Yb-doped mixed-sesquioxide films grown by pulsed laser deposition

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ABSTRACT

Growth and characterization of compositionally tuned, ytterbium-doped mixed lutetium-scandium oxide, and pure lutetia and scandia crystalline films are presented. Pulsed laser deposition was employed to grow these sesquioxide films, of thicknesses up to 20 μm, on (0 0 0 1)-sapphire substrates. By varying the atomic ratio of lutetium to scandium in the target, the lattice parameter of the resulting films could be tuned to match that of the single-crystal c-cut sapphire substrate and thereby achieve a lattice mismatch of <0.1%. Optimization of growth parameters led to a reduction of undesirable particulates and scattering points within the film. X-ray diffraction measurements show (2 2 2)-orientated epitaxial growth with crystallinity comparable to bulk crystals. Through pole figure and electron-backscatter imaging measurements, it was found that two inverted cubic lattice orientations grow with micron-scaled domains. Growth of these lattice-matched mixed sesquioxides paves the way for fabrication of high-quality waveguides suitable for generation of ultrashort laser pulses.

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1. Introduction

Sesquioxides, when doped with trivalent rare-earth ions, are established laser crystals, although difficult to source commercially [1], owing to their advantageous thermomechanical and optical properties compared with the exemplar medium yttrium aluminium garnet (YAG) [2,3]. When doped with ytterbium, they are well suited for high-power laser operation due to a low quantum defect between the pump and emission wavelengths and minimal residual heating of the material. Growth of high-quality sesquioxides is very challenging due to their high melting points ($\sim$2500 °C) [1], however, one growth method that does not require such high temperatures is pulsed laser deposition (PLD) [3–6]. PLD has been used to grow thin films of a range of materials including metals, semiconductors, and many oxide materials [7], which are the subject of this report. The target material can be either in single-crystal form, or as a ceramic in which a mix of powders is pressed into a disc and sintered to increase the density toward that of its constituents. Sintered ceramic targets allow for bespoke materials to be grown in which the stoichiometry of the film can be controlled by changing the relative proportions of the constituent components [8]. Furthermore, the film properties can be tuned by changing one of a number of basic deposition conditions, such as the laser pulse energy, background gas pressure, and substrate temperature, all of which have been shown to affect the film composition, crystallinity, and refractive index [9–11]. One key challenge for high-quality films grown via PLD is resultant scattering points in the film, originating from either particulates or the presence of multiple crystal domains. Fortunately, it has been shown that the number of scattering points can be reduced through optimization of the basic growth conditions [9,12].

Growing active sesquioxide films onto a sapphire substrate brings an additional advantage for potential use in high-power lasers through efficient heat sinking, owing to sapphire's high thermal conductivity, nearly 3 times higher than YAG (YAG – 11 W m^{-1} K^{-1} [13], sapphire – 30 W m^{-1} K^{-1} [14]). In addition, the lower refractive index of sapphire (n = 1.788 [14]) compared to scandia (n = 1.966 [1]) or lutetia (n = 1.911 [1]), enables waveguide structures to be realised. As a bulk laser crystal, Yb-doped lutetia (Yb:Lu$_2$O$_3$) has produced highly efficient, CW (continuous wave) lasers, producing in excess of 300 W with slope efficiencies of greater than 70% [13]. It also has a broad emission peak (13 nm FWHM [15]) in comparison to Yb:YAG (7 nm FWHM [6]) and will therefore support the broader spectral bandwidth of ultrashort-pulse mode-locked (ML) lasers or amplifiers. However, it has been shown that the use of mixed sesquioxides, in particular Yb:LuScO$_3$ (lutetium scandium oxide), broadens the emission band even further (22 nm FWHM [15]), theoretically allowing for pulses down to 50 fs [15]. The shortest pulse width demonstrated to date for a Yb:LuScO$_3$ laser has been 74 fs at a low output power (40 mW) [16]. In high-power ML thin disc lasers, sub-100 fs pulse durations are plausible with such crystal engineering [15].

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To be able to grow thicker films, which make possible large-mode-area pump-guiding waveguide devices (on the order of 10's of μm), compatible with high-power diode arrays, or allows for thin disc setups (on the order of 100's of μm [17]), lattice mismatch becomes important to the integrity of the film, due to the requirement to minimise residual strain [10]. The lattice constants for scandia and lutetia are 9.86 and 10.39 Å [1] and so when grown on (0 0 0 1) sapphire, there is a lattice mismatch of 2.8% and −2.5% for Lu_2O_3 and Sc_2O_3, respectively [3]. Using an epitaxial growth technique, such as PLD, it is possible however, to exploit compositional tuning of the ratio of scandium to lutetium in the film to obtain a near perfect quasi-lattice match [18] with a (0 0 0 1) sapphire substrate. Assuming Vegard's law [19], and with 5 at.% Yb doping, the optimum mix for the film in a scandia/lutetia mix is $(Yb_{0.05}Lu_{0.43}Sc_{0.52})_2O_3$. However, due to inhomogeneous material transfer from the target to the film, the optimum target composition will likely differ from this calculated value, and hence an experimental study is required.

