III}$ at 1525 and 1585 cm$^{-1}$ corresponding to C=C and C=O stretching are considerably diminished. An additional band corresponding to free C=O stretching at 1700 cm$^{-1}$ started to appear. This suggested that some of the ACAC were not bonded to the Sc$_{III}$ any more as bidentate ligands but were monodentate. The TEM image of precipitated particles (see Figure II-23) showed that this had an interesting foil-like structure, suggesting a two-directional favoured condensation. $b$ corresponds to the ratio of NH$_3$ to Sc$_{III}$. A mechanism for the basic catalysis may be as proposed below.

$$
H_2O + NH_3 = OH^- + NH_4^+ \quad \text{dissociation (1)}
$$

$$
Sc(ACAC)_3 + OH^- \rightarrow Sc(ACAC)_2(OH) + ACACH \quad \text{hydrolysis, exchange (2)}
$$

$$
2Sc(ACAC)_2(OH) \rightarrow (ACAC)_2Sc(OH)_2Sc(ACAC)_2 \quad \text{condensation by olation (3)}
$$

$$
\rightarrow \rightarrow ScO_x(OH)_y(ACAC)_{0.15} \quad \text{with } 2x+y=2.85, \text{condensed species.}
$$

Condensation occurred by olation for the same reasons as described for the acid routes (i.e. uncompleted coordination of the central Sc$_{III}$ ion and low ligand lability (i.e. $\delta(O)<0$)). Hydrolysis-condensation of Sc(ACAC)$_3$ in a basic medium produced scandium oxyhydroxide compounds. Unfortunately, reaction rates could not be controlled and precipitation and flocculation occurred leading to materials unsuitable to be used for sol-gel coatings.

**II-5 Conclusions on Scandia Sol-Gel Chemistry**

Hydrolysis-condensation of Sc(ACAC)$_3$ is a slow process because good stabilising ligands are present completely coordinating the metal. The use of scandium acetylacetonate as a precursor to the scandia colloidal particles was successful.
Neutral methoxyethanol (MOE) seemed to be a better medium for this because of its greater nucleophilic properties and its higher refluxing temperature favouring hydrolysis and condensation. Sols containing lozenge-platelet particles of scandia were produced in neutral MOE. This totally new method allows the formation of scandia sols that are suitable to be used for optical coating. ACAC ligands were removed by thermal decomposition at 773K or propane-1-ol extraction at 368K.

The first route to the synthesis of stable colloidal nanoparticles of scandia in an alcoholic medium has been developed and is now well understood. Particles, sols and xerogels have been characterised. The use of the sol to produce optical coatings by dip-coating will be explored in the following chapters.

Ethanoic acid was not suitable for sol-gel chemistry because it led to the formation of acetate groups, which are even less reactive and less soluble in alcohol. Basic conditions did increase the rate of the reactions, but prevented any control of them. Hence NH$_3$ catalysis led to scandium oxy-hydroxy-ACAC precipitates. Acid and base catalysts produced materials that were unsuitable for coating process. However interesting scandium-based particles of different morphologies were synthesised in different mediums at various conditions: All presented flat structures, as a result of condensations which were more favourable in two directions.

The main problem encountered with the chemistry of scandium pentanenedionate was its high prise (i.e. 10g of precursor, containing 1g Sc$^{III}$ was ~ £500). This meant the manipulation of very low quantity of material and solution, which is acceptable in a chemical laboratory or specific applications, but possibly not in production lines.

References

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[38] Swanson and Fuyat, *NBS Circular 539*, 3, (1953).
Chapter III

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Chapter III

The Sol-Gel Chemistry of Hafnia

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III-1  **Hafnium Oxide**

III-1-1  **Interesting Properties**

Hafnium is the second of the 5d-block elements and its outer shell configuration is \(4f^{14} 5d^2 6s^2\) (atomic number 72). The ionic radius of Hf\(^{IV}\) is 0.078nm. It has an oxidation state of 4 and its oxide (Hf\(_2\)O\(_2\)) is physically and chemically similar to zirconia [1]. It possesses a high melting point (i.e. near 3000K) and a good chemical stability. Its high refractive index (i.e. \(1.5 < n_H < 2.4\)) [2], its large band gap (i.e. 5.51eV), and its UV cut-off at 225nm make Hf\(_2\)O\(_2\) a good material for HR mirrors [3,4,2]. It will be seen that, despite its high price, it is of interest in other areas (e.g. catalysis, thermal resistant ceramics, paint industry, ...etc).

HfO\(_2\) is monoclinic \((a=0.511\text{nm}, b=0.517\text{nm}, c=0.529\text{nm} \text{ and } \beta=99^\circ11')\) at room temperature and transforms to tetragonal \((a=0.514\text{nm}, c=0.525\text{nm})\) at 1900K [1]. Further heating to 2950K leads to a transformation to a cubic structure [5,6]. In theory, the advantages of hafnia over zirconia are that Hf\(_2\)O\(_2\) does not undergo a transformation at moderate temperature and it has a lower expansion coefficient [7]. However, it will be shown that the transformation of amorphous hafnia (obtained from sol-gel chemistry) to monoclinic structure takes place at low temperature (i.e. 700K) and may also undergo unsuitable macroscopic changes.

Hafnia high refractive optical layers for high-power laser components have already been produced via vacuum deposition [8,9], electron beam evaporation [10], and liquid deposition [3,4]. Damage sites, created within these hafnium oxide coatings when radiated with a 1\(\omega\) laser, occurred via cumulative damaging effect [10], suggesting absorption possibly induced by impurities situated at the film/substrate interface. HfO\(_2\) was not the best candidate to be used at 1064nm (i.e. 1\(\omega\)), other material such as alumina presented better laser damage resistance. However hafnia is now considered to be used at 351nm (i.e. 3\(\omega\)) [8].
III-1-2 General Chemistry

Like most transition metals, hafnium can be obtained under stable salts such as chloride and oxychloreide, but also as organometallic oligomers (e.g. Hf(OEt)$_4$, Hf(OPr)$_4$, ...etc). Also, hafnium compounds are very hygroscopic and must be handled and stocked in inert gases. Condensation to HfO$_2$ leads to a white powder (if the oxidation is total) and to a black compound (if the oxidation is uncompleted). Monoclinic microcrystalline powders containing 0.8μm in size particles of hafnia can be prepared by precipitation of hafnium hydroxide from hafnium oxychloride in a solution of NaOH [7]. The dried solid has a high surface area that is reduced by densification at 973K. The chemical resistance of hafnia to basic condition [11] includes insolubility in NaOH solutions up to 2mol dm$^{-3}$ NaOH.

Hafnium sol-gel chemistry has been extensively studied and colloidal particles of different size and shape can be synthesised from organic and inorganic precursors. Elongated colloidal submicron-particles of hafnia can be obtained from HfCl$_4$ in aqueous solution upon thermohydrolysis [12]. These were composed of aggregates of polycrystalline nanoparticles. The same authors also reported a way of processing uniform spherical particles by calcination at 1173K of hafnium hydroxy-sulfate particles (these intermediate particles were previously synthesised from HfOCl in aqueous medium) [13]. The same authors have also reported a method of producing spherical amorphous hafnia particles from hafnium butoxide in an aerosol phase [14]. The shapes and sizes of these uniform micro and nanoparticles depended on the conditions applied to the hydrolysis-condensation process and on the nature of the counter-ion [15]. The synthesis of spherical colloidal nanoparticles of hafnium oxide (suitable for optical coating [4] or for modifying the surface properties of a core material [16]) can be synthesised in aqueous medium from hafnium oxychloride [17]. The sol-gel formation of nanometric particles of hafnia can also take place in organic solvents. Processing of alcoholic hafnia sols from alkoxide precursors is commonly used to produce highly porous gels or very thin optical coatings [18,19]. As alkoxide are very reactive toward nucleophile substitution, it is often essential that the reaction takes place in the presence of a stabilising agent such as ethanoic acid or ACAC.
III-1-3 Fields of Application

It is well known that ZrO₂ and HfO₂ are completely miscible in all proportions as binary oxides. HfO₂-TiO₂ system can be prepared [20] and, at 60 - 70% HfO₂, it is a near-zero thermal expansion material. If sintered at 1773K, it has the characteristic of an ultra refractory ceramic. More recently HfO₂ combined with Y₂O₃ has been studied as a material for nuclear applications and its solid neutron absorber property makes it a good material to be used as control rods or neutron shielding [11]. The incorporation of Y₂O₃ (or CaO or MgO or Nd₂O₃, etc [6]) in the monoclinic structure of HfO₂ allows the avoidance of the destructive transformation to tetragonal phase, but the direct formation of a stable cubic crystalline phase [5]. This latter is commonly called “stabilised HfO₂” or “fluoride phase” (because of its similarity with the mineral fluorite). HfO₂ is a good candidate for optical use at 351nm (i.e. 3ω laser), and can be prepared by several methods [21,4,8]. It is also of interest in catalysis, ceramics, and paint industries [22,23,12,13].

III-2 Sol-Gel Processing of HfO₂ from a Hf(OPr)₄ Precursor

Several tetravalent hafnium alkoxides are available as precursors for the formation of HfO₂ colloidal particles in alcohols. The rate of hydrolysis-condensation decreases with the size of the alkoxide group (see part I-5-5) due to increased steric hindrance and charge transition effect. The preparation of small hafnia particles requires a good control on the reaction rates difficult with highly reactive compounds. For the present work, hafnium n-propoxide (π-Chem, 99% pure, in propan-1-ol) was chosen to produce hafnia sols, xerogels and optical coatings, because of its higher stability towards nucleophilic substitution than hafnium ethoxide, and its high solubility in ethanol and propan-1-ol.

III-2-1 Introduction on Hafnium n-propoxide

In the present case, Hf⁴⁺ is surrounded by O atoms, and their radius are \( R_o = 0.078 \text{nm} \) for Hf⁴⁺ and \( R_o = 0.14 \text{nm} \) for \( O^2- \) [24]. Hence, according to Pauling (see part I-2-3), \( \rho = 0.55 \) suggested that Hf⁴⁺ is expected to be hexacoordinated in solution. In reality, its
coordination number is more often between 7 and 8. This is an important factor in the reactivity of precursors towards hydrolysis following an SN$_2$ mechanism. Molecular complexity increases with the atomic radius of the metal, but decreases with the size of the ligands. In Hf(OEt)$_4$, the covalent radii of Hf$^{IV}$ is 0.144nm and its molecular complexity is 3.6 [15]. n-Propoxide ligands are larger than OEt, therefore the molecular complexity of Hf(On-Pr)$_4$ is expected to be less than 3.6 at the same concentration. The charge distributions ($\delta$) have been calculated using the partial charge distribution model for both precursors in their monomeric state. The electronegativities ($\chi$) calculated from the Allred-Rochow values are given in Table III-1.

Table III-1: Partial charge distribution calculated for hafnium alkoxides.

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>$\chi$(Hf)</th>
<th>$\chi$(O)</th>
<th>$\chi$(C)</th>
<th>$\chi$(H)</th>
<th>$\chi$</th>
<th>$\delta$(Hf)</th>
<th>$\delta$(OR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf(Et)$_4$</td>
<td>1.36</td>
<td>3.5</td>
<td>2.5</td>
<td>2.1</td>
<td>2.30</td>
<td>0.59</td>
<td>-0.14</td>
</tr>
<tr>
<td>Hf(On-Pr)$_4$</td>
<td>1.36</td>
<td>3.5</td>
<td>2.5</td>
<td>2.1</td>
<td>2.28</td>
<td>0.58</td>
<td>-0.14</td>
</tr>
</tbody>
</table>

The calculation of the partial charges on O and Hf$^{IV}$ atoms does not take into account the molecular complexity and solvation by solvent molecules. Solvating by alcohol molecules takes place in solution to fulfill the potentially incomplete coordination sphere of Hf$^{IV}$. Therefore, it is very difficult to predict the relative reactivity of these precursors only from these charge values. However the attacking rate of entering groups and the leaving rate of ligands are expected to be slower with Hf(On-Pr)$_4$, because of the larger size of n-propoxide groups. The high value of $\delta$(Hf) suggests that the reaction rates would be high.

III-2-2 Experimental Synthesis of Spherical Hafnia Particles

In III-2-1 many sol-gel routes to colloidal HfO$_2$ were described. The method, developed now to produce homogeneous HfO$_2$ sol particles less than 5nm in diameter, was inspired by the route described by Larbot et al [18].

Hafnia sols were prepared from propan-1-ol solutions of hafnium n-propoxide (see Annex B-19) by hydrolysis under ethanoic acid conditions. The initial alkoxide solutions were first diluted to between 0.1 and 0.2M in anhydrous propan-1-ol in presence of ethanoic
acid (i.e. ratio $\text{CH}_3\text{CO}_2\text{H}/\text{Hf}^{IV}=f$). Hydrolysis took place at room temperature after addition of water (i.e. ratio $\text{H}_2\text{O}/\text{Hf}^{IV}=r$). Products were aged until the solutions presented a light bluish aspect that corresponded to the appearance of the particles. Table III-2 gives the gelation time ($T_g$) when the system stopped showing the characteristics of a fluid and the gel surfaces stood parallel to the bottom of the flask upon inclination.

Table III-2: Gelation times measured for hafnium n-propoxide solutions in propan-1-ol for different concentrations, hydrolysis ratios and ethanoic acid concentrations.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Acid/Hf$^{IV}$</th>
<th>Water/Hf$^{IV}$</th>
<th>Gelation time ($T_g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(f)</td>
<td>(r)</td>
<td>(h) (days)</td>
</tr>
<tr>
<td>0.2M</td>
<td>2</td>
<td>2</td>
<td>168</td>
</tr>
<tr>
<td>0.2M</td>
<td>2</td>
<td>3</td>
<td>0.75</td>
</tr>
<tr>
<td>0.2M</td>
<td>2</td>
<td>4</td>
<td>0.33</td>
</tr>
<tr>
<td>0.2M</td>
<td>3</td>
<td>3</td>
<td>120</td>
</tr>
<tr>
<td>0.2M</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>0.2M</td>
<td>4</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>0.1M</td>
<td>2</td>
<td>2</td>
<td>2280</td>
</tr>
<tr>
<td>0.1M</td>
<td>2</td>
<td>3</td>
<td>1440</td>
</tr>
<tr>
<td>0.1M</td>
<td>2</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>0.1M</td>
<td>3</td>
<td>3</td>
<td>1200</td>
</tr>
<tr>
<td>0.1M</td>
<td>3</td>
<td>4</td>
<td>360</td>
</tr>
<tr>
<td>0.1M</td>
<td>4</td>
<td>4</td>
<td>720</td>
</tr>
</tbody>
</table>

In order to be used at 351nm, a coating must have an optical thickness ($H$) of 88nm. For a coating with $n=1.5$, this corresponds to a physical thickness ($h$) of 67nm. Therefore, in order to obtain a better homogeneity (lower scattering), a coating has better being formed by 10 layers of 6.7nm particles than 2 layers of 34nm particles. The smaller are the particles the lower the scattering coefficient ($S$) is expected to be. Also, the processing of high reflective coatings requires very small particles leading to higher densities. The stability of the sol with time is also important because it is directly correlated with the reproducibility of the coating structure. Chemical and physical interactions, taking place between particles upon ageing, increase the viscosity of the sol, and during deposition,
porosity and refractive indices \((n)\) depend strongly on this factor. Therefore, the ideal sol would be formed of the smallest and most stable particles of hafnia that could be synthesised.

Table III-2 shows that the sols evolved quickly to the gels, and this evolution was faster for higher concentrations of the precursor and higher water contents \((r)\). On the other hand, the gelation time decreased when the concentration of ethanoic acid increased. It was also observed that the faster the gels formed, the more opaque they were, suggesting that rapid processes led to larger particles. The best compromise was thereby found for a precursor concentration of 0.2M, an \(r\)-value of 2, and an \(A\)-value of 2. The solution obtained with these conditions exhibited a slight bluish aspect after 48h of ageing suggesting that particles appeared after this period of time.

At this stage of hydrolysis and condensation (i.e. slight bluish aspect of the sol), polycondensation and aggregation of the particles to the gel were still very fast (i.e. 5 days). Hence, the process was quenched by further dilution to 0.1M with propan-1-ol and further addition of a ratio \(\text{CH}_3\text{CO}_2\text{H/Hf}^{IV}\) of 2. Sols were centrifuged to remove the bigger aggregates. Reproducible thin films had to be produced during a period of 3 weeks following the preparation in order to avoid changes of sol viscosity. During this period, the particle diameter remained <5nm.

Study of sols, produced from alcoholic solution of hafnium alkoxide via ethanoic acid catalysis, has shown that the viscosity of the sol remained stable and suddenly increases just before the gelation time [18]. This confirmed that gelation occurred by further condensation-aggregation of particles after a period of stability during which optical coating must be performed.

### III-2-3 Characterisation of Hafnia Particles by TEM

TEM micrograph in Figure III-1 shows \(\text{HfO}_2\) sol particles after having aged the sol for 2 weeks. Their compositions were obtained by X-ray probe analysis (see Figure III-2).
Figure III-1: TEM micrograph of spherical hafnia particles deposited on carbon-coated copper grids, (1cm=33nm, × 300 000).

HfO₂ particles appeared to be homogeneous and spherical, with an average diameter estimated at less than 5nm. The low accuracy of the present TEM image prevented the measurement of the exact particle size. X-ray probe analyses of TEM sample gave peaks at 1.65 KeV that corresponded to Hf M₄,₅, suggesting that the particles were rich in hafnium.

Figure III-2: X-ray probe energy dispersion for hafnia sol particles.
III-2-4  **Characterisation of Hafnia Xerogels by FTIR**

Hafnia xerogels were obtained by solvent evaporation at atmospheric pressure and temperature after keeping the sol sealed for 2 weeks. Xerogels were then vacuum dried at 373K before being analysed by FTIR as described in part II-2-6. Spectra (Figure III-3) exhibited broad vibration bands at 467, and 1050cm\(^{-1}\) that corresponded to Hf-O stretching. The broad band at 3400cm\(^{-1}\) corresponding to O-H stretching suggested that the precursor was partly hydrolysed. n-Propoxide ligands have not been fully exchanged by acetate or hydroxide groups as expressed by the absorption at 1027cm\(^{-1}\), corresponding to the stretching vibration of Hf-OR.

<table>
<thead>
<tr>
<th>Band (cm(^{-1}))</th>
<th>Attribution</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>(\gamma)(O-H) from M-OH</td>
<td>S, Broad</td>
</tr>
<tr>
<td>2936</td>
<td>(\gamma)(C-H) from organic</td>
<td>S, Sharp</td>
</tr>
<tr>
<td>1720</td>
<td>(\gamma)(C=O) from carbonate</td>
<td>S, Sharp</td>
</tr>
<tr>
<td>1555</td>
<td>(\gamma)(C-O) from CH(_3)COO(^{-}) symmetric</td>
<td>VS</td>
</tr>
<tr>
<td>1454</td>
<td>(\gamma)(C-O) from CH(_3)COO(^{-}) antisymmetric</td>
<td>VS</td>
</tr>
<tr>
<td>1417</td>
<td>(\delta)(CH) deformation</td>
<td>S</td>
</tr>
<tr>
<td>1337</td>
<td>(\delta)(CH) deformation</td>
<td>M</td>
</tr>
<tr>
<td>1027</td>
<td>(\gamma)(Hf-OC) from Hf-OC(_3)H(_5)</td>
<td>M, Sharp</td>
</tr>
<tr>
<td>851</td>
<td>(\gamma)(C-C) from CH(_3)COO(^{-})</td>
<td>M, Broad</td>
</tr>
<tr>
<td>656</td>
<td>(\gamma) (Hf-O) from Hf-OR</td>
<td>S,</td>
</tr>
<tr>
<td>617</td>
<td>(\pi)(OH) from Hf-OH</td>
<td>S, Sharp</td>
</tr>
<tr>
<td>467</td>
<td>(\pi)(OH) from Hf-OH</td>
<td>S, Broad</td>
</tr>
</tbody>
</table>

The characteristic asymmetric and symmetric absorption bands of chelating acetate are present at 1555 and 1454cm\(^{-1}\) (with \(\Delta\gamma=101\text{cm}^{-1}\)), suggesting that acetate groups were present and not fully exchanged with water. \(\Delta\gamma=101\text{cm}^{-1}\) suggests that they were essentially in a bidendate coordination mode, but it was impossible to described them as chelating one or bridging two hafnium atoms [25] (see Figure III-4).
The attribution of the absorption bands recorded for the hafnia xerogel dried at 373K is as proposed in Table III-3. When heated at 723K, for 1h, gels showed broad and
characteristic absorption bands of hafnium oxide (i.e. below 900 cm$^{-1}$). The additional low absorption bands at 1350 - 1550 cm$^{-1}$ corresponded to carbonated residues.

III-2-5 Characterisation of Hafnia Xerogels by TGA-DSC

TGA in air and DSC in N$_2$ and air were carried out on HfO$_2$ xerogels (2 weeks aged) by the method described in II-2-7. TGA and DSC of hafnia xerogels dried at 373K are given in Figure III-5 in air and nitrogen. DSC under air and nitrogen show endotherms below 500K, that, as for Sc$_2$O$_3$, might be ascribed to the loss of adsorbed water (at 350K) and adsorbed ethanoic acid (at 450K). DSC in air shows two exotherms (at 650K and 750K) that could correspond to the thermal decomposition of possibly two organic groups: n-propoxide ligands at low temperature and acetate ligands still chelating Hf$^{IV}$ at high temperature. The relative proportion of these two peaks expressed the rate of nucleophilic exchange between acetate and n-propoxide groups. Acetate groups were bound to hafnium by at least two different ways that are bridging two hafnium atoms or chelating one [25,15]. The hydrolysis rate was correlated to the ratio of weight lost during thermal treatment.

![Figure III-5: TGA-DSC plots obtained with a hafnia xerogel predried at 373K: (TGA in air (a), DSC in air (b), DSC in N$_2$ (c)).](image)
The total weight loss was 29% w/w. 17% w/w was associated with the process of organic compound decomposition. Unfortunately, the plots did not allow deduction of the exact content of acetate and n-propoxide groups contained in the xerogel. However, the loss of 7% of the total weight below 350K shows that hafnia xerogels had adsorbed water after being dried. No recrystallisation was recorded.

III-2-6 **Characterisation of Hafnia Xerogels by XRD**

XRD patterns in Figure III-6 were obtained using the method described in part II-2-8. Hafnia xerogel (from a 2 weeks aged sol) was XRD amorphous, but became monoclinic HfO₂ upon heating for 1 hour at 723K. No recrystallisation was observed by DSC. On the other hand, XRD peaks gradually increased in intensity and narrowed upon heating at higher temperature. Hence crystallisation started below 773K and occurred gradually with temperature increasing.

![XRD patterns of hafnia xerogels](image)

*Figure III-6: XRD patterns of hafnia xerogels dried at 373K (a), heated for 1 hour at 723K (b), and heated for 1 hour at 973K (c).*

Attributions of the diffraction peaks with the relevant miller indices are given in Table III-4. Peaks of highest intensities and intensities of background are also reported. TEM
analyses of heated hafnia xerogel (at 723K for 1h) redispersed in ethanol showed very large aggregates (see Figure III-7).

Table III-4: Relative XRD intensities, d spacing and Miller indices attribution of diffraction peaks obtained for standard monoclinic HfO₂, and scandia xerogels heated at 373K, 773K and 973K.

