Radiation effects in ceramics

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Abstract

Ceramics represent a large class of solids with a wide spectrum of applicability, whose structures range from simple to complex, whose bonding runs from highly ionic to almost entirely covalent and, in some cases, partially metallic, and whose band structures yield wide-gap insulators, narrow-gap semiconductors or even superconductors. These solids exhibit responses to irradiation which are more complex than those for metals. In ceramic materials, atomic displacements can be produced by direct momentum transfer to often more than one distinguishable sublattice, and in some cases radiolytically by electronic excitations, and result in point defects which are in general not simple. Radiation-induced defect interaction, accumulation and aggregation modes differ significantly from those found in metals. Amorphization is a frequent option in response to high-density defect perturbation and is strongly related to structural topology. These fundamental responses to irradiation result in significant changes to important applicable properties, such as strength, toughness, electrical and thermal conductivities, dielectric response and optical behavior. The understanding of such phenomena is less well-understood than the simple responses of metals but is being increasingly driven by critical applications in fusion energy production, nuclear waste disposal and optical communications.

1. Introduction

Radiation effects in solids comprise a wide range of phenomena, many of which are common to all solid types, but some of which depend on the details of structure, bonding and composition peculiar to a given solid. Ceramics comprise a readily identifiable class of solids, but the distinguishing characteristics are not always so easy to enumerate. Ceramics are generally strongly-bonded refractory materials, yet the melting points for example of the alkali halide model systems (1074 K for NaCl) are especially low. The bonding of refractory oxides, like MgO or Al₂O₃, is almost entirely ionic, but SiO₂ and refractory nitrides and carbides are substantially covalent. Ceramics are frequently good insulators, but the utility of electrical ceramics like zirconia, β-alumina and cuprate superconductors lies in facile electron or ion transport. Ceramics are often mechanically brittle, yet readily-cleavable halides deform as plastically as pure copper, and even refractory MgO deforms readily at room temperature under a microindentor. Ceramics are most frequently compounds, but elemental silicon and carbon yield bona-fide ceramic solids. There is perhaps some utility in the adage that one knows one when one sees one in the context of identifying ceramics. For the purposes of this review, we shall consider Si, SiC, Si₃N₄, SiO₂, ZrSiO₄, NaCl, MgO, BeO, CaF₂, Al₂O₃, MgAl₂O₄, CaTiO₃, Ca₂Nd₄(SiO₂)₅O₂, CaZrTi₂O₇ and UO₂ to be genuinely representative ceramic solids. Amongst them, a distinction can be made between compact structures (e.g., alkali halides, strongly ionic oxides) and the more open network structures (e.g., MgO, BeO, UO₂) and complex structures (e.g., MgAl₂O₄, CaZrTi₂O₇).

Ceramics are found in a variety of radiation environments. The study of radiation effects in ceramics began late in the last century with investigations of damage tracks and amorphization in uranium-
thorium-containing minerals. With the development of fission reactors, concern shifted to understanding the effects of radiation on (U, Pu)O\textsubscript{2} and (U, Pu)C fuels, SiC coatings, graphite moderators and B\textsubscript{4}C absorbers. Twenty years ago, concern shifted to the back end of the nuclear fuel cycle – nuclear waste disposal – with attention focussed on the role of self-irradiation in stability of solid nuclear wasteform ceramics. Fusion reactors bring another set of problems where ceramics are called upon to serve as electrical insulators, first-wall protection, tritium breeders, radiofrequency and optical windows, and diagnostic electrical devices in particularly intense radiation fields with a high ionizing component. The widespread use of microelectronics in space and military applications has occasioned further interest in the specifically electronic effects of radiation on ceramics used as coverslips on solar cells, substrates for devices, dielectric and insulating layers, high-temperature superconductors, and optical communications media. These environments subject ceramics to both particle and ionizing radiation at temperatures up to half the melting point (\(T_m\)) or more and to displacement doses up to 100 displacements per atom (dpa).

Despite the variety of composition, structure and applications of ceramics in radiation environments, the responses of ceramics to radiation nevertheless exhibit substantial similarities and sufficient commonality that they can be usefully described in ensemble [1]. Ceramic radiation responses are not wholly dissimilar to those of that other well-studied class of solids, metals, for both of which the principal considerations are much the same: point and aggregate defect production; dimensional, mechanical and thermal property alterations; and changes in electrical (and for transparent ceramics, optical) properties, each of which is successively discussed in the three following sections. The principal distinctions lie in the higher energy of bonding in ceramics, the possibility of electrical charge at point defects, the high energy of anti-site disorder and the directionality of bonding in covalent structures.

Table 1
Displacement energies in some ceramics

<table>
<thead>
<tr>
<th>Solid</th>
<th>Displacement energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>11–22</td>
</tr>
<tr>
<td>C (diamond)</td>
<td>80</td>
</tr>
<tr>
<td>SiC</td>
<td>Si 93 C 22</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg 60 O 65</td>
</tr>
<tr>
<td>BeO</td>
<td>O 76</td>
</tr>
<tr>
<td>(\alpha)-Al\textsubscript{2}O\textsubscript{3}</td>
<td>Al 24 O 79</td>
</tr>
<tr>
<td>MgAl\textsubscript{2}O\textsubscript{4}</td>
<td>O 56</td>
</tr>
<tr>
<td>UO\textsubscript{2}</td>
<td>U 60 O 40</td>
</tr>
</tbody>
</table>

Ceramic solids share much with geological materials, which are nature’s long-lived manifestations of ceramic chemistry and processing. An important geological application of synthetic ceramic processing is the long-term storage of high-level radioactive waste in ceramic wasteforms, a subject discussed in the final section.

2. Radiation damage processes in ceramics

The primary radiation damage event is displacement of one or more atom species and the consequent formation of Frenkel (vacancy–interstitial) pairs. The displacement may occur ballistically, by transfer of kinetic energy from an incident projectile (electron, proton, neutron, ion), or radiolytically by conversion of radiation-induced electronic excitations into atom (ion) motion. In compounds, the displacements may not always occur stoichiometrically, occasionally significant chemical effects. Implantation associated with ion irradiation can further shift solid-state chemistries. The responses to accumulation of primary displacement defects include defect recombination, defect aggregation and amorphization, all of which exhibit additional features distinct from those associated with such processes in metals. These distinctive features are discussed below.

2.1. Primary displacement spectra

Ceramic compounds are distinguished by the presence of more than one distinguishable sub lattice populated by distinct atom types which may have similar or very different masses and atomic (or ionic) radii. MgO, with the rocksalt structure for example, has two distinct interpenetrating fcc sub lattices for respectively the similarly-sized Mg\textsuperscript{2+} and O\textsuperscript{2−} ions, while the structure of \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (hereafter, alumina) is dominated by the anion sub lattice of the larger oxygen ions. The Mg\textsuperscript{2+} and Al\textsuperscript{3+} cations in MgAl\textsubscript{2}O\textsubscript{4} are partially or wholly ordered, so there can be more than one non-equivalent cation sub lattice, each with elemental or sometimes mixed populations. Even compact ceramic structures are in general not close-packed, and the interstices available to any displaced atom are a function of all sub lattices present. The dominant oxygen ions in alumina define octahedral interstices, only 2/3 of which are occupied by aluminum cations, so the 1/3 unoccupied octahedral interstices are the most spacious sites available to displaced cations. In strongly ionic solids, the local Coulomb field additionally determines which interstitial sites are available to (or prescribed for) which displaced ions; in covalent solids, the preferred bonding geometry may function similarly. An additional complication is that the displaced ion may change its charge (and hence size) during displacement, and both vacancy and interstitial components of
the resulting Frenkel pair may trap charge. The form of the interstitial may of consequence be quite unlike the simple atom interstitial in metals. Split interstitials have long been favored as the model in Si and Ge [2]; $X_2^+$ and $X_2^-$ molecular-ion interstitials are well-documented in MX halides [3], and $O_2^-$ or $O_2^{2-}$ interstitials are observed in silica [4] and suspected in other oxides.

Frenkel defect formation energies (about 13 eV for both cation and anion Frenkel defects in MgO [5]) are typically higher than for metals. Saddle-point energies in the displacement process may be largely determined by a dominant sublattice and reflect the generally large bonding energies. Consequently, displacement energies $T_d$ are usually large as compared to metals and are generally different for each sublattice. Table 1 shows some typical values determined experimentally or by molecular-dynamics simulations. These values are directionally-dependent and temperature-dependent as in metals, and the values for each sublattice can often be measured separately by using spectroscopic evidence from the resulting point defects. Oxygen displacement in compact oxides is generally difficult (typically requiring 60 eV); comparable values are measured for Mg displacement in compact cubic-structure MgO, though in the hexagonal counterpart, BeO, beryllium ions appear to be easier to displace [6]. The low value measured for Al displacement in alumina [7] reflects the ready availability of an accommodating interstitial site. Similarly, oxygen displacement in the fluorite structure of $UO_2$, in which only every other cube of oxygen ions is occupied by a $U^{4+}$ cation, may be cased by the ready availability of an adjacent cubic interstice.

The disparity in atom (ion) masses as well as their different displacement energies implies that different kinetic energies are transferred to them in ballistic collisions. For the low-energy transfers characteristic of electron or low-energy light-ion irradiations, it is possible that one or more atomic species is infrequently or never displaced, leading to a chemically-skewed primary displacement spectrum. Such is often the case in high-voltage electron microscope irradiations, where large differences in threshold accelerating voltage generally obtain for the different atomic species in ceramic compounds. Displacement of only a single species does not, however, mean that observable structural alterations are not encountered: preferential precipitation of a single displaced (or undisplaced) species may occur, or there may be efficient secondary displacement mechanisms operating, driven by the chemical imbalance in the displacement spectrum. With heavier and more energetic particle irradiation (fast neutrons, heavy ions, energetic radioactive decay products), collision cascades initiated by the energetic primary knock-on atom (PKA) have a mixing effect which evens out the chemical imbalance asymptotically with increasing PKA kinetic energy. Even so, persistent imbalances can arise for atomic components exhibiting large differences in mass or displacement energy [8,9].

An alternative displacement mechanism operating in a surprising number of insulating (or at least semiconducting) ceramics occurs as a consequence of electronic excitations generated by interaction with ionizing radiation [10]. The phenomenon is known as radiolysis, and in some solids, such as halides (the basis for the photograpic process) and silicates, can be more efficient than knock-on displacement per unit of energy deposited. The electronic losses along fast charged-particle and PKA trajectories far outweigh the energy transferred in mechanical collisions, so most of the particle kinetic energy is eventually available to generate radiolytic displacements where these are possible. Radiolytic displacement is also possible with strictly ionizing radiation where ballistic impact does not occur.

Four criteria must be satisfied to ensure efficient coupling of electronic stopping power to atomic displacements [1,10]. First, an electronic excitation must be localized to one or at most a few atom sites. Next, the excitation must have a lifetime (~0.1 ps) comparable with phonon periods in order to couple into a mechanical response of the nuclear mass, and the available excitation energy must be comparable to the displacement energy for an atom in its excited state. Finally, a (potential) energy-to-momentum conversion mechanism must exist and compete favorably with other excitation decay modes such as recombination luminescence. Metals fail the first two criteria because electronic excitations are rapidly (~1 fs) delocalized via the conduction band. In insulators and semiconductors, the most frequent electronic excitations involve valence electrons, corresponding to excitation energies of the order of the band gap (1-12 eV); narrow-gap semiconductors are thus likely to fail on the energy criterion. While sufficiently energetic (10-30 eV), collective excitations (plasmons) of valence or conduction electrons are not sufficiently localized. This leaves single electron excitations in wide-gap insulators as the candidate states for radiolysis, the most persistent form of which is bound electron-hole (self-trapped exciton) states, some of which are long-lived enough to be responsible for phosphorescence. Many strongly ionic wide-gap insulators, like most oxides, nevertheless still fail the energy criterion because the displacement energies scale with the square of the common ion charge, so radiolysis is likely only for univalent anions or substantially covalent bonding, or at surfaces where the sputtering displacement energy is lower than for interior displacements.

