OSTI

These pages replace the first 5 pages (before the table of content) and pages 38-41 of our original renewal proposal for #DE-FG03-93ER45498

DOE/ER/45498--T2

GRANT #DE-FG03-93ER45498

PARTICLE-INDUCED AMORPHOUS COMPLEX CERAMIC

Rodney C. Ewing
Lu-Min Wang
Department of Earth & Planetary Sciences
University of New Mexico
Albuquerque, New Mexico 87131

February 16, 1996 (revised)

Amount requested:	\$77,937.00 (first year)
	\$238,519.00 (three years)
Requested starting date:	August 1, 1996
Proposed duration:	3 years
Type of business:	Educational
Principal investigators:	R. C. Ewing (505) 277 4163
	L.M. Wang (505) 277 7536
Business contact:	Marla F. Wonn (505) 277 2968
Date of submission:	January 23, 1996

This proposal may be subjected to external review.

Rodney C. Ewing
Regents' Professor

Lu-Min Wang
Research Associate Professor

Office of Research
Administration

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

62
I/93/96
JPC

PRESENT RESEARCH PROGRAM (1993-1996)

The presently funded three-year research program, supported by the Division of Materials Sciences of the Office of Basic Energy Sciences, was initiated on August 1, 1993; during the period in which the grant will have been active, \$249,561 of support have been provided to date with an additional \$79,723 to be spent during the third, final year (ending July 30, 1996). The primary purpose of the program is to develop an understanding of heavy-particle radiation effects -- α -recoil nuclei, fission fragments, ion-irradiations -- on ceramic materials and the thermal annealing mechanisms by which crystallinity might be restored. During the past two years, we have completed major studies on zircon (ZrSiO_4), olivine (Mg_2SiO_4 and ten other compositions), spinel (MgAl_2O_4 and four other compositions), and silica polymorphs (quartz, coesite and stishovite), as well as berlinite (AlPO_4) which is isomorphous with quartz.

The work on zircon was particularly important in that we established the efficacy of actinide-doping and heavy-ion beam irradiations as techniques to simulate long-term damage (over hundreds of millions of years) of complex ceramics (Weber et al., 1994). Zircon is probably the most useful naturally occurring phase for such studies. Based on this fundamental research program, we (Ewing et al., 1995) proposed the use of zircon as a host phase of the immobilization of the plutonium that results from the dismantlement of nuclear weapons. The University of New Mexico and PNNL have applied for a patent based on this idea. This proposal generated considerable interest, particularly abroad, where zircon and monazite (CePO_4) are candidate materials for inert fuel matrices for the "burning" of actinides separated during reprocessing of nuclear fuel. Our proposal was cited by BES/DOE as having a "Significant Implication for Department of Energy Related Technologies" in the Metallurgy and Ceramics category of the 1995 Materials Science Research Competition. It was gratifying to see basic research find an important application. We are presently pursuing the applied aspects of this work with support from Los Alamos National Laboratory. The basic research will continue but with a focus on monazite, probably the only other naturally occurring phase for which such study is practical. This will be the basis of the Ph.D. dissertation of Al Meldrum.

The work on olivine (HCP derivative structure) and spinel (CCP structure) was in large part completed and a major manuscript has been prepared (Wang et al., submitted). Preliminary results were summarized in Ewing et al. (1995). The very close structural relation between these phases, as well as the wide compositional variety of these phases, allowed us to examine structural and bonding controls on radiation-induced amorphization. One important finding of this study is that the dose required for amorphization of a particular crystal structure may vary greatly with the changing composition. For compositions with the same structure-type, parameters such as bond ionicity, melting temperature, Debye temperature and free energy of formation may all be used as criteria for predicting the relative susceptibility for amorphization to a great extent. However, these criteria fail when comparing different structure-types. In close collaboration with LANL, we have made the observation that MgAl_2O_4 can be amorphized at low temperatures by a disordering process (Bordes et al., 1995b) after very high doses. The most interesting and important result was that irradiation "resistant" structure types, such as spinel, can be easily amorphized by changing the composition. This was determined on an Fe-Si-spinel which

*Renewed proposal
removed & filed
separately.*

is thermodynamically unstable under normal pressure condition (Wang et al., 1995). The results mean that thermodynamic stability, bonding type and strength, in addition to topological stability, play important roles in determining the "irradiation resistance" of a material. The success of this approach will serve as a basis for the systematic study of silicates, phosphates and vanadates of the tetragonal zircon and the monoclinic monazite structure-types by Al Meldrum. Universal criteria for amorphization, which may be a combination of several material parameters, can only be determined when more data from this type of systematic study become available.

In addition to these major studies, we continued work on a variety of complex ceramics: 1.) pyrochlores (Lumpkin and Ewing, 1995); 2.) zirconolite (Farges et al., 1993; White et al., 1995); samarskite (Warner and Ewing, 1993); vesuvianite (Eby et al., 1993); berlinite (Bordes and Ewing, 1995); monazite (Meldrum et al., 1995); TI-type high temperature superconductors (Wang et al., 1994b; Newcomer et al., submitted). Additionally, we have sought to apply our results to other fields, such as geochronology (Onstott et al., 1995) and nuclear waste disposal (Weber and Ewing, 1995). Some of these results are high-lighted in this proposal, and selected publications are included in the Appendix.

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 spectroscopy, EXAFS, (4) x-ray absorption near edge structure, XANES, (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 (10) *in situ* TEM analysis during ion irradiations. It is important to note that the HVEM- and IVEM- Tandem Facility at Argonne National Laboratory has become an essential facility for our research program.

As part of this research program, Professor Ewing was a co-organizer of the Materials Research Society symposium, "Scientific Basis for Nuclear Waste Management XVIII", held in Kyoto, Japan in October of 1994 and co-organizer of the symposium "Radiation Effects in Ceramics" of the Minerals Metals Materials Society Meeting held in Las Vegas in February of 1995. In 1996, Professor Ewing will co-chair (with W.J. Weber) a BES sponsored workshop on radiation effects in glasses to be held in Santa Fe in February and he is a member of the program committee for IBMM-96 to be held in Albuquerque in September.

Much of the research during the past two and one half years was carried out in collaboration with individuals at other universities and laboratories: G. W. Arnold (SNL), C.W. Allen and R.C. Birtcher (ANL), Gordon Brown and François Farges (Stanford University), Maryellen Cameron (NSF), Frank Clinard (LANL), R. Doremus (RPI), Yehuda Eyal (Technion University, Haifa, Israel), F.C. Hawthorne (University of Manitoba, Winnipeg), L.W. Hobbs (MIT), B. Morosin and J.C. Barbour (SNL), Takashi Murakami (Mineralogical Institute, University of Tokyo), T.C. Onstott and Alexandra Navrotsky (Princeton University), K.C. Sickafus (LANL), T.J. White (University of South Australia) and W.J. Weber (PNNL).

The results of these studies have appeared in a number of publications and abstracts and are summarized below (student authors are indicated by an asterisk; selected papers included in the Appendix are indicated by "A").

Journal Articles (1993 - present):

Julie K. Warner* and R.C. Ewing (1993) Crystal chemistry of samarskite. *American Mineralogist*, vol. 78, pp. 419-424.

R.K. Eby*, J. Janeczek, R.C. Ewing, T.S. Ercit, L.A. Groat, B.C. Chakoumakos, F.C. Hawthorne and G.R. Rossman (1993) Metamict and chemically altered vesuvianite. *Canadian Mineralogist*, vol. 31, part 2, pp. 357-369.

M.L. Miller* and R.C. Ewing (1993) Image simulation of partially amorphous materials. *Ultramicroscopy*, vol. 48, pp. 203-237.

L.M. Wang, R.C. Birtcher and R.C. Ewing (1993) Ion irradiation-induced nano-scale polycrystallization of intermetallic and ceramic materials. *Nuclear Instruments and Methods for Physics Research, B: Beam Interactions with Materials and Atoms*, vol. B80/81, pp. 1109-1113.

^A F. Farges, R.C. Ewing and G.E. Brown (1993) The structure of aperiodic, metamict, $(\text{Ca,Th})_2\text{Zr}_2\text{Ti}_4\text{O}_{14}$ (zirconolite): An EXAFS study of the Zr, Th, and U sites. *Journal of Materials Research*, vol. 8, no. 8, pp. 1983 - 1995.

L.M. Wang, M.L. Miller*, and R.C. Ewing (1993) HRTEM study of displacement cascades in krypton ion irradiated silicate -- olivine. *Ultramicroscopy*, vol. 51, pp. 339-347. Presented at the "Frontiers of Electron Microscopy in Materials Science" conference, Oakland, CA, 1992.

^A W.J. Weber, R.C. Ewing, and Lu-Min Wang (1994) The radiation-induced crystalline-to-amorphous transition in zircon. *Journal of Materials Research*, vol. 9, no. 3, pp. 688 - 698.

^A R.C. Ewing (1994) The metamict state: 1993 - The Centennial. *Nuclear Instruments and Methods in Physics Research*, vol. B91, 22-29.

^A L.W. Hobbs, F.W. Clinard, Jr., S.J. Zinkle, R.C. Ewing (1994) Radiation effects in ceramics. *Journal of Nuclear Materials*, vol. 216, 291-321 (cover article, only the first page is attached because of its length).

^A S. Ellsworth*, A. Navrotsky, and R.C. Ewing (1994) Energetics of radiation damage in natural zircon (ZrSiO_4). *Physics and Chemistry of Minerals*, vol. 21, 140-149.

N. Bordes, K.E. Sickafus, E.A. Cooper and R.C. Ewing (1995) Structural damage in spinel after ion irradiation. *Journal of Nuclear Materials*, vol. 225, pp. 318-323.

^A R.C. Ewing, W.J. Weber and F.W. Clinard, Jr. (1995) Radiation effects in nuclear waste forms. *Progress in Nuclear Energy: An International Review Journal*, vol. 29, no. 2, pages 63-127 (only the first page is attached because of its length).

R.C. Ewing, W. Lutze and W.J. Weber (1995) Zircon: A host-phase for the disposal of weapons plutonium. *Journal of Materials Research*, vol. 10, no. 2, pages 243-246.

T.C. Onstott, M.L. Miller, R.C. Ewing, G.W. Arnold and D.S. Walsh (1995) Recoil refinements: Implications for the $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique. *Geochimica et Cosmochimica Acta*, vol. 59, no. 9, pp. 1821-1834.

G.R. Lumpkin* and R.C. Ewing (1995) Geochemical alteration of pyrochlore group minerals: Pyrochlore subgroup. *American Mineralogist*, vol. 80, 732-743.

^A N. Bordes, L.M. Wang, R.C. Ewing and K.E. Sickafus (1995) Ion-beam induced disordering and onset of amorphization in spinel by defect accumulation. *Journal of Materials Research*, vol. 10, no. 4, pages 981-985.

L.M. Wang, W.L. Gong, N. Bordes and R.C. Ewing (1996, in press) A comparative study on ion beam induced effects in spinel structure-types. *Nuclear Instruments and Methods in Physics Research B*.