<table>
<thead>
<tr>
<th>d(hkl) (nm)</th>
<th>Miller indices (h, k, l)</th>
<th>Relative intensities I/Iₘₐₓ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HfO₂ standard</td>
<td>373K</td>
</tr>
<tr>
<td>1.2599</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>0.5051</td>
<td>001</td>
<td>6</td>
</tr>
<tr>
<td>0.3677</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>0.3616</td>
<td>011</td>
<td>10</td>
</tr>
<tr>
<td>0.3147</td>
<td>-111</td>
<td>100</td>
</tr>
<tr>
<td>0.2823</td>
<td>111</td>
<td>80</td>
</tr>
<tr>
<td>0.2608</td>
<td>200</td>
<td>25</td>
</tr>
<tr>
<td>0.2590</td>
<td>020</td>
<td>20</td>
</tr>
<tr>
<td>0.2524</td>
<td>002</td>
<td>25</td>
</tr>
<tr>
<td>0.2487</td>
<td>-201</td>
<td>10</td>
</tr>
<tr>
<td>0.2320</td>
<td>120</td>
<td>10</td>
</tr>
<tr>
<td>0.2201</td>
<td>-112</td>
<td>15</td>
</tr>
<tr>
<td>0.1980</td>
<td>-202</td>
<td>10</td>
</tr>
<tr>
<td>0.187</td>
<td>022</td>
<td>25</td>
</tr>
<tr>
<td>0.1793</td>
<td>-221</td>
<td>10</td>
</tr>
<tr>
<td>0.1648</td>
<td>310</td>
<td>15</td>
</tr>
</tbody>
</table>

Highest intensity (cps) | 165 | 120 | 48 | 125 |
Background intensity (cps) | - | 25 | 20 | 20 |
III-2-7 Determination of the Average Hafnia Particle Size by XRD

Only one broad diffraction was observed at low angle $2\theta=6.9^\circ$, characteristic of amorphous material. The particle size cannot be determined from this peak broadness, since it did not verify the Bragg’s law (i.e. $d_{hkl}=\lambda/(2\sin\theta)$). However, the position of the diffracted peak corresponds to a $d$-value that gives an idea of the particle dimension. For hafnia xerogel, $\theta=3.45^\circ$ and $d=1.26\text{nm}$, confirming that the particles were of nanometric dimension (i.e. less than 5nm) as observed by TEM (see Figure III-2).

III-2-8 Characterisation of Hafnia Xerogels by N$_2$-BET

The N$_2$ adsorption-desorption at 77K was investigated on a hafnia xerogel sample (sol aged for 2 weeks) heated at 723K for 1h (0.200g), as described in II-2-9. The N$_2$ adsorption-desorption isotherm obtained is shown in Figure III-8. This was of type-IV with a capillary condensation hysteresis loop. The total BET surface area was estimated, from the BET-plot, to be $8.5\text{m}^2/\text{g}$, while the Langmuir surface area plot gave $11.9\text{m}^2/\text{g}$. These values were just outside the limits of accuracy of the method.
The desorption cumulative pore volume was estimated at 0.028 cm$^3$/g and the desorption average pore diameter was found to be 7.1 nm (larger than the 2.4 nm in size particle). The very low surface areas deduced were consistent with a dense material.

III-3 Conclusions on HfO$_2$ Sol-Gel Chemistry

The control hydrolysis-condensation of propanoic solution of hafnium propanoxide [Hf(On-Pr)$_4$], in presence of ethanoic acid ($f=2$) and water ($r=2$), led to a hafnia sol (0.2 M) containing very small particles. In order to stabilise this sol, the growth of the particles had to be quenched by further dilution (to 0.1 M) and addition of more ethanoic acid ($f=2$). The final sol was formed of homogeneous particles of 2.4 nm in diameter (if aged for two weeks) and was stable for several weeks before gelation. The reactions involved are proposed to be:

\[
\text{CH}_3\text{COOH} + \text{n-PrOH} \rightarrow \text{CH}_3\text{COOC}_8\text{H}_8 + \text{H}_2\text{O} \tag{1}
\]

Esterification (production of water)
Hf(OPr)_4 + H_2O \rightarrow \text{Hf(OPr)}_3(\text{OH}) + \text{HOPr} \quad (2)

Hydroxylation (hydrolysis)

Hf(OPr)_4 + CH_3COOH \rightarrow \text{Hf(On-Pr)}_3(\text{OAc}) + \text{HOPr} \quad (3)

Acetylation (exchange with acetate)

(2) + (3) \rightarrow \text{(AcO)}\text{Hf(OPr)}_2(\text{OH}) \quad (4)

Hydroxylation and chelation with acetate

2\text{Hf(OPr)}_2(\text{AcO})(\text{OH}) \rightarrow (\text{OPr})_2(\text{AcO})\text{Hf}=\text{(OH)}_2=\text{Hf(OAc)(OPr)}_2 \quad (5)

Condensation olation type 2(OH)_2 (formation of two hydroxo bridges, the leaving groups are solvate molecules)

2\text{Hf(OPr)}_2(\text{OAc})(\text{OH}) \rightarrow (\text{OPr})_2(\text{AcO})\text{Hf-O-Hf(OPr)}_2(\text{OAc}) + \text{H}_2\text{O} \quad (6)

Condensation by oxolation type 2(O)_1

2\text{Hf(OPr)}_2(\text{OAc})(\text{OH}) \rightarrow (\text{OPr})_2(\text{OAc})\text{Hf-O-Hf(OPr)(OAc)(OH)} + \text{HOPr} \quad (7)

Condensation by alcoxolation type 2(O)_1

\rightarrow \text{hafnia sol made of particle containing 17\% } w/w \text{ n-propoxide and acetate groups.}

Esterification reactions led to an increase of the water content ($r$) in the solution [18]. As shown previously by FTIR and TGA-DSC, acetate groups formed very stable complexes by chelating one or two hafnium atoms. The stabilisation was due to the increasing of the hafnium coordination number preventing an easy attack of the entering group (HO⁻). By comparing the gelation time ($T_g$) (Table III-2), one observed that systems containing an equal ratio of water and acid ($f=r$) gelled faster when these ratios were 4 than when they were 2 and 3. This suggests that hydrolysis reaction was predominant upon the chelation with ethanoic acid. However, once the particles were formed (i.e. there was a bluish aspect of the solution), the addition of further acetate groupments in the sol underwent chelation of hafnium atoms at the particle surface. The hydrolysis sites were then blocked.
This effect added to the dilution effect prevented a fast condensation and aggregation between particles that would have lead to flocculation or fast gelling.

Particles obtained as described below were amorphous, in an XRD sense, due to their nanometric size. These underwent a progressive polymorphic transformation upon heating, leading to monoclinic structure. Remaining organics (i.e. acetate and propoxide) could be removed upon heating at 723K by thermal decomposition. Such bulk xerogels exhibited a dense structure that was suitable for high index optical coatings.

References


[19] N. Bazin, D. Spriggs and J. E. Andrew, 9th International Workshop on Glasses, Ceramics, Hybrids and Nanocomposites from Gels, (September 1997), (Sheffield, UK), Abstract GP17, p211.


Chapter IV

THE SOL-GEL CHEMISTRY
OF ZIRCONIA
IV-1  **Zirconium Oxide**

IV-1-1  **Interesting Properties**

Zr is the second element of the 4d-block (electronic configuration: 4d² 5s²). Its has an oxidation state of 4 and ZrO₂ has similar physical and chemical properties than hafnia [1] (e.g. ionic radius of Zr⁴⁺=0.079nm). ZrO₂ is monoclinic at room temperature (a=0.514nm, b=0.520nm, c=0.531nm and β=99° 14') and its lattice parameters differ very slightly from the hafnia ones. Zirconia transforms to tetragonal (a=0.512nm, c=0.525nm) at 1400K (500K lower than for HfO₂ [1]); a cubic structure can also be obtained at higher temperature. Despite these similarities, it will be shown that the transformation from amorphous to monoclinic ZrO₂, did not undergo the dramatic structure changes seen for HfO₂.

Zirconia made by sol-gel process is of growing interest because of its potential use in optics, integrated optics circuits, alkali protective films, catalysis, gas sensors and thermal barrier coatings. It is used as a high reflective optical coating because of its high refractive index (i.e. 1.6<n<2.3) [2], and its high band gap (Eg=5.39eV, corresponding to an UV cut-off of 230nm [3,4]). So far, its good optical properties at 351nm and its relatively cheaper price, make zirconia the best candidate for high index component in high refractive multilayer mirror. Furthermore, it offers an easy sol-gel synthetic process and a high flexibility in terms of the choice of precursor and condition [5-11].

IV-1-2  **General Chemistry**

In aqueous solution, Zr⁶⁺ can be complexed by most of the common anions (e.g. Cl⁻, ClO₄⁻, PO₄³⁻, NO₃⁻, SO₄²⁻) [12]. They have different degrees of polymerisation and can all be precursors or intermediates in hydrolysis-condensation processes. In acidic medium, Zr⁴⁺ hydrolysis and condenses under gelatinous precipitate with the formula ZrO₂₋ₓ(OH)ₓH₂O. This amorphous phase crystallises in tetragonal ZrO₂ if heated at 673K via oxolation-dehydration [13, 14]. Refluxing solutions of hydrolysed zirconium at pH=3-2 leads to sols
containing monoclinic ZrO₂ particles formed by oxolation. Organo-zirconium compounds (e.g. zirconium ethoxide, isopropanoxide, butoxide, oxalate etc), are used as precursors for sol-gel chemistry in organic medium. These alkoxides are highly hygroscopic and are usually purchased dissolved in their parent solvent. Some common sol-gel routes are given below:

- Zr(OPr)₄ in propan-1-ol and hydrolysed in presence of 1,2 ethanediol (stabilising agent) leads to hybrid material showing high ionic conductivity [8].
- Zr(OPr)₄ in propan-1-ol (or ethanol) and hydrolysed in presence of nitric acid [4], or ethanoic acid [5,9], leads to sols that are suitable for optical coatings.
- Zr(O₂C₃H₅)₄ in ethanol and hydrolysed in presence of ethanoic acid leads to sols suitable to be liquid deposited [15].
- Zr(OtBu)₄ in ethanol and thermohydrolysed at 353K in presence of HNO₃ can be combined with alumina to produce catalysis materials [16].

The possibilities are vast and methods can be adapted to obtain the right type of sol, gel, xerogel or aerogel.

**IV-1-3 Fields of Application**

The development of zirconia-based ceramic materials is of great interest because of their superior chemical resistance. The thermal stability of ZrO₂ can be improved if it is combined with other oxides such as hafnia (see III-A-3-1) [1,17], yttria and scandia [18], or yttria and ceria [19]. It has been shown that hafnia and zirconia are completely soluble in all proportion in the binary system. These stabilised tetragonal zirconia coatings are widely used in gas turbines to lower metal temperatures, and thereby to increase component life or improve engine efficiency. The best thermal stabilities are obtained by combining scandia with yttria and zirconia; yttria-ceria-zirconia shows lower low-temperature degradation.

Porous zirconia can be used as industrial filters, gas sensors, catalysis supports, or active elements in reactions such as hydrogenation and oxidation. Preparation of ZrO₂ from basic hydrolysis of zirconium chloride produces ceramics with 350m²g⁻¹. Their thermal and mechanical properties can also be improved by doping them with yttrium or
potassium [20,21]. Zirconia can also be combined with alumina to produce materials of superior mechanical properties used in catalysis. The surface area reached if zirconium and aluminium butoxide precursors are used, is 290 m$^2$g$^{-1}$ after calcination at 993K [16]. Also, impregnation of alumina-yttria-stabilised-zirconia with copper leads to materials of high surface areas (150 - 250 m$^2$g$^{-1}$) [22] used for atmospheric oxidation of CO below 723K.

Zirconia optical coatings are used in areas such as optical fibers, wave-guides, high refractive dielectric films, radiation filters, ...etc. ZrO$_2$ is already extensively used in high power UV-3ω-laser devices. Despite its poor laser fluence at 1056nm (1ω) [23], zirconia exhibited a high damage resistance at 351nm and the possibility to form up to 12 stable pairs of layers with colloidal silica [4,5]. ZrO$_2$ optical thin layers, produced by vacuum or electron-beam deposition methods [3], exhibited very high reflectivity but poor laser damage resistance compared to liquid deposited films.

### IV-2 Sol-Gel Processing of ZrO$_2$ from a Zr(OPr)$_4$ Precursor

Using Pauling’s method to determine the coordination number (N) [24] (see I-2-3), it was found that ρ=0.56, suggesting that Zr$^{IV}$ is hexacoordinated. However, in its monoclinic ZrO$_2$ structure, zirconium atoms have a coordination of 7 [13]. Also, it has been shown that the main intermediate to monoclinic zirconia, existing in aqueous medium, is the tetramer (i.e. [Zr$_4$(OH)$_{16}$(OH$_2$)$_8$]$^0$), exhibiting a coordination number of 8. Therefore, one expects Zr$^{IV}$, complexed with organic ligands in alcohol, to require more than 6 entities in its coordination sphere. Hydrolysis of such precursors or intermediates would thus be favourable through an SN$_2$ mechanism.

#### IV-2-1 Introduction on Zirconium n-Propoxide

For the same reasons given for hafnia (see III-2), sol-gel synthesis, Zr(OPr)$_4$ precursor (see Annexe B-19) was chosen for the present work. The molecular complexity of Zr(OEt)$_4$ was reported to be 3.6 [25], therefore the molecular complexity of Zr(OPr)$_4$ will
be inferior to 3.6 in the same conditions. Table IV-1 gives (\(\delta\)) and (\(\chi\)) calculated for Zr(OR)\(_4\) using the partial charge distribution model described in I-2-2.

\[\text{Table IV-1: Partial charge distribution calculated for zirconium alkoxides, (molecular complexion and the solvatation by solvent molecules are not taken in account).}\]

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>(\chi(\text{Zr}))</th>
<th>(\chi(\text{O}))</th>
<th>(\chi(\text{C}))</th>
<th>(\chi(\text{H}))</th>
<th>(\chi)</th>
<th>(\delta(\text{Zr}))</th>
<th>(\delta(\text{OR}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(OEt)(_4)</td>
<td>1.29</td>
<td>3.5</td>
<td>2.5</td>
<td>2.1</td>
<td>2.29</td>
<td>0.65</td>
<td>-0.16</td>
</tr>
<tr>
<td>Zr(On-Pr)(_4)</td>
<td>1.29</td>
<td>3.5</td>
<td>2.5</td>
<td>2.1</td>
<td>2.28</td>
<td>0.64</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

The attacking rate of entering groups and the leaving rate of ligands are expected to be slower with Zr(OPr)\(_4\) because of the larger size of propoxide groups compared to ethoxide groups. Charges calculated for Zr\(^{IV}\) are slightly higher than that for Hf\(^{IV}\), suggesting that, in the same conditions, the process for ZrO\(_2\) is expected to be faster than for hafnia. This was verified only for a low concentration of precursor and reactant. Once again, it is difficult to predict the relative reaction rates, knowing that many other factors than charge distributions influence the mechanism (e.g. coordination, solvatation, molecular complexion, concentration, possible stabilisation by a chelating agent, ...etc).

**IV-2-2 Experimental Synthesis of Spherical Zirconia Particles**

The same experimental procedure used for hafnia (see III-2-2) was applied to the synthesis of ZrO\(_2\) colloidal particles. Hydrolysis took place at room temperature with the conditions listed with the corresponding gelation times in Table IV-2. By comparing \(T_g\), one can observe that hydrolysis predominates over chelation. As with hafnia, the best compromise was found for \(C_\text{Zr}=0.2\text{M}, r=2\) and \(f=2\), and the bluish aspect appeared after 1 week. The process was then quenched by further dilution to 0.1M with propan-1-ol and further addition of a ratio \(\text{CH}_3\text{CO}_2\text{H}/\text{Zr}^{IV}\) of 2, before being centrifuge. Eventually, when \(\text{Zr}^{IV}=0.1\text{M}, \text{H}_2\text{O}=0.2\text{M}\) and \(\text{CH}_3\text{CO}_2\text{H}=0.4\text{M}\), the gel was obtained after 3 months. The viscosity of the sols increased slowly up to \(T_g/3\) and then accelerated [20]. Therefore, reproducible thin films had to be produced during the early period of 3 weeks following the preparation in order to avoid dramatic changes of sol viscosity. A TEM control of the particle sizes during this period showed that they remained smaller than 5nm in diameter.
Table IV-2: Gelation times measured for solutions of zirconium n-propoxide in propan-1-ol for different concentrations, hydrolysis ratios, and acid concentrations.

<table>
<thead>
<tr>
<th>Concentration Zr^{IV}</th>
<th>Acid/Zr^{IV} (f)</th>
<th>Water/Zr^{IV} (r)</th>
<th>Gelation time (Tg) (h)</th>
<th>Gelation time (Tg) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2M</td>
<td>2</td>
<td>2</td>
<td>1320</td>
<td>55</td>
</tr>
<tr>
<td>0.2M</td>
<td>2</td>
<td>3</td>
<td>36</td>
<td>1.5</td>
</tr>
<tr>
<td>0.2M</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>0.25</td>
</tr>
<tr>
<td>0.2M</td>
<td>3</td>
<td>3</td>
<td>1080</td>
<td>45</td>
</tr>
<tr>
<td>0.2M</td>
<td>3</td>
<td>4</td>
<td>432</td>
<td>18</td>
</tr>
<tr>
<td>0.2M</td>
<td>4</td>
<td>4</td>
<td>840</td>
<td>35</td>
</tr>
<tr>
<td>0.1M</td>
<td>2</td>
<td>2</td>
<td>2160</td>
<td>90</td>
</tr>
<tr>
<td>0.1M</td>
<td>2</td>
<td>3</td>
<td>240</td>
<td>10</td>
</tr>
<tr>
<td>0.1M</td>
<td>2</td>
<td>4</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>0.1M</td>
<td>3</td>
<td>3</td>
<td>1920</td>
<td>80</td>
</tr>
<tr>
<td>0.1M</td>
<td>3</td>
<td>4</td>
<td>1440</td>
<td>60</td>
</tr>
<tr>
<td>0.1M</td>
<td>4</td>
<td>4</td>
<td>1512</td>
<td>63</td>
</tr>
</tbody>
</table>

IV-2-3 Characterisation of Zirconia Particles by TEM

Figure IV-1: TEM micrograph of spherical zirconia particles deposited on carbon-coated copper grids, (1cm = 40nm, ×250 000).
Figure IV-1 shows homogeneous spherical ZrO₂ sol particles (aged for 2 weeks before being analysed as described in II-2-4). Particles diameter were evaluated to be less than 5nm. The corresponding EDX is given in Figure IV-2. These X-ray probe analyses gave peaks at 1.80 keV that corresponded to Zr M₄,₅, suggesting that the particles were rich in zirconium. The real particle diameter was estimated by XRD in part IV-2-7.

![X-ray probe energy dispersion](image)

*Figure IV-2: X-ray probe energy dispersion obtained for zirconia particles deposited on TEM carbon-coated copper grids.*

**IV-2-4 Characterisation of Zirconia Xerogels by FTIR**

Zirconia xerogels were obtained by solvent evaporation at room pressure and temperature of a 2 weeks aged sol, and then vacuum dried at 373K. These were analysed by FTIR as described in II-2-4. Spectra exhibited broad vibration bands at 460, 616, 647 and 1027cm⁻¹ that corresponded to Zr-O stretching from Zr-OR, Zr-O-Zr and Zr-OH. The broad band at 3392cm⁻¹ corresponded to O-H stretching, suggesting that the precursor was partly hydrolysed. Propoxide ligands were not fully exchanged by acetate or hydroxide groups as expressed by the absorption at 1027cm⁻¹ assigned to Hf-OPr. The characteristic antisymmetric and symmetric absorptions of acetate, chelating one or bridging two zirconium atoms [26], are present at 1536 and 1452cm⁻¹ (with Δγ=84cm⁻¹). These structures were already represented in Figure III-4 for Hf-acetate. Band attribution for a zirconia xerogels dried at 373K is as proposed in Table IV-3.
Figure IV-3: FTIR spectra of zirconia xerogels dried at 373K (a), heated for 1 hour at 723K (b), and, heated for 1 hour at 973K (c).

Table IV-3: FTIR bands for zirconia xerogel dried at 373K

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>Attribution</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3392</td>
<td>γ(O-H) from M-OH</td>
<td>S, Broad</td>
</tr>
<tr>
<td>2937</td>
<td>γ(C-H) from organic</td>
<td>S, Sharp</td>
</tr>
<tr>
<td>1705</td>
<td>γ(C=O) from carbonate</td>
<td>M, sharp</td>
</tr>
<tr>
<td>1536</td>
<td>γ(C-O) from CH₃COO⁻ symmetric</td>
<td>VS</td>
</tr>
<tr>
<td>1452</td>
<td>γ(C-O) from CH₃COO⁻ antisymmetric</td>
<td>VS</td>
</tr>
<tr>
<td>1416</td>
<td>δ(CH) deformation</td>
<td>VS</td>
</tr>
<tr>
<td>1338</td>
<td>δ(CH) deformation</td>
<td>M</td>
</tr>
<tr>
<td>1027</td>
<td>γ(Zr-O) from Zr-OC₃H₇</td>
<td>M, Sharp</td>
</tr>
<tr>
<td>798</td>
<td>γ(C-C) from CH₃COO⁻</td>
<td>M</td>
</tr>
<tr>
<td>647.5</td>
<td>γ(Zr-O) from Zr-OR</td>
<td>S, Broad</td>
</tr>
<tr>
<td>616</td>
<td>π(OH) from Zr-OH</td>
<td>S, Broad</td>
</tr>
<tr>
<td>460</td>
<td>π(OH) from Zr-OH</td>
<td>S, Broad</td>
</tr>
</tbody>
</table>
When heated at 723K, zirconia gels showed broad and characteristic absorption bands of zirconium oxide (i.e. high absorption below 900 cm\(^{-1}\)). The additional low absorption bands at 1350-1550 cm\(^{-1}\) corresponded to carbonated residues.

**IV-2-5 Characterisation of Zirconia Xerogels by TGA-DSC**

TGA in air and DSC in N\(_2\) and air of a zirconia xerogel prepared as for FTIR investigation is shown in Figure IV-4. Similar thermal activities as for HfO\(_2\) xerogels were observe. The total weight loss was 44% w/w:

- endotherm at 350K ascribed to the loss of adsorbed water (7% w/w)
- endotherm at 450K ascribed to the loss of adsorbed ethanoic acid
- exotherm at 650K and 750K corresponded to the thermal decomposition of organic groupments (27% w/w acetate and propoxide)
- presence of acetate under both chelating or bridging two Zr atoms

![TGA-DSC plots obtained with a zirconia xerogel pre-dried at 373K: (TGA in air (a), DSC in air (b), DSC in N\(_2\) (c)).](image)

The content in organic species is higher for zirconia than it has been for hafnia. Also, no recrystallisation was recorded.
IV-2-6  Characterisation of Zirconia Xerogel by XRD

The crystallinity of the zirconia xerogel (prepared as for FTIR investigation) was studied by XRD with the method given in II-2-8. It was XRD amorphous, but became tetragonal ZrO$_2$ upon heating, for 1 hour at 723K.

Figure IV-6: XRD patterns of a zirconia xerogel dried at 373K (a), heated for 1 hour at 723K (b), and heated for 1 hour at 973K (c).

Figure IV-7: TEM image of a ZrO$_2$ xerogel heated for 1h at 723K and redispersed in ethanol, (1cm=80nm, x125 000).
Table IV-4: Relative intensities, d(hkl) and Miller indices attribution of diffraction peaks obtained for standard tetragonal ZrO₂, and zirconia xerogels heated at 373K, 723K and 973K.

<table>
<thead>
<tr>
<th>d(hkl) (nm)</th>
<th>Miller indices</th>
<th>Relative intensities I/Iₘₐₓ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ZrO₂ tetragonal</td>
</tr>
<tr>
<td>1.2492</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>0.2948</td>
<td>111</td>
<td>100</td>
</tr>
<tr>
<td>0.2605</td>
<td>002</td>
<td>18</td>
</tr>
<tr>
<td>0.2532</td>
<td>200</td>
<td>25</td>
</tr>
<tr>
<td>0.1820</td>
<td>202</td>
<td>65</td>
</tr>
<tr>
<td>0.1541</td>
<td>131</td>
<td>45</td>
</tr>
</tbody>
</table>

|               | Highest intensity (cps) | 420 | 125 | 110 | 260 |
|               | Background intensity (cps) | -   | 25  | 25  | 25  |

The monoclinic structure of ZrO₂ has not been observed at low temperature. As a result, initial small particles of zirconia could have been under tetragonal or monoclinic structure before heating. Recrystallisation to tetragonal ZrO₂ started below 773K and occurred gradually with the temperature increasing. Miller indices, d(hkl), relative intensities, maximum intensities and intensities of background are given in Table IV-4 for each peak and compound. Redispersed in ethanol xerogel, after being heated at 723K for 1h, are shown as large aggregates in Figure IV-7.

