Femtosecond laser ablation of cadmium tungstate for scintillator arrays

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Ultrafast pulsed laser ablation has been investigated as a technique to machine CdWO$_4$ single crystal scintillator and segment it into small blocks with the aim of fabricating a 2D high energy X-ray imaging array. Cadmium tungstate (CdWO$_4$) is a brittle transparent scintillator used for the detection of high energy X-rays and $\gamma$-rays. A 6 W Yb:KGW Pharos-SP pulsed laser of wavelength 1028 nm was used with a tuneable pulse duration of 10 ps to 190 fs, repetition rate of up to 600 kHz and pulse energies of up to 1 mJ was employed. The effect of varying the pulse duration, pulse energy, pulse overlap and scan pattern on the laser induced damage to the crystals was investigated. A pulse duration of $\geq$ 500 fs was found to induce substantial cracking in the material. The laser induced damage was minimised using the following operating parameters: a pulse duration of 190 fs,fluence of 15.3 J cm$^{-2}$ and employing a serpentine scan pattern with a normalised pulse overlap of 0.8. The surface of the ablated surfaces was studied using scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy and X-ray photoelectron spectroscopy. Ablation products were found to contain cadmium tungstate together with different cadmium and tungsten oxides. These laser ablation products could be removed using an ammonium hydroxide treatment.

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1. Introduction

Cadmium tungstate is a commonly used material for the detection of X-rays and $\gamma$-rays, due to its high density of 7.9 g cm$^{-3}$ and average high atomic number [1]. It converts incident ionising radiation into visible photons which are isotropically emitted from the point of radiation absorption. These can be detected by an optical sensor coupled to the scintillator. Thick 2D arrays of optically isolated small pitch segments can be used for the detection of high energy X-rays whilst also giving positional information for imaging [2]. Any decrease in spatial resolution, typically associated with an increase in thickness, can be prevented using a material which is optically highly reflective between each segment. The manufacture of these arrays is typically undertaken by hand where scintillator crystals are mechanically cut, polished and assembled into large arrays. This approach is costly, time consuming and becomes difficult for higher resolution arrays containing segments with a width below 500 $\mu$m. In addition to handling difficulties, cadmium tungstate is difficult to machine into small segments due to its brittleness; with a reported fracture toughness of 0.2 MPa $m^{1/2}$ and a cleavage along the (010) plane [3]. Laser micromachining can potentially segment cadmium tungstate and other scintillator materials with minimal damage and in geometries which minimise the need for the handling of the small fragile segments. For the array to function efficiently, the laser machining should not induce any changes in the material which could negatively affect the light transporting properties of the array. Such changes include the formation of cracks and a heat affected zone including recast material which could absorb the scintillation light. Laser machining is one of only a few viable cutting methods and is cost effective, due to the fast cutting times.

Several groups have reported the use of lasers to structure or segment scintillators using either ablation or sub-surface laser engraving. These ablation studies have typically focussed on the use of Nd:YAG nanosecond pulsed lasers or nanosecond pulsed Excimer lasers, since many scintillators are transparent to UV wavelengths [4,5]. The researchers have encountered difficulties with crystal heating and segment melting [4] or have been forced to employ a lower energy laser beam to pre-score the crystal, enabling containment of any fractures [5]. Due to problems associated with the brittleness of many scintillator materials, attempts at segmenting scintillators using ablation were abandoned in favour of sub-surface laser engraving which had previously shown promise [6–9]. The sub-surface laser engraving technique relies on modifying regions of the scintillator crystal to either induce changes in refractive index or micro-cracks which act to reduce the spread of scintillation light from one segment to another via...
absorption and total internal reflection [6]. Compared to optical isolation in the segmentation method, the sub-surface laser engraving technique has a potentially worse spatial resolution since light can still pass through the low refractive index region between each segment.