A.N. Sreeram*, L.W. Hobbs, N. Bordes and R.C. Ewing (1996, in press) Irradiation-induced amorphization of AlPO_4 . *Nuclear Instruments and Methods in Physics Research*.

A. Meldrum*, L.M. Wang and R.C. Ewing (1996, in press) Ion beam induced amorphization of monazite. *Nuclear Instruments and Methods in Physics Research*.

G.R. Lumpkin* and R.C. Ewing (1996, in press) Geochemical alteration of pyrochlore group minerals: Betafite subgroup. *American Mineralogist*.

^A W.L. Gong, L.M. Wang, R.C. Ewing and Y. Fei (1996, in press) Surface and grain boundary amorphization: Thermodynamic melting of coesite below the glass transition temperature. *Physical Review B*.

P.P. Newcomer*, L.M. Wang, J.C. Barbour, R.C. Ewing, M.L. Miller and B. Morosin (submitted) Temperature dependent microstructural modification in ion irradiated Ti -type high temperature superconductors. *Physica C, Superconductivity*.

Symposia and Conference Proceedings:

R.C. Ewing (1993) The long-term performance of nuclear waste forms: The use of natural materials - Three case studies. Scientific Basis for Nuclear Waste Management XVI. C.G. Interrante and R.T. Pabalan, Eds., Proceedings of the MRS, vol. 294, Pittsburgh, Pennsylvania, pp. 559 - 568.

L.M. Wang, R.C. Ewing, W.J. Weber and R.K. Eby* (1993) Temperature and ion-mass dependence of amorphization dose for ion beam irradiated zircon (ZrSiO_4). Beam-Solid Interactions: Fundamentals and Applications. M. Nastasi, L.R. Harriott, N. Herbots and R.S. Averback, Eds., Proceedings of the Materials Research Society, vol. 279, Pittsburgh, Pennsylvania, pp. 451-456.

Y. Eyal and R.C. Ewing (1993) Impact of alpha-recoil damage on dissolution of thoriated glass. Proceedings of the International Conference on Nuclear Waste Management and Environmental Remediation, Vol. 1, Low and Intermediate Level Radioactive Waste

Management, Eds., D. Alexandre, R. Baker, R. Kohout and J. Marek, sponsored by the American Society of Mechanical Engineers, Prague, Czech Republic, September 5 - 11, pp. 191 - 196.

L.M. Wang, M. Cameron, W.J. Weber, K.D. Crowley and R.C. Ewing (1994) In situ TEM observation of radiation induced amorphization of crystals with apatite structure. Hydroxyapatite and Related Materials. P. W. Brown and B. Constantze, Eds. (CRC Press) pp. 243-249.

Rebecca X. Ai, Nicole Bordes, E.A. Cooper, K.E. Sickafus, R.C. Ewing, and Michael Nastasi (1994) Dislocation loops in spinel crystals irradiated successively with deep and shallow ion implants. Materials Synthesis and Processing Using Ion Beams. R.J. Culbertson, O.W. Holland, K.S. Jones and Karen Maex, Eds., Proceedings of the Materials Research Society, vol. 316, pp. 147-151.

^A L.M. Wang, W.L. Gong and R.C. Ewing (1994) Amorphization and dynamic recovery of A_2BO_4 structure types during 1.5 MeV krypton ion-beam irradiation. Materials Synthesis and Processing Using Ion Beams. R.J. Culbertson, O.W. Holland, K.S. Jones and Karen Maex, Eds., Proceedings of the Materials Research Society, vol. 316, pp. 247-252.

^A L.M. Wang, P.P. Newcomer*, R.C. Ewing and B. Morosin (1994) Quantitative analysis of displacement cascade damage in ion irradiated $TiBa_2CaCu_2O_7$ superconductor by digital HRTEM. Proceedings of the 13th International Congress on Electron Microscopy, B. Jouffrey and C. Colliex, Eds. (les éditions de physique, Les Ulis, France) pp. 957-958.

^A R.C. Ewing, L.M. Wang, W.J. Weber (1995) Amorphization of complex ceramics by heavy-particle irradiations. Microstructure of Irradiated Materials. I.M. Robertson, L.E. Rehn, S.J. Zinkle and W.J. Phythian, Eds., Proceedings of the Materials Research Society, vol. 373, pp. 347-358.

N. Bordes and R.C. Ewing (1995) Application of channeling techniques and high resolution transmission electron microscopy to ion-beam damaged zircon. Microstructure of Irradiated Materials. I.M. Robertson, L.E. Rehn, S.J. Zinkle and W.J. Phythian, Eds., Proceedings of the Materials Research Society, vol. 373, pp. 371-376.

N. Bordes and R.C. Ewing (1995) Ion-beam and electron-beam induced amorphization of berlinite ($AlPO_4$). Microstructure of Irradiated Materials. I.M. Robertson, L.E. Rehn, S.J. Zinkle and W.J. Phythian, Eds., Proceedings of the Materials Research Society, vol. 373, pp. 395-400.

^A L.M. Wang, W.L. Gong, N. Bordes, R.C. Ewing and Y. Fei (1995) Effects of ion dose and irradiation temperature on the microstructure of three spinel compositions. Microstructure of Irradiated Materials. I.M. Robertson, L.E. Rehn, S.J. Zinkle and W.J. Phythian, Eds., Proceedings of the Materials Research Society, vol. 373, pp. 407-412.

W.J. Weber and R.C. Ewing (1995) Radiation effects issues related to U.S. DOE site remediation and nuclear waste storage. Scientific Basis for Nuclear Waste Management XVIII, T. Murakami and R.C. Ewing, Eds. Proceedings of the Materials Research Society, vol. 353, pp. 1389-1396.

T.J. White, R.C. Ewing, L.M. Wang, J.S. Forrester and C. Montross (1995) Temperature dependence of amorphization for zirconite and perovskite irradiated with 1 MeV krypton

ions. Scientific Basis for Nuclear Waste Management XVIII, T. Murakami and R.C. Ewing, Eds. Proceedings of the Materials Research Society, vol. 353, pp. 1413-1420.

^A P.P. Newcomer*, L.M. Wang, M.L. Miller and R.C. Ewing (1995), Crystallization of nano-size thallous oxide during ion irradiation of Tl-Ba-Ca-Cu-O high temperature superconductors. JMSA Proceedings: Microscopy and Microanalysis 1995, G.W. Bailey, M.H. Ellisman, R.A. Hennigar and N.J. Zaluzec, Eds. Jones & Begell Publishing, New York, pp. 214-215.

^A L.M. Wang, R.C. Ewing and W.J. Weber, HRTEM Study of ion beam irradiation induced amorphization in ceramic materials, JMSA Proceedings: Microscopy and Microanalysis 1995, G.W. Bailey, M.H. Ellisman, R.A. Hennigar and N.J. Zaluzec, Eds. Jones & Begell Publishing, New York, pp. 360-361.

R.C. Ewing, W.J. Weber and W. Lutze (1996, in press) Crystalline ceramics: Waste forms for the disposal of weapons plutonium. NATO Workshop Proceedings, E. Merz, Editor, Disposal of Ex-Weapons Plutonium as Waste, Kluwer Academic Publishers, Dordrecht, The Netherlands.

L.M. Wang, W.L. Gong, R.C. Ewing and W.J. Weber (1996, in press) On the roles of interface and temperature on solid state amorphization. Thermodynamics and Kinetics of Phase Transformation, J.S. Im, B. Park, A.L. Greer and G.B. Stephenson, Eds. Proceedings of the Materials Research Society.

W.J. Weber, R.C. Ewing and W. Lutze (1996, in press) Performance assessment of zircon as a waste form for excess weapons plutonium under deep borehole burial. Scientific Basis for Nuclear Waste Management XIX, W.M. Murphy and D.A. Knecht, Eds. Proceedings of the Materials Research Society.

Book Chapters

R.C. Ewing and J. Akimoto (1995) "The Metamict State" in Higher Mineralogy. A.S. Marfunin, Ed., Springer-Verlag, Germany.

Volumes or Books Edited

Rodney C. Ewing and W. Lutze [guest editors] (1994) Special Issue on Nuclear Waste Disposal. Materials Research Society Bulletin, vol. XIX, no. 12, 72 pages.

T. Murakami and R.C. Ewing [co-editors] (1995) Scientific Basis for Nuclear Waste Management XVIII, Parts 1 and 2, Proceedings of the Materials Research Society, Pittsburgh, Pennsylvania, vol. 353, 1,455 pages.

Abstracts

(over 50 abstracts were published during the period 1993 to present)

Invited Presentations

- "The Future of Mineralogy: The Role of Materials Science" (R.C. Ewing): Aarhus University, Denmark, March 1, 1993.
- "Radiation Effects in Minerals and Ceramics: The Centennial" (R.C. Ewing): Aarhus University, Denmark, March 3, 1993.
- "Radiation-Induced Amorphization of Materials" (R.C. Ewing): Princeton Materials Institute symposium on "Materials Under Extreme Conditions", Princeton University, May 17, 1993.
- "Radiation Effects in Nuclear Waste Forms" (R.C. Ewing): International Summer School on the Fundamentals of Radiation Damage, University of Illinois at Urbana Champaign, August 4, 1993.
- "The Metamict State: 1993 - The Centennial" (R.C. Ewing): Radiation Effects in Insulators - 7, Nagoya, Japan, September 6, 1993.
- "Radiation-Induced Amorphization of Zircon" (R.C. Ewing): Department of Geological Sciences, University of Texas, Austin, October 14, 1993.
- "Crystalline Ceramics: Future Uses as Radioactive Waste Forms: A Review and Comparison" (R.C. Ewing): symposium on Emerging Technologies in Hazardous Waste Management VI sponsored by the American Chemical Society, I&EC Division, Atlanta, Georgia, September 20, 1994.
- "Radioactive Waste Forms: A Review and Comparison" (R.C. Ewing): seminar on Radioactive Waste Management Practices and Issues in Developing Countries sponsored by the International Atomic Energy Agency, Beijing, China, October 13, 1994.
- "The Development of Ceramic Nuclear Waste Forms" (R.C. Ewing): seminar presented at the Beijing Institute for Nuclear Engineering, Beijing, China, October 17, 1994.
- "Amorphization of Complex Ceramics by Heavy-Particle Irradiations" (R.C. Ewing): symposium on the Microstructure of Irradiated Materials, MRS, Boston, MA, November 30, 1994.
- "Amorphization of Coesite Induced by Electron- and Ion-Beam Irradiation" (W.L. Gong): symposium on Radiation Effects in Nonmetals, TMS 1996 Annual Meeting, Las Vegas, NV, February 13, 1995.
- "Digital Analysis of HRTEM Images of Ion-Beam Damaged Ceramic Materials" (L.M. Wang): symposium on Radiation Effects in Nonmetals, TMS 1996 Annual Meeting, Las Vegas, NV, February 13, 1995.
- "Zircon: A Host-Phase for the Disposal of Weapons Plutonium" (R.C. Ewing): workshop on the Elimination of Weapons Plutonium, sponsored by the German-American Academic Council Foundation and the U.S. National Academy of Sciences, Bonn, Germany, March 22, 1995.

