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HEAVY-PARTICLE IRRADIATIONS

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AMORPHIZATION OF COMPLEX CERAMICS BY HEAVY-PARTICLE IRRADIATIONS

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ABSTRACT

"Complex" ceramics, for the purpose of this paper, include materials that are generally strongly bonded (mixed ionic and covalent), refractory and frequently good insulators. They are distinguished from simple, compact ceramics (e.g., MgO and UO₂) by structural features which include: 1.) open network structures, best characterized by a consideration of the shape, size and connectivity of coordination polyhedra; 2.) generally, complex compositions which characteristically lead to multiple cation sites and lower symmetry; 3.) directional bonding; 4.) bond-type variations, from bond-to-bond, within the structure. The heavy particle irradiations not only include ion-beam irradiations, but also recoil-nucleus damage resulting from α -decay events from constituent actinides. The latter effects are responsible for the radiation-induced transformation to the metamict state in minerals. The responses of these materials to irradiation are complex, as energy may be dissipated ballistically by transfer of kinetic energy from an incident projectile or radiolytically by conversion of radiation-induced electronic excitations into atomic motion. This results in isolated Frenkel defect pairs, defect aggregates, isolated collision cascades or bulk amorphization; all may occur concurrently. Thus, the amorphization process is heterogeneous. Only recently have there been systematic studies of heavy particle irradiations of "complex" ceramics on a wide variety of structure-types and compositions as a function of dose and temperature. In this paper, we review the conditions for amorphization for the tetragonal orthosilicate, zircon [ZrSiO₄]; the hexagonal orthosilicate/phosphate apatite structure-type [X₁₀(ZO₄)₆(F,Cl,O)₂]; the isometric pyrochlores [A₁₋₂B₂O₆(O,OH,F)_{0-1p}H₂O] and its monoclinic derivative zirconolite [CaZrTi₂O₇]; the olivine (derivative - *hcp*) structure types, α -VI A₂^{IV}BO₄, and spinel (*ccp*), γ -VI A₂^{IV}BO₄.

INTRODUCTION

The earliest recognition of radiation effects in materials was in a "complex ceramic", the naturally occurring mineral gadolinite [(Ce, La, Nd, Y)₂Fe²⁺Be₂Si₂O₁₀]. Jacob Berzelius noted the release of stored energy on heating during blow-pipe analysis. Gadolinite is a sheet silicate in which SiO₄ and BeO₄ tetrahedra form sheets parallel to the (001) plane. The sheets are connected by FeO₆ octahedra, and rare-earth elements are in 8-fold coordination. In 1893, W.C. Brögger defined "metamikte" minerals as a third class of amorphous materials, but it was not until 1914 (18 years after the discovery of radioactivity) that Hamberg suggested that metamictization is a radiation-induced, periodic-to-aperiodic phase transition caused by α -particles which originate from the constituent radionuclides in the uranium and thorium decay series. By 1924, V.M. Goldschmidt had provided the first criteria for metamictization which presaged the criteria of Naguib and Kelly [1] nearly 50 years later for simpler compounds that were amorphized by ion-beam irradiations. In 1939, Stackelberg and Rottenback tried to test the hypothesis that metamictization was a radiation-induced phase transformation by bombarding a thin slab of zircon with α -particles. The results were inconclusive but this must have been one of the first experiments in which an "ion beam" was used to "modify" a ceramic material. The details of this early history are summarized in refs. [2-4].

Most recently, systematic studies have been completed on a wide variety of silicate,

