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The metamict state: 1993 – the centennial

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In 1893, a Norwegian mineralogist, W.C. Brøgger, defined "metamikte" as a third class of naturally occurring, amorphous materials. Metamict minerals were determined to be amorphous based on conchoidal fracture and isotropic optical properties; however, well developed crystal forms evidenced the prior crystalline state.

In 1914, A. Hamberg, based on the observation of pleochroic haloes, first suggested that metamictization is a radiation-induced, periodic-to-aperiodic transition caused by α-particles which originate from decay of constituent U and Th. Within a few years, F. Rinne and L. Vegard confirmed by X-ray diffraction that metamict minerals were either amorphous or finely crystalline. By 1940, M. v. Stackelberg and E. Rottenback had established that the decrease in density, refractive indices and birefringence correlated with the breakdown of the structure with increasing α-decay event dose. They tested this hypothesis by bombarding a thin slab of zircon, tetragonal $ZrSiO_2$, with α-particles. The result was inconclusive, but this must have been one of the first experiments in which an "ion-beam" was used to "modify" a ceramic material. Metamict minerals remained a curiosity and a daunting challenge, as compositions were exceedingly complex (lanthanides were abundant) and no structure remained, except that which was restored on heating. In 1952, Adolf Pabst, in his presidential address to the Mineralogical Society of America, carefully tabulated the changes in properties (e.g., release of stored energy and decreased resistance to leaching) which resulted from the radiation damage. Pabst specifically noted that some structures are "resistant" to damage accumulation (e.g., monoclinic $ThSiO_2$) while other polymorphs are often found in the metamict state (e.g., tetragonal $ThSiO_2$).

The use of zircon (isostructural with thorite) in U/Pb dating, however, focused substantive studies on the process of radiation damage. Holland and Gottfried (1955) investigated damage accumulation as an age-dating technique in a classic study of natural zircons (570 million years old; doses up to 10^{16} α-decay events/mg = 0.7 dpa); and developed a modern model of damage accumulation. Recent studies are reviewed which include Pu-doped and ion-beam irradiated zircons. With the exception of radiation effects on alumina and silica, zircon is now probably the most studied complex ceramic.

1. Introduction

During the past ten years, the words "metamict" or "metamictization" have been increasingly used synonymously for "amorphous" or "amorphization", particularly in referring to the effects of heavy-particle irradiations, such as α-decay event damage in ceramics and minerals [1]. Occasionally, the term has also been applied to the amorphization of phases such as α-quartz under electron beam irradiations [2]. The term "metamikte" was first defined in a Danish encyclopedia in 1893 by W.C. Brøgger [3] as part of a discussion of "amorf" solids. Metamict minerals were recognized as a third class of amorphous substances which had originally been crystalline. The amorphous state of such substances was inferred from their conchoidal fracture, optical isotropy, and "glass-like" appearance. The previous crystallinity was evidenced by well formed crystal faces.

On the occasion of the hundredth anniversary of the definition of the metamict state, this paper briefly summarizes the history of work on metamict minerals. This summary draws extensively on the work of Professor Adolf Pabst [4]. Additional reviews of the literature of metamict minerals can be found in refs. [5–7].

2. History

2.1. Prior to 1950

The earliest description of unique properties associated with radiation-damaged materials was by Jöns Jacob Berzelius [8]. Berzelius was a Swedish physician and mineral chemist and certainly one of the most eminent scientists of his century. Berzelius discovered the elements cerium, selenium and thorium. His treatise on blowpipe analysis was translated into German, French, English, Russian, and Italian, and his systematic application of this technique laid the analytical foundation for the discovery of new elements during the 19th century. The abundance of complex pegmatites (small rock units containing higher than normal concentrations of exotic elements, such as the rare

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earths, uranium and thorium) led to the inevitable study of U- and Th-bearing minerals and the observation that some glowed on moderate heating, releasing, sometimes violently, large amounts of energy. This "pyrognomic" behavior was first observed in gadolinite, $(REE)_2FeBe_2Si_2O_{10}$, a monoclinic silicate.

Brøgger's definition of metamict minerals in 1893 was based in part on the knowledge that there was a large class of materials that displayed this pyrgonomic behavior. Other workers during the second half of the 19th century [9,10] established that these phases were initially isotropic but became birefringent and increased in specific gravity on heating. As early as 1864, zircon, $ZrSiO_4$, was the focus of study [10].

