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FORMATION OF A METASTABLE CRYSTALLINE PHASE DURING ION IRRADIATION OF SPINEL

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ABSTRACT

We have examined the radiation resistance of magnesio-aluminate spinel by irradiating single crystals of MgAl_2O_4 with 400 keV Xe^{++} ions at 100 K. At low irradiation doses, the material transformed into a metastable crystalline phase with half the lattice spacing of the original crystal. Electron diffraction analysis revealed that this structural change can be explained in terms of the redistribution of cations among octahedral, tetrahedral, and three-fold coordinated interstitial sites of the close-packed anion lattice. Corresponding to this transformation, the hardness and elastic modulus increased with dose to values about 10% greater than those of unirradiated spinel. We believe that the formation of this metastable phase plays an important role in determining the radiation resistance of spinel.

INTRODUCTION

Magnesio-aluminate spinel is a radiation-resistant ceramic with potential applications in fusion reactors. Previous studies, performed at or above room temperature, have shown that spinel retains its crystal structure when irradiated with energetic particles. Clinard, Hurley, and Hobbs [1] irradiated MgAl_2O_4 with fast neutrons at 925 and 1100 K and found very little defect aggregation and no swelling. Sickafus *et al.* [2] examined spinel single crystals irradiated with fast neutrons at 658 K to about 250 displacements per atom (dpa). They observed cation disorder, but no amorphization. Zinkle [3] found no loss of crystallinity after irradiation of spinel at about 925 K with various ions with energies of the order of MeV. However, Yu, Sickafus and Nastasi [4] were able to amorphize spinel by irradiating at 100 K with 400 keV Xe^{++} ions. Prior to the amorphous transition, the first-order fundamental reflections became extinct in the electron diffraction pattern. These extinctions were subsequently observed by Sickafus *et al.* [5] in $\text{MgO} \cdot 3\text{Al}_2\text{O}_3$ under the same irradiation conditions and confirmed by Bordes *et al.* [6] following 1.5 MeV Kr^+ irradiation of MgAl_2O_4 at 20 K. It is evident from the change in the diffraction pattern that low-temperature ion-irradiated spinel undergoes a phase transformation to a metastable crystalline state before becoming amorphous. We have performed an electron diffraction analysis of several model crystals to determine the structure of this metastable phase. In this report, we discuss the nature and significance of this transformation.

CALCULATION

MgAl_2O_4 spinel belongs to the cubic $\text{Fd}3\text{m}$ space group and has a lattice parameter of 0.808 nm. In the 'normal' ordered state, each oxygen anion is bonded to a tetrahedral Mg cation and three octahedral Al cations as shown in figure 1. The anions form a close-packed lattice with a repeat distance of 0.404 nm. This arrangement leaves seven-eighths of the tetrahedral and one-half of the octahedral sites unoccupied and creates conditions favorable for cation site exchange known as inversion. The inversion parameter i is the fraction of Mg cations that reside in octahedral sites, and varies from 0 in 'normal' spinel to 1 in 'inverse' spinel. By varying this inversion parameter from 0 to 1, we calculated electron diffraction patterns from the spinel lattice for various levels of cation disorder. In addition, we studied several model crystals based on changes in the arrangement of the cation and anion sublattices in spinel. For each model crystal, the structure factors for various reflections were calculated based on the analytical expressions of Doyle and Turner [7] for scattering factors. These calculated reciprocal space intensity distributions were compared to the experimentally obtained diffraction pattern to determine the structure of the metastable phase.

Figure 1. The arrangement of cations in the close-packed anion lattice of spinel.

RESULTS AND DISCUSSION

The experimental electron diffraction patterns from unirradiated spinel and a region irradiated to 2×10^{15} Xe⁺⁺/cm² are shown in figures 2 (a) and (b), respectively. The first order reflections are missing in the diffraction pattern from the irradiated layer. The distributions of the damage and implanted ion in this layer were calculated using the TRIM [8] computer code and are shown in figure 3. The thickness of the irradiated layer predicted by TRIM shows reasonable agreement with that determined by cross-sectional transmission electron microscopy (TEM).

