Damage evolution of ion irradiated defected-fluorite $\text{La}_2\text{Zr}_2\text{O}_7$ epitaxial thin films

Tiffany C. Kaspar,^{1,*} Jonathan G. Gigax,² Lin Shao,² Mark E. Bowden,³ Tamas Varga,³ Vaithiyalingam Shutthanandan,³ Steven R. Spurgeon,¹ Pengfei Yan,³ Chongmin Wang,³ Pradeep Ramuhalli,⁴ Charles H. Henager, Jr.⁵

¹*Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

²*Department of Nuclear Engineering, Texas A&M University, College Station, TX 77843, USA*

³*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

⁴*National Security Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

⁵*Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

Abstract

Pyrochlore-structure oxides, $\text{A}_2\text{B}_2\text{O}_7$, may exhibit remarkable radiation tolerance due to the ease with which they can accommodate disorder by transitioning to a defected fluorite structure. The mechanism of defect formation was explored by evaluating the radiation damage behavior of high quality epitaxial $\text{La}_2\text{Zr}_2\text{O}_7$ thin films with the defected fluorite structure, irradiated with 1 MeV Zr^+ at doses up to 10 displacements per atom (dpa). The level of film damage was evaluated as a function of dose by Rutherford backscattering spectrometry in the channeling geometry (RBS/c) and scanning transmission electron microscopy (STEM). At lower doses, the surface of the $\text{La}_2\text{Zr}_2\text{O}_7$ film amorphized, and the amorphous fraction as a function of dose fit well to a stimulated amorphization model. As the dose

increased, the surface amorphization slowed, and amorphization appeared at the interface. Even at a dose of 10 dpa, the core of the film remained crystalline, despite the prediction of amorphization from the model. To inform future ab initio simulations of $\text{La}_2\text{Zr}_2\text{O}_7$, the bandgap of a thick $\text{La}_2\text{Zr}_2\text{O}_7$ film was measured to be indirect at 4.96 eV, with a direct transition at 5.60 eV.

Keywords: crystalline oxides; ion irradiation; structural disordering; STEM HAADF

*Corresponding author. *Email address:* tiffany.kaspar@pnnl.gov (T.C. Kaspar)

1. Introduction

Pyrochlore structure oxides ($A_2B_2O_7$) are of interest for the wide variety of physical, chemical, and electronic properties exhibited by the more than 500 known *A* and *B*-site cation combinations [1]. One particularly interesting property is the resistance of these compounds to structural amorphization when exposed to radiation. This property, along with the ability to incorporate radionuclides such as Pu and Am on the *A*-site in the pyrochlore structure, has led to much interest in pyrochlore oxides as a stable nuclear waste form [2-4]. Initial work focused on titanate pyrochlores ($A_2Ti_2O_7$), but zirconate pyrochlores ($A_2Zr_2O_7$) proved significantly more radiation-tolerant. For example, $Ga_2Ti_2O_7$ amorphizes at 0.2 displacements per atom (dpa) under 1 MeV Kr^+ irradiation at room temperature, while $Ga_2Zr_2O_7$ can withstand 15 dpa under 1.5 MeV Xe^+ irradiation at room temperature without amorphizing [2]. Likewise, $Er_2Zr_2O_7$ is highly radiation-resistant, while $Er_2Ti_2O_7$ is not [1].

The remarkable radiation resistance of pyrochlores arises, at least in part, from the unique properties of the pyrochlore crystal structure. The pyrochlore structure (space group $Fd\bar{3}m$) is a derivative of the fluorite structure (CaF_2 , space group $Fm\bar{3}m$), with ordered cations on two distinct sites (*A* and *B*) and one-eighth of the O sites (the 8a sites in Wyckoff notation) vacant [3]. The stoichiometry is formally $A_{1-2}B_2O_6Y_{0-1}$, with the *A*-site occupied by rare earths, actinides, or elements with inert lone-pair electrons of valence 2+ or 3+ and the *B*-sites occupied by transition or post-transition metals of valence 4+ or 5+ [1, 5]; $Y = O$ for pyrochlore oxides but can also be OH or F [2]. The radiation resistance has been shown to be related to the ease with which *A*- and *B*-sites can disorder (antisite defects); likewise, disorder can be introduced in the lattice positions of the oxygen vacancies. Thus, superior radiation resistance results from low energetic barriers to transform from the ordered pyrochlore to the disordered fluorite structure [3, 6, 7].

The ratio of atomic radii of the *A*- and *B*-site cations, r_A/r_B , can be used as a guide to determine whether an $A_2B_2O_7$ oxide crystallizes in the defected fluorite or pyrochlore structure [8]: for $r_A/r_B < 1.46$,

the defect fluorite structure is favored; for $1.46 < r_A/r_B < 1.78$, the oxide crystallizes in the pyrochlore structure, and for $r_A/r_B > 1.78$ less symmetric crystal structures such as the monoclinic perovskite-layered structure (PLS) [9, 10] or tetragonal ($P4_32_12$) [11] structures are energetically preferred. Using this analysis, $Gd_2Ti_2O_7$ ($r_A/r_B = 1.74$) is much further from the defect fluorite structure than is $Gd_2Zr_2O_7$ ($r_A/r_B = 1.46$); thus, $Gd_2Zr_2O_7$ can easily transition to the defect fluorite structure upon irradiation, while $Gd_2Ti_2O_7$ cannot. Likewise, $Er_2Zr_2O_7$ ($r_A/r_B = 1.39$) crystallizes in the defect fluorite structure and exhibits high radiation tolerance, while $Er_2Ti_2O_7$ ($r_A/r_B = 1.66$) crystallizes in the pyrochlore structure with poor radiation tolerance. A comprehensive study of the lanthanide stannate pyrochlores, $Ln_2Sn_2O_7$ ($Ln = La$ to Lu and Y) confirmed this trend of increasing radiation tolerance with decreasing r_A/r_B [12, 13]. A similar analysis of the oxygen positional parameter of the O 48f site, x , compared to that for the ideal pyrochlore structure ($x = 0.3125$) and the ideal (non-defective) fluorite structure ($x = 0.375$), leads to similar conclusions regarding radiation tolerance: those oxides which exhibit x values closer to the ideal fluorite value exhibit higher radiation tolerance than those with x values closer to the ideal pyrochlore structure [1, 7].