We present PLD growths and subsequent characterization of Sc_2O_3 and Lu_2O_3 films and three compositionally-tuned $(Yb_{0.05}Lu_{(0.975-x)}Sc_{(x-0.025)})_2O_3$ films, grown from targets with "x" values of 0.475, 0.575, and 0.675. Here for generality it is assumed that the ytterbium ion can replace either Lu^{3+} or Sc^{3+} in equal measure. It is found that for x = 0.575, the lattice constant of the resultant film provides a near perfect quasi lattice match between the (1 1 1) orientation of the film and the (0 0 0 1) hexagonal orientation of the sapphire substrate. We also show the optimization of growth parameters, X-ray diffraction spectra of the different materials, and demonstrate different orientations of growths in these mixed-sesquioxide films.

2. Experimental setup

PLD growths were performed using the setup shown in Fig. 1. PLD uses a pulsed laser beam to ablate a target material, creating a plume that travels in a vacuum or partial vacuum toward a heated substrate, and under the correct conditions the deposited material grows into a crystalline film. In our setup, a KrF Coherent COMPexPro 110 laser was used to generate ∼20 ns UV laser pulses at a repetition rate of either 20 or 100 Hz. The UV laser beam was focused onto a sintered ceramic target, to a fluence of ∼1.0 J cm^{-2}, inside a stainless-steel vacuum chamber, which was backfilled with oxygen to a pressure of 0.02 mbar. The targets were 50-mm-diameter and 5-mm-thick discs, and during deposition were rotated in combination with horizontal translation, to create an epitrochoidal path for successive ablation points across the surface, thus increasing the utilised area.

Following ablation, the plasma plume propagated toward a 10 × 10 × 1 mm^3 substrate, heated by a CO_2 laser (operating at a wavelength of 10.6 μm). The near-diffraction-limited CO_2 laser beam was directed into the chamber through a ZnSe tetraprism [20], reformatting the Gaussian spatial-profile into a quasi-top-hat distribution to match the square substrate.

All depositions were undertaken in a partial vacuum backfilled with oxygen to a pressure of 0.02 mbar. Various growths were performed with different ceramic target constituents, i.e. for the mixed sesquioxides $(Yb0.05Lu0.5Sc0.45)2O3$, $(Yb0.05Lu0.4Sc0.55)2O3$, and $(Yb0.05Lu0.3Sc0.65)2O3$, and for the binary sesquioxides Lu_2O_3 and Sc_2O_3. UV laser fluence values between 0.95 and 1.2 J cm^{-2}, and substrate temperatures between 1300 and 1740 °C were explored in order to optimise the crystalline properties of the films produced. Two different CO_2 lasers were used for these growths, Synrad UC-2000 with a maximum power of 40 W for the lower temperature growths (below ∼1500 °C) and Rofin OEM10IX 10.6 HP (maximum power 170 W) for the higher temperature growths (above ∼1500 °C).

2.1. Film characterization techniques

Dark-field microscopy of the respective films was carried out using a Nikon Eclipse LV100D, which allowed visualisation of
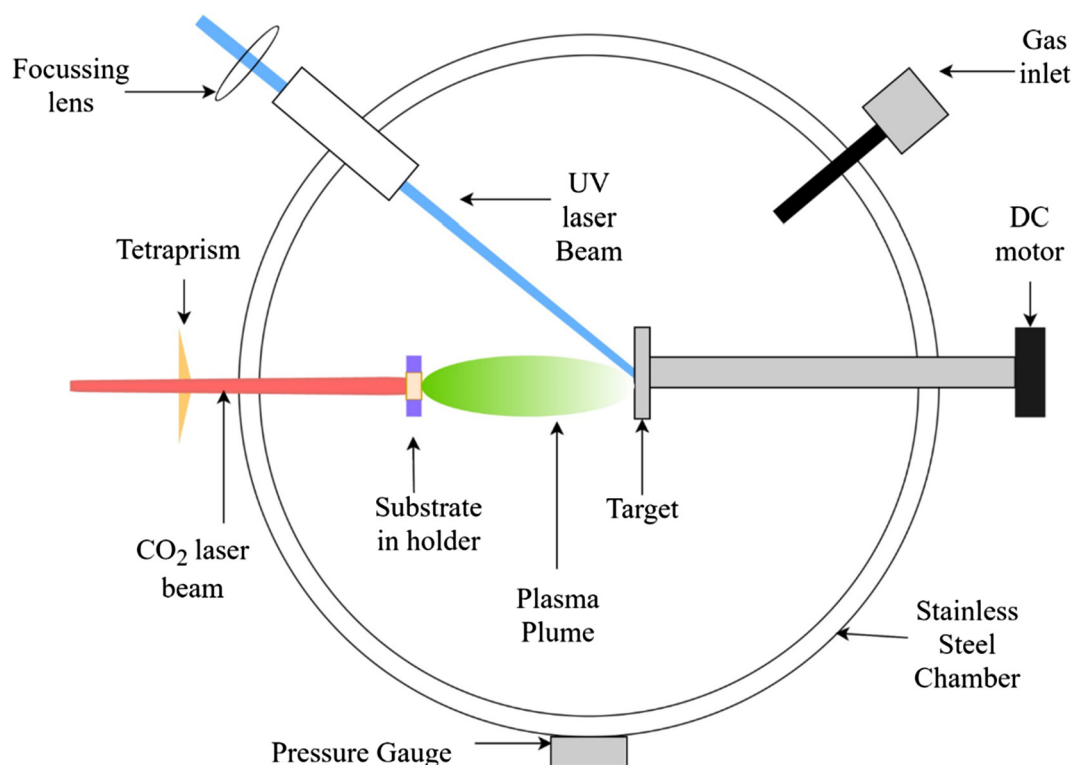