The absorption mechanisms of ultrashort pulse laser ablation make it a promising method to segment scintillators such as cadmium tungstate. The authors are not aware of any published research on the effectiveness of ultrashort pulsed laser ablation for segmenting brittle transparent scintillators. Due to the high intensities achievable in ultrashort laser ablation, the absorption process is due to a multiphoton non-linear process. As a result of this, matching of the optical absorption properties of the ablated material with the wavelength of the laser light is not as crucial as for ns pulse laser ablation or continuous wave laser ablation [10]. Ultrashort pulse laser ablation is also capable of ablating with minimal heating of the material due to the ablation process occurring faster than heat can diffuse into the neighbouring material [10]. Whilst ultrashort pulse laser ablation could enable rapid micromachining that does not melt or crack the scintillators, previous studies have not paid particular attention to the effect the ablation process might have on the surface of the material, and how this might influence the performance of a scintillator array. This work aims: (i) to establish the optimum laser operating conditions to efficiently cut the material but induce minimum damage; (ii) to investigate the nature of the ablated material and establish a methodology to clean the ablated surfaces to allow a scintillator array to be assembled.

A 6 W Yb:KGW 1028 nm laser was used in air with a Scanlab SCANCube 10 galvanometer scanner and telecentric f/6 lens system. The laser was capable of pulse durations in the range of 190 fs to 10 ps with pulse energies as high as 1 mJ. A series of experiments were conducted to determine the optimum laser parameters for the application. The following parameters were investigated: (i) the effect of pulse energy on the ablation rate; (ii) the scan speed with different repetition rates – to investigate the effect of the pulse overlap on definition of the cut; (iii) the degree of cracking induced by different cutting directions, pulse energy, pulse duration and scan pattern. The normalised pulse overlap (NPO) is the degree of overlap for subsequent pulses as they are scanned across the sample. It can be defined by the spot diameter D, the scan speed V, the pulse duration \( t_p \) and the laser repetition rate \( R \) as follows: \( D - (V/R) - V^*t_p]/(D) = \text{NPO} \) [11]. Hence, a higher NPO corresponds to a greater overlap of pulses.

Following ablation, Confocal laser scanning microscopy (CLSM) was used to study sub-surface damage, scanning electron microscopy (SEM) was used to study the morphology of the ablated regions, atomic force microscopy (AFM) was used to measure surface topography, energy dispersive X-ray spectroscopy was used to analyse the elemental composition of the bulk of the laser ablated regions and X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical composition of the laser ablated surfaces.

2. Method

The Yb:KGW pulsed laser was a Light Conversion Pharos-SP (supplied by Photonic Solutions Ltd. Edinburgh, UK) employing a wavelength of 1028 nm. A pulse compressor system enabled the pulse duration to be adjusted from 190 fs to 10 ps with a maximum power of 6 W and an adjustable repetition rate from single pulses up to 600 kHz giving pulse energies as high as 1 mJ. The laser was integrated into a CAM system which controlled a Scanlab SCANCube 10 galvanometer scanner coupled to a telecentric f/6 scanning lens. A slightly elliptical spot was formed due to astigmatism in the optics. The spot size was determined to be 30 μm by plotting the squared diameter of a series of single pulse holes against the logarithm of the pulse energy [12].

Cadmium tungstate was supplied by Hilger crystals in the form of sheets of 15 mm × 25 mm with the thickness varying from 340 to 470 μm. The laser was incident on the (010) plane to cut through the thickness of the sheets (Fig. 1). X-ray diffraction showed that the long edge of the sheet was 7.44° from the (101) plane and the short edge was 8.67° off the (10−1) plane. The sheets were supported at both ends giving a small air gap of 1 mm above the sample stage. This arrangement was employed following initial tests which showed that debris from the sample stage damaged the crystal as the laser cut, penetrated through the sheet and into the aluminium plate on the stage.

