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RADIATION EFFECTS AND ANNEALING KINETICS IN
CRYSTALLINE SILICATES, PHOSPHATES AND COMPLEX
Nb-Ta-Ti OXIDES

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ABSTRACT

The interaction of heavy-particles (alpha-recoil nuclei, fission fragments and implanted ions) with ceramics is complex because these materials have a wide range of structure types, complex compositions and chemical bonding is variable (not only from structure type to structure type, but also within the structure). Radiation damage can produce diverse results, but most commonly, crystalline periodic materials become either polycrystalline or aperiodic (the metamict state). We have studied the transition from the crystalline to the aperiodic state in natural materials that have been damaged by alpha recoil nuclei in the uranium and thorium decay series and in synthetic, analogous structure types which have been amorphized by ion implantation. The transition from the crystalline to aperiodic state has been followed by detailed analysis of x-ray diffraction data, high resolution transmission electron microscopy, and extended x-ray absorption fine structure spectroscopy/x-ray absorption near edge spectroscopy. The use of these techniques with increasing dose provided data on an increasingly finer scale as the damage process progressed. Results of these studies are summarized in the attached publications.

INTRODUCTION

The interaction between heavy-particles (alpha-recoil nuclei, fission fragments and implanted ions) and ceramics (insulators) or non-metals is an inherently complex process because these materials have a wide range of structure-types, considerable compositional variations and the chemical bonding may range from ionic to covalent to near metallic. The resulting radiation damage is caused by ionization as well as displacement collisions. The transition from the periodic to aperiodic state is not only governed by the damage process and the accumulation of isolated defects and defect aggregates (collision cascades or thermal spikes), but also by the mechanisms and kinetics of annealing. Impurities, diffusion of defects and phase transformations may all affect the end-result of heavy-particle and ceramic interactions. Numerous reviews of radiation effects in ceramics are available (Wilks, 1968; Hobbs, 1979; Kelly, 1981; Matzke, 1982; Crawford and Slifkin, 1972; Weber, 1983; Clinard and Hobbs, 1986).

Two broad approaches have been used in the study these types of radiation effects:

(1) Mineralogists and materials scientists (Broegger, 1890; Pabst, 1952; Ewing, 1975; Ewing and Haaker, 1980; Lumpkin et al., 1986; Bhandari et al., 1971; Bursill and McLaren, 1966; Fleischer et al., 1964, 1965, 1975) have studied the effect of alpha recoil nuclei and fission fragments on natural materials. In the mineralogic literature, the resulting aperiodic structure is known as the metamict state. The materials typically have complex compositions, but with structure types that are important in a wide variety of technological applications (e.g. the pyroclore structure type which has diverse applications (Chakoumakos, 1984).) Doses may reach values as high as 10^{17} alpha-events/mg which is equivalent to >50 displacements per atom (dpa), and there is a regular change in the structural and physical properties of the material with increasing dose (e.g. Holland and Gottsried, 1955; Murakami et al., 1987). The study of natural materials is limited by the number and types of samples available and the fact that samples with doses in the narrow range of interest (e.g. the crystalline to metamict transformation) sometimes cannot be found. Alteration and thermal annealing complicate the interpretation of microstructures found in natural materials (Ewing and Headley, 1983).

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Headley et al., 1981).

(2) Radiation damage in materials analogous to those found in nature have been experimentally studied by heavy ion bombardment (Cartz and Fournelle, 1979; Cartz et al., 1980, 1981a, 1981b, Karioris et al., 1981), heavy ion implantation (Dran et al., 1980, 1981; Headley et al., 1982); actinide doping experiments (Chick et al., 1979; Weber et al., 1980; Wald and Offerman, 1982; Turcotte, 1981; Turcotte et al., 1982; Weber et al., 1982, 1985, 1986; Weber, 1982; Clinard, et al., 1983 1984a, 1984b), fission fragment damage (Vance and Boland, 1975; Vance and Pillay, 1980), fast neutron irradiation (Crawford and Wittels, 1956; Reeve and Woolfrey, 1980) and thermal neutrons, that is radiation effects due to (n, alpha) reactions (Vance et al., 1982). The experiments which most closely produce the effects observed in natural materials are actinide-doping experiments which reach doses as high as 10^{25} alpha-events/m³ (= 10^{15} alpha-events/mg). Comparisons with observations for natural materials have been made for zirconolite (Ewing and Headley, 1983), pyrochlore (Lumpkin et al., 1986; Lumpkin and Ewing, in press) and zircon (Headley et al., 1982; Headley and Ewing, in press; Murakami et al., in press). Radiation effects caused by fission fragments, fast neutrons and thermal neutrons have not provided credible simulations for alpha-recoil effects.