Fig. 1. Diagram of setup used for PLD.

scattering points with a size greater than the optical diffraction limit ($\sim$0.5 μm). X-ray diffraction (XRD) analysis and pole figure measurements were performed with a Rigaku Smartlab diffractometer to examine the crystallinity, lattice constant and texture of the films. Finally, a Zeiss Evo 50 scanning electron microscope was used for backscatter electron analysis and energy-dispersive X-ray spectroscopy to study the growth structure and stoichiometry.

3. Fluence optimization

Initially, we studied the effect of ablation fluence on the quality of growth from the pure scandia and lutetia targets, with particular focus on the number of observable scattering points in the films. A range of undoped Sc_2O_3 and Lu_2O_3 films were grown with the substrate heated to 1430 °C with a UV laser repetition rate of 20 Hz. The films were grown for 30 min (36000 pulses) to thicknesses of 2 μm and 1 μm for the scandia and lutetia respectively. A range of ablation fluences were used. Fig. 2 shows the dark-field images of three Sc_2O_3 and three Lu_2O_3 films, where the white spots indicate the presence of particulates or scattering points in the film, which are detrimental for realising low-loss optical waveguides. In terms of film scattering points, the optimum ablation fluence for Sc_2O_3 was 1.05 J cm^{-2}, whilst for Lu_2O_3 it was 1.1 J cm^{-2}. Although not very different in value, it means that during mixed-sesquioxide growths, a compromise fluence value was needed.

3.1. Substrate temperature optimization

To find the optimum substrate temperature to grow mixed-sesquioxide films with high degrees of crystallinity, five films were grown using a target with composition $(Yb0.05Lu0.47Sc0.48)2O3$, and a laser fluence of 1.05 J cm^{-2}, at different substrate temperatures. All of the films were grown with 36,000 pulses to a thickness of approximately 1 μm. Fig. 3(a) shows the normalised peak XRD intensity and FWHM for the (2 2 2) peak of the five films, all

recorded under the same XRD scan settings. It can be seen that the temperature with the highest intensity and smallest FWHM is $\sim$1400° (temperature calibration is discussed in [21]). This trend is also demonstrated in Fig. 3(b), which shows the rocking curve FWHM, however the rocking curve for the highest-temperature growth was not measureable due to its polycrystalline structure. Growths performed at temperatures lower than $\sim$1300 °C became increasingly amorphous with decreasing temperatures.

3.2. Compositional tuning of mixed sesquioxides

The XRD spectra for three PLD-grown, compositionally tuned mixed-sesquioxide films, as well as a Sc_2O_3 film and Lu_2O_3 film are shown in Fig. 4. These were grown at 1430 °C with an ablation fluence of 1.05 J cm^{-2} to thicknesses of $\sim$1 μm. The peak positions for the (2 2 2) peak for Lu_2O_3 [22] and Sc_2O_3 [23], and the calculated optimum peak for sapphire are also shown for comparison purposes. All 5 films have narrow peaks with a FWHM of less than 0.05° implying good crystalline growth. Table 1 shows the target composition alongside the corresponding measured (via EDX) film composition. The measured values were used to calculate the effective lattice constant and lattice mismatch, with a target composition of $(Yb_{0.05}Lu_{0.4}Sc_{0.55})_2O_3$ (green line), a film with near perfect (<0.1% lattice mismatch) lattice match to the sapphire substrate is grown. This clearly shows the ability to compositionally tune the ratio of lutetia and scandia in the film in order to achieve a specific value of lattice constant.