$La_2Zr_2O_7$ has been investigated as a model zirconate pyrochlore material that exhibits relatively poor radiation resistance. $La_2Zr_2O_7$ is relatively far from the fluorite structure, with $r_A/r_B = 1.61$ and O 48f $x = 0.332$ [14]. An irradiation study of a polycrystalline monolith of $La_2Zr_2O_7$ with 1.5 MeV Xe^+ found that the material amorphized at a dose of 5.5 dpa at room temperature. A fit of the amorphization dose as a function of temperature found a critical amorphization temperature of ~ 310 K; above this temperature, recrystallization processes dominate and the material cannot be amorphized [1]. Because this study utilized transmission electron microscopy (TEM) to identify the onset of amorphization, the degree of damage that occurred at a given temperature as a function of dose could not be measured. Without this data, it is difficult to determine the damage mechanism. Theoretical molecular dynamics (MD) simulations of ion-induced defect cascades in $La_2Zr_2O_7$ confirmed that a low yield of cation antisites,

interstitials, and vacancies was the primary material response [15]. This was interpreted as the beginnings of a transition towards the disordered fluorite state, and follow-up simulations revealed that the key defect process is the generation of cation Frenkel pairs (interstitial + vacancy) [16]. More recent *ab initio* MD calculations found that the threshold displacement energies for both cations and anions are higher, and cation and anion Frenkel pair formation energies are lower, in $\text{La}_2\text{Zr}_2\text{O}_7$ than in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ [14]. These predictions correlate with the enhanced ion-beam-induced radiation resistance observed for $\text{A}_2\text{Zr}_2\text{O}_7$ ($\text{A} = \text{Nd}, \text{Sm}, \text{Gd}$) pyrochlores relative to $\text{La}_2\text{Zr}_2\text{O}_7$ [1]. Likewise, MD simulations predicted that substitution of Ti for a fraction of the Zr in $\text{La}_2\text{Zr}_2\text{O}_7$ would be detrimental to the radiation tolerance, since the *A*-site to *B*-site exchange energy increases with the addition of Ti [17].

To better understand the mechanisms of ion-induced radiation damage in pyrochlores such as $\text{La}_2\text{Zr}_2\text{O}_7$, it is preferable to study single crystal specimens. In contrast to polycrystalline powders, which are typically limited to a determination of the amorphization dose, the level of radiation damage in single crystal specimens can be more easily quantified (without contributions from grain boundary effects) with techniques such as TEM [18] or Rutherford backscattering spectrometry (RBS) in the channeling geometry (RBS/c) [19, 20]. Synthesis of bulk single crystals can be difficult and time-consuming, but deposition of epitaxial thin films can be done relatively quickly and easily, and dopants can be introduced in a controlled manner. Epitaxial thin films are suitable for ion-induced radiation damage studies [21], and are particularly amenable to RBS/c. In contrast to textured $\text{La}_2\text{Zr}_2\text{O}_7$ thin films deposited by solution methods [22, 23], there have been few reports of epitaxial $\text{La}_2\text{Zr}_2\text{O}_7$ thin films synthesized by vacuum deposition methods [24, 25]. Here we present the results of 1 MeV Zr^+ ion irradiation of $\text{La}_2\text{Zr}_2\text{O}_7$ epitaxial thin films which have crystallized in the defected fluorite structure. With RBS/c data collected from these films as a function of dose, we obtain detailed information on the mechanism of damage accumulation in defected-fluorite $\text{La}_2\text{Zr}_2\text{O}_7$, as well as an accurate measure of the dose required for full amorphization. The conclusions drawn from the RBS/c analysis are supported by

scanning transmission electron microscopy (STEM) cross-sectional images collected at key dose levels. These results are compared to previous reports [1] detailing radiation damage accumulation in pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$.

2. Experimental

Thin films of $\text{La}_2\text{Zr}_2\text{O}_7$ were deposited by pulsed laser deposition at a substrate temperature of 850 - 900°C in a background pressure of 25 mTorr O_2 . A KrF laser operating at 1 Hz was used to ablate the ceramic targets with a fluence of $\sim 2 \text{ J/cm}^2$. $\text{La}_2\text{Zr}_2\text{O}_7$ films were deposited from a ceramic $\text{La}_2\text{Zr}_2\text{O}_7$ target. Final film thicknesses were nominally 500 Å on $1 \times 1 \text{ cm}^2$ single crystal SrTiO_3 (STO), LaAlO_3 (LAO), and 8% Y:ZrO_2 (yttria-stabilized zirconia, YSZ) substrates. Except where noted below, substrates were adhered with colloidal silver paint to a 1" diameter Si(001) wafer to prevent the diffusion of metals (such as Mo) from the sample holder to the substrate; an additional benefit of this sample mounting arrangement is the improved thermal contact to the thin Si wafer, which allowed efficient heating of the substrate to the temperatures employed in this work. X-ray diffraction (XRD) patterns were collected on a Philips X'Pert Materials Research Diffractometer (MRD) using $\text{Cu K}\alpha_1$ radiation monochromated with a hybrid mirror/4 crystal monochromator. High-resolution θ - 2θ scans, ϕ scans, and reciprocal space maps (RSMs) were collected with fixed-slit detector optics. Ellipsometry data was collected as a function of incident photon energy with a variable-angle spectroscopic ellipsometer (V-VASE, J.A. Woollam) at angles of 50°, 60°, and 70°. Data were fit using the WVASE software program.

Ion irradiations were performed with 1 MeV Zr^+ ions at fluences ranging from 3.98×10^{13} to 7.96×10^{14} ions/ cm^2 produced by a 1.7 MV tandem accelerator at the Texas A&M University Ion Beam Lab. Zr^+ ions were incident on the sample at room temperature and an angle of 7° off normal. A corner of the sample, approximately 4 mm x 4 mm, was defined by masking the sample in a thick Al foil prior to irradiation. Displacements per atom (dpa) were calculated using the SRIM software, assuming a

displacement energy of 50 eV [1] (in reasonable agreement with later theoretical predictions [14, 15]), which resulted in a predicted average damage rate of 0.8 vacancies/ion*Å in the La₂Zr₂O₇ film. Films were analyzed before and after irradiation by RBS in the random and channeling (RBS/c) directions. RBS data were generated with 2 MeV He⁺ incident on a ~1.5 x 1.5 mm area of the film, and collected at a detector angle of 160°. Aligned spectra were obtained by adjusting the goniometer to the surface normal of the specimen. Random spectra were acquired by tilting one axis to a fixed value of 7° and rocking another axis of the goniometer by ±3° during acquisition. Various levels of charging were observed for different analysis locations and ion doses, affecting the backscattering yield and (to a lesser extent) the energy scale. To correct for this, individual channeling data were normalized such that the La peak of the respective random backscattering spectra matched across all measurements. Samples were prepared for STEM using an FEI Helios NanoLab Dual-Beam Focused Ion Beam (FIB) microscope and a standard lift out procedure. High-angle annular dark field (STEM-HAADF) images were collected using a C_s-corrected JEOL ARM 200-CF microscope operated at 200 keV, with a 1 Å probe size, a convergence angle of 27.5 mrad, and a collection angle of 83 mrad. Geometric phase analysis (GPA) was performed using the FRWR Tools plugin [26] with the YSZ substrate selected as a reference region.