Initially, a series of holes were ablated at increasing pulse energy using 1, 2, 5 and 10 pulses to assess the ablation rate as a function of energy and number of pulses. The pulse energies were controlled by changing the laser power and repetition rate. At a frequency of 25 kHz and pulse duration of 190 fs, ten power settings were employed. The power was initially set at 550 mW, which due to losses in the optics, delivered 450 mW to the sample. The power was then progressively increased up to a laser power of 5500 mW, delivering 4230 mW to the sample. The power was measured using a Coherent FieldMate power metre. A Zeiss LSM-400 CLSM was employed to image the holes generated and their volume and depth were measured with a Bruker Dimension Edge AFM in the non-contact tapping mode. The Gwyddion SPM analysis software was employed to analyse the AFM data [13].
The pulse overlap tests were performed by changing the scan speed and keeping the repetition rate fixed at 25 kHz using powers of 4400, 4950 and 5500 mW. NPO values of 0.3–0.8 in 0.1 increments were employed.

The damage induced by different laser parameters including cutting direction, pulse duration, pulse energy and cut width to depth ratio was investigated as follows. The differences in cutting direction were tested by cutting 3 trenches, one parallel to the long edge of the sheet, one parallel to the short edge of the sheet and one at 45° to the edges of the sheet. The sample was then rotated by 90° and another 3 trenches were ablated in the same configuration to study possible effects due to polarisation of the laser. To study the damage induced by the different pulse energies and pulse durations as a function of ablated depth three different pulse durations were tested, 1 ps, 500 fs and 190 fs. Pulse durations up to 10 ps were tested, but the significant damage induced at these pulse durations prevented detailed studies of the samples. The depth was controlled by the number of passes employed for each trench. The number of passes was controlled by the CAM system and 9 trenches were ablated for each of the pulse energies with a progressive increase in the number of passes from 5 passes for the first trench to 800 for the final trench. The NPOs were kept at a value of 0.8 and the pulse energies varied by changing the pulse repetition rate. The selected repetition rates were 100, 84.6, 73.3, 64.7 and 57.9 kHz which corresponded to pulse energies of 55, 65, 75, 85 and 95 μJ and fluences of 15.6, 18.4, 21.2, 24.1 and 26.9 μJ cm⁻² respectively. The samples were cleaned by immersion in a solution of 30 vol% NH₃ in H₂O at 45 °C for 15 min. This solution was used for cleaning as it has been shown to dissolve cadmium tungstate and tungsten oxides [14].

The morphology of the ablated surfaces was studied using a Hitachi S3200N SEM. An incident electron beam energy of 20 keV was employed in the low pressure mode (15 Pa) to prevent charging of the samples. This limited the SEM to the use of backscatter imaging only. A Bruker Dimension Edge AFM in the PeakForce tapping mode was employed to study the morphology of the trench walls before and after cleaning. XPS was performed on surfaces of a reference sample, an ablated sample and cleaned sample. The XPS instrument employed was a Thermo Scientific Theta Probe with a monochromated Al k-alpha X-ray source (hν = 1486.6 eV) operated at 15 kV and 20 mA using an X-ray spot with a radius of 400 μm for the reference sample and 200 μm for the ablated samples. The hemispherical analyser was operated with a pass energy of 50 eV and a step of 0.2 eV for the core level spectra. An electron flood gun was used to compensate for surface charging. The binding energies of the photoelectron peaks were referenced to the adventitious hydrocarbon C 1 s peak at 285.0 eV. Curve fitting was undertaken using a mixed Gaussian–Lorentzian lineshape and quantification of atomic concentrations was performed from the peak areas using the Thermo Scientific Avantage software which employs instrument modified Wagner sensitivity factors after a Shirley background subtraction.

3. Results and discussion

3.1. Material removal rate

The ablated volume of the 190 fs holes was measured by AFM. Two measurements were performed for each hole, with the scanning direction being reversed, minimising any effect of the steep sided walls of the holes on the results recorded.

The volume was determined for each ablated hole using the AFM dataset and an average taken of both measurements. The volume of ablated material was plotted against the total incident energy (Fig. 2). The 3 highest pulse energy holes ablated with 10 pulses were too deep to be measured by the AFM.

