RESPONSE OF ZIRCON TO ELECTRON AND Ne^+ IRRADIATION

R. Devanathan*, W. J. Weber*, and L. A. Boatner**

* Pacific Northwest National Laboratory, Richland WA 99352, ram@pnl.gov

** Oak Ridge National Laboratory, Oak Ridge, TN 37831

CONF-97/201--

RECEIVED

JAN 26 1998

OSTI

ABSTRACT

Zircon (ZrSiO_4) is an actinide host phase in vitreous ceramic nuclear waste forms and a potential host phase for the disposition of excess weapons plutonium. In the present work, the effects of 800 and 900 keV electron, and 1 MeV Ne^+ irradiations on the structure of single crystals of ZrSiO_4 have been investigated. The microstructural evolution during the irradiations was studied *in situ* using a high-voltage electron microscope interfaced to an ion accelerator at Argonne National Laboratory. The results indicate that electron irradiation at 15 K cannot amorphize ZrSiO_4 even at fluences an order of magnitude higher than that required for amorphization by 1.5 MeV Kr^+ ions. However, the material is readily amorphized by 1 MeV Ne^+ irradiation at 15 K. The temperature dependence of this amorphization is discussed in light of previous studies of radiation damage in ZrSiO_4 .

INTRODUCTION

Nuclear waste management, including the disposition of plutonium from weapons, is one of the most daunting challenges facing the United States Department of Energy. Zircon (ZrSiO_4), which is a durable mineral that occurs in nature with U and Th in its structure, has been proposed as a host phase for the immobilization of Pu and other actinides [1]. α -decay of these actinides results in an α -particle with an energy of about 5 MeV and a recoil nucleus that has an energy of about 80 keV. The α -particle loses most of its energy by ionization, while the recoil nucleus comes to rest mainly by elastic collisions with the lattice atoms that result in a damage cascade. Previous studies have examined the crystalline-to-amorphous transition due to recoil damage in zircon using heavy-ion irradiation (such as MeV Kr^+ and Xe^+) [2,3]. A systematic investigation of the irradiation temperature dependence of the amorphization of zircon by lighter ions is needed to gain an understanding of particle mass effects. Moreover, it has been shown that ionization can significantly influence the microstructural evolution of irradiated ceramics [4-6]. However, the effects of ionizing radiation on the structural evolution of irradiated zircon are not well understood. The present work addresses these issues by examining the structural changes brought about in ZrSiO_4 by energetic electron and Ne^+ irradiation.

EXPERIMENTAL DETAILS

The crystal structure of zircon is schematically shown in Fig. 1. Single crystals of synthetic ZrSiO_4 , grown by a flux technique [7], were irradiated with 800 and 900 keV electrons, and 1 MeV Ne^+ and examined *in situ* in the HVEM Tandem Facility at Argonne National Laboratory. This facility consists of a 1.2 MeV modified Kratos/AEI EM7 electron microscope interfaced to two National Electrostatics Corporation ion accelerators [8]. The details of the experimental setup have been discussed elsewhere [6]. The zircon samples were prepared by mechanical polishing and liquid nitrogen-cooled ion milling with 5 keV Ar ions at about 10° to

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

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, makes 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 electronic image products. Images are produced from the best available original document.

the sample surface. During irradiation, the sample temperature was maintained between 15 and 1075 K using a liquid He stage and a heating stage. The ion flux was about 1×10^{12} ions/cm²-s and the peak of the Gaussian electron flux profile was about 2×10^{19} e⁻/cm²-s with a half-width at half-maximum of about 2 μ m. The electron displacements per atom (dpa) were estimated from Oen's tables [9] and the ion dpa from TRIM 97 simulations [10] assuming a sample thickness of 100 nm and displacement energies of 80, 20, and 45 eV, respectively, for Zr, Si, and O [11]. The ion implant and damage profiles are shown in Fig. 2. Chemical effects due to the implant are negligible within 100 nm from the surface. The electronic to nuclear stopping power was about 25 for the ion irradiation and about 10000 at the peak of the electron beam.

Figure 1. Ball and stick model of the tetrahedral unit cell of ZrSiO_4 .

Figure 2. 1 MeV Ne^+ implant and damage profiles in ZrSiO_4 calculated using TRIM 97.

