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DAMAGE ACCUMULATION IN MgAl₂O₄ AND YTTRIA-STABILIZED ZrO₂ BY Xe-ION IRRADIATION

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ABSTRACT
Magnesium-aluminate spinel (MAS) and yttria-stabilized zirconia (YSZ) are being considered for use as ceramic matrices in proliferation resistant fuels and radioactive storage systems, and may be used either as individual entities or as constituents in multicomponent ceramic systems. It is worthwhile, therefore, to compare radiation damage in these two potentially important materials when subjected to similar irradiation conditions, e.g., ion beam irradiation. To compare radiation damage properties of these two materials, single crystals of spinel and zirconia were irradiated with 340 keV Xe⁺ ions at 120 K, and subsequently investigated by Rutherford backscattering and ion channeling (RBS/C), and optical absorption spectroscopy. Results indicate that damage accumulation in both spinel and zirconia follow a three stage process: 1) very slow damage accumulation over a wide range of dose; 2) rapid changes in damage over a range of doses from about 0.25 to 25 displacements per atom (dpa); 3) slower damage accumulation at very high doses and possibly saturation. Optical absorption results indicate that F-centers form in Xe ion-irradiated spinel and that the concentration of these centers saturates at high dose. Absorption bands are also formed in both spinel and zirconia that are due to point defect complexes formed upon irradiation. These bands increase in intensity with increasing Xe dose, and, in the case of zirconia, without saturation. Finally the rate of change in intensity of these bands with increasing Xe dose, mimic the changes in damage observed by RBS/C with increasing dose.

INTRODUCTION
Fully stabilized zirconia (FSZ) and magnesium-aluminate spinel (MgAl₂O₄) have been proposed for use in non-uranium-bearing, proliferation resistant fuels (PRFs) that incorporate plutonium and burnable poisons in neutronically inert and chemically durable matrices. PRFs, if properly engineered, may improve environmental characteristics regarding waste fuel stability. In the effort to achieve a closed nuclear cycle and develop proliferation resistant nuclear reactors, PRFs will play important role.

The choice of FSZ for PRF was made on the basis of the following facts:
1) Actinides are readily incorporated into the FSZ structure. Cubic zirconia is isostructural with PuO₂ and UO₂.
2) Chemical durability of FSZ is very high.
3) FSZ possesses excellent radiation stability characteristics.

These facts make FSZ a very good candidate for PRF design. However, FSZ exhibits poor thermal conductivity compared to UO₂ (the oxide in conventional nuclear fuel). Consequently, there is interest in identifying material with higher thermal conductivity than FSZ, for use as a PRF ceramic matrix. Researchers have proposed several designs to improve thermal conductivity. One way is to use magnesium-aluminate spinel as a matrix phase and FSZ as an actinide-host
second phase*. MgAl$_2$O$_4$ shows exceptional radiation tolerance[1], which is in part due to the relative ease with which the Mg$^{2+}$ and Al$^{3+}$ cations exchange positions on the tetrahedral and octahedral lattice sites.

Recent studies of radiation damage in zirconia and spinel have emphasized ion irradiation. It was found that spinel implanted at elevated temperature (670 K) with 370-400 keV Xe ions resists amorphization to a peak damage level of 50 displacements per atom (dpa) [2]. At cryogenic temperature (100 K), an amorphous layer is formed at the sample surface at a peak damage level of 25 dpa [3].

Most of the recent experiments with zirconia have attempted to demonstrate amorphization of this material. However, xenon ion irradiation of yttria-stabilized zirconia indicates no susceptibility to either amorphization or phase transformation [4, 240 keV Xe$^+$; 5, 400 keV Xe$^{++}$; 6, 1.5 MeV Xe$^+$ and 60 keV Xe$^{++}$; 7, 400 keV Xe$^{++}$; 8, 60 keV Xe$^{++}$; 9, 370 keV Xe$^{++}$]. Also, at cryogenic and room temperatures, no amorphization was observed in zirconia to peak atomic displacement damages of at least 100 dpa [4, 5, 7]; this peak dose exceeds the dose required for amorphization of spinel [3].

Because FSZ and spinel will be subjected to the same radiation conditions in PRFs, it is important to compare their radiation tolerance properties. It is known that formation of extended defects, such as dislocation loops and voids, originate from the condensation of point defects, namely vacancies and interstitials. Electron microscopy is usually not sufficiently sensitive to detect the production of point defects in solids. However, the technique of optical absorption spectroscopy is quite amenable to this task. Accordingly, we have employed optical absorption spectroscopy, in conjunction with Rutherford Backscattering Spectroscopy and ion-channeling (RBS/C), to investigate defect production by ion irradiation in MAS and YSZ.