Three technologically-significant examples are found in halides (monovalent ionic compounds), silica (substantially covalent oxide), and in surface sputtering of
transition metal oxides. Fig. 1 depicts two radiolysis sequences, the first well-documented in MX halides [11], the second suspected in silica [12], operating in the interiors of these respective compounds. In the first, a single electron excitation localizes on the halogen sublattice, the hole portion of the bound electron–hole pair forming an $X^+$ molecular ion occupying two halogen sites. The molecular ion is unstable in the resulting Coulomb field and moves rapidly off-center within a nanosecond, resulting in an $X^+$-crowd-ion molecular interstitial (called an H center) occupying a single halogen site and leaving behind a vacant halogen site which retains the excited electron (an F center). In effect, the exciton has mechanically dissociated into a halogen Frenkel pair. In the second, the exciton is associated with a Si–O bond and an oxygen atom moves off center to bond with an adjacent oxygen to form an $-\text{O}^\cdot\text{O}^-$ peroxy linkage between two Si atoms, leaving behind an oxygen vacancy occupied by two electrons in the form of dangling Si orbitals (E$^\cdot$ center); loss of one of these electrons causes one of the adjacent silicon to relax into a planar [SiO$_2$] triangular, rather than tetrahedral, geometry (E$^\cdot$ center).

Both radiolytic sequences are surprisingly efficient; displacements in alkali halides occur with quantum efficiency approaching 0.5, while those in silica occur with an efficiency $>10^{-4}$. Since most ionization events eventually decay to single electron excitations, the high quantum efficiency in halides means that about half the absorbed energy from ionization is available to produce atomic displacements. Operating with much reduced efficiency by comparison are surface desorption mechanisms in transition metal oxides. In one mechanism [13], which is a near-surface variant of the Varley mechanism [14] proposed much earlier for halide radiolysis, a cation core–hole excitation is followed by charge transfer to anions and additionally Auger electron emission; this sequence results in multiple hole localization at anion sites, consequent ejection of surface oxygen ions rendered into positive charge states unstable in the Madelung potential, and evaporation of metal ions reduced to neutral surface atoms. The much-reduced efficiency derives from the low probability of core (as opposed to valence) electron excitations and the infrequency of Auger events. Such surface mechanisms are nevertheless responsible for widespread and inconvenient rearrangement and erosion of insulator surfaces being examined by atomic-resolution transmission electron microscopy (TEM) [15,16]. All three mechanisms generate primary displacements initially on the respective anion sublattices, an extreme of skewed stoichiometry in the primary displacement spectrum.

2.2. Defect aggregation

The most probable fate for a newly produced Frenkel defect pair is self-(correlated) recombination, and the second most probable fate is annihilation of either component by the complementary component of a second Frenkel pair produced nearby (uncorrelated athermal recombination). For those defects which escape recombination, defect aggregation is a mechanism for reducing the elastic energy (and for most ceramics, the excess Coulomb energy also) associated with defect accumulation. Localization of defects in aggregates also decreases the probability of recombination with complementary defects and leads to a much higher fraction of initial displacements stored in the solid. As indicated earlier, the abstraction of energy from the incident radiation field occurs differentially for the different sublattice components, either because the target atom (ion) masses and displacement energies differ in simple binary collisions or because radiolytic displacement sequences occur on a single sublattice. Consequently, the numbers of displaced atoms (ions) are
Fig. 2. Interstitial condensation into dislocation loops. (a) \( \frac{1}{2}(110)\{110\} \) unfaulted loops in an MO rock-salt structure oxide like MgO formed from stoichiometric numbers of cation and anion interstitials, (b) equivalent loop resulting from anion interstitial condensation alone in MX rocksalt (NaCl)-structure halide, with additional formation of substitutional \( X_2 \) molecular defects [24].

unlikely to be stoichiometrically distributed, and this circumstance has significant implications for defect aggregation modes.

In crystalline solids, the most common aggregation mode for interstitials is planar condensation on a new set of atom sites, bounded by a dislocation loop (Fig. 2a). While the condensation may result in faulted or unfaulted stacking sequences through the loop plane, Coulomb repulsion in ionic solids proscribes faulted sequences which result in apposition of like ions. There is therefore a strong driving force for planar interstitial condensates to remain stoichiometric, or at least to balance anion and cation charges.

Stacking sequences in the complex unit cells of many ceramic crystal structures can be quite long, and because the elastic energy of a dislocation loop scales as the square of the Burgers vector, there is often no option but to tolerate faulted loops with smaller Burg-

Fig. 3. Interstitial aggregates in fission-neutron \((E > 0.1 \text{ MeV})\) irradiated ceramics. (a) Two-layer faulted interstitial dislocation loops in single-crystal MgAl\(_2\)O\(_4\) irradiated to \(2.3 \times 10^{26} \text{ n/m}^2\) (23 dpa) at 925 K (0.38\(T_m\)); A are \( \frac{1}{2}(110)\{110\} \) rosettes, B are \( \frac{1}{6}(111)\{111\} \) loops [20]. (b) Intersecting unfaulted dislocation loops and dislocation network arising in single-crystal Al\(_2\)O\(_3\) irradiated to \(3 \times 10^{25} \text{ n/m}^2\) (3 dpa) at 1015 K (0.44\(T_m\)) [19]. Weak-beam TEM images.
ners. The stacking arrangements in alumina along either [0001] or ⟨1010⟩, for example, are the 12-layer sequences AαBβAγBaAβBγA, where A, B are oxygen ion layers and α, β, γ are aluminum ion layers. Interstitials condense on [0001] basal or [0110] prism planes, without apparent preference, as \( \frac{1}{2} \langle 0001 \rangle \{0001 \rangle \). Either gen ion layers and α, β, γ are aluminum ion layers.

The stacking sequence AαBβAγBaAβBγA; this sequence faults only the cation sublattice, and not the larger oxygen anions, and maintains stoichiometry [17]. Either loop may unfault by the passage of a partial shear across the loop plane [18], e.g.

\[
\frac{1}{2} \langle 0001 \rangle + \frac{1}{2} \langle 1010 \rangle = \frac{1}{2} \langle 1011 \rangle.
\]

which permutes A → A, B → B and α → γ → β → α to regenerate the perfect stacking sequence. The resulting \( \frac{1}{2} \langle 1011 \rangle \) unfaulted loops are free to rotate on their glide cylinders, and their further growth leads to intersections and generation of dislocation networks [19] by at least 1 dpa in the temperature range 700–1200 K (0.3–0.5 \( T_g \)).

The behavior of MgAl₂O₄ spinel, with 56 atoms per unit cell, is particularly instructive as an example of the radiation response of more complex structures, in which it may not be possible with small Burgers vector loops to preserve stoichiometry, much less unfaulted stacking sequences. The cubic spinel structure can be described approximately as close-packed oxygen layers arranged in cubic ABCA packing, half of whose octahedral and one-eighth of whose tetrahedral interstices are occupied by cations. Along ⟨110⟩, the stacking sequence is the four layer sequence aδaε, where the a layers have mixed aluminum + oxygen population and the δ and ε layers have mixed Al + Mg + O population. Along ⟨111⟩ is found the twelve-layer sequence AγBaCβ AγBaCβA, where (in normal spinel) α, β, γ are aluminum layers and α', β', γ' are cation layers with mixed Al + Mg population.

Two-layer Frank loops (Fig. 3a) nucleate on both ⟨110⟩ and ⟨111⟩ planes in neutron- and ion-irradiated spinel irradiated in the temperature range 675–1100 K (0.28–0.46 \( T_g \)) [20,21]. The \( \frac{1}{2} \langle 110 \rangle \{110 \rangle \) loops preserve stoichiometry and fault only the cation sublattice, but the \( \frac{1}{2} \langle 111 \rangle \{111 \rangle \) loops, also faulting the cation sublattice, additionally alter the Al/Mg ratio – in either direction, depending on whether Aγ or Baα layers are inserted. The \( \frac{1}{2} \langle 111 \rangle \) loops therefore offer a vehicle for local accommodation of non-stoichiometry in the primary displacement spectrum. At elevated temperature, the equimolar MgO · Al₂O₃ line compound broadens into an aluminum-rich phase field, permitting an investigation of the effect of non-stoichiometry on radiation response. The role of non-stoichiometric \( \frac{1}{2} \langle 111 \rangle \) loops is clearly demonstrated in irradiation of an aluminum-rich MgO-2Al₂O₃ composition quenched from its stability field, which results in almost exclusive nucleation of \( \frac{1}{2} \langle 111 \rangle \) loops that are effectively precipitating the excess aluminum [22]. There is some indication that \( \frac{1}{2} \langle 111 \rangle \) loops are favored to nucleate first, even in stoichiometric spinel, and later convert to \( \frac{1}{2} \langle 110 \rangle \) loops [23].

The \( \frac{1}{2} \langle 110 \rangle \) loops grow as rossettes, with petals growing out on all equivalent ⟨110⟩ planes. No common junction dislocation is required for intersection along ⟨111⟩ of two such \( \frac{1}{2} \langle 110 \rangle \) faults, so the rosette form maximizes the loop area (and number of interstitials stabilized) with respect to the dislocation core perimeter. These loops grow to micrometer dimensions at 1100 K and still do not unfault, which is significant because faulted loops make poor interstitial sinks: the total fault energy increases linearly with each interstitial added, whereas in unfaulted loops the elastic energy per added interstitial decreases as the loop grows larger. Loop nucleation is also difficult, requiring at least a Frenkel septet. As a consequence, only about 0.05% of the total displacements in spinel are stabilized in loop aggregates in spinel, the vast majority simply recombining; by comparison, once the loops in alumina unfault and intersect to form climbing dislocation networks (Fig. 3b), the fraction is closer to 1% [19].

Fig. 2b depicts a more extreme accommodation to the gross displacement non-stoichiometry effected in NaCl undergoing radiolysis, where anion Frenkel pairs are the only primary displacement product. Driven together by elastic attraction, two Cl⁻ H-center molecular-ion interstitials react to form a neutral Cl₂⁺ interstitial molecule, which secondarily displaces a Na⁺ cation and a Cl⁻ anion from their ion sites in order to occupy a pair of substitutional sites; the secondarily-displaced ions nucleate a dislocation loop, which continues to grow by the adsorption of H-centers and to generate new substitutional chlorine molecules in its wake [24]. Dislocation loops are observed in electron-irradiated BeO at elevated temperatures at electron energies (80 keV) sufficiently small that only Be and not O ions are being primarily displaced [6,25,26]; similar observations have been made in alumina electron-irradiated below the oxygen displacement threshold [27]. Hence, secondary displacement mechanisms may operate more generally in response to imposed non-stoichiometries in the primary displacement spectrum [28].

Vacancy aggregation in irradiated ceramics can lead to void (pore) formation stabilized by radiation-produced insoluble-gas atoms, as in metals, provided efficient sinks for interstitials have first been established. Alumina is found to develop extensive pore arrays aligned along the c-axis (Fig. 4a), while spinel exhibits pore formation only immediately adjacent to polycrystalline grain boundaries which provide the only locally-efficient interstitial sinks (Fig. 4b). Non stoi-
chiometry in displacements or vacancy diffusion on the various sublattices can lead instead to precipitation of altered phases. An extreme example occurs in halides, where aggregation of F-center anion vacancies locally isolates the cation species, which incorporate the F-center electrons into a metallic conduction band to form colloidal metal precipitates of the cation species [29]. Sodium colloids are indeed a potential problem in rocksalt nuclear waste repositories [30,31], and calcium colloid lattices are observed in irradiated CaF$_2$ [29,32]. There is evidence for Al precipitation in electron-irradiated alumina thin foils [33], which may also arise from the dominance of Al displacements in such experiments. Substitutional molecular halogen defects in halides, upon acquiring sufficient mobility [34] can also aggregate to form halogen inclusions which may be gas bubbles or fluid inclusions, depending on the misfit [35]. An analogous aggregation of the oxygen molecular products of radiolysis may underlie the generation of oxygen bubbles in irradiated silicate glasses [36].