**IV-2-7 Determination of the Average Zirconia Particle Size by XRD**

As for hafnia xerogel, only one broad diffraction was observed at low angle 2θ=7°, characteristic of amorphous material. The d-value deduced from the Bragg’s law (i.e. \(d_{(hkl)}=\frac{\lambda}{2\sin\theta}\)) and the position of the diffracted peak is \(d=1.26\text{nm}\), confirming that the particles where of nanometric dimension (i.e. less than 5nm) as observed by TEM (see Figure IV-2).
N₂-BET investigation (as performed on scandia and hafnia xerogels, see II-9) of a zirconia xerogel heated at 723K did not show an isotherm of a specific type (see Annexe B-18). The total BET surface area was estimated at 10.3m²/g, while the Langmuir surface area gave 14.3m²/g. The desorption cumulative pore volume was negligible (0.0017cm³/g) and the desorption average pore diameter was not meaningful. As with hafnia, these values are below the accuracy limit of the apparatus, but they are consistent with a dense material.

**Conclusions on ZrO₂ Sol-Gel Chemistry**

Bulk zirconia xerogel was found to be dense and thus suitable for a high index coating. The controlled hydrolysis-condensation of a propanoic solution of [Zr(On-Pr)₄] with the conditions described in IV-2-2, led to colloidal particles of 3.2nm (if the sol is aged for 2 weeks). The xerogel was then highly dense and formed of very small condensed particles. These zirconia particles were XRD amorphous and transformed slowly to tetragonal ZrO₂ upon heating. Remaining acetate and isopropoxide were decomposed at 723K.

Chemical analysis showed that zirconia and hafnia xerogels had similar chemical environments and structures. Differences were noticed in the higher organic content, the slower kinetic of the hydrolysis-condensation process and the slightly larger average particle size measured for zirconia. Also, despite their very close oxide structures and properties, their sol-gel synthesis led to xerogels that do not crystallise in the same structure when heated. However, one expects the reactions involved in the hydrolysis-condensation process of zirconia to be similar to that of hafnia (see equations (1) to (7) in III-3).

Remarks that can be made for both zirconia and hafnia sol-gel chemistry are:

- esterification reaction leads to an increase of the water content in the solution [27].
- acetate groups formed very stable complexes one or two metal atoms (i.e. bidendate or bridge).
- the hydrolysis reaction dominates over the chelation with ethanoic acid.
once the particles are formed (i.e. the solution has a bluish aspect), the addition of further acetate groupments in the sol may undergoes chelation of metal atoms at the surface, blocking further hydrolysis on these sites.

dilution may prevent fast condensation or aggregation of particles that would lead to flocculation or fast gelling.

ZrO₂ particles had similar shape, size and structure than those prepared by other variable organic methods [5,7,9,11,28]. However, the high amount of CH₃CO₂H and the low concentration in water and zirconia precursor, prevent a fast gelation as noticed with other routes [9]. In addition, contrary to the results reported by Chaibi et al. [8], no transformation to the monoclinic phase of ZrO₂ was obtained within the range of temperature studied. Therefore, and as observed with HfO₂, such stable low-concentrated young-sols led to dense thermally stable xerogels by solvent evaporation. It will be shown now that these were suitable for high index optical coatings.

Zirconia, hafnia, and scandia sols which production conditions were selected and described in parts II-2-2, III-2-, and IV-2-2, were used for liquid deposition of optical coatings.

References


Chapter V

PROCESSING OF
OPTICAL COATINGS
V-1 Fundamentals Aspects of Liquid Deposition Methods

Liquid deposition methods can be performed with two kinds of sol-gel liquid systems: polymeric (i.e. obtained via the powder-free process) and colloidal (i.e. obtained via the powder process). The polymeric route consists of depositing the partially hydrolysed precursor on the substrate. The right conditions must be applied in order to prevent total polymerisation in the sol before coating. Once the film is formed, completion of the hydrolysis-condensation process takes place while the solvent evaporates. Unfortunately this method leads to thin films that craze and peel when heated, due to stresses induced at interfaces coating/substrates, resulting to shrinkage during the completion of the condensation.

Figure V-1: TEM image of a vertical cross-section of a silica coating on a Perspex substrate (x100 000, 1cm=100nm).

The colloidal route deposits the colloidal particles on the substrate surface and this is followed by evaporation of the solvent. It is advantageous over the polymeric one because it leads to coatings that are usually porous, soft and stress-free. Therefore, sols containing discrete particles are more appropriate to produce stacks of antireflective and highly reflective layers [1]. Porous materials can be more easily combined with binders,
fillers or other constituents that can change the properties of a film once deposited [2]. Hafnia, zirconia and scandia coatings were produced as discrete colloidal particles (as shown in Figure V-1, which is a TEM image of a vertical cross-section of a silica coating on a Perspex substrate). The coating is 300nm thick and is formed of discrete particles of 10nm in diameter. This TEM image could not be obtained with ZrO₂, HfO₂ or Sc₂O₃ coatings because these were removed from the Perspex during cutting. Four liquid deposition methods are capable of producing thin and homogeneous optical films. The two mostly used are dip and spin coatings. The two others (known as meniscus and spray coating) are more recent and require special equipment. In order to encourage a homogeneous sol diffusion onto the substrate surface, all coating processes require the use of solvents (colloid dispersing media) exhibiting good substrate wetability. That is why every effort was made to synthesis ZrO₂, HfO₂ or Sc₂O₃ discrete particles in alcohol (i.e. polar solvents were ideal).

V-1-1  Spray Coating

Scratch resistant SiO₂ thin films have been deposited by aerosol-gel process (spray coating) from a diluted TEOS solution (i.e. tetra ethoxy silane) [3]. The technique is based on sol-gel polymerisation of a liquid film, deposited from an ultrasonically sprayed aerosol. The condensation rate must be very slow in order to prevent a dramatic increase in the viscosity, and thus to control the transport of the sol. The polymerisation takes fully place after solvent evaporation from the substrate. The thickness depends on the amount of sol sprayed on the surface.

V-1-2  Meniscus Coating

Meniscus coating is also called laminar-flow coating. Substrates are coated in an upside-down position, using a vacuum chuck for substrate carriage. The sol to be deposited is pumped in a horizontal tube fitted with a slot at its upper part. Then, the sol flows out in a laminar manner through the slot forming a continuous and homogeneous liquid film at the outside top of the tube. The sol drains down into a collector to be recycled. The substrate is placed in contact with the liquid film such that a narrow meniscus is created
between it and the applicator tube. This later is then slowly moved horizontally relative to the substrate [1]. A liquid film is transferred to the substrate and the coating is formed while solvent evaporates. This method allows the coating of very large substrates, but is restricted to flat surfaces. The thickness depends on the deposition rate.

**V-1-3 Spin Coating**

Spin coating deposition process is more commonly used than the two previous methods. It consists in spinning a substrate at 200 - 4000rpm, while a certain volume of sol is deposited at its centre. Thanks to the centrifugal force induced by the rotation, the sol is spread out on the surface forming a homogeneous liquid film [4]. The coating is formed while solvent evaporates. The volume of sol deposited and the rate of solvent evaporation control the film thickness. Increasing the speed of rotation leads to thinner coatings because of the tendency of the sol to be pushed out of the substrate edges. As a result the thickness is adjusted mostly by controlling the spin rate. It has the advantage of simplicity over the two previous methods. It is well adapted for processing thin layers on circular substrates. The main disadvantage lays in the fact that a low percentage of sol remains as the actual coating, and most of it is lost after being dragged away by the centrifugal force.

**V-1-4 Dip Coating**

Dip coating is doubtless the easiest technique of liquid deposition methods. It involves withdrawing of a substrate from a sol. A meniscus forms at the contact between the fluid and the surface and leads to the formation of a liquid film. Gravitational draining and solvent evaporation accompanied by further condensation results in the deposition of a solid film. Dip coating requires less equipment and involves lower cost than other methods. It also has the advantage of minimising the waste of sol. The most important advantage of sol-gel dip coating is that it offers the possibility of controlling the microstructure of the deposited film. This depends on the following factors: concentration, size and structure of the colloidal particles, relative rates of condensation and evaporation, capillary pressure, and substrate withdrawal speed [5].
Figure V-2: Diagram of the dip coating process showing the sequential stages of structure development that result from draining, by solvent evaporation and a continued condensation reaction [5].

The substrate is withdrawn at a speed of $U_0$ and drags the sol, leading to the formation of a film over the surfaces of the substrate. Since the solvent is evaporated and the sol drained down by gravity, the remaining film becomes thinner and thinner and terminates at a well-defined drying line ($x=0$, see Figure V-2). When the velocity equals $U_0$, the process is steady. Therefore a constant evaporation rate of the solvent leads to the formation of a solid film of homogeneous thickness. The increasing concentration caused by solvent evaporation, leads to aggregation of particles into structures that depend on the withdrawal speed. For partially condensed species (e.g. oligomers or very small particles) a competition is established between compaction and condensation. Condensation creates shrinkage that prevents compaction. However, often in the case of thin film deposition, the drying stage overlaps with the aggregation-gelation stages, leaving a very brief time
for condensation reaction to occur. This results in the formation of film structures that have collapsed at the final stage of drying as explained when monoliths aerogels are dried too quickly (see I-7-3). The draining and evaporation that accompanied dipping cause the thickness \( h \) and the fraction of solids (i.e. concentration of particles in the sol) to change continuously with the distance between the liquid bath surface and the drying line.

*Influence of the withdrawal speed:* It has been shown for both category of sol (e.g. branched polymers or discrete condensed particles) that the higher is the withdrawing speed, the larger is the amount of material deposited. Plotting the thickness multiplied by the refractive index (i.e. a term that is proportional to the percentage volume of solid) versus the coating rate has given plots with positive gradients [5], because a faster withdrawal allows more sol to be dragged. A second effect of the withdrawal speed is on the refractive index. In the case of repulsive particles, increasing the speed of deposition increases the refractive index of the film. Inversely a decrease of refractive index was noticed with reactive polymeric sols [5]. In this second case, longer ageing times took place due to longer drying times induced by the thicker liquid films. Therefore the increase of porosity with \( U_0 \) is explained by the longer times required for shrinkage. For discrete particles, it is expected that particles will arrange themselves into close-packed structures that will lead to denser films. This arrangement (into a crystal-like structure) is favoured by the longer drying times in thicker liquid films giving more time for particle organisation.

*Influence of the intermediate structure:* Reduction of the condensation rate (i.e. precursor reactivity) by adjusting the pH causes a corresponding increase in the refractive index suggesting the formation of a denser film [5]. The possible structure of inorganic precursors ranges from weakly branched polymers to large condensed particles. The size and interaction between these entities also influence the film final structure.

*Influence of the capillary effect:* Close to the drying line \((x=0)\), further condensation causes the concentration of water to increase. This water enrichment is also enhanced by the faster evaporation of alcohol. A consequence of this water enrichment during sol deposition is the increase of the capillary pressure (due to the greater surface tension of
water over alcohol). On the other hand, the presence of a higher concentration of water at a certain stage will increase the ageing rate, leading to more porous material. A competition between these two effects takes place. For dip coating, it has been shown that increasing the water content of the system leads first to the formation of denser films due to capillary effect. Above a certain concentration of water, ageing is predominant over the capillary effect and an increase of the film porosity is observed. For spin coating, the evaporation rate is higher leaving no time for ageing; the refractive index of the film increases with the water content [5,6]. For the synthesis of ZrO2, HfO2 and Sc2O3, the choice of water concentration was driven by the stability of the sol upon other effects.

V-2 Optical Properties of Coatings

The optical properties of a material are characterised by its refractive index (n<sub>i</sub>) (depending on its density and porosity), transmittance (T), reflectivity (R), absorbance (A), and its intensity of scattering (S). When an electromagnetic wave of a specific wavelength (λ<sub>0</sub>) meets a substance, fractions of the radiation can be absorbed, reflected, scattered, or transmitted through the substance. Therefore one has I = T + S + R + A.

V-2-1 Dielectric Films

The determination of the optical thickness (H) and the refractive index (n<sub>i</sub>) of a homogeneous dielectric film requires the understanding of the Fresnel theory of interference taking place within a dielectric film. The properties of a homogeneous dielectric film situated between two homogeneous media is of particular interest in optics, especially for lenses protection, antireflection coatings, optical filters, polariser, ...etc. In the present section, it is shown how the refractive index and the optical thickness of a single layer deposited on an optical substrate can be deduced from the transmission and reflection spectra [7]. We assume all media to be non-magnetic (i.e. μ = 1, where μ is the magnetic permeability and corresponds to the ratio of flux density produced to the magnetic field strength producing it). The propagation of an electromagnetic wave through a homogeneous film is shown in Figure V-3.
Figure V-3: Propagation of an electromagnetic wave through a homogeneous film.

$n_i$ is the refractive index of the substrate, $n_2$ is the refractive index of the single layer and $n_3$ is the refractive index of the medium ($n_3=1$ if medium is air). According to the Fresnel formulae, the reflection and transmission coefficients at the interfaces 1-2 and 2-3 (i.e. $r_{12}$, $t_{12}$, $r_{23}$ and $t_{23}$) are given as follows.

\[
ar_{12} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2}, \tag{1}
\]
\[
t_{12} = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2}, \tag{2}
\]
\[
r_{23} = \frac{n_2 \cos \theta_2 - n_3 \cos \theta_3}{n_2 \cos \theta_2 + n_3 \cos \theta_3}, \tag{3}
\]
\[
t_{23} = \frac{2n_2 \cos \theta_2}{n_2 \cos \theta_2 + n_3 \cos \theta_3}. \tag{4}
\]

In terms of these expressions, the reflection and transmission coefficients ($r$ and $t$) for the whole system are expressed as followed in equation (5) and (6) [6].

\[
r = \left( r_{12} + r_{23} \cdot e^{2i\beta} \right) / \left( 1 + r_{12} \cdot r_{23} \cdot e^{2i\beta} \right), \tag{5}
\]
\[
t = \left( t_{12} + t_{23} \cdot e^{2i\beta} \right) / \left( 1 + r_{12} \cdot r_{23} \cdot e^{2i\beta} \right). \tag{6}
\]

And the reflectivity ($R$) and transmittance ($T$) are given from by relation (7) and (8).
\[ R = |r|^2 = \frac{r_{12}^2 + r_{23}^2 + 2 \cdot r_{12} \cdot r_{23} \cdot \cos 2\beta}{1 + r_{12}^2 \cdot r_{23}^2 + 2 \cdot r_{12} \cdot r_{23} \cdot \cos 2\beta} \]  
\[ T = \frac{n_3 \cdot \cos \theta_3}{n_1 \cdot \cos \theta_1} \cdot |r|^2 = \frac{n_3 \cdot \cos \theta_3}{n_1 \cdot \cos \theta_1} \cdot \frac{t_{12}^2 \cdot t_{23}^2}{1 + r_{12}^2 \cdot r_{23}^2 + 2 \cdot r_{12} \cdot r_{23} \cdot \cos 2\beta} \]  

where \[ \beta = (2\pi/\lambda_0) \cdot n_2 \cdot h \cdot \cos \theta_2. \]  

In relation (9), \( \lambda_0 \) is the incident wavelength. We observe that \( R \) and \( T \) remain unchanged if \( \beta \) is replaced by \( \beta + \pi \). In other words, \( R \) and \( T \) are unchanged if \( h \) is replaced by \( h + \Delta h \) with \( \Delta h \) being expressed as in equation (10).

\[ \Delta h = \frac{\lambda_0}{2n_2 \cos \theta_2} \]  

Hence, reflectivity and transmittance of dielectric films differing in thickness \( \Delta h \) by an integral multiple of \( (\lambda_0/2n_2 \cos \theta_2) \) are the same. The optical thickness \( (H) \) of a coating of refractive index \( n_2 \) is given by \( H = n_2 h \). The derivative of relation (7) is null (i.e. \( dR/dH = 0 \)) when \( \sin 2\beta = 0 \), thus we have a maximum or a minimum of reflection when relation (9) becomes (11).

\[ n_2 h = H = (m \cdot \lambda_0) / (4 \cdot \cos \theta_2), \quad \text{(with } m = 0, 1, 2, \ldots \text{)} \]  

- When \( m \) is odd: (i.e. \( m = 1, 3, 5, \ldots \text{etc}) \), \( \cos 2\beta = -1 \), and equation (7) is reduced to equation (12).

\[ R = [(r_{12} - r_{23})/(1 - r_{12} \cdot r_{23})]^2 \]  

For a normal incidence, we have

\[ r_{12} = (n_1 - n_2)/(n_1 + n_2) \]  

and \[ r_{23} = (n_2 - n_3)/(n_2 + n_3) \]
Hence the reflectivity \( R \) at normal incidence (i.e. \( \theta_2=0 \)) \( R \) corresponding to odd values of \( m \) is expressed by relation (15).

\[
R = \left[ (n_1 n_3 - n_2^2)/(n_1 n_3 + n_2^2) \right]^2 \quad (15)
\]

In the case where the coating has the highest refractive index and the medium the lowest (i.e. \( n_2>n_3>n_1 \)), the reflectivity \( R \) is maximal when \( dR/dH=0 \).

When \( m \) is even (i.e. \( m=2, 4, 6, \ldots \) etc), \( \cos 2\beta=1 \), equation (7) becomes equation (16).

\[
R = \left[ (r_{12} + r_{23})/(1 + r_{12} r_{23}) \right]^2 \quad (16)
\]

In particular for normal incidence and \( n_2>n_3>n_1 \), \( R \) is minimal and is expressed by (17). For this particular case, \( R \) seems to be independent of \( n_2 \).

\[
R = \left[ (n_1 - n_3)/(n_1 + n_3) \right]^2 \quad (17)
\]

A plate whose optical thickness is \( h=(m \lambda_0)/(4 \cos \theta_2) \) with \( (m=1, 3, 5, \ldots \) etc), has no influence on the intensity of the reflected or transmitted radiation. Usually, the first medium is air \( (n_1=1) \). One can observe that, with a film whose optical thickness has any of the value \( \lambda_0/4, 3\lambda_0/4, 5\lambda_0/4, \ldots \) etc, the reflectivity is a maximum or a minimum according to whether the refractive index of the film is greater or lower than the refractive index of the substrate. The opposite is the case if the film has an optical thickness \( (H) \) of \( 2\lambda_0/4, 4\lambda_0/4, 6\lambda_0/4, \ldots \) etc.

It is evident from the preceding analysis that a coating, whose optical thickness is a quarter of the incident light wavelength (i.e. \( H=\lambda_0/4 \)) and whose refractive index is high enough, may exhibit the best high-reflectivity property. According to relation (15), the reflectivity at normal incidence would be strictly zero if \( n_2=(n_1 n_3)^{1/2} \). This condition cannot be satisfied in practice.
V-2-2  Periodically Stratified Media

In order to achieve high reflection that cannot be reached with a single layer (e.g. $80\%<R<99.9\%$), it is necessary to stack pairs of low and high index thin quarter-wavelength layers ($H=\lambda /4$). A monochromatic light ($\lambda_o$) passing through such a device would undergo multi-reflections leading to high reflectivity. These optical devices are to be used as mirrors for laser beam transport [8]. A multi-layer stack usually consists of a succession of homogeneous layers of alternately low and high refractive indices ($n_2$ and $n_3$) and thickness ($h_2$ and $h_3$) [7], placed between two homogeneous media of refractive indices $n_1$ and $n_4$ (see Figure V-4). We assume the media to be non-magnetic ($\mu=1$). Equations (9') and (9'') are related to equation (9).

\[ \beta_2 = (2\pi/\lambda_o) n_2 h_2 \cos \theta_2 \quad (9') \]
\[ \beta_3 = (2\pi/\lambda_o) n_3 h_3 \cos \theta_3 \quad (9'') \]

\[ n_4 \]
\[ n_3 \]
\[ n_2 \]
\[ n_1 \]

\[ h_3 \]
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**Figure V-4:** Propagation of an electromagnetic wave through a multi-layers stack mirror.

To simplify the calculation, we study the case of particular interest when the incidence is normal (i.e. $\theta_1=0$) and the two basic layers are of the same optical thickness $H$ (i.e $H=\lambda /4=n_2 h_2=n_3 h_3$). Hence
\[ \beta_2 = \beta_3 = \frac{2\pi}{\lambda_0} n_2 h_2 = \frac{2\pi}{\lambda_0} n_3 h_3 \]  

(18)

The characteristic matrix \( M_2(h) \) of one period is then given by (19) [9].

\[
M_2(h) = \begin{bmatrix}
\frac{n_3}{n_2} & 0 \\
0 & -\frac{n_2}{n_3}
\end{bmatrix}
\]

(19)

The characteristic matrix of the multi-layers, whose basic period is such a pair, is given as can be directly verified multiplying \( M_2(h) \) \( N \) times by itself.

\[
M_{2N}(Nh) = \begin{bmatrix}
\left( -\frac{n_3}{n_2} \right)^N & 0 \\
0 & \left( -\frac{n_2}{n_3} \right)^N
\end{bmatrix}
\]

(20)

And the reflectivity \( R_{2N} \) becomes as expressed in equation (21) [9].

\[
R_{2N} = \left[ 1 - \frac{n_4 \left( \frac{n_2}{n_3} \right)^{2N}}{n_1 \left( \frac{n_2}{n_3} \right)^{2N}} \right]^{\frac{2}{2}}
\]

(21)

This shows that for a fixed number \( N \) of pair, \( R_{2N} \) increases when the ratio \( n_2/n_3 \) increases; further more, if this ratio is fixed \( R_{2N} \) increases with the number of pair \( N \).
In the present case, a monochromatic light \((\lambda_0)\), pumping on an optical surface coated with a material of high refractive index, is considered. In the following example, the medium is air (i.e. \(n_a=1\)), the substrate is fused-silica (i.e. UV cut-off~200nm, \(n_s=1.474\) at 351nm [8,10], (see Annexe B-5)), and the coating is a porous scandia xerogel film (i.e. unknown \(n_H\) and \(h\)), deposited and thermally treated as described later in this section. This case is schematised in Figure V-5.

![Figure V-5: Propagation of an electromagnetic wave through an thin layer, h is the layer physical thickness, \(n_a\), \(n_H\) and \(n_s\) are respectively the refractive indices of the medium, the coating and the substrate, \(R\) and \(T\) are the reflectivity and transmittance, and \(\theta_i\) is the incident angle.](image)

Figure V-6 displays the UV transmission spectrum of this scandia thin single face deposited on a fused-silica substrate. In order to measure only the transmission of the coating, a bare substrate was taken as reference when recording the spectrum (see Annexe B-5). In Figure V-6, it can be seen that \(T\) is minimal \((T_{\text{min}}=87.55\%, R\) maximal) at \(\lambda_0=330\text{nm}\). This minimal transmission corresponds to the first harmonic (i.e. \(m=1\)) of the wave interference caused by the thin film. According to relation (11), \(R\) is a maximal for \(n_Hh=(m\lambda_0)/(4\cos\theta_i)\) at a wavelength of \(\lambda_0\) if \(m\) is an odd integer and if the angle of incident is normal to the surface (e.g. \(\theta_i=0\)). Thus the optical thickness \(H\) can be deduced from equation (11) as follows in relation (22).
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\[ H = n_H \times h = \frac{\lambda_o}{4} \]  \hspace{1cm} (22)

Figure V-6: UV Transmission spectrum of a scandia thin film single face deposited on a fused silica substrate.

The reflectivity at \( \lambda_o \) (\( R_{\text{min}} \)) deduced from equation (15) is given through (23).

\[ R_{\text{min}} = \left[ \frac{n_s - n_H^2}{n_s + n_H^2} \right]^2 \]  \hspace{1cm} (23)

As a result of the conservation of light \( A+S+T+R=1 \) (where \( T \) is transmittance, \( R \) is reflectivity, \( A \) is absorption and \( S \) is scattering), one can deduce the relation (24), assuming that \( A \) and \( S \) are negligible and \( R' \) and \( T' \) correspond to the reflectivity and the transmittance of the bare substrate in (25).

\[ R + T + R' = 1 \]  \hspace{1cm} (24)

\[ R' = (1-T')/2 \]  \hspace{1cm} (25)

If, \( \lambda_o \) is the wavelength of minimal transmission, \( R_{\lambda_o} \) is the total reflectance of the system at \( \lambda_o \), \( T_{\lambda_o} \) is the transmission of the system recorded at \( \lambda_o \) and \( T'_{\lambda_o} \) is the transmission of the substrate alone recorded at \( \lambda_o \) (see Annexe B-5), therefore \( R_{\lambda_o} \) is expressed as in equation (26).
The refractive index of the thin film can also be written in terms of equation (23) as expressed in (27).

\[ n_H = \left[ n_s \left( \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \right) \right]^{\frac{1}{2}} \]  

For the present scandia coating exhibiting the UV transmission in Figure V-6, \( H = 82.5 \text{nm} \), \( n_H = 1.837 \) at 330nm, and \( h = H/n_H = 44.9 \text{nm} \).

