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Radiation damage kinetics in synthetic MgTiO₃ (geikielite) single crystals have been studied using the in situ ion beam facility at Los Alamos National Laboratory. The geikielite samples were irradiated at temperatures of 170, 300, and 470 K with 400 keV xenon ions and the radiation damage was sequentially measured with Rutherford backscattering using a 2 MeV He ion beam along a channeling direction. Threshold doses of 1 and 5x10¹⁵ Xe/cm² were determined for the crystalline-to-amorphous transformation induced by Xe ion irradiation at 170 and 300 K, respectively. However, geikielite retained its crystallinity up to a dose of 2.5x10¹⁶ Xe/cm² at the irradiation temperature of 470 K. This study has shown that MgTiO₃, which has a corundum derivative structure, is another radiation resistant material that has the potential for use in radiation environments.

INTRODUCTION

Radiation resistant ceramics are desired for many applications in radiation environments due to their unique electrical, optical, and mechanical properties. Considerable studies have been conducted to understand the radiation responses of various oxide ceramics [1-3], in particular magnesium aluminate spinel (Mg₃Al₂O₄) and its end compounds, alpha-alumina (α-Al₂O₃) and magnesia (MgO). Although spinel is considered to be one of the most radiation resistant oxides, it has recently been found that spinel undergoes phase transformations from its equilibrium phase through an intermediate crystalline phase to an amorphous phase under Xe ion irradiation at cryogenic temperatures [4]. However, similar ion irradiations at elevated temperatures do not induce such phase transformations [5]. These observations indicate that the phase transformations in spinel are promoted by radiation-induced cation redistribution [6]. The understanding of the rules that govern the phase transformations at different irradiation temperatures will provide a link to the development of materials criteria for radiation resistance.

We have recently extended the temperature effect study of radiation damage to other relevant oxides including α-alumina, geikielite (MgTiO₃), ilmenite (FeTiO₃), magnesia, and zirconia (ZrO₂). As reported previously [7-9], it is difficult to amorphize α-alumina at room temperature. Geikielite possesses a corundum-derivative structure and multi-component chemistry. We expect that geikielite is a radiation resistant oxide. In this study, we have examined in situ the kinetics of radiation damage accumulation induced by 400 keV Xe ion irradiation at a temperature range 170-470 K in synthetic geikielite single crystals.

EXPERIMENT

Synthetic MgTiO₃ single crystals were fabricated in the Crystal Growth Laboratory at Los Alamos National Laboratory (LANL). Geikielite samples were prepared to a dimension of 10x20 mm² width and 0.5 mm thickness with a c-cut orientation. Ion irradiation experiments were performed at the LANL in situ ion beam system [10]. The LANL system provides an efficient and
unique means to determine the radiation damage kinetics in single crystal materials. This system also plays a complementary role to the HVEM-tandem facility at Argonne National Laboratory for radiation effects studies. The sample for ion irradiation was mounted onto a sample stage with silver paint. The orientation and translational motions of the sample were controlled by a multi-axis goniometer in a surface modification target chamber. The chamber was interconnected with both an ion irradiation beamline form a 200 kV implanter and an analysis beamline from a 3 MV tandem accelerator. The sample orientation geometry with respect to the two ion beams is shown schematically in Figure 1. Prior to ion irradiation, the unirradiated sample was first aligned with its $<10\overline{1}4>$ axis along the 2 MeV He ion beam using Rutherford backscattering and ion channeling (RBS/C) measurements. The $<10\overline{1}4>$ axis has a 35° angle to the c-axis that is close to the sample normal. The sample temperature was then either cooled or heated to temperatures of 170, 300, and 470 K for sequential ion beam irradiation and analysis.

Radiation induced lattice disorder was monitored through RBS/C measurements following each irradiation of 400 keV Xe$^{2+}$ ions. The irradiation and analysis beam spots were co-centered on the sample surface with beam sizes of about 7 and 2 mm in diameter. The incident angle of the irradiation beam was 25° with respect to the sample normal. The irradiation doses varied from 4x10$^{12}$ to 2.5x10$^{16}$ Xe/cm$^2$ with the current density maintained at ~1 μA/cm$^2$. The irradiation experiment at a given temperature proceeded until the lattice disorder in the irradiated sample reached a certain saturation level. Following each irradiation experiment at a chosen temperature, the sample was translated to set an unirradiated area for the next irradiation experiment at a different temperature. The sample orientation was maintained throughout the entire experiment, which lasted about eight hours. The LANL in situ capability enhanced the experimental efficiency by a factor of ten and improved the experimental accuracy as compared to those of conventional ex situ measurements.