2.3. Amorphization

Defect aggregation is a highly-localized secondary defect response to primary displacements. A more global response is also possible in which the identity of individual defects is lost as the entire solid adopts a uniformly defective state. The most dramatic form of this response is the loss of long-range periodic order – amorphization – of an initially crystalline structure. The radiation-induced aperiodic condition was first studied in ancient minerals containing $\alpha$-particle emitting U and Th impurities and coined the *metamict* state by Norwegian mineralogist W.C. Brøgger a hundred years ago [37,38]. Amorphization of crystalline quartz (SiO$_2$) by neutron irradiation [39] and of crystalline zircon (ZrSiO$_4$) by $\alpha$-decay [40] were extensively studied forty years ago, and the metamict state was subsequently thought to be the exclusive province of inorganic ceramics and minerals (and, of course, organic solids, whose crystalline forms readily amorphize under irradiation [41]) until electron-irradiation-induced amorphization of intermetallic alloys was discovered within the last decade [42]. It is now clear that amorphization takes place at low displacement values (~ 1 dpa), occurs more readily at low temperatures for most solids, and usually involves substantial dimensional changes (both swelling and compaction are observed).

Comparison of irradiation results, particularly of ion-implantation studies in ceramics [43–45], has subsequently revealed a wide variation in susceptibility to

Fig. 4. Pore formation in fission-neutron irradiated ceramics. (a) Pore arrays aligned along the c-axis in Al$_2$O$_3$ irradiated to $3 \times 10^{22}$ n/m$^2$ (3 dpa) at 1015 K (0.44$T_m$). (b) Pore sheets forming adjacent to grain boundaries in polycrystalline MgAl$_2$O$_4$ irradiated to $2.3 \times 10^{22}$ n/m$^2$ (23 dpa) at 1100 K (0.46$T_m$). Underfocused Fresnel-contrast TEM images [19].
amorphization (Table 2). Alkali halides, for example, steadfastly retain crystalline order, preferring decomposition over amorphization, while silicas amorphize rather than forming aggregate defects. Such behavioral extremes have been correlated with bonding character, structure type, melting point, structural complexity and other physical and chemical attributes [46-51] - with at best limited success - in the hope of distinguishing criteria for explaining and predicting the amorphization response. Ion irradiations, though convenient, involve serious chemical effects from a high density of implanted ions, which are only beginning to be separated from the displacive effects [21]; tabulations such as Table 2 incorporating earlier data must therefore be viewed with caution.

Irradiation temperature is an important parameter because amorphization is, in some sense, the failure to crystallize from a radiation-disordered state exhibiting...
no initial long-range order; in this sense amorphization is not unlike glass formation, criteria for which have been recently redefined [51]. The principal parameter to be considered is available freedom for alternative structural arrangement, an evaluation of which lies in the realm of structural topology, enumerated by the branch of mathematics known as combinatorial geometry. The clearest formulation of the approach has been given independently by Cooper [52] and Phillips [53]. Cooper has considered the connectivity of structuring polytopes (for three-dimensional ceramic compounds, these are the familiar cation coordination polyhedra of Pauling’s rules) and shown that, for some combinations of polytope and connectivity, a structure is constrained (usually overconstrained) to be crystalline, while in other cases marginally- or underconstrained and free to adopt aperiodic configurations. Gupta [54,55] has extended Cooper's approach to establish an exact formulation of structural freedom

\[ f = d - C\delta - \left( \frac{\delta(\delta + 1)}{2V} \right) - (d - 1)(Y/2) \]

where \( f \) is the structural freedom available at each vertex of a polytope of dimensionality \( \delta \) with \( V \) vertices, each connected on average to \( C \) polytopes to generate a structure of dimensionality \( d \); the polytopes may each additionally share \( Y \) edges or \( Z \) \( p \)-sided faces. Structural connectivity is conveniently represented as \( \{V, C\} \). Enumerations for various ceramic structure types appear in Table 2 and correlate well with measured critical absorbed energies for amorphization during ion implantation.

An instructive illustration of the importance of structural topology to amorphization is the behavior of three of the crystalline polymorphs of silica, each of which amorphizes by radiolysis without nucleation of aggregate defects. (4, 2)-connected silicas comprise corner-sharing networks of \([\text{SiO}_4] \) tetrahedral structuring polytopes, each vertex of which is shared by two tetrahedra (Fig. 5a); the structures are only marginally constrained and determined only by boundary conditions. By contrast, \( \text{Si}_3\text{N}_4 \) is composed of \([\text{SiN}_4] \) tetrahedra, each vertex of which is shared with three tetrahedra, while the \([\text{SiC}_4] \) tetrahedra in \( \text{SiC} \) share each vertex with four tetrahedra; both structures are overconstrained and more jealous of their crystallinity. By way of evidence, neither \( \text{Si}_3\text{N}_4 \) nor \( \text{SiC} \) appears to amorphize under neutron or fast electron irradiation at room temperature, as do readily all three forms of \( \text{SiO}_2 \) cited, but instead both form dislocation loop aggregate defects [1]. \( \text{SiC} \) does amorphize at room temperature under ion bombardment and at 140 K under fast electron irradiation [51].) (6, 6)-connected \( \text{NaCl} \) (Fig. 5b) is even more redundantly-connected, with \([\text{NaCl}_6] \) octahedra sharing all edges, and as indicated earlier does not appear to be amorphizable.

The crystalline silica polymorphs cristobalite, tridymite (both high-temperature forms) and quartz (a low-temperature form) share the same network connectivity but differ in the linkages at third-neighbor tetrahedra [56]. Their network topologies are uniquely described by the sets of undecomposable rings (closed paths through linked tetrahedra) passing through a central tetrahedron in each respective structure. The set comprises exactly 12 6-rings in cristobalite and tridymite but predominantly 8-rings in quartz. The ring complement scales with density, structures with larger rings having higher densities. Metamict silica has a density almost exactly that of tridymite, but is 3% denser than vitreous silica, formed by cooling molten

![Fig. 6. Density changes in irradiated ceramics. (a) Swelling of \( \alpha \)-quartz and compaction of vitreous silica after neutron irradiation near room temperature [73]. (b) Swelling peaks for five other neutron-irradiated ceramics [63].](image-url)
SiO₂ through a glass transition, and 14% less dense than quartz (Fig. 6a). The inference is that the structure of metamict silica is dominated, like cristobalite and tridymite, by 6-rings. High-resolution TEM imaging reveals that tridymite and cristobalite proceed rapidly and seamlessly during radiolysis to the metamict state [57], whereas quartz locally nucleates misfitting amorphous inclusions which grow incrementally [58] and involve a large change in the structural topology required.

Unfortunately, TEM structure images of aperiodic materials provide information only about the microscope lens transfer function, and not about aperiodic structure [59]. However, electron diffraction (Fig. 7a) can provide useful information about radial density variations, provided inelastically-scattered electrons are removed from the diffraction patterns [60]. Radial density function sets, such as those depicted in Fig. 7b, provide such information about vitreous silica, neutron-amorphized quartz, and electron-amorphized quartz, cristobalite and tridymite. They reveal that, while the structure of electron-amorphized silicas is close to that of vitreous silica, the structures of the three electron-amorphized crystalline polymorphs differ from each other and significantly from that of neutron-amorphized quartz [61]. The structures of amorphized ceramics are therefore not unique, but depend on the precursor states and the modes of formation.

3. Mechanical and thermal property alterations

Ceramics and glasses can undergo significant changes in mechanical and thermal properties as a result of exposure to particulate irradiation (e.g., electrons and neutrons) and, in the case of materials sensitive to radiolytic damage, exposure to ionizing radiation (e.g., X- or gamma rays). In an irradiated ceramic the displaced ions can (1) remain in isolated form, (2) annihilate by recombination, or (3) aggregate into extended defects such as dislocation loops and pores. Isolated defects introduce dimensional changes, the integrated effect of which remains small if the defects remain isolated, because the athermal recombination volume is large for such a configuration, and defect content saturates at about 0.1%. Isolated defects also offer larger cross sections (per defect) than do aggregated defects for scattering of electrons and phonons, and so isolated defects give rise to large changes in electrical and thermal properties.

Dislocation loops, which commonly nucleate in ceramics with compact structures and overconstrained network structures, can expand and intersect (particularly if they unfault) to form dislocation networks (Fig. 3b) which can climb indefinitely with absorption of point defects and exhibit a bias for the interstitial component of Frenkel pairs because of the strain-field interaction. Vacancy aggregates (pores or colloids) can also expand indefinitely, but exhibit little bias for ei-

Fig. 7. (a) Amorphization of quartz in a TEM beam, with accompanying diffraction patterns [63]. (b) Species-averaged radial density functions derived from energy-filtered electron diffraction patterns of electron- and neutron-amorphized quartz compared to that of vitreous silica [61].
ther interstitial or vacancy species. The establishment of efficient, biased, unsaturable defect sinks, such as dislocation networks in compact solids, leads to lasting, essentially irreversible incorporation of new atom sites and attendant swelling. The kinetics can be modelled using rate theory, just as for void swelling in metals, and with similar predictions even if the displacements occur on only a single sublattice, the dislocation loops are complex composite aggregates, and the vacancy sinks are colloidal precipitates [62]. Such theoretical approaches predict a temperature of maximum swelling (Fig. 6b), which is widely observed for ceramics developing dislocation networks [63]. The lower temperature flank of the swelling curve represents, roughly, increasing vacancy mobility and the establishment of (neutral bias) vacancy aggregates, whereas the post-peak diminution at higher temperature corresponds to loss of vacancy sink stability.

The situation for rearrangeable network structures is analogous, in that the network rearrangements, to the extent that they are random and stochastic, also serve as unsaturable defect sinks until a steady-state aperiodic structure develops. The resulting dimensional changes may, however, be either positive (swelling) or negative (compaction), depending on the details of the network rearrangements, and the applicable rate theory derives from multiple-hit target theory [64].

It is instructive, for the purposes of this account, first to compare neutron damage effects in two extensively-studied ceramics, Al₂O₃ and MgAl₂O₄, in order to demonstrate how the different ways in which displacements are accommodated occasion major differences in property changes for these two compact-structure materials. After that comparison, the behavior of SiO₂, a marginally-constrained network compound with a damage response quite different from that observed in most ceramics, is considered.

### 3.1. Al₂O₃

Alumina (in the form α-Al₂O₃) is perhaps the best-known refractory ceramic for high-technology applications. When this material is irradiated with fast fission neutrons near room temperature, most vacancies and interstitials that do not recombine remain isolated or form small clusters such as divacancies. As a result, the roughly 1 vol% swelling observed at $1 \times 10^{25}$ n/m² results primarily from lattice dilatation around point-like defects. These fine-scale defects are efficient in scattering phonons, and so a large reduction in thermal conductivity can be expected.

Irradiation at higher temperatures results in greater defect aggregation and annihilation, and therefore a lower concentration of point defects, so that thermal conductivity is less degraded than at lower temperatures. Nevertheless, even when Al₂O₃ is irradiated to a fluence of $2 \times 10^{26}$ n/m² at temperatures as high as 1100 K, subsequent measurement of thermal diffusivity (a property that is closely proportional to thermal conductivity) at room temperature reveals degradation on the order of 50% (Fig. 9). Calculations [66] indicate that point defects will dominate the degradation process even with elevated-temperature irradiation, but that the observed porosity [19] can still be a major contributor to phonon scattering.

