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IN SITU TEM STUDY OF ION-BEAM-INDUCED AMORPHIZATION OF COMPLEX SILICATE STRUCTURES

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ABSTRACT

The in situ transmission electron microscopy (TEM) with ion-irradiation technique has been used for the first time to study the radiation-induced amorphization (metamictization) process of naturally occurring silicates: neptunite [$Na_2KLi(Fe,Mn)_2Ti_2(SiO_3)_8$], titanite ($CaTiSiO_5$), gadolinite ($REE_2FeBe_2Si_2O_{10}$), zircon ($ZrSiO_4$) and olivine [$(Mg,Fe)_2SiO_4$]. These phases were irradiated with 1.5 MeV Kr^+ ions in the Argonne HVEM-Tandem Facility at room temperature with the electron diffraction pattern monitored in situ. The critical doses required for amorphization of the electron transparent thickness of neptunite, titanite, gadolinite, zircon and olivine have been determined to be 1.7, 2.0, 2.3, 4.8 and 6.0×10^{14} ions/cm^2, respectively. The results show a correlation between amorphization dose and the chemical and structural complexity of these five phases. The most complex structure (e.g. neptunite) becomes amorphous at the lowest critical dose. The critical amorphization dose also increases with the increasing melting temperature of the minerals.

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DISCLAIMER

1. Introduction

Metamictization (amorphization) of minerals is a radiation-induced, periodic-to-aperiodic phase transition caused by α-decay of the constituent radioactive uranium and thorium in geological times (up to 10^9 years) [1]. Recently, there has been a significant interest in the metamict state and amorphization process in minerals because they are structurally and chemically analogous to phases that will be actinide hosts in ceramic nuclear waste forms [2]. Also, there is a fundamental interest in developing a better understanding of the solid-state crystalline-to-amorphous (c-a) transformation process because of the possible technological applications of amorphous materials [3].

In this study, in situ transmission electron microscopy (TEM) with ion-beam-irradiation is used to follow the amorphization process in diverse structurally-complex natural silicates. This technique not only simulates the metamictization process in just a few hours, but also allows one to study radiation effects in phases which are not actinide host; and thus, offer no examples of α-decay damage. This study is only preliminary to a larger effort in determining the controlling parameters for the c-a transformations of the complex ceramic materials.

2. Structure Description and Experimental Procedures

The silicate phases studied in this research include neptunite [$Na_2KLi(Fe,Mn)_2Ti_2(SiO_3)_8$], titanite ($CaTiSiO_5$), gadolinite ($REE_2FeBe_2Si_2O_{10}$), zircon ($ZrSiO_4$) and olivine [$(Mg,Fe)_2SiO_4$]. Gadolinite, zircon and titanite are known as naturally occurring actinide-host phases. While gadolinite [4] and zircon [5] have been found in metamict state, only certain localized alpha-decay damage has been reported for titanite [6]. Neptunite and olivine do not contain actinide elements, and thus, have never been found in metamict (or amorphous) state.

Basic structural parameters for the five silicates are listed in Table 1. Their structures are shown as polyhedral representations, which are drawn by using the STRUPLO program [8], in Fig. 1. In the illustrations, cation-anion "ionic" networks are drawn by representing their cation coordination groups as polyhedra, with the cations centrally located and the vertices of the polyhedra representing the anions (usually oxygen). All silicon tetrahedra have thick "stripes"; all octahedra have thin lines; and the more irregular and highly coordinated cations are drawn as circles in the illustrations (except in the case of zircon). The complexity of each silicate structure may be quantified by a number of topologic parameters. In this study, we simply indicate the number of distinct cation coordination geometries in the structure (Table 1).

The highly complex structure of neptunite consists of a box-like network of silicon tetrahedra, with interpenetrating chains of edge-sharing Fe-Ti octahedra (Fig. 1A). The remaining space is occupied by 6-coordinated Li (small solid circles), 7-coordinated Na (medium solid circles) and 10-coordinated K (large open circles).

The titanite structure consists of corner-sharing chains of Ti-octahedra, which are corner-linked by isolated silicon tetrahedra. Ca in 7-fold coordination, represented by open circles, fills the remaining structural cavities (Fig. 1B). The titanite sample used in this study contains a small amount of uranium (0.02 wt.% UO_2), and was annealed at 700 °C for 10 hours in order to eliminate the radiation damage caused by α-decay of uranium prior to ion irradiation [9].

Gadolinite consists of sheets of silicate and beryllium tetrahedra parallel to the (001) planes, which are interconnected by Fe octahedra and 8-coordinated rare-earth elements (REE), mainly yttrium. The Be tetrahedra are indicated by thin strips and the REEs are represented by open circles in Fig. 1C. The gadolinite used in this study contains 0.14 wt.% UO_2 and 0.13 wt.% ThO_2, and was hydrothermally annealed at 710 °C for 15 hours before ion irradiation.