The volume of ablated material was found to be greater using multiple lower energy pulses than fewer higher energy pulses delivering the same total incident energy. The holes ablated using 10 of the lowest energy pulses at 18 μJ, delivering a total incident energy of 180 μJ resulted in significantly more material being removed than those ablated using 5 pulses of the highest pulse energy of 169 μJ delivering a total incident energy of 846 μJ, despite 5 pulses at the highest energy being equivalent to 4.7 times the total incident energy of the lowest energy pulses. This increase in the material removal rate is consistent with incubation effects in the crystal where the initial pulses induce defects in the material which then increase absorption of the incident laser light in subsequent pulses [10].

Fractionating the total incident energy into more pulses was also found to influence the morphology of the ablated regions. Holes

![Fig. 2. The ablated volume as a function of total incident laser energy.](image-url)
Ablated using few high energy pulses were found to have a smooth crater that was surrounded by a raised lip (Fig. 3(A)). Holes ablated using many low energy pulses were not surrounded by a raised lip and the bottom of the holes exhibited a coarse ripple structure (Fig. 3(b)). The surrounding regions for both low and high energy holes were found to contain evidence of liquid phase material ejected from the ablation volume. The ripple formation in the holes ablated using low pulse energy is consistent with the evolution of nanoplasma bubbles [15]. The raised lip surrounding the holes ablated using high energy pulses was attributed to re-deposited ablated material. As the removal of material at higher pulse energies is less influenced by incubation effects than that at lower energies, it is thought that the material is removed before the ripple structure can form. Hence, the formation of ripples by nanoplasma bubbles is suppressed at higher pulse energies. This observation is contrary to what has been previously reported about the formation of coarse surface ripples [16]. The discrepancy is attributed to the fluences used in this study being significantly higher than those typically used for the study of surface ripples [16].

The formation of surface ripples is undesirable in the machined surfaces as they would lead to an increase in light leakage between each machined segment and poorer spatial resolution [17]. Therefore, despite the lower material removal rate, the higher pulse energies were considered to be more desirable for the segmentation of scintillators.

3.2. Pulse overlap

The trenches ablated using NPOs of 0.6 and above show much straighter edges than those with lower NPO values (see Fig. 4). This was due to low NPOs leaving a ‘neck’ of CdWO₄ in between each pulse giving rise to an undulating trench edge (Fig. 4(A)). The morphology of the ablated regions has a periodic structure which corresponds to the pulse overlap. The regions where the laser pulses strongly overlap (Fig. 4(B)) exhibits fewer pores than the regions which have only been exposed to only one or two pulses due to the low overlap (Fig. 4(A)). As a result of the reduction in porosity of the ablated regions and better definition of the trench edges an NPO of 0.8 was selected for this application.

The material adjacent to the trenches was also found to be modified by the lower intensity tails of the beam profile. The modified regions were found to have two types of fine surface ripples. The finer ripples had a spacing of 337 nm and the coarser ripples had a spacing of 884 nm (Fig. 4(C)). The spacing of the ripples was less than the laser wavelength of 1028 nm and is consistent with the initial stages of the formation of nanoplasma bubbles [15]. The widths of the trenches increased with NPO and were different for the two cutting directions, due to the elliptical laser spot. In the vertical cutting direction, the trenches ablated with an NPO of 0.3 were on average 11 μm narrower than those ablated with an NPO of 0.8, and due to the slightly elliptical spot 12 μm narrower in the horizontal direction. The increase in trench width was due to the higher overlap leading to more laser energy being deposited at the tails of the beam profile which ablated more material.

