DOE/ER/45396--4

DE93 013335

Progress Report on the Study of

RADIATION-INDUCED APERIODICITY IN IRRADIATED CERAMICS

DOE Grant DE-FG02-89ER45396

conducted by

Linn W. Hobbs
John F. Elliott Professor of Materials
Department of Materials Science & Engineering
Massachusetts Institute of Technology
Room 13-4062
Cambridge, MA 02139
(617) 253-6835
FAX (617) 252-1020

for the period

22 June 1992 - 1 February 1993

submitted to

Dr. William J. Weber
Division of Materials Science
Office of Energy Research
U. S. Department of Energy
Washington, D.C. 20545

February 1993

1. INTRODUCTION

This document summarizes progress in the investigation of Radiation-Induced Aperiodicity in Irradiated Ceramics conducted under support of DOE Grant DE-FG02-89ER45396 during the period 22 June 1992 to 1 February 1993 by Dr. Linn W. Hobbs, John F. Elliott Professor of Materials at Massachusetts Institute of Technology. This period represents approximately six months of the first budget period of a three-year continuing grant begun on 22 June 1992.

The current program is largely experimental and is designed to reveal details of the metamict (amorphization, or crystal-to-glass) transformation in irradiated ceramics using a variety of experimental approaches applied to two representative systems: network silica (SiO_2) in its various polymorphic manifestations (quartz, cristobalite, tridymite, keatite, coesite, vitreous silica) and less-connected lead phosphates (lead metaphosphate PbP_2O_6, lead pyrophosphate $Pb_2P_2O_7$, and lead phosphate glasses of intermediate compositions). The silica compounds have been amorphized using electrons, neutrons and ions, while the phosphates have been amorphized using ions (primarily) and neutrons.

Three methodologies are being employed: energy-filtered electron microdiffraction (EFED), high-resolution transmission electron microscopy (HRTEM), and high-performance liquid-phase chromatography (HPLC). Evidence appearing in HRTEM images is being evaluated using three techniques: image simulations of model transformations, selected-area Fourier-space analysis of local image periodicities, and real-space morphological filtering using mathematical morphological algorithms. Progress to-date with each of these approaches is detailed below.

2. IRRADIATIONS

In conjunction with the HRTEM studies described below, *in situ* 200-keV electron irradiations of three crystalline polymorphic forms of silica have been compared at an electron flux of 10^6 electrons/nm^2: α-quartz irradiated along [100], (x-cut), [120] (y-cut) and [001] (z-cut); α-cristobalite; and α-tridymite irradiated along [1 0 -1]. Z-cut quartz samples were found to withstand a larger electron fluence before amorphization, compared to x-cut or y-cut samples, reflecting the asymmetry of the structure, probably through the effect of anistropic surface constraints on nucleation of the disorder at the specimen surfaces. HRTEM images suggest that tridymite is amorphized through a similar radiolytic sequence as quartz, but both tridymite and cristobalite amorphize more rapidly than quartz. Cristobalite is the most sensitive of the three structures, undoubtedly because its density and structure are closest to the probable structure of metamict silica, as concluded from our earlier modelling studies.

In α-quartz, an amorphous region is confirmed to form first at the surface, and there is a diffuse boundary between this advancing amorphous front and the adjacent crystalline material. Amorphous inclusions subsequently nucleate throughout the crystal, growing to sizes of a few tens of nm with a sharp interface between inclusion and adjacent crystal, but these inclusions are relatively stable and grow more slowly than the boundary between crystalline and amorphized material moves at the overall amorphization front. The slower growth rate appears to be due to the strain barrier arising from the density difference between α-quartz and its metamict state. By contrast, no amorphous inclusions were found to form in irradiated cristobalite or tridymite, and amorphization under sustained irradiation is realized by the rapid advancement of a much sharper amorphization front. The sharpness of the crystal/metamict interface may, again, be due to the closeness of the cristobalite and tridymite structures to the metamict structure; in quartz, substantial rearrangement is required, owing to the abundant existence of primitive 8-rings that our modelling studies show are not consistent with the lower density of metamict material, which must be dominated by the primitive 6-rings found in cristobalite and tridymite.

In addition to 100-keV P^+ ion irradiations of lead pyrophosphate single crystals and lead pyrophosphate and lead metaphosphate glasses to fluences between $5x10^{18}$ and $2x10^{20}$ ions/m^2, we have continued to pursue irradiations with 58 keV O^{2+} ions and 540 keV Pb^{3+} ions. TEM cross sections have been examined for all these ion-irradiated materials and EFED data collected with the VG HB5 STEM, as described below.

3. ENERGY-FILTERED ELECTRON DIFFRACTION

A mode of operation for our Vacuum Generators VG HB5 100-kVfield-emission STEM has been devised for obtaining energy-filtered electron diffraction patterns from thin films which involves scanning the diffracted electron distribution across the electron spectrometer entrance aperture. This has enabled zero-loss electron diffraction data to be obtained from vitreous silica, neutron-amorphized quartz, ion-amorphized quartz and *in-situ* electron-amorphized quartz silica structures and from P^+ ion-amorphized crystalline and lead phosphates. In the last six months we have concentrated on two extensions of the technique. The first is analysis of a range of aperiodic silica films of varying densities deposited by chemical vapor deposition onto silicon substrates. The latter has been thinned away, and radial distribution functions (RDFs) generated from EFED data obtained from the silica films. The motivation is to try to relate density, which is a parameter which alters significantly during metamictization of both crystalline and glassy silicas, with silica structure, at least as deduced from site-averaged RDFs. The second new direction is to establish an operating EFED mode on MIT's new 300-kV VG HB603 field-emission STEM. This instrument features post-specimen lens optics, which provides more flexibility in acquiring EFED patterns, and will be shortly installed with a parallel-mode electron energy-loss spectrometer (PEELS), which is much more sensistive than the HB5 serial EELS spectrometer and will provide a better chance to record the EFED patterns, filtered at elemental edges, needed to produce partial RDFs specific to each elemental site. We have now succeeded in producing EFED patterns with the HB 603 in a mode analagous to that used for the HB5 but are continuing to experiment with alternative enregistration modes using post-specimen optics.

