Radiation-Induced Phase Transformations in Ilmenite-Group Minerals

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ABSTRACT

Transmission electron microscopy (TEM) is a powerful tool for characterizing and understanding radiation-induced structural changes in materials. We have irradiated single crystals of ilmenite (FeTiO₃) and geikielite (MgTiO₃) using ions and electrons to better understand the response of complex oxides to radiation. Ion irradiation experiments of bulk single crystals at 100 K show that ilmenite amorphized at doses of less than 1x10¹⁵ @ cm⁻² and at a damage level in the peak damage region of ~1 displacement per atom (dpa). Transmission electron microscopy and electron diffraction of a cross-sectioned portion of this crystal confirmed the formation of a 150 nm thick amorphous layer. Geikielite proved to be more radiation resistant, requiring a flux of 2x10¹⁵ Xe²⁺ cm⁻² to induce amorphization at 100 K. This material did not amorphize at 470 K, despite a dose of 2.5 x10¹⁵ Xe²⁺ cm⁻² and a damage level as high as 25 dpa. Low temperature irradiations of electron-transparent crystals with 1 MeV Kr⁺ also show that ilmenite amorphized after a damage level of 2.25 dpa at 175 K. Similar experiments on geikielite show that the microstructure is partially amorphous and partially crystalline after 10 dpa at 150 K. Concurrent ion and electron irradiation of both materials with 1 MeV Kr⁺ and 0.9 MeV electrons produced dislocation loops in both materials, but no amorphous regions were formed. Differences in the radiation response of these isostructural oxides suggests that in systems with Mg-Fe solid solution, the Mg-rich compositions may be more resistant to structural changes.

I. INTRODUCTION

Transmission electron microscopy (TEM) is a powerful and essential tool for characterizing and understanding radiation-induced structural changes in materials. Fundamental knowledge of the interaction between solids and various types of radiation are crucial for the development of reactor materials, identification of suitable nuclear waste forms, and the production of radiation-resistant materials for space applications. Of the numerous simple and complex oxides studied for these applications, spinel has been found to be exceptionally radiation resistant [1-4]. Sickafus et al. [5] suggested that several characteristics may enhance radiation resistance in oxides: complexity of composition and the tendency for cation disorder. Clinard et al. [2] were the first to show evidence that compositional complexity enhances radiation resistance, and it does so by suppressing the nucleation and growth of dislocation loops and voids. Good examples of the defect characteristics of complex and simple compounds are spinel and MgO. In spinel, the formation of a dislocation loop requires the condensation of two or more MgO₂Al₂O₃ anti-Schottky septets. Moreover, it is hard to condense point defects into loops because they are invariably faulted. Additionally, in spinel the formation of anti-site defects occurs at much lower energies than either Frenkel or Schottky defects [6]. Thus, the major low energy defect structure is cation disorder. In MgO, however, it is much simpler to condense MgO molecular units and the lack of stacking faults makes loop nucleation easier. Also, these loops grow readily during irradiation, leading to a vacancy bias, void formation, and concomitant swelling [2].
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To test the proposed radiation-resistance criteria and gain a better understanding of how complex oxides respond to radiation, we recently began an investigation of radiation damage response in ilmenite-group oxides. We chose this family of oxides because of their relative compositional complexity (two cations) and the tendency of Fe\(^{2+}\) and Ti\(^{4+}\) cations in ilmenite (FeTiO\(_3\)) to disorder at high temperatures. In this paper, we describe the results of electron and ion irradiations on natural and synthetic ilmenite (FeTiO\(_3\)) and synthetic geikielite (MgTiO\(_3\)) single crystals. We employed two types of experiments: (1) ion implantation followed by Rutherford backscattering spectrometry and ion channeling (RBS/C), with subsequent electron microscopy of cross-sectioned irradiated samples; and (2), in situ observation of electron and ion irradiation damage using the High Voltage Electron Microscopy Facility at Argonne National Laboratory. Both types of experiments show that FeTiO\(_3\) is less resistant to radiation damage than MgTiO\(_3\). The comparatively low ion irradiation tolerance of ilmenite suggests that chemical composition and crystal structure may be important in determining the radiation resistance of an oxide.