As this work predated the discovery of radioactivity in 1896 by Becquerel, metamictization was not recognized as a radiation-induced transformation. Brøgger speculated that metamictization was due to "outside influences" and that complicated structures might be more susceptible to this effect. Spencer [11] considered hydration as a possible cause, as the molecular water content of these phases could be exceedingly high (10 to 15 wt.%).

Goldschmidt [12], the first to establish principles, "Goldschmidt's Rules", which governed the distribution of elements in the Earth's crust, provided the first clear statement of criteria for metamictization:

1. The structure should be weakly ionic and possibly susceptible to hydrolysis.
2. The structure should contain ions which may change their "state of ionization" under ambient conditions.
3. The structure must necessarily be subjected to strong radiation, either from internal sources or from outside sources.

Hamberg [13] was the first to suggest 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. Vegard [14] in studies of thorite, $ThSiO_4$, confirmed the absence of X-ray diffraction maxima in metamict minerals, indicating that they were either amorphous or finely crystalline. Later work [15,16] supported the idea of a radiation-induced transformation. Stackelberg and Rottenback [17,18] established that the decrease in density, refractive indices and birefringence correlated with the breakdown of the structure with increasing α-decay dose. Stackelberg and Rottenback [17,18] tried to test this hypothesis directly by bombarding a thin slab of zircon with α-particles. The results were inconclusive because the slab fractured, but this must have been one of the first experiments in which an "ion beam" was used to "modify" a ceramic material. Machatschki [19] suggested that the instability of zircon might be due to structural considerations. In zircon, zirconium is in eight-fold coordination; however, zirconium's ionic radius is such that it is close to the limit of the range in which Zr is in six-fold coordination. Hutton [20] suggested that changes in ionic radius associated with transmutation or "auto-oxidation" of phases due to the α-particle capture of electrons may lead to an increased susceptibility to metamictization.

2.2. 1950 to 1975

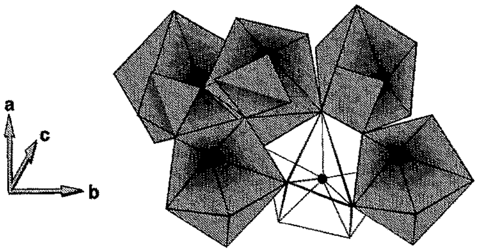
Careful, systematic work on the metamict state was not undertaken until the 1950s. In 1952, Pabst's presidential address to the Mineralogical Society of America [4], "The Metamict State", resurrected the use of the term and raised important fundamental questions concerning the stability of different structure types in a radiation field. In 1955, Holland and Gottfried [21] completed the first careful and systematic study of damage in-growth in zircon, $ZrSiO_4$.

Pabst summarized the early studies on metamictization and listed the known properties of metamict minerals. More importantly, the second half of his paper focused on the behavior of the polymorphs of $ThSiO_4$ monoclinic huttonite and tetragonal thorite. Huttonite, isostructural with monazite ($CePO_4$), is always found in the crystalline state in nature; while, thorite, isostructural with zircon, is often partially or completely metamict. The principal differences between the structures (see Fig. 1) are: 1) the ThO_9 coordination polyhedra in huttonite vs. the ThO_8 coordination polyhedra in thorite; 2) the close-packed structure in huttonite ($\rho = 7.35$ g/cm^3) vs. a more open structure in thorite ($\rho = 6.69$ g/cm^3) in which large voids (14 Å^3) are connected and form channels parallel to the c-axis. These structures were refined by Taylor and Ewing [22], and two observations were made concerning the susceptibility of thorite to α-decay event damage:

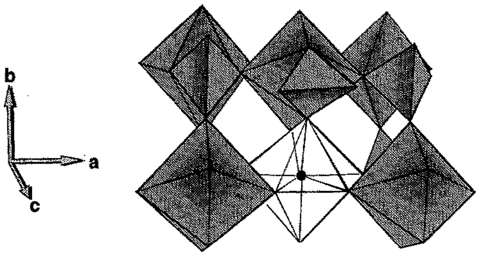
1) Stability criteria based on radius ratio and charge balance are inconclusive; the Th/O radius ratio (0.76) suggests that the nine-fold coordinated huttonite structure should be preferred, while a calculation of Pauling charge balance indicates that the O(1) oxygen of huttonite is overbonded ($\zeta = 2.5$). All oxygen atoms in thorite are exactly charge balanced ($\zeta = 2.0$).