4. HIGH-PERFORMANCE LIQUID-PHASE CHROMATOGRAPHY

Chemical evaluation of the connectedness of silica structures (for example by trimethylsilylation and chromatography) is not especially reliable, but the stability of condensed phosphates with respect to polymerization in an aqueous medium permits statistical evaluation of phosphate chain lengths and 3- and 4- rings, providing unique information about medium-range order in these materials. A high-performance liquid-phase chromatographic flow-injection analysis (HPLC-FIA) system has now been constructed in our laboratory for phosphate chain and ring analysis of metamict and glassy phosphate ceramics. The solvent delivery system consists of a Spectrum linear gradient elution apparatus, a Beckman Model 110A pump and a Rheodyne 7125 six-port injection valve equipped with 20 μl and 50 μl sample loops. The HPLC column being used is a Hamilton PRP-X100 high-resolution 8% cross-linked quaternary ammonium anion-exchange column (250 mm long x 4.1 mm internal diameter) equipped with a guard column. The reagent flow-injection system also consists of a Beckman Model 110A pump and a Rheodyne 7125 six-port injection valve (for total phosphate content determination). Both these flow-injection systems are coupled using a mixing-tee, and the reactants are subsequently heated to 414 K using an electrical heating tape and finally cooled using chilled water. A 658 nm detector window has been installed in a Waters 440 detector/integrator system on loan from Professor W. H. Orme-Johnson in the Department of Chemistry.

The system is at this writing being calibrated by using a series of standards: KH_2PO_4 (one-membered [PO4] chains), $Na_4P_2O_7$ (two-membered chains), $Na_5P_3O_{10}$ (three-membered chains), $(NH_4)_6P_4O_{13}$ (four-membered chains) and $Na_3P_3O_9$ (three-membered rings).

5. HIGH-RESOLUTION ELECTRON IMAGING

TEM is a useful irradiation soruce for silicas, which can be disordered radiolytically by the ionizing component of the electron field, so that *in situ* study of progressive irradiation disordering can be carried out at atomic resolution. MIT's Akashi-ISI EM002B 200-keV ultrahigh-resolution TEM (point resolution 0.18 nm) has been utilized for this purpose. For studies of lead phosphates, which we have shown do not undergo radiolysis, cross sections have been made of ion-irradiated material, so that it is possible to evaluate regions which are wholly crystalline, in transition, or wholly metamict.

High-resolution imaging techniques based on diffraction phenomena and information transfer now routinely provide precise information about crystalline structure and structural irregularities in periodic solids at the atomic level. It is by contrast notoriously difficult to extract definitive structural information from aperiodic solids suing imaging techniques, or even the diffraction phenomena on which they are based, neither of which provides sufficient resolution of medium-range order. How much can be understood about *one* aperiodic structure, the metamict state, from following the progressive degradation under irradiation of its crystalline precursor in a high-resolution imaging mode? To answer this question, image simulations of silicas in transition have been made by reworking the theory of HRTEM imaging to include the diffuse scattering arising from the presence of substantial disorder. The evidence is not wholly in, but two additional avenues of evaluating images are being pursued.

Diffractograms from small (10 nm) image areas of transition material are being made by digitizing the image using SEMPER 6 software on a Silicon Graphics personal IRIS machine and applying suitable rapid Fourier transform algorithms with "soft" apertures. Theese are not true diffraction patterns, since they come from projected images from which phase information has been lost, but the Fourier analysis provides a useful and spatially-resolved spectrum of image periodicities and their alteration with progressive alteration. Though it is commonly believed that a "soft" aperture should be used in Fourier analysis of images, in fact detailed analysis has revealed that it is the size of the aperture that is more important, and when an aperture of a definitive size is applied, a hard aperture gives results of higher quality. Where there are sharp boundaries between crystalline and amorphous regions, Fourier characterization of HRTEM images has so far revealed no direct evidence for existence of any intermediary periodic structure before the crystalline state transforms into the metamict state. Detailed examinations are currently being performed on HRTEM images of regions where gradual disordering has occurred.

Auto-correlation algorithms have also been applied to reveal the presence of any local order in a structure image. Compared with Fourier methods, which are most useful for relatively large areas, correlation functions establish the similarities of two individual features when they are compared in image space. A more elegantly comprehensive approach is total image analysis using mathematical morphological algorithms. For this purpose, the LISP-based image processing software XLIM, developed at the Centre de Morphoplogie Mathematique (CMM), Ecole des Mines in Fountainebleau, France, has been implemented on our DEC VAX II GPS workstation. (Professor Hobbs has maintained a close working relationship with the CMM over the last two years, through a shared student, and Ms. Lewis has spent six months at the Image Processing Laboratory in Grenoble, where many of the CMM algorithms are employed.) In this approach, morphological filtering methods are used as an alternative to Fourier space methods and define certain criteria that can be useful in detecting characteristic structural features in the image. Other more complex algorithms, such as distance functions and geodesic reconstructions, are also being applied The main focus is to establish a relationship between periodic contrast in the image and the presence of remanent periodicity in the structure; the methods are being currently applied to characterization of partially ordered transition zones appearing in the images, located between periodic and aperiodic regions.

END

DATE
FILMED
6/11/93