

Synthesis and structural characterisation of the new K_2NiF_4 -type phases, $A_2In_{0.5}Sb_{0.5}O_4$
(A=Sr, Ba)

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Abstract

In this paper we report the synthesis and structural characterisation of two new K_2NiF_4 -type phases, $Ba_2In_{0.5}Sb_{0.5}O_4$ and $Sr_2In_{0.5}Sb_{0.5}O_4$. To our knowledge these are the first examples of K_2NiF_4 compounds of general formula $A_2M^{III}_{0.5}M^V_{0.5}O_4$ with both 3+ and 5+ cations in the octahedral sites. $Ba_2In_{0.5}Sb_{0.5}O_4$ is shown to have a tetragonal cell (space group $I4/mmm$, $a=4.1651(1)$, $c=13.299(1)$ Å) with an essentially disordered arrangement of In and Sb. In the case of $Sr_2In_{0.5}Sb_{0.5}O_4$, however, ordering of In and Sb is observed leading to an expanded unit cell ($Pmcb$, $a=5.7592(1)$, $b=5.7740(1)$, $c=12.543(1)$ Å). The results therefore show that varying the size of the alkaline earth cation has a pronounced effect on the ordering of In and Sb within the structure.

Keywords: K_2NiF_4 structure, neutron diffraction, Indium, Antimony

Introduction

Materials with the perovskite structure have attracted considerable interest due to such systems displaying a range of properties of technological importance, e.g. superconductivity, ionic and electronic conductivity, magnetoresistance, dielectric properties, catalysis. Although the general formula for a stoichiometric perovskite oxide can be written AMO_3 , this simple formula does not indicate the diverse range of compositions that can be prepared. For example it is possible to have more than one cation on both the A and M sites, provided the total charge is 6+, with considerable attention having been focused on mixed M site cation systems, such as $LaM_{0.5}M'_{0.5}O_3$ (M is a 2+ cation, e.g. Mg, Ni, Cu; M' is a 4+ cation, e.g. Ti, Zr), $(Ba/Sr)M_{0.5}M'_{0.5}O_3$ (M is a 2+ cation, e.g. Ni, Zn; M' is a 6+ cation, e.g. W), or $(Ba/Sr)M_{0.33}M'_{0.67}O_3$ (M is a 2+ cation, e.g. Mg, Ca, Ni, Cu; M' is a 5+ cation, e.g. Nb, Ta).[see for example 1-14]

A related structure to that of perovskite is the K_2NiF_4 structure in which perovskite-type layers are separated by rock salt layers (figure 1). A wide range of materials with this structure-type have been prepared and studied including the well-known La_2CuO_4 based superconductor $La_{2-x}Ba_xCuO_4$ [15-17]. The general formula of these compounds can be written A_2MO_4 , although in contrast to the wide range of materials reported with two cations of different charge on the octahedral M site in perovskites (as outlined above), there have been few reports of such compounds with the K_2NiF_4 structure. In order to rectify this, we have tried to prepare some examples of such samples, and in this paper we report the synthesis and structures of the novel compounds $A_2In_{0.5}Sb_{0.5}O_4$ (A= Sr, Ba). To our knowledge these are the first examples of K_2NiF_4 compounds of general

formula $A_2M^{III}_{0.5}M^{V}_{0.5}O_4$ with both 3+ and 5+ cations in the octahedral sites. We show that the alkaline earth cation size can have a key effect on the ordering of In and Sb on the octahedral (M) site.

Experimental

High purity, $SrCO_3$, $BaCO_3$, In_2O_3 and Sb_2O_3 were used to prepare the compounds $A_2In_{0.5}Sb_{0.5}O_4$ (A=Sr, Ba). The powders were ground in the required stoichiometric proportions and heated at $1100^\circ C$ for $Ba_2In_{0.5}Sb_{0.5}O_4$, and $1000^\circ C$ for $Sr_2In_{0.5}Sb_{0.5}O_4$ for 12 hours, before regrinding and reheating at $1200^\circ C$ and $1100^\circ C$ respectively for a further 12 hours. Phase purity was confirmed using powder X-ray diffraction (Seifert XRD 3003TT diffractometer). Attempts to prepare a similar compound containing Ca, i.e. $Ca_2In_{0.5}Sb_{0.5}O_4$, were unsuccessful, showing that there is a minimal alkaline earth size for the stabilisation of these phases.

Neutron diffraction data were collected for $Sr_2In_{0.5}Sb_{0.5}O_4$ and $Ba_2In_{0.5}Sb_{0.5}O_4$ on diffractometers HRPD and POLARIS, ISIS, Rutherford Appleton Laboratory. Refinement of the neutron diffraction data employed the GSAS suite of programs [18].

