

RECEIVED

CONF-970834--27

AUG 12 1997

ANL/MSD/CP--92835

OSTI

**HVEM-TANDEM AND EELS STUDY OF
RADIATION DAMAGE IN ZIRCONOLITE***

Katherine L. Smith¹, Nestor J. Zaluzec², and Gregory R. Lumpkin¹

¹Materials Division
Australia Nuclear Science and Technology
LMB 1, Menai 2234
Australia

²Materials Science Division
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439

March 1997

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, non exclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 

Submitted to the Microscopy & Microanalysis, Cleveland, Ohio, August 10-14, 1997.

*Work supported in part by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

DISCLAIMER

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

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.

HVEM-TANDEM AND EELS STUDY OF RADIATION DAMAGE IN ZIRCONOLITE

Katherine L. Smith*, Nestor J. Zaluzec#, Gregory R. Lumpkin*

*Materials Div., Aust. Nuclear Sci. & Tech. Org., LMB 1, Menai 2234, Australia

#Materials Science Div., Argonne National Laboratory, Argonne, IL 60439, USA

Zirconolite ($\text{CaZrTi}_2\text{O}_7$) is the major host phase for actinides in Synroc, a promising waste form for the immobilisation of high-level radioactive waste¹. The effect of radiation damage on the structure and durability of zirconolite are important to predictive modelling of zirconolite's behaviour in the repository environment and risk assessment.

In this study, radiation damage effects in zirconolite were investigated by irradiating samples with 1.5 MeV Kr^+ ions using the HVEM-Tandem at Argonne National Laboratory (ANL) and energy loss electron spectroscopy (EELS). The HVEM-Tandem consists of a modified AEI high voltage transmission electron microscope interfaced to a 2 MV tandem ion accelerator. EELS spectra were collected using a Philips 420 TEM, operated at 120 kV, fitted with a Gatan Model 607 Serial EELS. EELS data were recorded at resolutions of ~ 1.0 eV and at a dispersion of about ~ 0.25 eV.

Selected area diffraction patterns (SADs) of individual grains of various zirconolites were monitored as a function of dose to establish the critical dose for amorphisation (D_c). A representative sequence is shown in Figure 1 and results for all samples are summarised in Table 1. We found that i) D_c (zirconolite) is independent of the atomic weight of dopants in zirconolite and the mean atomic weight of the sample and that ii) the Bragg reflections in SAD patterns which persist to the highest doses are firstly those resulting from the fluorite sublattice and secondly the four (110)-type reflections which lie on the innermost of the two diffuse rings representative of amorphous zirconolite. Within experimental error, our D_c (undoped zirconolite) value agrees with that measured by Ewing and Wang² (4×10^{14} ions cm^{-2}) and disagrees with that measured by White et al.³ (1×10^{15} ions cm^{-2}). However on the basis of computer simulations of ion irradiation Smith et al.⁴ suggest that White et al.'s D_c (undoped zirconolite) value may be high. Assuming this to be true, it may also explain why White et al.'s data suggested that D_c (zirconolite) depended on the atomic weight of dopant species, which is in contradiction to the trend we observed.

The Ti L edges of undoped zirconolite before and after ion irradiation, and two Ti standards (TiO_2 and Ti_2O_3) are shown in Figure 2. Comparison of the zirconolite and Ti-oxide spectra suggests that Ti predominantly exhibits a valence of 4+ in both unirradiated and irradiated zirconolite and that the bond lengths in zirconolite are similar to those in TiO_2 . The electron energy loss near edge structure (ELNES) of the Ti L shell is consistent with the Ti changing from octahedral coordination to tetrahedral coordination⁵. As the irradiated material is amorphous at this point, analysis of the ELNES is one of the few ways that this change in the electronic structure can be determined at the local level. To quantitatively measure the changes due to irradiation, we fitted the zirconolite Ti-L spectra with four Lorentzians (in a similar manner to Morrison et al.⁶) and calculated L_2/L_3 and L^*_2/L^*_3 and $L_3 - L^*_3$ (Table 2). L_2/L_3 is the same before and after irradiation which suggests that radiation damage does not significantly affect the number of holes in the d-band (and hence valence). L^*_2/L^*_3 increases and $L_3 - L^*_3$ decreases after irradiation which suggests that radiation damage in zirconolite causes a distortion of the octahedral field around Ti atoms toward a tetrahedral configuration, consistent with previous X-ray absorption near edge structure and the extended x-ray absorption fine structure studies of natural zirconolite⁷.

References

- 1.) Ewing R.C., Weber W.J. and Clinard Jr. F.W., Progress in Nuclear Energy, 29(2) (1995) 63-127.
- 2.) Ewing R.C. and Wang L.M. (1992). Nuc. Instr. Meths. Phys. Res. B65, 319-323.
- 3.) White T.J., et al. (1995) Mat. Res. Soc. Symp. Proc. Vol. 353, 1413 - 1420.
- 4.) Smith K.L., et al. Submitted to J. Nuclear Materials.
- 5.) Brydson R., et al. (1987) Sol. State Comm., 64, 609-612.

6.) Morrison T.L. et al. (1985) Phys. Rev. B, 35(5), 3107-3111

7.) Lumpkin G.R. et al. J. Mater. Res., 1, (1986) 564-576

8.) The authors thank the HVEM-Tandem Facility staff at ANL for assistance during ion irradiations and partial support by the U.S. DOE, Basic Energy Sciences, under contract W-31-109-ENG-38. The authors thank Peter Fielding (UNE), Lou Vance (ANSTO) and Alan Cuelho (UTS) for making and kindly providing the samples.