II. BACKGROUND

The family of compounds that we refer to as the ilmenite-group oxides are related by the fundamental composition A\(^{2+}\)Ti\(^{4+}\)O\(_3\). In natural crystals, the divalent cation A can be Fe (ilmenite), Mg (geikielite), Mn (pyrophani te), Zn (ecandrewsite), or Cd, Ni in the A site have also been synthesized. In nature, ilmenite is by far the most common of the rhombohedral titaniumates. Rhombohedral oxides such as il menite have crystal structures based on the hexagonal close-packing scheme. The cations sit on two-thirds of the available octahedral sites. The ilmenite structure is essentially an ordered version of the \(\alpha\)-alumina structure (R\(3\)c). The occupation of Fe\(^{2+}\) and Ti\(^{4+}\) instead of Al\(^{3+}\) doubles the number of crystallographically nonequivalent cation sites, reducing the space group symmetry to R\(3\). As shown in Fig. 1, Fe and Ti cations are layered along the [0001] direction. This ordering results in displacement of the anions away from the layers with larger cations toward the layers with the smaller cations.

Figure 1. Model of the ilmenite structure. Cations that can occupy the A site are Fe\(^{2+}\) (ilmenite), Mg\(^{2+}\) (geikielite), Mn\(^{2+}\) (pyrophani te), Zn\(^{2+}\) (ecandrewsite), Cd\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\).

In the geological sciences, ilmenite-silicate phase equilibria are a useful tool for constraining the crystallization conditions of igneous and metamorphic rocks. Ilmenite also often makes a large contribution to the magnetic signature of a rock, and is thus useful in paleomagnetic investigations. This mineral also a variety of current and potential industrial applications, such as a substrate material for high T\(_c\) superconducting films [7], as a high-temperature, wide band gap semiconductor [8], and as a component of heavy concrete for radiation shielding in fission reactors [e.g., 9]. Ilmenite has been studied as a source for oxygen on proposed lunar bases [10], as a resource for He\(^{3+}\) for space fusion energy applications [11], and as a radiation-resistant semiconductor for satel-
lites and related space applications [12]. Geikielite is a dielectric ceramic, with possible uses in microwave oscillators, narrow-band microwave filters, communications devices, and geographic positioning satellites [13].

The physical properties of ilmenite are closely linked to its solid solution relations with hematite (Fe2O3). The properties of this solid-solution series are the result of cation and magnetic order-disorder and low temperature immiscibility. The phase diagram (Fig. 2) of the system Fe2O3-FeTiO3 has several important features: (1) a cation ordering transition; (2) a miscibility gap between disordered (hematite) and ordered (ilmenite) phases; and (3) a magnetic order-disorder transition. At room temperature, ilmenite with <27% hematite component is a p-type conductor, whereas if the hematite component is >27%, it is a n-type conductor [14]. The magnetic properties of ilmenite-hematite solid solutions range from paramagnetic to ferrimagnetic to antiferromagnetic [15, 16]. Except under extremely reducing conditions, natural ilmenite tends to have some component of Fe2O3. Ilmenite grains in volcanic rocks cool rapidly and Fe2O3 remains dissolved in the quenched ilmenite. In rocks cooled over long periods of time, the hematite and ilmenite components will exsolve and form composite crystals, with the abundance of these phases controlled by bulk chemical composition. Lunar ilmenite has no hematite component due to the absence of Fe3+ on the Moon.

The natural crystal used for this study cooled slowly over millions of years and has approximately 20 volume% hematite that occurs as micron-scale ovoid exsolution structures. The cation order-disorder transition temperature for a crystal with this bulk composition is much higher than the temperature during our experiment (100 K). However, neutron- and ion-irradiated spinel crystals show greatly increased cation disordering at temperatures lower than capable of producing equivalent thermally induced disorder [17, 18]. Thus, we anticipate that disordering in ilmenite may be similarly influenced by irradiation.