Irradiation to high fluences at temperatures up to 1100 K ($0.48T_m$) can result in swelling as great as 4 vol% (Fig. 8b) [67]. Expansion at this temperature is highly anisotropic (Fig. 8a); the anisotropy results from preferential retention of interstitial dislocation loops with Burgers vectors that induce dilatation predominantly resolved along the c-axis [19,68]. One ominous consequence of such anisotropy in damage response is extensive grain boundary separation [19], leading to gross fracturing of polycrystalline alumina [65]. Thus,

![Fig. 8. Dimensional changes in fission-neutron irradiated ceramics [19]. (a) Anisotropic a-axis and c-axis dilatation in neutron-irradiated single-crystal Al₂O₃ as a function of irradiation temperature. (b) Swelling of single-crystal Al₂O₃ and MgAl₂O₄ as a function of neutron fluence at three irradiation temperatures.](image-url)
large reductions in strength of polycrystalline alumina can be anticipated. Strength of single-crystal Al₂O₃, where anisotropic growth is not a consideration, does not degrade after irradiation to a fluence of 2 × 10²⁶ n/m² at 680 and 815 K and in fact shows a slight increase [69]. This behavior has been attributed to an observed increase of fracture toughness, which is thought to result from interaction of cracks with the void field [70].

3.2. MgAl₂O₄

Magnesium aluminate spinel is the most radiation-resistant ceramic known. In both single-crystal and polycrystalline forms, MgAl₂O₄ shows near-zero swelling (Fig. 8b) after neutron irradiation to 2 × 10²⁶ n/m² at 680 and 815 K and in fact shows a slight increase [69]. This behavior has been attributed to an observed increase of fracture toughness, which is thought to result from interaction of cracks with the void field [70].

3.3. SiO₂

Silicon dioxide is found both in the aperiodic form (vitreous silica) and in at least six crystalline polymorphs. The latter are sometimes generically (but incorrectly) referred to as quartz in irradiation properties literature, although that name correctly applies only to the trigonal form (α-quartz) or its higher-temperature β variant, which is hexagonal. As shown in Fig. 6a, irradiation with even a low fluence of neutrons (of order 10²⁴ n/m²) has a dramatic effect on both vitreous silica and quartz: the former densifies by 3 vol%, while the latter swells 14 vol% [78]. Both starting forms move to a common density and share related, if not identical, metamict states. The major changes induced in SiO₂ by low levels of atomic displacement are a consequence of the ease with which [SiO₄] tetrahedra can be rearranged into alternative network configurations [51]. It should be recalled from Section 2.1 that SiO₂ can be damaged by radiolysis as well as by collisional events [112].

There are few data on changes in mechanical properties of SiO₂ resulting from radiation damage. Since irradiation-induced alterations in atomic arrangement...
are global rather than local (that is, defects such as pores and dislocation loops are not observed), it may be anticipated that a strength value similar to those characteristic of vitreous silica (~100 MPa) would be found for the metamict condition. However, the large volume changes observed indicate that SiO₂ components which are subjected to mechanical constraint (e.g., optical fibers and sealed windows) will likely have to be limited to neutron fluences of order 5 × 10²¹ n/m², unless periodic annealing can be utilized. This limitation arises because, at that fluence, the induced strain of ~4 × 10⁻⁴ for both vitreous silica and quartz is sufficient to put constrained systems at risk of fracture [74].

Room-temperature thermal conductivity of unirradiated quartz is 5–8 W/mK, depending on crystallographic direction. The corresponding value for vitreous silica is approximately 1 W/mK. Again, few data exist for irradiated material, but it would seem reasonable to expect that vitreous silica, which has an aperiodic structure to begin with that is unlikely to differ substantially in topology from metamict silica, would show little change in thermal conductivity upon irradiation. On the other hand, the thermal conductivity of quartz would be expected to decrease upon irradiation to about 1 W/mK, the value for vitreous silica.

4. Changes in electrical and optical properties

Ceramics have a much broader range of electrical and optical properties than do metallic solids, ranging from highly insulating to superconducting and from colorless and transparent over km lengths to opaque and highly reflective. This variety is being increasingly exploited in applications involving radiation environments, from fusion reactor designs which require electrical insulators, dielectric waveguides and diagnostic windows to optical communications fibers and superconducting computers for the military. The largest changes in electrical and optical responses of ceramics in fact occur during irradiation because of a significant alteration in the populations of charge states and charge carriers induced by both ionizing and displacive components. The properties altered are electrical conductivity (both transient and permanent), dielectric response (breakdown strength, the value of the dielectric constant, and dielectric loss), and light transmission (edge shifts and transparency). Such important changes affect the utility of ceramics in these applications and are discussed here in turn.

4.1. Electrical conductivity

It has long been known that the electrical conductivity of insulating and semiconducting materials can be dramatically increased by energetic radiation, due to the excitation of valence electrons into the conduction band. The phenomenon of radiation-induced conductivity (RIC) was apparently first discovered in 1873, when the semiconductor selenium was observed to become more conductive during exposure to light [75]. Similar photoconductivity experiments on different insulating materials followed around the turn of the century using X-ray [76] and gamma ray [77] sources. Radiation-induced conductivity was subsequently observed to be a general phenomenon in insulators irradiated with ionizing radiation, including electron and alpha-particle sources [78,79]. Despite these early experimental observations, a sound theoretical understanding of RIC incorporating the general features of carrier excitation, trapping and recombination did not occur until the 1950s when models by Rose [80] and Fowler [81] were published. There are numerous books and review articles devoted to photoconductivity and RIC [82–89]. The term photoconductivity has historically been limited to induced conductivity associated with photon radiation sources, viz. light, X-ray and gamma rays, whereas RIC is the more general term for any type of ionizing radiation source [83].

Accurate measurement of RIC in ceramic insulators requires several experimental precautions. A suitable guard ring geometry [90] is required to minimize surface leakage currents. However, it should be recognized that significant surface leakage currents may occur during irradiation, even when guard rings are utilized, due to the deposition of conductive surface films from the surrounding atmosphere [91]. Ionization of the surrounding atmosphere can produce spurious currents unless the pressure is below about 0.1 Pa, and the maximum ionization currents occur at intermediate pressures of ~10–100 Pa [92]. This gas ionization is a particularly difficult problem for fission-reactor RIC measurements. The measured radiation-induced current depends strongly on the behavior of the metallic electrodes that are in contact with the insulator [83–86]. Two general categories of electrode behavior are possible, depending on specimen surface preparation, the method of electrode deposition, and the relative work functions (electron affinities) of the electrode and insulator. Many vacuum-deposited metals act as blocking electrodes (also known as rectifying contacts) at low and intermediate field strengths, i.e., charge carriers are not easily transferred from the electrode to the insulator, but charge carriers may be removed from the insulator by the electrode [85]. This can lead to the formation of Schottky barriers at the electrode–insulator interface. The preferred contacts are ohmic electrodes, which produce a linear relation between current and voltage. However, all ohmic contacts tend to inject excess charge carriers into the insulator when the applied electric field exceeds a certain value [83,84]. This
leads to space-charge-limited current flow and non-ohmic behavior. RIC associated with ionizing radiation tends to increase the upper limit of the electric field for ohmic behavior by reducing space-charge effects in the insulator. In practice, ohmic behavior must be experimentally verified (with and without ionizing radiation) in both the forward and reverse current direction to determine the allowable range of electric fields.

4.1.1. Transient radiation-induced conductivity

Any source of radiation that is sufficiently energetic to ionize the atoms in a ceramic insulator by imparting kinetic energy to the valence electrons in excess of the band gap energy (typically a few eV) can produce radiation-induced conductivity. Many of the ionized electrons and associated holes recombine within ~10^{-11} s in the vicinity of their parent ion and do not contribute to any current flow (geminate recombination) [86]. Electrons and holes that escape geminate recombination can diffuse under an applied electric field and produce RIC. Structural imperfections in the crystal, such as impurities, create trapping sites for the diffusing electrons and holes which further modify the RIC behavior. Two types of trapping sites are possible: recombination centers, where the captured charge carrier recombines with a carrier of opposite charge, and trapping centers, where a charge carrier is temporarily captured and is thermally re-excited into the conduction band before recombination occurs [84,86]. The demarcation between recombination and trapping centers is approximately the Fermi energy level (E_F). Electrons captured in sites lying more than E_F from the conduction band will generally experience recombination with a hole since thermal re-excitation into the conduction band is negligible, whereas electrons residing in sites lying within E_F from the conduction band will generally be thermally excited back into the conduction band before recombination occurs and are therefore temporary trapping centers [84].

There is a large data base on the instantaneous increase in electrical conductivity of ceramics induced by exposure to ionizing radiation [83,86–89,92–108]. The high mobility and capture cross sections of electrons and holes in the conduction band generally result in recombination of the electron–hole pairs created by ionizing radiation within < 10^{-8} s [86]. Hence, RIC measurements must be performed in situ while the specimen is being irradiated. The electrical conductivity of the ceramic generally reverts to a value very near its pre-irradiation value immediately after the irradiation source is turned off [86,92,102], although in some cases the time constant for decay of the RIC can be seconds or days [85,109]. This delayed conductivity is due to thermal emission of charge carriers from trapping centers which are located near the Fermi energy level (“deep” traps).

Fig. 10 shows a typical example of the temperature-dependent RIC of alumina measured during exposure to ionizing radiation [100]. The RIC is only weakly dependent on temperature at low irradiation temperatures, which is an indication of predominantly deep trapping sites. Various studies have observed either a slight increase [99,100,104,107] or decrease [99] in the RIC with increasing temperature in the range of 298 to 673 K. At high irradiation temperatures, the RIC curve gradually merges with the electrical conductivity curve for unirradiated material.

The electrical conductivity measured during irradiation can generally be described by the simple power law relation

$$\sigma = \sigma_0 + KR^\delta,$$  \hspace{1cm} (3)

where $\sigma_0$ is the conductivity in the absence of irradiation, $R$ is the ionizing dose rate, and $K$ and $\delta$ are constants which depend on the material and irradiation conditions [80,86,88,98]. The proportionality constant $K$ has typical room temperature values of 10^{-12} to 10^{-9} s/(Gy·Ω·m) for ceramic insulators. The dose-rate exponent $\delta$ has been observed to vary between 0.5 and 1 for most materials [83,84,88,89]. Several experimental studies have shown that the detailed behavior of $\delta$ depends on both temperature and defect concentration [84,88,99,100,106,107], with reported values as low as 0.5 and as high as 3 to 5. The supralinear behavior is generally only observed over a narrow range
Also, except for those of Hodgson and Clement [106] and Pells [107] which were made on MgO and MgAl$_2$O$_4$, respectively. The data of Farnum et al. [102] which were made on MgO and MgAl$_2$O$_4$ are previously unpublished results on a specimen irradiated at 298 K to 10$^3$ dpa with 3-MeV protons.

Most RIC studies performed to date have considered only the overall magnitude of the ionizing radiation and have assumed that the spatial distribution of the ionization is not important. There is some theoretical [112] and experimental [95] evidence that the prompt RIC may be less in insulators exposed to densely-ionizing radiation sources, as compared to diffuse or weakly-ionizing radiation, a result of enhanced electron–ion geminate recombination. However, the overall effect of ionization density appears to be small, since there is no correlation between ionization density and RIC behavior for high-purity Al$_2$O$_3$ irradiated with X-rays, gamma rays, electrons, protons, or neutrons (e.g. Fig. 11) [92,98,102].

4.1.2. Permanent electrical conductivity changes

There have been numerous studies of the effect of prolonged irradiation on the electrical conductivity of ceramic insulators. Under certain irradiation conditions, it is possible to inject charge carriers into the insulator and thereby increase the post-irradiation electrical conductivity for a limited period of time [85]. However, prolonged irradiation without an applied electric field generally produces either no change or a moderate decrease in the post-irradiation electrical conductivity compared to the pre-irradiation value [89, 91,94,102,103,110,111,113]. The decrease in conductivity occurs in specimens subjected to displacement damage, which produces trapping sites for the charge carriers.