3. Results

3.1 Crystalline structure and epitaxy

The pyrochlore crystal structure of La₂Zr₂O₇ is closely related to the cubic fluorite structure of YSZ, although the lattice parameter difference ($a_{\text{La}_2\text{Zr}_2\text{O}_7} = 10.786 \text{ Å}$ [24] and $a_{\text{YSZ}} = 5.125 \text{ Å}$) leads to a lattice misfit of $\delta = (a_{\text{La}_2\text{Zr}_2\text{O}_7}/2 - a_{\text{YSZ}})/a_{\text{YSZ}} * 100\% = 5.3\%$. Despite this misfit, high quality epitaxial La₂Zr₂O₇(111) thin films can be obtained on YSZ(111) substrates, as shown in Fig. 1(a). Only (*l*l) reflections are observed in the θ -2 θ scan. Surprisingly, only reflections with even index *l* are observed; the (111) (10.68° 2 θ) and (333) (43.49° 2 θ) reflections of the pyrochlore structure are not present [27]. This indicates that the cations in the La₂Zr₂O₇ film have not ordered in the pyrochlore crystal structure, as

expected, but instead the film has crystallized in the defected-fluorite structure. Despite this, the finite thickness fringes flanking the $\text{La}_2\text{Zr}_2\text{O}_7(222)$ peak indicate that the film exhibits well-ordered crystallinity with sharp and smooth interfaces. The RSM in Fig. 1(b) shows the YSZ(133) and $\text{La}_2\text{Zr}_2\text{O}_7(266)$ reflections. The single spot observed for the $\text{La}_2\text{Zr}_2\text{O}_7(266)$ reflection confirms the epitaxial relationship with the YSZ substrate. From the q_{xy} position of the film reflection relative to that of the substrate, the film appears to be relaxed, as expected from the large δ and film thickness.

Deposition under similar conditions on LAO(001) results in epitaxial (001)-oriented $\text{La}_2\text{Zr}_2\text{O}_7$ films, as presented in Fig. 1(c). A very low lattice mismatch of $\delta = -0.2\%$ is possible if the $\text{La}_2\text{Zr}_2\text{O}_7(001)$ film rotates by 45° about the surface normal. In addition to the strong $\text{La}_2\text{Zr}_2\text{O}_7(00l)$ diffraction peaks, an additional peak is observed in the θ - 2θ pattern (marked with an asterisk in Fig. 1(c)), which is assigned as Mo(110) arising from contact with the Mo sample holder during deposition. Figure 1(d) presents a ϕ scan of the $\text{La}_2\text{Zr}_2\text{O}_7(440)$ and LAO(110) in-plane peaks. The four-fold symmetry of the $\text{La}_2\text{Zr}_2\text{O}_7(440)$ reflections reveals a single in-plane orientation for this film, and the relationship with the four-fold LAO(110) peaks confirms the expected epitaxial orientation between film and substrate: the $\text{La}_2\text{Zr}_2\text{O}_7$ film rotates by 45° relative to the LAO substrate. In the (001) orientation, the out-of-plane diffraction patterns of pyrochlore and fluorite structures are identical. A search for the (333) in-plane diffraction peak (not shown) did not reveal any diffraction intensity, indicating that this film has crystallized in the defected fluorite structure. Deposition of $\text{La}_2\text{Zr}_2\text{O}_7$ on STO(001) might be expected to result in a similar epitaxial relationship as $\text{La}_2\text{Zr}_2\text{O}_7/\text{LAO}(001)$, despite the somewhat larger lattice mismatch ($\delta = -2.3\%$); however, as indicated in Fig. 1(d), (111)-oriented $\text{La}_2\text{Zr}_2\text{O}_7$ films result instead; as with the $\text{La}_2\text{Zr}_2\text{O}_7$ film deposited on YSZ(111) and discussed above, the (333) reflection is not observed, confirming that this film also possesses the defected fluorite structure. The (111) orientation of the pyrochlore structure is a low-energy surface, although a recent modeling study found the (110) surface to be the lowest-energy surface [28]. As illustrated by the very weak and unevenly spaced peaks in the ϕ scan of the

La₂Zr₂O₇(440) reflection in Fig. 1(e), no preferential in-plane orientation exists. Thus, La₂Zr₂O₇/STO(001) can be considered, at best, textured in the out-of-plane direction, but the film is not epitaxial.

The film structure results obtained by XRD are corroborated by RBS/c measurements of the La₂Zr₂O₇ films deposited on STO(001), YSZ(111), and LAO(001), as shown in the RBS random and channeling spectra in Fig. 2(a), and scans of the La peak region of interest as the film is rocked through the channeling direction in Fig. 2(b). In all cases, the single crystal oxide substrate exhibits strong channeling (channel number < ~380 in Fig. 2(a)), with LAO(001) returning the lowest yield. Due to the difficulty in separating the La signal due to the film from that of the substrate for La₂Zr₂O₇ / LAO(001), the minimum yield ($\chi_{\min} = I_{\text{channeling}}/I_{\text{random}}$, where I is the yield in counts) was calculated for the Zr peak (after subtraction of the La background) and found to be 14%. The angular scan for this film in Fig. 2(b), which was obtained for the La peak, indicates a similar channeling yield but is likely influenced by La channeling in the LAO substrate. In Fig. 2(a), a somewhat higher yield of 21% is obtained for the La peak from the La₂Zr₂O₇ / YSZ(111) heterostructure (for reference, the minimum yield obtained for a bare YSZ substrate is 12%). In this case, the La peak in the channeling direction exhibits clear surface and interface peaks in addition to the yield from the bulk of the film. The surface peak arises from backscattering from the top surface of the film, where no shadowing can occur. The interface peak indicates the presence of disorder at the film/substrate interface. The fairly low $\chi_{\min}$ values for these two films are consistent with the well-ordered epitaxial structure observed by XRD (Fig. 1). In contrast, the La₂Zr₂O₇ film on STO(001) exhibits essentially no channeling ($\chi_{\min} = 95\%$), as confirmed by the identical La and Zr backscattering peak intensities in the random and channeling directions in Fig. 2(a), and the lack of features exhibited by the angular scan in Fig. 2(b). This is actually somewhat surprising considering the XRD results in Fig. 1(d) and (e), which indicated an out-of-plane texture in the (111) direction. Although the film grains are oriented randomly in-plane, RBS/c in the out-of-plane direction normal to the film surface should still reveal some degree of channeling. The lack of channeling

indicates the presence of film defects that were not detected by XRD, suggesting that more local probes are needed.

3.2 Irradiation with 1 MeV Zr⁺

Inspection of Fig. 2(a) reveals that La₂Zr₂O₇ / STO(001) is the ideal choice for the irradiation study because both the La and Zr peaks are well-separated from the substrate Sr peak. Unfortunately, the La₂Zr₂O₇ film deposited on STO(001) is not epitaxial and thus shows no channeling, making it impossible to monitor the increase of disorder in the film with increasing dose. Instead, La₂Zr₂O₇/YSZ(111) was chosen as an alternative for the irradiation measurements. Although only the La peak from the film can be analyzed due to interference of the Zr peaks from the film and substrate, the La peak is well-resolved, with clear surface, bulk, and interface regions. Each region can be monitored independently to ascertain whether disorder or amorphization occurs preferentially in a particular region.

The effect of 1 MeV Zr⁺ irradiation on the La backscattering peak collected in the channeling geometry is illustrated in Fig.3(a) as a function of ion dose (dpa). As the La₂Zr₂O₇ film is irradiated, the channeling yield for the La peak decreases, indicating that disorder is increasing. For low ion doses (0.5 – 2 dpa), the characteristic “U” shape of the channeling peak remains, indicating that the disorder in the bulk of the film (B) is less than at the interface (I), and the surface backscattering peak (S) can be resolved. The approximate positions of these three regions are shown as shaded areas in Fig. 3(a). As the dose increases to > 4 dpa, this characteristic shape disappears and the distinction between interface, bulk, and surface regions can no longer be made.