Results

X-ray diffraction showed the successful synthesis of the compounds $Ba_2In_{0.5}Sb_{0.5}O_4$ and $Sr_2In_{0.5}Sb_{0.5}O_4$, and so the structures of these materials were determined by neutron

diffraction. Both materials were initially run on diffractometer Polaris. However, for $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ it was shown that significant changes to the sample had occurred. These changes were attributed to water incorporation into the sample, supported by TGA studies, leading to an expansion along the c axis (as evidenced by a shift in the (002) peak to lower angle) and a loss of crystallinity. A similar ability to readily incorporate water has been previously reported in the related K_2NiF_4 system, Ba_2ZrO_4 [19,20]. As a result of these problems with the original $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ sample, the sample was re-examined on diffractometer HRPD after heating at 1000°C for 2 hours to remove this water, before collecting the neutron diffraction data.

Further studies on the effect of water incorporation in these materials, as well as fluorination studies, are in progress, and will be reported later. Here we report the structures of these novel phases.

Structure refinement: $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ and $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$

Refinement of the data for $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ was attempted using the tetragonal space group $I4/mmm$ commonly observed for K_2NiF_4 -type compounds. Using this space group a good fit to the data was obtained and the refined structural parameters are given in table 1 with selected bond distances in table 2 and the neutron profiles in figure 2. This model does not allow for any ordering of In and Sb, and so assumes a random distribution of both cations on the octahedral sites within the structure.

Attempts to refine the data for $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ with space group $I4/mmm$ gave a poor fit to the data with evidence for a number of unfitted peaks. The unfitted peaks could be

indexed on a $\sqrt{2} a \times \sqrt{2} b \times c$ cell, with a small orthorhombic splitting. It was thought that this expanded cell may be due to In/Sb ordering. Therefore, a number of space groups were attempted, allowing for possible ordering of In and Sb in the octahedral sites, to include ordering of In and Sb within a layer, and ordering based on alternate layers of In and Sb. The best fit was obtained for the orthorhombic space group Pmcb, with ordering of In and Sb within each layer (figure 3). The refined data indicated that there was complete ordering of In and Sb in the structure, with attempts at placing some In on the Sb site and vice-versa giving rise to zero occupancy after refinement. For the oxygen sites (O2, O3), the thermal displacement parameters were initially quite high, and so these oxygens were allowed to move off-site creating split sites for these positions. This resulted in improved R factors and significantly reduced thermal parameters for these oxygen atoms. The final refined structural data are given in table 3 with selected bond distances in table 4. The neutron profile fits are shown in figure 4.

In order to confirm that there was no ordering in $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$, the ordered $\sqrt{2} a \times \sqrt{2} b \times c$ structural model for $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ was also examined for this sample., although this refinement proved unstable. Therefore, since a good fit to the data had been achieved for space group I4/mmm (table 1), and there were no extra peaks observed for this sample, it was concluded that the initial model, with a random distribution of In and Sb, was valid.

Discussion

The synthesis and structural characterisation of the new K_2NiF_4 type compounds $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ and $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ have been shown. The structural studies have

demonstrated that the size of the alkaline earth cation has a key influence on the ordering of In and Sb within the structure. In $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$, the neutron diffraction data shows no evidence for any long range ordering of In and Sb in the octahedral sites, although it is possible that some short range ordering may exist. In addition, the bond distances (table 2) show that the In/Sb- O_6 octahedra are regular. In the case of $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$, however, long range ordering of In and Sb does occur, leading to alternating In and Sb within the layers. This ordering results in an expanded $\sqrt{2} a \times \sqrt{2} b \times c$ cell, and a small orthorhombic distortion. In this structure there is also some significant tilting of the octahedra (figure 3). This can be explained from calculations of the tolerance factors for both $\text{Ba}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ and $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$. For the former, a tolerance factor of 0.97 is obtained, consistent with the near ideal K_2NiF_4 structure observed. In contrast, the tolerance factor for $\text{Sr}_2\text{In}_{0.5}\text{Sb}_{0.5}\text{O}_4$ is significantly lower (0.91), which is consistent with a need for tilting of the octahedra to alleviate structural strain. In addition to such tilting, the octahedra are non-regular with significant differences between apical and equatorial bond lengths (table 4). The smaller size of Sb versus In causes the equatorial oxygens (O1) to move closer to the Sb, leading to the four equatorial bonds for the SbO_6 octahedra being significantly shorter than those for the InO_6 octahedra (1.965 vs 2.126Å). In contrast, the apical bond lengths are shorter for the InO_6 octahedra (2.008 vs 2.114Å). Overall therefore, the SbO_6 octahedra have four short equatorial bond lengths and two long axial bond lengths, while for the InO_6 octahedra the situation is reversed. In terms of the average bond distances, the value for the SbO_6 octahedra is smaller than that for the InO_6 octahedra, as expected from ionic radii considerations.