The projected range of 400 keV Xe ions at a 25° incident angle was estimated to be 75 nm, as determined by the TRIM code [11] using a mass density of 4.05 g/cm$^3$ for geikielite. The damage level in the peak damage region was estimated to be 25 displacements per atom (dpa) for a dose of 1x10$^{16}$ Xe/cm$^2$ if a displacement energy of 40 eV was assumed for all elements. The peak concentration of Xe in geikielite was about 2 at.% for 1x10$^{16}$ Xe/cm$^2$.

RESULTS

Figure 2 shows sequential in situ RBS/C spectra from a MgTiO$_3$ crystal following the 400 keV Xe ion irradiations at room temperature. Minimum backscattering yield, defined as the RBS yield ratio of an aligned to a random spectrum, is an indication of the single crystal quality of the material. For the aligned spectrum from the unirradiated geikielite sample, the minimum yield from the Ti signal near the sample surface is 10%. This indicates good single crystallinity of the as-grown sample. The aligned spectrum shows high dechanneling yields after the irradiation of 4x10$^{14}$ Xe/cm$^3$. The dechanneling yields are higher in the 150 nm thick Xe irradiated layer, indicating the presence of radiation induced lattice disorder. The dechanneling yields from sample depths greater than the irradiated layer are due to dechanneling by the defects present in the irradiated layer. The amount of the dechanneling in the irradiated layer represents the amount of radiation damage. The ion channeling results in Figure 2 clearly show that the amount of radiation damage increases with increasing irradiation dose. The backscattering yields from the peak damage region where a maximum lattice disorder occurs coincides with that of the random spectrum after irradiation to a dose of 5x10$^{15}$ Xe/cm$^2$. This suggests that a buried amorphous layer is formed around the peak damage region.
The ion irradiation and *in situ* RBS/C measurements performed at 170 K revealed that a buried amorphous layer was formed in geikielite at a much lower dose, \(1 \times 10^{15}\) Xe/cm\(^2\). Further irradiation to \(2 \times 10^{15}\) Xe/cm\(^2\) produced an extended amorphous layer of 150 nm thickness on the geikielite surface. For the Xe irradiation at 470 K, however, the rate of radiation damage accumulation is lower as compared to that for irradiation at room temperature. Figure 3 shows *ex situ* channeling and random RBS spectra from the MgTiO\(_3\) sample after the 400 keV Xe ion irradiation at 470 K to an integrated dose of \(2.5 \times 10^{16}\) Xe/cm\(^2\). The average minimum yield for the Ti signal over the entire irradiated layer is \(80\%\), indicating that no amorphization occurred in the irradiated geikielite. A small dip that appears in the Ti RBS signal near the surface in Figure 3 is due to the presence of a high concentration of implanted Xe. The TRIM calculation estimated that there is 5 at.% of implanted Xe accumulated in the peak concentration region.

The kinetics of radiation damage accumulation in geikielite have been determined from a series of *in situ* RBS/C spectra following the incremental dose of Xe irradiation. Figure 4 shows the fraction of damaged volume integrated over the entire Xe irradiated MgTiO\(_3\) layer for the Ti sublattice as a function of Xe irradiation dose and irradiation temperature. The kinetic curve obtained from the sample irradiated at 170 K shows the highest rates of damage accumulation. The damage fraction value quickly approaches 100% as the irradiation dose reaches \(1 \times 10^{15}\) Xe/cm\(^2\). This indicates that the threshold dose for the complete crystalline-to-amorphous phase transformation is about \(1 \times 10^{15}\) Xe/cm\(^2\) for the Xe irradiation at 170 K. The damage accumulation becomes slower for the irradiation at 300 K. The complete amorphization occurs at a dose of \(5 \times 10^{15}\) Xe/cm\(^2\). The lowest rates of damage accumulation occur at the irradiation temperature of 470 K. The damaged volume fraction saturates at about 80% as the irradiation dose increases to \(8 \times 10^{14}\) Xe/cm\(^2\). This clearly shows that geikielite is not susceptible to amorphization at elevated temperatures.