Fig. 5 shows dark field microscopy image of two mixed sesquioxide films, $(Yb_{0.05}Lu_{0.4}Sc_{0.55})_2O_3$ (a) and $(Yb_{0.05}Lu_{0.5}Sc_{0.45})_2$-$O_3$ (b) grown at 1430 °C with an ablation fluence of 1.05 J cm^{-2}. This demonstrates a low density of scattering points.

We performed pole figure measurements to investigate the crystallographic texture of the sesquioxide films. It is expected that pole figures for (1 1 1)-orientated cubic crystals have three peaks separated by 120° around a central peak, due to the threefold symmetry of the lattice. In Fig. 5 (a) this is confirmed for a measurement made on a (1 1 1)-orientated Sc_2O_3 crystal. However, Fig. 5
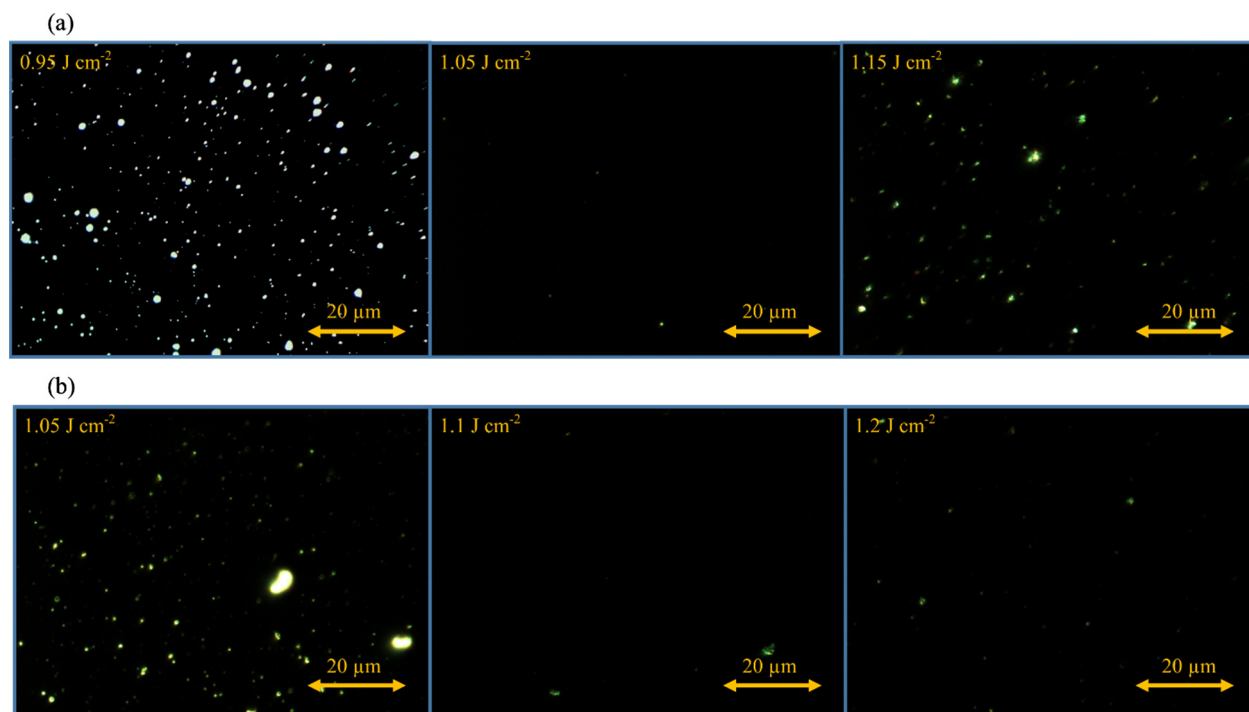