- "Radiation-Induced Amorphization in Ceramics" (R.C. Ewing): research conference on Kinetic Processes in Minerals and Ceramics, sponsored by the European Research Conferences, Blankenberge, Belgium, March 25, 1995.
- "Zircon: A Host-Phase for the Disposal of Weapons Plutonium" (R.C. Ewing): seminar at Plutonium Facility, Los Alamos National Laboratory, April 12, 1995.
- "Crystalline Ceramics: Alternative Waste Forms for the Disposal of Plutonium" (R.C. Ewing): NATO Advanced Research Workshop on "Disposal of Weapons Plutonium - Approaches and Prospects", St. Petersburg, Russia, May 15, 1995.
- "Radiation-Induced Amorphization in Nuclear Waste Forms" (R.C. Ewing): Annual meeting of the American Crystallographic Association, Montréal, Canada, March 29, 1995.
- "Radiation Effects in Nuclear Waste Forms" (R.C. Ewing): IVEM Workshop on Major Issues in Irradiation Effects Research organized by the Electron Microscopy Center for Materials Science at Argonne National Laboratory, October 25, 1995.
- "Where Is the Materials Science in Radioactive Waste Disposal?" (R.C. Ewing): Symposium X, "Frontiers in Materials Science", Fall meeting, Materials Research Society, Boston, MA, November 29, 1995.

PROPOSED RESEARCH PROGRAM (1996-1999)

FUNDAMENTAL ISSUES

The interactions between heavy particles (alpha-recoil, fission fragments and implanted ions) and complex ceramics are more complex than in metals, semiconductors and intermetallics because of variations in structure-type, complex compositions and mixed bond type. In addition, ceramic materials are often structurally anisotropic so that damage effects may be channeled and are certainly orientation dependent. Four fundamental questions arise in such a research program:

◇ What is the process, at the atomic level, by which a ceramic material is transformed from the periodic, crystalline state to the aperiodic, amorphous, state? The process must inevitably involve the formation of isolated defects and defect aggregates (e.g., collision cascades) followed by relaxation and recovery. In the case of alpha-decay damage, the defects include interstitials that result from the alpha particle and "aggregates" caused by the alpha-recoil nucleus. Migration and recombination of point defects in complex structures are expected to be more difficult than in simple structures, because of the existence of many unique structural sites which make replacement events less likely to occur. The identification of the types of defects, the kinetics of defect mobility, the effect of defect overlap, and the annealing kinetics of the defects -- all affect the process by which damage ingrowth develops and affect the change in the physical and structural properties of the material with increasing dose. The temperature dependence of these processes is critical to the final state of the irradiated material.

◇ What is the structure (both short-range for nearest-neighbor coordination geometries and long-range at the molecular component scale) of the final damaged state? F. C. Hawthorne (1985) has demonstrated that crystalline structures can be characterized by the polymerization of "fundamental building blocks." An important contribution to the understanding of radiation effects would be the determination of whether these "fundamental building blocks" persist from the crystalline state to the fully damaged aperiodic state. HRTEM of microlite (Lumpkin and Ewing, 1988a) and zircon (Murakami et al., 1991) and EXAFS of zirconolite (Farges et al., 1993) suggest that these structural elements persist in highly damaged materials. There is also the question of whether the aperiodic state goes through further transformations with increasing dose beyond the "apparent" saturation dose (i.e., complete loss of crystallinity).

◇ What are the mechanisms and kinetics of annealing for point and aggregate defects? To what extent do the kinetics of the annealing or relaxation processes determine whether some phases continue to exist in the crystalline state (e.g., UO_2 despite high doses), or whether they become polycrystalline or aperiodic? Recent work at UNM by Newcomer et al. (submitted) has correlated changes in thermal conductivity with the formation of either aperiodic or crystalline domains within cascades. What are the structural and compositional controls on the annealing process? Can we use a basic or derived material parameters as criteria for predicting the susceptibility of materials to amorphization?

◊ What are the products of recrystallization of the final damaged state? From previous studies (e.g., titanite, Hawthorne et al., 1991), it is clear that the proportion of damaged material can have a profound effect on the results of recrystallization experiments.

These are the same fundamental questions that we posed in our proposal three years ago. Although we have made important progress in answering each of these questions, these issues still remain the principal guides to our proposed future work. A much larger data base is required to answer these questions and to test and extend the existing models.

FUNDAMENTAL APPROACHES

The fundamental approach in our previous work was to focus on naturally occurring phases (e.g., zircon, titanite, pyrochlore and uraninite) and to use a combination of techniques (mainly detailed x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and extended x-ray absorption spectroscopy (EXAFS)/x-ray absorption near-edge spectroscopy (XANES) to follow the transition from the periodic to the aperiodic state. The progression of techniques provided a view on a finer and finer scale of the damage accumulation process. This limited most of our work to an examination of radiation effects in natural phases caused by α -particle and α -recoil nuclei in the uranium and thorium decay series. We believe that now, with the important exception of monazite (CePO_4), we have exhausted the important work that can be completed on natural phases.

During the past three years, we have used the HVEM-Tandem Facility at Argonne National Laboratory to study the temperature dependence of the critical amorphization doses of many compositions with specific structure types (olivine, spinel and zircon) under various ion beams. This approach allowed us to expand our study to include structure types which do not contain U and Th in their naturally occurring, analogous structure type.

We propose to continue our studies of ion beam irradiation on more fundamental structure types of various compositions (listed in the next section) concentrating on the crystalline-to-amorphous (c-a) transformation under well controlled experimental conditions. The recent addition of an intermediate voltage electron microscope (IVEM) with a higher spatial resolution to the HVEM-Tandem Facility at Argonne National Laboratory (IVEM-Tandem) has provided us with a great new tool to follow the microstructure change at a much smaller scale *in situ* during ion irradiation. Although the resolution of the IVEM is still limited as compared to most high resolution TEMs of the same voltage because of the larger pole-piece gap required for the ion interface, it is adequate for lattice imaging of many of the complex ceramic materials proposed in our study, which generally have much larger unit cell parameters than metals and semiconductors. The lattice imaging is especially important as it allows us to study the initial stages of the amorphization process, the role of interfaces and the morphology of surviving displacement cascades. The old HVEM-Tandem system is still very useful to our studies because of its wide temperature range (25 K to 1000 K) and its high energy electron source (up to 1.2 MeV). The wide temperature range is needed for determining the temperature dependence of critical amorphization doses (D_c) and the critical amorphization temperature. From the D_c -T curve, an activation energy associated with a dynamic defect annealing process can be determined based on a model developed by Weber et al. (1994).

The high energy electron source is required for determining the displacement energies of the phases under investigation by the method outlined by Inui et al. (1990). Thus, we plan to make extensive use of the HVEM- and IVEM- Tandem Facilities at Argonne National Laboratory in order to follow the amorphization process in well selected targets.

We also plan to do cross-sectional TEM (XTEM) studies on bulk samples irradiated using the ion beam facilities at LANL and SNL and to study the depth dependence of irradiation effects to better understand the role of free surfaces on amorphization. Although surfaces may act as point defect sinks resulting in a defect denuded zone in most irradiated metallic materials, we have obtained evidence that free surfaces are more favorable sites for nucleation of amorphous volumes in complex ceramics (Wang et al., in press). This phenomenon may be associated with a certain irradiation temperature and may also be related to the high ionization energy loss of ions at the irradiation surface. The present sample geometry for irradiation in the HVEM-Tandem Facility prevents a detailed study on the role of free surfaces. XTEM study can also provide information on the extent to which the data obtained from the *in situ* irradiation/TEM study are valid for the bulk material.

Data collected from the above studies will be compared with the material parameters (e.g., structure-type, bond type and strength, thermodynamic data, etc.), previous results from pressure induced amorphization studies and classical glass formation studies in order to extract insight into the controlling mechanisms for amorphization of complex ceramic materials.

PHASES PROPOSED FOR STUDY AND JUSTIFICATIONS

The principal considerations of irradiation effects in ceramics include point and aggregate defect production; the crystalline-to-amorphous transition; dimensional, mechanical and thermal property alteration; and changes in electronic, magnetic, and optical properties. Comparison of irradiation results in ceramics has revealed a wide variation in susceptibility to amorphization. Gupta (1993) considered a topologic parameter, freedom for alternative structural arrangement, in the evaluation of glass-formation ability. Based on the parallels between glass-formation and amorphization, Hobbs (1994) proposed that this structural topology parameter be used to evaluate the susceptibility of ceramics to amorphization. However, the structural topology does not consider chemical influences on irradiation-induced amorphization. The structure-types proposed for study comprise a large number of compositions so that chemical and thermodynamic parameters, such as bond-type and strength and free energy of formation, can be used to evaluate the susceptibility to amorphization under the condition of a fixed topology. Also included in the proposed phases are polymorphs of fixed composition, so that the effect of structural complexity or topological stability can be studied without the confusion introduced by variations in chemical composition, as has been encountered in previous studies.

1. Monazite and zircon structure types (ABO_4):

There are a wide variety of ABO_4 structure types (Muller and Roy, 1974; Aldred, 1984) that include silicates (zircon, $ZrSiO_4$ and thorite, $ThSiO_4$), phosphates (xenotime, YPO_4 and monazite, $CePO_4$) and vanadates ($REEVO_4$). The phases selected for study are

orthosilicates, that is the BO_4 tetrahedra are not polymerized, but exist as isolated tetrahedra bonded across corners and edges to the A-site cation coordination polyhedra. There are no bridging oxygens in such structures. Based on studies of α -decay damage in natural phases, one may anticipate a different response when comparing silicates and phosphates (Lumpkin and Chakoumakos, 1988; Chakoumakos et al., 1990). Bond energies for the P-O bond are roughly 200 kJ/mol lower than for the Si-O bond. Thus, phases with a greater proportion of P-O to Si-O bonds have a lower energy barrier to recrystallization. This point has been emphasized by Robinson (1983) using MARLOWE to simulate collision cascades in monazite (a phase under study, see later section). Although cascades produced by different types of ions may vary in their structure and effect on the periodic structure, Robinson concludes that it is unlikely that the crystal structure of the target itself plays more than a minor role in the structure of the collision cascades. The differences between the response of different minerals must be attributed mainly to the stability of the defect arrays produced in the collision cascades, not to processes occurring during cascade production. There is also recently cited evidence that some phosphates are amorphized as a result of electronic processes during ion-beam amorphization (Sales et al., 1992), although we have found that the electronic energy loss had little effect in the amorphization of zircon (Wang and Ewing, 1992). Additionally, different structure types (e.g., the monoclinic monazite vs. tetragonal zircon) have different susceptibilities to heavy particle irradiations and metamictization. The monoclinic structure type (e.g., monazite) is not found in the metamict state, while the tetragonal structure type (e.g., zircon and thorite) are often metamict (Pabst, 1952). Thus, the ABO_4 -structure types offer a wide variety of stoichiometries and structures for the investigation of effects of bond-type on amorphization and defect annealing. A comprehensive study on zircon (ZrSiO_4) as been completed in collaboration with W.J. Weber (Weber et al., 1994). We propose to study the following phases for comparison to zircon.