To quantify the level of disorder in the film, the fraction of amorphous material within the film was calculated from the intensity of the La backscattering peak at a given ion dose ($I_{\text{irradiated}}$) as $(I_{\text{irradiated}} - I_{\text{channeling}}) / (I_{\text{random}} - I_{\text{channeling}})$. The value of $I_{\text{irradiated}}$ was taken as the average of the counts in the interface peak region, the film bulk region, or the surface peak region, as indicated by the shaded areas in Fig.

3(a), or the area under the entire La backscattering peak. The values of I_{random} and $I_{\text{channeling}}$ were taken from the unirradiated film. The amorphous fraction of $\text{La}_2\text{Zr}_2\text{O}_7$ as a function of ion dose is plotted in Fig. 3(b). A monotonic increase in amorphization is observed to a dose of 6 dpa, after which amorphization appears to plateau; at 10 dpa, the $\text{La}_2\text{Zr}_2\text{O}_7$ film exhibits a very similar fraction of amorphous material as at a dose of 6 dpa. Subtle differences in damage rate can be seen for the interface, bulk, and surface regions. The disorder in the surface peak region increases quickly at low doses, then increases more slowly at higher doses. In contrast, the interface peak increases more slowly initially, then at higher doses the damage rate increases. The film bulk region appears to exhibit a plateau at 2 dpa, but more data points as a function of dose are required to confirm this trend.

To correlate the RBS results to structural changes in the film, cross-sectional STEM-HAADF images were collected from three areas, corresponding to nominally pristine LZO and ion doses of 2 dpa and 10 dpa. As shown in Fig. 4(a), the nominally pristine LZO crystal structure is cubic, as expected. The superstructure indicative of the pyrochlore crystal structure [1] is not observed in fast Fourier transform (FFT) of the image, consistent with the assessment by XRD that this film possesses the defect fluorite structure. This cross-section was collected from an area between the pristine region utilized for He^+ RBS channeling alignment and the 2 dpa Zr^+ region, and thus a low level of damage may have occurred from either irradiation (or both). Evidence of this damage is also observed as a surface amorphous region in some of the STEM images (not shown), and the observation of ion tracks on the film surface (see inset to Fig. 4(a); the STEM cross-section was collected from an area between ion tracks). Figures 4(b-c) show details of the LZO / YSZ interface, indicating the presence of misfit dislocations to accommodate the lattice mismatch between the film and substrate. GPA analysis was used to calculate the in-plane strain component (ϵ_{xx}) relative to the substrate and highlight the location of the misfit dislocations. The dislocations are spaced 7-8 nm apart and act to relax the film strain, yielding a 3-4% in-plane expansion relative to the substrate, in good agreement with our XRD measurements.

Figures 5(a-b) show that, after a dose of 2 dpa, the top portion of the film has transformed to a damaged layer consisting of substantial amorphization. The thickness of this damaged layer in the region imaged in Fig. 5(b) is approximately 8 nm. Some radiation-induced amorphization (~ 4 nm) is also observed at the LZO/YSZ interface in certain regions, although in other regions the LZO exhibits crystallinity in contact with the YSZ substrate. The central portion of the film remains crystalline; as with the nominally pristine film shown in Fig. 4, the superstructure indicative of the pyrochlore crystal structure is not apparent in the lattice image or the associated FFT. The thickness of this crystalline region, in the areas which exhibit amorphization at the YSZ interface, is approximately 26 nm. The original film thickness was 56 nm, which indicates that FIB sample preparation of the STEM cross-section has removed some of the amorphous film at the surface. If the assumption is made that, other than a 26 nm thick central region of crystalline material, the rest of the 56 nm thick film has amorphized, an amorphous fraction of 0.53 can be estimated. The RBS channeling results in Fig. 3(b) indicated an amorphous fraction of 0.46 at a dose of 2 dpa, which matches well with the ratio of damaged to crystalline regions in the STEM images.

Further irradiation to 10 dpa does not continue to uniformly thicken the surface damage layer, as illustrated in Fig. 5(c); in this case, the damage layer possesses a thickness of approximately 14 nm compared to a total film thickness 46 nm, with an uneven and somewhat poorly defined interface between the amorphized surface layer and the central crystalline region. At this higher ion dose, the majority of additional damage has occurred at the LZO/YSZ interface. In Fig. 5(c), the average thickness of the amorphous region at the interface is approximately 9 nm. Pitting of the substrate is observed at regular intervals, as shown in Fig. 5(d), likely originating from the misfit dislocations shown in Figs. 4(b-c). However, it is difficult to ascertain whether the misfit dislocations promoted damage in these regions, or conversely if they acted as sinks for radiation-induced damage [21] while the areas between dislocations experienced higher damage levels. In some places, the amorphous regions at the interface

and surface infringe on the central crystalline region, and touch or nearly touch. In these regions, evidence of faceting of the crystalline material is evident; this faceting is likely along a direction equivalent to the corner-sharing TiO_6 octahedra in the pyrochlore $\langle 112 \rangle$ direction [29]. An estimate of the ratio of amorphous to crystalline regions in the STEM image in Fig. 5(c) is 0.40, which is well below that found by RBS/c (0.87). This discrepancy may be explained by fact that the crystalline region in the center of the film is partly damaged. Thus, a fraction of the backscattering observed in RBS/c occurs in this region, whose amorphous level cannot be quantified from the STEM images. The estimate of amorphous fraction also does not account for the amorphous regions which have infringed on the central, crystalline region. Nonetheless, the STEM images confirm that the LZO film has not fully amorphized at a dose of 10 dpa.

3.3 Electronic structure of $\text{La}_2\text{Zr}_2\text{O}_7$

The electronic structure of $\text{La}_2\text{Zr}_2\text{O}_7$ is not well established, which hinders efforts to model the radiation damage properties of the material [14]. To this end, the optical properties as measured by spectroscopic ellipsometry of a 3000 Å thick $\text{La}_2\text{Zr}_2\text{O}_7$ thin film deposited on YSZ(111) are presented in Fig. 6. The XRD patterns of this film were similar to those presented in Fig. 6(a,b), indicating that the film possesses the defected fluorite structure and the epitaxial strain has been relaxed. In the visible light region ($\sim 1.8 - 3.5$ eV), the index of refraction of $\text{La}_2\text{Zr}_2\text{O}_7$ ranges from 2.09 to 2.20, which matches well with the index of refraction determined by Kinata *et al.* [30] on a bulk sample of polycrystalline pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ in a similar wavelength range. The bandgap values of defected-fluorite $\text{La}_2\text{Zr}_2\text{O}_7$ are determined from the Tauc plots in Fig. 6(b-c). A direct bandgap of 5.60 eV and indirect bandgap of 4.96 eV are determined by extrapolating the linear region of each plot to zero. From this analysis, defected-fluorite $\text{La}_2\text{Zr}_2\text{O}_7$ is found to be an indirect-gap semiconductor. As summarized in Table 1, these bandgap values are considerably larger than those measured experimentally on polycrystalline powder

material with the pyrochlore structure (3.5 – 3.9 eV) [31, 32]. Density functional theory (DFT) calculations which model the pyrochlore structure typically predict bandgap values in the range of 4.0 – 4.2 eV [31, 33, 34], although a recent *ab initio* molecular dynamics calculation predicted a bandgap of 3.33 eV [14]. In most cases, the bandgap prediction was assumed to be an underestimation of the true value, due to the well-known deficiency of both the local density approximation (LDA) and Perdew-Burke- Ernzerhof (PBE) functionals in correctly accounting for electron correlation effects [14, 34]. Interestingly, analysis of the pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ band structure predicted by DFT indicates that the lowest-energy band transition should be direct [31, 33, 34], while the experimental results in Fig. 6 indicate that defect-fluorite $\text{La}_2\text{Zr}_2\text{O}_7$ possesses an indirect bandgap. Analysis of the optical properties of $\text{La}_2\text{Zr}_2\text{O}_7$ at photon energies > 6 eV may provide a more accurate measure of the indirect bandgap value, but are not possible with the current ellipsometry setup.