Fig. 2. Influence of the ablating laser fluence on the number of scattering points in Sc_2O_3 (a) and Lu_2O_3 (b). The top left number in each image is the ablation fluence.
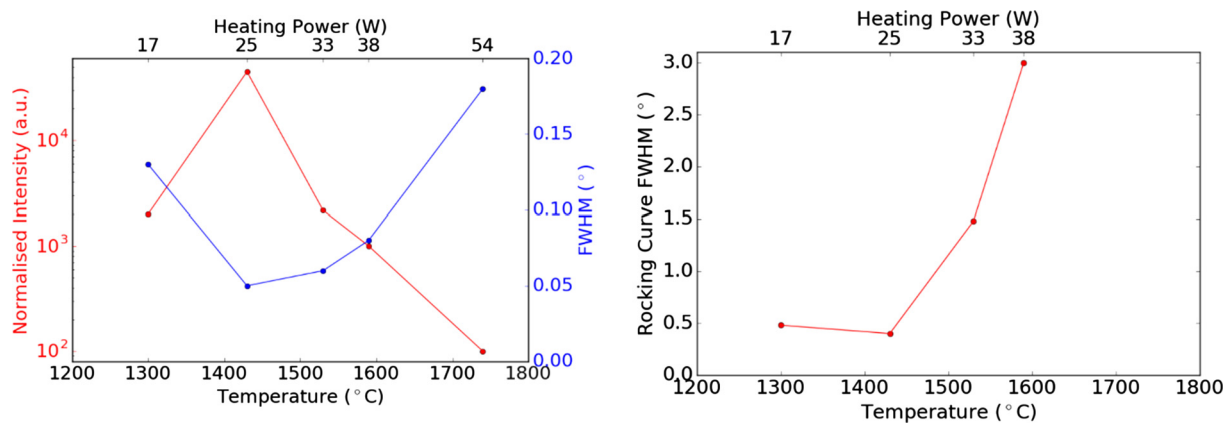
Fig. 3. (2 2 2) XRD peak characteristics for mixed-sesquioxide films grown with different substrate temperatures. (a) the intensity (red dots) of the peaks normalised to the thickness of the films/FWHM (blue triangles) of these XRD peaks and (b) the FWHM of the rocking curve measurements. The heating power provided to the substrate by the CO_2 laser is also indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
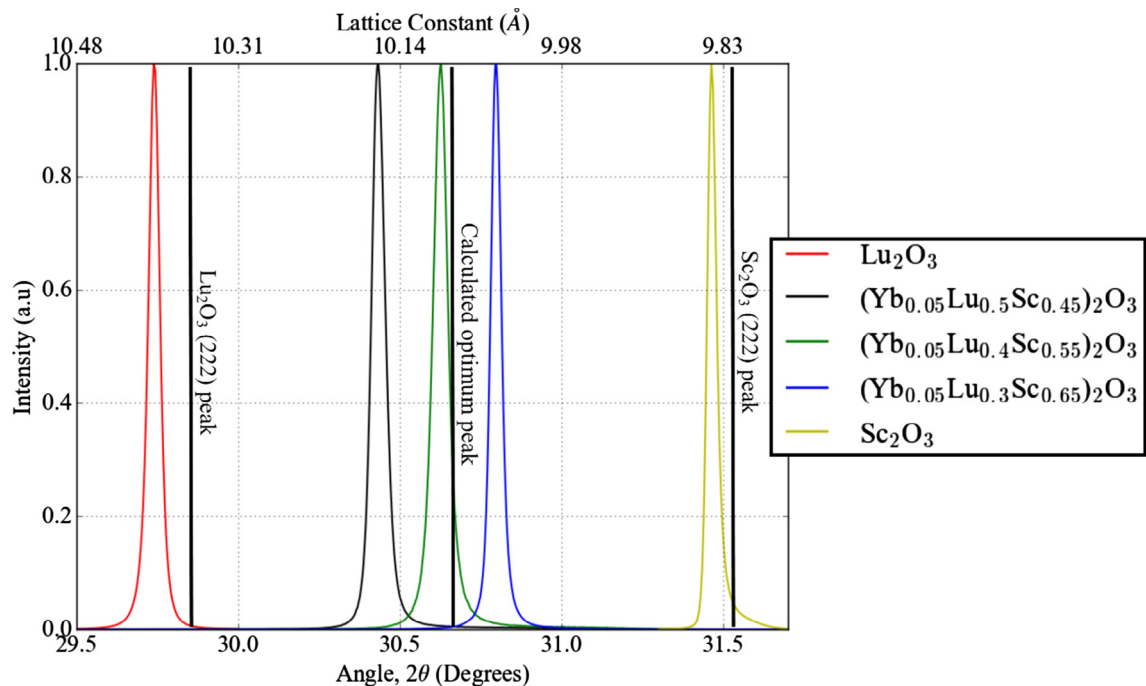

Fig. 4. XRD spectra of five films grown from three-mixed sesquioxide targets, a Sc_2O_3 target and a Lu_2O_3 target. The expected lattice constants for scandia (2 2 2), lutetia (2 2 2) according to the national chemical database and the calculated optimum lattice constant for quasi lattice matching with sapphire (assuming Vegard's law) is indicated.

Table 1
Target and film constituents' comparison, measured via EDX, with the effective lattice constant and percentage quasi-lattice mismatch (to the optimum 10.09 Å) calculated using Vegard's law.