**V-3 Experimental Dip Coating**

Dip coating has been chosen over the other deposition methods because of its advantages in terms of low cost, simple processing and possibility of coating substrates of complex shapes. Also, the high price of Sc(ACAC)_3 precursor (i.e. £500 for 10g of precursor containing 1g of Sc^{III}) made dip coating advantageous because no waste of sol was induced. The production of high reflective optical films to be used at 351nm required a substrate that did not absorb at this wavelength. As a result coatings have been deposited on fused silica substrates (thickness=5mm, diameter=45mm, refractive index=1.474 and UV cut-off<200nm) [11]. The following part states the importance of the pre-cleaning step of the fused silica substrate surface. Experimental procedures of deposition are described for each material. Treatment methods applied on scandia coatings are detailed.

**V-3-1 Substrate Preparation for Dip Coating**

In order to underline the importance of cleansing the substrate before performing the deposition, surfaces of a raw and a cleansed substrates were analysed by AFM (the principle of AFM is described in Annexe A-10).
Surfaces were first cleaned with an aqueous solution of HNO₃ (2M), before being washed with H₂O, dried with anhydrous propanol-1-ol, and stored in a dust-free box. Before deposition, substrates were dipped in a propane-1-ol bath to remove the eventual dusts adsorbed on the surface during transport. AFM images and data of the raw and cleansed fused silica substrates are given in Figures V-7 and V-8 and Table V-1.

Figure V-7: AFM image of the surface of an unwashed fused silica substrate (x and y: 1cm=0.66μm; z: 1cm=0.066μm).

Table V-1: AFM-derived characteristics of raw and cleansed fused silica substrate surfaces, (± 5%).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Analysed area (μm²)</th>
<th>Rp-ν (nm)</th>
<th>Rms (nm)</th>
<th>R (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cleansed</td>
<td>36μm²</td>
<td>8 nm</td>
<td>0.7 nm</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>raw</td>
<td>25μm²</td>
<td>36 nm</td>
<td>2.8 nm</td>
<td>1.4 nm</td>
</tr>
</tbody>
</table>

Rp-ν, Rms and R correspond to the distance between the highest peak and the lower valley, the root mean square of the roughness, and the average roughness, respectively calculated for the scanned surface. These are mean values given with an error of 5% (see Annexe A-10).
Large defects present on raw surfaces (see Figure V-7) corresponded to impurities or dust particles (of 30-300nm in dimension) on the fused silica. Knowing that the physical thickness of the coatings was only 40 - 70nm, the presence of such particles at the interface film/substrate was unacceptable. The AFM image of the cleansed substrate (see Figure V-8) showed very few particles of dimension all smaller than 8nm, and exhibited an acceptable smoothness ($R=0.5\,\text{nm}$). After being exposed 1h to the laboratory environment, recontamination of the surface was found to have occurred and large particles were once more seen. Here, the state of surface achieved after cleansing was not as good as had been wished. The purity could have been increased by performing the washing and the coating in a white room (filtered air).

**Sols and Method of Dip Coating**

ZrO$_2$, HfO$_2$ and Sc$_2$O$_3$ xerogel coatings were produced by dipping the substrates in the adequate sols under the conditions listed in Table V-2. The scheme of the dip coating process is shown in Figure V-9.
Table V-2: Characteristics of sols used to produce optical coatings via dip coating.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sc$_2$O$_3$</th>
<th>HfO$_2$</th>
<th>ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>methoxyethanol</td>
<td>0.025</td>
<td>0.1</td>
</tr>
<tr>
<td>Ageing time (weeks)</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Viscosity (cp)</td>
<td>1.55</td>
<td>2.28</td>
<td>2.57</td>
</tr>
<tr>
<td>Withdrawal rate (cm/min)</td>
<td>18</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

For the present repulsive discrete particles (sols given in Table V-2), it was expected that a high withdrawal speed would allow particles to arrange into close-packed structures, leading to denser films. Therefore, a high deposition rate would have been well appropriated to produce high refractive index films. On the other hand, the withdrawal speed had to be adjusted to lead to the right optical thickness ($\lambda_0/4$). As for scandia no stable sols of concentration higher than 0.025M could be produced. Several dips were needed to obtain the quarter-wavelength thickness.
V-3-3 Adjustment of the Withdrawal Rate

The optical coating thickness was deduced from the coating UV spectra, as described in V-2-3. The withdrawal rate was adjusted until the coating exhibited a minimum transmission (corresponding to the first harmonic of the interference) at ideally 351nm. Before interpreting the UV-transmittance data (determination of $H$ and $h$), multiple reflections due to the film present on the rear face of the substrate had to be eliminated. As a result, rear face coatings had been removed for each sample with HNO$_3$/H$_2$O/EtOH-PrOH.

No species absorbing at 351nm were present in the hafnia and zirconia coatings, thus no treatment was required for these two materials. On the other hand, ACAC ligands in the scandia xerogel appeared to absorb in UV at $\lambda_{\text{max}}=312$nm. These absorptions are due to $\pi\pi^*$ and $n\pi^*$ electronic transitions taking place in the C=O groups of the ACAC ligands. In order to produce good optical coatings to be used at 351nm, the removal of this organic of scandia coatings was investigated via treatments described now.

V-3-4 Thermal Treatment of Scandia Coatings

TGA-DSC characterisation of the scandia xerogel (see Figure II-10) showed that the remaining organic ligands, bound on the surface of the platelet particles, were thermally decomposed at 750K (see Figure II-10). This result was confirmed by the work of Beech et al., reporting the beginning of the thermal decomposition of scandium acetylacetonate at 773K with an activation energy of $E_a=51$ kJ.mol$^{-1}$ [12]. XRD investigation of the scandia xerogel heated at 773K for 1h showed that the particles retained their morphology and that no dramatic polymorphic transformation occurred. Such temperature did not affect the fused silica substrate. Thus, in order to decompose the absorbing organic, scandia coatings were deposited on fused silica substrates and were then heated under room condition at 773K for 15mn after each 3 dips. This treatment was accompanied by densification of the coatings as deduced later in part VI-3.
Another treatment method was the removal of the remaining organic species by solvent extraction. This treatment consisted in removing ACAC ligands from the thin film by dissolution in propane-1-ol near its boiling point (i.e. 368K). The principle was the same as that of soxhlet extraction but no sock was required. The extraction system is shown in the Figure V-10.

![Diagram of solvent extraction method applied to coated optical samples.](image)

**Figure V-10: Solvent extraction method applied to coated optical samples.**

The extraction took place for 5h until the absorption at 312nm (related to the presence of ACAC in the coating) ceased to be detected by UV-spectrometry. It will be shown later that some of the superficial particles may have redispersed or dissolved during the purification. In addition, a slight densification of the coating may have occurred that might be attributed to further condensation, removing of the ACAC and rearrangement of the particles. Such extractions are usually applied to bulk materials with the help of a cellulose sock (soxhlet extraction). This could not be performed on scandia bulk material because of the very small particles, diffusing through the socks.
Chemical Treatment of Scandia Coatings

Chemical treatment of scandia coatings consisted of completing the condensation of the deposited *intermediate* particles, composing the film, by immersing samples in aqueous solutions containing an oxidising agent such as H$_2$O$_2$ or highly reactive hydroxyl groups from NH$_4$OH, for example. In presence of such reagents, ACAC ligands were expected to be easily exchanged. Coatings were dipped 10min in the following solutions:
- Aqueous solution of H$_2$O$_2$ (5% w/w) at pH=4.
- Aqueous solution of NH$_3$ (2% w/w) at pH=11.

The disappearance of the absorption at 312nm on UV-spectrophotometry was observed for each treatment, suggesting the removal of the ACAC ligands from the coating. It will be shown later in VI-1 that these purification techniques were accompanied by a degradation of the surfaces possibly due to redispersion or redissolution of the particles in the media. This phenomenon is known as the Ostwald ripening and favours the redissolution of smaller particles [13]. Unfortunately it was impossible to evaluate the amount of scandia that had redissolved because of the very low amount of material loss (e.i. equivalent to loss of 15nm in thickness, see Table VI-9), and the redispersion of particles that can not be accounted in the dissolution.

Characterisations of such treated scandia coatings in addition to untreated scandia, hafnia and zirconia coatings are now presented.

**References**


Chapter VI

CHARACTERISATION
OF COATINGS
VI-1  **AFM Characterisation of Coatings**

Atomic force microscopy (AFM) is a physical, non-destructive, technique that allows for the visualisation of a surface topography and the determination of roughness. Its advantage lies in the fact that it is highly accurate in the z direction and that a computationally-derived image of the surface can be processed and displayed. Its principle is summarised in Annexe A-10. The following investigation on surfaces of scandia, hafnia and zirconia coatings allowed the author to select which treated and untreated coatings were to be considered further.

AFM investigations were performed with an AUTOPROBE CP (Park Scientific Instrument). Surface topographies were recorded in contact mode by scanning 5μm×5μm areas of the coatings. Images of these areas were obtained after correction of the slopes induced by substrate curvature defaults. To obtain clearer patterns, magnifications in the z direction (height) were chosen to be greater than magnifications in the x and y directions. Origins of z-axes have been arbitrary chosen. Values of surface average roughness (R), mean square roughness (Rms) and maximal height difference between peaks and valleys (Rp-v) are given with errors of 5%. Samples submitted to AFM analysis were hafnia, scandia and zirconia untreated and treated coatings produced on fused silica substrates by dip coating (as described in part V). Optical thickness (H) were adjusted at 351nm for each sample.

VI-1-1  **Determination of Cracks in a Silica Gel Coating by AFM**

Figure VI-1 shows the AFM image of a silica thin film. This SiO₂ gel film was the top layer of a coating sample composed of three alternate pairs of high index zirconia and low index silica. Both materials were produced via sol-gel chemistry (as described in [6]), and deposited via dip coating to produce films of 0.27μm in optical thickness. Cracks shown in Figure VI-2 were attributed to interfacial forces taking place between layers. These forces were due to the difference in the thermal coefficients of both materials [1,2], explained by their structural difference (i.e. high density of zirconia
films and the high porosity of silica ones). This phenomenon is greater with thick layers, and it can also be observed when the drying to xerogel is too fast [3,4]. Zirconia, hafnia and scandia coatings, produced here with an optical thickness about 88nm (see UV investigation part VI-3), did not exhibit such cracks in AFM analysis (see Figure VI-2 to VI-10). This suggests that the drying process used for scandia, hafnia and zirconia sols, was slow enough to produce crack-free ceramic thin films to be used at 351nm.

![AFM image of a silica-zirconia film showing cracks](image)

**Figure VI-1: AFM image of a silica-zirconia film showing cracks (x and y: 1cm = 0.66μm; z: 1cm=0.20μm).**

**VI-1-2 Scandia Coatings**

Surfaces of untreated and treated scandia coatings were AFM scanned. Relevant images are displayed in Figures VI-2 to VI-6. They all presented the same aspect of uniformed coatings containing uniform peaks or valleys spread all over their surfaces. No significant structural defects were observed. The maximal distance between the highest peak and the lowest valley ($R_{p-v}$), the root mean squares of the roughness ($R_{rms}$) and the average roughness ($R$) are listed in Table VI-1.
Figure VI-2: AFM image of an untreated scandia coating surface, (x and y: 1cm = 0.66μm; z: 1cm = 0.066μm).

Figure VI-3: AFM image of an propane-1-ol extracted scandia coating surface (x and y: 1cm = 0.66μm; z: 1cm = 0.066μm).
Figure VI-4: AFM image of a thermally-treated (773K, 1h) scandia coating surface (x and y: 1cm = 0.66μm; z: 1cm = 0.066μm).

Figure VI-5: AFM image of a H₂O₂/H₂O (5% w/w, pH=4, 10min) treated scandia coating surface (x and y: 1cm = 0.066μm; z: 1cm = 0.066μm).
Figure VI-6: AFM image of a NH$_3$/H$_2$O (2% w/w, pH=11, 10min) treated scandia coating surface (x and y: 1cm = 0.066µm; z: 1cm = 0.066µm).

Table VI-1: Average roughness of scandia coatings, obtained from AFM (± 5%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Treatments</th>
<th>Surface ($\mu m^2$)</th>
<th>$R_p$-$v$ (nm)</th>
<th>$R_{ms}$ (nm)</th>
<th>$R$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused-silica</td>
<td>cleaned</td>
<td>36</td>
<td>8</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>untreated</td>
<td>25</td>
<td>18</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>n-PrOH soxhlet 5h (368K)</td>
<td>25</td>
<td>22</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>heated under air (773K, 1h)</td>
<td>36</td>
<td>17</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>H$_2$O$_2$/H$_2$O (5% w/w pH=4, 10min)</td>
<td>25</td>
<td>32</td>
<td>3.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>NH$_3$/H$_2$O (2% w/w pH=11, 10min)</td>
<td>26</td>
<td>31</td>
<td>3.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

VI-1-3 Zirconia Coatings

AFM analysis of the surface of a thermally treated (1h at 723K under air) zirconia coating was performed for comparison with the surface of a thermally treated scandia coating. The temperature of 723K was chosen because it corresponded to that required
for the decomposition of acetate ligands (see TGA Figure IV-4). AFM images obtained for both untreated and heated ZrO₂ coatings are shown in Figures VI-7 and VI-8. They presented smoother surfaces than scandia samples.

Figure VI-7: AFM image of an untreated zirconia coating surface (x and y: 1cm = 0.66μm; z: 1cm = 0.066μm).

Figure VI-8: AFM image of a thermally treated (723K, 1h) zirconia coating surface (x and y: 1cm = 0.66μm; z: 1cm = 0.066μm).
The small crater (1 μm in diameter) appearing on the surface of thermally-treated zirconia coating is assumed to be due to the ejection of an impurity upon heating. The statistical calculations of the characteristic $Rp-v$, $Rms$ and $R$ values, listed in Table VI-2, did not take into account the presence of such craters.

### Table VI-2: Average roughness of zirconia coatings obtained from AFM (± 5%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Treatments</th>
<th>Surface ($\mu m^2$)</th>
<th>$Rp-v$ (nm)</th>
<th>$Rms$ (nm)</th>
<th>$R$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused-silica</td>
<td>cleaned</td>
<td>36</td>
<td>8</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>$ZrO_2$</td>
<td>untreated</td>
<td>25</td>
<td>8</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>$ZrO_2$</td>
<td>Heated (air, 1h, 723K)</td>
<td>25</td>
<td>12</td>
<td>1.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**VI-1-4 Hafnia Coatings**

The same procedure was used in AFM investigation of hafnia surfaces. Images of both untreated and thermally treated $HfO_2$ coating surfaces are shown in Figure VI-9 and VI-10. The characteristic values of $Rp-v$, $Rms$, and $R$ are listed in Table VI-3.

*Figure VI-9: AFM image of an untreated hafnia coating surface (x and y: 1cm=0.66 μm; z: 1cm=0.066μm).*
The untreated hafnia coating had a good surface homogeneity. But, contrary to scandia and zirconia, hafnia smooth coating surfaces disappeared upon thermal-treatment leading to very large clusters (200 and 600nm in diameter and between 40 and 80nm in height). The gradual recrystallisation by heating shown by XRD, might have led to these cluster formation. The same transformation has not been observed with the tetragonal phase of ZrO$_2$.

Table VI-3: Average roughness of hafnia coatings obtained from AFM (± 5%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Treatments</th>
<th>Surface ($\mu m^2$)</th>
<th>$R_{p-v}$ (nm)</th>
<th>$R_{ms}$ (nm)</th>
<th>$R$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused-silica</td>
<td>cleaned</td>
<td>36</td>
<td>8</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>untreated</td>
<td>25</td>
<td>12</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>Heated under air (723K, 1h)</td>
<td>65</td>
<td>162</td>
<td>10.9</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Figure VI-10: AFM image of a thermally-treated (723K, 1h) hafnia coating surface (x and y: 1cm = 1 $\mu$m; z: 1cm = 0.10$\mu$m).
VI-1-5 Discussion on Surface Topography

Surfaces of untreated hafnia and zirconia coatings were not as smooth as surfaces of bare clean substrates, but they were smoother than surfaces of scandia coatings. This difference could be attributed to the smaller sizes and the spherical shapes of ZrO\textsubscript{2} and HfO\textsubscript{2} particles compared to the larger dimensions of the Sc\textsubscript{2}O\textsubscript{3} platelets (i.e. $d_{\text{ZrO}_2}=3.2\text{nm}$, $d_{\text{HfO}_2}=2.4\text{nm}$, $d_{\text{Sc}_2\text{O}_3}=8\times40\times70\text{nm}$). Despite the smaller size of hafnia particles, zirconia presented a smoother surface suggesting that not only the particle size but also the coating structuring influenced the roughness. None of the surfaces exhibited cracks.

The high temperature applied had different effects on the samples due to the different structures and thermal resistances. The comparison of $R$ and $R_{p-v}$ for each material (see Tables VI-II) showed that thermal treatment slightly degraded the surfaces of zirconia but produced clusters with hafnia. These can be formed through the slow polymorphic transformation to monoclinic structure taking place below 700K for hafnia only (see XRD Figure III-6). As for zirconia, the slow transformation into tetragonal form, also occurring below 700K (see XRD Figure VI-6), did not create dramatic structural changes in the coating. In the case of scandia, the smoothing of the surface can be explained by a rearrangement of the particles at high temperature.

For scandia, soxhlet extraction treatment in propan-1-ol reduced the $R$-value from 1.7nm to 1.5nm. Annealing at 773K for 1h decreased it to 1.2nm. Scandia samples treated in ammonia or hydrogen peroxide exhibited dramatic increasing of $R$ suggesting that these chemical treatments induced degradation by redissolution or redispersion of the particles into the medium, as explained in part V-3-5. Thermal-treatment and extraction produced a successful purification of organic species in addition to a reorganisation of the particles leading to smoother surfaces. Comparison between untreated and solvent extracted scandia surfaces shows that $R_{p-v}$ increased and $R$ decreased upon extraction. No explanation was found for this observation.
The \( R_{p-v} \) values correspond to the heights recorded between the highest peaks and the lowest valleys of the scanned areas. These values gave an idea of the maximum size of structural defects existing on the surfaces. They corresponded to 5 times the dimension of the primary particles of untreated hafnia and to 2.5 times the dimension of primary particles of untreated zirconia. For scandia, the ratio of \( R_{p-v} \) divided by the primary particle thickness \( T=8\text{nm} \) gave 2.25 for untreated coatings, 2.8 for extracted in propan-1-ol coatings, and 2.1 for thermally treated coatings. This observation suggested that for each case, surfaces of coatings were homogeneous and contained default sizes of only a few particles. Concerning scandia coatings, nothing allows one to affirm that the platelet particles were self-organised horizontally on the surface.

Untreated hafnia and zirconia coatings exhibited good surface homogeneity making them good materials for optical applications. Zirconia surface had the lowest roughness.
and hafnia coating was not thermally stable. Scandia surfaces also exhibited a good smoothness after being annealed 1h at 773K.

### VI-2 XPS Characterisation of Coatings

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is a technique that allows the determination of the chemical composition of a material surface (i.e. to a depth of a several hundreds of nanometre). In addition, the chemical environment of an element can be detected. The principle of XPS is explained in details in Annexe A-II. Investigations were performed with an ESCALAB instrument using Mg Kα₁,₂ (0.75eV) as source of photoelectron excitation. As this method did not require the use of fused silica substrates, scandia, hafnia, and zirconia coatings were produced on glass substrates by dip coating. The optical thicknesses were adjusted at 87.5nm for each sample as described in chapter V. Five thin film samples were submitted to XPS analysis: untreated hafnia, untreated zirconia, untreated scandia, extracted in propane-1-ol scandia, and thermally treated at 773K scandia. They were mainly composed of metal oxi-hydroxides and organic species remaining from the sol-gel-deposition-treatment process. Therefore X-ray photoelectron spectra were expected to contain peaks corresponding to C 1s and O 1s binding energy. Sc 2p¹/₂, Sc 2p³/₂, Zr 3d³/₂, Zr 3d⁵/₂, Hf 4d³/₂, Hf 4d⁵/₂, Hf 4f⁵/₂ and Hf 4f⁷/₂ peaks were also analysed. Spectra of each region were recorded under the experimental conditions listed in Table VI-4. Small peaks at 1072eV, 103eV and 686eV present in each spectrum corresponded to the binding energies of Na 1s, Si 2p and F 1s from the glass substrate composition. For each sample, a charge correction ($\Delta E$) must be applied on the binding energy of each peak. The charge correction depends on the apparatus work function ($\phi$), the position of the sample, and the physical nature of the coating. As described in Annexe A-11, $\Delta E$ were calculated for each sample in relation to the reference C1s binding energy peak ($\alpha'$) (see Annexe A-11) at 285 eV, and are given in Table VI-5. Relative intensities were also reported in relation to the intensity of the $\alpha'$ reference peak of the corresponding spectrum.
Table VI-4: Conditions used for XPS investigation for the different regions scanned.

<table>
<thead>
<tr>
<th>Regions (eV)</th>
<th>Emission correspondence</th>
<th>∆E applied</th>
<th>Step size (eV)</th>
<th>Acquisition time / step (ms)</th>
<th>Number of scans</th>
</tr>
</thead>
<tbody>
<tr>
<td>to 1200</td>
<td></td>
<td>No</td>
<td>1.00</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>390 to 420</td>
<td>Sc2p</td>
<td>Yes</td>
<td>0.10</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>170 to 190</td>
<td>Zr3d</td>
<td>Yes</td>
<td>0.10</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>200 to 235</td>
<td>Hf4d</td>
<td>Yes</td>
<td>0.10</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>9 to 28</td>
<td>Hf4f</td>
<td>Yes</td>
<td>0.10</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>516 to 536</td>
<td>O1s</td>
<td>Yes</td>
<td>0.10</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>270 to 295</td>
<td>C1s</td>
<td>Yes</td>
<td>0.10</td>
<td>100</td>
<td>5</td>
</tr>
</tbody>
</table>

Table VI-5: Charge corrections (ΔE) calculated from the shift corresponding to the C1s (α') binding energy of adsorbed carbonated species.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Eb uncorrected, C1s (α') (eV)</th>
<th>Eb corrected, C1s (eV)</th>
<th>ΔE, (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc₂O₃ untreated</td>
<td>294.3</td>
<td>285</td>
<td>9.3</td>
</tr>
<tr>
<td>Sc₂O₃ propanol extracted</td>
<td>294.1</td>
<td>285</td>
<td>9.1</td>
</tr>
<tr>
<td>Sc₂O₃ heated at 773K</td>
<td>294.9</td>
<td>285</td>
<td>9.9</td>
</tr>
<tr>
<td>ZrO₂ untreated</td>
<td>294.3</td>
<td>285</td>
<td>9.3</td>
</tr>
<tr>
<td>HfO₂ untreated</td>
<td>296.2</td>
<td>285</td>
<td>11.2</td>
</tr>
</tbody>
</table>

The entire C1s-corrected 0-1200eV spectrum of thermally treated scandia is shown in Figure VI-12. Annexes B-1 to B-4 show 0 to 1200eV non-corrected spectra of coatings made of untreated scandia, extracted in propane-1-ol scandia, untreated zirconia and hafnia.

VI-2-1 Experimental Results

Figures VI-13, VI-14 and VI-15 display the C1s-corrected spectra obtained in the regions where Sc, Zr and Hf characteristic peaks are present. Table VI-6 details the
deduced chemical environments for each sample. Binding energy data from literature are reported in Annexe B-17 [13].

Figure VI-12: C1s-corrected XPS of a thermally treated at 773K Sc$_2$O$_3$ coating.

