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Letter to the Editors

Amorphization of $MgAl_2O_4$ spinel using 1.5 MeV Xe^+ ions under cryogenic irradiation conditions

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Abstract

Single crystal thin foils of stoichiometric magnesium aluminate spinel ($MgAl_2O_4$) were irradiated with 1.5 MeV Xe^+ ions at 30 K. Structural evolution during irradiation was monitored in situ by transmission electron microscopy and using selected area electron diffraction. A transition to a metastable crystalline phase was observed at an ion dose equivalent to 4 displacements per atom (dpa) at a depth in the thin foil specimen of 50 nm. The spinel was ultimately rendered amorphous at an ion dose equivalent to 35 dpa at 50 nm foil depth. These results are compared to previous observations of amorphization in single crystal spinel by Yu et al. [Philos. Mag. Lett. 70 (1994) 235].

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1. Introduction

Stoichiometric magnesium aluminate spinel ($MgAl_2O_4$) is a candidate insulating oxide for application in neutron radiation environments such as fusion reactors. Interest in spinel arises because deleterious effects associated with high dose exposure to neutrons are minimal in this ceramic [2–5]. Studies of single crystals exposed to high neutron damage levels (up to 250 displacements per atom or dpa) at temperatures between 385 and 750 °C, showed that: (1) spinel crystals remained single crystalline, though irradiation-induced cation sublattice disorder was observed [6]; (2) the crystals exhibited minimal dimensional changes and no alterations in elastic constants [7]; (3) the spinel crystals showed no significant changes in microhardness [8] and (4) the irradiations produced modest accumulations of microstructural damage in the form of interstitial loops, stacking fault networks and small voids [9].

The ultimate radiation resistance of a material is often assessed according to its susceptibility to loss of crystallinity and amorphization. Radiation-induced amorphization is undesirable in materials for engineering applications due to the volume swelling and elastic softening that typically accompany this transformation. In radiation-resistant materials like spinel, very high irradiation doses are required to induce amorphization, unless the material is susceptible to electronic damage mechanisms. It should be noted that spinel has been shown to amorphize under very high electronic stopping conditions (>6 keV/nm), based on irradiation experiments with swift heavy ions [10,11]. But no reports are found in the literature indicating amorphization of spinel by neutron irradiation, where damage is more attributable to ballistic events. However, ion irradiations may be used to accelerate damage rates as compared to neutrons, and several attempts to amorphize spinel using ions are reported in the literature. At elevated temperature, e.g. at 650 °C, no amorphization of spinel has been reported by ion irradiation for peak damage levels up to ~100 dpa [12]. At room temperature, no

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amorphization was reported in ion irradiations to peak damage levels of 50–90 dpa [12–14]. At cryogenic temperatures and in an electron-transparent specimen, no amorphization was observed to a damage level of about 6 dpa, assuming a foil thickness less than 100 nm [15]. On the other hand, in a bulk spinel specimen irradiated at 30 K, amorphization was achieved at a peak damage level of ~25 dpa [1]. However, in this last-mentioned study, the irradiating ion (Xe^{2+}) did not possess sufficient energy to separate the region of peak damage from the implantation region. Consequently, questions concerning a 'chemical effect' due to the implanted ions remain unresolved. Amorphization phenomena in ceramics due to chemical effects associated with implanted ions are well-documented [16]. The purpose of the present study was to irradiate spinel with ions and ion energies that produce peak damage and implantation regions that are spatially well-separated, so that amorphization mechanisms attributable to chemical effects are inconsequential.

2. Experimental procedure

Synthetic single crystals of stoichiometric $MgO \cdot Al_2O_3$ ($MgAl_2O_4$) spinel with (0 1 1) orientations were used for this study. One side of each crystal was polished to a mirror finish. Plan-view transmission electron microscopy (TEM) specimens were prepared as follows: samples were sectioned, mechanically polished to a thickness of about 20 μm, and finally thinned by ion-milling to electron transparency using 6 keV Ar ions at a 12° glancing incidence angle. During ion-milling, the samples were cooled using a standard liquid nitrogen cold-stage. TEM samples were irradiated with 1.5 MeV Xe^+ ions at a dose rate of 4.3×10^{15} Xe $m^{-2}\,s^{-1}$ using the HVEM-Tandem Facility at Argonne National Laboratory [17]. The maximum ion fluence obtained in this experiment was 3.6×10^{20} Xe m^{-2}. Periodically during the irradiation, TEM samples were inspected in situ, using selected-area electron diffraction (SAED), with the HVEM operating at 400 kV. The foil thickness in the sample regions from which SAED information was obtained ranged from ~50 to 100 nm. Temperature was monitored using a thermocouple attached to the sample holder near the sample position. Temperature was maintained at 30 ± 3 K throughout the irradiation.