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phosphate, and oxide structure types which have been amorphized by α -decay event damage [5-7] or by ion-beam irradiations [8-10]. This review focuses on selected results which best exemplify the characteristics of "complex" ceramics. The basic approach involves the detailed study of carefully selected *structure types over a wide range of compositions*. Structure types are considered on the basis of their topologic relations, e.g., zircon and apatite are both orthosilicates/phosphates (the tetrahedral monomers are not connected to one another, but rather are linked across corners and edges to other cation coordination polyhedra). Ideally, polymorphous structures of the same composition (e.g., the α - and γ - forms of Fe_2SiO_4 which are respectively the olivine (derivative *hcp*) and spinel (*ccp*) structure types) may be studied to determine the critical amorphization dose as a function of structure-type and temperature. This allows for the analysis of the structural and topologic controls on the final damage microstructure and critical amorphization dose [11]. For each structure type compositional variations allow the evaluation of the role of bond-type and bond-strength. As an example, in the olivine structure, the tetrahedral sites may be comprised of SiO_4 , GeO_4 , or PO_4 tetrahedral monomer units. These substitutions can dramatically change the calculated ionicity. The compositional substitutions also have dramatic effects on the physical and chemical properties. The melting point of Mg_2SiO_4 is 1890°C vs. $1,205^\circ\text{C}$ for Fe_2SiO_4 . The pressure-induced olivine-to-spinel transition occurs at approximately 150 kb for Mg_2SiO_4 and at 50 kb for Fe_2SiO_4 . Thus, careful selection of the structure-type and composition can be used to analyze the important controlling parameters in the amorphization process.

Finally, one should comment on the fine previous studies [refs. 1 and 12 are good examples] and very recent exciting work [13-15]. The initial studies [1, 12] were, by and large, restricted to a consideration of binary compounds most of which are compact ceramics (e.g., Al_2O_3 and UO_2). More recent studies [13-15] have focused on binary intermetallic compounds of various stoichiometries and with some variety in their structure types. In these compounds, disordering on crystallographic sites (exchange of atoms) and the introduction of isolated defects are important processes. The principal advantage of studying the intermetallic compounds is that interatomic potentials are available, and this allows molecular dynamic simulations of the radiation-induced amorphization, as well as the calculation of electron diffraction patterns for comparison to actual experiments. The resulting model, derived from the study of intermetallic compounds, has been used to place radiation-induced amorphization into the wider context of processes that cause solid-state amorphization by establishing the thermodynamic relationships between static atomic displacements (i.e., expansion of the unit cell), melting, and elastic softening [15]. Although similar phenomenon have been observed for complex ceramics (e.g., expansion of the unit cell, correlation to melting point, and dramatic decreases in elastic modulus with increasing dose), it is not yet possible to extend the model to the description of complex ceramics. In particular, the radiation-induced amorphization in complex ceramics is heterogeneous. The transition from the periodic to aperiodic state occurs over a range of doses with a distinctive microstructure, mixed aperiodic and periodic domains, the proportions of which change with increasing dose.

STRUCTURE TYPES

Zircon

Zircon (ZrSiO_4) is the most extensively studied metamict mineral and "complex" ceramic. Zircon is tetragonal, *I41/amd*, ($Z=4$). The zircon structure (Fig. 1) consists of edge-sharing ZrO_8 dodecahedra forming chains parallel to [010] and chains of alternating, edge-sharing, SiO_4 tetrahedral monomers and ZrO_8 coordination polyhedra parallel to [001]. The chains are crosslinked by isolated SiO_4 tetrahedra forming an open network structure.

Natural zircons containing up to 5,000 ppm U and Th undergo a radiation-induced

Figure 1. Structure of zircon as seen down [100] axis. Edge-sharing dodecahedra (8-coordinated Zr, dotted) form chains parallel to [010]. The chains are cross-linked by SiO_4 tetrahedra (striped).

crystalline-to-amorphous transformation as a result of α -decay event damage [7,16]. This transformation has also been studied in synthetic zircon in which ^{238}Pu has been incorporated on 8.1% of the Zr sites [6,17,18] and *in situ* by ion-beam-irradiation of natural zircon crystals [18,19]. Amorphization from α -decay event damage is complete after 1×10^{19} α -decay events/g (~ 0.6 dpa) for both natural zircons and for Pu-doped zircon, even though the dose rates differ by 10^8 . Data analysis indicates that amorphization in zircon occurs as a result of defect accumulation rather than directly in the displacement cascades of the recoil nuclei [6,17]. This crystalline-to-amorphous transformation is shown in Fig. 2. The contributions of defect accumulation in the crystalline phase and volume change associated with the crystalline-to-amorphous transformation to the total macroscopic swelling has been modeled [17,18].