Table VI-6: XPS C1s-corrected binding energies of Sc, Hf and Zr.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peaks</th>
<th>Reference (eV) [13]</th>
<th>$E_b$ corrected (eV)</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_2$O$_3$</td>
<td>Sc 2p$_{3/2}$</td>
<td>-</td>
<td>406.8</td>
<td>Sc-OR with</td>
</tr>
<tr>
<td>untreated</td>
<td>Sc 2p$_{3/2}$</td>
<td>401.8 - (Sc$_2$O$_3$)</td>
<td>402.3</td>
<td>R: (Sc, H, C)</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>Sc 2p$_{3/2}$</td>
<td>-</td>
<td>406.7</td>
<td>Sc-OR with</td>
</tr>
<tr>
<td>propanol extracted</td>
<td>Sc 2p$_{3/2}$</td>
<td>401.8 - (Sc$_2$O$_3$)</td>
<td>402.3</td>
<td>R: (Sc, H, C)</td>
</tr>
<tr>
<td>at 773K</td>
<td>Sc 2p$_{3/2}$</td>
<td>-</td>
<td>406.0</td>
<td>Sc-O from</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zr 3d$_{3/2}$</td>
<td>-</td>
<td>185.2</td>
<td>Zr-OR with</td>
</tr>
<tr>
<td>untreated</td>
<td>Zr 3d$_{5/2}$</td>
<td>182.2 - (ZrO$_2$)</td>
<td>182.9</td>
<td>R: (Zr, H, C)</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>Hf 4d$_{3/2}$</td>
<td>-</td>
<td>224.5</td>
<td>Hf-OR with</td>
</tr>
<tr>
<td>untreated</td>
<td>Hf 4d$_{5/2}$</td>
<td>213.0 - (HfO$_2$)</td>
<td>213.8</td>
<td>R: (Hf, H, C)</td>
</tr>
<tr>
<td></td>
<td>Hf 4f$_{5/2}$</td>
<td>-</td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hf 4f$_{7/2}$</td>
<td>16.7 - (HfO$_2$)</td>
<td>17.4</td>
<td></td>
</tr>
</tbody>
</table>
For each scandia sample, the binding energy difference ($\Delta E_b$) between the Sc2p$^{3/2}$ and Sc2p$^{1/2}$ peaks were close to 4.3eV (i.e. value of $\Delta E_b$(Sc2p$^{3/2}$ - Sc2p$^{1/2}$) given in the literature [13]), confirming that these peaks corresponded to scandium element. For zirconia and hafnia, the literature gives $\Delta E_b$(Zr3d$^{3/2}$ - Zr3d$^{5/2}$)=2.4eV and $\Delta E_b$(Hf4f$^{5/2}$ - Hf4f$^{7/2}$)=1.5eV [13]. These were also verified in the present spectra of zirconia and hafnia samples. Each coating exhibited peaks characteristic of Sc, Zr and Hf atoms in an electron-donor-element (e.g. F, Cl, O, P, N, ...etc) environment (see Annexe B-17). In order to obtain more information on the chemical environment of Sc, Zr, and Hf, C 1s and O 1s data were investigated (see Figure VI-16 to VI-22). Tables VI-7 and VI-8 give C1s-corrected binding energy peaks recorded in O 1s and C 1s regions.

**Table VI-7: XPS C1s-corrected binding energies O 1s peaks.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>O1s Peaks</th>
<th>$E_b$ corrected (eV)</th>
<th>$I_{(a,b)}/I_\alpha$</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_2$O$_3$ untreated</td>
<td>$\alpha$</td>
<td>530.2</td>
<td>2.4</td>
<td>Sc-O, O environment</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>531.6</td>
<td>3.1</td>
<td>Sc-OR, R=C or R=H</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ propanol</td>
<td>$\alpha$</td>
<td>530.3</td>
<td>2.9</td>
<td>Sc-O, O environment</td>
</tr>
<tr>
<td>extracted</td>
<td>$\beta$</td>
<td>531.5</td>
<td>2.9</td>
<td>Sc-OR, R=C or R=H</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ heated at 773K</td>
<td>$\alpha$</td>
<td>529.8</td>
<td>3.8</td>
<td>Sc-O, from Sc$_2$O$_3$,</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>531.5</td>
<td>1.8</td>
<td>Sc-OR, R=C, carbonate species</td>
</tr>
<tr>
<td>ZrO$_2$ untreated</td>
<td>$\alpha$</td>
<td>530.6</td>
<td>2.3</td>
<td>Zr-O</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>531.7</td>
<td>3.4</td>
<td>Zr-OR, R=C or H</td>
</tr>
<tr>
<td>HfO$_2$ untreated</td>
<td>$\alpha$</td>
<td>530.4</td>
<td>2.4</td>
<td>Hf-O</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>531.9</td>
<td>3.8</td>
<td>Hf-OR, R=C or H</td>
</tr>
</tbody>
</table>

In Table V-7, the presence of two peaks (\(\alpha\) and \(\beta\)) suggested that mainly two types of O atoms, differed by two chemical environments, were contained in the coatings. No data were found in literature for the presently analysed compounds. Nevertheless, regarding the data found for other metal oxy-hydroxides (see Annexe B-17), one can suggest that 529.8<$E_b<$530.6eV corresponded to M-O-M and 531.5<$E_b<$5301.9eV corresponded to M-OR (with M=Sc, Zr, HF and R=C, H)
In Table VI-8, the presence of two Peaks ($\alpha'$ and $\beta'$) suggested that C atoms with two types of chemical environment composed the coating. Peak ($\alpha'$) was due to the carbon species adsorbed at the surface and used as reference to calculate the charge corrections ($\Delta E$). Peaks ($\beta'$) corresponded to carbonated organic species from remaining ligands, or residue of thermal decomposition for heated Scandia. As expected and in accordance with results obtained from previous chemical analysis techniques (e.g. FTIR, TGA, ...etc see chapter II, III, and IV), Sc, Hf, and Zr atoms were in an oxygen environment.

### Scandia Coatings

In Figure VI-13, untreated and extracted in propane-1-ol scandia coatings exhibited the same $E_b$-values suggesting that the environment of Sc atoms did not change after purification by solvent extraction. In the case of thermally treated scandia coating, $E_b$ were slightly shifted to lower energies (i.e. 401.6 and 406eV) which corresponded exactly to the Sc2p peaks of Sc2O3.
In Figure VI-13, Cls-corrected Sc2p XPS peaks obtained with untreated Sc2O3 (a), extracted in propanol Sc2O3 (b), and heated at 773K Sc2O3 (c) coatings.

In Figure VI-14, O1s peaks (β) recorded at about Eb=531.5eV for each scandia sample corresponded to oxygen atoms that were bound to H or C confirming that hydroxide and carbonate groups were composing the chemical environment of Sc atoms. The relative intensity of this β peak slightly decreased after propanol extraction and decreased significantly on heating the coating at 773K (see Table VI-7), expressing successful purification of organics. O1s peaks (α) at about 530.3eV corresponded to oxygen atoms in an oxide or hydroxide structure suggesting that oxo or hydroxo bridges were present in the untreated and propanol extracted scandia coatings. The shift of this α peak to 529.8eV, observed for the thermally treated sample, was attributed to the Sc2O3 denser structure formed at high temperature.

In Figure VI-15, the first peak (α') (at Eb=285eV) corresponded to C1s from C-H and C-C of adsorbed CnHm species [5], also used as reference. The β' peak (at 289.3eV) corresponded to C1s from O-C=O, confirming the presence of carbonated residue in the vicinity of the scandium atoms. The relative intensity of the β' peak (see Table VI-8) decreased upon solvent extraction or thermal treatment at 773K of the coating, expressing a successful removal of carbonated species by these treatments. The low
intense peak at 289 eV corresponded to the carbonate residue from thermal decomposition trapped in the structure.

Figure VI-14: Cls-corrected O1s XPS peaks obtained with untreated Sc$_2$O$_3$ (a), extracted in propanol Sc$_2$O$_3$ (b), and heated at 773K Sc$_2$O$_3$ (c) coatings

Figure VI-15: Cls-corrected C1s XPS peaks obtained with untreated Sc$_2$O$_3$ (a), extracted in propanol Sc$_2$O$_3$ (b), and heated at 773K Sc$_2$O$_3$ (c) coatings
The carbonated group, entering the composition of scandia xerogel optical thin films, was logically deduced to be ACAC ligands remaining bound to Sc atoms. Therefore and as already shown by previous analysis on bulk scandia xerogels (e.g. FTIR and TGA-DSC), scandia coatings were composed with ACAC and OH groups in addition to Sc-O-Sc bridges. Heating the thin film 1h at 773K led to a condensed Sc₄O₃ structure that contained trapped carbonate residues from thermal decomposition. Extraction in propane-l-ol for 5h at refluxing temperature did unfortunately remove only a small ratio of ACAC ligand.

VI-2-3 Zirconia Coatings

Zr3d⁵/₂ peaks (at 182.9eV and 185.2eV) of an untreated zirconia coating are shown in Figure VI-16. They corresponded to Zr atoms bound to OH or O-C-R groups as reported in literature (see Annexe B-17). Figure VI-17 showed a main O1s peak (β) at 531.7eV corresponding to OH and MeCOOH groups. The low intensity shoulder (α) at 530.6eV was attributed to O atoms taking part in Zr-O-Zr bridges (oxide structure).

![Figure VI-16: C1s-corrected Zr3d XPS peaks obtained with an untreated ZrO₂ coating.](image)
As for scandia, C1s peak (α’) corresponded to C-C-H from adsorbed C\textsubscript{n}C\textsubscript{m} species. This was also used as reference (see Figure VI-18). The presence of a second C1s peak (β’) (at 289eV) suggested that organic species containing O-C=O sequences remained coordinated to Zr; no doubt these were acetate groups chelating one or bridging two
zirconium atoms as previously shown by FTIR (see Figure III-4). The lower relative intensity of O1s peak (α) compared to O1s peak (β) suggested that zirconium based particles were partially condensed and hydrolysed (i.e. high ratio of hydroxide and acetate groups).

VI-2-4 Hafnia Coatings

Figure VI-19 exhibited the Hf4f spectrum recorded for an untreated HfO2 coating. The Hf4f7/2 peak (at 17.4eV) corresponded to Hf atoms in an oxygen environment. O1s peak (β) at 531.9eV showed in Figure VI-20 corresponded to OH and MeCOOH groups. As for zirconia, the low intense shoulder (α) at 530.4eV was attributed to O atoms taking part in Hf-O-Hf bridges (oxide structure). In Figure VI-21, peak (α') was used as the calibration peak. The second peak (β') (at 289.1eV) was attributed to O-C=O from acetate groups remaining bound to Hf atoms.

![Figure VI-19: C1s-corrected Hf 4f XPS peaks obtained with an untreated HfO2 coating.](image)
These observation confirm the fact that hafnium based particles were partially condensed and hydrolysed and were composed with a high ratio of hydroxide and acetate groups. As expected, there was a high similarity in the XPS results for hafnia and zirconia coatings.
VI-2-5 Discussion on Coating Composition

Scandia, zirconia and hafnia optical coatings showed XPS results that matched previous chemical analyses performed on bulk materials and reported in Chapter II-IV. They appeared to be composed of an oxy-hydroxide structure containing organic impurities that depends on the precursor and the catalyst used. These results are satisfactory in the sense that these coatings exhibited the characteristic compositions of transition metal xerogels to be used as optical thin films. We will see later that the content of carbonated species did not affect dramatically the optical performances of the present coatings at 351nm. For scandia xerogels, Sc$_2$O$_3$ was formed and ACAC ligands were decomposed at high temperature, leaving carbonate species trapped in the oxide network. The next section gives information concerning the optical properties of these coatings.

VI-3 UV-Transmission Characterisation of Coatings

Scandia, hafnia, and zirconia pure materials, having their UV cut-off below 250nm, do not absorb at 351nm making them suitable for 3ω optical coating. However, present coatings were not pure, and amongst the organic species used for processing the xerogels, only ACAC in scandia synthesis, presented an electronic absorption close to 351nm (i.e. ACAC $\lambda_{\text{max}}=312$nm).

The following UV investigations led to the calculation of refractive indices and physical thickness of thin films as described in part V-2-3. These were of great interest to determine the potential application of scandia, zirconia, and hafnia xerogels at 351nm, and also to compare these materials one to the others. Transmission spectra of thin xerogel films, single side (SS) and double side (DS) deposited on fused silica substrates, were recorded at normal incidence (Perkin Elmer UV-NIR lambda 9). Every effort was made to produce SS coatings of quarter-wavelength thick with $\lambda_o=351$nm. The background was previously recorded with two bare fused silica substrates disposed at normal incidence of the reference and analysing beams. Then the bare substrate, placed
in the path of the analysing beam, was replaced with the sample for spectrum recording. Wavelength of minimal transmission ($\lambda_0$), transmittance ($T_{\lambda_0}$), refractive indices ($n_{\lambda_0}$), optical thickness ($H$) and physical thickness ($h$), were deduced for each scandia, hafnia, and zirconia quarter-wavelength coating. Refractive indices and physical thickness were reported with errors of $\delta(n_{\lambda_0}) = \pm 0.002$ and $\delta(h) = \pm 0.3\text{nm}$.

VI-3-1 Scandia Coatings

UV transmission spectra and derived optical data are shown in Figure VI-22 and Table VI-9 for scandia coatings, SS deposited on fused silica substrates.

![UV transmittance of SS deposited scandia coatings. (untreated (a), extracted in propane-1-ol (b), ammonia treated (c), hydrogen peroxide treated (d) and thermally treated at 773K (e)).](image)

*Figure VI-22: UV transmittance of SS deposited scandia coatings. (untreated (a), extracted in propane-1-ol (b), ammonia treated (c), hydrogen peroxide treated (d) and thermally treated at 773K (e)).*
Table VI-9: Optical properties of scandia SS deposited on fused silica substrates, $(\delta(n_{Ao})= \pm 0.002$ and $\delta(h)= \pm 0.3 \text{nm}$).

<table>
<thead>
<tr>
<th>Sc$_2$O$_3$ Treatment</th>
<th>$\lambda_o$ (nm)</th>
<th>$T_{Ao}$ (%)</th>
<th>$H$ (nm)</th>
<th>$n_{Ao}$</th>
<th>$h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>380</td>
<td>96.2</td>
<td>95.0</td>
<td>1.596</td>
<td>60.3</td>
</tr>
<tr>
<td>n-PrOH soxhlet 5h (368K)</td>
<td>355</td>
<td>95.6</td>
<td>88.5</td>
<td>1.618</td>
<td>54.7</td>
</tr>
<tr>
<td>heated in air 1h (773K)</td>
<td>330</td>
<td>87.6</td>
<td>82.5</td>
<td>1.837</td>
<td>44.9</td>
</tr>
<tr>
<td>H$_2$O$_2$/H$_2$O 5% w/w pH=4 (10mn)</td>
<td>310</td>
<td>93.4</td>
<td>77.5</td>
<td>1.688</td>
<td>45.9</td>
</tr>
<tr>
<td>NH$_3$/H$_2$O 2% w/w pH=11 (10mn)</td>
<td>265</td>
<td>93.3</td>
<td>66.3</td>
<td>1.708</td>
<td>38.8</td>
</tr>
</tbody>
</table>

Each spectrum exhibited the characteristic transmittance of a high index coating of physical thickness $h$ of about several tens of nanometres. Calculation were performed with absorption and scattering effects taken negligible (i.e. $A + S = 0$).

First, one can see that for each treated sample, the ACAC absorption band (present at $\lambda_{max}=312$ nm for the untreated scandia) has disappeared, suggesting that each purification method has induced at least a partial removal of ACAC (as also confirmed by XPS). These treatments also induced a densification of the coatings, expressed by the increasing of refractive indices $n_{Ao}$ accompanied by a decreasing of physical thickness $h$.

AFM investigation (see VI-1-2) has shown a dramatic increase of surface roughness for NH$_3$ and H$_2$O$_2$ chemically treated coatings, leading to a loss of transmittance by scattering shown for (c) and (d) in Figure VI-22. These coatings also exhibited a diminishing of physical thicknesses that may be due to redispersion or redissolution of superficial particles in the treatment solutions. Therefore no further interest was shown for these techniques.

The solvent extraction method seemed to be interesting because it did not degrade and roughen the surface of the film (see Figure V-22 (a) and (b)). The thickness decrease (from 60.3 to 54.7 nm) was associated with a slight increasing of the refractive index (from 1.596 to 1.618). However it was difficult to conclude if the coating had
underwent a densification process or if particles from the surface had redispersed themselves in the hot propane-1-ol.

UV-spectra in Figure VI-23 correspond to DS scandia coatings that were built with 6 dips and untreated for (b), 6 dips and after solvent extracted for (c), and 12 dips and solvent extracted for (a). They all exhibited the same high index characteristic as SS scandia thin films, and the clear disappearance of the ACAC absorption upon treatment between (b) and (c). For the thicker coating (a), a maximal transmittance (99.95%) was recorded at about 400nm, suggesting that scattering and absorption represented only 0.05% of the incident light intensity at around $\lambda=400$nm. As a result, the absorption due to the remaining ACAC and the scattering induced by a surface roughness $R=1.5$nm (after extraction) were assumed to be negligible (i.e. $A+S\approx0$).

![Figure VI-23: UV transmittance of DS scandia coatings, 12 dips and propane-1-ol extracted (a); 6 dips and untreated (b) and 6 dips and propane-1-ol extracted (c).](image)

Thermal treatment induced a surface roughness decreasing and a densification through ACAC removal and a possible reorganisation of the particles (annealing). A high improvement of the reflectivity was recorded when the coating was thermally treated at 773K for 1h after each 3dips. The refractive index reached the value of 1.837 at $\lambda_0=329$nm.
Figure V-24 shows the evolution of UV-transmission with increasing optical thickness (60-250nm), for thermally treated DS coated samples. Maximum transmittances close to 100% were recorded at second harmonic wavelengths (i.e. $T$ from 99.3% at 300nm to 99.85% at 560nm). This shows that thermally treated scandia coatings induced mainly reflection and transmission between 300 and 500nm. Therefore, absorption and scattering could be taken to be negligible when a temperature of 773K is applied on scandia coatings (i.e. $0.7%<A+S<0.15%$ between 300 and 560nm).

![Figure VI-24: UV transmittance of DS scandia coatings thermally treated at 773K each 3 dips. (a) to (h) were produced with an increasing number of dips (6, 9, 12, 15, 18, 21, 30 and 45) in a 0.025M scandia sol (prepared as described in II-2-2).](image)

Such evaluation of $A$ and $S$ could not be investigated on untreated scandia DS coatings because of the perturbing absorption band of ACAC ligands at $\lambda_{\text{max}}=312$nm.

VI-3-2 **Zirconia Coatings**

Figure VI-25 shows the UV-transmission of an untreated zirconia xerogel SS coating on a fused silica substrate with the optical properties reported in Table VI-10.
Table VI-10: Optical properties of untreated zirconia and hafnia SS coatings on fused silica substrates, (δ(n_λ)= ±0.002 and δ(h)= ±0.3nm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>λ_0 (nm)</th>
<th>T_λ0 (%)</th>
<th>H (nm)</th>
<th>n_λ0</th>
<th>h (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>none</td>
<td>329</td>
<td>96.7</td>
<td>82.2</td>
<td>1.589</td>
<td>55.6</td>
</tr>
<tr>
<td>HfO₂</td>
<td>none</td>
<td>350</td>
<td>97.3</td>
<td>87.5</td>
<td>1.567</td>
<td>55.8</td>
</tr>
</tbody>
</table>

Figure VI-25: UV transmittance of untreated SS zirconia coating (F) on fused silica substrate.

Figure VI-26: UV transmittance of untreated DS zirconia coatings. (c), (b) and (a) were produced with 1, 2 and 3 dips.
The refractive index calculated (Table VI-10) was in accordance with 1.59 reported in literature for sol-gel zirconia coatings [6]. As for scandia, scattering and absorption could be approximately deduced from an UV investigation of untreated zirconia DS coatings of variable thickness (Figure VI-26). Maximum transmissions showed that very little absorption and scattering were induced by the present zirconia xerogel (i.e. $T=99.3\%$ at 260nm and $T=99.6\%$ at 330nm). Therefore $A+S\approx0$.

**VI-3-3 Hafnia Coatings**

Figure VI-27 shows the UV transmission of untreated hafnia SS coating. It exhibited the characteristic optical properties of high reflective coatings (see Table VI-10). Its deduced refractive index (1.567 at 350nm) was close to that of the zirconia xerogel. UV transmittance investigation of DS hafnia coatings, at different thicknesses, (Figure VI-28) confirmed the fact that $A$ and $S$ were negligible for $HfO_2$ (i.e. $T=99.5\%$ at 260nm and $T=99.7\%$ at 380nm).

![Figure VI-27: UV transmittance of untreated SS hafnia coating (H) on fused silica substrate.](image-url)
VI-3-4 Discussion on Coating Optical Properties

Scandia, zirconia and hafnia coatings all exhibited the characteristics of high reflective thin films. However, they were different in terms of texture, impurity nature and content, hardness, and refractive indices, making them possibly useful only for specific applications. The thermally treated scandia coating had the highest reflectivity, in addition to an acceptable roughness and purity (inducing low level of scattering and absorption). Unfortunately it required heating at 773K, and some substrates are unable to support such a temperature. Optical characteristics achieved by extracting ACAC from the scandia coating in hot propane-1-ol, were not as good as those obtained with thermal treatment, but the method was easier to perform. The main disadvantage of the solvent extraction technique was that it allowed the possibility of superficial particle redispersion. Chemically treated scandia coatings induced unwanted degradation of the surfaces. Hafnia and zirconia coatings exhibited refractive indices that were in accordance with values reported in literature, and close to that of untreated scandia coating. They also had good optical properties (e.g. low surface roughness, low levels of absorption and scattering). The low thermal resistant of hafnia xerogel films may be a
handicap when radiated at 351nm. The zirconia coating has advantages over other materials in terms of thermal stability, homogeneity, surface roughness, processing and cost.

VI-4  **PD Characterisation of Coatings**

UV spectrophotometry has been used to characterise scandia, hafnia, and zirconia coatings in terms of transmission ($T$) and reflectance ($R$), with $(A+S)$ deduced to be $<1\%$ for each case. Absorption taking place within a coating or at its interfaces can be the result of its *intrinsic* absorption and/or absorption by centres such as dusts, impurities, contamination residues, defects, ...etc. Scattering increases with the level of geometric imperfections in the material such as structural non-homogeneity, roughness (related to particle size), scratches, holes, polishing residues, substrate defects, ...etc (this latter can be the starting point of thin film defect formation during coating [7]). As the coatings were to be used at 355nm, it was important to be able to evaluate the absorbance and scattering at this wavelength. The sensitive photothermal deflection (PD) analysis (described in Annexe A-12) can give mappings of absorption and scattering of a 200x200µm selected area at 1/10 ppm sensitivity [8-10]. This technique was also very useful to determine mean values $A$ and $S$, and also to picture sizes, shapes, and concentrations of absorbing centres and defects likely to induce laser damage.

The LOSCM laboratory system was used to perform partial scattering and absorption measurements. Conditions were as follows:

- Scanned areas: 200 x 200 µm.
- Increment: 10 µm.
- Pump laser: argon, 200mW at $\lambda=514.5$nm, beam diameter: 10µm.
- Probe laser: He-Ne, 0.8mW at $\lambda=632.8$nm, beam diameter: 10µm.
- Acquisition time: 10s/per increment.
- Shooting frequency: 27 Hz.
- Angle of scattered light measurement: 45°.
- Detector: SPOT 9D characteristics (15V, 47kΩ).
Irradiation of the sample surfaces with a pumping laser at 351nm (instead of 514.5nm) would have been more appropriated to the present work, unfortunately the system used here did not contain a pump laser YAG emitting at 3ω. However, the mean absorption $A$ is representative of the intrinsic absorption coefficient of the material composing the thin film. Hence samples exhibiting a certain mean absorption ($A$) at 514.5nm are expected to show higher mean absorption at 351nm.

The presence of absorbing or scattering centres at 514.5nm, that could be related to the contamination and imperfections at the substrate surfaces or in the coating, could induce an additional loss of transmittance and reflectance at 351nm (even though the PD analysis were performed at 3ω). Figures VI-29 and VI-30 represent the absorption ($A$) and partial scattering ($S$) maps of scandia coatings that had been thermally treated at 773K.

Figure VI-29: Absorption map of scandia coating thermally treated at 773K on fused silica substrate.