4.0 Discussion

Several physical models have been proposed for the evolution of amorphization as a function of ion dose [18, 35]. Among these, Gibbons [19] discussed a defect accumulation model (also referred to as a cascade overlap model), which assumes that the defects and disorder created by each irradiation-induced collision cascade accumulate in the sample until the defect concentration exceeds the critical concentration necessary for amorphization; this tends to occur when individual collision cascades overlap. The cascade overlap model predicts a sigmoidal dependence of amorphous fraction on ion dose, as is typically observed for light ion irradiation (i.e., He^+). For example, synthetic coesite (a high pressure polymorph of SiO_2) was found to amorphize through a cascade overlap model when irradiated with 1.5 MeV Kr^+ [36]. As an alternative, Gibbons [19] also proposed a direct amorphization model, which predicts that the highly disordered region generated by each collision cascade is quenched more rapidly than recrystallization can occur. Analogous to the rapid thermal quenching employed to create

glasses, this rapid quenching of the collision cascade results in an amorphous core surrounded by crystalline material. As the ion dose increases, these small amorphous volumes accumulate until the entire material is amorphized. In this model, the amorphous fraction follows an exponential dependence on ion dose, as is observed for heavy ion irradiation. For example, zircon (ZrSiO_4) mineral samples irradiated by naturally-occurring U were found to follow the direct amorphization model [37].

In the cascade overlap model (specifically, the cascade double overlap model [19]), the rate of amorphization as a function of ion dose, D , is given by [37]:

$$f_a = 1 - \left[\left(1 + B_d D + \frac{1}{2} B_d^2 D^2 \right) e^{-B_d D} \right] \quad (1)$$

where f_a is the fraction of amorphous material, B_d is the total area of disordered or damaged material (projected onto the material surface) [19], and the ion dose, D , is given as total ions/cm². In Fig. 3(b), the best fit of the defect accumulation model (Equation (1)) to the experimental amorphization data for $\text{La}_2\text{Zr}_2\text{O}_7$ is plotted. A value of $B_d = 1.73 \times 10^{-14} \text{ cm}^2$ was found to best fit the amorphous fraction calculated from La backscattering data averaged over the entire region. Clearly, the sigmoidal shape of the model curve is not reproduced in the experimental data, and the discrepancy between model and experiment increases at higher ion doses. In contrast, the direct amorphization model fits the data well at ion doses up to 6 dpa. The direct amorphization model is given by [19, 37]:

$$f_a = 1 - e^{-B_a D} \quad (2)$$

where B_a is analogous to B_d in Equation (1) (i.e., the total area of amorphous material, projected onto the film surface). A value of $B_a = 4.54 \times 10^{-15} \text{ cm}^2$ was found to fit the amorphous fraction calculated from the entire La backscattering region satisfactorily for ion doses ≤ 6 dpa. This value of B_a corresponds to a radius of 380 Å for each amorphous cluster generated by an implanted ion, if a cylindrical geometry of the collision cascade is assumed [19].

A disorder accumulation model has also been developed [20, 38], in which the amorphous fraction (f_a) is given by a direct impact/defect-stimulated model which includes both direct-impact amorphization and growth of the amorphous region at the crystalline/amorphous interface stimulated by defects, cascades, or implanted ions [39]:

$$f_a = 1 - (\sigma_a + \sigma_s) / \{\sigma_s + \sigma_a \exp[(\sigma_a + \sigma_s)D]\} \quad (3)$$

where σ_a and σ_s are the cross-sections for direct and stimulated amorphization, respectively (σ_a is analogous to B in Eqn. (1) and (2) above). Because ion channeling analysis is sensitive to both amorphization and the presence of interstitials and small interstitial clusters in crystalline regions, the total relative disorder, S , is given by:

$$S = f_a + S_d \quad (4)$$

where S_d is the relative disorder from interstitials in the crystalline regions of the material. The dependence of S_d on ion dose is given by a simple point defect accumulation model, multiplied by the probability, $(1-f_a)$, of a defect being generated in the crystalline region:

$$S_d = S_d^* [1 - \exp(-BD)] (1 - f_a) \quad (5)$$

where S_d^* is the saturation value for the defect-induced disorder observed along a specified ion channeling direction and B is proportional to the effective recombination volume for the interstitial defects giving rise to S_d . The best fit of Eqn. (4) to the amorphization data as a function of dpa is presented in Fig. 3(b), and the fit parameters are given in Table 2. The model is able to fit the data well, including the slight plateau between 1 and 2 dpa. The resulting σ_a and σ_s values from the fit are one to two orders of magnitude smaller than those obtained at 300 K for the Sm sublattice of $\text{Sm}_2\text{Ti}_2\text{O}_7$ ($\sigma_a = 1.0 \text{ dpa}^{-1}$, $\sigma_s = 66 \text{ dpa}^{-1}$) [20]. This is intuitively reasonable, given the ease with which the bulk single crystal of $\text{Sm}_2\text{Ti}_2\text{O}_7$ was amorphized (full amorphization at 0.1 – 0.15 dpa) compared to the $\text{La}_2\text{Zr}_2\text{O}_7$ epitaxial film in Fig. 3(b), which has not reached full amorphization at 10 dpa. However, the mechanism of amorphization appears to be somewhat similar for both materials: in both cases, σ_s is significantly

larger than σ_a . In addition, the value in Table 2 for S_d^* is quite similar to that obtained for $\text{Sm}_2\text{Ti}_2\text{O}_7$ ($S_d^* = 0.28$), although the value of $B = 10 \text{ dpa}^{-1}$ is somewhat larger than that obtained for $\text{La}_2\text{Zr}_2\text{O}_7$.

Previous MD simulations of the ion irradiation properties of pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ by Chartier *et al.* [15, 16] predicted a low yield of cation antisites, interstitials, and vacancies as a result of irradiation. This low yield of defects occurs as $\text{La}_2\text{Zr}_2\text{O}_7$ transitions towards the disordered fluorite state. Ion implantation of a polycrystalline $\text{La}_2\text{Zr}_2\text{O}_7$ sample by 1.5 MeV Xe^+ by Lian *et al.* [1] partially corroborated these results. At low ion doses, $\text{La}_2\text{Zr}_2\text{O}_7$ tended to form a disordered fluorite structure observed by *in situ* TEM, as predicted by the MD simulations, but as the dose increased, the material amorphized; total amorphization (as judged by the loss of diffraction features in selected area electron diffraction patterns) occurred at a dose of 5.5 dpa.