**III. RADIATION-INDUCED PHASE TRANSFORMATIONS**

Several types of radiation-induced phase transformations have been evidenced in oxides. The most common transformation is amorphization, the complete loss of crystal structure. However, amorphization can be preceded by the formation of a metastable crystalline layer that is structurally distinct from both the amorphous region and the precursory material. These phenomena have recently been described in spinel (MgAl2O4), and are also known to occur in α-alumina [19, 20]. In spinel, the metastable phase is cubic, but the structural repeat unit is half that of unirradiated spinel (0.4 and 0.8 nm, respectively) [20].

Several studies have shown interesting phase transformations in ilmenite-group oxides. Although pressure- and temperature-induced phase transformations in FeTiO3 had been known since 1980 [21], the nature of these transitions were not understood until Leinenweber et al. [22] observed high-pressure (16 GPa) orthorhombic perovskite polymorphs from a starting composition of LiNbO3-structured FeTiO3. Mehta et al. [23] later reported that the lithium niobate (R3c) structure is metastable with respect to the il-
menite-perovskite phase boundary, and that perovskite is the stable form for FeTiO₃ at high pressures. In NiTiO₃, a transition from the ordered ilmenite structure (R₃) to the disordered alumina structure (Rk) was found to occur at 1560 K [24]. Thorough investigation of MnTiO₃ has shown three phases are possible: (1) MnTiO₃, I, normal ilmenite structure (R₃); (2) MnTiO₃, II, LiNbO₃ structure (R₃c) at high pressures and temperatures (>900 C, >40 kbar); and (3) MnTiO₃, III, orthorhombic perovskite structure (Pnma) at high pressures and lower temperatures (>45 kbar, <900 C) [25-27]. The transformation from II to III involves a 5% decrease in volume, is reversible, and has a pronounced hysteresis [26].

Although the pressures and temperatures described in the above experiments are high for most materials science applications, the response of materials to high levels of radiation may result in structural changes that are similar to those caused by pressure and temperature. At high pressures, orthorhombic (Mg,Fe)₂SiO₄ olivine transforms to the spinel structure [28, 29]. A similar transformation may be analogous to radiation-induced transformations in spinel [19, 20]. Additionally, olivine and silica have been found to amorphize at high pressures [30, 31], a process well-documented in numerous studies on radiation damage in a variety of materials. Therefore, the temperature- and pressure-induced phase transformations in ilmenite-structure oxides, in conjunction with the appearance of metastable crystalline phases in irradiated spinel and alumina, suggest that ilmenite and related oxides may also produce metastable phases during ion and electron irradiation.

IV. EXPERIMENTS

A variety of samples were used for this study. The natural single crystal of ilmenite was collected in the Adirondack Mountains, New York (supplied by G.L. Nord, Jr.). A synthetic ilmenite crystal was grown using the Czochralski method at Texas A&M University (supplied by K. Pandey). The geikielite crystal was grown using the floating-zone method at Los Alamos National Laboratory. All crystals were oriented using Laue x-ray back reflection, cut into wafers perpendicular to the c-axis, and polished to an optical finish on one side for ion-irradiation studies. Rutherford backscattering spectrometry combined with ion channeling (RBS/C) and ion irradiations were conducted at the Ion Beam Materials Laboratory (IBML) at Los Alamos National Laboratory. The High Voltage Electron Microscopy Facility at Argonne National Laboratory was used for dual beam electron and ion irradiations and in situ observation of radiation damage in electron transparent crystals.