More recently there has been great interest in the formation of the aperiodic state in ceramics as a result of ion implantation (Naguib and Kelly, 1975; R. Kelly, 1981; Hj. Matzke, 1982; Arnold and Borders, 1984). This work is summarized by McHargue et al. (1986) in the proceedings volume of a Symposium on Irradiation Effects Associated with Ion Implantation (Andersen and Picraux, 1985). This work has, in general, been limited to relatively simple phases, such as alumina, silicon-carbide, titanium diboride and magnesia; but the complexities that govern the transition from the crystalline to amorphous state in natural materials are also found in these simpler compounds (Brimhall and Simonen, 1986). Ion implantation of these phases, however, shows very clearly the potential application of ion implantation combined with Rutherford backscattering-channeling experiments (McHargue et al., 1986) and analytical electron microscopy (Bentley, 1986) to more complex phases.

The basic approach of the research in this program has been to study

heavy particle interactions with ceramic materials that are a result of alpha-decay damage in naturally occurring materials. Preliminary work on the simulation of this type of damage using ion implantation techniques was completed in collaboration with R. B. Gregor (Boeing Research) and George Arnold (Sandia National Laboratories). The results of this research should be generally applicable to the understanding of the behavior of ceramics in radiation fields (e.g. fission reactors - nuclear fuels and SiC coatings; long-term stability of ceramic, nuclear waste forms; sensitivity of electrical and optical devices to radiation in space).

RESEARCH PROGRAM

This research program was initiated on August 1, 1983; and during the four year period in which the contract/grant will have been active, \$317,800 of support has been provided by the Division of Materials Sciences, Office of Basic Energy Sciences, DOE.

The grant has provided support for a post-doctoral fellow, Bryan Chakoumakos, a Ph.D. candidate, Gregory R. Lumpkin, and partial summer salary for Professor R. C. Ewing. Lumpkin will defend his Ph.D. dissertation during the Fall-1987 semester.

The primary purpose of the program was to develop an understanding of heavy particle radiation effects (e.g. alpha-recoil nuclei and fission fragments) on ceramic materials and thermal annealing mechanisms by which crystallinity might be restored. The study concentrated on naturally occurring materials which have been extensively damaged by the radioactive decay of constituent U/Th nuclides and their daughter products over periods of hundreds of millions of years. This provided a unique opportunity to study dose rate effects by comparing our results to those obtained by varied experimental procedures (e.g. neutron irradiations, ion implantation and actinide doping experiments).

The research focused on naturally occurring pyrochlore structure types, as these are abundant in nature, can have a wide range of compositions and exhibit a variety of potentially useful properties, which include catalysis, ferroelectricity, ferromagnetism, luminescence, ionic conductivity and are potential host phases for nuclear waste in ceramic materials (Chakoumakos, 1984). Other phases included in this period of study were zircon ($ZrSiO_4$), thorite ($ThSiO_4$), uraninite (UO_2), thorianite (ThO_2) and titanite ($CaTiOSiO_4$).

The analytical techniques used in the research program have involved: (1) detailed x-ray diffraction analysis **XRD**, (2) high resolution transmission electron microscopy **HRTEM**, (3) extended x-ray absorption fine structure **EXAFS** spectroscopy, (4) x-ray absorption near edge structure **XANES** spectroscopy, (5) complete electron microprobe analysis **EMPA**, (6) scanning electron microscopy **SEM**, (7) differential thermal analysis and

differential scanning calorimetry DTA/DSC, (8) thermal gravimetric analysis TGA, (9) instrumental neutron activation analysis INAA, and Fourier transform infrared spectroscopy FT-IR.