Several recent studies indicate that severe permanent increases in the electrical conductivity of ceramic insulators may occur during extended irradiation if an electric field is applied during the irradiation [110,111, 114–123]. This radiation-induced electrical degradation (RIED) apparently develops in oxide ceramics at moderate temperatures of about 473 to 873 K after irradiation to the rather low damage levels of 10$^{-5}$ to 0.1 dpa. RIED has been reported for single-crystal and polycrystalline Al$_2$O$_3$ [110,111,114–123], MgO [114] and MgAl$_2$O$_4$ [111], irradiated with electric fields greater than about 20 V/mm. The effect of RIED is to

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**Fig. 11.** Radiation-induced conductivity of pure oxide ceramics measured during irradiation near room temperature [92,98–102,106,107]. All of the measurements were made on Al$_2$O$_3$, except for those of Hodgson and Clement [106] and Pells [107] which were made on MgO and MgAl$_2$O$_4$, respectively. The data of Farnum et al. [102] which were made on MgO and MgAl$_2$O$_4$ are previously unpublished results on a specimen irradiated at 298 K to 10$^3$ dpa with 3-MeV protons.
crease the base conductivity ($\sigma_0$ in Eq. (3)). Some studies have reported permanent post-irradiation electrical conductivities > $10^{-4}$ S/m in degraded samples [111], which could severely limit the usefulness of ceramic insulators in radiation environments.

Significant degradation in the electrical resistivity of electron-irradiated $\text{Al}_2\text{O}_3$ has been reported for electric fields as low as ~20 V/mm, and the degradation process is accelerated if the electric field is greater than ~75 V/mm [117,118]. It is worth noting that most insulator applications in nuclear radiation environments require continuously-applied electric fields of 10–1000 V/mm (e.g., Ref. [89]). In contrast to the well-known phenomenon of electrothermal dielectric breakdown in unirradiated ceramics [124], RIED has been reported to occur not only in dc electric fields, but also in ac fields up to at least 126 MHz [117,118].

There is apparently a strong temperature dependence for the RIED process, with the largest degradation in insulators such as $\text{Al}_2\text{O}_3$ occurring near 723 K [89,119,120]. Little or no degradation has been observed in $\text{Al}_2\text{O}_3$ or $\text{Y}_2\text{O}_3$ for neutron doses of 0.01 to 0.5 dpa at temperatures of 888 to 1373 K with an applied dc electric field of ~40 to 150 V/mm [125–128]. Similarly, RIED was not observed in $\text{MgAl}_2\text{O}_4$ or $\text{Al}_2\text{O}_3$ irradiated with 18 MeV protons at temperatures > 873 K [129]. Electron irradiation studies indicate that the lower temperature limit for RIED in $\text{Al}_2\text{O}_3$ is about 423 K [120], whereas proton irradiations conducted to a somewhat higher damage rate showed that significant levels of RIED did not occur if the irradiation temperature was below ~573 K [111]. RIED was not observed in $\text{Al}_2\text{O}_3$ irradiated with fission neutrons at 353 K up to ~0.11 dpa with an applied electric field of 130 V/mm [130].

The phenomenon of RIED has been observed only in specimens subjected to radiation sources which produce displacement damage, suggesting that the physical degradation mechanism involves some type of point defect aggregation. Unfortunately, the physical process responsible for the electrical degradation remains uncertain. Hodgson [110,116–121] has suggested that colloid (small metallic precipitate) formation may be the cause, based on light-optical microscopy, the general temperature and dose-rate dependence of the process, and optical absorption (F and F+ oxygen vacancy center) measurements. However, transmission electron microscopy has failed to detect colloid formation in either degraded or undegraded samples irradiated with an applied electric field [123,129,131]. Furthermore, the irradiation temperature corresponding to the peak electrical degradation (~723 K) is several hundred degrees below the peak void swelling temperature for these materials [63]. Since colloid formation and void swelling both involve nucleation and growth of vacancy-type defects, a similar temperature dependence would be expected for both processes.

Fig. 12 compares the results of several RIED studies on $\text{Al}_2\text{O}_3$ that were performed near the peak degradation temperature of 723–773 K [110,111,122,131]. Significant permanent degradation was observed in the electron-irradiated specimens after < $10^{-4}$ dpa, whereas ~0.1 dpa was required to induce RIED during fission neutron irradiation. The inability to correlate the RIED results obtained in different irradiation sources with displacement damage level suggests that additional physical parameters need to be considered, such as damage rate [121] and irradiation spectrum [21]. From Fig. 12, it appears that irradiation sources such as electrons, which produce isolated point defects and high levels of ionization per atomic displacement, may cause accelerated RIED kinetics as compared to...
fission neutrons, which produce relatively dense populations of defects in spatially localized regions and low levels of ionization per atomic displacement. It is well established that irradiation spectrum can have a strong influence on the microstructural evolution of ceramic insulators such as Al$_2$O$_3$ and MgAl$_2$O$_4$, and that point defect diffusion in ceramics can be greatly enhanced by ionizing radiation [21]. Hodgson [121] has also recently noted that the lower damage rates employed in the electron irradiation experiments would be expected to induce RIED at lower damage levels, as compared to high damage rate (fission neutron) experiments, if point defect aggregation is responsible for RIED (simple chemical-rate theory predicts a square-root dependence on dose rate).

Several recent studies have suggested the possibility that RIED may be due to surface leakage currents, instead of bulk conductivity changes [91,132]. It was concluded in these studies that hydrocarbon deposition onto the specimen surface from residual gases in an evacuated target chamber could modify the optical absorption and surface electrical conductivity during irradiation, thereby creating an apparent “bulk” RIED effect. Application of an electric field during irradiation was found to increase dramatically the electrical conductance of the surface film compared to the zero-field case (perhaps by modifying the chemical nature of the deposited film) [132]. Further support for the importance of atmospheric contamination was obtained from a side-by-side neutron irradiation experiment on Al$_2$O$_3$ [128]. No evidence for RIED was obtained in capsules filled with Ar gas during irradiation to about 0.03 dpa at temperatures of 668, 888 and 928 K with dc applied fields of 50 and 150 V/mm. On the other hand, conductivity increases similar to the RIED curves (Fig. 12) were observed in specimens irradiated with an ac applied field of 130 V/mm in capsules that were evacuated and sealed before irradiation. Post-irradiation examination of the specimens from the evacuated capsules is currently in progress and will help determine if a conductive surface film caused the RIED-like behavior for these specimens. It should be noted that the neutron irradiation study shown in Fig. 12, which reported evidence for RIED, was performed in a capsule that was evacuated and sealed prior to irradiation [122].

Further work is clearly needed to resolve the questions surrounding the RIED phenomenon, viz. is RIED a bulk or a surface irradiation effect, and what are the physical mechanisms responsible for RIED? Colluid formation does not appear to be a likely mechanism for the electrical degradation, since a high volume fraction of metallic precipitates would be required to increase the electrical conductivity of Al$_2$O$_3$ to $> 10^{-5}$ S/m. In addition, colloid formation has not been observed by electron microscopy, even in specimens which have apparently suffered RIED [123]. On the other hand, the work by Zong et al. [123] indicates that specimens subjected to an electric field during irradiation experience significant bulk microstructural changes in their dislocation density. The average dislocation density in single-crystal Al$_2$O$_3$ irradiated with an electric field of $\sim 210$ V/mm was found to be $\sim 10^{13}$/m$^2$, compared to $\sim 10^9$/m$^2$ in regions irradiated without an electric field. The dislocations were heterogeneously grouped in low-angle subgrains [123], suggesting that RIED may be somehow associated with polygonization. The microstructures observed in the regions exposed to the electric field are reminiscent of the microstructure observed in dielectrics subjected to high-temperature thermoelectric breakdown [133].

Recent work by Hodgson [119,120] suggests that the production of F$^+$ centers (oxygen vacancy containing a single trapped electron) is enhanced during irradiation with an applied electric field. The F$^+$ center is expected to be more mobile than the F center [134], which could lead to defect aggregation at lower temperatures than normally occurs (i.e., without an applied electric field) and could explain the discrepancy between the location of the RIED and void swelling temperature peaks. Radiation effects studies on semiconductors suggest that applied electric fields may also enhance the defect production rate [134]. Finally, the possible role of space charge effects on the development of RIED needs further study. Large inhomogeneous electric fields can be induced in dielectrics by trapped charges [135] and by electromagnetic radiation [136,137]. It is conceivable that local amplification of the electric field applied during the RIED experiments may occur, which could lead to localized dielectric breakdown.

4.2. Dielectric breakdown strength

Most ceramic insulators can withstand electric fields up to about $10^7$ V/m at room temperature without suffering permanent dielectric breakdown. Bulk dielectric breakdown occurs by either the avalanche or the thermal (Joule heating) mechanisms, depending on the material, temperature, and duration of applied voltage [138]. The avalanche mechanism is dominant at low temperatures and for short voltage pulses and occurs when electron motion induced by the electric field is sufficiently energetic to produce ionization from electron–electron collisions. The thermal mechanism is associated with the increased electrical conductivity that occurs with increasing temperature in insulators. If the Joule heating associated with current flow in a dielectric is sufficiently high to increase the bulk temperature, further increases in current are produced until runaway and breakdown occur. The dielectric breakdown strength of ceramics generally decreases
with increasing temperature, due to the increased importance of thermal breakdown at elevated temperatures. Typical breakdown strengths for oxide insulators at 1473 K are $\sim 10^5$ V/m [139].

Irradiation appears to have a relatively minor effect on the dielectric breakdown strength of ceramic insulators. Post-irradiation tests have shown that the room-temperature breakdown strength was essentially unchanged in Al$_2$O$_3$ and other oxide ceramics following irradiation at 373 to 613 K to a fluence of 0.15 to $2.2 \times 10^{26}$ n/m$^2$ ($E > 0.1$ MeV) [140]. Similar results were also obtained for Al$_2$O$_3$ irradiated at 923 and 1103 K to a fluence of $(1-2) \times 10^{26}$ n/m$^2$ ($E > 0.1$ MeV) [141]. A slight degradation in the dielectric breakdown strength of Al$_2$O$_3$, ThO$_2$ and ZrO$_2$ was found during exposure to an X-ray field of about 5 Gy/s at temperatures below 473 K [142]. The X-rays did not affect the breakdown strength at temperatures above 473 K, owing to the increased importance of field-enhanced thermal emission compared to RIC effects [142]. Concurrent ionizing radiation of 0.5 Gy/s did not affect the breakdown strength of BeO or Al$_2$O$_3$ at any temperature between 298 and 923 K [104].

4.3. Dielectric properties: dielectric constant and loss tangent

The power absorbed by a low-loss dielectric from an incident electromagnetic wave is dependent on two material parameters, the dielectric permittivity ($\varepsilon$) and the loss tangent (tan $\delta$). The loss angle $\delta$ is related to the phase difference between the applied ac field and the resulting current. For an ideal loss-free dielectric, the current leads the voltage by 90$^\circ$ and the loss angle $\delta$ is zero, whereas in real dielectrics the phase difference between the current and voltage is 90$^\circ$ $-$ $\delta$ [143]. Rigorously, the loss tangent is defined as the ratio of the imaginary to the real part of the permittivity, $\varepsilon''/\varepsilon'$. From an integration of the product of the voltage and current, the power absorbed in the dielectric is given by [143]

$$P = \omega \varepsilon \tan \delta E^2,$$

where $\omega$ is the angular frequency of the ac electric field with root-mean-square amplitude $E$. The product $\varepsilon \tan \delta$ is commonly referred to as the dielectric loss factor.