The amorphization data presented in Fig. 3(b) indicates that, at low ion irradiation dose, the defected-fluorite $\text{La}_2\text{Zr}_2\text{O}_7$ film amorphizes more readily than either the direct amorphization or cascade overlap models would predict. Inclusion of stimulated amorphization (σ_s) in the disorder accumulation model (Eqn. (3)) is required to adequately fit the data in the low-dose regime. The best-fit parameters shown in Table 2 indicate that stimulated amorphization is more influential than direct amorphization (σ_a). The STEM image presented in Fig. 5(b) clearly shows an amorphous layer which has formed in the surface region of the film; in this region, we can conclude that growth of the amorphous region at the crystalline/amorphous interface after the radiation damage has occurred, stimulated by defects, cascades, or implanted ions, is a primary amorphization mechanism in $\text{La}_2\text{Zr}_2\text{O}_7$. As the irradiated dose increases, similar amorphization appears at the $\text{La}_2\text{Zr}_2\text{O}_7/\text{YSZ}(111)$ interface. Interestingly, though, the amorphous regions do not easily encroach on the center portion of the $\text{La}_2\text{Zr}_2\text{O}_7$ film, which remains crystalline with the defected fluorite structure in the STEM image in Fig. 5(d). As the damage level increases, the film becomes more resistant to amorphization, in agreement with the previous MD simulations [[15, 16]. Surprisingly, though, while Lian *et al.* [1] observed full amorphization of

pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ at a dose of 5.5 dpa, in this work the epitaxial film of defected fluorite $\text{La}_2\text{Zr}_2\text{O}_7$ exhibited an amorphous fraction of only 78% at a dose of 6 dpa; this damage level did not increase as the dose was increased to 10 dpa. Clearly, the surface and interface of the epitaxial thin film play a large role in the amorphization mechanism at lower doses, in contrast to the spatially uniform amorphization observed in large-grained polycrystalline pyrochlore-structure $\text{La}_2\text{Zr}_2\text{O}_7$ [1]. The resistance of thin film $\text{La}_2\text{Zr}_2\text{O}_7$ to amorphization at higher doses, however, may be related to the difference in structure between $\text{La}_2\text{Zr}_2\text{O}_7$ which originally possessed the pyrochlore structure but has disordered into a defected fluorite-type structure as a result of irradiation, and $\text{La}_2\text{Zr}_2\text{O}_7$ which is fully disordered as-synthesized.

Two plateaus in the damage accumulation data presented in Fig. 3(b) are evident: a weak plateau in the range of 1 – 2 dpa, and a clear plateau between 6 and 10 dpa. These plateaus cannot be explained by the presence of recombination centers. Instead, they typically correspond to the formation of extended planar defects such as stacking faults and dislocation loops, facilitated by the high mobility of interstitials during irradiation near the critical amorphization temperature [38]. Lian *et al.* [1] predicted that the critical amorphization temperature for $\text{La}_2\text{Zr}_2\text{O}_7$, above which amorphization does not occur, is ~ 310 K. Thus, the room temperature irradiation in the current study is close to the critical temperature, and the formation of planar defects is a possible source of the observed damage plateaus. These planar defects may play a role in the observed change in amorphization behavior observed by STEM: at doses up to 2 dpa, most of the amorphization occurs in the top half of the film, but at higher doses, this surface amorphous region remains relatively static, and further amorphization is observed at the film/substrate interface.

5.0 Conclusions

The structural and optoelectronic properties of epitaxial, pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ thin films were explored. Epitaxy was realized on YSZ(111) and LAO(001) substrates, but not on STO(001). The bandgap

of a thick $\text{La}_2\text{Zr}_2\text{O}_7$ film was measured to be indirect at 4.96 eV, in contrast to the lower values obtained by previous experimental reports, which is likely due to the lack of grain boundaries and defects in the epitaxial film. Irradiation of $\text{La}_2\text{Zr}_2\text{O}_7$ / YSZ(111) with 1 MeV Zr^+ ions resulted in an exponential increase in amorphization, as measured by RBS backscattering of the La peak in channeling geometry. At lower doses, the amorphization fraction as a function of ion dose fit well to a stimulated amorphization model. Full amorphization was not observed even at a dose of 10 dpa, although the stimulated desorption model predicted amorphization at a dose of approximately 8 dpa. A dose of 10 dpa is also considerably higher than the critical amorphization dose observed by Lian *et al.* [1] for polycrystalline $\text{La}_2\text{Zr}_2\text{O}_7$. A plateau in the amorphization data at high ion flux might be attributed to the formation of planar defects. The results presented here can be used to refine the models developed to predict the radiation response of pyrochlore oxides, and provide insight into the underlying physical mechanisms of radiation-induced defect formation.

6.0 Acknowledgments

The authors are grateful to Dr. Weilin Jiang (PNNL) for technical suggestions and discussions. The research described in this paper was conducted under the Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. A portion of the research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. Ion irradiations and RBS characterization were carried out at the Texas A&M University Ion Beam Lab.