Figure 2. Amorphous fraction, f_a , as a function of dose in Pu-doped and natural zircons. The solid curve for Pu-doped zircon is based on a fit of the data to a double overlap model [18]. The dashed curve for natural zircon is based on a fit of the double overlap model, with an incubation dose (0.05 dpa), to the optical and density data of Holland and Gottfried [16].

Based on thermal recovery data [6], the volume change associated with the fully amorphous state in zircon does not exhibit a significant temperature dependence. The dose for complete amorphization under heavy ion (Kr^+ and Xe^+) irradiation is the same as that determined for natural and Pu-doped zircon. In addition, high-resolution TEM indicates that the microstructural changes with dose are the same for natural and Kr^+ -irradiated zircon. The temperature dependence of amorphization in zircon has been determined *in situ* under Kr^+ irradiation (Fig. 3) and may be understood as a two stage process in which different annealing mechanisms dominate [18]. The dose for amorphization increases with temperature in two stages with activation energies of 0.02 and 0.31 eV, respectively, for the recovery processes.

The process for irradiation-induced amorphization in zircon is now well understood. Models for the dose and temperature dependence (Fig. 3) of the amorphization process in zircon have been developed [18]. Consequently, it is possible to model the effect of temperature and time on recovery kinetics for the amorphization process in zircon, and similar structures, over geologic time periods (i.e., hundreds of millions of years). This is significant because zircon is an important mineral for geochronological studies, and radiation damage may lead to disturbed U and Pb isotopic ratios. Additionally zircon has been identified as an actinide host phase in ceramic nuclear waste forms [20]. The work summarized here confirms that radiation damage over geologic time scales can be simulated in crystalline waste forms by shorter term actinide-doping or ion beam-irradiation experiments.

Figure 3. Temperature dependence of the dose for complete amorphization of zircon under 1.5 MeV Kr^+ irradiation. [18]. The data show two stages associated with defect annealing that decrease the rate of amorphization.

Apatite Structure Type

The apatite group of minerals are the most abundant of the phosphate minerals and include fluorapatite, $Ca_{10}(PO_4)_6F_2$, and hydroxyapatite, $Ca_{10}(PO_4)_6(O,H)_2$, which are the materials of teeth and bone [21]. Several rare-earth orthosilicates are isostructural with natural apatites, and those with the composition, $Ca_2(La,Nd,Gd)_8(SiO_4)_6O_2$, have been studied because of their occurrence in nuclear waste forms.

Orthophosphate and orthosilicate apatites are hexagonal, $P6_3/m$, ($Z=2$). The PO_4 or SiO_4

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tetrahedra are isolated from one another, but linked by larger cations. There are two asymmetric large cation sites for which 2/5 of the large cations (usually Ca) are surrounded by six closest oxygens in the form of trigonal prisms and 3/5 of the cation sites are coordinated by five oxygens and one F. The resulting structure is a complex, open framework.

In situ irradiation of hydroxyapatite and carbonate-substituted apatite at room temperature in a TEM with 200 keV electrons results in the rapid formation (< 5 min) of hexagonally-shaped voids (1.5 to 10 nm in diameter) on the anion sublattice as a result of F center aggregation [22]. After longer periods of electron irradiation (> 20 min), local amorphization and collapse of the apatite structure occurs; however, complete amorphization has not been reported. Selected area electron diffraction indicates that polycrystalline CaO may form as a decomposition product within the amorphous matrix. A similar susceptibility to electron-irradiation damage at room temperature has been reported for fluorapatite [23]; however, the void-like structures coalesced, forming a complex labyrinth with channels or voids 5 nm in diameter and amorphization was not observed. Ion-beam irradiation of fluorapatite does result in amorphization, and the dose for amorphization increases with temperature [24].