4.1. Ion Beam Materials Laboratory, Los Alamos National Laboratory

At the IBML, 2 MeV He⁺ ion beam RBS/C measurements were performed on the samples to verify the orientation of the crystal and to assess the quality of the polished surface. Aligned RBS spectra were obtained while the incident He⁺ beam was aligned along the <0001> axis of the crystal. Minimum backscattering yield ($\chi_{min}$), defined as the RBS yield ratio of the aligned spectrum to that of the random spectrum, was used to quantify the quality of the sample surface. The initial high $\chi_{min}$ (~30%) of the natural ilmenite indicated substantial residual damage in the near-surface region due to mechanical polishing. The damaged layer was effectively removed by etching the sample in a 50:50 mixture of hydrofluoric acid and water at room temperature for ~5 minutes, as indicated by the reduction in $\chi_{min}$ to ~6% along the c-axis. Etching of the geikielite crystal reduced the $\chi_{min}$ from 8% down to ~4% along the c-axis.

Due to the comparatively poor channeling characteristics of the ilmenite, two types of experiments were used for the different materials. The ilmenite was irradiated using the ex situ technique, which involves using separate chambers for ion irradiation and surface analysis. The geikielite crystal was studied using the in situ chamber, which allows for sequential irradiation and RBS analysis. Thus, nearly continuous monitoring of damage accumulation is possible. The conditions used for both experiments are summarized in Table 1.
The irradiated ilmenite sample was prepared in cross section for transmission electron microscopy (TEM) observation to assess changes in microstructures induced by ion irradiation. Two portions of the irradiated crystal were glued face-to-face and then ground and polished to a thickness of ~20 microns. The sample was further thinned by ion milling using 3-5 keV Ar ions. The finished sample was examined using a Philips CM30 TEM operating at 300 kV.

The Monte Carlo code TRIM [32] was used to calculate the ranges of ions and damage parameters. In the ilmenite experiment, the projected range of 200 keV Ar$^{+}$ ions is about 125 nm. The peak concentrations of implanted Ar ions were 0.1 atomic % at a dose of 1x10$^{15}$ Ar$^{+}$ cm$^{-2}$. At this dose, the peak damage level is ~1 displacement per atom (dpa) [33]. In the geikielite experiments, the projected range of 400 keV Xe$^{2+}$ ions at a 25° incident angle (as required by the geometry for all in situ experiments) is 75 nm. The damage level in the peak damage region is 25 dpa for a dose of 1x10$^{16}$ Xe$^{2+}$ cm$^{-2}$, with a peak concentration of implanted Xe of about 2 atomic % at this dose.

**Table 1.** Conditions for irradiation experiments reported in this paper.

<table>
<thead>
<tr>
<th></th>
<th>200 keV Ar$^{+}$</th>
<th>400 keV Xe$^{2+}$</th>
<th>1 MeV Kr$^{+}$</th>
<th>1 MeV Kr$^{+}$ &amp; 0.9 MeV e$^{-}$</th>
</tr>
</thead>
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<tr>
<td>n FeTiO$_3$</td>
<td>100K</td>
<td>-</td>
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<tr>
<td>s FeTiO$_3$</td>
<td>-</td>
<td>-</td>
<td>50-300K</td>
<td>50-300K</td>
</tr>
<tr>
<td>MgTiO$_3$</td>
<td>170-470K</td>
<td>30-150K</td>
<td>30-150K</td>
<td></td>
</tr>
</tbody>
</table>

n = natural; s = synthetic

4.2. HVEM Facility, Argonne National Laboratory

The HVEM Facility allows for in situ observation of ion- (1 MeV Kr$^{+}$) and electron-induced radiation damage in electron-transparent crystals. The ilmenite crystal used for these experiments was a synthetic sample grown using the Czochralski method at Texas A&M University. The geikielite sample was from the same crystal used in the IBML experiments. Samples were cooled to ~100-150 K on a He-cooled stage prior to irradiation. Experimental conditions are shown in Table 1.