Absorption and partial scattering maps, corresponding to surfaces of the bare fused silica, the untreated scandia coating, the solvent extracted scandia coating, and the untreated hafnia and zirconia coatings, are given in Annexe B-6 to B-15. They were all prepared at $H=87\pm 5\text{nm}$, as given in V-3-2, and exhibited the same aspect as scandia thermally treated in Figures VI-29 and VI-30.
Table VI-11 reports the mean absorption $A$, the partial scattering $S$, the maximum $A_p$ and $S_p$ peak values for each coating deduced from the PD technique. Values of $(A+S)$ at 351nm from the UV transmission analysis in VI-3 are also given.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$A$</th>
<th>$A_p$</th>
<th>$S$</th>
<th>$S_p$</th>
<th>$(A+S)$ (ppm) at 350nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaned bare FS</td>
<td>4.3</td>
<td>30</td>
<td>0.67</td>
<td>1.2</td>
<td>500</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ untreated</td>
<td>15.4</td>
<td>90</td>
<td>0.46</td>
<td>2.2</td>
<td>5000</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ PrOH treated</td>
<td>29</td>
<td>180</td>
<td>0.41</td>
<td>0.8</td>
<td>5000</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ treated at 773K</td>
<td>7.7</td>
<td>120</td>
<td>0.24</td>
<td>0.5</td>
<td>5000</td>
</tr>
<tr>
<td>ZrO$_2$ untreated</td>
<td>7.8</td>
<td>70</td>
<td>0.22</td>
<td>0.9</td>
<td>4000</td>
</tr>
<tr>
<td>HfO$_2$ untreated</td>
<td>5.7</td>
<td>15</td>
<td>0.35</td>
<td>0.7</td>
<td>3000</td>
</tr>
</tbody>
</table>

One could observed that the scandia extracted in propan-1-ol had a high $S$ and $A$ by PD, but exhibited the lowest $(A+S)$ value by UV-transmittance. Such contradictory results suggested that a correlation of both techniques was difficult to establish because too many acquisition parameters differed. UV-transmittance obtained at 351nm, on 50mm$^2$ areas with $S$ corresponding to intensities scattered in the whole space differed from PD results obtained at 514.5nm, on 0.04mm$^2$ areas with $S$ corresponding to scattered...
intensities detected in a spatial cone of 45° angle. In addition, only one PD scanned could be performed for each sample, hence the areas of 0.04mm² were taken to be representative of the whole surfaces. Also, a correlation of the AFM roughness (given in part VI-1) with the partial scattering was not appropriated because the 10μm increment in PD investigation corresponded to twice the dimension of AFM whole analysed areas (5x5μm). Therefore, PD technique did not take into account the effects of macro-imperfection.

Both absorption and scattering maps of each sample exhibited a homogeneous background with localised peaks of higher value. As expected, cleaned fused silica surface exhibited lower mean absorption than coated samples. However, it showed localised absorption peaks (10 - 40μm in diameter) up to \( A_p = 30 \text{ppm} \), suggesting that the fused silica surfaces were locally defective or more probably contaminated during handling (see V-3-1). After coating, these impurities were supposed to be localised at the interface substrate/film. Surprisingly, the partial scattering level \( S = 0.67 \text{ppm} \) of the bare fused silica was higher than for the coating samples, revealing that the polished substrate also contained physical imperfections (e.g. polishing residues, non-homogeneity, scratch, etc). Thus, the coatings contained lower level of physical imperfections and diminished the effects of imperfect substrate surfaces.

VI-4-1 Scandia Coatings

The three scandia coatings exhibited absorbing and scattering centres of a few tens of micrometer in dimension (see Figure VI-29, Figure VI-30 and Annexe B-8, B-9, B-10, B-11). Scattering maxima did not correspond to absorption maxima, suggesting that physical imperfections and dust were both present with different effects. Centres absorbing up to 180ppm at 514.5nm were recorded for untreated and treated scandia coatings suggesting that dramatic localised absorption could also result at 351nm. A for the treated at 773K coating was half the value of the untreated coating (as a result of ACAC thermal loss), but increased by a factor of two after extraction in propan-1-ol (possibly due to a transformation into a more absorbing material induced by the
treatment). In terms of scattering, $S$-values for scandia coatings were similar before and after propan-1-ol extraction. However, it significantly decreases to $S=0.25$ ppm after thermal treatment, possibly due to the densification into Sc$_2$O$_3$ and reorganisation of the particles via removal of ACAC (already shown by AFM, XPS and UV-transmittance techniques).

VI-4-2 **Zirconia Coatings**

The untreated zirconia coating contained physical imperfections and impurity residues inducing scattering ($S_p$) and absorption ($A_p$) localised maxima. Mean $A$ and $S$ values were found similar to those of the thermally treated scandia film. However, absorption centres were less intense, but in a higher concentration than for scandia (see Annexe B-12, B-13).

VI-4-3 **Hafnia Coating**

No absorption maxima were recorded for the hafnia coating, suggesting that it contained no residual impurity in the scanned area (see Annexe B-14 and B-15). The mean value of absorption $A=5.7$ ppm was lower than the other coatings, but $S$ was higher than for zirconia and thermally treated scandia coatings. Therefore, the hafnia coating seemed to contain only structural imperfections (on the study area), and possessed a low intrinsic absorption at 514.5 nm.

VI-4-4 **Discussion on Absorption and Scattering of Coatings**

Additional PD scanned effectuated on adjacent or distant areas of these scandia, zirconia and hafnia surfaces would have been more representative of the samples. However, for each coating, mean absorption and partial scattering were low (i.e. $4<A<29$ ppm and $0.2<S<0.7$ ppm), suggesting that Sc$_2$O$_3$, HfO$_2$ and ZrO$_2$ coatings had low intrinsic absorption coefficients at 514.5 nm. The initial size of the particles forming the coating may have influenced $S$ as explained in III-2-2. Mean scattering ($S$)
of hafnia coating (particle size 2.4nm) was expected to be the lowest, but was even higher than $S$ obtained for the thermally treated scandia (initial particle size: 40x70x8nm). This suggested that the particles size but also the way they were structured in the xerogel influenced the mean scattering.

On the other hand, they all exhibited maxima in absorption and scattering profiles, that did not correspond one to another. These revealed contamination by residual impurities (i.e. absorbing centres) and the presence of structural imperfections (i.e. scratches, region of high density, polishing residues, ...etc). It has been shown that absorbing and scattering centres could be present on bare substrate and could also arise during deposition of the xerogels (from impurities content in the sols or possibly induced by substrate surface imperfections). Thus, they can be located anywhere on the sample (i.e. randomly at the interface, in the coating or at the surface). Thereby, since the representative area was only 0.02mm², the fact that hafnia absorption map did not show maxima did not mean that there were no absorbing centres on the sample. These impurities and imperfections are expected to be the main reason of absorption, scatterisation, and therefore induced laser damage at 3ω (some local absorption reached $A_p=180$ppm at 514.5nm and could induce dramatic absorption and damages at 351nm). The purity of the sol, the environment during deposition and the optical flatness of the substrate were then of great importance. The hafnia coating presented the lowest absorption, the zirconia one presented the lowest mean scattering and the thermally treated scandia coating was not very far from these.

VI-5 **Conclusions on Characterisation of Coating**

Fused silica bare substrates and scandia, hafnia and zirconia coatings have been analysed in terms of surface nanoscopic roughness, chemical composition and environment, transmittance and reflectance in UV, refractive index at 351nm and absorption and partial scattering at 514.5nm. They all exhibited good homogeneity, optical flatness, high reflectivity and high purity making them suitable to be used as
optical films. At $\lambda_0=351\,\text{nm}$, $\text{Sc}_2\text{O}_3$, $\text{HfO}_2$ and $\text{ZrO}_2$ SS ($H=\lambda_0/4$) coatings on fused silica showed the properties in Figure VI-31.

![Figure VI-31: $h$, $n_\text{H}$, $R$, $A$ and $S$ compared for $\text{Sc}_2\text{O}_3$, $\text{HfO}_2$ and $\text{ZrO}_2$ coatings.](image)

Dividing the physical thickness ($h$) by the roughness ($R$) gives a ratio that is constant for treated and untreated scandia coatings (i.e. $h/R=2.8$). This suggests that the rough surface layer and the coating thickness decreased simultaneously with the same intensity upon treatment, expressing a homogeneous purification. ($h/R$) values (1.3 for hafnia and 1.5 for zirconia) revealed a homogeneity, between interfacial layer and coating, that is twice as good as scandia coatings.

Imperfections and dusts particles showed through PD mapping could be the starting points of damage formation upon laser irradiation [11] and nowadays, every effort is made to diminish the concentration and sizes of these optical-defects [12]. Except these defects, all materials exhibited low absorbance (i.e. <5ppm at 514.5nm). However, Figure VI-31 shows that each coating had some strong and weak points. Zirconia
exhibited excellent surface flatness and good thermal stability, but low refractive index. *Hafnia* had good surface homogeneity, low absorption with low refractive index in addition to low thermal stability. Thermally treated *scandia* was highly reflective (i.e. $n_H=1.87$) and despite its slightly higher surface roughness, exhibited low absorption and scattering levels. It had a good thermal stability but the disadvantage to be highly expensive and to require a purification stage. XPS showed that each coating was composed of metal ions condensed via oxo and hydroxo bridges, and contained trapped and bound organic residues. These did not affect the optical performance of zirconia and hafnia coatings at $\lambda=351\text{nm}$, but had induced absorption (at $\lambda=312\text{nm}$) in untreated scandia xerogels. Therefore, ACAC ligands had had to be removed from the scandia xerogel. Both thermal decomposition and solvent extraction methods succeeded at least partly in this task, but despite its higher refractive index, may make Sc$_2$O$_3$ less technically attractive than cheaper and easier to produce ZrO$_2$ and HfO$_2$.

**References**


Chapter VII

APPLICATION OF COATINGS TO $3\omega$ LASER OPTICAL DEVICES
VII-1 LIDT Measurement Techniques

Coatings produced here were designed to be applied to optical devices that are to be incorporated in high-power laser systems for study of nuclear fusion in inertial confinement. In order to have a better idea of the "size" of lenses and other optics involved and also to understand the importance of the technology involved in the design of these optics, the laser facility Nova (in California) is briefly described.

VII-1-1 The Inertial Confinement Fusion Program: the Nova Facility

Inertial Confinement Fusion (ICF) program is focused on the goal of demonstrating thermonuclear fusion ignition and energy gain in the laboratory. In the Lawrence Livermore National Laboratory, programs are built around the existing Nova and Beamlet Laser Fusion Facilities. NIF (the new National Ignition Facility) is under construction in support of defence and energy related issues. This is composed of a battery of 10 high power UV lasers and a target chamber into which the lasers can shoot simultaneously. The cutaway view in Figure VII-1 shows the relevant layout.

Figure VII-1: Scheme of the target chamber of the Nova facility.

Within the laser bay (see Figure VII-2), a space frame supports the 10 laser amplifier chains about 100m long. A system of mirrors and lens causes the 10 laser beams to simultaneously illuminate the fusion fuel target (<100μm), centred in a spherical target chamber (3m in diameter).
Figure VII-2: The Nova laser bay containing 10 lasers.

Lenses required by such laser chains can be massive, as shown in Figure VII-3, representing a 200Kg block of glass designed to be reflective at the infrared wavelength.

Figure VII-3: A 200kg IR reflective mirror.

The Nova laser facility can deliver 15 trillion watts of ultraviolet light for a 3ns pulse, that can be "shaped" in time and intensity, increasing fuel compression efficiency. In addition an array of crystals can "tune" the laser system to produce laser light pulses of different wavelengths (e.g. invisible infrared, visible green, ultraviolet blue). Optical coatings involved had to be highly resistant to such
radiation. Nova's diagnostic capabilities are world-class and this combination of powerful features makes Nova an invaluable tool for gathering data about nuclear fusion.

VII-1-2 Measurement of Laser Induced Damage Threshold (LIDT)

Coatings can be applied as component in HR transport mirrors, AR coatings, blast shield, harmonic converter, debris shield and polariser. Such coatings must fulfil requirements in terms of laser damage resistance that varies with the nature of the device and the type of laser. Therefore, for the present work, measurement of laser induced damage thresholds (LIDT) was to be performed on the $\lambda_{o/4}$ scandia, hafnia and zirconia coatings at $\lambda_o=351\text{nm}$.

VII-1-3 Experimental Procedure of LIDT Measurement

LIDT measurements were performed by shooting the laser on the sample until damages occurred. The energy reaching the coating depends on the laser power, the number of shots, their frequency and duration. As a result, the way of shooting influences the nature of the damage and the flux at which they appear. Three different shooting methods were used (i.e. 1-on-1, N-on-1 and R-on-1 modes).

- The 1-on-1 mode consisted of one shot on one area of the coating. The next shot was applied on another area at greater energy (if the previous shot had not caused damage). The threshold was the mean value of the lowest flux at which damage had been observed and the highest flux at which no damage had occurred.

- The N-on-1 mode consisted of shooting at a flux lower than the 1-on-1 threshold on an area and increasing the number of shots until destruction occurred. The threshold was computed in an identical way to the 1-on-1 mode.

- The R-on-1 mode was similar to the N-on-1 mode except that the laser flux was increased after each shot until the destruction occurred.

Laser damage testing was carried out on single layer coatings with the system shown in Figure VII-4. A Nd-YAG laser was used to produce radiation at 351nm of 0.7ns
pulse duration at a repetition rate of 1.5Hz. The output energy yielded at 351nm was 60mJ per pulse. The sample position was adjusted as to obtain a surface irradiation area equivalent to 1mm². The laser beam was incident upon the sample in S-polarisation at an incident angle of 45°. Damage was detected in-situ with a Normanski interference contrast microscope and a CCD camera display [49].

Figure VII-4: System for LIDT analysis at 351nm.

LIDT depend on the number of damage per area, the average size of the damaged spots, the total percentage of total damage area and the scattering induced by the damage. Some damages cannot be detected by optical or electronic microscopes but only with an interference microscope. Here, LIDT values were taken when visible defect appeared and continued to grow with subsequent laser pulses or if the initial damage was considered to be catastrophic (i.e. damage spot was of similar size than the laser spot size).

VII-1-4  Mechanisms of Damage Formation

The mechanisms involved in damage formation are not fully understood but may include
Formation of small cracks (<0.05mm in diameter) at 1ω, by downward collapsing, [1] with no debris scattered out from the centre of the damage.

Melting due to absorption of the laser radiation accompanied by a reduction of the coating thickness [1]. Such damage has been observed on sol-gel deposited tantala [1] and silica [4,5] or electron beam evaporated HfO$_2$ [6]. To avoid this, the materials must possess high transparency at the chosen wavelength (i.e. be of high band gap), and be as free as possible of any absorbing impurity (e.g. organic, dust, ...etc).

Absorbing impurities, dust, atom clusters [7,8] carbonated species adsorbed at the surface of the substrate, increase the UV absorption and decrease the laser resistance [9]. These damages are usually the first to be observed; nodules are located within layers or at their interfaces [9], and the larger they are the greater the resulting damage is [10]. If the energy absorption is high enough then rapid fluid vaporisation and melting on the edge of the craters are also observed.

Ion beam evaporated Sc$_2$O$_3$ and multilayer stacks scandia/magnesium fluoride had been reported to exhibit crazing [11], peeling or delamination at λ=248nm. These were due to differences in thermal expansion coefficient between layers and adsorption/desorption of pore water, creating compressive or tensile stresses (i.e. convex or concave deformation) [12].

Topographic modification can occur at high intensity. The particles repulse apart one to another consequently generating structure changes in the layer. According to this observation, damages can also be explained in terms of vacancy generation or particle rearrangement. As a result, photoelectronic mechanism which produces energetic electrons in the surface region of an insulating material (laser irradiation of a dielectric film) can lead to strong mutual repulsion affecting the organisation of layers. Binding zirconia particles with polyvinylpirrolidone (PVP) led to coatings highly resistant to laser damage [13]. J. Dijon et al have shown that linear absorption in submicron size region causes heating and then damaging possibly due to a long relaxation time (or a low thermal conductivity). Clusters of nanometric size were proposed to be mostly responsible, and it has been shown that the temperature induced by such absorption can reach
more than $10^4 \text{K}$ on a small (100nm) surrounding material volume. This was proposed to be the first step of the damage formation mechanism [7].

**VII-2 Analysis of Damage and Laser Resistance**

Scandia, zirconia and hafnia single layer coatings of thickness $H = \lambda_0/4$ were obtained by dip coating on fused silica as described. Previous to coating, substrates were cleaned with acid, water and alcohol. After coating, in order to analyse single face coated samples, the film was removed from one face of the substrate by the same method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mode</th>
<th>Number measures</th>
<th>Fluence (J/cm²)</th>
<th>Comments on damages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sc$_2$O$_3$</strong></td>
<td>N-on-1</td>
<td>7</td>
<td>7.6</td>
<td>slight damage do not deteriorate, catastrophic damage at higher energy</td>
</tr>
<tr>
<td>treated</td>
<td>R-on-1</td>
<td>3</td>
<td>13.8</td>
<td>no damage</td>
</tr>
<tr>
<td><strong>Sc$_2$O$_3$, propanol</strong></td>
<td>N-on-1</td>
<td>11</td>
<td>9.9</td>
<td>slight damage, do not deteriorate</td>
</tr>
<tr>
<td>extracted.</td>
<td>R-on-1</td>
<td>3</td>
<td>13.6</td>
<td>no damage</td>
</tr>
<tr>
<td><strong>Sc$_2$O$_3$, thermally</strong></td>
<td>N-on-1</td>
<td>10</td>
<td>6.8</td>
<td>slight marks leading to catastrophic damages</td>
</tr>
<tr>
<td>treated at 773K</td>
<td>R-on-1</td>
<td>5</td>
<td>9.3</td>
<td>series of small damage spots of approximately 1µm large</td>
</tr>
<tr>
<td><strong>ZrO$_2$</strong></td>
<td>N-on-1</td>
<td>3</td>
<td>14</td>
<td>no damage</td>
</tr>
<tr>
<td>untreated</td>
<td>R-on-1</td>
<td>3</td>
<td>13.7</td>
<td>no damage</td>
</tr>
<tr>
<td><strong>HfO$_2$</strong></td>
<td>N-on-1</td>
<td>3</td>
<td>14.9</td>
<td>no damage</td>
</tr>
<tr>
<td>untreated</td>
<td>R-on-1</td>
<td>3</td>
<td>14.6</td>
<td>no damage</td>
</tr>
</tbody>
</table>

LIDT measurements were performed at $3\omega$ with the AWE system shown in Figure VII-4. The conditions applied are given below.

- **Mode**: N-on-1 and R-on-1.
- Angle with incident beam: 45° (S-polarisation)
- Number of shot: 50
- Beam diameter: 1mm

Table VII-2: LIDT values reported in literature for scandia, hafnia and zirconia coatings on fused silica surface (L-LIDT and H-LIDT represent the lowest and the highest values obtained for 6 different areas tested on each sample).

<table>
<thead>
<tr>
<th>Sample identification</th>
<th>L-LIDT (J.cm⁻²)</th>
<th>H-LIDT (J.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂, Sol-Gel, [66]</td>
<td>9.1</td>
<td>9.8</td>
</tr>
<tr>
<td>ZrO₂, Sol-Gel, [74]</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Sc₂O₃, CVD, [142]</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>ZrO₂, Sol-Gel, AWE [253]</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>HfO₂, Sol-Gel, AWE [253]</td>
<td>13</td>
<td>-</td>
</tr>
</tbody>
</table>

Zirconia, hafnia and scandia quarter wavelength coatings were analysed in N-on-1 and R-on-1 modes. Between 3 and 11 measurements were necessary for each sample to give representative LIDT values. LIDT in Table VII-1 corresponded to the highest energies at which no damage occurred. They can be compared with values reported in literature for N-on-1 mode (see Table VII-2).

VII-2-1 Scandia Coatings

Before interpreting these results, it is important to show that a coating can be entirely destroyed by a laser shot. The following SEM picture (see Figure VII-5) shows a massive damage site produced on a scandia coating thermally pre-treated, at 8.4 Jcm⁻² with the following laser conditions: N-on-1 mode, 0.8mm beam diameter, 0° incident angle, 50 shots. EDX map and profiles of this damage site are given in Figures VII-5 and VII-6 in terms of O, Si and Sc elements. The damage is a 0.75cm in diameter circular crater fitting the 0.8mm diameter laser beam. The highest concentration of scandium appeared to be on the edge of the damage site and the
lowest concentration in the centre of the site. In addition, the crater centre exhibits a higher oxygen and silicon content than the non-irradiated area. The later remarks suggest that most of the scandia film corresponding to the whole irradiated area was blasted away leading to a great crater (80% of the diameter of the beam). SEM picture of the crater is shown in Annexe B-16.

Figure VII-5: SEM picture of a whole laser damage performed on thermally treated scandia film, over 8.4J/cm² (x 120). Si, O and Sc ratio content mappings of the damage have been measured by EDX.

Figure VII-6 also provided a profile of the crater in terms of electronic signal showing that most of the material was blasted on the edge. Both edges and centre of this damage area showed little grains of size \((d)\) \((20\text{nm}<d<100\text{nm})\) as seen in the SEM image in Figure VII-7.
Figure VII-6: Si, O and Sc energy dispersive profiles and electronic signal profile of the damage shown in Annexe B-16 and Figure VII-5.

Figure VII-7: SEM image of the surface of the laser damage centre (similar to the edge one) created on a thermally treated scandia film over 8.4Jcm$^{-2}$(×25 000).

The undamaged areas (around the damage site) showed a homogeneous surface composed of non-spherical particles randomly arranged (see SEM image in Figure VII-8). Comparison of Figures VII-7 and VII-8 suggested that the temperature rose over 773K upon irradiation, inducing a polymorphic transformation of the initial
lozenge scandia particles (i.e. they might be melting). Such a temperature rise may have been created by massive energy absorption due to the intrinsic absorption of the coating material or by the presence of absorbing centres (impurities).

Figure VII-8: SEM picture of undamaged area surface of a thermally treated scandia film over 8.4Jcm$^{-2}$ ($\times 25000$).

In Table VII-I, LIDT values measured for untreated and treated scandia coatings were superior in the R-on-l mode than when measured in the N-on-l mode, suggesting that coatings had a better resistance when the energy was progressively applied. Thereby, the scandia untreated and treated xerogel coatings did not permit sufficiently fast diffusion of the energy, since the thermal relaxation time of a material depended on its thermal conductivity and structure.

Despite the removal of the ACAC organic, LIDT values for both modes were lower for thermally-treated dense scandia coatings. In the other hand, when scandia xerogel had been previously purified in hot propanol, LIDT values increased to 9.9Jcm$^{-2}$ in N-on-l mode. As a result, removal of the organic species led to a higher resistance, but densification of the coating led to a lower resistance. The thermal relaxation time of the scandia coatings was suspected to be longer after structural densification. Therefore the structure of scandia coatings (influencing the thermal diffusion
property) was directly linked to their laser resistance and its influence dominated over the concentration of ACAC. However, LIDT values measured on scandia xerogels here were higher than values reported for CVD deposited scandia in Table VII-2 [11]. This confirmed the fact that dense scandia coatings (CVD and thermally treated xerogel) exhibited lower LIDT values at 351nm than more porous xerogel coatings (see Table VII-1).

In the R-on-1 mode, small spots (1μm in diameter) were observed only for thermally treated scandia coatings at 9.3Jcm\(^{-2}\); these have been assigned to local absorptions by impurities or structural defects (likely to arise from incorporation of dust) and densification occurring during heating. These potentially absorbing centres may have been the damage initiators of the small craters in Figure VII-9.

![SEM image of small (<1μm) damage sites produced in thermally-treated scandia coatings above 9.3 Jcm\(^{-2}\) in the R-on-1 mode.](image)

In the N-on-1 mode, small damage sites appeared for each untreated or treated scandia coating over the energy thresholds shown in Table VII-1. They were of various types and shapes: some deteriorated with further irradiation and some did not.
Damage sites that continued to deteriorate could be attributed to linearly absorbed photons (see Figure VII-5 or Annexe B-16). On the other hand, damage sites that did not deteriorate were due to localised absorption (see Figure VII-10), inducing the material to collapse into small particles at the centre of the damage site.

Figure VII-10: SEM image of a 100μm damage site occurred on untreated scandia coating above 7.6 Jcm⁻² in N-on-1 mode. The white spots corresponded to scandia particles collapsed during damage formation.