Computer simulations of ion transport obtained using the Monte Carlo code TRIM-95.xx [18] indicate that the vast majority of the 1.5 MeV Xe^+ ions pass completely through an electron transparent (<100 nm thick) spinel TEM sample. The projected range of 1.5 MeV Xe ions in spinel is about 360 nm, with a longitudinal straggling of about 70 nm (TRIM). TRIM indicates that at foil depths between 50 and 100 nm, the component of damage due to atomic displacements ranges from about 0.95 to 1.1 dpa per 10^{19} Xe^+ ions/m^2, averaged over the sublattices of spinel (assuming a threshold energy for displacement of 40 eV for Mg, Al, and O; this is a reasonable average based on values published in the literature [19,20]). The depths between 50 and 100 nm cover the range of thickness from which diffraction patterns were obtained in this experiment. It should be noted that based on published estimates for the displacement threshold energies for Mg, Al, and O in $MgAl_2O_4$ (see references above), all three constituents are displaced by 400 keV electrons during SAED observations. Based on the estimate that all SAED measurements were completed within some fraction of an hour (accumulated over the time of the entire experiment), we estimate that electron-induced displacements add approximately 1 dpa to the total displacement damage due to the Xe^+ ion irradiation. Though this represents a few percent of the total dose, we do not address this effect any further in our discussion. This is partly because we have shown that electron irradiation also induces recovery of ion damage microstructures in spinel (i.e., electron irradiation works against rather than contributes to the ion damage) [21].

3. Results

Fig. 1 shows SAED patterns from an $MgAl_2O_4$ single crystal prior to ion irradiation (Fig. 1(a)) and following exposure at 30 K to 1.5 MeV Xe^+ ions to fluences of 5.2×10^{18} (Fig. 1(b)), 1.3×10^{19} (Fig. 1(c)), 4.2×10^{19} (Fig. 1(d)), 1.0×10^{20} (Fig. 1(e)) and 3.6×10^{20} (Fig. 1(f)) Xe^+ ions/m^2. Damage levels are indicated in Fig. 1 in dpa; these values correspond to a foil depth of 50 nm and were obtained using the conversion factor 0.95 dpa per 10^{19} Xe^+ ions/m^2 (based on TRIM). The electron beam direction (**B**) in Fig. 1(a) is [0 1 1], while **B** = [1 1 1] in Fig. 1(b)–(d). The thin foil changed orientation dramatically upon exposure to the ion beam, so it was not possible to monitor the [0 1 1] pole throughout the irradiation experiment. Nevertheless, it is apparent in Fig. 1(b)–(d), that the first-order spinel reflections become gradually fainter with increasing dose, until they are almost absent (Fig. 1(d)). The faint, first-order reflections in Fig. 1(c) are ⟨2 2 0⟩-type reflections, while the strong reflections persisting in both Fig. 1(c) and (d) are ⟨4 2 2⟩-type reflections.

This radiation-induced crystal transformation has been observed in spinel before, in both bulk [1,22] and thin film samples [15,23]. The transformation is attributed to a combination of both cation disordering and cation occupation of interstitial sites to produce a 'rock-salt-like' cation arrangement within a pseudo-cubic close-packed anion sublattice [24,25]. The SAED pattern in Fig. 1(d) can still be indexed with a face-centered cubic (fcc) Bravais lattice, but the lattice parameter necessary to index the pattern is 0.404 nm, i.e. half the