(a) Xenotime (YPO_4) is tetragonal and isostructural with zircon (Ewing and Chakoumakos, 1982), but xenotime has not been found in the metamict state, suggesting low-temperature annealing of this phosphate. For xenotime, we propose to complete a series of *in-situ* ion irradiations and HREM investigations that are identical to the conditions used in the irradiation study of zircon. We want to investigate the importance of bond type on the amorphization process by comparing isostructural silicates and phosphates.

(b) Thorite (ThSiO_4) is tetragonal and isostructural with zircon (Ewing and Chakoumakos, 1982) and commonly found in the metamict state and often displays low temperature alteration and annealing effects leading to the formation of secondary thorite phases containing H_2O and the substitution of 4H^+ for Si^{4+} in the B-site (Fron del, 1953; Robinson and Abbey, 1957; Speer, 1982; Lumpkin and Chakoumakos, 1988). Structure refinements of the ThSiO_4 polymorphs were completed by Taylor and Ewing (1978), and observed radiation effects in natural materials were discussed by Ewing and Haaker (1980) and Ewing (1994). Ion bombardment (Kr^+ and Ar^+) experiments were completed on monoclinic ThSiO_4 and tetragonal ZrSiO_4 powders (Karioris et al., 1981; Cartz and Fournelle, 1979) and both became metamict at fluences of 5 ions/ nm^2 (3 MeV). We propose to further characterize (using HRTEM) the structure of partially metamict and completely metamict thorite. These results can then be compared to ion irradiation experiments (HVEM Tandem Facility, ANL). In addition, we want to complete an EXAFS/XANES study of the Th-coordination polyhedron with increasing α -decay dose. Results by Farges et al. (1991, 1993) suggest that there is a difference in distortions

observed in the Zr-coordination polyhedron of zircon and the Th-coordination polyhedron of thorite with increasing α -decay dose. The nearest neighbor structure is readily distorted during the damage ingrowth process of thorite, but apparently this is not the case with zircon. This is a good system to study the effects of bonding, structural topology, and molecular water on the radiation damage ingrowth process.

(c) Huttonite (monoclinic polymorph of ThSiO_4) is isostructural with monazite and in nature is always found in the crystalline state. We propose to characterize natural samples by HRTEM and to compare the results to those obtained on tetragonal thorite. We will complete parallel irradiations (1.5 MeV Kr^+ in a temperature range of 20-800 K) and *in-situ* TEM and HRTEM examination of both thorite and huttonite.

(d) Monazite ($(\text{Ca,Ce,Nd})\text{PO}_4$) in nature is always found in the crystalline state (Boatner and Sales, 1988) despite relatively high concentrations of Th and U. Samples from Amelia, Virginia (300 million years old) contain up to 20 wt. % ThO_2 and remain crystalline up to doses of approximately 6×10^{16} alpha-events/mg. Monazite has, until recently, been the only single phase crystalline material proposed to be a waste form for high level nuclear waste. Its remarkably low dissolution rate, its negative temperature coefficient of solubility, its high physical and chemical durability, and its ease of annealing make it an attractive nuclear waste form. Insofar as the physical properties of a material may change significantly as a result of amorphization, this research is important in that the amorphization and annealing processes can affect nuclear waste form properties. The response of monazite to irradiation also has important implications for geochronology. Monazite typically has undisturbed U-Pb systematics relative to zircon, the phase most frequently used in the U-Pb age dating of geological materials (Parrish, 1990).

We propose to characterize alpha-decay damaged monazite specimens by HRTEM and to complete *in situ* annealing experiments on these samples. Again, we will also complete parallel irradiations and *in-situ* TEM examination of the amorphization process for monazite. Our preliminary results from the *in situ* irradiation study have shown that although monazite amorphized at lower ion doses than zircon at temperatures below ~360K, it has a much lower critical amorphization temperature than zircon (430K vs. 1100K) (Meldrum et al. in press; see figure 1). This and the results from an earlier comparative study on apatite (Wang et al., 1994c) indicate that the defects anneal much faster in phosphates than in silicates at elevated temperatures, although monazite (a phosphate) has a much higher melting temperature (2045°C) than that of zircon (a silicate, 1676°C).

(e) Rare earth vanadates (MVO_4), such as LnVO_4 , CeVO_4 and NdVO_4 , have the tetragonal zircon structure but are not found in nature. The structure of many rare earth vanadates have been solved by Chakoumakos et al. (1994). It has been found that V-O distance decreases slightly with increasing Z of the metal cation in the Ln series. The displacement of the oxygen atoms about their mean position in the vanadates is considerably higher than for the corresponding phosphates: this difference has been attributed to the more compact and rigid nature of the PO_4 relative to the VO_4 tetrahedron (Chakoumakos et al., 1994). A comparative ion irradiation study between silicates, phosphates and vanadates with the same zircon structure-type provides a wonderful opportunity for understanding the role of bonding and anion tetrahedron types on the susceptibility of complex ceramics to amorphization.

Figure 1. Comparison of temperature dependence of critical amorphization dose of monazite and zircon under 1.5 MeV Kr^+ irradiation (Meldrum et al., in press).

2. Perovskite structure type (ABO_3):

There are a huge number of compositions with the perovskite structure-type (Navrotsky, 1989; Burns, 1989):

- (1) $\text{A}^{3+}\text{B}^{3+}\text{O}_3$
 $\text{A} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er}$
 $\text{B} = \text{Al, Ga, Cr, Fe, In, Ni, V, Co, Sc}$
- (2) $\text{A}^{2+}\text{B}^{4+}\text{O}_3$
 $\text{A} = \text{Mg, Ca, Sr, Ba, Cd, Pb, Mn, Fe, Zn}$
 $\text{B} = \text{Ti, Zr, Mn, Sn, Ce, Th}$
- (3) $\text{A}^+\text{B}^{5+}\text{O}^{2-}_3$
 $\text{A} = \text{K, Li}$
 $\text{B} = \text{Nb, Ta}$
- (4) High pressure polymorphs of MgSiO_3 and CaGeO_3 which are metastable phases at ambient pressure.

The ideal cubic structure of perovskite is a network of regular BO_6 octahedra linked by their corners that extend symmetrically in three dimensions. The A-site cation occupies the cubic cavity formed by the eight octahedra, and each is surrounded by 12 nearest neighbor oxygens. Due to variations in ionic size and small displacements of atoms, the actual structure found in a majority of perovskites is a pseudosymmetric variant (hettotype) of the

ideal (aristotype) arrangement ($Pm\bar{3}m$), resulting from a small distortion of the unit cell and a reduction of the overall symmetry. This distortion is responsible for the ferromagnetic, and ferroelastic properties of perovskites (Rao et al., 1977). The polymorphic phase transition of perovskites can be exemplified by $BaTiO_3$. On cooling from high-temperature, the structure of $BaTiO_3$ undergoes three displacive phase transitions with atomic movements of 0.1 Å or less. At the Curie temperature of 130 °C, the point group symmetry changes from cubic $m\bar{3}m$ to tetragonal $4mm$. The tetragonal structure, with spontaneous polarization along [001], persists down to 0 °C, where it transforms to orthorhombic symmetry ($mm2$). On further cooling, the orthorhombic structure transforms to rhombohedral ($3m$) near -90 °C.

Perovskite structure-types have a wide range of engineering applications in modern industry (Newnham, 1989) as optoelectrical and microelectrical materials. The perovskite structure-type can also be developed for a new generation of catalysts (Tejucá, 1989). Microelectric and optoelectric devices of perovskites may be operated in irradiation environments, such as nuclear reactors and during space exploration. The irradiation effects in perovskites for these devices must be thoroughly understood, as irradiation may cause significant modification or degradation (Chen et al. 1994, Rankin et al. 1995). Ion-beam processing technology is capable of controlling crystallinity, composition, and characteristics under nonthermal equilibrium conditions and produces high-performance materials and devices, such as ion-beam modification of opto-electronical crystals for better performance. Basic aspects of irradiation effects in the perovskite structure-type such as irradiation-induced effects on physical properties and microstructures and irradiation-induced amorphization are of critical importance in engineering applications of perovskites. Additionally, perovskite is one of the primary phases in the ceramic nuclear waste form, SYNROC (Ringwood et al., 1988). Perovskite is the primary host phase for Sr and trivalent actinides; thus, radiation effects as a function of perovskite structure type (e.g. cubic, orthorhombic or rhombohedral) are of critical importance in waste form evaluation.

From a thermodynamic point of view, the enthalpy of formation of perovskite represents the energy requirement for recrystallization of perovskite from the amorphous state, that is, the stability of crystalline perovskite under irradiation. If this is true, we should be able to predict the relative susceptibility to amorphization of perovskite phases based on a rather complete set of thermodynamic data available in the literature (Takyama-Muromachi, 1988). For example, for the $ATiO_3$ system, the order should be: $CdTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$, with $BaTiO_3$ being the most stable phase because it has the highest enthalpy of formation. Naturally occurring perovskites $(Ca,Na,Ce,Th)(Ti,Nb)O_3$ are sometimes found to be metamict due to α -decay damage. Ferroelectric PLZT, $(Pb,Ln)(Zr,Ti)O_3$, has been completely amorphized after a dose of 1.9×10^{14} ions/cm² by 1.5 MeV krypton irradiation at room temperature (Wang et al, 1992d). Even more interesting, a series of other important parameters are available in the literature for many perovskite phases, such as the Madelung energy (Navrotsky, 1989), the tolerance factor, Debye temperatures (Anderson, 1995), Néel temperatures (Burns, 1989), thermal expansion coefficient (Touloukian et al., 1977) and elasticity (Liebermann et al., 1977). The tolerance factor, a useful parameter related to the stability of perovskite structures, is given by

$$t = (r_A + R_O)/2(R_B + R_O)$$

where r_A , R_B , and R_O are empirical radii of the respective ions. By geometry, the ideal cubic structure should have $t = 1$. These parameters may be closely linked to the relative susceptibility to amorphization for the various compositions within the perovskite structure types.

In addition, we will study the nonstoichiometric influences on irradiation-induced amorphization using selected nonstoichiometric perovskite compositions. Most crystalline materials have a well-defined phase with a chemical composition precisely reproducible and are referred to as stoichiometric. However, some compounds are characterized by a single phase over a range of chemical compositions, and these are referred to as nonstoichiometric. Compared to the corresponding stoichiometric compound, the nonstoichiometric composition has a higher concentration of inherent defects. The energy associated with these extra defects may make a significant contribution to the total energy required for irradiation-induced amorphization. Electron microscopy may be used to advantage in characterizing the detailed structure of defects in nonstoichiometric materials (Hayes and Stoneham, 1985). One of the nonstoichiometric perovskite phases under consideration is CaTiO_3 , which can tolerate excess Ca, as the Ca^{2+} ion is small enough to substitute in small amounts for Ti in the octahedral cation sites (Smith, 1987).