For high power applications, such as radio-frequency heating of the plasma in fusion reactors, it is desirable to have the lowest possible loss factor in order to minimize thermal stresses associated with power absorption. The dielectric permittivity of most ceramic insulators is approximately $10^6 \varepsilon_0$ over a wide range of temperature and frequency, where $\varepsilon_0$ is the permittivity of free space [143]. On the other hand, the value of tan $\delta$ exhibits a pronounced dependence on temperature and frequency [144–146]. Impurities have a relatively minor effect on the permittivity, but they can cause dramatic increases in the loss tangent over several decades in frequency [143–146]. The loss tangent can be represented as the sum of contributions from electrical conduction and polarization losses [143,148]

$$\tan \delta = \frac{\sigma}{\varepsilon \omega} + \frac{\chi'' \varepsilon_0}{\varepsilon},$$

where $\sigma$ is the electrical conductivity (Eq. (3)) and $\chi''$ is the imaginary part of the electric susceptibility. The electrical conductivity term is generally negligible compared to the polarization term, unless there is a large amount of RIC. A typical loss tangent for a low-loss dielectric such as Al$_2$O$_3$ at 100 MHz is tan $\delta$ $\approx 10^{-4}$ at room temperature, and the electrical conductivity required to produce this large a loss tangent would be $\sigma \approx 5 \times 10^{-6}$ S/m. The loss tangent generally decreases at all frequencies with decreasing temperature below room temperature. Loss peaks associated with impurities can produce complex behavior in the loss tangent at elevated temperatures, but the general trend is an increase in the loss tangent with increasing temperature [144–146].

Post-irradiation measurements indicate that radiation-induced changes in the permittivity are generally small ($\sim 1$–5%), with either slight increases [148,150–152] or decreases [149] reported. A slight decrease ($\sim 1$%) in the permittivity of several ceramic insulators was measured during pulsed neutron irradiation with peak ionizing dose rates up to $4 \times 10^3$ Gy/s at room temperature, due to electrical conductivity increases associated with RIC [92].

Displacement damage can produce large increases in the loss tangent, with the magnitude of the increase depending on the material, irradiation conditions, and measurement frequency [145,147–160]. Most of the loss-tangent measurements in irradiated material have been performed on Al$_2$O$_3$, with relatively few studies performed on MgAl$_2$O$_4$ [92,154,158,160], BeO [149,157], AlN [92,154], Si$_3$N$_4$ [92,158,160] and “AlON” (Al$_{25}$O$_{37}$N$_6$) [156,158,160]. All these ceramic appear to behave in a qualitatively similar manner, although significant quantitative differences can occur (due mainly to as-yet unresolved impurity effects). Fig. 13 summarizes some of the post-irradiation loss tangent measurements made at frequencies greater than 1 MHz on Al$_2$O$_3$ irradiated near room temperature [147,148,153,154]. Neutron irradiation fluences up to about $1 \times 10^{22}$ n/m$^2$ ($\sim 0.001$ dpa) produce only small increases in the room temperature loss tangent. Large increases in the loss tangent occur over a wide frequency range for neutron fluences above $1 \times 10^{22}$ n/m$^2$.

Irradiation at elevated temperatures requires progressively higher neutron fluences to induce comparable degradation in the loss tangent. For example, the
Fig. 13. Effect of neutron irradiation near room temperature on the loss tangent of polycrystalline (pc) and single crystal (sc) Al$_2$O$_3$ [147,148,153,154]. All of the measurements were performed post-irradiation at room temperature at the indicated frequency.

Room-temperature loss tangent of Al$_2$O$_3$ measured at 95 GHz increased from $3.9 \times 10^{-4}$ to $8.3 \times 10^{-4}$ after irradiation to a neutron fluence of $1 \times 10^{26}$ n/m$^2$ ($E > 0.1$ MeV) at 658 K [149], whereas a similar amount of degradation was observed in this frequency range for Al$_2$O$_3$ irradiated to only $\sim 3.5 \times 10^{23}$ n/m$^2$ ($E > 0.1$ MeV) at 333 K [153]. Radiation-induced point defects that contribute strongly to dielectric loss are known from post-irradiation annealing experiments on Al$_2$O$_3$ to be thermally unstable at temperatures above room temperature [153,161,162]. That instability causes the rate of loss-tangent degradation to decrease with increasing temperature above room temperature. In addition, the predominant type of defect produced during irradiation changes from point defects at low temperatures (which are effective in increasing the loss tangent) to defect aggregates and dislocation loops at elevated temperatures (which are less effective at increasing the loss tangent per atomic defect).

There is evidence that significant annealing of the induced loss-tangent degradation in ceramics may occur at room temperature. Post-irradiation measurements on Al$_2$O$_3$, MgAl$_2$O$_4$ and AlON irradiated with protons near room temperature to damage levels of $\sim 0.02$ dpa found that a substantial part of the loss-tangent increase at 100 MHz was recovered within a matter of hours [158,160]. Since most loss-tangent measurements on neutron-irradiated samples are typically made several months after the irradiation (to allow for the decay of radioactivity), post-irradiation measurements made on samples irradiated near or below room temperature may underestimate the in-situ loss tangent. There have only been a few attempts to measure the in-situ loss tangent of ceramics during irradiation [92,157,159]. Pulsed fission-reactor irradiation at very high damage rates ($\sim 4 \times 10^4$ Gy/s) caused a significant prompt increase in the loss tangent at 100 MHz of several ceramics due to radiation induced conductivity (cf. Eq. (5)), but the damage levels in this study were not high enough to investigate point-defect annealing behavior [92]. A measurable increase in the loss tangent of Al$_2$O$_3$ was detected during proton irradiation at 300 K for damage levels greater than $\sim 10^{-4}$ dpa, and the loss tangent became larger than $10^{-3}$ for damage levels $> 10^{-3}$ dpa [159]. This in-situ degradation is about an order of magnitude higher than that determined from post-irradiation tests performed on neutron-irradiated samples (cf. Fig. 13).

4.4. Optical properties

One of the characteristic features of dielectric materials is their good transmission at frequencies corresponding to the optical part of the electromagnetic spectrum [163]. Absorption of light is generally small in ceramic dielectrics between the infrared and ultraviolet wavelengths of $\sim 100$ µm and $\sim 100$ nm, respectively. Irradiation-induced defects in dielectric materials can reduce transparency by serving as resonant absorption and scattering centers. The strong coloration of irradiated ceramics results from defects having energy levels of opposite parity within the band gap [164,165]. This produces a unique resonant scattering frequency for each individual type of point defect (anion vacancy, anion vacancy with one trapped electron, etc.). Much of the present understanding of point defects in non-metals has been obtained from studies on the optical absorption and luminescence associated with irradiation. Defect concentrations below $10^{22}$/m$^3$ (0.1 appm) can be detected by optical techniques [123,166]. Vacancies on the anion sublattice in oxides are historically referred to as F-type centers, whereas vacancies on the cation sublattice are called V-type centers [165]. Numerous reviews on the optical properties of irradiated ceramics have been published [164,165,167,168].

Optical absorption and luminescence measurements have been used to determine fundamental parameters such as the threshold displacement damage energy in Al$_2$O$_3$ [88,169,170] and the effect of irradiation spectrum [171–173] and temperature [88,162,173] on the defect production rate in Al$_2$O$_3$ and MgO. These studies have shown that the defect production rate decreases with increasing temperature, and that energetic collision cascades generally produce a smaller fraction of the calculated Kinchin-Pease displacements compared to low-energy displacement events. The aggregation of point defects into defect clusters during
annealing at elevated temperatures has also been studied by optical techniques in ceramics such as Al$_2$O$_3$ [162,174].

Numerous radiation effects studies have been performed on quartz and vitreous silica optical fibers, owing to their technological importance [165,168,175–185]. The optical fibers are often in reality glassy silicates with significant concentrations of dopants such as Ge, P and OH and low concentrations of other impurities. The basic design of an optical fiber consists of a transparent core surrounded by a concentric transparent cladding which has a lower index of refraction. This design causes transmitted light to be confined to the core due to reflection at the interface between core and cladding. Optical fibers composed of pure silica cores and fluorine-doped silica cladding have been found to have the best transmission properties in a radiation environment [179,184,185]. Since SiO$_2$ suffers permanent damage during exposure to ionizing radiation, most studies have been conducted with X-rays or gamma rays. Several neutron irradiation studies have also been performed [175–178]. The fluence required to produce significant degradation in optical transmission depends on the wavelength of interest. For example, an attenuation of 10 dB/m was produced at 500 nm and 700 nm in silica fibers after room temperature neutron irradiation to fast neutron fluences of $1 \times 10^{21}$ and $1 \times 10^{22}$ n/m$^2$, respectively [178].

Radiolytic damage in optical fibers is characterized by breaking of bonds, which are then available as electron or hole traps with absorption bands outside of the wavelengths of interest has been used to decrease the sensitivity of optical fibers to radiation [181]. However, more recent work has shown that pure silica has superior radiation resistance compared to that of silica doped with elements such as Ge or P [184,185]. Similarly, low levels (~1 ppm) of impurities such as Al or the alkali metals or moderate levels (~100 ppm) of Cl can greatly reduce the radiation resistance of silica at certain wavelengths. Silica containing up to 1000 ppm OH (a common natural impurity) has better transmission characteristics than pure silica for wavelengths below 650 nm, but there are conflicting results on whether high-OH silica maintains this advantage after irradiation [184].

For most optical fibers, the transmission is significantly better at long wavelengths (1.5 mm) compared to short wavelengths (0.2 mm), and this wavelength dependence is maintained after irradiation [178,183–185]. The effect of irradiation temperature on optical absorption is complex. Point-defect annealing generally results in reduced optical degradation with increasing temperature, particularly above 473 K [184]. However, severe optical degradation can occur at high temperatures (above about 573 K), most likely due to deterioration in the optical cladding [179]. Periodic exposure of the irradiated optical fiber to an intense light source can cause significant recovery of the radiation induced attenuation by a process known as photobleaching [180].

5. Radiation effects in nuclear waste forms

One of the most important applications of the study of radiation effects in ceramics during the past decade has been radiation effects in nuclear waste forms, e.g. borosilicate glasses, single and polyphase phase crystalline ceramics, and the UO$_2$ in spent nuclear fuel. In the latter case, the radiation dose due to the in-reactor neutron irradiation has already been substantial, and damage accumulation during disposal is not anticipated to be significant. High-level waste (HLW) in the United States has three major sources: (1) spent nuclear fuel from commercial nuclear reactors; (2) high-level liquid waste produced at West Valley, New York, in the 1960’s during the reprocessing of commercial spent nuclear fuel; (3) high-level waste generated by the nuclear weapons program. Much of the defense waste is stored in tanks at the Hanford and Savannah River sites in Washington and South Carolina, respectively. The volumes are substantial. At the Hanford site alone the inventory includes 11 million m$^3$ of fluids and 6900 metric tons of nuclear materials, which includes 4100 metric tons of uranium and 15 metric tons of Cs and Sr capsules. The total activity is estimated to be 446 million curies [186]. Although the defense wastes account for 95% of the current total United States’ HLW inventory, they account for only 9% of the total radioactivity. The majority of the radioactivity is contained in commercial spent nuclear fuel [187]. Except in the case of direct disposal of spent fuel, these wastes must be treated and solidified prior to permanent disposal. The effect of radiation on waste form solids is a critical concern. As an example, the cumulative alpha-decay doses per gram which are projected for the nuclear waste glasses to be used for the West Valley Demonstration Project (WVDP) and the Savannah River Plant (SRP) reach values of $10^{16}$ in 100 years [187]. Similarly, crystalline waste forms, e.g. the titanate assemblage Synroc, reach values of $> 10^{18}$ alpha-decay events/g in 1000 years for a 20 wt% waste loading. For this Synroc composition, the total accumulated dose at the end of 10000 years is nearly equivalent to 0.5 dpa. This is well within the range for which one may expect important changes in physical and chemical properties, most notably transitions from crystalline to aperiodic (metastable) states.

Although present performance assessments of ra-
dionuclide containment rely primarily on the geologic repository, the physical and chemical durability of the waste form can contribute greatly to successfully isolation of nuclear wastes [188]. Thus, the effect of radiation on physical properties and chemical durability are of critical concern. The changes in chemical and physical properties occur over the relatively long periods of storage, $10^4$ to $10^8$ years, and at relatively low temperatures (less than 473 K depending on waste loading, age of the waste, depth of burial, and the repository-specific geothermal gradient). Thus, one of the challenges is to effectively simulate radiation damage at relatively low fluences over long periods of time. This is why studies of naturally-occurring U- and Th-bearing phases that are structurally and chemically analogous to waste-form phases have provided important data [189].