In conclusion, these phases are, to our knowledge, the first examples of K_2NiF_4 compounds of general formula $A_2M^{III}_{0.5}M'^V_{0.5}O_4$ with both 3+ and 5+ cations in the octahedral sites, and suggest that further studies in this area are worthwhile. The neutron diffraction data shows that varying the size of the alkaline earth cation has a pronounced effect on the ordering of In and Sb within the structure.

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Table 1 Refined structural data for Ba₂In_{0.5}Sb_{0.5}O₄

Atom	Site	x	y	z	U ₁ (x100)	Site occ.
Ba	4e	0	0	0.3531(2)	*	1.0
In	2a	0	0	0	0.64(6)	0.5
Sb	2a	0	0	0	0.64(6)	0.5
O1	4c	0	0.5	0	*	1.0
O2	4e	0	0	0.1565(1)	*	1.0

I4/mmm, a=b= 4.1651(1), c=13.299(1) Å. R_{wp}=8.17%, R_p=7.36%, $\chi^2 = 1.825$

*Anisotropic thermal parameters

Atom	U ₁₁ (x100)	U ₂₂ (x100)	U ₃₃ (x100)	U ₁₂ (x100)	U ₁₃ (x100)	U ₂₃ (x100)
Ba	1.18(6)	1.18(6)	0.5(1)	0	0	0
O1	1.4(1)	2.2(1)	1.0(1)	0	0	0
O2	1.85(6)	1.85(6)	1.1(1)	0	0	0

Table 2 Selected bond distances for Ba₂In_{0.5}Sb_{0.5}O₄

Bond	Bond distance (Å)
In/Sb- O1	2.083 (x4)
In/Sb- O2	2.081 (x2)
Ba - O1	2.856 (x4)
Ba - O2	2.614 (x1)
Ba - O2	2.948 (x4)

Table 3 Refined structural data for Sr₂In_{0.5}Sb_{0.5}O₄

Atom	Site	x	y	z	U ₁ (x100)	Site occ.
Sr1	4g	0	0.0098(4)	0.3516(2)	*	1.0
Sr2	4h	0.5	0.4834(4)	0.3552(1)	*	1.0
Sb	2a	0	0	0	0.38(5)	1.0
In	2b	0.5	0.5	0	0.22(6)	1.0
O1	8i	0.2360(4)	0.2442(5)	0.0130(1)	*	1.0
O2	8i	0.0249(9)	-0.0392(7)	0.1672(2)	*	0.5
O3	8i	0.4687(9)	0.5397(6)	0.1584(2)	*	0.5

Pmcb, a= 5.7593(1), b= 5.7740(1), c=12.543(1) Å. R_{wp}=1.91%, R_p=3.13%, χ^2 =3.371

*Anisotropic thermal parameters

Atom	U ₁₁ (x100)	U ₂₂ (x100)	U ₃₃ (x100)	U ₁₂ (x100)	U ₁₃ (x100)	U ₂₃ (x100)
Sr1	2.07(9)	0.51(8)	1.20(6)	0	0	0.05(8)
Sr2	0.83(7)	1.41(8)	0.00(4)	0	0	-0.14(7)
O1	0.59(5)	1.52(6)	2.51(5)	-0.42(4)	0.09(7)	-0.90(9)
O2	0.4(3)	0.4(1)	0.70(7)	-0.23(8)	0.1(1)	-0.07(7)
O3	1.5(3)	1.7(1)	0.01(6)	-0.3(1)	-0.70(9)	-0.46(8)

Table 4 Selected bond distances for Sr₂In_{0.5}Sb_{0.5}O₄

Bond	Bond distance (Å)
In - O1	2.126 (x4)
In - O2	2.008 (x2)
Sb - O1	1.965 (x4)
Sb - O3	2.114 (x2)
Sr1 - O1	2.662 (x2)
Sr1 - O1	2.821 (x2)
Sr1 - O2	2.335
Sr1 - O2	2.619
Sr1 - O2	3.182
Sr1 - O3	2.708
Sr1 - O3	3.068
Sr2 - O1	2.705 (x2)
Sr2 - O1	2.821 (x2)
Sr2 - O2	2.754
Sr2 - O2	3.039
Sr2 - O3	2.496
Sr2 - O3	2.574
Sr2 - O3	3.222