Irradiation-induced amorphization in rare-earth silicate isomorphs of natural apatite was first observed in Cm-doped glass [25] and ceramic [26] waste forms. Extensive investigations of α -decay-induced amorphization in Cm-doped $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$ [17,27] and ion-beam-induced amorphization in $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ [28] have been completed. Unlike zircon, amorphization in Cm-doped apatite primarily occurs directly in the cascade of the recoil nucleus released by α -decay. This amorphization results in significant volume expansion (up to 9.5%), stored energy (130 J/g), increased fracture toughness, and enhanced dissolution. The contributions of defect accumulation and amorphization to the total macroscopic swelling have also been determined and modeled [17]. The temperature dependence of amorphization under 1.5 MeV Kr⁺ ion irradiation has been determined for both $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ and fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, (Fig. 4). The dose for complete amorphization increases more rapidly with temperature and exhibits no distinct stages for the fluorapatite. In the case of $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$, amorphization increases with temperature in two stages [28], similar to the

Figure 4. Comparison of temperature dependence of critical amorphization doses in displacement per atom (dpa) for 1.5 MeV Kr⁺ ion-irradiated apatite structure types [24].

behavior in zircon. Given the same structure and identical irradiation conditions, the difference in the temperature dependence for the two apatite compositions (Fig. 4) is due to the higher rate of recovery (more mobile defects, fewer cation species) for the fluorapatite. At 15 K, the dose for complete amorphization in $\text{Ca}_2\text{La}_3(\text{SiO}_4)_6\text{O}_2$ is independent of ion mass (recoil-energy spectrum) for Ne^+ , Kr^+ and Xe^+ ion irradiations [28]. As the temperature increases, the dose for complete amorphization increases inversely with the mass of the bombarding ion.

Pyrochlore and Zirconolite

The pyrochlore structure-type, isometric $\text{A}_{1.2}\text{B}_2\text{O}_6(\text{O},\text{OH},\text{F})_{0.1}$, encompasses more than 500 synthetic compositions and occurs in a wide variety of compositions in nature (pyrochlore, betafite and microlite are the principal minerals). The structure is similar to that of fluorite, but rather than the AX_2 stoichiometry, one-eighth of the anions are missing and there are two cation sites. The main framework of the pyrochlore structure consists of BO_6 octahedra which share corners to form six- and three-membered rings in sheets parallel to the (111) plane. The large A-site cations are in 8-fold coordination polyhedra [29]. The different polytypes, such as monoclinic zirconolite (Fig.5) are a result of different stacking sequences for the BO_6 sheets. Despite a wide variety of potentially useful properties (catalytic activity, ferroelectricity, ferromagnetism, luminescence, ionic conductivity, and high thermal stability), the study of radiation effects has been restricted nearly exclusively to the monoclinic derivative, zirconolite $[(\text{CaZr})\text{Ti}_2\text{O}_7]$ which is an actinide-host phase in Ti-based, crystalline ceramics. In waste form zirconolite, Pu, Cm and Am may occupy the A-site. For compositions such as $(\text{Ca},\text{Pu})\text{Ti}_2\text{O}_7$ a cubic pyrochlore structure forms. Radiation damage studies of natural, as well as ^{238}Pu - and ^{244}Cm -doped, pyrochlore and zirconolite have been summarized in detail by Ewing et al. [30].

Figure 5. Polyhedral structure diagram of zirconolite in the (001) projection, that is looking down on the sheets of corner-sharing TiO_6 . The octahedra represent TiO_6 ; the small spheres, Zr; the large spheres, Ca [30]. Crystal structure diagram courtesy of B.C. Chakoumakos.