**EXPERIMENTAL DETAILS**

The (100) oriented cubic-stabilized zirconia (9.5 mole % Y$_2$O) single crystals used in this study were obtained from Zirmat Corp. FSZ crystals contained Y$_2$O to stabilize the cubic structure. The crystals were 0.5 mm thick and polished on both sides. Single crystals of (111)-oriented MgAl$_2$O$_4$ spinel (0.5 mm thick) polished on both sides were obtained from Linde Division, Union Carbide Corp.

Samples were irradiated with 340 keV Xe$^{++}$ ions using a 200 kV ion implanter in the Ion-Beam Materials Laboratory (IBML) at Los Alamos National Laboratory. Ion fluences ranged from $1-10^{15}$ to $1-10^{21}$ ions/m$^2$. The ion flux was $5-10^{14}$ ions/m$^2$-sec for fluence $1-10^{15}$ ions/m$^2$, $5-9-10^{15}$ ions/m$^2$-sec for fluences $1-10^{16}–1-10^{17}$ ions/m$^2$, and $1-10^{17}$ ions/m$^2$-sec for fluences $1-10^{18}–1-10^{19}$ ions/m$^2$. Samples were tilted about 6° for implantation to minimize ion-channeling effects during the irradiation. The sample stage was cooled to 120 K by liquid nitrogen conduction cooling. After implantation samples were warmed to room temperature for measurement.

Optical absorption measurements on the irradiated spinel crystals were performed at room temperature using a Cary 5E spectrophotometer. For all the samples, optical absorption was measured prior to and after implantation. The measured wavelength range was 190-3000 nm (6.53-0.41 eV).

Rutherford Backscattering Spectroscopy and ion-channeling (RBS/C) were used to analyze the radiation-induced damage accumulation following ion irradiation. For RBS/C, we used an analyzing beam of 2.0 MeV helium normal to the sample, with the detector located 13 degrees from the normal. The measurements were done ex-situ at room temperature.

Calculations of ion range and energy deposition were made using the Monte Carlo code SRIM-2000 (version 2000-10) by J.F.Ziegler et al [10]. For the calculations we used a density of

* Because of a nearly cubic-close-packed spatial arrangement of oxygen anions, large cations such as actinide species cannot be incorporated into the spinel structure.
3.58 g·cm⁻³ for stoichiometric spinel (JCPDS file 21-1152 [11]) and 5.96 g·cm⁻³ for yttria-cubic-stabilized zirconia (from JCPDS file 30-1468 [11], for composition Zr₀.₈₅Y₀.₁₅O₁₉₃, close to the composition of our samples). A threshold displacement energy of 40 eV was used for all target elements. The results of SRIM simulations are presented in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Average range</th>
<th>Straggling</th>
<th>Position of peak in damage</th>
<th>Peak displacement damage in displacements per atom (dpa) per 1·10²¹ ions/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>88 nm</td>
<td>21 nm</td>
<td>63 nm</td>
<td>265</td>
</tr>
<tr>
<td>Zirconia</td>
<td>71 nm</td>
<td>26 nm</td>
<td>45 nm</td>
<td>328</td>
</tr>
</tbody>
</table>

During Xe implantation microstructural changes are introduced within a very narrow layer of material at the surface. According to SRIM, the projected range of 340 keV Xe ions is ~90 nm in spinel and ~80 nm in yttrium stabilized zirconia (Table 1). During optical absorption measurements light passes through both implanted and unimplanted layers. To segregate effects produced by ion implantation in the material, we subtracted absorbance of the material before any damage had been produced from absorbance after implantation. The difference spectra obtained in this way show features attributable to the defects produced by implantation with Xe ions.

RESULTS AND DISCUSSION

RBS/C data for spinel irradiated with 340 keV Xe⁺⁺ ions are shown in Fig. 1. The minimum yield (the ratio of the backscattering yield of an aligned spectrum to that of a “random” spectrum at some depth below the surface scattering peak) measured from an unirradiated spinel single crystal is ~6 %. This indicates good crystalline quality of the substrate. Due to accumulation of radiation-induced lattice disorder following Xe irradiation, RBS/C spectra exhibit additional dechanneling yields for Al, Mg, and O below the surface. Damage accumulation increases with

![Figure 1](attachment:image.png)

Figure 1. Ion channeling spectra obtained from spinel (MgAl₂O₄) single-crystals irradiated with 340 keV Xe ions at 120 K to fluences ranging from 1·10¹⁷-1·10²¹ Xe/m².
increasing radiation dose and approaches a fully "random" level at a fluence of $3 \times 10^{19} \text{Xe/m}^2$. This result is consistent with previous experiments, where it was found that spinel transforms to a metastable crystalline phase at around $5 \times 10^{16} \text{ions/m}^2$, and eventually to an amorphous state at $5 \times 10^{19} - 1 \times 10^{20} \text{ions/m}^2$ (400 keV Xe$^{2+}$ implanted at 100 K) [12].