Target composition	Film composition	Lattice constant (Å)	% Lattice mismatch
(Yb0.05Lu0.5Sc0.45) 2O3	(Yb0.03Lu0.56Sc0.41) 2O3	10.14	0.5
(Yb0.05Lu0.4Sc0.55) 2O3	(Yb0.03Lu0.45Sc0.52) 2O3	10.087	−0.03
(Yb0.05Lu0.3Sc0.65) 2O3	(Yb0.03Lu0.34Sc0.63) 2O3	10.03	−0.6

(b) shows an example pole figure measurement for a film grown at ∼1430 °C with a fluence of 1.05 J cm^{-2} from a target with composition $(Yb_{0.05}Lu_{0.4}Sc_{0.55})_2O_3$, which has six peaks separated by 60°.

This indicates the presence of two rotationally-inverted domains [3], highlighting the textured nature of the film, but also that the relatively sharp peaks support the conclusion of high-quality crystalline-film growth due to the narrow XRD 2θ FWHM bandwidths for the mixed-sesquioxide films. A backscattered electron detector was used to visualise these different domains (Fig. 6), on the polished facet of a 10-μm thick sample grown from the same target and growth conditions. Domains were randomly generated and were typically sub-micron in dimensions, however, the boundaries of these domains will likely cause scattering of light and hence contribute to the linear propagation losses in a waveguide (see Fig. 7).

Despite the domains shown in these growths, the ability of PLD to tune the constituents of the crystalline films to lattice match with the substrate is evident. A negligible lattice mismatch paves the way for growth of films without scattering points caused by lattice defects, this will increase the efficiency of an active waveg-
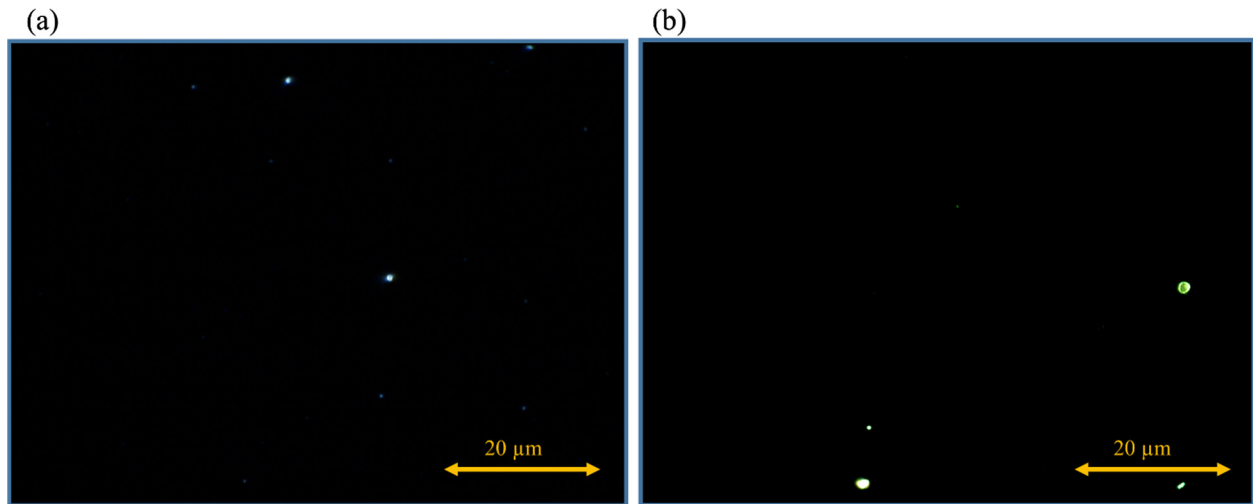
Fig. 5. Dark field images of a $(Yb_{0.05}Lu_{0.4}Sc_{0.55})_2O_3$ film (a) and a $(Yb_{0.05}Lu_{0.5}Sc_{0.65})_2O_3$ film (b) grown at 1430 °C and an ablation fluence of 1.05 J cm^{-2}.