In this review, we will only discuss the results of ion beam-irradiation experiments, which have only been completed on the zirconolite structure. TEM studies of samples irradiated with 3 MeV Ar^+ ions showed damage buildup similar to that observed in material damaged by α .

decay of ^{238}Pu or ^{244}Cm , namely, accumulation of small defects (α -recoil tracks) to the point where the material became globally disordered [31]. The most recent study has been on a suite of compositions irradiated with 1 MeV Kr^+ : $\text{CaZrTi}_2\text{O}_7$, $\text{Ca}_{0.75}\text{Gd}_{0.50}\text{Zr}_{0.75}\text{Ti}_2\text{O}_7$, and $\text{Ca}_{0.75}\text{U}_{0.50}\text{Zr}_{0.75}\text{Ti}_2\text{O}_7$ over a range of temperatures from 20K to 675K [32]. The most interesting result was the wide range of critical doses for amorphization. At 475 K, the pure zirconolite required nearly an order of magnitude higher dose than the Gd-doped zirconolite. The uranium-doped zirconolite was amorphized by the ion milling, 4 kV Ar^+ , during sample preparation. This suggests that the susceptibility to amorphization of a nuclear waste form zirconolite may be sensitive to the composition, particularly the content of high-Z actinides.

Natural zirconolites have also been used in ion-beam irradiation simulations of α -decay event-induced amorphization [33]. Recrystallized samples (1,400 K for 8 hours in air) were irradiated with 1.5 MeV Kr^+ ions using the HVEM-Tandem Facility at Argonne National Laboratory. The Kr^+ dose rate used during the irradiation was 3.4×10^{11} ions/ cm^2s , which is a damage rate 2×10^{12} times higher than that which has occurred in the natural zirconolite due to decay of uranium. *In-situ* transmission electron microscopy was completed during the ion irradiation. After a Kr^+ dose of 4×10^{14} ions/ cm^2 ($= 0.3$ dpa), the zirconolite grains were amorphized. The dpa level for ion beam-induced amorphization is six times lower than that calculated for the natural α -decay induced process. Some of the α -decay event damage may have recovered by point defect migration over geologic periods of time. Inclusions of thorianite, ThO_2 , in the zirconolite did not become amorphous at equivalent doses. This is consistent with the already mentioned apparent radiation "resistance" of UO_2 . The resistance of thorianite to amorphization compared to zirconolite is consistent with a model of damage accumulation in insulators in which the critical dose for amorphization is inversely proportional to the topologic and chemical complexity of the phase [8]. Thorianite is isometric with only one unique cation site. Zirconolite is monoclinic with three unique cation sites. Such criteria may be useful in evaluating the response of waste form ceramics to α -decay event damage.

Dose-dependence of damage in zirconolite has been studied by Headley et al. [34] using Pb^+ ions of 40 to 240 keV at ambient temperature. The amorphization process is heterogeneous and proceeded in four stages: isolated tracks, track overlap, domination by aperiodic domains, and finally complete amorphization. Results were compared with those for natural zirconolite self-irradiated to various damage levels by α -decay over geologic times. Both the nature and extent of damage were similar, regardless of the large difference in damage rates. Clinard et al. [35] extended the comparison to include ^{238}Pu -substituted zirconolite and showed that damage at the intermediate rate characteristic of zirconolite was similar to that observed in natural and Pb^+ ion-bombarded material.

In summary, these preliminary studies confirm the efficacy of using heavy ion-beam irradiations to simulate the longer-term radiation effects that result from α -decay event damage in nuclear waste forms. Systematic studies of zirconolites of variable composition over a range of temperatures should provide the necessary information for performance assessments as a function of waste form composition, thermal history, and cumulative α -decay event dose.

A_2BO_4 Compounds: Olivine, Spinel and Phenakite

The A_2BO_4 system is characterized by a rich variety of compositions (e.g., $\text{A} = \text{Mg, Fe, Mn, Ca, Ni, Co, Be, Li, and REE}$; $\text{B} = \text{Si, Ge, Be and P}$), extensive solid-solutions between pure, end-member compositions, and a variety of structure types (e.g., the *hcp* derivative olivines, the *ccp* spinels, and the hexagonal phenakite structure). The temperature dependence of the critical amorphization dose, D_c for many of the A_2BO_4 compositions was investigated by *in situ* TEM during ion beam irradiation in order to investigate structural and bonding controls on the amorphization and recovery processes. The phases studied so far include: forsterite (Mg_2SiO_4), fayalite ($\alpha\text{-Fe}_2\text{SiO}_4$), phenakite (Be_2SiO_4), synthetic Mg_2GeO_4 , spinel