Much of this work was carried out in collaboration with individuals at other laboratories: Frank Clinard (LANL), Lynn Boatner (ORNL), T. J. Headley, G. W. Arnold and B. Doyle (SNL), Yehuda Eyal (Technion University, Haifa, Israel), R. B. Greegor and F. W. Lytle (Boeing Research), Takashi Murakami (Japanese Atomic Energy Research Institute, on leave to the University of New Mexico), F. C. Hawthorne (University of Manitoba, Winnipeg), B. H. W. S. de Jong (Corning Research), S. R. Garcia (LANL) and S. A. Howard (Univ. of Missouri-Rolla).

The results of these studies have appeared in a number of publications and abstracts (some of which are included as attachments) and are summarized below:

Journals and Conference Proceedings:

R. C. Ewing and T. J. Headley (1983)* Alpha-recoil damage in natural zirconolite ($\text{CaZrTi}_2\text{O}_7$). Journal of Nuclear Materials, 119, 102-109.

R. B. Greegor, F. W. Lytle, R. C. Ewing and R. F. Haaker (1984)* Ti-site geometry in metamict, annealed and synthetic complex Ti-Nb-Ta oxides by x-ray absorption spectroscopy. Nuclear Instruments and Methods in Physics Research, B1, 587-594.

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actinide host phases in radioactive waste forms. In Scientific Basis for Nuclear Waste Management VIII, C. M. Jantzen, J. A. Stone and R. C. Ewing, Eds., Materials Research Society, Pittsburgh, Pennsylvania, 647-654.

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R. B. Gregor, F. W. Lytle, B. C. Chakoumakos, G. R. Lumpkin and R. C. Ewing (1986) An investigation of uranium L-edges of metamict and annealed pyrochlore. In Scientific Basis for Nuclear Waste Management IX, L. Werme, Ed., Materials Research Society, Pittsburgh, Pennsylvania, 387-392.

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G. R. Lumpkin, B. C. Chakoumakos, R. C. Ewing (1986) Mineralogy and radiation effects of microlite from the Harding pegmatite, Taos County, New Mexico. American Mineralogist, 71, 569-588.

G. R. Lumpkin, E. M. Foltyn and R. C. Ewing (1986) Thermal recrystallization of alpha-recoil damaged minerals of the pyrochlore structure type. Journal of Nuclear Materials, 139, 113-120.

G. R. Lumpkin, R. C. Ewing, B. C. Chakoumakos, R. B. Gregor, F. W. Lytle, E. M. Foltyn, F. W. Clinard, Jr., L. A. Boatner and M. M. Abraham (1986) Alpha-recoil damage in zirconolite. Journal of Materials Research, 1, 564-576.

T. J. Headley and R. C. Ewing (1986) TEM study of the microstructure of metamict minerals. Microanalysis-1986, pp. 141-144.

G. R. Lumpkin and R. C. Ewing (1986) High resolution transmission electron microscopy of microlite from the Harding pegmatite, Taos County, New Mexico. Microanalysis-1986, pp. 145-148.

T. Murakami, B. C. Chakoumakos and R. C. Ewing (1986) X-ray powder diffraction analysis of alpha-event radiation damage in zircon. In Advances in Ceramics, vol. 20, D. E. Clark, W. B. White and A. J. Machiels, Eds., American Ceramic Society, Columbus, Ohio, pp. 745-753.

Y. Eyal, G. R. Lumpkin and R. C. Ewing (1987) Natural annealing of alpha-recoil damage in metamict thorite-group minerals. In Scientific Basis for Nuclear Waste Management X, J. K. Bates and W. B. Seefeldt, Eds., Materials Research Society, Pittsburgh, Pennsylvania, pp. 635-643.