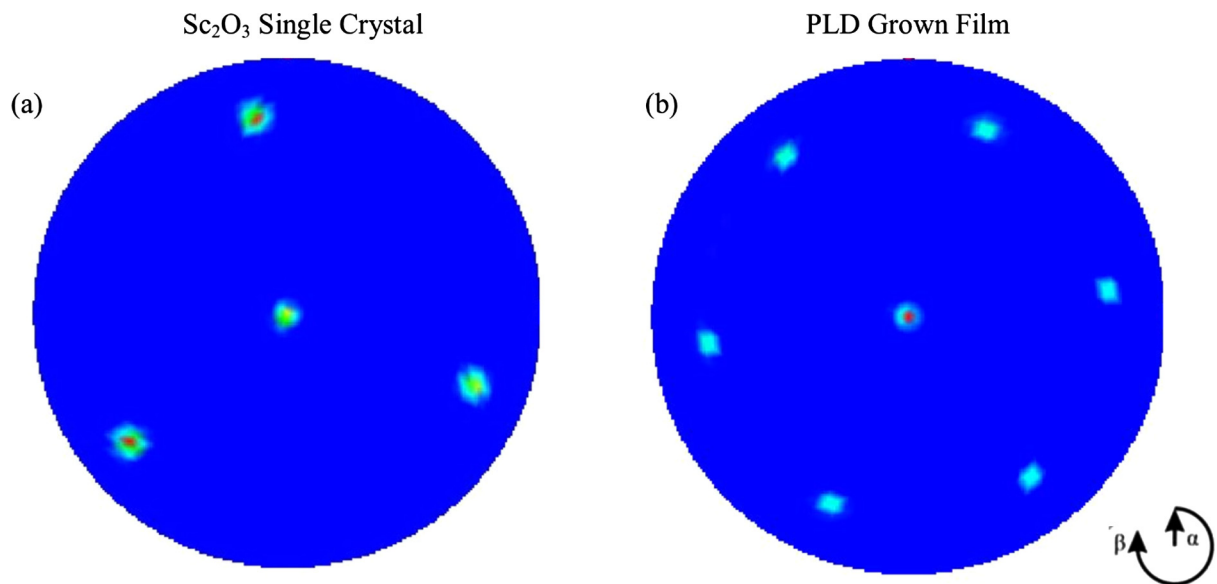**Fig. 6.** Pole figure measurements of a (a) scandia singe-crystal and (b) a film grown from a target of composition $(Yb_{0.05}Lu_{0.4}Sc_{0.55})_2O_3$.
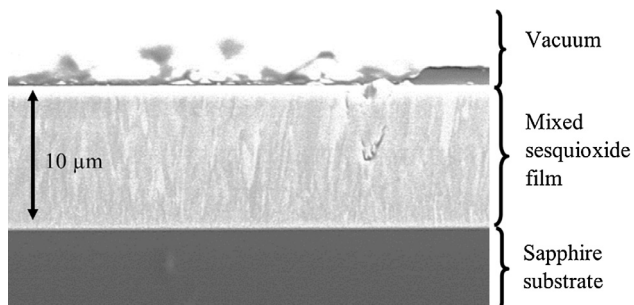

Fig. 7. A backscattered electron image of a facet of a mixed-sesquioxide thin film. Illustration of the formation of domains in PLD mixed sesquioxide growth.

uide device. In particular, ytterbium-doped mixed-sesquioxide films grown onto a sapphire substrate will enable compact, ultrashort-pulse waveguide lasers with reasonable power-scaling potential [17,24].

4. Conclusion

In summary, we have presented the growth of the first compositionally tuned mixed-sesquioxide thin films that have a quasi-lattice mismatch to sapphire of <0.1%. We have demonstrated the optimum growth conditions for low-surface-defect, high-crystallinity growth in a 10-μm thick film as demonstrated by XRD FWHM bandwidths as narrow as a bulk crystal. These materials, grown via PLD, have the potential to be gain media for ultrashort-pulse lasers with enhanced spectroscopic parameters compared to using single constituent sesquioxides.

Acknowledgements

References

[1] C. Krankel, Rare-earth-doped sesquioxides for diode-pumped high-power lasers in the 1-, 2-, and 3um spectral range, IEEE J. Sel. Top. Quantum Electron. 21 (1) (2015) 250–262.

[2] P.B.W. Burmester, T. Ishii, G. Huber, M. Kurfiss, M. Schilling, Characterization of crystalline europium doped α-Y_2O_3 PLD-films grown on α-Al_2O_3, Mater. Sci. Eng. B 105 (1–3) (2003) 25–29.

[3] S. Bär, G. Huber, J. Gonzalo, A. Perea, A. Climent, F. Paszti, Europium-doped sesquioxide thin films grown on sapphire by PLD, Mater. Sci. Eng. B 105 (1–3) (2003) 30–33.

[4] Y. Kuzminykh, H. Scheife, S. Bär, K. Petermann, G. Huber, PLD-grown Yb-doped sesquioxide films on sapphire and quartz substrates, J. Phys. Conf. Ser. 59 (2007) 462–465.

[5] T.L. Parsonage, S.J. Beecher, A. Choudhary, J.A. Grant-Jacob, P. Hua, J.I. Mackenzie, D.P. Shepherd, R.W. Eason, Pulsed laser deposited diode-pumped 7.4 W $Yb:Lu_2O_3$ planar waveguide laser, Opt. Exp. 23 (25) (2015) 31691–31697.

[6] S.J. Beecher, T.L. Parsonage, J.I. Mackenzie, K.A. Sloyan, J.A. Grant-Jacob, R.W. Eason, Diode-end-pumped 1.2 W $Yb:Y_2O_3$ planar waveguide laser, Opt. Exp. 22 (18) (2014) 22056–22061.