3.3. Damage and cracking

Nine parallel trenches were ablated at a constant power of 5500 mW with an increasing number of passes from 5 to 800

![Fig. 3. 3D AFM topographic images of two ablated holes ablated using 5 × 169 μJ pulses (A) and 10 × 18 μJ pulses (B).](image-url)

![Fig. 4. SEM micrographs of: (A) a trench ablated with an NPO of 0.3; (B) a trench ablated with an NPO of 0.8 and (C) fine ripples at the edge of a trench ablated with an NPO of 0.3.](image-url)
passes at 1 ps, 500 fs and 190 fs pulse duration for 5 different repetition rates of 100, 84.6, 73.3, 64.7 and 57.9 kHz. This corresponded to pulse energies at the sample of 43, 50, 58 and 73 µJ and fluences of 12.1, 14.1, 16.4, 18.7 and 20.7 µJ cm⁻² respectively. CLSM was used to non-destructively evaluate sub-surface damage. The sub-surface damage was seen as bright regions in the images, where the laser light was reflected off the crack interfaces as the microscope was focused into the crystal.

The anisotropic thermal and mechanical properties of cadmium tungstate make it highly susceptible to thermal shock [18]. This resulted in pulse durations of 500 fs and longer inducing more damage for the same pulse energy than 190 fs. The sub-surface cracks were observed closer to the illuminated surface as the pulse energy and pulse duration were increased. Both 1 ps and 500 fs pulses were found to induce significant cracking at the lowest tested pulse energy of 43 µJ. The cracking was found to begin when the trench extended to a depth of 20 µm for the 500 fs pulses and a depth of 10 µm for the 1 ps pulses. Significant sub-surface cracking could be observed to a depth of 120 µm.

For trenches ablated using 190 fs pulses significant sub-surface damage was only observed for pulse energies of 66 µJ and greater. Smaller scale damage was observed in some cases at pulse energies above 50 µJ. The degree of sub-surface damage was found to be a function of the orientation of the cut with respect to the dimensions of the CdWO₄ sheet (Fig. 5).

The damage was found to be more severe for cut orientation 2 (Fig. 1) which was parallel to the 25 mm edge of the CdWO₄ sheet (Fig. 5(A)). Significantly less damage was observed for cut orientation 1 (Fig. 1) which was parallel to the 15 mm edge of the CdWO₄ sheets (Fig. 5(B)). Cutting at a 45° angle to either edge produced less damage than cutting along the 25 mm edge but significantly more than cutting along the 15 mm edge. It was possible to machine along the short edge direction without causing observable damage by reducing the scan speed from 707 mm s⁻¹ to 175 mm s⁻¹. The sheets were cut into a series of strips for assembly into a scintillator array. Sequentially machining the strips was found to induce a large amount of cracking (Fig. 6(A)). The cracking could be avoided through the use of a serpentine scan pattern giving each trench one pass of the laser at a time (Fig. 6(B)).

The time delay between each pass was found to influence the amount of cracking. If the delay was too short, then large cracks would begin from the ends of the cuts and span to other cuts. This was attributed to the build-up of heat in the trench [19]. Arranging the laser cuts in the form of a serpentine scan pattern also enabled a pulse energy of 54 µJ to be used without inducing cracking which corresponded to a fluence of 15.3 µJ cm⁻², as opposed to 12.1 µJ cm⁻² when not using a serpentine scan pattern. The reduction in damage due to the serpentine scan pattern was also attributed to the reduction in the build-up of heat in the trench.

While the edges of the sheet were not aligned to any specific crystal plane, the angle of the planes to the edge of the sheet is small and the extent of the cracking obscures the exact relationship between the cracking and the crystal planes. The increase in cracking seen with an increased pulse duration and energy together with a reduction in cracking observed when using a serpentine scan pattern would suggest that the edges of the ablation volume experience a rapid increase in temperature during the machining leading to a thermal up-shock. Sabharwal et al. measured a 60% difference in the coefficient of thermal expansion of CdWO₄ along the (100) plane compared to the (010) plane but the coefficient of thermal expansion along the (001) plane was not measured [18]. Macavei et al. showed that there was a significant difference in the mechanical properties of CdWO₄ between the a-, b- and c-axes with the c-axis showing the highest stiffness and the b-axis showing the lowest stiffness [20]. This suggests that the anisotropic cracking is due to the differences in the mechanical and thermal properties of CdWO₄, but detailed characterisation of the thermal and mechanical properties of CdWO₄ would be needed to investigate this phenomenon further, which is beyond the scope of this study.