2) The voids in the thorite structure provide channels for the diffusion of molecular water into the structure (some metamict thorites contain up to 70 mol% water); thus, highly polarizing impurities such as water may inhibit or prevent recrystallizaion of radiation-damaged thorite under ambient conditions. Pabst ends his paper by noting that ··· powerful sources of radiation are now available ··· and it is surprising that so few attempts have been made to produce it [the metamict state] artificially."

At the same time as Pabst's presidential address, there was renewed interest in the use of radiation



Huttonite



Thorite

Fig. 1. Perspective polyhedral representations of the huttonite and thorite structures. Smaller tetrahedra are SiO_4 groups and the larger polyhedra are ThO_9 (huttonite) and ThO_8 (thorite). After Taylor and Ewing [22].

damage as a tool for geochronology [23] either by measuring stored energy or the degree of damage (via changes in physical and structural properties) as a function of α-decay event dose which depends on the concentrations of U and Th. The watershed paper by Holland and Gottfried [21] provided one of the most detailed studies of damage development in a complex ceramic, zircon, as a function of increasing α-decay event dose. A suite of zircons (570 million years old) from Sri Lanka with a range of U and Th concentrations was analyzed to determine changes in density, refractive indices and unit cell volume as a function of increasing α-decay dose up to saturation values of 10^{16} α-decay events/mg. At this dose, the zircon became X-ray diffraction amorphous. This study was different from previous efforts in that it: 1) clearly established the range of dose over which the periodic-to-aperiodic transition occurred, 10^{15}–10^{16} α-decay events/mg; 2) precisely determined the change in density (−17%), the decrease in birefringence until the material was isotropic, and the anisotropic expansion of the unit cell (5%). Their interpretation: 1) clearly distinguished between the role of α-particles, which dissipate most of their energy by electronic excitation and ionization events, from that of the recoil nucleus which dissipates most of its energy by elastic collisions and causes upwards to 2000 atomic displacements; 2) modelled damage in-growth and proposed the formation of new crystallites, "phase 2", of an undamaged zircon structure type at intermediate doses (i.e., radiation enhanced crystallization); 3) discussed the role of annealing in determining the final state of a material.

2.3. 1975 to 1990

During this period, renewed interest in the effects of α-decay event damage on radioactive waste forms led to increased funding and research. Weber [24,25] studied defect accumulation in UO_2 as a function of α-particle, α-recoil and fission fragment damage combined with detailed studies of the annealing kinetics [26]. This work demonstrated the different effects of various types of radiation and their temperature dependence.

Eyal and co-workers [27,28] developed an ingenious chemical probe of α-recoil tracks that has proved particularly valuable in calculating the mean life, τ, of α-recoil tracks in crystalline and metamict minerals. Powdered samples were leached in a bicarbonate solution at room temperature for periods up to hundreds of days. The radioactivities of ^{238}U, ^{234}U, ^{232}Th, ^{230}Th and ^{228}Th in each solution were determined by α-spectrometry. The leaching data are presented in terms of the quantity, R, which is the relative leaching rate given by the fractions of activities leached. The ratios are with respect to the initial radioactivities in the mineral. The most important feature of the technique is that the magnitude of the fractionation varies for different isotope pairs $^{228}Th/^{232}Th$ and $^{234}U/^{238}U$. Commonly the $^{228}Th/^{232}Th$ fractionation is much enhanced relative to the $^{234}U/^{238}U$ fractionation. Taking into account the time scales for radioactive decay, this observation suggests the annealing of individual α-recoil tracks. The short-lived nuclide ^{228}Th (mean life = 2.7 yr) is formed by the decay of the short-lived α-recoil atom ^{228}Ra (mean life = 8.3 yr). Therefore the enhanced leaching of ^{228}Th displays the effect of α-recoil damage that is always relatively fresh (mean life = 11 yr). On the other hand, the nuclide ^{234}U is relatively long-lived (mean life = 3.53×10^5 yr), and its enhanced dissolution relative to ^{238}U is governed by the older damage. Using this method, Eyal and Fleischer [27,28] determined a mean annealing time for an α-recoil track in minerals (e.g., UO_2, ThO_2 and $CePO_4$) as being in the range of 15000 to 18000 yr. These phases are important because they retain their crystallinity even at high α-decay doses (> 10 dpa). This is in contrast to the calculated mean life of an α-recoil track of 10^8 yr in complex pyrochlore structure types which are commonly found in the metamict state.