3. $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ternary system phases:

The $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ternary system is an important and well studied system in both ceramic sciences and mineralogy. Many irradiation experiments have been performed on some of the phases in this system, e.g. Mg_2SiO_4 olivine and MgAl_2O_4 spinel. However, there has not been a systematic irradiation study of the phases in this system as a whole. The irradiation study of well selected phases in this system can provide important insights into the relationship between classical glass formation and irradiation-induced amorphization, as well as the topological control on amorphization of ceramics.

Very recently, we have noted a parallel behavior between ion beam induced amorphization and classical glass formation in oxides based on preliminary results from several phases in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ternary system (S. Wang, in preparation; see Figure 2). In the classification of simple oxides for glass formation, SiO_2 is a network former (or glass former), Al_2O_3 is an intermediate, and MgO is a network modifier. The role of a network modifier is to make a network easier to crystallize. The roles of oxides in glass formation can be determined by the use of field strength measurements, as introduced by Volf (1984). The network formers generally have a field strength >1 , while good network modifiers have field strength around 0.5. Our preliminary results have shown that, in a complex ceramic material, the higher the concentration of network formers, the lower the critical ion dose for amorphization. This observation needs to be further tested and refined on more phases because it implies very important insights into the processes of ion beam induced amorphization of oxide systems.

(a) $\text{Al}_2\text{O}_3\text{-SiO}_2$ binary system and related phases

The $\text{Al}_2\text{O}_3\text{-SiO}_2$ binary includes the silica polymorphs (SiO_2), alumina (Al_2O_3), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), and the three aluminosilicate polymorphs (Al_2SiO_5).

There has never been any previous work on radiation effects in the aluminosilicate structure types; however, the three polymorphs (kyanite, Al_2OSiO_4 ; andalusite, AlAlOSiO_4 ; sillimanite, AlSiAlO_5) offer interesting structural contrasts. All of the polymorphs are orthosilicates with isolated silicon-oxygen tetrahedra (in this regard similar to zircon, olivine and garnet). In all three structures, the Si is in tetrahedral coordination, and one of two Al^{3+} cations is in octahedral coordination. A major difference in the structures is the coordination of the remaining Al^{3+} , being four-coordinated with oxygen in sillimanite, five-coordinated with oxygen in andalusite, and six-coordinated in kyanite. This difference is indicated in the manner the formulas are expressed. The polymorphs also differ in the degree of polymerization of the octahedra. Kyanite consists of "sub-chains" of edge-shared octahedra that are parallel to the [001] direction. Andalusite has isolated chains of edge-shared octahedra parallel to [001]. Sillimanite is similar to the andalusite structure, but the Al-site occupancy of the octahedral chains is different. The chains may also be distinguished on the basis of the Al-occupancy arrangement in the octahedra. The differences in thermodynamic stability of these three phases are illustrated in Figure 3. Ion beam irradiations of these polymorphs will allow us to evaluate the effect of coordination geometry, polymerization and thermodynamic stability on the damage/annealing process. We will attempt to use surface EXAFS on irradiated samples to evaluate whether the structure of the amorphous state is identical for each of the three polymorphs after they have been amorphized.

Figure 2. Variation of activation energies with chemical composition in the Al_2O_3 - SiO_2 binary for the viscous flow of melts (indication of the degree of difficulty for glass formation) and for a dynamic defect annealing process during ion beam amorphization (extracted from the D_c -T curves). The similarity of these two curves suggests a parallel between glass formation and ion beam amorphization processes (Wang, S., in preparation).

Figure 3. Experimentally determined stability fields for the polymorphs of Al_2SiO_5 (Holdaway, 1980).

The high temperature and high pressure polymorphs of silica provide an excellent set of phases, not only for examining the effects of topology, but also for evaluating the effect of thermodynamic stability on amorphization.

According to Lam and Okamoto (1994), in disordered crystals, atomic defects create significant static displacements, μ_{sta} in addition to displacements resulting from thermal vibrations, μ_{vib} . The c-a transformation in such structures has been interpreted as solid-state “melting” which occurs when the sum of the dynamic (thermal) and static mean-square displacements, $\langle \mu^2_{\text{T}} \rangle$, reaches a critical value, $\langle \mu^2_{\text{cri}} \rangle$, identical to that of melting for the correspondingly perfect crystalline structures:

$$\langle \mu^2_{\text{T}} \rangle = \langle \mu^2_{\text{sta}} \rangle + \langle \mu^2_{\text{vib}} \rangle \geq \langle \mu^2_{\text{cri}} \rangle$$

Lam and Okamoto (1994) have proposed that $\langle \mu^2_{\text{T}} \rangle \approx \langle \mu^2_{\text{sta}} \rangle \geq \langle \mu^2_{\text{cri}} \rangle$ for the irradiation-induced amorphization, while $\langle \mu^2_{\text{T}} \rangle = \langle \mu^2_{\text{vib}} \rangle \geq \langle \mu^2_{\text{cri}} \rangle$ ($\langle \mu^2_{\text{sta}} \rangle = 0$) when an unirradiated compound melts on heating. The temperature effects on amorphization were considered to only result in annealing, that is a recovery of the damaged structure. We have made a preliminary study on the thermodynamic metastabilities of silica polymorphs on irradiation-induced amorphization. In the case of coesite (a high pressure phase), there is a greater thermal contribution, $\langle \mu^2_{\text{vib}} \rangle$, to irradiation-induced amorphization (Gong et al., submitted), as coesite undergoes solid-state amorphization by annealing alone. We

propose that the expanded thermodynamic condition for irradiation-induced amorphization is:

$$\Delta G_{\text{tot}} = \Delta G_{\text{therm}} + \Delta G_{\text{def}} + \Delta G_{\text{dis}} \geq \Delta G_{\text{amorph}}$$

where ΔG_{tot} is the total energy of the irradiated crystal; ΔG_{therm} is the thermal contribution due to the temperature increase; ΔG_{def} and ΔG_{dis} are the free energy increases due to defect buildup and chemical disordering caused by irradiation, respectively, and ΔG_{amorph} is the free energy of the amorphous solid. More investigations of irradiation-induced amorphization on metastable crystalline phases are necessary to determine the thermal contribution in promoting solid-state amorphization under irradiation.

We consider the following metastable crystalline phases to be important in testing our new model:

- (1) Stishovite, another high-pressure polymorph of SiO_2 stable above 9.5 GPa. This phase has the rutile structure in which Si is six-coordinated by oxygen atoms. It is thermodynamically unstable relative to glass or liquid SiO_2 at any temperature.
- (2) The related GeO_2 phase with the rutile structure is also a high-pressure metastable phase. The rutile structure-types of SiO_2 and GeO_2 are also another good system for testing the structural topology theory of glass-formation and amorphization, as proposed by Gupta (1993) and Hobbs (1994).

From a thermodynamic standpoint, glass formation below the glass transition temperature raises some questions, for example, whether the structure and thermodynamic properties of the amorphous phase (or glass) can be regarded as an equilibrium undercooled liquid at its low formation temperature, which cannot be obtained by cooling a liquid because of slow kinetics. Kauzmann (1948) has argued that an undercooled liquid whose entropy falls below that of the corresponding crystalline phase must undergo massive "freezing" to a glass. Irradiation-induced amorphization of these metastable crystalline phases can be used to demonstrate the glass formation ability of these phases if solid-state amorphization is a process parallel to glass formation. In these metastable phases, Si and Ge are all coordinated by six oxygen atoms because they are high pressure phases. However, in the lower pressure polymorphs of these metastable phases, the cations are coordinated to four oxygens. Therefore, two basic questions arise concerning glass formation by irradiation: (i) whether Si and Ge cations in the amorphous phase immediately produced by irradiation have six-fold oxygen coordination; (ii) whether the six-fold coordination undergoes a relaxation process to four-fold coordination at lower, ambient pressure. These two questions are important to understanding the glass-formation process which can be induced by irradiation. Raman spectroscopy will be a useful technique for determining the coordination configuration changes in these metastable phases before and after irradiation. Energy-filtered electron diffraction can also be used to obtain quantitative results on the coordination configuration changes.

Although rutile (TiO_2) does not easily amorphize under ion irradiation, GeO_2 may because it is known to be a good glass former. Since the field strength of GeO_2 is smaller than that of SiO_2 , it is expected that GeO_2 requires higher doses than SiO_2 for amorphization.

In addition, BeF_2 , another isomorph of quartz is known as a good glass former, perhaps the best in fluoride system. Because the bond type of BeF_2 is almost purely ionic, it is a good phase for testing the ionicity criterion for the amorphization of ceramics. The experiment on BeF_2 will also be a good test of the hypothesis of the parallel between radiation-induced amorphization and ease of glass formation. It is important to understand the controlling factors on irradiation induced amorphization by comparing the results from SiO_2 , GeO_2 , AlPO_4 (Bordes and Ewing, 1995) and BeF_2 .

(b) MgO-SiO_2 binary system

The MgO-SiO_2 binary contains the refractory material periclase (MgO) and the compounds forsterite (Mg_2SiO_4) and enstatite (MgSiO_3). Experiments on irradiation-induced amorphization of forsterite and periclase has been completed (Wang et al., submitted and Wang, S. et al, in preparation). We still need to complete the dose-temperature curve for enstatite. This will provide a strong experimental test of the glass-formation hypothesis.

(c) $\text{MgO-Al}_2\text{O}_3$ binary system and related phases

The $\text{MgO-Al}_2\text{O}_3$ binary contains the important phase spinel (MgAl_2O_4). Many experiments have been done on spinel (Zinkle et al., 1990; Yu et al. 1994) and other isostructural compositions (Wang et al., 1995). MgO is not a glass former, as determined by its low field strength value and compact crystalline structure, and MgO is very hard to amorphize by ion irradiation (Matzke, 1982). From the point of view of classical glass formation, the resistance to amorphization of MgAl_2O_4 spinel may be related to the presence of MgO . To test this hypothesis, we propose to complete a study on a related phase—hercynite (FeAl_2O_4). Hercynite has the spinel structure. Because FeO has a higher field strength than MgO (0.58 vs. 0.51), it is expected that FeAl_2O_4 will be easier to amorphize than MgAl_2O_4 . Additional support for this hypothesis comes from the comparison between fayalite (Fe_2SiO_4) and forsterite (Mg_2SiO_4), with fayalite being much easier to amorphize than forsterite (Wang et al, 1994a). It is also important to compare the $\text{FeAl}_2\text{O}_4/\text{MgAl}_2\text{O}_4$ (spinel) pair with $\text{Fe}_2\text{SiO}_4/\text{Mg}_2\text{SiO}_4$ (olivine) pair to obtain better a understanding the effect of chemistry on amorphization within the same structure type.