[7] R.W. Eason, Pulsed Laser Deposition of Thin Films, John Wiley & Sons inc, 2007.

[8] J.A. Grant-Jacob, S.J. Beecher, T.L. Parsonage, P. Hua, J.I. Mackenzie, D.P. Shepherd, R.W. Eason, An 11.5 W Yb:YAG planar waveguide laser fabricated via pulsed laser deposition, Opt. Mater. Exp. 6 (1) (2015), 91.

[9] J.A. Grant-Jacob, S.J. Beecher, H. Riris, A.W. Yu, D.P. Shepherd, R.W. Eason, J.I. Mackenzie, Dynamic control of refractive index during pulsed-laser-deposited waveguide growth, Opt. Mater. Exp. 7 (11) (2017) 4073.

[10] T.C. May-Smith, K.A. Sloyan, R. Gazia, R.W. Eason, Stress engineering and optimization of thick garnet crystal films grown by pulsed laser deposition, Cryst. Growth Des. 11 (4) (2011) 1098–1108.

[11] S.J. Beecher, J.A. Grant-Jacob, P. Hua, J.J. Prentice, R.W. Eason, D.P. Shepherd, J.I. Mackenzie, Ytterbium-doped-garnet crystal waveguide lasers grown by pulsed laser deposition, Opt. Mater. Exp. 7 (5) (2017) 1628.

[12] P.K. Schenck, M.D. Vaudin, D.W. Bonnell, J.W. Hastie, A.J. Paul, Particulate reduction in the pulsed laser deposition of barium, Appl. Surf. Sci. 127 (129) (1998) 655–661.

[13] R. Peters, C. Kränkel, S.T. Fredrich-Thornton, K. Beil, K. Petermann, G. Huber, O. H. Heckl, C.R.E. Baer, C.J. Saraceno, T. Südmeyer, U. Keller, Thermal analysis and efficient high power continuous-wave and mode-locked thin disk laser operation of Yb-doped sesquioxides, Appl. Phys. B 102 (3) (2011) 509–514.

[14] S.H. Waeselmann, S. Heinrich, C. Kränkel, G. Huber, Lasing of Nd^{3+} in sapphire, Laser Photonics Rev. 10 (3) (2016) 510–516.

[15] K. Beil, C.J. Saraceno, C. Schriber, F. Emaury, O.H. Heckl, C.R. Baer, M. Golling, T. Südmeyer, U. Keller, C. Kränkel, G. Huber, Yb-doped mixed sesquioxides for ultrashort pulse generation in the thin disk laser setup, Appl. Phys. B 113 (1) (2013) 13–18.

[16] A. Schmidt, V. Petrov, U. Griebner, R. Peters, K. Petermann, G. Huber, C. Fiebig, K. Paschke, G. Erbert, Diode-pumped mode-locked $Yb:LuScO_3$ single crystal laser with 74 fs pulse duration, Opt. Lett. 35 (4) (2010) 511–513.

[17] K.A. Sloyan, T.C. May-Smith, R.W. Eason, Hybrid garnet crystal growth for thin-disc lasing applications by multi-beam pulsed laser deposition, Appl. Phys. A 110 (4) (2012) 799–803.

[18] K.E. Youden, R.W. Eason, M.C. Gower, N.A. Vainos, Epitaxial growth of $Bi_{12}GeO_{20}$ thin-film optical waveguides using excimer laser ablation, Appl. Phys. Lett. 59 (16) (1991) 1929–1931.

[19] A.R. Denton, N.W. Ashcroft, Vegard's law, Phys. Rev. A 43 (6) (1991) 3161–3164.

[20] M. Ajroud, M. Haouari, H. Ben Ouada, H. Mâaref, A. Brenier, B. Champagnon, Energy transfer processes in (Er^{3+}–Yb^{3+})-codoped germanate glasses for mid-infrared and up-conversion applications, Mater. Sci. Eng. C 26 (2–3) (2006) 523–529.

[21] A. Sposito, Pulsed laser deposition of thin film magneto-optic materials and lasing waveguides, in: Optoelectronics Research Centre, University of Southampton, 2014.

[22] 40471, Inorganic Crystal Structure Database, <http://iscd.cds.rsc.org>.

[23] 26841, Inorganic Crystal Structure Database, <http://icsd.cds.rsc.org/>.

[24] D.P. Shepherd, A. Choudhary, A.A. Lagatsky, P. Kannan, S.J. Beecher, R.W. Eason, J.I. Mackenzie, X. Feng, W. Sibbett, C.T.A. Brown, Ultrafast high-repetition-rate waveguide lasers, IEEE J. Sel. Top. Quantum Electron. 22 (2) (2016) 16–24.