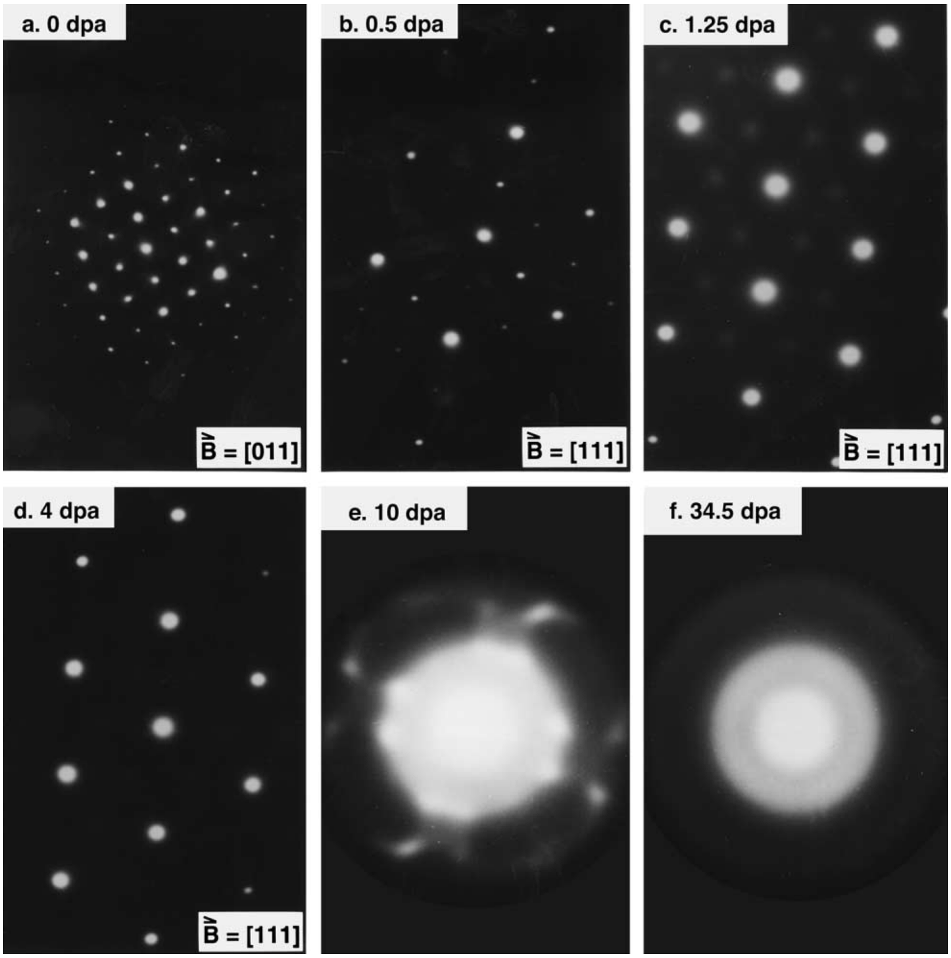

Fig. 1. SAED patterns from an (0 0 1)-oriented $MgAl_2O_4$ thin foil: (a) prior to ion irradiation and (b)–(f) following exposure at 30 K to 1.5 MeV Xe^+ ions to fluences of 5.2×10^{18}, 1.3×10^{19}, 4.2×10^{19}, 1.0×10^{20} and 3.6×10^{20} Xe^+ ions/m^2, respectively.

lattice parameter of ordinary spinel, which is about 0.808 nm.

Following this disordering transformation and with continued ion irradiation, a gradual diminution of the intensity of Bragg reflections is observed, along with increasing levels of diffuse scattering (Fig. 1(e)), and a gradual appearance of diffuse rings of intensity. Finally, as shown in Fig. 1(f), no evidence of crystalline diffraction is visible; only diffuse halos are apparent, which is indicative of the presence of amorphous material. These results indicate that at 30 K, $MgAl_2O_4$ single crystal spinel is amorphized by 1.5 MeV Xe^+ ions at a dose of about 35–40 dpa, for foil thicknesses ranging from 50 to 100 nm.

4. Discussion

The previous observation by Yu et al. [1] of amorphization of bulk spinel using 400 keV Xe^{2+} ions may be attributed to a chemical effect, since the Xe ion range overlapped the region containing the amorphous phase. However, in this experiment, the range of 1.5 MeV Xe^+ ions falls well beyond the foil thickness used to monitor radiation damage accumulation. Fig. 2 shows a comparison of TRIM calculations for target atom displacements (dpa) and Xe ion implanted concentration as a function of depth in $MgAl_2O_4$, for 400 keV and 1.5 MeV Xe. It is apparent that for the ion fluence used by Yu et al., 1×10^{20} ions/m^2 [1], the peak concentration of 1.8 at.% Xe at 100 nm lies within the thickness of the observed amorphous layer (130 nm). But the TRIM results in Fig. 2 for 1.5 MeV Xe ions, indicate that the concentration of implanted Xe ions in samples 100 nm or less in thickness, is less than 5 ppm per 10^{19} Xe ions/m^2. For the maximum fluence used in this experiment, the implanted Xe concentration does not exceed 180 ppm. This suggests that the amorphization of spinel observed in this experiment is due to displacement damage

