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Ion irradiation-induced crystal structure changes in inverse spinel $MgIn_2O_4$

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ABSTRACT

400 keV Ne and 200 keV He ion irradiations were performed on fully inverse $MgIn_2O_4$ samples at cryogenic temperature (~77 K), in order to examine the influence of radiation-induced cation disordering on crystal structure. In the case of $MgIn_2O_4$ samples irradiated with Ne ions to a peak displacement damage dose of 4 displacements per atom (dpa), a spinel-to-rocksalt phase transformation was observed. By contrast, for $MgIn_2O_4$ samples irradiated with He ions to a peak displacement damage dose of 5 dpa, the only observed structural effect involved cation rearrangements from an inverse to a "random" spinel structure.

The crystal structure of spinel with the general formula AB_2O_4 was first determined in 1915 by Bragg [1] and Nishikawa [2]. One unit cell, belonging to the $Fd\bar{3}m$ space group, contains eight AB_2O_4 units arranged in a pseudo-cubic close-packed (CCP) anion sublattice that contains tetrahedral and octahedral interstices. In a normal II–III structure, one-eighth of the 64 tetrahedral sites are occupied by A^{2+} cations (Wyckoff equipoint 8*a*) and half of the 32 octahedral interstices are taken up by B^{3+} cations (Wyckoff equipoint 16*d* for Setting 1 of $Fd\bar{3}m$).[1] One fascinating feature of the spinel structure is its ability to accommodate large amounts of cation disorder. This disordering process leads a wide range of cation distributions with the general formula $(A_{1-x}B_x)_{tet}(A_xB_{2-x})_{oct}O_4$ (*tet* and *oct* represent tetrahedral and octahedral cation sites, respectively). Here *x* is the inversion parameter, specifying the fraction of B cations occupying tetrahedral sites, with values ranging between 0 (a so-called *normal* spinel such as $MgAl_2O_4$: $(Mg_1)_{tet}(Al_2)_{oct}O_4$) and 1 (an *inverse* spinel like $MgIn_2O_4$: $(In_1)_{tet}(Mg_1In_1)_{oct}O_4$). Many spinel oxides exhibit remarkable electrical, magnetic, and other physical characteristics [3]. Among them, $MgAl_2O_4$ has been considered for potential application as the non-fertile phase in an inert matrix nuclear fuel due to its high radiation tolerance [4,5].

Irradiation-induced structural evolution in many spinel compounds, especially $MgAl_2O_4$, has been extensively studied under various radiation conditions. Although $MgAl_2O_4$ shows excellent amorphization resistance and low volume swelling under ion irradiation at room and elevated temperature [6–9], this compound can be amorphized when irradiated with 400 keV Xe at cryogenic temperature [10]. Additionally, observation of a cation disordering transition from $x = 0$ to $x \sim 2/3$, (the latter inversion indicating a *random* spinel) was reported following swift ion irradiation [11] and following neutron irradiation [12]. In addition, a phase transformation of $MgAl_2O_4$ from the spinel crystal structure to a disordered *rocksalt* structure (space group $Fm\bar{3}m$) has been observed in studies using both low energy ions [13,14] and swift heavy ions [15]. This phase transformation involves not only a mixing of cations, as in the disorder transition, but the movement of cations from tetrahedral to octahedral sites in the crystal lattice. Some experimental and theoretical studies have shown that cation disorder plays a crucial role in controlling radiation tolerance and defect mobility in spinels [10,16–18]. Therefore, in order to optimize materials for nuclear energy applications, it is important to understand how the presence of cation disorder might affect the formation of metastable phases under radiation environments. However, the irradiation-induced rocksalt transformation in $MgAl_2O_4$ is the subject of some controversy [11,19]. This is partly due to the fact that the X-ray atomic form factors for Mg and Al are too similar, such that X-ray diffraction (XRD) is not conclusive in identifying the spinel-to-rocksalt and order-to-disorder phase transformation.

In this letter, we describe results of ion irradiation damage experiments performed on fully-inverse $MgIn_2O_4$ spinel ($x \sim 1$), experiments designed to examine radiation-induced cation disorder and concomitant structural evolution of a model spinel compound. To our knowledge, few studies of irradiation stability have been performed on compounds possessing the inverse spinel structure [20,21]. We performed 400 keV Ne and 200 keV He ion irradiations on $MgIn_2O_4$ at cryogenic temperature (~77 K). Importantly, in contrast to $MgAl_2O_4$, the X-ray atomic form factor

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[1] Note that the remaining vacant octahedral and tetrahedral interstices in spinel correspond to the 16*c* and 8*b*/48*f* Wyckoff sites, respectively, in Setting 1 of $Fd\bar{3}m$. This becomes important later in interpretations of radiation-induced phase transformations.