3.4. Analysis of the trench wall composition

The ablation process deposited a significant amount of fine powder debris on the surface of the cadmium tungstate (Fig. 7). As the laser cut deeper into the crystal, layers of debris were deposited on the walls of the ablated trench. Immersion in an ammonium

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**Fig. 5.** CLSM images of the sub-surface damage spanning from the trenches ablated at a power of 5500 mW using 190 fs pulses and a repetition rate of 25 kHz: (A) parallel to the 25 mm edge; (B) parallel to the 15 mm edge.

**Fig. 6.** A schematic diagram of the different scan patterns showing: (A) the sequential pattern and (B) the serpentine scan pattern. The dotted lines show the path of the scanner between each cut.
Hydroxide solution was used to remove the debris from the ablated surfaces. Trench walls ablated using 190 fs pulses at a pulse energy of 54 μJ and an NPO of 0.8 were imaged using SEM before (Fig. 7(A)) and after cleaning (Fig. 7(B)). The micrographs show that the surface after cleaning is smoother and there are fewer traces of particles on the surface (Fig. 7). The micrographs also showed a series of light and dark bands on the top half of the trench. The banding appeared to be ridges that were smoothed out by the cleaning process. SEM micrographs looking down an ablated trench showed the extent of the debris and the effectiveness of the cleaning process (Fig. 7(C) and (D)). The width of the trench before (Fig. 7(C)) and after (Fig. 7(D)) cleaning was measured and the width after cleaning had increased by an average of 2 μm, indicating that the debris was up to 1 μm thick on each side of the trench.

An AFM was used to measure the topography of an 80 μm × 80 μm region at the top of a trench before (Fig. 8(A)) and after cleaning (Fig. 8(B)). These images confirmed that the banding observed in the SEM micrographs were ridges formed during the ablation process. The height of the ridges was not constant and the cleaning process had a smoothing effect on the ridge morphology, although the ridges were still evident after cleaning (Fig. 7(B)). This suggests that the ablation debris was depositing on the surface in a manner which enhanced the ridged morphology. The ridges were not present in the bottom half of the trench which corresponded to the depth at which the trench width became constant. Therefore, the ridges correspond to points at which the power delivered at the edges of the laser spot becomes lower than the threshold required for ablation.

Energy dispersive X-ray spectroscopy was performed on the ablated wall of a trench which had not been cleaned and on one that had been cleaned in ammonium hydroxide. Before cleaning the ratio of cadmium to tungsten was found to vary significantly from the top (Fig. 7(A) and (B) analysis point 1) to the bottom of the trench (Fig. 7(A) and (B) analysis points 10 and 13 respectively). The results show an increase in the cadmium concentration at the top of the trench and a large depletion in the cadmium concentration at the bottom of the trench. In agreement with the SEM images in Fig. 6, the ammonium hydroxide cleaning process removes the surface debris, exposing the underlying CdWO₄ bulk.

Fig. 7. SEM micrographs of the machined CdWO₄. The upper images show the trench wall: (A) before cleaning and (B) after cleaning. The lower images show the CdWO₄ surface and a view down an ablated trench: (C) before cleaning and (D) after cleaning.

Fig. 8. 3D AFM topographic images of the wall of an ablated trench before (A) and after (B) cleaning.
and giving rise to a more consistent cadmium to tungsten ratio as a function of depth (Fig. 9).