- [1] J. Lian, X.T. Zu, K.V.G. Kutty, J. Chen, L.M. Wang, R.C. Ewing, Ion-Irradiation-Induced Amorphization Of $\text{La}_2\text{Zr}_2\text{O}_7$ Pyrochlore, *Phys. Rev. B* 66(5) (2002) 054108.
- [2] S.X. Wang, B.D. Begg, L.M. Wang, R.C. Ewing, W.J. Weber, K.V.G. Kutty, Radiation Stability Of Gadolinium Zirconate: A Waste Form For Plutonium Disposition, *J. Mater. Res.* 14(12) (1999) 4470-4473.
- [3] K.E. Sickafus, L. Minervini, R.W. Grimes, J.A. Valdez, M. Ishimaru, F. Li, K.J. McClellan, T. Hartmann, Radiation Tolerance Of Complex Oxides, *Science* 289(5480) (2000) 748-751.
- [4] R.C. Ewing, W.J. Weber, J. Lian, Nuclear Waste Disposal-Pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$): Nuclear Waste Form For The Immobilization Of Plutonium And "Minor" Actinides, *J. Appl. Phys.* 95(11) (2004) 5949-5971.
- [5] M.A. Subramanian, G. Aravamudan, G.V.S. Rao, Oxide Pyrochlores - A Review, *Prog. Solid State Chem.* 15(2) (1983) 55-143.
- [6] Y. Li, P.M. Kowalski, G. Beridze, A.R. Birnie, S. Finkeldei, D. Bosbach, Defect Formation Energies In $\text{A}_2\text{B}_2\text{O}_7$ Pyrochlores, *Scripta Mater.* 107 (2015) 18-21.
- [7] X.J. Wang, H.Y. Xiao, X.T. Zu, Y. Zhang, W.J. Weber, Ab Initio Molecular Dynamics Simulations Of Ion-Solid Interactions In $\text{Gd}_2\text{Zr}_2\text{O}_7$ And $\text{Gd}_2\text{Ti}_2\text{O}_7$, *J. Mater. Chem. C* 1(8) (2013) 1665-1673.
- [8] S. Park, M. Lang, C.L. Tracy, J.M. Zhang, F.X. Zhang, C. Trautmann, M.D. Rodriguez, P. Kluth, R.C. Ewing, Response Of $\text{Gd}_2\text{Ti}_2\text{O}_7$ And $\text{La}_2\text{Ti}_2\text{O}_7$ To Swift-Heavy Ion Irradiation And Annealing, *Acta Mater.* 93 (2015) 1-11.
- [9] M. Gasperin, Lanthanum Dtitanate, *Acta Crystallogr. Sect. B-Struct. Commun.* 31(AUG15) (1975) 2129-2130.
- [10] S. Nanamatsu, M. Kimura, K. Doi, S. Matsushita, N. Yamada, New Ferroelectric - $\text{La}_2\text{Ti}_2\text{O}_7$, *Ferroelectrics* 8(1-2) (1974) 511-513.
- [11] G.J. Redhammer, G. Roth, G. Amthauer, Yttrium pyrogermanate, $\text{Y}_2\text{Ge}_2\text{O}_7$, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* 63 (2007) I93-I95.
- [12] J. Lian, K.B. Helean, B.J. Kennedy, L.M. Wang, A. Navrotsky, R.C. Ewing, Effect Of Structure And Thermodynamic Stability On The Response Of Lanthanide Stannate-Pyrochlores To Ion Beam Irradiation, *J. Phys. Chem. B* 110(5) (2006) 2343-2350.
- [13] C.L. Tracy, J. Shamblin, S. Park, F.X. Zhang, C. Trautmann, M. Lang, R.C. Ewing, Role Of Composition, Bond Covalency, And Short-Range Order In The Disordering Of Stannate Pyrochlores By Swift Heavy Ion Irradiation, *Phys. Rev. B* 94(6) (2016) 064102.
- [14] H.Y. Xiao, W.J. Weber, Y. Zhang, X.T. Zu, Ab Initio Molecular Dynamics Simulations Of Ion-Solid Interactions In Zirconate Pyrochlores, *Acta Mater.* 87 (2015) 273-282.
- [15] A. Chartier, C. Meis, J.P. Crocombette, L.R. Corrales, W.J. Weber, Atomistic Modeling Of Displacement Cascades In $\text{La}_2\text{Zr}_2\text{O}_7$ Pyrochlore, *Phys. Rev. B* 67(17) (2003) 174102.
- [16] A. Chartier, C. Meis, J.P. Crocombette, W.J. Weber, L.R. Corrales, Molecular Dynamic Simulation Of Disorder Induced Amorphization In Pyrochlore, *Phys. Rev. Lett.* 94(2) (2005) 025505.
- [17] A. Chartier, C. Meis, W.J. Weber, L.R. Corrales, Theoretical Study Of Disorder In Ti-Substituted $\text{La}_2\text{Zr}_2\text{O}_7$, *Phys. Rev. B* 65(13) (2002) 134116.
- [18] J. Lian, L. Wang, J. Chen, K. Sun, R.C. Ewing, J.M. Farmer, L.A. Boatner, The Order-Disorder Transition In Ion-Irradiated Pyrochlore, *Acta Mater.* 51(5) (2003) 1493-1502.
- [19] J.F. Gibbons, Ion Implantation In Semiconductors. 2. Damage Production And Annealing, *Pr. Inst. Electr. Elect.* 60(9) (1972) 1062-1096.
- [20] Y. Zhang, W.J. Weber, V. Shutthanandan, R. Devanathan, S. Thevuthasan, G. Balakrishnan, D.M. Paul, Damage Evolution On Sm And O Sublattices In Au-Implanted Samarium Titanate Pyrochlore, *J. Appl. Phys.* 95(5) (2004) 2866-2872.
- [21] C.M. Wang, T.C. Kaspar, V. Shutthanandan, A.G. Joly, L. Kovarik, B.W. Arey, M. Gu, A. Devaraj, B.D. Wirth, R.J. Kurtz, Structure And Radiation Damage Behavior Of Epitaxial $\text{Cr}_x\text{Mo}_{1-x}$ Alloy Thin Films On Mgo, *J. Nucl. Mater.* 437(1-3) (2013) 55-61.

- [22] X. Obradors, T. Puig, A. Pomar, F. Sandiumenge, N. Mestres, M. Coll, A. Cavallaro, N. Roma, J. Gazquez, J.C. Gonzalez, O. Castano, J. Gutierrez, A. Palau, K. Zalamova, S. Morlens, A. Hassini, M. Gibert, S. Ricart, J.M. Moreto, S. Pinol, D. Isfort, J. Bock, Progress Towards All-Chemical Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ -Coated Conductors, *Supercond. Sci. Technol.* 19(3) (2006) S13-S26.
- [23] Y. Wang, Y.F. Lu, L. Zhou, C.S. Li, Z.M. Yu, J.Q. Feng, L.H. Jin, P.F. Wang, H. Wang, Effect Of Annealing Atmosphere On The Epitaxial Growth Process Of $\text{La}_2\text{Zr}_2\text{O}_7$ Films On Different Substrates, *Ceram. Int.* 39(1) (2013) 829-833.
- [24] J.W. Seo, J. Fompeyrine, A. Guiller, G. Norga, C. Marchiori, H. Siegwart, J.P. Locquet, Interface Formation And Defect Structures In Epitaxial $\text{La}_2\text{Zr}_2\text{O}_7$ Thin Films On (111)Si, *Appl. Phys. Lett.* 83(25) (2003) 5211-5213.
- [25] L.L. Ying, Y.M. Lu, Z.Y. Liu, F. Fan, B. Gao, C.B. Cai, T. Thersleff, E. Reich, R. Huhne, B. Holzapfel, Thickness Effect Of $\text{La}_2\text{Zr}_2\text{O}_7$ Single Buffers On Metallic Substrates Using Pulsed Laser Deposition For $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ -Coated Conductors, *Supercond. Sci. Technol.* 22(9) (2009) 095005.
- [26] C.T. Koch, Determination Of Core Structure Periodicity And Point Defect Density Along Dislocations, Ph.D. Thesis, Arizona State University, Tempe, Arizona, 2002.
- [27] M. Bolech, E.H.P. Cordfunke, F. Janssen, A. Navrotsky, Standard Enthalpy Of Formation Of Lanthanum Zirconate, *J. Am. Ceram. Soc.* 78(8) (1995) 2257-2258.
- [28] P.P. Dholabhai, R. Perriot, B.P. Uberuaga, Atomic-Scale Structure and Stability of the Low-Index Surfaces of Pyrochlore Oxides, *J. Phys. Chem. C* 120(19) (2016) 10485-10499.
- [29] G. Xu, W.B. He, Y.G. Zhao, Y. Liu, Z.H. Ren, G. Shen, G.R. Han, Hydrothermal Synthesis, Characterization And Growth Mechanism Of Single Crystal Lead Titanate Pyrochlore Dendrites, *Crystengcomm* 13(5) (2011) 1498-1503.
- [30] Y. Kintaka, T. Hayashi, A. Honda, M. Yoshimura, S. Kuretake, N. Tanaka, A. Ando, H. Takagi, Abnormal Partial Dispersion in Pyrochlore Lanthanum Zirconate Transparent Ceramics, *J. Am. Ceram. Soc.* 95(9) (2012) 2899-2905.
- [31] M. Uno, A. Kosuga, M. Okui, K. Horisaka, H. Muta, K. Kurosaki, S. Yamanaka, Photoelectrochemical Study Of Lanthanide Zirconium Oxides, $\text{Ln}_2\text{Zr}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$ and Sm), *J. Alloy. Compd.* 420(1-2) (2006) 291-297.
- [32] Q. Wang, T. Hisatomi, Y. Moriya, K. Maeda, K. Domen, Physicochemical Properties And Photocatalytic H_2 Evolution Activity Of Rh-Doped $\text{La}_2\text{Ti}_2\text{O}_7$ Prepared By Molten Salt Synthesis, *Catal. Sci. Technol.* 3(8) (2013) 2098-2103.
- [33] J. Feng, B. Xiao, C.L. Wan, Z.X. Qu, Z.C. Huang, J.C. Chen, R. Zhou, W. Pan, Electronic Structure, Mechanical Properties And Thermal Conductivity Of $\text{Ln}_2\text{Zr}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ and Gd) Pyrochlore, *Acta Mater.* 59(4) (2011) 1742-1760.
- [34] J. Yang, M. Shahid, M. Zhao, J. Feng, C.L. Wan, W. Pan, Physical Properties Of $\text{La}_2\text{B}_2\text{O}_7$ ($\text{B} = \text{Zr}, \text{Sn}, \text{Hf}$ and Ge) Pyrochlore: First-Principles Calculations, *J. Alloy. Compd.* 663 (2016) 834-841.
- [35] S.X. Wang, L.M. Wang, R.C. Ewing, Irradiation-Induced Amorphization: Effects Of Temperature, Ion Mass, Cascade Size, And Dose Rate, *Phys. Rev. B* 63(2) (2001) 024105.
- [36] W.L. Gong, L.M. Wang, R.C. Ewing, J. Zhang, Electron-Irradiation- And Ion-Beam-Induced Amorphization Of Coesite, *Phys. Rev. B* 54(6) (1996) 3800-3808.
- [37] S. Rios, E.K.H. Salje, M. Zhang, R.C. Ewing, Amorphization In Zircon: Evidence For Direct Impact Damage, *J. Phys.-Condes. Matter* 12(11) (2000) 2401-2412.
- [38] Y. Zhang, W.J. Weber, W. Jiang, C.M. Wang, V. Shutthanandan, A. Hallen, Effects Of Implantation Temperature On Damage Accumulation In Al-Implanted 4H-SiC, *J. Appl. Phys.* 95(8) (2004) 4012-4018.
- [39] W.J. Weber, Models And Mechanisms Of Irradiation-Induced Amorphization In Ceramics, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms* 166 (2000) 98-106.