Another important development was the use of highly active actinides, mainly ^{238}Pu (87.7 yr half-life) and ^{244}Cm (18.1 yr half-life), to accelerate the damage in-growth process and to allow the observation of the periodic-to-aperiodic transition in phases which were potential actinide hosts in nuclear waste forms [29,30]. Although these highly radioactive samples were difficult to handle, it was possible to precisely monitor density changes and follow damage in-growth using X-ray diffraction analysis and electron microscopy. The ^{244}Cm-doped phases included: $Ca_2Nd_8(SiO_4)_6O_2$ [31–33]; $Gd_2Ti_2O_7$ [34–36]; $CaZrTi_2O_7$ [36]. The ^{238}Pu-doped phases included: zircon [37,38]; $CaZrTi_2O_7$ [39–42].

Finally, nearly 30 years after the initial suggestion by Pabst, Cartz and others [43] irradiated powders of monoclinic huttonite and tetragonal thorite, $ThSiO_4$, with Ar^+ ions at 3 MeV to investigate structural controls on radiation damage. Using X-ray diffraction analysis, they demonstrated that both thorite and huttonite can become metamict (the damage cross-section for thorite is nearly twice that of huttonite); however, low temperature annealing studies showed that the huttonite recrystallized more easily than thorite. Under ambient conditions over geologic time, huttonite may recrystallize; therefore, huttonite is not found in the metamict state. Unfortunately, to date, there are still no systematic studies of the $ThSiO_4$ polymorphs; however, Cartz's work anticipated the use of ion beam irradiations to study the susceptibility of different minerals to radiation damage.

Work continued on natural zircons. Chakoumakos et al. [44] examined in detail a single zircon crystal with zones (5 to 400 μm thick) of variable U and Th concentrations which lead to a range of α-decay doses which spanned the periodic-to-aperiodic transition. Their work [44,45] confirmed the earlier work of Holland and Gottfried [21]. Recent work [46] on this crystal was extended by using the mechanical properties microprobe to measure changes in mechanical properties with increasing dose (40% decrease in hardness, 60% decrease in elastic moduli, and an increase in fracture toughness). Also, using a suite of natural zircons, the periodic-to-aperiodic transition was studied for the first time using high resolution transmission electron microscopy [47]. The same samples were used in leaching experiments [48] and showed a factor of ten increase in leach rate as a function of this radiation-induced transformation.

In addition to detailed studies of zircon, similar systematic studies [49] were initiated on natural, isometric pyrochlore structure types, $A_{1-m}B_2O_6(O,OH,F)_{1-n}\ pH_2O$, and its monoclinic derivative, zirconolite, $CaZrTi_2O_7$. These phases are important actinide hosts in the titanate nuclear waste form, Synroc. Although results from these studies were similar to those for zircon, Lumpkin [49] made a significant contribution by noting that if one analyzed suites of pyrochlores from different localities (of different ages), the calculated dose for the crystalline-to-metamict transition increased with the age of the geologic deposit (Fig. 2). This is clear evidence for the annealing of α-recoil damage over geologic time. The change in critical amorphization dose with age was modelled assuming "fading" of the recoil-nucleus "tracks" in a fashion similar to that used to describe fission fragment track fading. Critical parameters are the α-decay event dose, age of the sample, and the mean life of an α-recoil track in the mineral. The variation of dose as a function of age for natural pyrochlores can then be corrected by consideration of recoil track annealing. Fig. 3 illustrates such a correction when the mean life of a track, τ_a, is assumed to be 100 million years. A similar analysis of data for zircon and zirconolite gave mean lifetimes of 400 million years and 700 million years, respectively. This is in contrast to the mean lives determined by Eyal and co-workers of tens of thousands of years for phases which retain their crystallinity despite high doses (> 10 dpa). Thus, the natural samples provide clear evidence for annealing over geologic time under ambient conditions. The final state of the material depends on the mean life of the α-recoil track, a material dependent property.

