LA-UR- 00 - 4469

Approved for public release;
distribution is unlimited.

Title: A Comparison Between Radiation Damage Accumulation in
Oxides with Pyrochlore and Fluorite Structures

Author(s): Kurt E. Sickafus, MST-8
Licia Minnervini, Imperial College - London, UK
Robin W. Grimes, Imperial College - London, UK
James A. Valdez, MST-8
Thomas Hartmann, MST-8

Submitted to: For Publication in: Radiation Effects and Defects in Solids
Proceedings of: ICDIM 2000 International Conference on Defects
in Insulating Materials, April 3-7, 2000, Johannesburg, Midrand,
South Africa

Los Alamos

NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A comparison between radiation damage accumulation in oxides with pyrochlore and fluorite structures

Kurt E. Sickafus,¹ Licia Minervini,² Robin W. Grimes,² James A. Valdez,¹ and Thomas Hartmann¹

¹Division of Materials Science and Technology, MS-G755, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

²Department of Materials, Imperial College, Prince Consort Road, London SW7 2BP, UK.

ABSTRACT

Ion irradiation damage experiments were performed on single crystals of the pyrochlore compound $\text{Er}_2\text{Ti}_2\text{O}_7$ and the fluorite compound $\text{Er}_2\text{Zr}_2\text{O}_7$. Results indicate that the pyrochlore compound is far more susceptible to defect accumulation and amorphization than the fluorite compound. In particular, $\text{Er}_2\text{Ti}_2\text{O}_7$ irradiated with 350 keV Xe^{++} ions succumbs to a amorphization transformation by a fluence of 1×10^{15} Xe/cm^2 , while $\text{Er}_2\text{Zr}_2\text{O}_7$ remains crystalline with no change in crystal structure to at least 5×10^{16} Xe/cm^2 . Atomistic computer simulations were used to explain this difference in radiation damage behavior between compounds with similar structures. Simulations of defect formation energies reveal that point defects induced by irradiation, such as cation antisite and anion Frenkel pairs, are far more stable in the fluorite compound than in the pyrochlore compound.

KEYWORDS: ion irradiation, pyrochlore, fluorite, amorphization, point defects

Submitted to *Radiation Effects and Defects in Solids*. Proceedings of ICDIM 2000 – International Conference on Defects in Insulating Materials, April 3-7, 2000, Johannesburg – Midrand, South Africa

RECEIVED

SEP 28 2000

OSTI

In this report, we compare the radiation damage behavior of two types of $A_2B_2O_7$ oxides, pyrochlores and fluorites. It is already well-established that titanate pyrochlores such as $Gd_2Ti_2O_7$ are highly susceptible to amorphization under ion irradiation (e.g. (1)), while fluorite-structured oxides such as UO_2 and ZrO_2 (cubic-stabilized) are highly radiation tolerant (for UO_2 , (2); for ZrO_2 , (3)). However, until now we have lacked a fundamental explanation for this distinction between the damage response of compounds with similar structures. We will demonstrate here using atomistic computer simulation techniques, that there are substantial differences in point defect formation energies between pyrochlores and fluorites. These differences help to explain the radiation damage susceptibility of pyrochlores versus the damage tolerance of fluorites.

Single crystals of $Er_2Ti_2O_7$ and $Er_2Zr_2O_7$ were grown in a Crystal Systems, Inc. floating-zone crystal growth unit. Crystal dimensions were approximately 5 mm diameter and 10 mm length. X-ray diffraction (XRD) measurements on powders obtained from the crystal boules indicated that both the $Er_2Ti_2O_7$ and $Er_2Zr_2O_7$ are cubic, with lattice parameters given by $a = 1.0095(1)$ nm for $Er_2Ti_2O_7$ and $a = 0.5198(1)$ nm for $Er_2Zr_2O_7$ (using a silicon internal standard). XRD results are consistent with a pyrochlore structure for the $Er_2Ti_2O_7$ crystal and a fluorite structure for the $Er_2Zr_2O_7$ crystal. Disks of ~ 1 mm thickness were cut from each crystal boule and polished for ion irradiation. Samples were irradiated under cryogenic conditions ($T \sim 120$ K) using 350 keV Xe^{++} ions to fluences ranging from 1×10^{15} to 5×10^{16} Xe/cm^2 . Irradiated samples were then prepared in cross-section for analysis using transmission electron microscopy (TEM).

Figure 1a shows a TEM image indicating the damage microstructure for an $Er_2Ti_2O_7$ pyrochlore sample irradiated to a fluence of 1×10^{15} Xe/cm^2 . Similarly, Figure 1b shows the microstructure for an $Er_2Zr_2O_7$ fluorite sample irradiated to a fluence of 5×10^{16} Xe/cm^2 .

Electron microdiffraction patterns (insets in Figs. 1a and 1b) indicate that the pyrochlore is amorphized by fluence 1×10^{15} Xe/cm², while the fluorite remains crystalline to at least 15 times this ion fluence. An interesting void microstructure (consisting of chains of voids parallel to the sample surface) develops in the fluorite at the highest ion dose (Fig. 1b). These voids are not apparent at a fluence of 1×10^{16} Xe/cm² (4) and the origin of these voids is unclear at present. Nevertheless, the fluorite compound is able to resist an amorphization transformation to at least 15 times the amorphization dose for the pyrochlore compound.

To help explain this dramatic difference in radiation damage behavior between similar compounds, we performed an investigation using atomistic computer simulation methods, into the detailed crystal structure of a variety of $A_2B_2O_7$ compounds. We considered A^{3+} cations ranging from lanthanum to lutetium and B^{4+} cations ranging from titanium to cerium. We examined not only the perfect crystal lattice for each compound, but we also predicted, via calculations, the extent to which a given lattice accommodates irradiation-induced point defects. Calculations were carried out using the CASCADE code (5). Details are presented elsewhere (6).