Other types of damage site were observed. SEM images in Figures VII-11, VII-12 and VII-13 are of coating stacks consisting of substrate/low index materials/scandia layers. Figure VII-11 shows a homogeneous damage site in a thermally-treated silica/scandia pair (0.6mm diameter). The surface of this damage site is magnified in Figure VII-12 and shows a multitude of small craters (~0.5μm) with high and low index layer delamination (possibly due to stress generated by differences in thermal expansion coefficient between layers [11]). Thus the top scandia layer had partly detached itself from the low index silica aerogel coating underneath.
Figure VII-11: SEM image of a $600 \mu m$ large damage observed on a silica/scandia pair heated at 773K above 2.1 Jcm$^{-2}$ in the N-on-1 mode.

Figure VII-12: SEM image showing delamination in the centre of the damage site seen in Figure VII-11.
Figure VII-13: SEM image of a 1µm damage site observed in a MgF₂/scandia pair heated at 773K above 3.1 Jcm⁻² in the N-on-1 mode.

Figure VII-13 represents a 1µm crater in a pair of MgF₂/scandia layers; these may be blasted away separately (on the right of the damage) or together. In these low/high index pairs, LIDT values were lower than for single layers, due to the difference in thermal expansion coefficient of the porous low index and the dense high index materials [11].

VII-2-2 Zirconia Coatings

The only damage sites observed for zirconia sample were substrate cracks localised on the rear face of the substrate (free of zirconia coating). Fused silica damaged at over 11Jcm⁻² [5]. No laser damage was observed in the coating at 14 Jcm⁻² in the R-on-l mode and 13.7 Jcm⁻² in the R-on-1 mode. These results matched previously reported values [14]. The SEM analysis of the irradiated surface showed undamaged smooth surface.
Chapter VII  Application of Coatings to Laser Optical Devices

VII-2-3  **Hafnia Coatings**

No damage sites were observed in both modes in hafnia xerogel coatings at the thresholds. (LIDT values reached 14.6 Jcm\(^{-2}\) in the R-on-1 mode and 14.9 Jcm\(^{-2}\) in the R-on-l mode). Similar results have been reported previously [15]. Such damage thresholds were above those of the bare fused silica substrate (i.e. 11Jcm\(^{-2}\)).

VII-3  **Conclusion, Comparison between Scandia, Zirconia and Hafnia LIDT**

LIDT results are summarised in Figure VII-14, for each sample.

![Figure VII-14: LIDT values measured for untreated (unt.) zirconia, hafnia, scandia and treated scandia coatings in N-on-1 and R-on-1 modes.](image)

Damage occurred through different mechanisms (i.e. probably due to local and intrinsic absorption) and a variety of types of site are obtained. The LIDT values for hafnia and zirconia coatings were higher than for scandia coatings because they did not contain ACAC groups, absorbing at \(\lambda=312\)nm. Also, the more complicated the procedure for scandia xerogel coatings (e.g. involving several steps, dips or treatments) the lower the LIDT because they might have favoured contamination by dust and impurities [9].
Untreated and solvent extracted scandia coatings showed better resistance to 3ω-laser than the denser thermally treated one, suggesting that ACAC absorption was not as expected the main cause of damaging. The scandia coating may have melted. This was confirmed by the fact that LIDT in the R-on-l mode is higher than those obtained in the N-on-l mode. Propan-1-ol extracted scandia exhibited the highest absorption by PD, but the lowest LIDT, suggesting that intrinsic absorption could be only one factor in damage formation.

Each coating reached a LIDT value close to that of pure fused silica (i.e. 11Jcm$^{-2}$). From the present results, the resistance to 3ω Nd-YAG laser radiation was better for hafnia and zirconia coatings. In R-on-l mode, each coating exhibited an excellent laser damage resistance, except for the denser thermally treated scandia.

**References**


Conclusion

Sol-gel chemistry of Sc(ACAC)$_3$ has been studied in acid, basic and neutral media. The first ever reported preparation method of scandia particles in alcohol has been developed and presented. These particles exhibited an anisotropic lozenge platelet shape (8×40×70nm in size) and were stable as a colloidal sol for several months. The hydrolysis/condensation to such particles was difficult due to the stabilizing effect of the ACAC groups, preventing an easy hydrolysis-substitution on the Sc(ACAC)$_3$ precursor. Initiation of the scandia particle formation required thermohydrolysis at 398K (allowed by the MOE solvent). The refluxing time controlled the particle size. The platelet shape was explained by the effect of the ACAC ligands. For comparison purpose, stable alcoholic sols of hafnia and zirconia were investigated. They were prepared in propan-1-ol from hafnium and zirconium isopropoxides with ethanoic acid as a stabilizing agent. Hafnia particles presented a spherical shape and were 2.5nm in diameter. Zirconia particles were also spherical but slightly larger with a diameter of 3.2nm. Scandia, hafnia and zirconia sols had to be used in their early periods after synthesis (i.e. 3 months for scandia and 3 weeks for hafnia and zirconia), before gelation. The chemical stabilisation by ACAC and ethanoic acid were studied and sol-gel mechanisms were proposed for each case. Despite the fact that scandia sols have been produced from a different organometallic precursor, in a different solvent and at a lower concentration than hafnia and zirconia sols, their evolution with time, the compositions and structures of their bulk xerogels and the optical properties of their coatings on fused silica substrates were compared.

Scandia, hafnia and zirconia xerogels, obtained via solvent evaporation from the sols, exhibited the characteristic FTIR, TGA and XPS of colloidal oxy-hydroxy-organometallic particles, with a raw formula corresponding to MO$_x$(OH)$_y$(OR)$_z$ (with M=Sc, Hf or Zr and OR=ACAC, MeCO$_2$H or OPr, depending on the material). The remaining concentration of organic species was found to be higher for hafnia and zirconia than for scandia, suggesting a higher level of condensation for the latter. The
content of such organic species did not influence significantly the UV cut-off of the xerogels produced here. For zirconia and hafnia, UV cut-offs, deduced from their transmission (Figures VI-26 and 28), were close to those of the pure bulk materials (i.e. $\lambda_{\text{cut-off}}(\text{HfO}_2)=225\text{nm}$, $\lambda_{\text{cut-off}}(\text{ZrO}_2)=230\text{nm}$). The scandia xerogel also had a UV cut-off close to that of pure $\text{Sc}_2\text{O}_3$ ($\lambda_{\text{cut-off}}(\text{Sc}_2\text{O}_3)=215\text{nm}$) (see Figure VI-23), but had an absorption band at 312nm attributed to ACAC $n\pi^*$ and $\pi\pi^*$ electronic transitions. This organic species could be removed by thermal decomposition at 723-773K. Thus, the process used here allowed the formation of xerogels as optically transparent as their pure parent materials, except for scandia for which a purification stage was required to eliminate the absorption at near 312nm. It was demonstrate that irradiation of such xerogels with a laser source may induce an increase in the temperature by absorption. Amorphous scandia xerogels transformed gradually to cubic $\text{Sc}_2\text{O}_3$ (which is thermally stable until 1273K), with no dramatic particle morphology transformation. Zirconia amorphous xerogels transformed into tetragonal $\text{ZrO}_2$ when gradually heated until 723K (this transformation usually takes place at 1400K for pure monoclinic $\text{ZrO}_2$). Crystallisation of hafnia amorphous xerogel to monoclinic $\text{HfO}_2$, occurring gradually upon heating until 723K, created a dramatic structural transformation. Therefore, the thermal stability varied for each xerogels, but they all gradually crystallised from amorphous particles with temperature (the initiation of recrystallisation started with the thermal decomposition of the organic content).

Hafnia, zirconia and scandia sols were then used to produce thin optical films on fused silica substrates by dip coating. This method of liquid deposition was very appropriate because of the wetting capacity of the solvents, the simplicity of the equipment involved, and the ease of control of the layer thickness. Quarter wavelength thick coatings of scandia, zirconia and hafnia xerogels, to be used at 351nm, were characterised in terms of chemical composition, structural homogeneity, optical properties, and resistance to 3w-laser radiation. They all exhibited good optical properties, homogeneity and resistance to laser damage.
However each material presented different characteristics that made them likely to be used for specific applications.

Untreated and treated coatings were smooth enough to be used as optical thin films; only hafnia exhibited a dramatic polymorphic transformation upon thermal treatment that destroyed totally the layer morphology. No cracks were found by AFM, suggesting that the drying process was slow enough to prevent extensive high particle compaction. As characterised for bulk xerogels, films were composed of $\text{MO}_x(\text{OH})_y(\text{OR})_z$, suggesting that no reactions occurred with atmospheric CO$_2$, O$_2$ or H$_2$O (see XPS investigation in part VI-2). ACAC groups in scandia coatings were expected to cause the increasing of the intrinsic absorption of the xerogels at 351nm. The attempts to purify scandia coatings from this absorbing organic, by completion of condensation in an acidic peroxide bath or an ammonia solution, were successful but led to the degradation of the surface. These phenomena (expressed by a roughness $(R)$ increasing from 1.7 to 2.7nm) were attributed to the redispersion or redissolution of the superficial particles into the solution. The extraction in hot propan-1-ol allowed for the removal of part of the remaining ACAC, but did not degrade the coating (i.e. the roughness even decreased to $R=1.5$nm). The thermal treatment, inducing the decomposition of ACAC, smoothened and densified the coating (via particle rearrangement). This led to a cubic Sc$_2$O$_3$ thin films (containing residual carbonate species) with a roughness of 1.2nm and a refractive index of 1.84. Despite the lozenge-platelet shape of scandia particles, nothing suggested that they arranged themselves horizontally during deposition. Scandia coatings never reached the surface homogeneity of zirconia and hafnia. The smoother surfaces of untreated hafnia and zirconia coatings (i.e. $R_{\text{ZrO}_2}=0.7$nm and $R_{\text{HfO}_2}=0.9$nm) were attributed to the smaller size of their spherical particles (i.e. $d_{\text{ZrO}_2}=3.2$nm and $d_{\text{HfO}_2}=2.5$nm) compared to the scandia platelet dimension (i.e. 70nm long). It was observed that the smaller hafnia particles did not produce smoother surfaces, suggesting that the coating structure (particle arrangement during drying) was also an important factor in surface topography.
Optically clean fused silica surface had a mean absorption ($A$) of 5.2ppm. The fused silica substrates used here were optically polished and exhibited relatively low mean absorption and scattering (i.e. $A=4.3$ppm and $S=0.67$ppm). By comparison, photothermal-deflection showed that scandia, hafnia and zirconia coatings exhibited excellent mean absorption and scattering values (i.e. $4<A<29$ppm and $0.2<S<0.5$ppm), making them suitable to be used at 514nm. The higher scattering ($S=0.67$ppm, but very acceptable to for optical application), found for the polished substrate, was related to the polishing process. On the other hand, coatings produced lower level of scattering than the bare fused silica substrates, denoting a good distribution of the particles at the surface and thus a higher smoothness. Comparing the mean absorptions $A$ and the particle sizes $d$ showed, once more, that the optical efficiency depended on the coating structure (governed not only by the size of particles, but also their arrangement). This observation is highlighted by the fact that AFM roughness (statistically calculated for a different area of scanned surface than for PD) showed a higher smoothness for zirconia than for hafnia despite the smaller size of hafnia particles. Absorption and scattering maps also displayed peaks that corresponded to contamination and structural faults present at different levels in the coatings and arising from handling and processing. For most of the time, these imperfections were absorbing or scattering, but some were found to exhibit both effects (see maps of untreated scandia coating in Annexes B-10 and B-11). Absorbing peaks were attributed to the presence of impurities of a different chemical nature (dust). Scattering peaks are thought to be induced by local differences of refractive indices (holes, scratches or high-density clusters). Hence, peaks present at the same place in both maps corresponded to absorbing impurities of higher or lower density than the coating. This suggested that coatings were contaminated by imperfections of a different nature. Such imperfections could be localised at the surface of the substrate, at the interface substrate/coating, in the coating or at its surface. The lowest absorption was seen for hafnia and the lowest scattering for zirconia. The highest concentrations of dust and structural imperfections were seen for scandia coatings, and was due to the complexity of the deposition method. Investigation by photothermal deflection can produce a depth profiling of such contaminated coatings and therefore can show where certain types of defect are most
likely to be found. Such information could be useful to the optimisation of the substrate preparation (cleaning, storage, atmosphere used in handling, ... etc) and the coating process (i.e. method of coating, characteristics of the sol, ... etc) with the goal of improving the optical properties.

At 351nm, each coating exhibited a high refractivity when deposited on fused silica substrates, characteristic of high index materials with refractive indices superior to that of fused silica (i.e. \( n > 1.474 \)). They all had low absorption and scattering and most of the light intensity was transmitted or refracted. Refractive indices of zirconia and hafnia xerogel coatings reached the values of \( n_{\text{HfO}_2} = 1.57 \) and \( n_{\text{ZrO}_2} = 1.59 \), in accordance to those reported in the literature. Scandia xerogel coatings exhibited the highest index of refraction with \( n_{\text{Sc}_2\text{O}_3} = 1.6 \). However, these refractive indices were far from those of the pure bulk materials (given to be 1.91 for scandia, 2.10 for hafnia and 2.00 for zirconia), suggesting that they were of lower density. A thermal treatment may induce densification of the layers, as shown for scandia, but also a total degradation as found for hafnia. The thermal treatment of scandia layers not only decomposed the remaining ACAC, but allowed controlled densification of the coating up to a refractive index of 1.86, without creating dramatic structural defects (a technique already used with CVD deposited scandia). For the present purpose of mirror design, a high refractive index suggests a lower number of high/low index coating pair to stack. But, most of all, the coating resistance to laser radiation damage must be as good as that of the fused silica alone. As a result, the LIDT values were the predominant requirement of high refractive coatings.

Determination of damage (LIDT) requires specially adapted equipment (such as the one described in Figure VII-4). High power laser damage mechanisms are not fully understood because of the many factors involved (i.e. laser type, shot duration, substrate, dielectric material, measurement method, ...etc). However, damages are mostly described in terms of the excitation of the electron in the conduction band, the potential heat increase by radiation and the transfer of the energy to the lattice [1]. In correlation with the analysis performed here, the influence of these effects was also verified for pulse duration longer than \( 5 \times 10^{-12} \) s on fused silica samples. The threshold
in fused-silica was found to be 1.5 Jcm$^{-2}$ when irradiated with a Ti:sapphire laser at 780nm for a pulse duration of 10$^{-14}$s. This is lower than the value of 11 Jcm$^{-2}$ obtained here on an optically polished fused silica substrate in the R-on-1 mode with a 3ω-Nd-YAG laser. Unfortunately, it is difficult to compare these two levels because of the difference of both lasers and condition used. LIDT measurements were performed at 351nm. Each coating exhibited a threshold of laser-induced damage equal to or superior to this value, making them suitable to be used at 351nm (i.e. in the R-on-1 mode, scandia resisted up to 13.8 Jcm$^{-2}$, hafnia to 14.9 Jcm$^{-2}$, and zirconia to 14.0 Jcm$^{-2}$). As shown in part VII, values for hafnia and zirconia are similar to those found in the literature. In the R-on-1 mode, the energy applied is more progressive than in the N-on-1 mode. In the N-on-1 mode, the LIDT values measured for hafnia and zirconia were as high as in R-on-1 mode, suggesting a good resistance and a good thermal conductivity allowing for fast relaxation. The N-on-1 LIDT value for an untreated scandia coating (i.e. 7.6 Jcm$^{-2}$) was higher than for the thermally treated one (i.e. 6.8 Jcm$^{-2}$) and lower than for the solvent-extracted one (9.9 Jcm$^{-2}$). This suggested that the soft removal of ACAC increased the resistance, but the densification that accompanied the thermal decomposition lowered it. Therefore the influence of the coating structure on the diffusion of energy through the coating (thermal relaxation) complicated the influence of ACAC absorption. More porous scandia xerogels showed better thermal diffusion and resistance than the denser one. Hafnia and zirconia coatings contained no organic species absorbing at 351nm, and were composed of networks of small particles. They had higher LIDT values than the scandia xerogel. These two coatings could not be damaged below the threshold of fused silica alone in both modes. Therefore they are more appropriate for use at a 3ω wavelength than scandia prepared by the presently developed methods.

As a result, hafnia and zirconia xerogel coatings are more appropriate to the design of 3ω mirror because of their higher stability than scandia coatings. Despite the low stability of hafnia xerogels at 723K, hafnia coatings had the highest LIDT at 351nm, followed very closely by that of Zirconia. But the higher cost of hafnium isopropoxide compared to that of zirconium isopropoxide must influence
significantly the choice of zirconia as high index component. Scandia coatings are more difficult to produce, involve more expense and showed lower 3ω-laser stability. On the other hand untreated or treated scandia coatings remained interesting in terms of high thermal stability and controllable refractive index. Thereby the potential applications in other areas of such scandia coatings at other wavelengths (i.e. far from ACAC $\lambda_{\text{max}}=312\text{nm}$) have to be investigated in the future.

**Further Work**

In terms of sols and coatings produced here, it is possible to increase indefinitely their purity and optical efficiency. In order to reduce the amount of contaminant coming from the air, syntheses, depositions, and potential treatments of scandia, hafnia and zirconia coatings could have been performed in a clean room equipped with an atmosphere controller. In addition, precursors could have been further purified via sublimation and condensation at high temperature in vacuum (e.g. the cold finger method). Also, solvents and reagents could have been further purified via distillation. The use of a dip-coater containing an IR-lamp, allowing for a fast and homogeneous drying, could have improved the quality of the coatings.

When coated by the CVD method, scandia coatings have shown higher stability with regard to laser irradiation than others CVD deposited thin films such as yttria, zirconia and hafnia coatings [2]. Scandia xerogel coatings may exhibit better stability at other irradiation conditions. Therefore, it might be interesting to investigate the LIDT of scandia sol-gel coatings at other wavelengths, and for a shorter time of irradiation (since powerful lasers are available and shot durations down to a few $10^{-15}\text{s}$ are possible) [1]. Also, such lasers give high quality beams (free from high intensity spots) that lead to a more regular distribution of the energy and thus more regular and exploitable morphology of the damage sites.
It was shown that scandia porous xerogels have catalytic activities in terms of dehydration, and CO oxidation. These studies have been performed on aqueous precipitates with surface areas of 6-100 m²g⁻¹. The organically produced scandia xerogels (thermally stable and exhibiting a N₂-BET surface-area of 130-182 m²g⁻¹) may show higher potential catalytic activities than the lower surface-area aqueous materials. As a result, the study of acidic and basic site levels within the xerogels, as well as the adsorption-desorption of molecules such as CO, H₂O or O₂, have to be investigated on this novel scandia material in the future. The present study of the sol-gel chemistry of scandia had the aim of producing particles suitable to be used for optical coatings. The sol-gel synthesis conditions (sol concentration, water content, temperature, refluxing and ageing times, drying process, thermal treatment, ...etc) could be adjusted to optimise the scandia xerogel structure for catalytic applications (porosity, surface area, ... etc). Such investigation would have to be based on analytical techniques such as N₂-BET, mercury porosimetry, TPD, ...etc.

In terms of the characterisation of scandia, hafnia and zirconia coatings, future analyses by depth profiling methods would certainly give additional information on the composition and structure of the layers from their surface to their substrate interfaces. Potential interpenetration between layers could be shown in the case of fully build mirrors. Secondary ion mass spectroscopy (SIMS) or secondary neutral mass spectroscopy (SNMS) must be performed to determine the eventual difference in residual organic species and the presence of potentially adsorbed species (CO₂, H₂O, O₂) at different depths. An X-ray photoelectron spectroscopy (XPS) depth profiling would show the potential difference in the xerogel structure induced during deposition (i.e. oxo, hydroxo bridges relative ratios and residual organics levels). In addition, a photothermal deflection investigation would provide three-dimensional maps of the coatings, showing the localisation of impurities and structural imperfections.

The novelty of the thesis lies in the production of colloidal nanoparticles of scandia, exhibiting controlled morphology, small size and high stability for the first time. Some already known and well-studied materials contain Sc^{III} in their structures. The
preparation methods of such composites used finely ground particles of $\text{Sc}_2\text{O}_3$ (or precipitates from aqueous solutions) and treatment of the component mixture. The controlled hydrolysis-condensation, allowed by the sol-gel technique developed here for scandia, could be used to incorporate $\text{Sc}^{\text{III}}$ into such materials under nanometric particles. Therefore, new methods of synthesis of such materials have to be investigated in the future. These are scandia-yttria-stabilised zirconia, $\text{Sc}_2\text{Cu}_2\text{O}_3$ sensor material or $\text{Ba}_2\text{ScO}_3\text{F}$ semiconductor (see II-1-3). Another application could be found to produce single layers of $\text{Sc}_2\text{O}_3$ of controlled refractive index and thickness as required for InGaAsP antireflective quarter-wavelength coatings (i.e. $n=1.8$).

This shows that scandia may find a multitude of other applications in the future. Thus, the concept of such nanometric lozenge-shaped particles, presented in this work, will be of great interest.


Annexes A: Principles of Techniques

A-1 Transmission Electron Microscopy (TEM) and Shadowing

Transmission electron microscopy is a very well adapted technique for the determination of particle shapes and sizes. It consists in depositing a drop of sol, containing the particles to analyse, on a 200μm holey grid before being placed in vacuum. An electron beam passes through the grid and is collected on the other side by a fluorescent screen. The grid plays the role of sample holder. It is usually made of copper and is CVD-coated with a thin layer of carbon that aims to sustain the particles. Because of the difference in atomic mass, electrons interfere in different ways with the particles and their carbon support. Therefore, the outlines of the particles placed in the path of the electron beam are projected on the fluorescent plate composing the screen. The magnification can then be adjusted by a set of electromagnetic fields.

TEM pictures allow for the measurement of two dimensions of the outlined objects. As a result, if the particles are physically anisotropic, it is difficult to determine their third dimension (e.g. thickness). However, this information can be obtained via shadowing the particles. This method consists in vacuum depositing a very thin layer of Au or Pt on the grid supporting the particles. The deposition takes place at an angle of incidence (α) different than 0° in order to permit an edge of the particles to be protected from the deposition (see Figure A-1). The coated sample is then analysed with the microscope and the thickness of the particles (T) is given by \( T = a \cos(\alpha) \) where \( a \) is the shadow width measured on the picture. Thus if \( \alpha = 60^\circ \) then \( T = a/2 \).
A-2 **X-Ray Probe Analysis (EDX)**

Recent TEM apparatus are generally equipped with X-ray probe analysis (i.e. EDX, also called Energy Dispersive Analysis X-ray: EDAX). This system analyses the X-rays emitted from a sample being bombarded by an electron beam. An X-ray spectrum is collected that contains peaks characteristic of the present elements. This technique is non-destructive. The energies of the X-rays emitted by a sample range from zero to the maximum energy of the incident electrons. An incoming electron, interacting with an electron from an atom electronic configuration, allows for the departure of this latter leaving a vacancy. The atom is unstable in this state and an electron from an outer shell tends to fill this vacancy. The energy difference between the inner electron shell and the outer one is lost under X-ray radiation collected in the spectrum. As each element has an unique electronic configuration, the energy spectrum from any particular element will be unique. Peaks created from the ejection of an electron from the K, L, and M shells are called the K, L, M lines respectively. Further more, the X-ray energy created by the electron jump can also be caught by another electron giving it sufficient energy to escape from the atom. This is called the Auger process; this fluorescence yield process depends on the atomic number.
A-3 Small Angle X-Ray Scattering (SAXS)

Amorphous or crystalline condensed matter scatters X-rays at very small angles as a result of electronic density heterogeneity existing at very small scales (e.g. few nanometres). Micelles or suspended particles in a medium of different electronic density are common studied cases. A monochromatic incident beam, of wavelength $\lambda$, meeting with such a particle leads to the formation of a diffusion zone. The scattering intensity decreases with the angle of diffusion and becomes almost nil for an order of $\lambda/D$, where $D$ is the particle diameter and $\theta$ is the incident angle. This corresponds to an angle of $1^\circ$ with the CuKα emission (i.e. $\lambda=0.1544\text{nm}$) and particles of 9nm in diameter ($D$).