Olivine is a common rock-forming mineral. The structure consists of zig-zag chains of edge-sharing Mg-Fe octahedra, parallel to [001], forming layers of octahedral chains on the (010) plane. The octahedral chains are cross-linked by isolated silicon tetrahedra into a closely arranged polyhedral framework (Fig. 1D). The Mg:Fe ratio is 9:1 in the olivine used in this study.

The structure of zircon consists of edge-sharing triangular dodecahedra (8-coordinated Zr) forming chains parallel to [010] (dotted polyhedra in Fig. 1E). The chains are joined by cross-linked silicon tetrahedra. Although zircon may contain U and Th up to several thousand ppm, no U or Th was detected via electron microprobe analysis in this sample.

The materials used in this study were first sliced and mechanically polished to < 100 μm in thickness. TEM sample discs were then drilled out of the thin slices using an ultrasonic disc cutter. Electron transparent regions were obtained by Ar ion milling.

The pre-thinned TEM samples were irradiated with 1.5 MeV Kr^+ ions in the HVEM-Tandem Facility at Argonne National Laboratory [10] at a dose rate of ~ 3.5×10^{11} ions/cm^{2}s. The facility consists of a modified Kratos/AEI EM7 high-voltage electron microscope (HVEM) and a 2 MV tandem ion accelerator. The ion beam comes into the microscope at an angle of 30° from the electron beam. During ion irradiation, the sample was tilted 20-25° so that the normal to the foil is 5-10° from the ion beam. Irradiations were performed at room temperature (~ 25 °C), and the maximum sample temperature increase due to beam heating was 20 °C. The electron diffraction pattern was monitored in situ with ion irradiation and the electron energy was set at 300 keV. Because of their high energy, most of the Kr ions completely penetrate the electron transparent thickness (< 300 nm) of the samples, and the Kr concentration introduced in the region of study is negligible at the doses used in the irradiation experiments. Due to the complexity of the material compositions, accurate determination of the dpa/dose relation is difficult. Assuming 15 eV as the displacement energy, it is estimated by the TRIM code [11] that a dose of 1×10^{16} Kr^+/cm^2 would create a displacement damage of ~ 16 dpa at a depth of 100 nm in titanite. The dpa/dose values for the other minerals are assumed to be within the same order of magnitude.

Before and after ion irradiation, the samples were also examined by high resolution electron microscopy (HREM) with a JEOL 2000FX analytical electron microscope at the University of New Mexico, which was operated at 200 kV.

3. Results and Discussion

Fig. 2 shows a series of selected area electron diffraction patterns (SAD) for each of the five silicates obtained before and during in situ ion irradiation. As in Fig. 2.I.A, before irradiation, a typical single crystal pattern was obtained from neptunite. A faint diffuse ring was obvious after a dose of 6.8×10^{13} ions/cm^2 (Fig. 2.I.B) and became more intense with increasing dose, indicating the formation and expansion of the amorphous volume. Meanwhile, the crystalline spots in the SAD faded and finally disappeared after a dose of 1.7×10^{14} ions/cm^2 (Fig. 2.I.D), the dose at which the amorphization process is complete. HREM micrographs of neptunite, showing perfect crystalline and typical amorphous images before and after amorphization, are in Fig. 3. Similar images have been obtained for the other silicates too.

The data for these minerals are presented in order of the increasing critical dose for complete amorphization. As can be seen from Fig. 2.V.A, after 1.5×10^{14}

ions/cm^2, a dose which nearly amorphizes neptunite completely, the crystalline SAD pattern of olivine is still unchanged. The doses required for the completion of amorphization in titanite, gadolinite, zircon and olivine are 2.0, 2.3, 4.8 and 6.0x10^{14} ions/cm^2, respectively. Based on the previously mentioned calculation, critical amorphization dose for titanite is equivalent to an average displacement damage of ~ 0.3 dpa in a 200 nm thick foil. Although the five silicates studied became amorphous at ion doses within the same order of magnitude, there is a correlation between the critical amorphization dose and: (1) structural complexity (e.g. number of distinct cation sites); (2) chemical complexity (e.g. number of different atom types); (3) melting points (a qualitative measure of the strength of bonding). While the phase which has the most complex structure (5 distinct cation sites) and composition, neptunite, becomes amorphous at the lowest critical dose, the simplest structures, zircon and olivine (only 2 distinct cation sites and isolated SiO_4 tetrahedral monomers), have the highest critical doses for amorphization. Gadolinite and titanite are intermediate in structural and chemical complexity as indicated by the number of unique cation sites, 3, and their critical amorphization doses are in between. The required critical amorphization dose increase with the melting points for all five phases.