XPS was performed on three samples; a sheet of cadmium tungstate before ablation, a segment of cadmium tungstate that had been ablated using 190 fs pulses at a pulse energy of 54 μJ and an NPO of 0.8 and a similarly ablated segment of cadmium tungstate that was cleaned using ammonium hydroxide. The reference sample was a cadmium tungstate sheet in an as-received state. For this sample, the XPS O 1 s peak exhibited two components, one at 530.6 eV corresponding to oxygen bonded to cadmium and tungsten (CdWO4) and a second component at 532.2 eV attributed to absorbed hydroxide species. The Cd 3d peaks had binding energies of 405.2 and 412.9 eV respectively. The W 4f peaks (Fig. 11) showed a convolution of 2 sets of overlapping peaks. The higher energy pair of W 4f7/2 and W 4f5/2 peaks have binding energies of 35.5 and 37.7 eV respectively. The lower energy pair of W 4f7/2 and W 4f5/2 peaks have binding energies of 33.5 and 35.8 eV respectively peaks associated with the W5⁺ state which is found in non-stoichiometric tungsten binary oxides such as WnO3n/C0 or a tungsten bronze such as Cd0–0.18WO3 [14,22–25].

The XPS spectra from the ablated surface showed a significant change in the surface composition compared to the native cadmium tungstate. The Cd 3d peaks do not typically show a strong chemical shift due to their filled 4d shell, but oxidation to CdO or CdO2 leads to a progressive shift to lower binding energies [19,20]. Consequently, the Cd 3d peaks for the ablated sample (Fig. 10) were fitted with: (i) Cd 3d5/2 and 3d3/2 peaks at binding energies of 405.2 and 412.0 eV respectively, associated with the Cd binding energies measured in the reference CdWO4 sample (however, these binding energies also correspond to the compounds CdO and CdCO3 [21]); (ii) Cd 3d5/2 and 3d3/2 peaks at binding energies of 403.6 eV and 410.6 eV corresponding to reported binding energies for CdO2 [21].

The W 4f peaks (Fig. 11) showed a convolution of 2 sets of overlapping peaks. The higher energy pair of W 4f7/2 and W 4f5/2 peaks have binding energies of 35.5 and 37.7 eV respectively, corresponding to tungsten in the hexavalent W6⁺ state such as in CdWO4 and WO3. The lower energy pair of W 4f7/2 and W 4f5/2 peaks have binding energies of 33.5 and 35.8 eV respectively peaks associated with the W5⁺ state which is found in non-stoichiometric tungsten binary oxides such as WnO3n/C0 or a tungsten bronze such as Cd0–0.18WO3 [14,22–25].
The O 1s peak was fitted with three components (Fig. 12), a low energy peak at 528.7 eV, corresponding to the reported binding energy of CdO [19], a peak at 530.5 eV corresponding to the reference CdWO₄ sample (but also reported for O²⁻ compounds which include CdO₂ and WO₃ [14,20]), and a high energy peak attributed to adsorbed hydroxides at 532.3 eV. With regard to this latter peak, a high energy O 1s component has also been attributed to a defective oxide state that is present in tungsten bronzes and tungsten sub-oxides [24,25].

From the XPS peak fits, the concentrations for each of the elements in the different chemical states were compared to the expected stoichiometry for the compound(s) identified and reasonable agreement was found in each case. The relative elemental fraction for the identified compounds (%) at the surface was then estimated and is given in Table 1. The XPS results in Table 1 indicate that the cadmium and the tungsten species in the ablated plume form cadmium tungstate, cadmium oxides and tungsten oxides.