From the measurement of the scattering intensity versus the incident angle, one can obtain parameters of the analysed system that are well defined. For homogeneous particles in suspension, the calculation of the mean gyration radius $R_g$ (corresponding to the inertial momentum of the particles in respect to their centres of gravity) is possible. Results obtained from SAXS analysis alone do not allow the complete determination of the particle morphology, because this requires comparison to a standard model. A picture taken by electronic microscopy is commonly used to obtain previous information on the shape of the particles, leading to the choice of a model (i.e. method of SAXS plots interpretation). The advantages of SAXS over electron microscopy, are a higher resolution and the possibility of analysing particles in solution. X-ray and neutron diffraction at small angles are now very useful techniques to characterise a system of condensed matter of very small dimensions dispersed in a medium. SAXS provides determination of particle or micelle size and morphology. On the other hand, SANS gives information at a molecular level. For the neutron the theory is the same as for X-rays but the diffraction is produced by heterogeneity of neutron density between phases (instead of electronic density as for SAXS). Interpretation of experimental results requires the fitting of relevant models. The theory of small angle X-ray diffraction was well explained by Guinier in the middle of this century [1-3].
Usually results are given in terms of scattered intensity \( I \) versus the scattering vector \( q \) (\( \text{Å}^{-1} \)) where

\[
|q| = \frac{(4\pi \sin \theta)}{\lambda}
\]

\( 2\theta \) is the scattering angle. Calculations were made using the approximation of Guinier where secondary diffraction (and interactions due to scattered waves) are neglected. For a system, the \( \ln(I) \) versus \( \ln(q) \) plot gives primary information (shape) on the particle morphology leading to the choice of a model taken for interpretation: For spherical particles, the Guinier plot \( \ln(I) \) versus \( q^2 \) allows for the calculation of the mean gyration radius \( (R_g) \). For lamellar particles, where two dimensions are greater than the third one \((x,y>z)\), the Guinier plot \( \ln(I,q^2) \) versus \( q^2 \) allows for the calculation of the platelet thickness \( (T) \) in the \( z \) dimension. For rod-like particles, one dimension is greater than the two others \((z>x,y)\), and the Guinier plot \( \ln(I,q) \) versus \( q^2 \) allows for the calculation of the rod diameter [1-3]. The particular case of platelet particles is described in part II-2-5.

### A-4 Spectrophotometry IR (FTIR)

Fourier transformed infra red spectrometry gives molecular fingerprints in terms of frequencies and intensities of characteristic vibrations of functional groups. Analysis usually takes place in the wavenumber range 400 to 4000 cm\(^{-1}\). This technique consists of recording the absorption of infrared radiation (i.e. energy and intensity) at a particular wavelength, induced by twisting, bending, rotating and vibrational motions of atoms in a molecule. Therefore, wavelengths and intensities of absorption depend on atomic masses, bond distances and geometric factors. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is characteristic of the functional groups composing the molecule.
A-5 **Thermogravimetry (TGA-DSC)**

Thermogravimetric analysis, combined with differential scanning calorimetry (DSC), is generally used to study the chemical and polymorphic transformations in a solid while its temperature is increased. TGA records a sample weight as a function of temperature, DSC measures thermal activities as a function of temperature. The parallel interpretation of both results determines at which temperature what type of transformation or reaction occurs (e.g. desorption, decomposition, oxidation, polymorphic transformation, recrystallisation, combustion, etc). In order to determine which processes involve oxidation, it is often necessary to perform the experiment in both presence and absence of oxygen.

A-6 **X-ray Diffraction (XRD)**

This analytical technique allows one to determine the crystallinity of a fine powder. Intensity and angle of X-ray diffraction depend strongly on the relative disposition of atoms in a material. If this one is amorphous (i.e. with a random disposition of atoms) X-rays are scattered in every directions. If atoms are well organised in planes, a diffraction pattern is obtained and narrow-intense peaks are exhibited. The condition of diffraction of X-rays in a crystal is given by the Bragg equation shown below:

\[ m \lambda = 2d \sin \theta \]

where \( \theta \) is the angle of diffraction, \( \lambda \) is the wavelength of the incident (and diffracted) radiation, \( m \) is the order of diffraction and \( d \) is the interplanar distance in the crystal lattice. A finely ground powder composed of homogeneous macro- or nano-crystals presents crystal planes oriented randomly in the three directions of space. Therefore, recording the diffraction of X-ray for \( 3<\theta<90^\circ \) on such a powder sample, leads to a pattern containing peaks that can be attributed to each type of crystal planes. Diffraction phenomena can be interpreted with the help of the reciprocal lattice concept. A plane can be represented by a line drawn normal to the plane. The spatial orientations of these vectors describe the orientations of the planes. They are also called
the Miller indices. The length of a vector is inversely proportional to the interplanar spacing of the plane that it represents. When normals are drawn from the same origin for each plane of a crystal lattice, the terminal points of these normals constitute a lattice array that is also called the reciprocal lattice.

From the diffraction peaks of an unknown compound and the Bragg equation, one can work out the interplanar distances within the crystal lattice. The crystalline structure can then be deduced [4]. This can also be done by fitting the Miller indices with equations that are characteristic of the crystal structure. The following equation characterises the cubic structure where $a$ represents the dimension of the unit cell, $d$ represents the interplanar distance and $h, k$ and $l$ the Miller indices.

$$d(hkl) = a(1/h^2 + 1/k^2 + 1/l^2)^{1/2}$$

### A-7 Determination of Particle Sizes by XRD

If the nano-crystals, composing the powder sample, have an average dimension less than 100nm, a broadening effect is noticed on the of X-ray diffraction peaks [5]. The extent of the broadening is given by the following equation.

$$B = (0.9\lambda) / (t \cos \theta)$$

where $B$ corresponds to the broadening measured at half of the maximum intensity of the diffraction peaks (in radians), and $t$ corresponds to the average diameter of the crystal particles. All diffraction peaks have measurable breadths that are due to the divergence of the incident beam and size of the particles. However $B$, in the equation above, refers only to the extra broadening caused by the particle size and is accurate only if $t<100$nm.
At angles higher than $2\theta = 40^\circ$, the diffraction effect of the Kα$_2$ emission from the copper source must be subtracted before measurement of the breadths [6]. This effect usually shows as main diffraction peak shoulders at higher angle. As a result, the smaller the particles are, the more accurate the measure is. In the present work, we have measured particle average diameter of less than 3nm, (see part III-2-7). At average diameters ($D$) lower than 2nm, the broadening effect flattens considerably the pattern making $B$ and $\theta$ difficult to read. SAXS would then be more appropriate for the determination of such small dimensions.

### A-8 UV spectrophotometry

A radiation meeting a substance is submitted to four phenomena: absorption ($A$), scattering ($S$), transmission ($T$), and reflection ($R$). The initial incident light intensity is then decomposed in four intensities such as $I=A+S+T+R$. UV-visible spectrophotometry allows for the determination of $T$ and $A$ (and also $R$, if $S$ is negligible).

Absorptions in the UV-visible wavelength range are due to non-forbidden electronic transitions from fundamental to conduction energy levels. The lower the radiation wavelength is, the higher the energy given to the system and the more probable the promotion of an electron to a superior level are. For carbonate organic absorbents, these transitions are called $\pi\pi^*$ and $n\pi^*$ because they correspond to the transition of an electron from the orbital $\pi$ of a Csp$^2$, or from the doublet $n$ of an O atom to the excited orbital $\pi^*$ from the molecular orbital distribution. In an oxide, the absorption threshold corresponds to the energy necessary to promote an electron from the fundamental to the conduction level. The greater the band gap of a material is, the lower its wavelength limit of absorption is, and the lower its UV cut-off is. Such UV investigation can also lead to the calculation of refractive indices and physical thickness of thin films as explained in details in part V-2-3.
A-9 Nitrogen Adsorption-Desorption Analysis (N₂-BET)

Adsorption-desorption isotherms (i.e. variations of the amount of gas adsorbed on a surface as its pressure is increased and then decreased at a specified temperature) are commonly used for determining the surface area, the porosity and the pore size distribution of solids. The six types of isotherm seen are shown in Figure A-2. The equation of the BET isotherm (i.e. Brunauer, Emmet and Teller [7]) is usually applied to determine the surface area:

\[
\frac{p}{(p_o-p)} V = 1 / (V_m C) + p (C-1) / (V_m C p_o)
\]

where:
- \( p \) is the pressure of the adsorbed gas,
- \( p_o \) is the vapour pressure of bulk liquid adsorbate,
- \( V \) is the volume adsorbed,
- \( V_m \) is the volume adsorbed at monolayer coverage and
- \( C = (k_a / k_d) / (k'_a / k'_d) \), with \( k \) and \( k' \) corresponding to the adsorption/desorption rate constants for monolayer and for subsequent layers respectively.

By plotting \( p / [(p_o-p) V] \) versus \( p / p_o \), one may deduce the values for \( C \) and \( V_m \) from the intercept and the gradient. Knowing the molecular cross-sectional of the adsorbate, usually calculated from the liquid density (i.e. 0.164nm² for N₂), the surface area of the sample can be calculated. During adsorption, a surface heterogeneity may cause a variation of the heat of adsorption with coverage. In the present BET theory, it is not taken in account. In addition, interactions between molecules in the adsorbed layer are neglected. The Langmuir plot limits adsorption to a monolayer. Thus, the BET method is more appropriate to the present study. Nitrogen is considered the most suitable adsorbate for most solids because it usually gives an isotherm with a \( C \)-value high enough to give a pronounced variation in the rate of adsorption, but not too high to suggest excessively localised adsorption.
The type II isotherm (associated with non-porous or macroporous materials) represents unrestricted multilayer of adsorption. The first linear section (plateau) corresponds to the surface covered by the first layer of molecules before further ones develop. The type IV isotherm is associated with mesoporous materials. The characteristic hysteresis loop corresponds to capillary condensation in the mesopores. Maximum coverage occurs at high pressure and the characteristics of type II isotherm can be applied to the first part of the type IV one. The other types of isotherm were not relevant to the present work, but details can be found in literature [8].

![Types of physisorption isotherms.](image)

**Figure A-2: Types of physisorption isotherms.**

### A-10 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is usually used to picture surface topography (e.g. showing structural defects, cracks, holes, peaks, ...etc). Also, recent apparatus are equipped with softwares that can perform statistical calculations of the roughness ($R$), and other characteristics (e.g. $Rp$-$v$, linear profile, ...etc). In AFM, a very thin flexible tip, cut in $Si_3N_4$ or $SiO_2$ foils, is slowly allowed to approach the surface until contact is made. By scanning a selected area of the surface and applying a constant force on the tip, a topographic image of varying heights is obtained. In the contact mode, the
The detectable force threshold is in the order of 10 to 100 eV/nm or $10^{-8}$ to $10^{-9}$ N. Therefore, if the tip is ideally thin enough and the surface ideally flat enough, individual atoms can be pictured. The sample is fixed on a piezoelectric scanner with the surface to be analysed directed horizontally on top. The tip is fixed above the sample surface on a force-deflection detection device that can be moved manually in the z direction. The raster scan in the x and y directions is applied by the piezoelectric sample holder. The whole system is also equipped with a vibration isolation device and a computer control system that converts the raw signals into a computerised image of the surface. In order to provide a well-defined interaction with the sample surface, the tip must be finished with a sharp end, ideally terminated with a single atom on its apex [9].

Figure A-3: Optical beam deflection method applied for feedback signal detection in the contact mode of AFM.

In the present case, the deflection, induced by the force acting between the flexible tip and the surface, was detected by an optical beam deflection (see Figure A-3). This method is the more commonly used because it allows for the detection of a large range of forces. A light beam, typically from a solid-state laser, is reflected by the top surface of the tip and the reflected light is detected with a photodiode. In order to
produce an almost perfect reflection, the tip surface is coated with gold by CVD. The mechanical bending of the flexible tip deflects the optical beam, thus changing the proportion of light falling onto the photodiode. The difference of light intensities detected by the photodiode is the basis of the raw signals. After treatment (e.g. filtration, slope correction, ...etc) these signals are computerised to produce an image of the surface topography.

A-11 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (or Electron Spectroscopy for Chemical Analysis (ESCA)) is a technique that allows the determination of the chemical composition of a material surface. Moreover, the chemical environment of an element can be detected. An atom excited by losing an electron from its outer shell, usually returns to an intermediate state by promoting an electron from an inner orbital. This phenomenon is accompanied by releasing energy under X-ray form. Thus, emitted photons are of high energy and of short wavelength (i.e. several nanometres). Excitation can be performed by electron bombardment or by irradiation with X-rays of shorter wavelengths [10-11]. Sources of excitation used for XPS are usually Mg Kα1,2 or Al Kα1,2.

When a material is bombarded with such a source of energy, an emission of electrons occurs from inner-shelves. Electrons whose binding energies are less than the energy of the exciting X-ray can be ejected. The kinetic energies $E_k$ of these emitted photoelectrons are then measured. Binding energies $E_b$ are characteristic of these electron-ion systems and are given as

$$E_b = h\nu - E_k - \phi$$

where $h\nu$ is the energy of the excitation source and $\phi$ is the spectrometer work function. ($\phi$ is constant for a given analyser). Therefore, the energy $E_k$ of an ejected electron is characteristic of the emitting atom and of its chemical environment. The concentration detection limit varies with the nature of the atom but can be estimated at 1% for light elements such as C, O and N to 0.1% for heavy element, such as Hf or Zr. The work function $\phi$ also depends on the position of the sample from the electron detector. If the material is a poor conductor (e.g. a metal oxide) the loss of electrons
creates a positive charge at the surface that tends to decrease the kinetic energy of the ejected electrons. As a result, $E_b$ tends to be higher than real values. In order to determine the intensity $\Delta E$ of this phenomenon, also called the charge correction, a reference binding energy (e.g. of C 1s) is usually used when the material to analysed contain C atoms in another environment than the reference ones. Substrate surfaces, containing adsorbed carbon-based species, give C 1s peaks at 285 eV. They correspond to C-H and C-C binding energies. $\Delta E$ takes in account the work function $\phi$ and is then calculated in relation to this reference C 1s binding energy [12]. Usually, when the analysed material contains many carbons (polymers), Au reference is needed. Such reference is not required when C 1s reference is well defined.

Binding energies are affected by electrons involved in covalent bonds, hence by the chemical environment of the atom. Generally parameters such as coordination, oxidation-state or ligand electronegativity affect the electron density around the atom creating a chemical shift in the electron binding energies seen. Such a shifting allows the analysis of the material chemical composition. References on the binding energy shifts can be found in literature [13].

A-12 Photothermal Deflection (PD)

When an electromagnetic wave is absorbed by a material, part of energies is converted to heat, inducing a local variation of refractive index. The heat propagation and the induced temperature change can create damage. Therefore, the resistance of a material toward radiation depends on its intrinsic absorption coefficient and its thermal conductivity. The basic process of photothermal deflection involves measuring the heating of a material caused by optical absorption. An area of the coating is irradiated perpendicular to the surface with a pump laser. A local temperature rise occurs and a thermal wave propagates within the material structure. This temperature rise is accompanied by a spatial variation in the refractive index leading to a bulking. This local dilatation, appearing on the sample surface, depends on the thermal expansion coefficient of the material. A second laser (i.e. probing laser) measures the local optical deflection induced by the refractive index gradient and the thermal bulking of the sample surface. As a result, the amplitude of the deflected signal depends on the
absorbing and thermal expansion properties of the thin film. PD is a direct measurement of absorbed energy. Hence the photothermal response is linear over a large range of absorbed optical power and is null when there is no absorption. As PD gives a reflected signal, it is insensitive to scattered light. In addition to being a non-destructive method, it is a very sensitive method that can measure absorption at ppm levels. Its advantages also lay in the possibility of producing maps of surface absorption with increment of 10\(\mu\)m by 10\(\mu\)m. This method can be used on a thin film for the determination of absorbing centres, the measurement of mean absorption, or the study of thermal characteristics. Studies have shown that this method also allows the localisation of absorption centres at the interface substrate-layer [14-16]. For the present cases, only absorption and scattering maps of optical coatings were investigated. PD measurements also depend on the nature of the substrate. As a result, experiments have to be performed with the same substrate. The thermal properties of a coating vary with the material, its structure, the deposition technique, and the thickness. Any comparison between two samples assumes that these parameters have little influence on the deflection. That it to say that only thin films of thickness less than 1000nm can be analysed [17].

The mean value of absorption is deduced from the detection by a photodetector of the deviation of the probing laser beam. This photodetector is divided in its middle in two equal parts \(V_A\) and \(V_B\). These correspond to the voltages delivered by both parts of the detector when the beam hits them. When the absorption is null, the probe laser spot is adjusted at the centre of the detector and both \(V_A\) and \(V_B\) are balanced (i.e \(V_A = V_B\)). When absorption occurs, the refractive index changes and the laser spot is displaced on the detector leading to \(V_A - V_B = \Delta V \neq 0\). One can show that the value \((\Delta V / V_A + V_B)\) is proportional to the angle of deviation \(\theta\) [18]. For classical conditions of irradiation, a variation of absorbance of \(10^{-4}\) corresponds to a deviation of \(10^{-8}\) radians. \((\Delta V / V_A + V_B)\) is then independent of the energy received and of the distance sample-detector. Hence it is independent of scattering effects. However, \(\theta\) varies linearly with the energy of the pump laser. In order to subtract the influence of the energy of the pump laser, the photothermal signal is given as \(PS = (\Delta V / V_A + V_B) / V_o\), where \(V_o\) is the voltage delivered by the photodetector measuring the power of the pump laser.
The numeric value of absorption is then obtained by comparing the photothermal signals measured for the samples and for coatings of known absorption (references). These absorptions were previously measured by classical photometry. Therefore, a simple proportionality relation is used to calculate the mean value of absorption.

![Diagram of PD measurements](image)

**Figure A-4: Principle of PD measurements.**

Scattering maps can be obtained as follows. When a transparent material is illuminated with a source of high enough power, light is scattered out of the spectral direction. A large aperture lens collects the light scattered by the coated face outside of the reflection direction, and directs it on a silicon photodiode. This one delivers a voltage $V_S$ when a non-null energy is collected. This measurement corresponds only to a spatial cone defined by a certain angle. The partial diffusion factor $DP$ is given by $DP = V_S / V_I$, where $V_I$ corresponds to the tension induced by the incident radiation of the laser pump. A value of total scatterisation can be obtained by integrating $DP$ over the all space. [14]. The principle of simultaneous absorption-diffusion measurement is shown in Figure A-4. Conditions usually used to perform partial scattering and absorption measurements are the following:
- Scanned areas: 200 × 200 μm.
- Increment: 10 μm
- Pump laser: argon, 200mW at λ=514.5nm, Ø=10μm.
- Probe laser: He-Ne, 0.8mW at λ=632.8nm, Ø=10μm
- Acquisition time: 10s/per increment
- Shooting frequency: 27 Hz
- Angle of scattered light measurement: 45°
- Detector: SPOT 9D (15V, 47kΩ)

**A-13 Viscosity**

Viscosity is deduced from the time ($T_s$) needed by a fixed volume of the scandia sol, of viscosity ($\eta_s$) and density ($\rho_s$), to pass through a capillary of a constant diameter. This method requires knowledge of the time ($T_L$) needed by the same volume of a liquid, of known viscosity ($\eta_L$) and density ($\rho_L$), to pass through the same capillary. ($\eta_s$) is deduced from the equation given below:

$$\frac{\eta_s}{\eta_L} = \frac{T_s \rho_s}{T_L \rho_L}$$

The viscosity of a liquid phase decreases when the ambient temperature increases. As a result, the given equation can be used if measurements are made at the same temperature for both liquids. Two capillaries of different diameters are immersed in a water bath at 298K. $T_s$ and $T_L$ are recorded for each capillary for each sample and viscosity is then deduced from the previous equation.

**References**


Annexes B: Additional Figures

Annexe B-1: C1s-corrected XPS of an untreated Sc₂O₃ coating.

Annexe B-2: C1s-corrected XPS of a propan-1-ol extracted Sc₂O₃ coating.
Annexe B-3: C1s-corrected XPS of an untreated ZrO$_2$ coating.

Annexe B-4: C1s-corrected XPS of an untreated HfO$_2$ coating.
Annexe B-5: UV transmission spectrum of a bare cleaned fused-silica substrate.

![UV Transmission Spectrum](image)

Annexe B-6: PD absorption map of the bare cleaned fused silica substrate.

![PD Absorption Map](image)
Annexe B-7: PD scattering map of the bare cleaned fused silica substrate.

Annexe B-8: PD absorption map of the propan-1-ol extracted scandia coating.

Annexe B-9: PD scattering map of the propan-1-ol extracted scandia coating.
Annexe B-10: PD absorption map of the untreated scandia coating.

Annexe B-11: PD scattering map of the untreated scandia coating.

Annexe B-12: PD absorption map of the untreated zirconia coating.
Annexe B-13: PD scattering map of untreated zirconia coating.

Annexe B-14: PD absorption map of the untreated hafnia coating.

Annexe B-15: PD scattering map of the untreated hafnia coating.
Annexe B-16: SEM image of a site of laser-induced damage, taken on a single layer of scandia coating at more than 6.9 J cm$^{-2}$, (1 cm=66 μm, ×150), and the corresponding EDAX profile analysis.

<table>
<thead>
<tr>
<th>Peak</th>
<th>compound</th>
<th>( E_b ) (eV)</th>
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<tbody>
<tr>
<td>Sc2p(^{3/2})</td>
<td>Sc</td>
<td>398.3</td>
</tr>
<tr>
<td></td>
<td>Sc(_2)O(_3)</td>
<td>401.8</td>
</tr>
<tr>
<td></td>
<td>ScCl(_3)</td>
<td>402.0</td>
</tr>
<tr>
<td></td>
<td>ScS</td>
<td>402.9</td>
</tr>
<tr>
<td></td>
<td>ScF(_3)</td>
<td>405.0</td>
</tr>
<tr>
<td>Zr3d(^{5/2})</td>
<td>Zr</td>
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<tr>
<td></td>
<td>ZrO(_2)</td>
<td>182.2</td>
</tr>
<tr>
<td></td>
<td>Zr(_4)(OH)(_8)salanine(_8)Cl(_8)</td>
<td>182.8</td>
</tr>
<tr>
<td></td>
<td>ZrF(_4)</td>
<td>185.3</td>
</tr>
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<td>Hf4f(^{7/2})</td>
<td>Hf</td>
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<td></td>
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<td>HfO(_2)</td>
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<tr>
<td>O1s</td>
<td>NiO</td>
<td>529.5</td>
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<td></td>
<td>Cr(_2)O(_3)</td>
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<td></td>
<td>KOH</td>
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<tr>
<td></td>
<td>Poly (methyl methacrylate)</td>
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<td>SiO(_2)</td>
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<td>Al(OH)(_3)</td>
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<td>C1s</td>
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<td>(CH(_2))(_n)</td>
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<td></td>
<td>CCl(_4)</td>
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Annexe B-18: N$_2$-adsorption isotherm at 77.5K of a zirconia xerogel preheated at 723K.

![Graph showing N$_2$-adsorption isotherm at 77.5K for a zirconia xerogel preheated at 723K.]

Annexe B-19: Chemical sources

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
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</thead>
<tbody>
<tr>
<td>Sc(ACAC)$_3$</td>
<td>Purity 99%, Chemat Technology, INC</td>
</tr>
<tr>
<td>MOE</td>
<td>2-methoxyethanol anhydrous, purity 99.8%, Aldrich</td>
</tr>
<tr>
<td>Hf(OPr)$_4$</td>
<td>99% pure, 70% w/w in propan-1-ol, π-Chem</td>
</tr>
<tr>
<td>Zr(OPr)$_4$</td>
<td>99% pure, 70% w/w in propan-1-ol, Aldrich</td>
</tr>
<tr>
<td>n-PrOH</td>
<td>Purity 99% +, Aldrich</td>
</tr>
<tr>
<td>EtCOOH</td>
<td>Acetic acid purity 99.99% glacial, Aldrich</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_4$OH 30% NH$_3$ in water, purity 99.99%, Aldrich</td>
</tr>
</tbody>
</table>
ERRATA


p 20: MPEOU stands for N-triethoxysilylpropyl O-polyethylene oxide urethane.

p 31: Read “the particles are pushed apart by electrostatic or chemical effects of the solvent encombrement. On the other hand, they attract themselves by the Van der Waals’ dipolar interactions”.

p 46: Read “Sc$_2$Cu$_2$O$_5$”.

p 47: Read “(CO)$_2^-$“.

p 84: Read “fluorite”

p 108: In *Figure VI-6*, XRD pattern (a) stands for (b), and pattern (b) stands for (a).

p 48, 49, 57, 58, 89, 106, 149-152, and 194: Replace “carbonate” by “carboxylate”.

p 144, 192 and 194: “2.4nm” hafnia and “3.2nm” zirconia average particle sizes must be replaced by “<5nm”.