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differences between Mg and In allow for more conclusive identification of irradiation-induced phases. Microstructural characterization revealed a phase transformation of $MgIn_2O_4$ from an inverse spinel to a disordered rocksalt structure, following Ne ion irradiation to a peak displacement damage dose of 4 displacements per atom (dpa). At this ballistic damage dose, we also observed evidence of partial amorphization of the $MgIn_2O_4$, based on grazing incidence X-ray diffraction (GIXRD) measurements. On the other hand, in the case of He ion irradiations, our study found no evidence for an amorphization transformation or a spinel-to-rocksalt transformation. However, we did observe a disordering transition of $MgIn_2O_4$ from an inverse ($x \sim 1$) to a random ($x \sim 2/3$) spinel structure, following He ion irradiation to a dose of 5 dpa. These results indicate that several different structural changes are possible in irradiated spinels. Our study provides new insights into the behavior of complex oxides exposed to energetic ion irradiation conditions.

High purity MgO and In_2O_3 powders from Alfa Aesar (99.9% purity) were used to produce sintered polycrystalline $MgIn_2O_4$ pellets. X-ray diffraction (XRD) measurements showed the fabricated pellets to be phase pure and in good agreement with published powder diffraction data for $MgIn_2O_4$ spinel with space group $Fd\bar{3}m$ (PDF# 73-2414 [22]).

Ion irradiations were performed at cryogenic temperature (~77 K) in the Ion Beam Materials Laboratory at Los Alamos National Laboratory, using a Danfysik High Current Research Ion Implanter operating at 200 kV. 400 keV Ne^{++} and 200 keV He^{+} ions were used in this study, in order to assess the effect of different ion species on the radiation damage response of the material.

I$MgIn_2O_4$ samples were examined before and after irradiation using GIXRD with a Bruker AXS D8 Advanced X-ray diffractometer. Ne ion irradiated samples were also prepared in cross-sectional geometries for transmission electron microscopy (TEM) examination using both Philips CM-30 and FEI Tecnai F30 electron microscopes, each operating at 300 kV.

Fig. 1(a) Ishows GIXRD patterns obtained from pristine $MgIn_2O_4$ and $MgIn_2O_4$ irradiated with 200 keV He^{+} ions to fluences of 1×10^{17} and 2×10^{17} He/cm^2, corresponding to peak displacement damage doses of ~2.5 and 5 dpa (as determined by SRIM [23] calculations, using a displacement threshold energy of 40 eV for all atomic constituents). The first observation in Fig. 1(a) is that in pristine $MgIn_2O_4$, the {111} reflection, which is very sensitive to the occupation of the tetrahedral and octahedral sites, is not observed. Structure factor calculations indicate that the extremely weak {111} reflection in $MgIn_2O_4$ is an indication of a highly-inverted spinel, $0.9 < x \leq 1.0$, depending on the oxygen dilation parameter, u. Thus, we can assume that prior to irradiation, our $MgIn_2O_4$ spinel approximates a fully-inverse spinel, i.e., $(In_1)_{tet}(In_1Mg_1)_{oct}O_4$.

The GIXRD patterns in Fig. 1(a) reveal that the {111} reflection appears upon He ion irradiation, and the {111} intensity increases with increasing ion fluence (or dose), while no amorphization is observed. Upon irradiation, atoms are displaced from their initial lattice sites, mixing the cation occupation of the tetrahedral 8*a* and octahedral 16*d* sites in the spinel structure, progressing toward a "random" arrangement of Mg and In cations on 8*a* and 16*d* sites. Specifically, for irradiated $MgIn_2O_4$, the inverse $(In_1)_{tet}(Mg_1In_1)_{oct}O_4$ structure transitions toward a random $(Mg_{1-x}In_x)_{tet}(Mg_xIn_{2-x})_{oct}O_4$ ($x \sim 2/3$) cation arrangement. Supplementary Figs. 1 and 2 show simulated powder XRD patterns for an inverse $MgIn_2O_4$ ($x = 1$, $u = 0.375$) and a *random* $MgIn_2O_4$ spinel ($x = 2/3$, $u = 0.375$), respectively. The oxygen parameter $u = 0.375$ is a hypothetical value for an "ideal" spinel crystal in which all octahedral and tetrahedral lattice interstices are regular. The measured GIXRD patterns from pristine and He irradiated $MgIn_2O_4$ shown in Fig. 1(a) are consistent with the simulated XRD patterns for inverse and random $MgIn_2O_4$ spinel, respectively. These observations indicate that He irradiation in $MgIn_2O_4$ induces a cation disordering transition from an inverse spinel to a random spinel structure.