Tanaka et al. published several papers on pulsed laser deposition of cadmium tungstate from cadmium tungstate targets and targets composed of a mix of CdO and WO₃, in both vacuum and in oxygen [26–30]. They were unable to grow cadmium tungstate films in vacuum but were successful in depositing cadmium tungstate in an oxygen atmosphere. An increased cadmium to tungsten ratio in the deposited films was observed at higher oxygen pressures and target to substrate distance [28]. This result would agree with our EDX findings where high cadmium to tungsten ratios are observed at the top of the trench and low cadmium to tungsten ratios occur deep within the trench. Within the ablated plume there is a higher concentration of Cd species at angles close to the surface normal which leads to an increase in the cadmium to tungsten ratio in the debris deposited at the top of the trench. In the middle of the trench the high number of collisions between the ablated species and oxygen leads to the formation of CdWO₄. At the base of the trench, the cadmium to tungsten ratio is much lower due to lighter species being more forward peaked than the heavier species [28,30], yielding a higher
4. Conclusion

Ultrashort pulsed laser ablation was investigated as a method for cutting CdWO₄ with the ultimate aim of forming 2-dimensional arrays of high aspect ratio structures for high energy X-ray imaging applications. The laser cutting process was shown to initiate material damage from thermal shock within the bulk of the brittle cadmium tungstate, limiting the pulse energy and scan speed which could be employed. Incubation effects were observed showing that effective ablation could be achieved using lower pulse energies at higher repetition rates rather than high pulse energies at low repetition rates. But lower pulse energies at higher repetition rate led to the formation of undesirable ripples on the ablated surfaces.

Pulse durations of 500 fs and longer were found to induce significant cracking at low pulse energies of \( \leq 50 \mu \text{J} \) Scanning the beam in a serpentine pattern rather than a normal sequential raster mode delocalised the laser energy enabling pulse energies of \( \leq 54 \mu \text{J} \) to be used without inducing cracking in the crystal. The laser induced damage was minimised using the following operating parameters: a pulse duration of 190 fs, fluence of 15.3 J cm\(^{-2}\) and employing a serpentine scan pattern with a normalised pulse overlap of 0.8.

XPS analysis showed that following ablation, ablation products of cadmium tungstate, cadmium oxides and tungsten oxides were deposited onto the trench walls and on the surface of the CdWO₄ crystal, close to the trench. Immersing the ablated CdWO₄ segments in boiling ammonium hydroxide was found to be a useful method of removing the ablation products from the CdWO₄ surface. The ammonium hydroxide treatment led to the formation of a thin layer of white cadmium hydroxide on the surface which could be beneficial to the optical efficiency of the cadmium tungstate scintillator array.

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References


Table 1

XPS Cd 3d, O 1s and W 4f components identified from the peak fits, associated compounds and relative surface fractions for the laser ablated CdWO₄ surfaces.

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak binding energy (eV)</th>
<th>Peak FWHM (eV)</th>
<th>Atomic %</th>
<th>Compounds identified</th>
<th>Relative elemental fraction for identified compounds (%)</th>
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<tr>
<td>Cd 3d₃/₂ (Cd²⁺)</td>
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<td>14.3</td>
<td>CdWO₄</td>
<td>7.4</td>
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<td>1.6</td>
<td>3.1</td>
<td>Cd(O)/Cd(OH)₂</td>
<td>6.9</td>
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<td>2.0</td>
<td>3.1</td>
<td>CdO₂</td>
<td>3.1</td>
</tr>
<tr>
<td>Cd 3d₃/₂ (Cd⁺⁺)</td>
<td>403.6</td>
<td>2.0</td>
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<td>9.3</td>
<td>OH⁻[Cd(OH)₂]/W₇O₃₋₁</td>
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<tr>
<td>W 4f₅/₂ (W⁶⁺)</td>
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<td>1.4</td>
<td>8.0</td>
<td>OH⁻/Cd(OH)₂/W₇O₃₋₁</td>
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<tr>
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<td>1.4</td>
<td>8.0</td>
<td>CdWO₄</td>
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</tr>
<tr>
<td>W 4f₁/₂ (W⁷⁺)</td>
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<td>1.4</td>
<td>8.0</td>
<td>WO₃</td>
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</tr>
<tr>
<td>O 1s (Cd0.18WO₃/W₇O₃₋₁)</td>
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<td>1.7</td>
<td>9.3</td>
<td>W₇O₃₋₁ and/or Cd₀.1₈WO₃</td>
<td>3.7</td>
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