(d) $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ternary compounds

Two important ternary compounds will be studied: cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) and sapphirine ($\text{Mg}_2\text{Al}_4\text{SiO}_{10}$). From the high SiO_2 mole concentration and the $(\text{Al,Si})\text{O}_4$ -tetrahedral network structure, we expect cordierite to amorphize easily if the ease of glass-formation criterion is correct. Glass with the cordierite composition is commonly known (Scholze, 1991).

4. Garnet structure type ($\text{X}_{32}\text{Y}_{23}(\text{SiO}_4)_3$):

Garnet is an isometric orthosilicate which consists of a distorted cubic close-packed array of oxygens. The polyhedral arrangement consists of a corner-sharing framework of alternating SiO_4 -tetrahedra and YO_6 -octahedra, and XO_8 triangular dodecahedra fill the remaining structural voids. In addition to a wide variety of natural compositions in which endmember compositions include: $\text{X} = \text{Mg, Fe, Ca and Mn}$; $\text{Y} = \text{Al, Cr, and Fe}$, there are

many synthetic compositions which include lanthanides (e.g., YAG). Different stoichiometries show a wide variation in melting points (from 800°C to 1200°C) and considerable variation in bond-type. However, preliminary studies by Eby et al. (1992) using 1.5 MeV Kr⁺ ions, showed no regular variation of critical amorphization dose with melting point. In fact, in Eby's systematic study of structure-types and bond-types, the garnets are problematic because no systematic relationship to critical amorphization dose could be determined. Eby's study included only four endmember compositions for natural garnets. We propose to repeat Eby's study (ion irradiation/HVEM Tandem Facility, ANL), but to use a wider range of garnet compositions, including synthetic and natural garnets, and to investigate the result of simple binary changes in composition.

SUMMARY

The fundamental approach in this research program will be to apply principally *in-situ* TEM/ion irradiations and high resolution TEM, energy filtered TEM, EXAFS/XANES, and other spectroscopic techniques to the study of the transition from the crystalline-to-aperiodic state in multi-cation complex ceramic materials (complex oxides, silicates, phosphates and vanadates). We are particularly interested in utilizing the HVEM- and the newly established IVEM-Tandem Facility at Argonne National Laboratory to systematically investigate the c-a transition for a variety of complex ceramic structure types over a wide temperature range. Detailed study at the sub-cascade level on the initial stages of amorphization, effects of the grain boundary and free surfaces on amorphization will be carried out at the University of New Mexico with our newly acquired high-resolution TEM.

This proposal outlines a program to study the effects of structure/bonding, chemical composition, thermodynamic stability, cascade energy and temperature on the amorphization of complex ceramic materials in order to establish unified criteria for predicting a material's susceptibility to amorphization. The proposed work is unique in that complex structure types of variable chemistries and polymorphs of fixed compositions are the focus of the study, so that the roles of structure and chemistry on amorphization can be better understood. The results from this study will provide the basis for extending current understanding and allow the development of new models of solid-state amorphization. We anticipate collaboration with other BES-funded programs and colleagues at national laboratories and other universities.

COLLABORATIVE INTERACTIONS

A number of collaborative efforts have resulted from this BES supported program (1993-1996). We expect that many of the following collaborations will continue:

G. Arnold	SNL	ion implantation of silicate structure types; member of Ph.D. committee for A. Meldrum
C.W. Allen R.C. Birtcher	ANL	use of the HVEM-Tandem Facility at ANL;
L. A. Boatner	ORNL	ion implantation and Rutherford backscattering-channeling studies. member of Ph.D. committee for A. Meldrum
G. Brown F. Farges	Stanford U.	EXAFS study of metamict zirconolite
M. Cameron	NSF	HRTEM study of fission tracks in apatite
F. Clinard (retired)	LANL	radiation effects in nuclear waste forms
R. Doreums	RPI	amorphization of ceramics (spent 95-96 academic year at UNM on sabbatical)
K. Sickafus	LANL	ion beam implantation studies at LANL
Y. Eyal	Technion U. Israel	irradiation studies of glass; bubble formation
F. C. Hawthorne	U. Manitoba	analysis of structural distortion as a result of radiation damage
L.W. Hobbs	MIT	irradiation study of berlinite
B. Morosin J.C. Barbour	SNL	radiation damage & flux pinning in Tl-type high temperature superconductors
T. Murakami	U. Tokyo	HRTEM and XRD study of metamict zircons
Alex. Navrotsky T.C. Onstott	Princeton U.	high temperature calorimetric studies of partially damaged zircon and zirconolite and radiation effects on $^{40}\text{Ar}/^{39}\text{Ar}$ dating
E. Salje	Cambridge U.	low angle scattering studies of defect annealing in metamict zircon
W.J. Weber	PNNL	radiation effects in complex silicates; member of Ph.D. committee for A. Meldrum
T.J. White	U. South Australia	ion beam irradiation study of zirconolite

STUDENTS & POST-DOCTORAL FELLOWS SUPPORTED BY THE BES PROGRAM

During the period 1993 to 1996, a number of students and post-doctoral fellows have been funded by or associated with this BES program. They are listed below with their present employment.

Mark Miller	Research scientist	University of New Mexico
Nicole Bordes	Post-doctoral fellow shared with LANL	Microscopy Unit, University of Sydney
Peter Burns	Post-doctoral fellow NSERC Fellowship	University of New Mexico
W.L. Gong	Visiting Scholar Chinese Academy Sc.	University of New Mexico
T.J. White	Fulbright Fellow	University of South Australia
Paula Newcomer	M.S., 1995	Sandia National Laboratories
Shixin Wang	Ph.D. candidate	University of New Mexico
Al Meldrum	Ph.D. candidate	University of New Mexico

REFERENCES

- Aldred, A. T. (1984) *Materials Letters* 3, 37.
- Andersen, H. H. and S. T. Picraux (1986) Eds. of *Proceedings of Symposium on Irradiation Effects Associated with Ion Implantation. Nuclear Instruments & Methods in Physics Research B16* (North-Holland, Amsterdam).
- Anderson, O.L. (1995) *Equations of State of Solids for Geophysics and Ceramics Science*, Oxford University Press, New York, Oxford.
- Arnold, G. W. and J. A. Borders (1984) Eds. of *Proceedings of the Second International Conference on Radiation Effects in Insulators. Nuclear Instruments and Methods in Physics Research B1* (North-Holland, Amsterdam).
- Bentley, J. (1986) *Nuclear Instruments & Methods in Physics Research B16*, 111.
- Bhandari, N. S. , S. G. Bhat, D. Lal, G. Rajagopalan, A. S. Tamhane, V. S. Venkatavaradan (1971) *Earth Planet. Sci. Letters* 13, 191.
- Birtcher, R.C. and L. M. Wang (1991) *Nuclear Instruments and Methods in Physics*, B59/60, 966.
- Boatner, L.A. and B.C. Sales (1988) in *Radioactive Waste Forms for the Future. North-Holland Physics*, Amsterdam, 778 pages.
- Bordes, N. and R.C. Ewing (1995) *Microstructure of Irradiated Materials. I.M. Robertson, L.E. Rehn, S.J. Zinkle and W.J. Phythian, Eds., Proceedings of the Materials Research Society*, 373, 395-400.
- Bordes, N., K.E. Sickafus, E.A. cooper and R.C. Ewing (1995a) *J. Nuclear Mater.* 225, 318.
- Bordes, N., L.M. Wang, R.C. Ewing and K.E. Sickafus (1995b) *J. Mater. Res.* 10, 981.
- Broegger, W. C. (1890) *Z. Kristallogr.* 16, 110; 122-126; 174-180; 389.
- Brown, W.L. (1988) *Nuclear Instruments and Methods in Physics Research B32*, 1-10.
- Burns, R. (1989) in *Perovskite: A Structure of Great Interest to Geophysics and Materials Science*, edited by A. Navrotsky and D.J. Weidner (AGU, Washington, D.C.), pp. 81.
- Bursill, L. A., L. G. Mallinson, S. R. Elliott and J. M. Thomas (1981) *J. Physical Chemistry* 85, 3004.
- Bursill, L. A. and A. C. McLaren (1966) *Phys. Status Solidi* 13, 331.
- Bursill, L. A. and J. M. Thomas (1981) *J. Physical Chemistry* 85, 3007.
- Bursill, L.A. and G. Braunshausen (1990) *Philosophical Magazine A* 62, 395-420.
- Cartz, L. and R. Fournelle (1979) *Radiation Effects* 41, 211.
- Cartz, L., F. G. Karioris, R. A. Fournelle, K. A. Gowda, K. Ramasami, G. Sarkar and M. Billy (1980) Ed. J. G. Moore, *Scientific Basis for Nuclear Waste Managment Vol. 3* (Plenum Press, New York).
- Cartz, L., F. G. Karioris, R. A. Fournelle, (1981a) *Radiation Effects* 54, 57.
- Cartz, L., F. G. Karioris and K. A. Gowda (1981b) *Radiation Effects Letters* 67(3), 83.
- Chakoumakos, B. C. (1984) *J. Solid State Chemistry* 53, 120.
- Chakoumakos, B.C. and R. C. Ewing (1985) *Annual Meeting of the Geological Society of America*, abstract, p. 542.