Figure 2 shows a contour plot of the formation energies for isolated point defect complexes in a wide range of $A_2B_2O_7$ compounds. The specific defect complex considered in Fig. 2 consists of a cation antisite (via reaction $A_{A(16d)} + B_{B(16c)} \longrightarrow A'_{B(16c)} + B^{\bullet}_{A(16d)}$) along with an anion Frenkel (via reaction $O_{O(48f)} \longrightarrow V^{\bullet\bullet}_{O(48f)} + O^{\bullet}_{i(8a)}$).[§] This point defect cluster occurs with the lowest energy expense compared to all other point defect reactions considered in this study (6). The above reactions are equivalent to a local transformation from an ordered pyrochlore into a disordered fluorite structure. The cation antisite and anion Frenkel defect

[§] The Wyckoff notation used in the defect reactions described here refers to equipoints in the space group for pyrochlore, i.e., $Fd\bar{3}m$. The point defect products on the right-hand sides of these reactions could alternatively be described using the space group for fluorite, $Fm\bar{3}m$. In this case, the A and B cations are randomly distributed on a 4a equipoint, while the O anions and anion vacancies are randomly distributed on an 8c equipoint.

reactions are consistent with typical point defects generated in a displacive radiation environment. The plot in Fig. 2 indicates that cation antisite and anion Frenkel defect formation is accompanied by high energy cost in compounds containing large A cations and comparatively smaller B cations. The lowest defect energies are associated with compounds in which A and B radii are more similar. As cation antisite defects and anion Frenkels are an inevitable consequence of a displacive radiation environment, Fig. 2 can also be interpreted as a predictor of radiation damage behavior: compounds with highly dissimilar cationic radii, $r(A^{3+}):r(B^{4+})$, should exhibit the greatest susceptibility to lattice destabilization (and possible amorphization), while compounds with similar $r(A^{3+}):r(B^{4+})$ should behave more robustly in a radiation environment.

This prediction is consistent with the observations in Fig. 1. The $\text{Er}_2\text{Zr}_2\text{O}_7$ fluorite with $r(\text{Er}_{\text{VII}}^{3+}):r(\text{Zr}_{\text{VII}}^{4+}) \approx 1.21$ resists amorphization, while the $\text{Er}_2\text{Ti}_2\text{O}_7$ pyrochlore with $r(\text{Er}_{\text{VIII}}^{3+}):r(\text{Ti}_{\text{VI}}^{4+}) \approx 1.66$ succumbs to amorphization at relatively low ion dose (ionic radii based on Shannon (7)). Based on our results, we make the following prediction: fluorite structured oxides will be more radiation tolerant than pyrochlore structured oxides, because fluorites more readily accept disordering defects into their lattices.^{§§}

^{§§} This work was sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences.

REFERENCES

1. S. X. Wang, L. M. Wang, R. C. Ewing, G. S. Was, G. R. Lumpkin, *Nuclear Instruments and Methods in Physics Research B* **148**, 704-709 (1999).
2. H. Matzke, M. Kinoshita, *Journal of Nuclear Materials* **247**, 108-115 (1997).
3. K. E. Sickafus *et al.*, *Journal of Nuclear Materials* **274**, 66-77 (1999).
4. K. E. Sickafus *et al.*, *Science*, submitted for publication (2000).
5. M. Leslie, "DL/SCI/TM31T" *Technical Report* (SERC Daresbury Laboratory, 1982).
6. L. Minervini, R. W. Grimes, K. E. Sickafus, *Journal of the American Ceramic Society*, in press (2000).
7. R. D. Shannon, *Acta Crystallographica A* **32**, 751-767 (1976).

FIGURE CAPTIONS

Figure 1. Cross-sectional transmission electron microscope (TEM) bright-field (BF) images obtained from (a) a Xe-ion irradiated $\text{Er}_2\text{Ti}_2\text{O}_7$ single crystal and (b) a Xe-ion irradiated $\text{Er}_2\text{Zr}_2\text{O}_7$ single crystal. The sample in (a) was irradiated under cryogenic conditions ($T \sim 120\text{K}$) using 350 keV Xe^{++} ions to a fluence of $1 \times 10^{15} \text{ Xe/cm}^2$. The sample in (b) was irradiated using the same conditions as in (a) to a fluence of $5 \times 10^{16} \text{ Xe/cm}^2$. The BF image and the corresponding electron microdiffraction patterns (insets) in (a) indicate that the irradiated layer (approximately 70 nm thick) in $\text{Er}_2\text{Ti}_2\text{O}_7$ is completely amorphized by the ion irradiation. The BF image and corresponding electron microdiffraction patterns (insets) in (b) indicate that the irradiated layer (approximately 130 nm thick) in $\text{Er}_2\text{Zr}_2\text{O}_7$ remains crystalline with no change in structure, even to 15 times the ion exposure used to irradiate the titanate.

Figure 2. Contour map showing the calculated isolated defect complex formation energy (complex consisting of cation antisite plus anion Frenkel pairs), for a variety of compounds with $\text{A}_2\text{B}_2\text{O}_7$ stoichiometry. A cations are arranged in order of increasing radii along the ordinate; likewise for B cations on the abscissa (ionic radii based on Shannon (7)). For each compound, calculations were performed assuming a pyrochlore cubic unit cell containing eight formula units. Not all compounds indicated here are known to form pyrochlores. Experimentally confirmed pyrochlores are indicated with open symbols, while checkered symbols represent compounds known to form fluorites. For compounds labeled with gray symbols, structural data was not available or the compounds have not been observed experimentally.

(a)

(b)

Figure 1

Figure 2