(MgAl_2O_4), chromite (FeCr_2O_4) and $\gamma\text{-SiFe}_2\text{O}_4$, a spinel phase formed at high pressure. Among these phases, Mg_2SiO_4 , $\alpha\text{-Fe}_2\text{SiO}_4$, Mg_2GeO_4 have the olivine structure, and Mg_2SiO_4 , $\alpha\text{-Fe}_2\text{SiO}_4$ are the end-members of a complete solid-solution ($\text{Mg,Fe})_2\text{SiO}_4$ series (several intermediate compositions of this series have also been studied at room temperature). The olivine structure ($Pbnm$) is an orthorhombic derivative of hcp of the oxygens; Mg and Fe are in octahedral coordination and Si in tetrahedral coordination (Fig. 6). The SiO_4 tetrahedral monomers are isolated from one another, but are joined along three edges and one apex to the edge-sharing chains (parallel to c) of A-site octahedra. In Mg_2GeO_4 , Ge substitutes for Si in tetrahedral sites, but the increased covalency of the Ge-O bond leads to lengthening of the shared edges. Phenakite (Be_2SiO_4) is trigonal, and the A- and B-site cations are in tetrahedral coordination. The tetrahedra form corner-sharing 6- and 4-membered rings (perpendicular to c); Be and Si atoms alternate. The rings are stacked (parallel to c) to form a corner-sharing three dimensional network. MgAl_2O_4 , FeCr_2O_4 and $\gamma\text{-SiFe}_2\text{O}_4$ all have the spinel structure ($Fd\bar{3}m$; $Z=8$), which, with the general formula of $\gamma\text{-VI A}_2\text{IV BO}_4$, is a face-centered ccp structure in which $1/8$ of the tetrahedral sites and $1/2$ of the octahedral sites are occupied by A- and B-site cations, respectively.

Figure 6. Structure of olivine as seen down $[100]$ axis. Si atoms are in tetrahedral sites. Mg and Fe^{2+} are in M1 and M2 octahedral sites. Oxygen atoms are at the corners of the polyhedra [39].

The temperature dependence of the critical doses required for amorphization, D_c (in dpa), for five A_2BO_4 phases, Mg_2SiO_4 , $\alpha\text{-Fe}_2\text{SiO}_4$, Mg_2GeO_4 , Be_2SiO_4 and $\gamma\text{-SiFe}_2\text{O}_4$ under 1.5 MeV Kr^+ ion beam irradiation are plotted in Fig. 7. The D_c 's are comparable at 15 K for all five phases (0.2-0.5 dpa), but D_c increases with temperature at different rates. During ion beam irradiation, two competing processes, amorphization and relaxation/annealing occur dynamically. Although the diffusion driven recovery is increased by irradiation-enhanced diffusion, this process is suppressed at low temperatures. Thus, the analysis of the temperature dependence of the critical amorphization dose, D_c , allows the two processes to be examined separately. The D_c -temperature curve is the result of competition between amorphization and dynamic recovery processes. While D_c increases with the increasing temperature in general, the slope of the D_c -temperature curve is indicative of a material's ability to recover. The D_c rate of increase (highest to lowest) is, as shown in Fig. 7: Be_2SiO_4 , Mg_2SiO_4 , Mg_2GeO_4 , $\alpha\text{-Fe}_2\text{SiO}_4$ and $\gamma\text{-SiFe}_2\text{O}_4$. The differences in the recovery rates change with temperature and results in the differences in amorphization "resistance" at elevated temperatures. Thus, the previous order for the D_c rate of increase can also be regarded as a relative ranking of "resistance" to amorphization at elevated temperatures. More accurately, the material's relative

Figure 7. Temperature dependence of critical amorphization dose of five A_2BO_4 phases under 1.5 MeV Kr^+ irradiation.

resistance to amorphization is a measure of a material's capability to recover when amorphized by displacement damage.