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R. C. Ewing, B. C. Chakoumakos, R. G. Lumpkin, T. Murakami, R. B. Greegor and F. W. Lytle (in press) Metamict minerals: Natural analogues for

radiation damage effects in ceramic nuclear waste forms. Proceedings volume of the Radiation Effects in Insulators-4 meeting held in Lyon, France, July 6-10, 1987.

G. R. Lumpkin and B. C. Chakoumakos (submitted) Thorite group minerals from the Harding pegmatite, Taos County, New Mexico. In a special issue of Geochimica et Cosmochimica Acta.

Abstracts:

R. C. Ewing (1983)* Transition from the crystalline to the metamict state in zirkelite. Annual Meeting of the Geological Association of Canada and the Mineralogical Association of Canada, Victoria, p. A21.

R. B. Gregor, F. W. Lytle, R. C. Ewing and R. F. Haaker (1983)* Investigation of Ca in metamict minerals using x-ray absorption spectroscopy. Stanford Synchrotron Radiation Laboratory Users Group Meeting, Stanford, California.

R. B. Gregor, F. W. Lytle, R. C. Ewing and R. F. Haaker (1984) EXAFS studies of metamict materials. Invited paper at the Third International EXAFS Conference, Palo Alto, California.

R. C. Ewing, R. B. Gregor and F. W. Lytle (1984) TEM, EXAFS and XANES examination of metamict, orthorhombic, Nb-Ta-Ti oxides. 27th International Geological Congress, Moscow, vol. V, sections 10 & 11, pp. 41-42.

R. B. Gregor, F. W. Lytle, B. C. Chakoumakos, G. R. Lumpkin, R. C. Ewing, R. J. Livak and F. W. Clinard, Jr. (1985) EXAFS investigation of actinides in natural pyrochlore and synthetic zirconolite, Stanford Synchrotron Radiation Laboratory Users Group Meeting, Stanford, California, p. 23.

B. C. Chakoumakos and R. C. Ewing (1985) Anisotropic lattice deformation in crystals due to alpha-decay damage. Mineralogical Society of America and Geological Society of America Annual Meeting, Orlando, Florida, p. 542.

T. Murakami, B. C. Chakoumakos and R. C. Ewing (1986) X-ray diffraction analysis of alpha-event radiation damage in zircon. 88th Annual Meeting of the American Ceramic Society, Chicago, Illinois, p. 513.

B. C. Chakoumakos, G. R. Lumpkin and R. C. Ewing (1986) Synthesis and ion exchange study of alkali tantalate-tungstate, defect pyrochlores. Joint Annual Meeting of the Geological Association of Canada and the Mineralogical Association of Canada, Ottawa, Canada, p. 54.

G. R. Lumpkin and B. C. Chakoumakos (1986) Thorite group minerals from the Harding mine, Taos County, New Mexico. Joint Annual Meeting of the Geological Association of Canada and the Mineralogical Association of Canada, Ottawa, Canada, p. 96.

L. A. Groat, F. C. Hawthorne, M. Raudsepp, C. McCammon, R. Gaba, G. R. Lumpkin and R. C. Ewing (1986) Crystallinity/metamictization variations in natural titanites. Annual meeting of the American Crystallographic Association, McMaster University, Hamilton, Ontario, Canada.

T. Murakami, B. C. Chakoumakos and R. C. Ewing (1986) High resolution electron microscopy of crystalline, partially metamict and metamict zircons. 14th General Meeting of the International Mineralogical Association, Stanford, California.

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R. C. Ewing, B. C. Chakoumakos, G. R. Lumpkin, T. Murakami, R. B. Gregor and F. W. Lytle (1987) Metamict minerals: Natural analogues for radiation damage effects in ceramic nuclear waste forms. Radiation Effects in Insulators-4, Lyon, France.

*These papers were submitted or completed during the period of the grant, but a major portion of the work was completed prior to the initiation of the grant.