V. RESULTS

RBS/C spectra of the three portions of the ilmenite crystal are shown with the random spectrum in Fig. 3. The spectrum from the unirradiated portion of the crystal is characterized by a low $\chi_{\text{min}}$ and very small Fe, Ti, and O surface peaks. The presence of hematite exsolution structures may have increased the dechanneling in this spectrum. The spectra acquired from sample regions irradiated to 1 and 2x10$^{15}$ Ar$^{+}$ cm$^{-2}$ are virtually identical, with the latter resulting in slightly higher RBS yields. The dechanneling yield from the irradiated layer at fluences of 1 and 2x10$^{15}$ Ar$^{+}$ cm$^{-2}$ coincide with the backscattering yield in a random-orientation spectrum. This is indicative of the formation of an amorphous layer in the irradiated region, or that the irradiated zone has become polycrystalline. The RBS/C results do not indicate the presence of defective crystalline material in the irradiated region, as has been observed in spinel [20, 21].

![Figure 3. RBS channeling spectra for 200 keV Ar$^{+}$-irradiated natural ilmenite. A 150 nm thick amorphous surface layer formed as a result of the irradiation.](image-url)
Results for the *in situ* experiments on geikielite are shown in Fig. 4. At 170 K, the RBS spectrum after a total dose of $2 \times 10^{16}$ Xe$^{2+}$ cm$^{-2}$ coincided with the random spectrum, consistent with the formation of an amorphous surface layer. The thickness of this amorphous layer, calculated using the width of the surface peak, is 150 nm. At room temperature (300 K), a flux of $6 \times 10^{15}$ Xe$^{2+}$ cm$^{-2}$ was required to produce a similar amorphous surface layer. Temperature-dependence of damage rate kinetics is further evidenced in the 270 K experiments, where crystalline material is still present even after a total dose of $2.5 \times 10^{16}$ Xe$^{2+}$ cm$^{-2}$. Although different energies and ion species were used for the ilmenite and geikielite experiments, it is quite clear that MgTiO$_3$ is significantly more resistant to radiation than FeTiO$_3$.

A more direct way to assess the nature of the damage in the irradiated region is by transmission electron microscopy of cross-sectioned samples. Using this technique, we observed in the sample portion irradiated with $1 \times 10^{15}$ Ar$^{2+}$ cm$^{-2}$ a thin (150 nm) homogeneous layer (Fig. 5a). Bend contours terminate at the interface between this layer and the substrate, indicating an abrupt transition from a crystalline to amorphous material. Selected-area electron diffraction (SAED) patterns of this layer show diffuse rings around the transmitted beam, indicating that the layer is amorphous (Fig. 5b). In contrast, an SAED pattern of the substrate reveals the rhombohedral symmetry of ilmenite (Fig. 5c). No hematite was observed in the thin regions of the TEM foil, but its widespread presence in the bulk sample suggests that the lack of hematite in the foil is probably just by chance.

Experimental results at the HVEM Facility were comparable to those from the IBML, but the addition of electron irradiation added some interesting complexities. As shown by the SAED pattern in Fig. 6a, ilmenite irradiated with 1 MeV Kr$^+$ to 2.25 dpa at 175 K completely amorphized. However, a dual-beam irradiation using 1 MeV Kr$^+$ to damage levels of 2.25 dpa and 0.9 MeV electron to damage levels of 2.4 dpa produced dislocation loops but did not amorphize the irradiated region (Fig. 6b-c). After ions-only irradiation at 150 K to damage levels of 10 dpa, MgTiO$_3$ formed a “salt and pepper” texture, as shown in Fig. 7a. A diffraction pattern from this region is characterized by a large, diffuse central spot and haloes, but also contain distinct reflections (Fig. 7b). A closer look at this texture (Fig. 7c) indicates that it is formed by crystalline regions (dark) in an amorphous matrix (light). Dual-beam irradiation produced dislocation loops but no amorphous regions (Fig. 7d-e). As in similar
Figure 6. Transmission electron micrographs of ions-only 1 MeV Kr$^+$ and dual beam 1 MeV Kr$^+$ and 0.9 MeV e$^-$ irradiations of FeTiO$_3$ at 175 K. (a) SAED pattern of ions-only irradiated region. The diffuse central spot and haloes are consistent with amorphization. (b) SAED pattern after dual-beam irradiation. (c) Bright-field micrograph of dislocation loops formed during dual-beam irradiated region. Note lack of features attributable to amorphization in (b) and (c).
Figure 7. Results of *in-situ* ions-only 1 MeV Kr⁺ and dual 1 MeV Kr⁺ and 0.9 MeV e⁻ irradiations of MgTiO₃ at 150 K. (a) bright-field micrograph of "salt-and-pepper" texture formed by ions-only irradiation to 10 dpa. (b) SAED pattern from (a). (c) close-up view of dark crystalline region surrounded by lighter amorphous matrix. (d) bright-field image of dual-beam irradiated region. (e) SAED pattern after dual-beam irradiation. Note the lack of features indicative of amorphization.
experiments on other materials, electron irradiation appears to aid in the annealing of ion-induced damage and either delays or inhibits amorphization.