Fig. 1(b) shows GIXRD patterns obtained from $MgIn_2O_4$ before and after 400 keV Ne ion irradiations with fluences of 1×10^{15} and

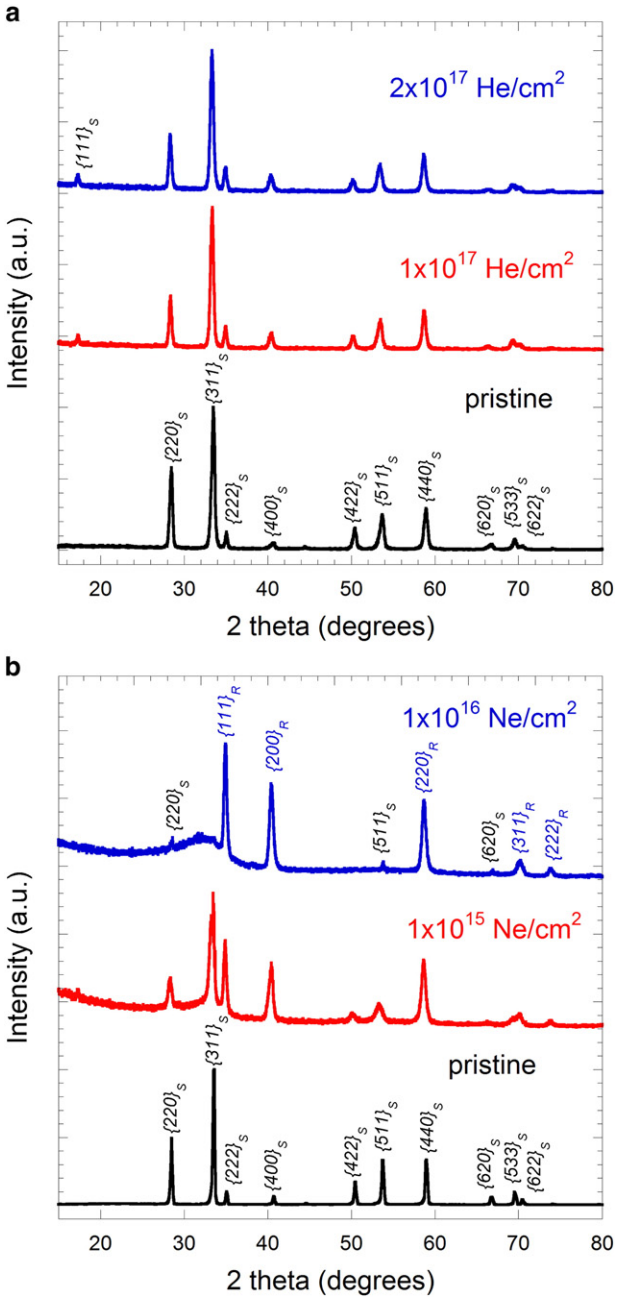

Fig. 1. (a) GIXRD patterns obtained from pristine $MgIn_2O_4$ and $MgIn_2O_4$ irradiated with 200 keV He^{+} ions to fluences of 1×10^{17} and 2×10^{17} He/cm^2, corresponding to peak displacement damage doses of ~2.5 and 5 dpa. {*hkl*} reflection subscript, *S*, represents the spinel phase. (b) GIXRD patterns obtained from pristine $MgIn_2O_4$ and $MgIn_2O_4$ irradiated with 400 keV Ne^{++} ions to fluences of 1×10^{15} and 1×10^{16} Ne/cm^2, corresponding to peak displacement damage doses of ~0.4 and 4 dpa. {*hkl*} reflection subscripts, *S* and *R*, represent the spinel and rocksalt phases, respectively.

1×10^{16} Ne/cm^2, corresponding doses of ~0.4 and 4 dpa, respectively. The most important diffraction effect observed following Ne irradiation is that the intensities of the primary spinel peaks (including (220), (311), (422) and (511)) are greatly diminished, while other initially weak reflections such as (222), (400) and (440) become strong in the irradiated spinel. Based on previous studies (see, e.g., Ref. [16]), these observations suggest that Ne ion irradiation is causing more than simple cation disorder on spinel lattice sites; on the other hand, an entirely new phase is being formed in the irradiated $MgIn_2O_4$. To determine the crystal structure of this altered crystalline phase, simulated powder XRD patterns were calculated for several structures proposed in earlier studies [19,24], including cation disordered rocksalt, sphalerite, and