The essential questions to be addressed in the study of radiation effects in nuclear waste forms are:

1. What are the changes in physical properties (e.g., volume, fracture toughness, and hardness), chemical properties (e.g., thermodynamic stability and leach rate), and stored energy as a function of radiation dose, temperature, and time?
2. How can the changes in physical and chemical properties be simulated in accelerated experiments to relevant radiation doses (for a waste form age of $10^4$–$10^8$ years)?

This section briefly summarizes and compares results which address these issues for borosilicate glasses and the crystalline ceramic waste form Synroc. The latter, a polyphase assemblage of titanates, was selected because most of the work on crystalline waste forms has been on Synroc phases [190,191]. The discussion focuses on actinide-bearing phases - isometric pyrochlores ($A_2B_2O_7$) and the monoclinic derivative structure zirconolite ($CaZr Ti_4O_9$). More detailed descriptions of waste forms can be found in the summary of Lutze and Ewing [192] and of radiation effects in waste form glasses in those of Weber [187,193].

### 5.1. Types of radiation

The chief sources of radiation in high-level nuclear waste forms are the beta decay of fission products (e.g., $^{137}$Cs and $^{90}$Sr) and the alpha decay of actinide elements (e.g., U, Np, Pu, Am and Cm). There are minor contributions to the damage process from spontaneous fission events of the actinides, and alpha-neutron reactions are sources of fission fragments and neutrons, but the production rates are low. Therefore, these events are not considered in this discussion. Beta decay is the primary source of radiation during the first 500 years of storage, because it originates from the shorter lived fission products (e.g., the half-life of $^{137}$Cs is 30.2 years and the half-life of $^{90}$Sr is 28.1 years). The beta decay of fission products is responsible for heat generation and the “thermal event” early in the history of waste-form storage. Alpha-decay damage becomes and remains important after approximately 1000 years (e.g., the half-life of $^{239}$Pu is $2.411 \times 10^4$ years).

The beta- and alpha-decay events can cause three types of radiation damage in the waste form: (1) collision cascades which cause atomic displacements, and the creation of Frenkel defect pairs due to elastic collisions between nuclear particles (e.g., alpha particles or the alpha-recoil nuclei); (2) ionization effects associated with beta particles or the alpha-particle during the highest velocity portion of its trajectory; (3) the transmutation of radioactive parent nuclei into different elements. Of these three effects, the most important are processes which cause atomic displacements, since these are responsible for the atomic-scale rearrangement of the structure and hence lead to the greatest change in physical and chemical properties. Each alpha-decay event results in approximately 1500 atomic displacements, while a beta-decay event results in only 0.15–0.10 displacements. There is no compelling evidence that ionization events result in important structural changes in the material [194–196]; however, more recent work by DeNatale and Howitt [36] and summarized by Weber [187] have shown that complex borosilicate glasses can decompose by an ionization-driven radiolytic process that produces bubbles which contain molecular oxygen. Although systematic studies are lacking, the bubble formation, glass decomposition, and even changes in chemical durability may correlate with the ionizing component of energy deposition.

### 5.2. Alpha-decay event damage and methods of study

Alpha-decay damage in nuclear waste forms is the result of the decay of actinides. The damage is caused by two separate, simultaneous processes associated with the alpha-decay event: (1) An alpha particle (kinetic energy 4.5–5.0 MeV) with a range of 10000 nm dissipates most of its energy by ionization; however, at low velocities near the end of its track, it displaces several hundred atoms creating Frenkel defect pairs. (2) The alpha-recoil atom (kinetic energy 0.07–0.09 MeV) with a range of 10 nm produces several thousand atomic displacements, creating “tracks” of disordered material. These two damaged areas are separated by thousands of unit-cell distances and are expected to have different effects on the crystalline structure [197].

There is a number of different techniques used to simulate alpha-decay damage effects in waste forms. These have been ably summarized by Weber and Roberts [195]. The most-preferred simulation techniques are doping-experiments in which short-lived actinide isotopes such as $^{238}$Pu (half-life of 87.7 years) or...
beta-gamma radiation. Neutron irradiations damage all tinides. Other phases will experience only alpha- and the recoil damage are those which contain alpha-phases in polyphase waste forms which will experience numerous atomic displacements. This provides a good simulation of alpha-recoil damage, but there is no simulation of the effect of helium buildup due to the alpha-particle damage. Additionally, the only phases in polyphase waste forms which will experience alpha-recoil damage are those which contain actinides. Other phases will experience only alpha- and beta-gamma radiation. Neutron irradiations damage all of the phases in the waste form. Also, boron-containing or boron doped waste forms can be irradiated in a slow neutron flux and, owing to the high \(^{10}\)B(n, \(\alpha\))Li cross section, an alpha particle \(E_{\text{max}} = 1.78\) MeV is generated. With this technique, high rates of He formation are possible, but this does not simulate the alpha-decay damage event. Lastly, thermal neutron capture by selected nuclides (e.g., \(^{235}\)U) can lead to spontaneous fission which results in the formation of extensive zones of atomic displacements, viz. fission tracks. This is not a good simulation of alpha-decay damage, and the number of fission events in nuclear waste forms is too low as to make the process an unimportant damage mechanism.

Finally, charged particle irradiations using electrons, protons, alpha particles or heavy ions have been used to simulate damage. Significant doses can be reached in short periods of time (e.g., fractions of a second), but analysis of the results is difficult because the damaged areas are thin surface layers of restricted lateral extent. Implanted layers also can change their characteristics (e.g., apparent leach rates) as a result of compositional changes that are enhanced in thin layers. Still, the alpha-particle irradiation is a good simulation of alpha-particle damage, and heavy-ion implantation (\(\text{Pb}^{2+}\)) provides a good simulation of alpha-recoil damage [198]. In fact, the two techniques used together can be used to unravel the relative contributions of alpha-particle and alpha-recoil damage to the changes in the properties of the solid. All of these techniques have been used to study alpha-decay damage effects in borosilicate glass and Synroc phases.

Most recently, Weber et al. [199] have completed a detailed study of the radiation-induced crystalline-to-amorphous transition in zircon in which they made a comparison between damage caused by alpha-decay events \(^{238}\)Pu-doped synthetic zircon and U-bearing natural zircons) and ion-beam-irradiated zircon (0.8 MeV Ne\(^+\), 1.4 MeV Ar\(^+\), 1.5 MeV Kr\(^+\), 0.7 MeV Kr\(^+\), 1.5 MeV Xe\(^+\)). The results demonstrated that the amorphization dose under the high dose rates of the ion irradiation \(10^{-4}\) to \(10^{-5}\) dpa/s) for heavy-ion irradiations is nearly identical to that for Pu-doped zircon \(3 \times 10^{-9}\) dpa/s), which suggests that the amorphization process is largely independent of the damage source and the dose rate for heavy particles (alpha-recoil particles or heavy ions). This in turn suggests that heavy ion beam irradiations can be used to simulate alpha-decay event damage in nuclear waste forms.

5.3.3 Comparison of radiation effects in borosilicate glass and Synroc waste forms

5.3.1 Physical properties

The principal difference between the two waste forms is the density change and hence the volume
expansion as a function of increasing radiation dose. Borosilicate glasses show only a limited density change (±1.5%), reaching saturation doses at $10^{24}$ alpha-decay events/m$^3$ [193,195]. In contrast, crystalline ceramic waste forms (single phase and polyphase aggregates) expand by as much as 6%, reaching saturation doses at $10^{25}$ alpha-decay events/m$^3$. As an example, $^{238}$Pu-doped polycrystalline aggregates of the pyrochlore-derivative zirconolite (CaZr$_2$Ti$_2$O$_7$) swell by 5% (dilatometric measurement on bulk sample) at a dose of $2 \times 10^{25}$ alpha-decay events/m$^3$ at ambient temperatures [200]. At higher temperatures (575 K), maximum swelling is 4% at a saturation dose of $4 \times 10^{25}$ alpha-decay events/m$^3$; at 875 K, swelling is less than 0.5%. This behavior illustrates the importance of annealing during the damage ingrowth process. Even at the highest level of volume expansion (5–6%), microcracking was not observed. In $^{244}$Cm-doped zirconolite, unit cell volume expansion was determined by X-ray diffraction for doses of up to $10^{25}$ alpha-decay events/m$^3$ [201]. The volume expansion is very anisotropic, with the expansion of the monoclinic cell along the c-axis over five times that along the a-axis. However, even with this large, anisotropic expansion, no microcracking was observed.

Natural zirconolites which have been exposed to doses between $10^{24}$ and $10^{26}$ alpha-decay events/m$^3$ also show this dramatic anisotropic expansion [202]. A detailed EXAFS study [203] of metamict zirconolites suggested that very little of the volume expansion was associated with changes in nearest-neighbor coordination number or bond length, but rather was caused by tilting of coordination polyhedra across shared oxygens (i.e., changes in the cation-oxygen-cation angles). Farges et al. [203] also noted that the structural environments of Zr$^{4+}$ and Th$^{4+}$ are different from those in silicate and borosilicate glasses in which they are commonly six-coordinated by oxygens. This suggests that there are fundamental structural differences in cation environments between radiation-induced aperiodic (metamict) phases and glasses quenched from melts. Additionally, natural zirconolites have been amorphized by ion beam irradiations (1.5 MeV Kr$^+$ ions) at doses of $4 \times 10^{18}$ ions/m$^2$ (= 0.3 dpa). This dose is about six times lower than that observed for natural alpha-decay induced processes in which annealing may occur over the great age, 550 million years, of the natural samples [204].

Very recently, Weber et al. [199] have demonstrated that the volume expansion of a ceramic phase, zircon, is nearly identical for natural zircons (600 million years old) and $^{238}$Pu-doped zircons (experiments of 6.5 years). The volume expansion consists of two components: at low doses (< 0.2 dpa), most of the volume increase is associated with the expansion of the unit cell; at higher doses (> 0.2 dpa), the increase in volume is due to the relative volume change associated with the crystalline-to-amorphous transition (Fig. 15).

The fracture toughness of both glasses and crystalline phases increases with alpha-decay dose [204]. In the case of borosilicate glasses, the increase in fracture toughness is approximately 25 percent. Bonninaud et al. [206] reported a slight decrease of the microhardness in glass with increasing alpha-decay dose as measured by the Knoop test. For $^{238}$Pu-doped zirconolite, there is a significant change in hardness (30 percent decrease) and an associated increase in fracture toughness [206]. For a $^{244}$Cm-doped apatite structure, Ca$_2$Nd$_4$(SiO$_4$)$_3$O$_2$, a 30% increase in fracture toughness was observed [207]. This is consistent with similar measurements on metamict and annealed euxenite, a mineral which is commonly amorphous due to alpha-decay damage associated with the presence of uranium and thorium, in which a 30% increase Vicker's hardness
was measured on annealing to the fully crystalline state [208]. The increased fracture toughness with increasing alpha-decay dose is associated with crack bowing, crack deflection, internal stresses associated with the coherency of second-phase particles, and differences in elastic properties of phases at different stages of the damage process. The most dramatic example of this process is shown in a complex-zoned zircon, ZrSiO$_4$, which has variable concentrations of U and Th such that the full range of damage microstructures is represented for the crystalline-to-aperiodic transition [209,210]. Those zones which have experienced the highest alpha-decay dose, and are therefore aperiodic (metamict), have no cracks, while the low dose zones contain fractures. This is the type of fracture pattern that might develop in crystalline materials that are complex-zoned relative to actinide concentrations.