VI. DISCUSSION

Ilmenite is less radiation-resistant than geikielite, and several factors may play a role in their different behavior. First, both the natural and synthetic ilmenite crystals contain small amounts of hematite precipitates. Matzke [34] reported that ion-irradiated hematite became quasi-amorphous at a flux of $2 \times 10^{16}$ ions cm$^{-2}$, although the ion type, energy, and experiment temperature are not specified. Comparison between the experiment reported in this paper and those of Matzke [34] are difficult, but if hematite amorphizes more easily than ilmenite, the hematite grains present in our samples may act as amorphization nuclei and result in premature amorphization of the bulk crystal. However, the absence of hematite in the portion of the crystal that we studied with TEM suggests that ilmenite may have amorphized without the local influence of hematite. A more detailed investigation is needed to explore this potential relationship.

Second, it is possible that the ion-irradiation process is not inert and that chemical reactions took place during the experiment [35]. Of particular concern is the possibility that redox reactions during irradiation may assist the precipitation of new phases, such as Fe$_2$O$_3$, Fe$_3$O$_4$, and TiO$_2$, resulting in a polycrystalline surface layer. RBS/C spectra taken from such a layer would be similar to those acquired from an amorphous surface layer. Korenevskii et al. [36] reported that iron in hematite was partially reduced to Fe$^{2+}$ during exposure to a fluence of $1.3 \times 10^{20}$ neutrons cm$^{-2}$ at a temperature of 150 °C. Nevertheless, the electron diffraction pattern of the surface layer of the irradiated ilmenite in this experiment is consistent with an amorphous material, though we have not examined the valence state of iron in this region. Finally, geikielite and ilmenite are isostructural, differing only in composition. In the olivine solid solution system (Mg$_2$SiO$_4$, Fe$_2$SiO$_4$), Fe-rich olivine is less ion radiation resistant than Mg-rich olivines [37]. Similarly, pressure-induced amorphization takes place at considerably higher pressures for Mg-rich olivine than for Fe-rich olivine [30]. Thus, chemical composition and insusceptibility to redox reactions may also play a role in determining ion radiation resistance.

Although the existence of metastable crystalline phases was not evidenced directly, such phase transformations may still be observed in future experiments. Ion fluences may have been too high in these experiments, or other conditions such as temperature may have been too low for their occurrence. Indeed, results of the 470 K irradiation suggest the existence of such a metastable phase, and TEM of a cross-sectioned sample should reveal the nature of this RBS-evidenced feature.

The early stages of damage accumulation need to be examined to better discern the relationship between possible redox reactions and amorphization in composite ilmenite-hematite crystals. Also, ion-irradiation experiments on pure hematite would be useful to predict the behavior of hematite during irradiation of ilmenite-hematite intergrowths. In general, it does appear that ilmenite is easily amorphized by ion irradiation under low and ambient temperature conditions. However, as demonstrated by 900 keV electron exposure [38], it may be useful in environments where a semiconducting material that is resistant to light particle bombardment is needed. Similarly, MgTiO$_3$ may be a useful dielectric material for high-radiation environments.

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