Data for the two spinel compositions, $MgAl_2O_4$ and $FeCr_2O_4$, were not included in Fig. 7 because $MgAl_2O_4$ was not amorphized at temperatures as low as 20 K at a dose as high as 7.5 dpa; $FeCr_2O_4$ amorphized at 20 K, but only at a dose of ~ 5 dpa which is more than ten times higher than that for the materials plotted in Fig. 7. Recently, Yu et al. [36] reported 400 kV Xe^+ ion-induced amorphization of $MgAl_2O_4$ at 100 K; however, the dose was 25 dpa, and the implanted Xe ions in the damage layer may have played a role in the amorphization. The unique amorphization resistance shown by the spinel structure is discussed in a separate paper in this proceedings [37].

Although the values for D_c are determined by electron diffraction at the maximum electron transparent thickness (with 300 kV electrons) [38], high resolution TEM has also been conducted on samples irradiated at various ion doses. The results for forsterite confirmed the cascade driven, heterogeneous nature of the amorphization process.

Table 1 lists important materials parameters which can be related to the amorphization of the A_2BO_4 phases studied (listed in order of increasing amorphization "resistance").

Table 1. Materials parameters of the A_2BO_4 phases in this study (phases are listed in the order of increasing amorphization "resistance").

Phase	ΔG^*_f	Ionicity	O-O ($\text{\AA}$)	β (Mbar ⁻¹)	dR/dA	Φ
γ - Fe_2SiO_4 (sp)	/	0.504	2.965	/	1.294	0.383
α - Fe_2SiO_4 (ol)	-1379.4	0.504	3.049	146	1.324	0.383
Mg_2GeO_4 (ol)	/	0.658	/	138	/	/
Mg_2SiO_4 (ol)	-2051.3	0.668	2.944	135	1.294	0.295
Be_2SiO_4 (ph)	-2033.7	0.554	2.750	66	/	0.177
Cr_2FeO_4 (sp)	/	0.574	/	107	/	0.292
Al_2MgO_4 (sp)	-2174.9	0.629	2.792	96	1.001	0.198

The meaning of the parameters and their relationship to the relative amorphization resistance of the phases are discussed as follows:

ΔG_f° is the standard free energy of formation from pure elements at 298 K. With the exception for Be_2SiO_4 , the phase with the lower value of ΔG_f° , or a phase more thermodynamically stable, is more resistant to amorphization at the elevated temperatures.

The ionicity, calculated by Pauling's equation, is a measure of the average bond type. For a given crystal structure, the phase with the higher ionicity is more "resistant" to amorphization at elevated temperatures. This confirms the results of a previous study on five different $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$ compositions irradiated with 1.5 MeV Kr^+ at room temperature [39]. Note, in comparisons between structure types, this criterion does not work.

Average O-O distances provide an indication of the resistance to disruption between polyhedra in structure. In general, resistance to amorphization should increase with decreasing O-O distance. This is basically confirmed by the data in Table 1; however, because $\gamma\text{-SiFe}_2\text{O}_4$ was formed under high pressure and is thermodynamically metastable, the small O-O distance is an unstable, high pressure configuration. As noted by Zemann [40], phenakite has the lowest interpolyhedral O-O distance among the silicates (2.75 Å). Phenakite is, thus far, the silicate with the highest "resistance" to ion beam-induced amorphization. Al_2MgO_4 has a larger average O-O distance than Be_2SiO_4 ; yet exhibits higher amorphization "resistance" because the oxygen atoms are in a near perfect ccp array.

The average M-O bond compression coefficient, β , is a quantitative indication for the bond strengths in the structure (inverse of the bond strength value). Within a structure type, "resistance" to amorphization increases with decreasing β because a stronger bond has a high tendency to recover when broken. The lowest β value among the listed phases is that of phenakite. However, the crystal structure of phenakite only consists of BeO_4 and SiO_4 tetrahedra, while the crystal structures of spinel and olivine are comprised of BO_6 octahedra and AO_4 tetrahedra. Their structural topologies are quite different. These data emphasize the importance of structure type (between comparable compositions) in evaluating the relative "resistance" to amorphization.