There have been several detailed discussions on the mechanisms for radiation-induced c-a transformation in recent years [12-15]. Although most of the arguments in these discussions are based on data obtained from intermetallic compounds, some features of these models may apply to ceramic materials. For example, the chemical disordering model [13] have suggested that complex materials are easier to amorphize. Another model [14] shows radiation-induced amorphization may require the accumulation of point-defects to a critical concentration prior to full amorphization. However, this mechanism may dominate only at lower temperatures [14]. At temperatures above 200 K, it is indicated that heavy-ion induced c-a transformations may be entirely due to the process of direct amorphization within the cascade [14]. In the preliminary study of some of these silicate phases, HREM suggests that cascade overlap is required to create individual regions which are fully aperiodic [16]. Still, the silicate phases in this study become fully aperiodic at fractions of a dpa (e.g. 0.3 for titanite). This suggests that the interaction of point defects with the remaining areas of crystallinity can lead to a fully aperiodic state for the bulk material. This may be expected in phases with mixed, covalent-ionic, directional bonding in which a single atomic defect may cause a distortion of the surrounding coordination geometries and the loss of long-range periodicity.

4. Summary

The in situ TEM/ion-irradiation technique has been used to study the radiation-induced amorphization process of five crystalline natural silicates: neptunite [$Na_2KLi(Fe,Mn)_2Ti_2(SiO_3)_8$], titanite ($CaTiSiO_5$), gadolinite ($REE_2FeBe_2Si_2O_{10}$), zircon ($ZrSiO_4$) and olivine [$(Mg,Fe)_2SiO_4$]. Despite the large differences in the crystal structure and chemical composition, all five phases were amorphized within the same order of magnitude of ion dose (10^{14} ions/cm^2). Critical doses at which amorphization was completed in neptunite, titanite, gadolinite, zircon and olivine are 1.7, 2.0, 2.3, 4.8 and 6.0x10^{14} ions/cm^2 respectively. For the five silicates studied, critical amorphization dose decreases with increasing structural complexity and decreasing melting point.

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References

[1] R.C. Ewing, B.C. Chakoumakos, G.R. Lumpkin and T. Murakami, MRS Bulletin (May/June, 1987) 58.

[2] W. Lutze and R.C. Ewing, in: Radioactive Waste Forms for the Future, eds. W. Lutze and R.C. Ewing (Elsevier Science Publishers B.V., New York, 1988) p. 699.

[3] R.W. Cahn, Contemp. Phys., 21 (1980) 43.

[4] J. Ito and S.S. Hafner, Am. Mineral. 59 (1974) 700.

[5] B.C. Chakoumakos, T. Murakami, G.R. Lumpkin and R.C. Ewing, Science 236 (1987) 1493.

[6] F.C. Hawthorne et al., Am. Mineral., in press.

[7] R.A. Robie, B.S. Hemingway and J.R. Fisher, Geol. Surv. Bull. 1452 (1979) 1.

[8] R.X. Fischer, J. Appl. Cryst. 18 (1985) 258.

[9] R.K. Eby and R.C. Ewing, MRS Proc. 183 (1990) 297.

[10] C.W. Allen, L.L. Funk, E.A. Ryan and S.T. Ockers, Nucl. Instr. and Methods in Phys. Res. B40/41 (1989) 553.

[11] J.F. Ziegler, J.P. Biersack and U. Littmark, The stopping and Range of Ions in Solids (Pergamon Press, New York, 1985).

[12] A.V. Drigo, M. Berti, A. Benyagoub, H. Bernas, J.C. Pivin, F. Pons, L. Thome and C. Cohen, Nucl. Instr. and Methods in Phys. Res. B19/20 (1987) 533.

[13] D.E. Luzzi and M. Meshii, J. Less-common Met. 140 (1988) 193.

[14] D.F. Pedraza, J. Less-common Met. 140 (1988) 219.

[15] D.F. Pedraza, Met. Trans. 21A (1990) 1809.

[16] T. Murakami, B.C. Chakoumakos, R.C. Ewing, G.R. Lumpkin and W.J. Weber, Am. Mineral., to be published.

Table 1. Basic material parameters of the studied natural silicates

Material Name	Formula	Crystal System	a	b (nm)	c	β	Space Group	Cation§ Sites	Density (g/cm^3)	Melting Point (K)
neptunite	$Na_2KLi(Fe,Mn)_2Ti_2(SiO_3)_8$	monoclinic	1.646	1.250	1.001	115.43°	C2/c	5	3.24	1055*
titanite	$CaTiSiO_5$	monoclinic	0.707	0.872	0.657	113.86°	A2/a	3	3.53	1670 [7]
gadolinite	$REE_2FeBe_2Si_2O_{10}$	monoclinic	1.000	0.757	0.477	90.31°	$P2_1/a$	3	4.44	1745*
zircon	$ZrSiO_4$	tetragonal	0.660	0.660	0.598	90°	$I4_1/amd$	2	4.67	1949† [7]
olivine	$(Mg,Fe)_2SiO_4$	orthorhombic	0.476	1.023	0.599	90°	Pbnm	2	3.27	2163 [7]

§ Number of distinct cation coordinations in the structure.

* Measured in this study.

† Zircon decomposes to ZrO_2+SiO_2 at 1949 K.