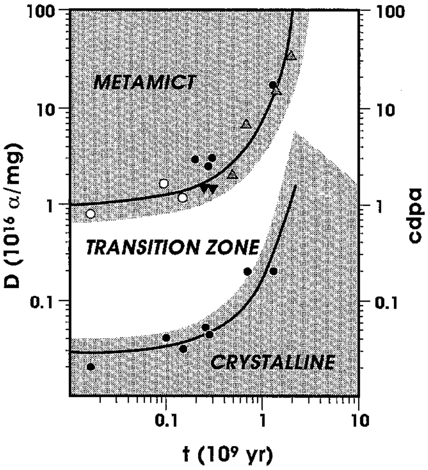


Fig. 2. Variation of α-decay event dose as a function of age for natural pyrochlores. The upper curve and data represent the saturation dose estimated from slightly crystalline and metamict samples. The lower curve and data represent the onset of detectable α-decay damage defined by X-ray diffraction analysis ($I/I_0 = 0.8–1.0$). After Lumpkin and Ewing [49].

2.4. 1990 to present

The most recent work is not summarized in detail, as the references cited provide the best description of approach and results. During the 1990s, much effort has been devoted to the synthesis of data for related

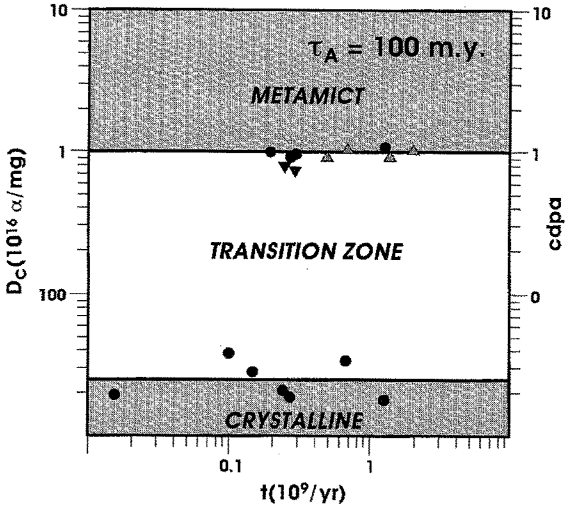


Fig. 3. Variation of dose as a function of age for natural pyrochlores after correcting the annealing of α-decay damage using a mean track life, τ_a, of 100 million years. The upper line is the saturation dose and the lower line is the onset of α-decay damage detectable by X-ray diffraction analysis. The corrected dose in dpa, cdpa, includes the correction for annealing. After Lumpkin and Ewing [50].

structure types under different types of irradiation. [50–52].

The study of natural zircons culminated with the very detailed analysis [53] of damage in-growth in suites of zircons from Sri Lanka (570 million years old) which had experienced variable α-decay event doses due to variable U and Th contents (0.06×10^{15} to 6.8×10^{15} α-decay events/mg). In addition to the physical and optical property changes with dose determined by Holland and Gottfried in 1955, later workers applied detailed X-ray diffraction analysis, electron microprobe analysis, high resolution transmission electron microscopy, infrared spectroscopy, and X-ray absorption spectroscopy to the study of this radiation-induced transition [53–56]. Murakami et al. [53] described three stages of damage in-growth. Stage-I ($< 3 \times 10^{15}$ α-decay events/mg) is characterized by sharp Bragg diffraction maxima with a minor contribution from the diffuse-scattering component. Electron diffraction patterns were sharp. Damage is dominated by the accumulation of isolated point defects which cause unit-cell expansion and distortion that account for most of the decrease in density. These defects may partially anneal over geologic time. Stage-II (3×10^{15} to 8×10^{15} α-decay events/mg) is characterized by significant decreases in the intensity of the Bragg diffraction maxima which become asymmetric due to increased contributions from the diffuse-scattering component. High-resolution transmission electron microscopy revealed that the microstructure consisted of distorted crystalline regions and amorphous "tracks" caused by α-recoil nuclei. With increasing α-decay dose, damaged crystalline regions are converted into aperiodic regions, but with no further significant expansion of the unit cell in the remaining crystalline regions. Stage-III ($> 8 \times 10^{15}$ α-decay events/mg) consists of material which is entirely aperiodic as far as can be determined by X-ray or electron diffraction. There was no evidence for the formation of ZrO_2 or SiO_2 as final products during the last stage of metamictization. Based on modeled density changes, aperiodic regions continued to experience a change in structure as they were redamaged. During Stage-II of the process, the modeled density of aperiodic regions changed from 4.5 g/cm^3 to 4.1 g/cm^3. Fission fragment damage does not contribute to the process of metamictization. The amorphization process is consistent with a model for the multiple overlap of displacement cascades, suggesting amorphization occurs as a result of defect accumulation rather than directly within a single displacement cascade. Comparison of results for natural zircon with those for Pu-doped zircon [57] showed that dose-rate variations (even as great as a factor of 10^8) had no substantial effect on the damage accumulation process. Unit cell parameters increased and density decreased more for the Pu-doped zircon than for natural zircon in the early stages of damage accumulation ($< 3 \times 10^{15}$ α-decay events/mg), suggesting that annealing of point defects in the early stages of the damage accumulation process occurs in natural zircon under ambient conditions. This accounts for the distinct sigmoidal shape of the damage curves for natural zircon and the apparent incubation period before the onset of amorphization.

