CONF-841157--94 .94

BOEING

DE85 014040

[PAPER PRESENTED AT SCIENTIFIC BASIS NUCLEAR WASTE MANAGEMENT, BOSTON, NOVEMBER 1984]

INVESTIGATION OF ANNEALED AND METAMICT PYROCHLORE MINERALS BY X-RAY ABSORPTION SPECTROSCOPY, R. B. Greegor, F. W. Lytle, The Boeing Company, Seattle, Washington 98124, R. C. Ewing, B. C. Chakoumakos, G. R. Lumpkin, University of New Mexico, Albuquerque, New Mexico 87131. FG06-84ER45121

Materials of the pyrochlore structure type exhibit a variety of interesting properties including phases capable of acting as hosts for actinides in radioactive wastes. Studies of curium doped gadolinium titanate phases ($Gd_2Ti_2O_7$) have been made which showed that the radiation damage ingrowth followed an exponential relationship of the form $\Delta V/V_0 = A[1-\exp(-BD)]$.[1] For the study reported here a series of synthetic pyrochlores were produced having the titanate phase with the general formula $(RE)_2Ti_2O_7$, RE = Er, Y_2, Gd_2, Dy, La. Additionally a set of metamict (radiation damaged) pyrochlores was examined in both a natural and post temperature annealed state.

Experiments were conducted on these samples using the Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) techniques. The EXAFS/XANES data were taken at the Stanford Synchrotron Radiation Laboratory (SSRL) on Beam Line IV-1 at a beam energy of 3 GeV and a current of ~ 80 mA. The measurements were made in a fluorescent mode using the Berkeley software.

The structural formula for an ideal pyrochlore is $A_2B_2X_6Y$, where A and B are metal cations and X and Y are anions. By removing combinations of A and Y ions a variety of defect structures can be produced. In the titanate pyrochlore phase the titanium oxygen octahedra share corners to form a network in which other cations (e.g., RE) occupy the holes. The Ti K-edge XANES for two pyrochlores (#186 Finland, #214 Canada) in natural and annealed condition are shown in figure 1. The feature on the steeply rising absorption edge just above the zero of energy is due to a transition having 1s-3d character. In perfect octahedral symmetry this transition is forbidden but as the inversion symmetry about the Ti is relaxed the transition becomes allowed.[2] In both the metamict samples shown in figure 1 this 1s-3d feature is more intense than the annealed counterpart, indicating greater asymmetry in the metamict Ti-O cage. Also the spectra of the annealed samples exhibit a finer detail of structure both in the 1s-3d like transition as well as in the features at the top of the absorption edge. The features at the top of the absorption edge are thought to be a mix of 1s-4p transitions and EXAFS multiple scattering.

The usable EXAFS range of data for the samples studied was shortened to approximately +300 eV above the Ti K-edge due to interference by the absorption edge of another element. The Fourier transforms of this range of data are shown in figure 2. All the transforms in figure 2 were made using the same background removal technique (3 region cubic spline), K range of data (~ 3.5 to 8.5 $Å^{-1}$) and weighting (K^3). Even though the K range of EXAFS data was limited the metamict and annealed specimens show important differences. Both metamict samples show a lower height of the first major peak (due to oxygen near neighbors) which is shifted to shorter Ti-O bond distances with respect to the annealed samples. This is indicative of a loss of and/or increasing disorder of the oxygen atoms about the Ti site resulting from alpha-recoil damage from the radioactive constitutents of the minerals.

In summary, these studies show that in pyrochlore structure types the Ti-O cage undergoes changes due to radiation damage. The individual Ti-O bonds become more disordered which leads to a loss of short and long range order and, ultimately, to expansion of the bulk material.

This research was supported by the Office of Basic Energy Science of the Department of Energy.

1. J. W. Wald and P. Offermann, "A Study of Radiation Effects in Curium-Doped $Gd_2Ti_2O_7$ (PYROCHLORE) and $CaZrTi_2O_7$ (ZIRCONOLITE)," Sci. Bas. Rad. Waste, Mgt.-V, Elsevier Pub. Co. 1982.

2. P. R. Sandstrom, F. W. Lytle, P. S. P. Wei, R. B. Greegor, J. Wong, and P. Schultz, "Coordination of Ti in TiO_2 Glass by X-ray Absorption Spectroscopy," J. Non. Cryst. Sol., 41, 201-207, 1980.

Figure 1. XANES

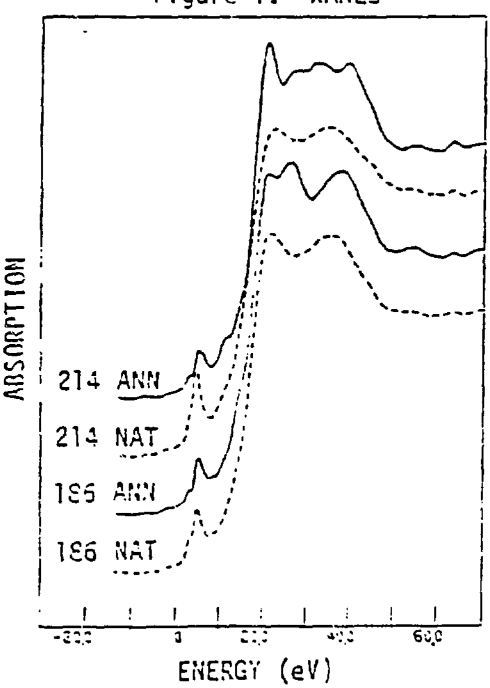
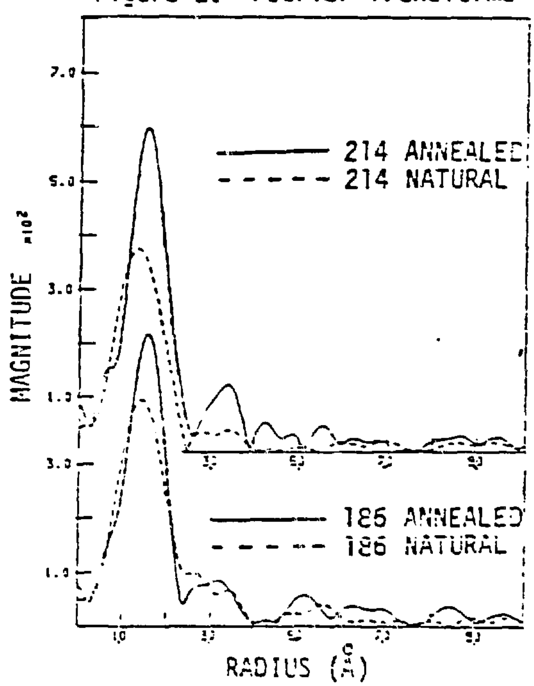


Figure 2. Fourier Transforms



DISCLAIMER