Optical absorption of spinel after implantation is shown in Fig. 2. Before irradiation, the absorption spectrum is dominated by two bands with maxima at 4.75 and 6.4 eV (Inset of Fig 2, curve a). These bands are traditionally assigned to Fe$^{3+}$ impurities [13]. In the implanted samples, a new band develops at 5.3 eV (Inset of Fig 2, curve b), which is attributed to F-centers (two electrons trapped at an oxygen vacancy) [14, 15]. Another feature of the absorption spectra of implanted spinel is growth of absorption above 6 eV. The highest recordable photon energy for our spectrometer is 6.5 eV, so a Gaussian fit was used to estimate the spectral position of this band. The spectra could be fit satisfactorily with three absorption bands at 5.3, 6.2 and 6.9 eV. The 6.2 eV band is very weak and will not be considered further in this work. The origin of 6.9-eV band is unknown, but it is probably associated with point defect complexes. This band begins to grow rapidly at the same dose in which the F-center band (5.3 eV) reaches saturation. The band at 6.9 eV (the magnitude of absorbance at 6.5 eV was used) reaches saturation at about the same dose where the formation of amorphous layer is observed. More detailed description of optical absorption results for Xe implanted spinel can be found elsewhere [16].

"The "random" level represents the backscattered He yield from a crystal oriented along a high-index direction, so that the yield is maximized.

Figure 2. Inset: Optical density of spinel (MgAl$_2$O$_4$) single-crystals. Curve a, before irradiation; curve b, after implantation with 340 keV Xe$^{2+}$ ions to a fluence of $3 \times 10^{17}$ ions/m$^2$ at 120K. Main figure: Difference absorption spectra obtained from MgAl$_2$O$_4$ crystals implanted with 340 keV Xe$^{2+}$ ions at 120 K to ion fluences ranging from $1 \times 10^{17} - 1 \times 10^{18}$ Xe/m$^2$. To obtain each difference spectrum, the absorption spectrum from a pristine, unirradiated sample was subtracted from the absorption spectrum obtained from an ion-implanted sample.
There is a large difference in threshold displacement energy between anions (60 eV) and cations (20 eV) in spinel [17]. Considering this fact, N. Yu et al. [18] suggested that the anion sublattice should be more radiation resistant than the two cation sublattices. Taking also into account that Mg$^{2+}$ and Al$^{3+}$ ions can exchange sites rather easily, they proposed a two-stage radiation-damage scenario to describe damage evolution in spinel. First, there occurs a transition to a metastable crystalline phase. This transition was presumed to take place on the cation sublattice, due to a displacement process dominated by cations within a less disturbed anion sublattice. Upon further irradiation, a second transformation occurs in both the anion fcc sublattice and the altered cation sublattice. Additional radiation damage accumulates in the modified structure and results in a final collapse of the fcc structure to produce an amorphous state in spinel. However, from the present optical absorption data we conclude that the anion sublattice is not altered before and during formation of the metastable spinel phase. This sublattice sustains significant damage prior to amorphization. Using Smakula formula [19], we estimate the concentration of saturated F-centers to be $N_{\text{def}} \approx 3 \times 10^{19}$ defects/cm$^3$.

**Figure 3.** Ion channeling spectra obtained from yttria-stabilized zirconia single-crystals irradiated with 340 keV Xe ions at 120 K to fluences ranging from $1 \times 10^{17}$-$1.5 \times 10^{19}$ Xe/m$^2$.

RBS/C spectra in Fig. 3 indicate the progression of damage accumulation in zirconia with increasing Xe dose. The calculated minimum yield, $Y_{\text{min}}$, based on the Zr peak, for an unimplanted zirconia crystal is 8%, indicating good crystallinity of these samples. A subsurface damage peak is apparent at low doses (for example, at an ion fluence of $1 \times 10^{19}$ ions/m$^2$), but it broadens with increasing dose until it meets the surface scattering position. The height of the damage peak also rises with increasing dose. However, this increase is partially due to the overlap of the implanted Xe peak and the Zr surface scattering peak. To overcome this interference between the Xe scattering (of He ions) and scattering from the damage layer, we selected a set of channels (600-630) below the Zr surface scattering peak, and estimated damage by integrating the He backscattered yield within this energy window. We define a damage accumulation parameter, $\chi$, as the ratio of this integral with the crystal oriented for channeling, versus the integral when the crystal is "randomly" oriented (same integration window). Using this method we determined that $\chi$ increases with increasing Xe dose, and, at a fluence of $1 \times 10^{21}$ ions/m$^2$, saturates at a value of 1. This may be interpreted as due to the formation of either an amorphous or polycrystalline layer at
the surface of zirconia samples. Fleischner et al. [4] did not observe saturation at \( x=1 \), although they used a large fluence, \( 1 \times 10^{21} \text{ ions/m}^2 \). However, in their case, the energy of Xe ions was lower (240 keV). Other Xe ion irradiation studies used fluences only up to \( 3 \times 10^{19} \text{ ions/m}^2 \). Sickafus et al. [20] performed irradiations of cubic zirconia with 72 MeV \( \Gamma^+ \) ions, and using RBS/C observed radiation induced dechanneling to the "random" level. However, transmission electron microscopy studies of 72 MeV \( \Gamma^+ \)-irradiated zirconia crystals did not reveal any evidence for amorphization of FSZ crystals by ion irradiation [21].