Most recently, particle irradiations (2 MeV He^+ [58]; 0.8 MeV Ne^+, 1.5 MeV Ar^+, 1.5 MeV Kr^+, 0.7 MeV Kr^+, 1.5 MeV Xe^+ [59]) have been used to induce amorphization in zircon, and the results are compared to the results of α-decay event damage [52]. The time scales in this comparison range from 0.5 hours to 570 million years! The defects are produced in varying concentrations along each particle track, depending on mass and energy. The amorphization process is nearly independent of the damage source (α-decay events vs. heavy-ion beam irradiations) and is consistent with models based on the multiple overlap of particle tracks, indicating amorphization occurs as a result of a critical defect concentration [52]. These results from natural zircons, Pu-doped zircons, and ion-beam irradiated zircons provide a basis for an understanding of not only the long-term behavior of materials in natural and man-made radiation environments (e.g., minerals used in geochronology and nuclear waste forms), but also the relatively short-term processes associated with ion-beam modification of ceramic properties for specific technologic applications (e.g., optical waveguides).

The work on mineral phases has continued and has been extended beyond those phases which become metamict due to their natural abundances of U and Th. Minerals now provide a wide variety of structure types by which irradiation-induced amorphization can be investigated as a function of structural topology, structural complexity and bond type. Initial studies by Wang et al. [60] and Wang and Ewing [61–63] have shown the relationship between structural topology (e.g., degree of complexity), melting point (e.g., bond strength), and bond type (e.g., degree of ionicity) to the critical amorphization dose. A much more systematic study of twenty-five silicate structure types [64] has shown that melting point, structure (e.g., degree of polymerization and atomic packing), and bonding (e.g., proportion of Si–O bonds) correlate with the critical amorphization dose (Fig. 4). As an example, Fig. 5 illustrates the variation of the mean amorphization dose with the degree of silicate polymerization (DOSP). The required dose for amorphization decreases as the connectivity of the SiO_4 tetrahedral monomers increases (DOSP = 0 for structures in which the silicon–oxygen tetrahedra are not connected, that is there are no bridging oxygens; DOSP = 3 for framework silicates in which every corner of every silicon–oxygen tetrahedron is connected to another silicon–oxygen tetrahedron, that is there are 100% bridging oxygens in the structure).

Despite the recent emphasis on ion beam irradiations, mineralogists still continued their detailed studies of natural phases. Hawthorne and colleagues [65] completed a monumental description of α-decay event damage in titanite, $CaTi(SiO_4)O$, a phase that shows only the earliest stages of damage, as uranium concentrations are low (up to 0.2 wt.%). I describe the study as monumental because the suite of ten specimens was examined by a full array of techniques – electron microprobe analysis, thermal gravimetric and evolved gas analysis, X-ray powder diffraction, single-crystal X-ray diffraction structure refinements, Mössbauer spectroscopy, magic-angle spinning NMR for ^{29}Si, high resolution transmission electron microscopy, and X-ray absorption spectroscopy. One of the most interesting results was that the damage process is accompanied by the reduction of Fe^{3+} to Fe^{2+}, which resides mainly in the aperiodic domains.