Fig. 1. Optical coefficients extracted from fits to spectroscopic ellipsometry data collected on 3000 Å $\text{La}_2\text{Zr}_2\text{O}_7 / \text{YSZ}(111)$. Insets: Tauc plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs. photon energy and linear extrapolations to determine the direct and indirect bandgap values, respectively.

Fig. 2. Out-of-plane XRD pattern (a) and reciprocal space map (b) of $\text{La}_2\text{Zr}_2\text{O}_7$ / YSZ(111). (c) Out-of-plane XRD pattern of $\text{La}_2\text{Zr}_2\text{O}_7$ / LAO(001). Unidentified peak is marked with an asterisk. (d) Phi scan of $\text{La}_2\text{Zr}_2\text{O}_7$ (440) and LAO(110) peaks from sample in (c). (e) Out-of-plane XRD pattern of $\text{La}_2\text{Zr}_2\text{O}_7$ / STO(001). (f) Phi scan of $\text{La}_2\text{Zr}_2\text{O}_7$ (440) peak from sample in (e).

Fig. 3. (a) RBS spectra collected with 2 MeV He^+ ions. Spectra were collected in both the random geometry (7° off normal, black lines) and the normal-incidence channeling geometry (colored lines), as judged by the minimum in the backscattering yield of the substrate. $\chi_{\min}$ values are given, as described in the text. (b) Angular scans of the La backscattering yield for $\text{La}_2\text{Zr}_2\text{O}_7$ on each substrate. Curves were shifted to align the peak minimum with 0° (surface normal).

Fig. 4. (a) RBS spectra of $\text{La}_2\text{Zr}_2\text{O}_7 / \text{YSZ}(111)$ as a function of increasing 1 MeV Zr⁺ dose. Interface (I), bulk (B), and surface (S) regions of the film are indicated as shaded areas. Inset: SRIM calculation results for 1 MeV Zr⁺ implantation. Dashed line indicates $\text{La}_2\text{Zr}_2\text{O}_7 / \text{YSZ}(111)$ interface. (b) Amorphous fraction of $\text{La}_2\text{Zr}_2\text{O}_7$, calculated from the La backscattering peak, as a function of ion dose. Dash-dot, dash, and wide dash lines represent the best fits of the direct amorphization, cascade overlap, and disorder accumulation models, respectively, to the experimental data.

Fig. 5. Representative STEM-HAADF images and GPA analysis of the unirradiated $\text{La}_2\text{Zr}_2\text{O}_7$ / YSZ(111). (a) Nominally pristine region, inset with a fast Fourier transform (FFT) taken from the outlined region of $\text{La}_2\text{Zr}_2\text{O}_7$ film. The SEM image at bottom shows ion tracks on the film surface in this region. (b) Detail of the $\text{La}_2\text{Zr}_2\text{O}_7$ / YSZ(111) interface region. (c) Corresponding map of in-plane strain component (ϵ_{xx}) relative to the substrate calculated using GPA. Arrows in (b) and (c) indicate the presence of dislocations at the interface.

Fig. 6. (a-b) Representative STEM-HAADF images of $\text{La}_2\text{Zr}_2\text{O}_7$ / YSZ(111) irradiated with 1 MeV Zr^+ to a dose of 2 dpa. The approximate thickness of amorphous regions is indicated by the dashed lines. The FFT shown in the inset was taken from the outlined region of the $\text{La}_2\text{Zr}_2\text{O}_7$ film in (b). (c-d) Images of the sample irradiated to a dose of 10 dpa. The approximate thickness of the amorphous regions is given by the dashed lines. The arrows indicate the presence of pits at the YSZ interface in (d).

Table 1

Summary of measured (film, powder) or calculated (DFT) bandgap of $\text{La}_2\text{Zr}_2\text{O}_7$.

Method	Bandgap (eV)	Reference
Ellipsometry of epitaxial film	4.96 eV (indirect)	This work
	5.60 eV (direct)	
Diffuse reflectance of powder	3.9 eV	[22]
Photocurrent of powder	3.52 eV	[21]
DFT (PBE-GGA)	3.33 eV	[7]
DFT (LSDA)	4.1 eV (direct)	[23]
DFT (CASTEP with LDA)	4.01 eV (direct)	[24]
DFT (CASTEP with GGA)	~4.2 eV (direct)	[21]

Table 2

Best-fit parameters obtained by fitting the disorder accumulation model (Eqn. 4) to the amorphization data in Fig. 4(b).

Parameter	Value
σ_a	0.08 dpa ⁻¹
σ_s	0.55 dpa ⁻¹
S_d^*	0.33
B	2.64 dpa ⁻¹