A major part of the results from this study period remain to be published, but they will be submitted for publication. The results include: (1) A detailed study of alteration effects observed in metamict pyrochlores from numerous localities throughout the world and a second paper on the crystal chemistry and radiation effects in natural pyrochlores. This work required the completion of approximately 300 electron microprobe analyses with accompanying SEM, XRD and selected HRTEM. (2) Cation exchange studies of synthetic, alkali tantalate-tungstate, defect pyrochlores. (3) Analysis of the considerable amount of EXAFS/XANES data which have been collected on natural and synthetic pyrochlores over the past three years. (4) XRD and HRTEM study of radiation damaged zircons and titanites. Particular attention will be paid to the analysis of alpha-recoil effects on the shape and intensity of diffraction maxima. The analysis of the titanite data will include single crystal x-ray diffraction structure refinements, infrared spectroscopy and Mossbauer spectroscopy. (5) Annealing study of UO_2 and ThO_2 .

FUTURE WORK

Although we have developed the techniques and assembled suites of samples to follow the alpha-decay induced phase transformation in detail, important questions remain to be answered. The most important issue requires an explanation for the persistent crystallinity of certain phases (e.g. uraninite, UO_2 , and monazite, $CePO_4$) despite high alpha-event doses (>100 dpa). It is clear from the work of Eyal and coworkers that the mean life of an alpha-recoil track varies significantly depending upon the matrix material. Thus, the annealing kinetics of alpha-decay damage are of paramount importance. Natural materials provide a unique opportunity to study such annealing under ambient conditions over extended periods of time (10^9 years). The annealing kinetics will vary not only as a function of the structure type, but also as a function of the composition (or chemical bonding) of the material.

In addition, we need to extend our examination of the damage process from the point where the material first reaches the saturation dose through the dose for which physical properties (e.g. density) continue to change. It is quite clear that the aperiodic structure can change as a function of increasing dose and in response to continuing alpha-decay damage. It is unlikely that suites of natural specimens will provide samples for this type of research, so we must look to ion implantation techniques to simulate the alpha-decay damage. This has the great advantage that a wider range of structure types (in various orientations) and compositions can be examined in materials simpler than natural systems and for which critical parameters (e.g. temperature) are controlled. The techniques used to characterize these thin, damaged layers are developed directly from the expertise gained in the ion beam modification and analysis of materials (see MRS Bulletin, vol. XII, no. 2, 1987).

Finally, of direct interest to those who propose various polyphase ceramics as potential nuclear waste forms, we must understand and be able to predict changes in physical properties with increasing alpha-decay dose. Over long periods of time, we must be able to predict the recrystallization and alteration products of metamict materials.

SUMMARY OF COLLABORATIVE INTERACTIONS

A number of collaborative efforts have resulted from this BES supported program. During the course of the work, the following collaborations occurred:

L. A. Boatner	ORNL SMAC/CRC	ion implantation and Rutherford backscattering-channeling studies (particularly zircon)
F. W. Clinard	LANL	comparison of radiation effects in actinide-doped and natural thorites (ThSiO_4); EXAFS/XANES on actinide phases
R. B. Gregor & F. W. Lytle	Boeing Res.	EXAFS/XANES
G. W. Arnold & B. Doyle	SNL	ion implantation and Rutherford backscattering-channeling studies
Y. Eyal	Technion Un. Israel	leaching studies of natural phases to determine alpha-recoil track annealing times
T. Murakami	JAERI	HRTEM and XRD study of metamict zircons
F. C. Hawthorne	Un. of Manitoba	collaborative study on natural titanites
B.H.W.S. de Jong	Corning Research	^{29}Si MASNMR of metamict zircon
S. R. Garcia	LANL	INAA for U and Th in natural samples
S. A. Howard	Un. of Missouri- Rolla	IRD line-broadening studies

In addition to these specific collaborations, the University of New Mexico group has participated in the Working Group on Radiation Effects. This group of BES-funded investigators has met twice during the past three years (Santa Fe, New Mexico in March of 1984, and Bryson City, North Carolina in August, 1985). A direct result of the meetings of this working group was a paper on radiation effects in zirconolite which was published in the Journal of Materials Research.

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20

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