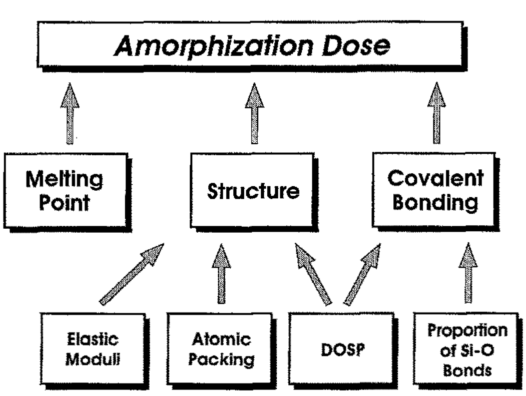


Fig. 4. Summary of the critical materials properties that correlate with the critical amorphization dose based on ion beam irradiations of different silicate structure types. After Eby et al. [64].

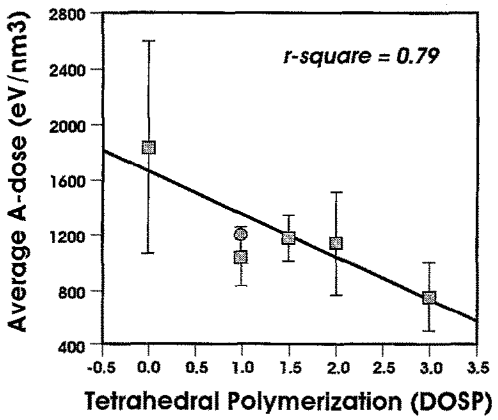


Fig. 5. The mean values (error bars are standard deviations) of the critical amorphization dose as a function of the degree of SiO_4 group polymerization (DOSP). Polymerization increases with increasing values of DOSP. DOSP = 0 for orthosilicates (no polymerization); DOSP = 1.0 for single chain silicates; DOSP = 1.5 for ring silicates; DOSP = 2.0 for sheet silicates; DOSP = 3 for framework silicates. After Eby and others [64].

Work also has continued on minerals of interest for nuclear waste form development. Despite its relative rarity, zirconolite, $CaZrTi_2O_7$, has been a subject of continuous study. Recent work using EXAFS/XANES has systematically examined the nearest neighbor environments of Ca, Zr, Ti, and U in fully metamict specimens. Farges and others [66] have confirmed that the stereochemistry of large cations such as Zr^{4+} and Th^{4+} in fact does play an important role in controlling the short-range environments of these cations; however, the structural environments of these elements in silicate and borosilicates glasses (6-coordinated environments in glasses quenched from a melt) are clearly different from radiation-induced aperiodic phases. Such studies emphasize the importance of structural descriptions of the aperiodic state that allow one to distinguish between different amorphization processes.

In phosphates, high performance liquid chromatography has been used to determine the degree of polymerization of PO_4 groups in aperiodic solids, e.g., the mineral griphite, as well as in quenched glasses and radiation-induced aperiodic phases [67,68].

3. Future work

Future work will inevitably mean the examination of more complex ceramic structures in carefully controlled ion beam irradiation experiments. There are three outstanding areas of research that will require attention:

1) We must determine the displacement energies of the different atoms in complex ceramics in order to model basic damage parameters, such as the range of particles, the distribution of defects along the path of the particle, and finally, the cascade geometry.

2) We must complete systematic studies, particularly at low temperatures, of related structure types, over a range of compositions in order to investigate the roles of structural topology, bond type/strength, and defect mobility during the relaxation (10^{-11} to 10^{-12} s) and annealing (seconds to millions of years) stages of irradiated ceramics.

3) We must investigate the aperiodic structure of radiation-induced amorphized materials and compare them to other aperiodic structures, e.g., quenched melts or pressure-induced amorphized solids.

Acknowledgements

This summary is written in tribute to Professor Adolf Pabst whose work and encouragement focused me on the subject of metamict minerals, a topic considered esoteric even by mineralogists. The results summarized in this paper come from nearly twenty-years of collaborations, as indicated by the co-authors of the papers in the references. Much of the insight into radiation damage in ceramics and minerals comes from these colleagues and students. Any errors and shortcomings in this paper are the responsibility of the author. This work has been supported by the Office of Basic Energy Sciences of the Department of Energy, Grant DE-FG03-93ER45498.

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