An interesting feature of the RBS spectra of Xe implanted zirconia is the fact that the Xe peak stops growing for fluences exceeding \( 1 \times 10^{21} \text{ ions/m}^2 \). Using RUMP program [22], we analyzed this peak and found that it corresponds to \( 5 \times 10^{20} \text{ Xe/m}^2 \). We suggest that this is the amount of Xe that can be accommodated by zirconia at this ion energy. Similarly, in the experimental results published by Fleischner et al. [4], one observes that the Xe peak has the same area at fluences of \( 3 \times 10^{20} \) and \( 1 \times 10^{21} \text{ ions/m}^2 \). This implies that saturation occurred at a fluence of \( 3 \times 10^{20} \text{ ions/m}^2 \) or lower. Fleischner et al. used lower energy (240 keV) Xe ions than we used in our experiment, so the results are quite consistent.

![Figure 4. Inset: Optical density of yttria-stabilized zirconia single-crystals. Curve a, before irradiation; curve b, after implantation with 340 keV Xe\(^{++}\) ions to a fluence of \( 3 \times 10^{20} \) ions/m\(^2\) at 120K. Main figure: Difference absorption spectra obtained from zirconia crystals implanted with 340 keV Xe\(^{++}\) ions at 120 K to ion fluences ranging from \( 1 \times 10^{17} - 1.5 \times 10^{21} \) Xe/m\(^2\). To obtain each difference spectrum, the absorption spectrum from a pristine, unirradiated sample was subtracted from the absorption spectrum obtained from an ion-implanted sample.](image)

The optical absorption spectra of zirconia after Xe ion irradiation are presented at Fig. 4. Before irradiation, there are no detectable absorption bands in this material (Inset of Fig. 4, curve a); rapid growth of absorption at higher energies is caused by nearness of the zirconia absorption edge. The spectrum after implantation (Inset of Fig. 4, curve b) is dominated by a broad band at 2.3 eV that can be fit with a Gaussian whose full-width at half-maximum is equal to 1.3 eV. No shift of absorption edge was observed in this study, even at the highest ion doses. The origin of this band is not known. The closest known band is the one at 480 nm (2.58 eV) observed in heavily reduced zirconia samples [23] and tentatively assigned to C-defects; C-defects are hepta-coordinated Zr\(^{4+}\) ions. It should be noted that this band did not reach saturation, even at the highest
Xe dose. It is quite possible that the 2.3 eV band has a similar origin with the 6.9 eV band in spinel, namely defect aggregates. The behavior of both absorption bands with increasing ion dose mimic the behavior of the corresponding RBS/C damage accumulation curves (Fig. 5). Studies are in progress to elucidate the origins of these as yet unidentified bands in spinel and zirconia.

CONCLUSIONS
To compare radiation damage properties of magnesium-aluminate spinel and yttria-stabilized zirconia, single crystals of these two materials were irradiated with 340 keV Xe ions at 120 K, and subsequently investigated by Rutherford backscattering and ion channeling (RBS/C), and optical absorption spectroscopy. Results indicate that damage accumulation in both spinel and zirconia follow a three stage process: 1) very slow damage accumulation over a wide range of dose; 2) rapid changes in damage over a range of doses from about 0.25 to 25 displacements per atom (dpa); 3) slower damage accumulation at very high doses and possibly saturation. Optical absorption results indicate that F-centers form in Xe ion-irradiated spinel and that the concentration of these centers saturates at high dose. Absorption bands are also formed in both spinel and zirconia that are due to point defect complexes formed upon irradiation. These bands increase in intensity with increasing Xe dose, and, in the case of zirconia, without saturation. Finally, the rate of change in intensity of these bands with increasing Xe dose, mimic the changes in damage observed by RBS/C with increasing dose.

Figure 5. a) Comparison of the lattice damage accumulation parameter, $\chi$, in spinel (A) and zirconia (D) as a function of Xe ion fluence as measured using RBS/C. Channels 370-410 for spinel and 600-630 for zirconia were used for integration.

b) Comparison of difference absorption bands: 6.9 eV in spinel and 2.3 eV in zirconia.
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