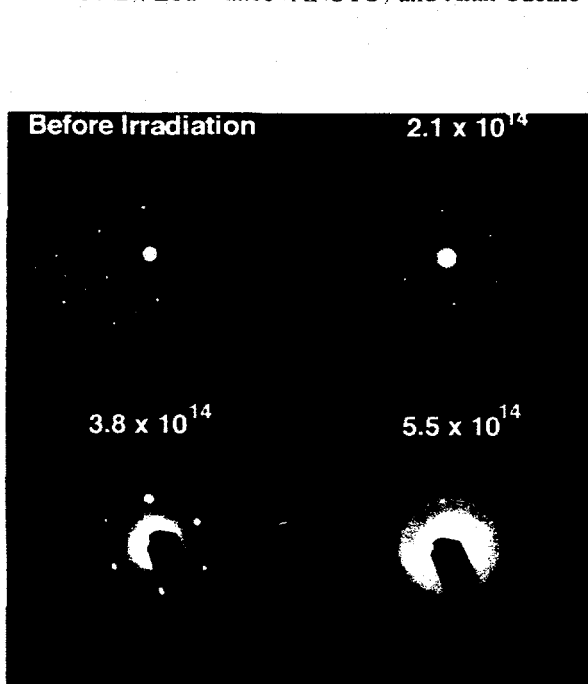


Figure 1. SADs of a zirconolite-2M grain viewed down [110] showing the effect of increasing dose. a) Before irradiation. After b) 0.85, c) 2.6, d) 3.0, e) 3.5, f) 4.7×10^{14} ions cm^{-2} .

Material

**Critical Dose
(ions cm^{-2})**

Undoped Zirconolite - 2M Mean At. No. = 14.6 $(\text{Ca}_{0.96}\text{Zr}_{0.01})_{0.97}\text{Zr}_{1.0}(\text{Ti}_{1.95}\text{Zr}_{0.05})_{2.0}\text{O}_{7.0}$	5.5×10^{14}
Nd + Zirconolite- 2M Mean At. No. = 15.2 $(\text{Ca}_{0.81}\text{Nd}_{0.17})_{0.98}\text{Zr}_{0.97}(\text{Ti}_{1.89}\text{Zr}_{0.11})_{2.0}\text{O}_{7.0}$	5.3×10^{14}
Nd + Zirconolite - 3T Mean At. No. = 15.3 $(\text{Ca}_{0.77}\text{Nd}_{0.19})_{0.96}\text{Zr}_{0.97}(\text{Ti}_{1.89}\text{Zr}_{0.11})_{2.0}\text{O}_{7.0}$	3.9×10^{14}
U + Zirconolite - 2M Mean At. No. = 14.9 $(\text{Ca}_{0.88}\text{U}_{0.08})_{0.96}(\text{Zr}_{0.99}\text{U}_{0.01})_{1.0}(\text{Ti}_{1.76}\text{Al}_{0.23}\text{Zn}_{0.01})_{2.0}\text{O}_{7.0}$	3.8×10^{14}
Th - Zirconolite 3T Mean At. No. = 16.5 $(\text{Ca}_{0.82}\text{Th}_{0.10})_{0.92}(\text{Zr}_{0.89}\text{Th}_{0.11})_{1.0}(\text{Ti}_{1.52}\text{Zr}_{0.48})_{2.0}\text{O}_{7.0}$	6.1×10^{14}

Table 1. Compositions, mean atomic numbers and critical amorphisation doses of samples.

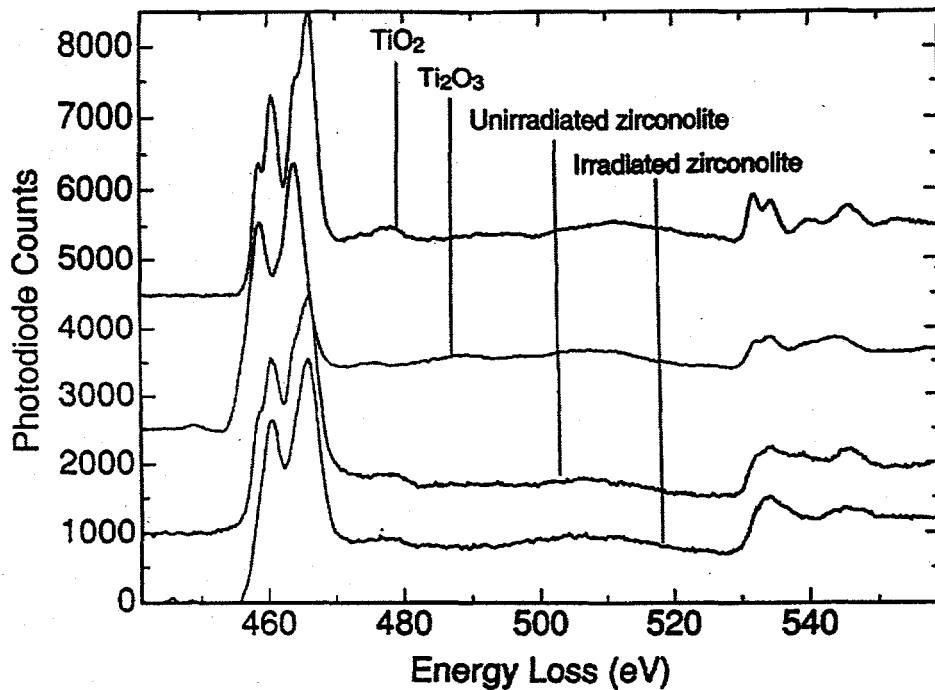


Figure 2. EELS spectra of TiO_2 , Ti_2O_3 , unirradiated and irradiated undoped zirconolite.