Figure 2. [001] electron diffraction patterns from (a) unirradiated MgAl₂O₄ (b) MgAl₂O₄ irradiated with 400 keV Xe⁺⁺ at 100 K to 2×10^{15} ions/cm².

Figure 3. Distributions of Xe ions and displacements in spinel for a dose of 2×10^{15} ions/cm².

The calculated diffracted intensity distribution from unirradiated normal spinel is shown in figure 4 (a) along with an experimental plot of this distribution from spinel irradiated to 2×10^{15} Xe⁺⁺/cm² shown in figure 4 (b). The disappearance of first order fundamental reflections, such as (220), following irradiation indicates a phase transformation. From the symmetry of the diffraction pattern in 2 (b) and similar patterns taken at other orientations, it is clear that the new phase is single crystalline and cubic, and has a lattice spacing that is half that of unirradiated spinel. Since the oxygen sublattice has this spacing, we started with the assumption that the anion sublattice remains intact while the cations exchange sites leading to inversion. However, inversion does not bring about significant changes in the electron diffraction pattern, because the scattering factors for Mg and Al are almost identical. The calculated values of the square of the structure factor are shown in figure 4 (c), as functions of the reciprocal of the interplanar distance, following complete inversion. From this plot, it is clear that cation site exchange on a 0.808 nm spinel lattice cannot explain this transformation. The lattice periodicity has to be halved to explain the extinction of the first order reflections. Therefore, we assumed a 0.404 nm face-centered cubic oxygen lattice with cations randomly distributed at the interstitial positions. By choosing, different combinations of interstitials we arrived at different model lattices.

Figure 4 (d) is a plot of the square of the structure factor for a rocksalt-like structure obtained by placing Mg and Al cations on three-quarters of the octahedral sites. For this model, the all-odd reflections are extremely weak, which is inconsistent with our experimental observations. It must be pointed out that in going from a 0.808 to a 0.404 nm cubic lattice, the Miller indices of corresponding reflections will be halved. Thus, the reflection corresponding to (400) of normal spinel would be indexed as (200). Figure 4 (e) represents a plot of the square of the structure factors for the case where the cations are randomly distributed on tetrahedral sites. Depending on whether all or half the tetrahedral sites are available for occupation one obtains the anti-fluorite or zinc-blende structure, respectively. In both instances, the diffraction patterns are quite similar in that the (200) reflection is quite weak. This is not observed in our experimental diffraction pattern [figure 2 (b)].

We also examined models that use various combinations of octahedral and tetrahedral cation occupancy. Although, in some cases, these models represented an improvement over the models discussed above, the calculated intensity distribution was inconsistent with experiment. For instance, the calculated (220) intensity was four times stronger than that of (111) and (200)

reflections, while the (311) intensity was weaker than that of the (422). On the contrary, our experimental results show that the (111), (200), and (220) reflection intensities are comparable, while the (311) is stronger than the (422). These results suggest that cations may have to be present at other interstitial sites to account for the observed intensity distribution.

Figure 4 (f) is the calculated reciprocal space intensity distribution from a 0.404 nm f.c.c. oxygen lattice with cations randomly distributed over interstitial sites with three-fold

Figure 4. The distribution of diffracted intensity in reciprocal space for the following cases: (a) Normal spinel; (b) spinel irradiated to $2 \times 10^{15} \text{ Xe}^{++}/\text{cm}^2$; (c) inverse spinel; (d) rocksalt-like structure; (e) anti-fluorite structure; and (f) f.c.c. anion lattice with cations in three-fold, octahedral, and tetrahedral sites. The lattice periodicity a is indicated for each structure. (b) is an experimental distribution, while the rest represent calculated values.

coordination in addition to six-fold (octahedral) and four-fold (tetrahedral) coordinated sites. The three-fold coordinated site is shown in figure 5. This model provides a good fit to the experimental diffraction pattern. In an ideal f.c.c. anion lattice, the three-fold site would be considerably less stable than the octahedral and tetrahedral interstices. However, in this case, the anion lattice is likely to be highly distorted as a result of ion irradiation. In such a distorted lattice, the three-fold sites may become as stable as the other two sites. Moreover, these distortions, which are not accounted for in the present calculation, may improve the fit between experiment and calculation.