RESULTS AND DISCUSSION

Fig. 3 shows $[1\bar{1}0]$ selected area diffraction (SAD) patterns from zircon before and after irradiation with 800 keV electrons for 12,000 s at 15 K. The co-existence of diffraction spots with a halo in Fig. 3(b) shows the occurrence of partial amorphization. The maximum energies transferred to Zr, Si, and O by an 800 keV electron are 34, 110, and 195 eV, respectively. The calculated displacement energy for Zr [11] is much higher than 34 eV. Hence, 800 keV electrons cannot displace Zr directly, and the partial amorphization probably occurs by the inefficient process of electrons displacing O which subsequently displace Zr. The maximum possible energy transfer from O to Zr is about 97 eV. Similar results were obtained for 900 keV electron irradiation of ZrSiO_4 at 15 K.

The peak electron dose was estimated to be 1.3 dpa which is several times the dose of about 0.35 dpa required for cryogenic heavy-ion induced amorphization of zircon [2]. The persistence of crystallinity, in this case, after a dose of 1.3 dpa may be due to a combination of the inefficiency of the displacement process, and enhanced migration of point defects as a result of ionization [12] and sub-threshold energy transfers [13]. Our assumption that Zr displacement occurs indirectly leads to the conclusion that the displacement energy for Zr is higher than 41 eV (inability to directly displace with 900 keV electrons) but less than 97 eV (indirect displacement by 800 keV electrons via the oxygen sublattice). The value of about 80 eV for Zr determined recently by computer simulation [11] fits within this broad range.

Figure 3. $[1\bar{1}0]$ selected area diffraction patterns of ZrSiO_4 (a) before and (b) after irradiation with 800 keV electrons at 15 K to about 1.3 dpa.

Fig. 4 shows a sequence of SAD patterns from zircon irradiated with 1 MeV Ne^+ at 15 K. As the irradiation proceeds, a halo appears in the diffraction pattern indicating the occurrence of amorphization. The crystalline spots become weaker and eventually disappear indicating complete amorphization of zircon at about 4×10^{15} ions/cm² which corresponds to a dose of about 0.2 dpa for the displacement threshold energies mentioned above. Thus zircon is readily amorphized by 1 MeV Ne^+ irradiation at 15 K.

Figure 4. A sequence of SAD patterns obtained *in situ* during the irradiation of ZrSiO_4 with 1 MeV Ne^+ at 15K. (a) unirradiated; (b) 2.5×10^{15} ; (c) 3×10^{15} and (d) 4×10^{15} ions/cm².

Fig. 5 shows the temperature dependence of the critical fluence for the amorphization of ZrSiO_4 . Complete amorphization occurred readily in the temperature range 15-600 K. The error bars of $\pm 10\%$ reflect the uncertainty in the determination of the fluence during irradiation. The temperature dependence of the amorphization fluence was fitted using the model proposed by Weber [2] and is shown as a curve through the data points in fig. 5. This model assumes that the effect of increasing temperature is to decrease the cascade volume per ion by intracascade annealing. The fluence, D , can be expressed in terms of the zero-temperature fluence, D_0 , activation energy for the dynamic damage recovery process, E_a , Boltzmann constant, k , temperature, T , and critical temperature, T_c as

$$D = \frac{D_0}{1 - \exp\left[\frac{-E_a}{k} \left(\frac{1}{T} - \frac{1}{T_c}\right)\right]} \quad (1)$$

Figure 5. The temperature dependence of the critical fluence for the amorphization of ZrSiO_4 by 1 MeV Ne^+ . The curve is a fit to the data using the Weber model.

The best fit to the experimental data was obtained for values of 0.06 eV and 1040 K, respectively, for E_a and T_c . A previous study determined the critical temperature for amorphization of ZrSiO_4 by 1.5 MeV Kr^+ to be 1100 K [2]. This decrease in critical temperature with decreasing projectile mass has been previously observed by Koike [14] in intermetallic compounds. Koike attributed this trend to the need for multiple overlaps of ion-tracks for amorphization by Ne^+ ions as opposed to the occurrence of amorphization within a single ion track for Kr^+ irradiation. The damage produced by Kr^+ is more stable against thermal recovery compared to that produced by Ne^+ . The activation energy for recovery of damage produced by energetic Ne ions, 0.06 eV, lies between the previously reported values of 0.02 eV for intracascade close-pair recombination and 0.31 eV for Kr^+ irradiation-enhanced defect mobility.