The parameter, dB/dA , is the ratio between M-O distances in the tetrahedral and octahedral sites. This parameter quantifies the relative stability of spinel or olivine structure types (A_2BO_4). For instance, if dB/dA is less than 1.19, then the spinel structure is stable. At higher values the olivine structure is stable at normal pressures [41]. This ratio for $\gamma\text{-Fe}_2\text{SiO}_4$ is 1.294 (> 1.19). Thus, topologically this high pressure phase is not stable, and a lower "resistance" to ion-beam induced amorphization is expected (although it has the spinel structure). Finally, based on the similar amorphization doses between $\alpha\text{-Fe}_2\text{SiO}_4$ and $\gamma\text{-Fe}_2\text{SiO}_4$ (Fig. 7), similar compositions may be more important than the difference in structure type in determining the critical amorphization dose.

The structural deviation parameter, Φ , [defined in ref. 37], is a measure of the deviation from perfect *ccp* and *hcp* of the oxygen anions. Distortion (resulting from cations which do not fit perfectly into the tetrahedral and octahedral interstices) of the perfect anion packing contributes to the relative instability of the structure. For an ideal spinel structure, Φ equals to zero. With the exception for BeO_4 , which does not have occupied octahedral sites in the structure, the resistance to amorphization does indeed increase with decreasing Φ . We note that this type of analysis may not only apply to a consideration of ion-beam induced amorphization, but it might also be applied to other amorphization processes. For example, the pressure required to amorphize various (Fe,Mg)-olivine compositions also increases with the increasing Mg-content in the pressure-induced amorphization of olivine [42].

Finally, the slope of the D_c -temperature curves is also a function of the density of the material. The lower the target density, the faster the curve rises (resulting in a lower activation energy for recovery and lower critical amorphization temperature). The effect of the lower target density is similar to the observations of Koike et al. [43] on the effect of smaller projectile-mass on the amorphization dose for CuTi. This dependence and similarity can be

qualitatively explained in terms of the collision cascade size. For a fixed target, the cross-section for nuclear collision is larger when a greater projectile mass is used, thus, creating a larger displacement cascade. The same relation is true for a fixed projectile mass in a target of greater density. As shown in ref. [38], the per ion vacancy production in a 200 nm thick foil varied from 2,200 for Be_2SiO_4 (2.96 g/cm^3) to 3,500 for Fe_2SiO_4 (4.392 g/cm^3). The greater the vacancy production per ion, the larger the displacement cascade. Because the activation energies for the recovery process calculated by the Weber et al. model [18] for these A_2BO_4 phases ($< 0.1 \text{ eV}$) are too low for crystal nucleation (usually several eV), it is assumed that the recovery in the amorphous cascade region was mainly through the epitaxial regrowth of the surrounding crystalline volume [38]. The recovery rate for a smaller cascade (smaller amorphous domain) is faster than that of a larger one because the surface area to volume ratio is larger for smaller cascades, thus allowing more efficient epitaxial recrystallization (i.e., shrinkage of the amorphous volume). With this consideration, the effects of other material parameters listed in Table 1 may be overestimated.

In summary, through the analysis on temperature dependence of amorphization dose for seven A_2BO_4 phases, we find that the structure type is important in determining the amorphization "resistance", with the exception noted for $\alpha\text{-Fe}_2\text{SiO}_4$ and $\gamma\text{-Fe}_2\text{SiO}_4$. Within a single structure type, many material parameters can be indicative of a material's "resistance" to amorphization; however, these criteria cannot be applied to the comparison of different structure types.

CONCLUSIONS

This brief survey of radiation effects in "complex" ceramics illustrates that the complexity in compositions and diversity in structure types is amenable to systematic studies which allow an analysis of the role of structural topology and bonding on the damage microstructure of this class of materials. The comparison to natural materials of similar compositions and structures that have accumulated equivalent doses over longer periods of time (e.g., hundreds of millions of years) provides a unique opportunity to study dose rate effects which may vary by as much as eight or nine orders of magnitude. Such studies have specific applications to the study of the long-term durability of ceramic nuclear waste forms.

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