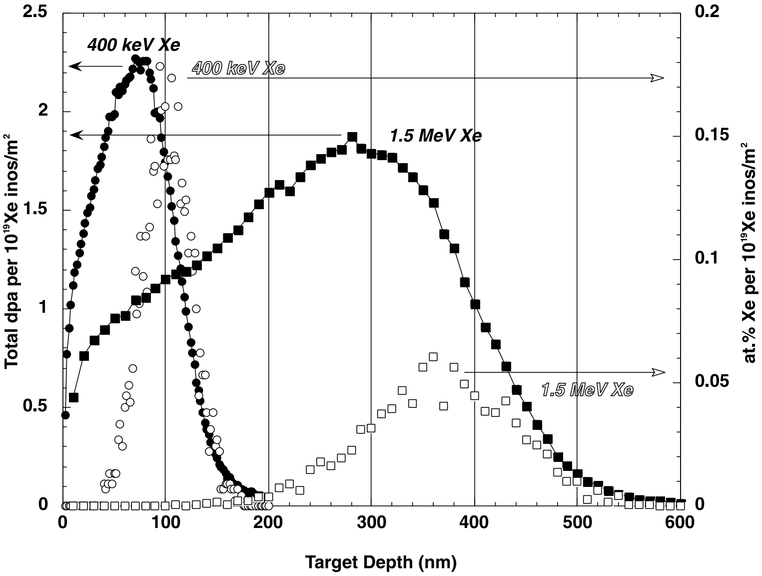

Fig. 2. TRIM simulations of: (1) total target atom displacements (averaged over all sublattices of the material) in dpa, and (2) the concentration of implanted Xe ions, in $MgAl_2O_4$ spinel as a function of target depth, for irradiations using 400 keV and 1.5 MeV Xe ions. Values on the ordinates are normalized to a fluence of 1×10^{19} ions/m^2. TRIM simulations based on 2000 ions. A typical sample thickness for the measurements shown in Fig. 1 lies between 50 and 100 nm along the abscissa.

accumulation, not to a chemical effect associated with the irradiating ion species. Defect annihilation at nearby surfaces in these thin film samples may have delayed the onset of the observed amorphization, but the cryogenic temperature used in this experiment probably minimized this effect.

The results presented here indicate that it is possible to induce an amorphization transformation in spinel by displacement damage-induced defect accumulation. One possible explanation for the observed transformation is that root mean square static and thermal atomic displacements in the crystal ultimately exceed a critical value, in accordance with a generalized form of the Lindemann criterion for melting and amorphization (e.g., see [26]). The observation by Bordes et al. [23] that pre-implanted ions can assist ion-induced amorphization of spinel seems to support this idea, though a chemical effect may also have influenced their observations.

It is noteworthy that a transformation to a metastable crystalline phase is always observed prior to amorphization of spinel. This phase was described earlier as consisting of cations occupying interstitial sites. Interestingly, a recent model due to Granato [27–29] describes amorphous transformations in fcc metals in terms of an accumulation of frozen-in lattice interstitialcies. On the other hand, Granato predicts large elastic softening of the shear modulus for crystals containing interstitialcies. In spinel, point-defect hardening is observed to accompany metastable phase formation, followed by elastic softening upon amorphization [30]. Clearly, the physical basis for amorphization in spinel and related materials is not yet explained satisfactorily.

5. Conclusions

Single crystal thin foils of $MgAl_2O_4$ magnesium aluminate spinel were irradiated with 1.5 MeV Xe^+ ions at 30 K to a maximum fluence of 3.6×10^{20} Xe^+ m^{-2}. Structural evolution was monitored using electron diffraction. A transition to a metastable crystalline phase was observed to be complete by a fluence of 4.2×10^{19} Xe^+ m^{-2}, which at a depth in the foil of 50 nm is equivalent to about 4 dpa. By a fluence of 3.6×10^{20} Xe^+ m^{-2}, no evidence of crystallinity remained in the thin foil specimen. This amorphization dose is equivalent to 35 to 40 dpa, for a foil thickness range of 50–100 nm. The range of 1.5 MeV Xe^+ ions extends beyond the foil thickness used for electron diffraction observations. This suggests that the amorphization phenomenon observed in this study is due to displacement damage accumulation in spinel, not to a chemical effect associated with the irradiating ion species.

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