The stability of amorphous zircon against recrystallization was examined by irradiating the amorphous material with 300 keV electrons at 1000 K. The peak electron flux was about $7 \times 10^{17} \text{ e}^-/\text{cm}^2\text{-s}$. Recrystallization was not observed after 3000 s. The temperature was then increased to 1075 K, the highest temperature attainable in the Argonne HVEM, and irradiated for 3000 s with 300 keV electrons. Once again, the amorphous material did not recrystallize. This is consistent with previous findings [2] that thermal recrystallization of zircon occurs above 1300 K. However, Meldrum *et al.* [15] have reported beam-induced crystallization of ZrSiO_4 at 300 K following 200 keV electron irradiation at a current density of 90 A/cm^2 for 300 s. The zircon crystallized into an assemblage of crystalline ZrO_2 and amorphous SiO_2 . The current density used by Meldrum *et al.* was three orders of magnitude higher than that used in the present work ($\sim 0.09 \text{ A/cm}^2$) which may explain the differences in the results.

CONCLUSIONS

We have examined the amorphization of ZrSiO_4 by 800 and 900 keV electrons and 1 MeV Ne^+ ions. Zircon is only partially amorphized at 15 K by electron irradiation to 1.3 dpa. This may be due to inefficient displacement processes, and defect re-arrangement by ionization and sub-threshold energy transfers. The threshold energy for Zr displacement is greater than 41 eV. Irradiation with 1 MeV Ne^+ leads to complete amorphization and the critical temperature for the process was determined by curve fitting to be 1040 K. Electron irradiation of amorphous zircon at 1075 K did not lead to crystallization. Further experiments and computer simulations are needed to obtain a better understanding of single displacement and cascade damage events in zircon and other waste form materials.

ACKNOWLEDGEMENTS

This work is sponsored by the U. S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract DE-AC06-76RLO 1830. The authors are grateful to Edward A. Ryan, Stanley T. Ockers, Peter M. Baldo, and Anthony W. McCormick of the HVEM-Tandem Facility at Argonne National Laboratory for their kind assistance with the irradiations.

REFERENCES

1. R. C. Ewing, W. J. Weber, and F. W. Clinard, Jr., *Prog. Nucl. Energy*, **29**(2), p.63 (1995).
2. W. J. Weber, R. C. Ewing, and L. M. Wang, *J. Mater. Res.* **9**(3), p.688 (1994).
3. L. M. Wang and R. C. Ewing, *Nucl. Instrum. Methods* **B65**, p.324 (1992).
4. S. J. Zinkle, *J. Nucl. Mater.* **219**, p. 113 (1995).
5. S. J. Zinkle and L. L. Snead, *Nucl. Instrum. Methods* **B116**, p.92 (1996).
6. R. Devanathan, K. E. Sickafus, W. J. Weber, and M. Nastasi, *J. Nucl. Mater.* (1998) (in press).
7. L. A. Boatner and B. C. Sales, in *Radioactive Waste Forms for the Future*, edited by W. Lutze and R. C. Ewing (Elsevier, Amsterdam, 1988), p.495.
8. C. W. Allen, L. L. Funk, E. A. Ryan, and A. Taylor, *Nucl. Instrum. Methods* **B40-41**, p.553 (1988).
9. O. S. Oen, U. S. Atomic Energy Commission Report, ORNL-4897 (1973).
10. J. F. Ziegler, J. P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon, Oxford, 1985.
11. R. E. Williford, R. Devanathan, and W. J. Weber, *Nucl. Instrum. and Methods B* (1998) (in press).
12. J. C. Bourgoin and J. W. Corbett, *Rad. Effects* **36**, p.157 (1978).
13. H. Abe, C. Kinoshita, P. R. Okamoto, and L. E. Rehn, *J. Nucl. Mater.* **212-215**, p.298 (1994).
14. J. Koike, Ph. D. thesis, Northwestern University (1989).
15. A. Meldrum, L. A. Boatner, and R. C. Ewing, *J. Mater. Res.* **12**(7), p.1816 (1997).