Figure Legends

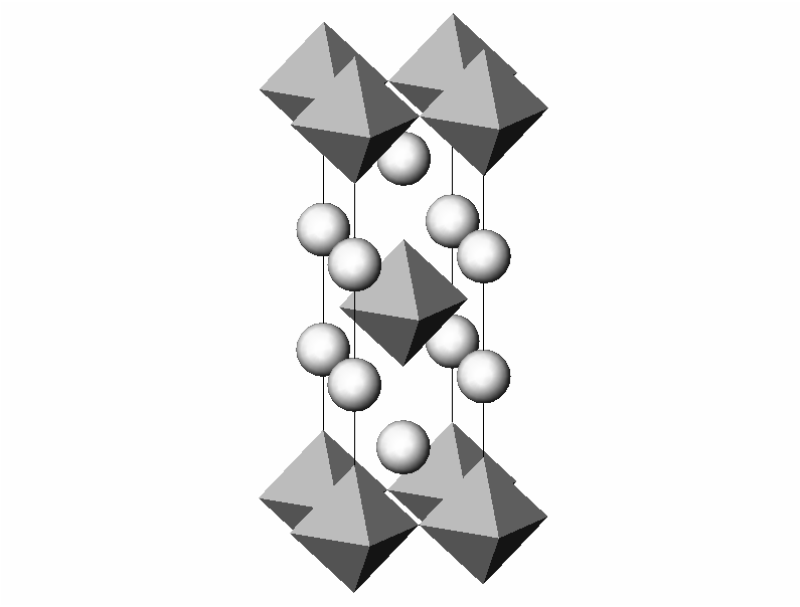
Figure 1(b). K_2NiF_4 structure (Octahedra: NiF_4 , Spheres: K)

Figure 2. Observed, calculated and difference neutron diffraction profiles for $Ba_2In_{0.5}Sb_{0.5}O_4$.

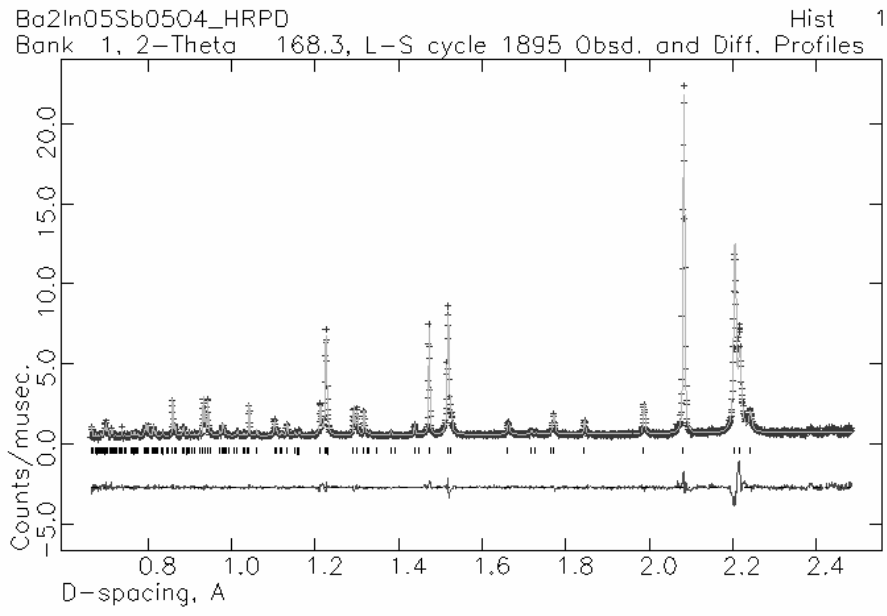
Figure 3. Structural model for $Sr_2In_{0.5}Sb_{0.5}O_4$ showing the ordering of In and Sb. (Light Octahedra: SbO_6 , Dark Octahedra: InO_6 , Spheres: Sr)

Figure 4. Observed, calculated and difference neutron diffraction profiles for $Sr_2In_{0.5}Sb_{0.5}O_4$.

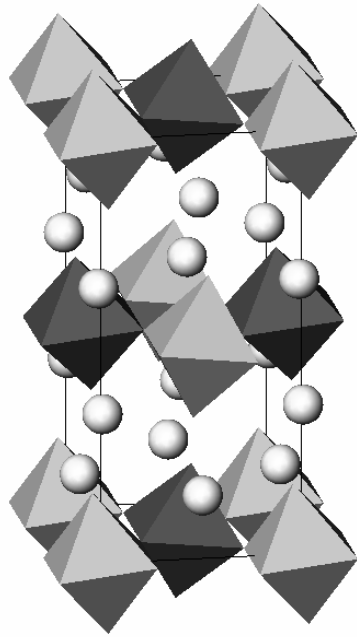
1.



2.



3.



4.