**DISCUSSION**

The temperature dependence of ion irradiation damage, observed in Figure 4, indicates the presence of annealing effects for the point defects introduced into the lattice by atomic cascade collisions. The rate of point defect annihilation reduces with decreasing irradiation temperature due to the reduction in the mobility of point defects. The behavior is consistent with that of many other materials including spinel. A comparative study has demonstrated that both geikielite and alpha-alumina are of similar radiation resistance under ion beam irradiation at cryogenic temperatures [12]. Therefore, geikielite and other related chemically stable compounds (ABO\(_3\)) with the corundum structure may have the potential for use in radiation environments.

As shown in Figure 4, there are two stages for lattice damage accumulation in geikielite under Xe irradiation at room temperature. For the dose regime below \(5 \times 10^{14}\) Xe/cm\(^2\), the damage accumulates at high rates. The damage accumulation slows down appreciably when the dose exceeds \(5 \times 10^{14}\) Xe/cm\(^2\). A plateau appears in the kinetic curve at a damage level of 60% for doses around \(0.5-1 \times 10^{15}\) Xe/cm\(^2\). The plateau represents the transition of damage accumulation from the high rates to the low rates as the dose increases. Close examination of the kinetic curve obtained at the irradiation temperature of 170 K has also revealed a small plateau present at the similar damage level. The behavior of two-stage radiation damage accumulation bears analogy to that in MgAl\(_2\)O\(_4\) spinel [4]. This suggests a possible radiation induced metastable crystalline phase present in the MgTiO\(_3\) crystal prior to amorphization. It is known that the dominant metastable phase in alumina is \(\gamma\)-phase with a defective spinel structure. We thus propose that a similar \(\gamma\)-alumina structure may represent such an intermediate phase. A detailed study using cross-
CONCLUSIONS

1. The kinetics of radiation damage accumulation in synthetic MgTiO$_3$ single crystals have been studied by in situ RBS and ion channeling measurements following 400 keV Xe ion beam irradiations at temperatures of 170, 300, and 470 K. The LANL in situ ion beam system has been demonstrated to be a unique and efficient means for radiation effects studies in single crystal materials.

2. The threshold doses for the crystalline-to-amorphous phase transformation have been determined to be 1 and 5x10$^{15}$ Xe/cm$^2$, respectively, for the Xe irradiations performed at 170 and 300 K. At 470 K, no amorphization has been observed up to an irradiation dose of 2.5x10$^{16}$ Xe/cm$^2$. This study indicates that MgTiO$_3$ is a radiation resistant oxide.

3. Close examination of the damage kinetic curves obtained at 170 and 300 K suggests a possible radiation induced metastable crystalline phase prior to amorphization in geikielite. We propose that a defective spinel structure, an analogue of γ-alumina, may represent such an intermediate phase.

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REFERENCES

**Figure 1** Schematic representation of the geikielite sample orientation with respect to the irradiation beam and analysis beam during *in situ* ion beam experiments.

**Figure 2** *In situ* RBS/C spectra obtained from a MgTiO₃ crystal when the 2 MeV He incident ion beam was aligned along the <1014> axis and following the 400 keV Xe ion irradiations at room temperature to indicated doses, along with a random spectrum of the same sample.

**Figure 3** *Ex situ* RBS/C spectra obtained from a MgTiO₃ crystal when the 2 MeV He incident ion beam was aligned along the <0001> axis and after the 400 keV Xe ion irradiation at 470 K to an integrated dose of 2.5x10¹⁶ Xe/cm², along with a random spectrum of the same sample.

**Figure 4** Fraction of damaged volume in the Xe-irradiated MgTiO₃ layer for Ti sublattice versus Xe irradiation dose at the irradiation temperatures of 170, 300, and 470 K.
Fig. 1

2 MeV He$^+$, 400 keV Xe$^{2+}$, MgTiO$_3$
Figure 2

Energy (MeV)

Normalized Yield

Channel

2 MeV He\(^{+}\) – MgTiO\(_3\)

400 keV Xe\(^{2+}\) Irrad.

- 0, 300 K
- 4x10\(^{14}\), 300 K
- 5x10\(^{16}\), 300 K

Random

Fig. 2