Figure 5. The three-fold coordinated cation site in the f.c.c. anion sublattice.

In addition to these cation disorder models, we have evaluated 0.404 nm cubic lattices in which the anion sublattice is considerably different from that in spinel. If the anions and cations are distributed on a perovskite-like structure, a simple-cubic diffraction pattern is obtained. A good fit to experiments is obtained if the ions are arranged at random on a 0.404 nm f.c.c. lattice. Since all the interstices would have to be empty, this model requires an unrealistic volume expansion of 75%. Thus, the most likely model for the structure of the metastable phase is the close-packed distorted anion lattice with cations in six-, four- and three-fold coordination.

In conjunction with this diffraction analysis, we have also studied the Young's modulus of irradiated spinel using the nano-indentation technique [9]. For each sample, indentations were made at three different depths (20, 40 and 80 nm). At each depth, the modulus was averaged over 10 indents. For an indentation depth of 40 nm, the Young's modulus increased monotonically with irradiation dose from a value of about 295 GPa for unirradiated spinel to about 325 GPa following a dose of $1.75 \times 10^{15} \text{ Xe}^{++}/\text{cm}^2$. Similar increases were also observed for indentations made at 20 and 80 nm. At higher doses where amorphization is observed, the modulus decreases to about 200 GPa. Yu et al. [10] have suggested that the metastable phase may be more covalent than unirradiated normal spinel and that this bonding change may be responsible for the observed elastic stiffening. The change in covalency may arise from local charge transfer brought about by the rearrangement of cations and the distortion of the anion lattice.

Recently, Chen *et al.* [11] used shell-model potential calculations to investigate the feasibility of several candidate structures for the metastable phase. They also studied the energetics of point defects in the spinel lattice. They found that the inverse spinel structure and several of the 0.404 nm lattices had higher lattice energies than normal spinel, which suggests that they are all good candidates for the metastable phase. Moreover, of all the point defects examined, site exchange between Mg^{+2} and Al^{+3} had the smallest energy of formation of 0.92 eV. This was an order of magnitude less than that of oxygen defects (vacancies and interstitials at 16c, 8b and 48f sites). The most favored interstitial position was neither the octahedral nor the tetrahedral site but an intermediate interstice. The equilibrated configurations of the 0.404 nm metastable lattices were found to possess non-cubic symmetry.

The results of Chen *et al.* [11] provide strong support for the findings of the present study. First, the fact that cation disorder is the most favored defect supports the idea that Mg and Al cations become randomly distributed among interstitial sites. Because of the low energy of formation of these defects, local cation disorder could provide favorable conditions for the nucleation of the metastable phase. Second, since the interstitial position with the lowest energy is neither octahedral nor tetrahedral, it is quite possible for cations to take up interstitial sites with three-fold coordination in addition to the six-fold and four-fold coordinated sites. Third, the non-cubic symmetry of the equilibrated configuration of the 0.404 nm lattices (rocksalt-like, antiferite etc.) indicates the possibility of local anion lattice distortions. Finally, the relatively high energy of anion lattice defects suggests that the anion lattice is not as likely as the cation lattice to undergo disorder. Thus, the anion lattice is likely to be retained intact with the exception of local distortions.

CONCLUSIONS

Magnesium-aluminate spinel transforms into a metastable crystalline phase when irradiated with 400 keV Xe ions at 100 K to low doses (2×10^{15} ions/cm²). This transformation is accompanied by an elastic stiffening. At higher doses, the material becomes amorphous and elastically soft. We have used electron diffraction analysis to determine the structure of this metastable phase. Our results indicate that the transformation of interest is to a distorted close-packed anion lattice with cations in octahedral, tetrahedral and three-fold coordinated interstices. This new lattice has half the spacing of unirradiated spinel, which explains the disappearance of the first-order fundamental reflections. We believe that the formation of the metastable phase plays an important role in the amorphization of spinel. Our findings show good agreement with recent shell model potential calculations of the energetics of point defects and possible metastable states in spinel.

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