- Chakoumakos, B. C. T. Murakami, G. R. Lumpkin, and R. C. Ewing (1987) *Science* 236, 1556-1559.
- Chakoumakos, B.C., J. C. McCallum, L.A. Boatner, W. C. Oliver, G.R. Lumpkin and R. C. Ewing (1989) *Radiation Effects in Insulators-5*, Hamilton, Ontario, Canada, June 19-23, p. 127.
- Chakoumakos, B.C., B.C. Sales, and L.A. Boatner (1990) *Amer. Mineral.* 75, 1447-1450.
- Chakoumakos, B.C., Abraham, M.M. and Boatner, L. (1994) *Journal of Solid State Chemistry*, 109, 197-202.
- Chen, Y., F.W. Clinard, B.D. Evans, E.H. Farnum, R.H. French, R. Gonzalez, J.J. O'Dwyer, F.W. Wiffen, X.F. Zong (1994) *J. Nucl. Mater.* 217, 32.
- Chick, L. A., G. L. McVay, G. B. Mellinger, F. P. Roberts (1979) PNL-3465 (Battelle Pacific Northwest Laboratories).
- Clinard, F.W., Jr. (1986) *Ceramic Bulletin* 65, 1181-1187.
- Clinard, F. W., Jr., L. W. Hobbs, C. C. Land, D. E. Peterson, D. L. Rohr and R. B. Roof (1982) *J. of Nuclear Materials* 105, 248.
- Clinard, F. W., Jr., D. L. Rohr, and R. B. Roof (1984a) *Nuclear Instruments and Methods in Physics Research B1*, 581.
- Clinard, F. W., Jr., D. E. Peterson, D. L. Rohr, L. W. Hobbs (1984b) *J. of Nuclear Materials* 126, 245.
- Clinard, F. W., Jr. and L. W. Hobbs (1986) Eds. R. A. Johnson and A. N. Orlov. *Physics of Radiation Effects in Crystals* (North-Holland, Amsterdam).
- Crawford, J. H., Jr., and L. M. Slifkin (1972) Eds. *Point Defects in Solids*, Vol. 1 (Plenum Press, New York).
- Crawford, J. H., Jr., and M. C. Wittels (1956) *International Conference on the Peaceful Uses of Atomic Energy* (U.N. Publication, Geneva).
- Devanathan, R., K.E. Sickafus, N. Yu and M. Nastasi (1995) *Philos. Mag. Lett.* 72, 155.
- Dran, J. C., M. Maurette and J. C. Petit (1980) *Science* 209, 1518.
- Dran, J. C., M. Maurette, J. C. Petit, B. Vassent (1981) Ed. J. G. Moore *Scientific Basis for Nuclear Waste Management* vol. 3 (Plenum, Press, New York).
- Eby, R.K., R.C. Ewing and R.C. Birtcher (1992) *J. Mater. Res.* 7, 3080.
- Eby, R.K., J. Janeczek, R.C. Ewing, T.s. Ercit, L.A. Groat, B.C. Chakoumakos, F.C. Hawthorne and G.R. Rossman (1993) *Canadian Mineralogist* 31, 357.
- Ellsworth, S., A. Navrotsky, and R.C. Ewing (1994) *Physics and Chemistry of Minerals* 21, 140.
- Ewing, R. C. (1975) *Amer. Mineral.* 60, 728.
- Ewing, R.C. (1994) *Nuclear Instru. Meths. in Physics Res.* B59, 22.
- Ewing, R.C. and B.C. Chakoumakos (1982) *Mineralogical Association of Canada Short Course Handbook*, vol. 8, 239-265.
- Ewing, R. C., B. C. Chakoumakos, G. R. Lumpkin and T. Murakami (1987) *Materials Research Society Bulletin* 12, 58-66.
- Ewing, R. C., B.C. Chakoumakos, G.R. Lumpkin, T. Murakami, R.B. Gregor and F. W. Lytle (1988) *Nuclear Instruments and Methods in Physics Research B32*, 487-497.
- Ewing, R. C. and R. F. Haaker (1980) *Nuclear and Chemical Waste Management* 1, 51.

- Ewing, R. C. and T. J. Headley (1983) *J. of Nuclear Materials* 119, 102.
- Ewing, R.C. and L.M. Wang (1992) *Nuclear Instruments and Methods in Physics Research B* 65, 319.
- Ewing, R.C., L.M. Wang, W.J. Weber (1995) *MRS Proceedings* 373, 347.
- Ewing, R.C., W.J. Weber and F.W. Clinard, Jr. (1995) *Progress in Nuclear Energy* 29, 63.
- Farges, F. and G. Calas (1991) *Amer. Mineral.* 76, 60-73.
- Farges, F., R.C. Ewing and G.E. Brown (1993) *J. Mater. Res.* 8, 1983.
- Fecht, H.J. and W.L. Johnson (1988) *Nature* 334, 50-51.
- Fleischer, R. L., P. B. Price, E. M. Symes and D. S. Miller (1964) *Science* 143, 349.
- Fleischer, R. L., P. B. Price and R. M. Walker (1965) *J. Geophys. Res.* 70 (6), 1497.
- Fleischer, R. L., P. B. Price and R. M. Walker (1975) *Nuclear Tracks in Solids* (Univ. of California Press, Berkeley).
- Fron del, C. (1953) *American Mineralogist* 38, 1007-1018.
- Gong, W.L., L.M. Wang, R.C. Ewing and Y. Fei (in press) *Physical Review B*.
- Gupta, P.K. (1993) *J. Am. Cer. Soc.* 76, 1088.
- Guyot, F. and B. Reynard (1992) *Chemical Geology* 96, 411-420.
- Handa, Y.P., J.S. Tse, D.D. Klug, and E. Whalley (1991) *J. Chem. Phys.* 94, 623-627.
- Hawthorne, F. C. (1985) *Amer. Mineral.* 70, 455.
- Hawthorne et al. (1991) *Amer. Mineral.* 76, 370-396.
- Hayes, H. and A.M. Stoneham (1985), *Defects and Defect Processes in Nonmetallic Solids*, John Wiley & Sons, New York.
- Headley, T. J., R. C. Ewing and R. F. Haaker (1981) *Proceedings of the 1981 Annual Meeting of the Electron Microscopy Society of America*, 112.
- Headley, T. J., G. W. Arnold and C. J. M. Northrop (1982) Ed. W. Lutze. *Scientific Basis for Nuclear Waste Management V* (North-Holland, New York).
- Headley, T. J. and R. C. Ewing (1986) *Microanalysis-1986* (San Francisco Press, San Francisco) pp. 141-144.
- Hemley, R.J., A.P. Jephcoat, H.K. Mao, L.C. Ming and M.H. Manghnani (1988) *Nature* 334, 52-54.
- Hemley, R.J., L.C. Chen and H.K. Mao (1989) *Nature* 338, 638-640.
- Hobbs, L. W. (1979) *J. Amer. Ceram. Soc.* 62, 267.
- Hobbs, L.W. (1994) *Nucl. Instru. and Meths. in Physics* B91, 30.
- Hobbs, L.W. (1995) *J. Non-Cryst. Solids* 182, 27.
- Hobbs, L.W., F.W. Clinard, Jr., S.J. Zinkle, R.C. Ewing (1994) *J. Nucl. Mater.* 216, 291.
- Holdaway, M.J. (1980) in: *Orthosilicates, Reviews in Mineralogy Vol. 5*, Mineralogical Society of America, Washington, D.C.
- Holland, H. D. and D. Gottfried (1955) *Acta. Cryst.* 8, 291.

- Inui, H., H. Mori and H. Fujita (1990), *Phil. Mag.* B61, 107.
- Karioris, F. G., K. A. Gowda and L. Cartz (1981) *Radiation Effects Letters* 58(1-2), 1.
- Kauzmann, W. (1948) *Chem. Rev.* 43, 219.
- Kelly, R. (1981) *Nuclear Instruments and Methods in Physics Research* 182 & 183, 351.
- Kinoshita, C., K. Fukumoto, K. Fukuda, F.A. Garner, and G.W. Hollenbert (1995) *J. Nucl. Mater.* 219, 143.
- Krishnaswami, S., D. Lal, N. Prabhu and D. MacDougall (1974) *Earth and Planetary Science Letters* 22, 51-59.
- Kruger, M.B., R. Jeanloz, M.P. Pasternak, R.D. Taylor, B.S. Snyder, A.M. Stacy and S.R. Bohlen (1992) *Science* 225, 703-705.
- Lam, N.Q. and P.R. Okamoto (1994) *MRS Bulletin* XIX(7), 41.
- Liebermann, R.C., L. Jones, and A.E. Ringwood (1977) *Earths. and Planet. Inter.* 14, 165.
- Lumpkin, G. R. and B. C. Chakoumakos (1986) *Mineral. Assoc. Canada Ann. Meeting, Program with Abstracts* 11, 96.
- Lumpkin, G.R. and B. C. Chakoumakos (1988) *American Mineralogist* 73, 1405-1419.
- Lumpkin, G. R., B. C. Chakoumakos and R. C. Ewing (1986) *Amer. Mineral.* 71, 569.
- Lumpkin, G.R., 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) *Journal of Materials Research* 1, 564-576.
- Lumpkin, G. R. and R. C. Ewing (1985) Eds. C. M. Jantzen, J. A. Stone and R. C. Ewing. *Scientific Basis for Nuclear Waste Management VIII.* vol. 44 (Materials Research Society, Pittsburgh, Pennsylvania).
- Lumpkin, G. R. and R. C. Ewing (1986) *Microanalysis-1986* (San Francisco Press, San Francisco) pp. 131-134.
- Lumpkin, G. R. and R. C. Ewing (1988a) *Physics and Chemistry of Minerals* 16, 2-20.
- Lumpkin, G. R. and R. C. Ewing (1988b) *Microanalysis-1988* (San Francisco Press, San Francisco) pp. 470-471.
- Lumpkin, G.R., R. C. Ewing and Y. Eyal (1988) *Journal of Materials Research* 3, 357-368.
- Lumpkin, G.R., B. C. Chakoumakos, R. C. Ewing, R. B. Gregor and F. W. Lytle (1989) 28th International Geological Congress, Washington, D.C., July 9-19.
- Lumpkin, G.R. and R.C. Ewing (1995) *American Mineralogist* 80, 732.
- Lumpkin, G.R. and R.C. Ewing (in press) *American Mineralogist*.
- Mansur, L.K. (1987) in *Kinetics of Nonhomogeneous Processes*, edited by G.R. Freeman (Wiley & Sons, New York), Chapter 8, p. 401.
- Mansur, L.K. (1991) *Journal of the Minerals, Metals & Materials Society* 43, 34.
- Matzke, HJ. (1982) *Radiation Effects* 64, 3.
- Matzke, HJ. (1992) *Nuclear Instruments and Methods in Physics Research* B65, 30-39.
- Matzke, HJ. and J.L. Whitton (1966) *Canadian Journal of Physics* 44, 995-1010.

- Mazzoldi, P. and G. W. Arnold (1987) *Ion Beam Modification of Insulators* (Elsevier, Amsterdam) 740 pages.
- McHargue, C.J. (1991) *Journal of the Minerals, Metals & Materials Society* 43, 40-44.
- McHargue, C. J., G. C. Farlow, G. M. Begun, J. M. Williams, C. W. White, B. R. Appleton, P. S. Sklad and P. Angelini (1986) *Nuclear Instruments and Methods in Physics Research B* 16, 212.
- Meier, W.M. and Villiger, H. (1969) *A Fortran Computer Program for Least-Squares Refinement of Interatomic Distances*, Program Manual, 26 pages.
- Meldrum, A., L.M. Wang and R.C. Ewing (in press) *Nucl. Instru. Methods in Physics*.
- Muller, O. and R. Roy (1974) *The Major Ternary Structural Families*. Springer-Verlag, Heidelberg, 487 pp.
- Murakami, T., B. C. Chakoumakos and R. C. Ewing (1986a) *Advances in Ceramics, Nuclear Waste Management*, D. E. Clark, W. B. White and A. J. Machiels, eds. (American Ceramic Society, Columbus, Ohio) pp. 745-753.
- Murakami, T., B. C. Chakoumakos and R. C. Ewing (1986b) Abstract volume for the International Mineralogical Association meeting, Stanford, California, July 14-19.
- Murakami, T., B.C. Chakoumakos, R.C. Ewing, G.R. Lumpkin and W.J. Weber (1991) *Amer. Mineral.* 76, 1510-1532.
- Naguib, H. M. and R. Kelly (1975) *Radiation Effects* 25, 1.
- Nastasi, M. and J. W. Mayer (1991) *Materials Science Reports* 6, 1.
- Navrotsky, A. (1989) in *Perovskite: A Structure of Great Interest to Geophysics and Materials Science*, edited by A. Navrotsky and D.J. Weidner (AGU, Washington, D.C.), pp. 67.
- Newcomer, PP., L.M. Wang, J.C. Barbour, R.C. Ewing, M.L. Miller and B. Morosin (submitted to *Physica C*).
- Newnham, R.E. (1989) in *Perovskite: A Structure of Great Interest to Geophysics and Materials Science*, edited by A. Navrotsky and D.J. Weidner (AGU, Washington, D.C.), pp.91-98.
- Okamoto, P.R., L.E. Rehn, J. Pearson, R. Bhadra, and M. Grimsditch (1988a) *J. of the Less-Common Metals* 40, 231.
- Okamoto, P.R., and M. Meshii (1988) in: *Proc. ASM Symp. on Science of Advanced Materials*. Eds. H. Wiedersich and M. Meshii, 33-97.
- Onstott, T.C., M.L. Miller, R.C. Ewing, G.W. Arnold and D.S. Walsh (1995) *Geochimica et Cosmochimica Acta* 59, 1821.
- Pabst, A. (1952) *Amer. Mineral.* 37, 137.
- Parkin, D.M. (1991) *Journal of the Minerals, Metals & Materials Society* 43, 45-46.
- Parrish, R.R. (1990) U-Pb dating of monazite and its application to geological problems. *Canadian Journal of Earth Sciences* 27, 1431-1450.
- Petit, J.-C., J.-C. Dran, and G. Della Mea (1987) *Bull. Minéral.* 110, 25-42.
- Rankin, J., J.C. McCallum and L.A. Boatner (1995) *J. Appl. Phys.* 78(3), 1519.
- Rao, R. and L.K. Rao, *Phase Transitions in Solids*, McGraw-Hill, New York, 1977.
- Reeve, K. D. and J. L. Woolfrey (1980) *J. of Australian Ceramic Society* 16, 10.

- Ringwood, A. E., S.E. Kesson, K.D. Reeve, D.M. Levins, and E.J. Ram (1988) Synroc in: *Radioactive Waste Forms for the Future*, Eds. W. Lutze and R.C. Ewing, Elsevier Physics, Amsterdam, pp. 233-334.
- Robinson, M. T. (1983) *Physical Review B* 27, 5347.
- Robinson, S. C. and S. Abbey (1957) *Canadian Mineralogist* 6, 1.
- Sales, B.C., R.A. Zuhr, J.C. McCallum and L.A. Boatner (1992) *Physical Review B* 46, 3215.
- Scholze, H. (1991) *Glass—Nature, Structure and Properties*, Springer-Verlag, New York, pp. 107.
- Schwardz, R.B. and W.L. Johnson, editors (1988) *J. Less-Common Met.* 140, 1-393.
- Sickafus, K.E., A.C. Larson, N. Yu, M. Nastasi, G.W. Hollenberg, F.A. Garner, and R.C. Bradt (1995) *J. Nucl. Mater.* 219, 128.
- Smith D.M. (1987) Ternary-oxide systems, in *Nonstoichiometric Compounds*, edited by C.R. A. Catlow and W.C. Mackrodt (*Advances in Ceramics*, Vol. 23), pp. 339-350.
- Speer, J. A. (1982) *Reviews in Mineralogy*, Vol. 5, Orthosilicates (Mineralogical Society of America).
- Takyama-Muromachi, E., and A. Navrotsky (1988) *J. Solid State Chem.* 72, 244-256 (1988).
- Taylor, M. and R. C. Ewing (1978) *Acta Cryst.* B34, 1074.
- Tejuca, L.G. (1989) *J. Less-com. Met.* 146, 261.
- Touloukian, Y.S., K.K. Kirby, R.E. Taylor and T.Y.R. Lee (1977) *Thermal Expansion, Nonmetal Solids (TPRC 13)*, IFI/Plenum Press, New York.
- Tse, J.S. and D.D. Klug (1992) *Science* 225, 1559-1561.
- Turcotte, R. P. (1981) *Radioactive Waste Management* 2(2), 169.
- Turcotte, R. P., J. W. Wald, F. P. Roberts, J. M. Rusin and W. Lutze (1982) *J. of American Ceramic Society*, 589.
- Vance, E. R. and J. N. Boland (1975) *Radiation Effects* 26, 135.
- Vance, E. R. and K. K. S. Pillay (1980) Ed. J. G. Moore. *Scientific Basis for Nuclear Waste Management Vol. 3* (Plenum Press, New York).
- Vance, E. R., M. Y. Khalil, K. K. S. Pillay, H. J. Milledge, D. W. Kneff and A. G. Pard (1982) *J. of Nuclear Materials* 108-109, 726.
- Volf, M.B. (1984) *Chemical Approach to Glass*, Elsevier, New York.
- Wald, J. W. and P. Offermann (1982) Ed. W. Lutze. *Scientific Basis for Nuclear Waste Management V* (North-Holland, New York).
- Wang, L.M., R.K. Eby, J. Janeczek and R.C. Ewing (1991) *Nuclear Instruments and Methods in Physics Research B* 59/60, 395-400.
- Wang, L.M. and R.C. Ewing (1992a) *MRS Bulletin*, May, 38-44.
- Wang, L.M. and R.C. Ewing (1992b) *Mat. Res. Soc. Symp. Proc.*, vol. 235, 333-338.
- Wang, L.M. and R.C. Ewing (1992c) *Nuclear Instruments and Methods in Physics Research B* 65, 324-329.
- Wang, L.M., Y. Wu and R.C. Ewing (1992) Amorphization of PLZT material by 1.5 meV Krypton ion irradiation with in situ TEM observation. *Proceedings of the Materials Research Society*, vol. 268, 343-347.
- Wang, L.M., R.C. Ewing, W.J. Weber and R.K. Eby (1993) *MRS Proceedings* 279, 451.

- Wang, L.M., W.L. Gong and R.C. Ewing (1994a) MRS Proceedings 316, 247.
- Wang, L.M., P.P. Newcomer*, R.C. Ewing and B. Morosin (1994b) Proc. of the 13th International Congress on Electron Microscopy, B. Jouffrey and C. Colliex, Eds. (les éditions de physique, Les Ulis, France), 957-958.
- Wang, L.M., M. Cameron, W.J. Weber, K.D. Crowley and R.C. Ewing (1994c) in: Hydroxyapatite and Related Materials. P. W. Brown and B. Constantze, Eds. (CRC Press), 243-249.
- Wang, L.M., W.L. Gong, N. Bordes, R.C. Ewing and Y. Fei (1995) MRS Proceedings 373, 407.
- Wang, L.M., W.L. Gong, R.C. Ewing and W.J. Weber (in press) MRS Proceedings 398.
- Wang, L.M., W.L. Gong, R.C. Ewing (submitted to Phil. Mag. A).
- Warner, J.K. and R.C. Ewing (1993) American Mineralogist 78, 419-424.
- Weber, W. J. (1981) J. of Nuclear Materials 98, 206.
- Weber, W.J. (1982) Journal of the American Ceramic Society 65, 544-548.
- Weber, W. J. (1983a) J. of Nuclear Materials 114, 213.
- Weber, W. J. (1983b) Radiation Effects 70, 217.
- Weber, W. J. (1983c) Ed. D. G. Brookins The Scientific Basis for Nuclear Waste Management V, MRS vol. 15 (Elsevier North-Holland, New York).
- Weber, W. J. (1984) Radiation Effects 83, 145.
- Weber, W.J. (1990) J. Mater. Res. 5, 2687-2697.
- Weber, W.J. (1991) Radiation Effects and Defects in Solids 115, 341-349.
- Weber, W.J. (1991) Journal of the Minerals, Metals & Materials Society 43, 35-39.
- Weber, W.J. (1992) Nuclear Instruments and Methods in Physics Research B65, 88-82.
- Weber, W.J. and R.B. Gregor (1990) Nuclear Instruments and Methods in Physics Research B46, 160-164.
- Weber, W. J. and G. D. Maupin (1988) Nuclear Instruments and Methods in Physics Research B32, pp. 512-515.
- Weber, W. J., J. W. Wald, W. J. Gray (1980) Ed. J. G. Moore. Scientific Basis for Nuclear Waste Management Vol. 3 (Plenum Press, New York).
- Weber, W. J., R. P. Turcotte and F. P. Roberts (1982) Radioactive Waste Management 2(3), 295.
- Weber, W. J. and F. P. Roberts (1983) Nuclear Technology 60, 178.
- Weber, W. J., J. W. Wald, and HJ. Matzke (1985) C. M. Jantzen, J. A. Stone and R. C. Ewing. Scientific Basis for Nuclear Waste Management VIII (Materials Research Society, Pittsburgh, Pennsylvania).
- Weber, W. J., J. W. Wald, HJ. Matzke (1986) J. of Nuclear Materials 138, 196.
- Weber, W. J., and L.M. Wang (1994) Nucl. Instr. and Meth. B91, 63.
- Weber, W.J., R.K. Eby and R.C. Ewing (1991) J. Mater. Res. 6, 1334-1345.
- Weber, W.J., L.K. Mansur, F.W. Clinard, and D.M. Parkin (1991) J. Nucl. Mater. 184, 1-21.

Weber, W.J., N.J. Hess and G.D. Maupin (1992) Nuclear Instruments and Methods in Physics Research B65, 102-106.

Weber, W.J., R.C. Ewing and L.M. Wang (1994) J. Mater. Res. 9, 688.

Weber, W.J., R.C. Ewing and W. Lutze (in press) Scientific Basis for Nuclear Waste Management XIX, Proceedings of the Symposia of the Materials Research Society, vol. 412, Eds. W.M. Murphy and D.A. Knecht (Materials Research Society, Pittsburgh, Pennsylvania).

White, C. W., P. S. Sklad, L. A. Boatner, G. C. Farlow, C. J. McHargue, B. C. Sales and M. J. Aziz (1986) Proceedings of the Symposia of the Materials Research Society, vol. 60 (Materials Research Society, Pittsburgh, Pennsylvania) p. 337.

White, C.W., C.J. McHargue, P.S. Sklad, L. A. Boatner and G. C. Farlow (1989) Materials Science Reports, vol. 4, pp. 41-146.

White, T.J., R.C. Ewing, L.M. Wang, J.S. Forrester and C. Montross (1995) MRS Proceedings 353, 1413.

Wilks, R. S. (1968) J. Nuclear Materials 26, 137.

Yada, K., T. Tanji and I. Sunagawa (1981) Physics and Chemistry of Minerals 7, 47.

Yada, K., T. Tanji and I. Sunagawa (1987) Physics and Chemistry of Minerals 14, 197-204.

Yu, N., K.E. Sickafus, and M. Nastasi (1994) Philos. Mag. Lett. 70, 235.

Zinkle, S.J. and S. Kojima (1990) Nucl. Instr. and Meth. B46, 165.

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.