5.3.2. Stored energy

Stored energy measurements are perhaps even more difficult to compare between waste forms than volume or hardness changes. Most measured values are less than 150 J/g. For HLW borosilicate glasses the stored energy resulting from alpha-decay events is generally less than 150 J/g and saturates at a dose of $0.1 \times 10^{18}$ to $0.3 \times 10^{18}$ alpha-decay events per gram. This saturation dose is considerably less than the dose required for saturation of volume changes (viz. $10^{18}$ alpha-decay events/g).

Stored energy values for crystalline ceramics are

Fig. 16. High-resolution TEM micrographs of self-irradiation damage in natural zircons, showing an increased degree of amorphization with increasing dose: (a) 0.0025 dpa, (b) 0.091 dpa, (c) 0.32 dpa, and (d) 0.5 dpa. The spacing marked in (c) is the 0.33-nm (200) d-spacing. The small rotation of remanent crystallites in the amorphous matrix in (c) is caused by local strain fields induced by amorphization (from Ref. [199]). Very similar microstructures are observed in ion-beam-irradiated zircon [199].
difficult to access because of the variety of phases. Most actinide-bearing phases are derivatives of pyrochlore structure types, and Lumpkin et al. [211] have summarized recrystallization data for natural pyrochlores and compared them to data available for $^{238}$Pu- and $^{244}$Cm-doped pyrochlores and zirconolites. (Zirconolite is a monoclinic derivative of the cubic pyrochlore structure type.) The natural pyrochlores (completely metamict prior to annealing) have recrystallization energies in the range of 125 to 210 J/g. In contrast, Pu-doped zirconolite has a value of 50 J/g at $15 \times 10^{26}$ alpha-decay events/m$^3$ [212]; Cm-doped zirconolite has a value of 127 J/g at $2 \times 10^{25}$ alpha-decay events/m$^3$ [213]. Activation energies of recrystallization for natural pyrochlores are between 0.29 and 0.97 eV [211]. These activation energies are intermediate between those measured for a $^{248}$Cm-doped glass (0.25 eV) and those found for Pu-doped zirconolite (1.22 eV [212]) and Cm-doped zirconolite (5.8 eV [213]).

The most interesting feature of these studies is that synthetic samples doped with highly-active actinides generally have lower values of "stored" energy than the natural samples. In considering this difference, one must clearly distinguish between the heat of crystallization (released on annealing of completely disordered materials) and stored energy that is directly related to alpha and alpha-recoil damage. In the latter case, stored energy will be related to the removal of isolated Frenkel defect pairs (created by the alpha-particle) and "track" fading (annealing of the alpha-recoil collision cascade). These results suggest that the stored energy will never be greater than the heat of crystallization which spans only a slightly larger range (50 to 200 J/g) than the stored energy values of borosilicate glasses (less than 150 J/g in most cases).

More recently, a comparison [214] has been made between the stored energy of $^{238}$Pu-doped zirconolite and that of naturally-damaged zirconolite (up to 20 wt% ThO$_2$ and UO$_2$, 550 million years old). Despite a dose rate difference of $10^8$, the released stored energy at saturation damage was in the range of 35–60 J/g. The $^{238}$Pu-doped zirconolite reached a maximum value of 100 J/g in the early stages of damage, $10^{25}$ alpha-decay events/m$^3$, but decreased until it was nearly the same as that of natural zirconolite, 40 J/g, at a dose of $10^{26}$ alpha-decay events/m$^3$. Most recently, measurements of stored energy in natural zircons using transposed temperature-drop calorimetry have been completed on a suite of samples that have reached doses of $10^{17}$ [215] alpha-decay events/g. The enthalpy of annealing at room temperature varies sigmoidally as a function of radiation, reaching a saturation plateau at doses greater than $5 \times 10^{18}$ alpha-decay events/g. The large magnitude of the enthalpy of the annealing plateau, $-322 \pm 16$ J/g, suggests that the damage to the structure is pervasive on the scale of 1 nm, and this has been confirmed by high-resolution transmission electron microscopy (Fig. 16).

5.3.3. Chemical durability

The chemical durability of a waste form is its most important property. The difficulty in comparing changes in chemical durability between waste forms is that the corrosion process must be extrapolated over time, and during this time critical parameters of the waste form environment change, such as the temperature, flow rate, or solution composition. Thus, there is no straightforward comparison that can be made between the corrosion of a single, aperiodic phase (a borosilicate glass) and a crystalline polyphase material such as Synroc. The only issue addressed in this discussion is whether under some set of specified conditions alpha-decay damage causes fundamental structural modifications which lead to an increased corrosion rate. Although alpha-decay damage has been simulated by a number of techniques (e.g., ion implantation), we restrict ourselves almost entirely to the data derived from actinide-doping experiments and actinide-bearing (U and Th) natural analogue structure types.

For borosilicate glasses, corrosion rate changes in actinide-doped glasses have been compiled by Weber and Roberts [195] and Weber [187]. For most of the experiments, alpha-decay doses reached values of $10^{24}$–$10^{25}$ alpha-decay events/m$^3$. Based on these results, the maximum change in bulk corrosion rate (network dissolution) is no more than a factor of 3 [187]; however, these tests are based mainly on weight loss measurements which can underestimate the radiation-induced increase in leach rate by a factor of 3–4 [216]. One should note, however, that during the early 1980's considerable controversy was generated by ion implantation results which suggested increases in corrosion rates by as much as a factor of 50 [217]. The fundamental question that resulted from the ion implantation studies was whether ion implantation can provide a reasonable simulation of alpha-recoil damage. The ion implantation results were never corroborated by the actinide-doping experiments; the discrepancy in the results between the two techniques could be due to differences in dose rate, thermal annealing or compositional changes associated with the implantation process.

In crystalline waste forms, one may expect a more dramatic change in the corrosion rate because of the transition from a stable, periodic atomic array to a metastable, aperiodic atomic array [218]. Not surprisingly, there is really very little in the way of systematic data relating changes in corrosion rate to alpha-decay damage. Bulk Synroc samples have been irradiated by fast neutrons up to a dose of $2.6 \times 10^{24}$ neutrons/m$^2$, and, based on Cs release, no systematic effect of radiation dose on leach rate was observed; however, the
interpretation in terms of alpha-decay damage of a single element's release into solution, for a polyphase material which has been irradiated by neutrons, leaves much to be desired. More relevant experiments provide results on actinide-doped single phases. Weber et al. [216,219,220] have reported results on nuclear waste phases: Ca$_3$Nd$_2$(SiO$_4$)$_3$O$_2$, Gd$_2$Ti$_2$O$_7$, and CaZrTi$_2$O$_7$-doped with $^{244}$Cm with accumulated doses of $10^{25}$ alpha-decay events/m$^3$. Their results show an order of magnitude increase in corrosion rate (normalized elemental mass loss based on at least five elements measured in solution for each sample). In addition, these results are consistent with similar measurements of natural phases in which annealing experiments are not part of the leaching experiments (see the discussion of zircon data following). This is a critical issue that requires additional, well-designed experiments for actinide-doped single phases.

Of particular relevance to the discussion of radiation damage effects in crystalline phases are the results and observations obtained on natural analogues. Perhaps the most important results are those that have been reported on zircon, ZrSiO$_4$. Although zircon is seldom suggested as a waste form phase, results on $^{238}$Pu-doped zircons and natural zircons, which commonly contain U and Th, can be compared [40,189,709,710,221–225]. These rather detailed results demonstrate that the changes in the physical and chemical properties which occur in $^{238}$Pu-doped zircons over a period of 5–6 years ($10^{26}$ alpha-decay events/m$^3$) are very similar to the changes observed in natural zircons which have accumulated equivalent alpha-decay doses in $10^8$ years. For natural zircons of variable alpha-decay dose spanning the range from the crystalline to metamict transition, Ewing et al. [226] have reported a ten-fold increase in the corrosion rate. These results are consistent with observations concerning the dissolution kinetics of crystalline and metamict zircon [227] and "disturbed" uranium/lead systematics in metamict zircons used in geologic age dating [228].

Few other natural phases, besides zircon, have simple enough compositions or variable enough U and Th concentrations that they can provide a full suite of samples which cover the dose range of the crystalline-to-metamict transition; however, geochemical alteration effects may be studied. For pyrochlore structure types, alteration patterns can be extensive and complex, with cation exchange playing a major role [229,230]. Some samples which are over 500 million years old (e.g., zirconolite), however, show no evidence of geochemical alteration [202]. The geochemical alteration of these phases over long periods of time remains an important area of future research. Thus far, the present discussion has been restricted to alpha-decay damage effects on the bulk dissolution of phases. In the case of glasses, this effect is minor, and in the case of crystalline materials the periodic to aperiodic transition has demonstrably important effects on the bulk corrosion rate. One should also note that there is important evidence for selective leaching of alpha-recoil nuclei from damaged areas in periodic as well as aperiodic materials [231]. This is a well known effect which is responsible for such phenomena as the isotopic disequilibrium within heavy-element decay chains and the differential solubility observed among actinide bearing phases [232]. The effect has been observed in potential actinide-bearing waste phases (e.g., monazite [233]; UO$_2$ [234,235]; pyrochlore-structure types [231]). The two demonstrated mechanisms for recoil release are: (1) direct ejection of a recoil nucleus into pore water [236] and (2) leaching along the recoil track [237–239]. The selective loss of radionuclides at the end of recoil tracks may not cause significant loss of actinides – but this phenomena has provided an experimental means of measuring the kinetics of alpha-recoil track fading. Eyal and Fleischer [234,235] have used the extent of isotopic disequilibrium in the $^{238}$U and $^{232}$Th decay series to infer how long alpha-recoil damage is retained in certain minerals. The effect is seen in crystalline and aperiodic (metamict) materials. The half-life of the alpha-decay track in aperiodic materials is substantially less than that of crystalline materials which become aperiodic with increasing alpha-decay dose [240]. Although there is still discussion concerning the nature of the release mechanism, and hence the nature of the damage [241], further studies are certainly warranted. Recently, Eyal and Ewing [242] have conducted leaching experiments on a 17-year old borosilicate glass containing 4 wt% ThO$_2$. For the unannealed glass, the initial $^{230}$Th leach rate was enhanced relative to the initial $^{231}$Th leach rate by 15–45% due to the selective removal of radiogenic $^{232}$Th nuclides from $^{228}$Ra-recoil tracks. A similar enhanced dissolution of alpha-decay products may occur in nuclear waste glasses, but experiments to identify this phenomenon have never been conducted.

5.4. Conclusions about waste

This brief summary of the literature concerning radiation effects in nuclear waste forms mainly illustrates that there are few systematic studies of the mechanisms and effects of interactions of radiation with nuclear waste form materials [243]. This was further emphasized in a workshop convened by the Division of Materials Sciences, Office of Basic Energy Sciences, US Department of Energy in 1990 on the radiation effects on materials in high-radiation environments. The workshop (summarized in Ref. [244])
identified high priority research areas on nuclear waste forms:
(1) effects of electronic energy deposition on glass structure and decompositions;
(2) dose-rate effects;
(3) effects of radiation on waste-form dissolution measurements;
(4) effects of radiation on mechanical properties (e.g., microfracturing).
Thus, nuclear waste management is an area which still requires careful and systematic studies of radiation effects in complex ceramics and glasses.

6. Concluding remarks

A treatment of radiation effects in such an extensive class of materials as ceramics, constrained here to the length of a single composite manuscript in a volume, the remainder of which is almost entirely devoted to the singular class of metals, is bound to suffer from unavoidable omissions. The study of such effects in inorganic non-metallic solids is both older than the corresponding interest in metals and necessarily more complex because the materials are more complex, and the authors hope that at least the principal issues have been raised and sufficient resources provided in the extensive citation list. That the behavior of metals in radiation environments has occasioned so much consideration, and that of ceramics so little comparatively, is more a comment on the narrow perspective of designers than on the fascination or relevance of problems encountered in the radiation responses of nonmetals. It is to be hoped, as the number and variety of radiation environments proliferates and their demands on materials escalate, that a more catholic consideration will be given to both the prospects and the problems of all materials classes.

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[183] E.J. Friebele and M.E. Gingerich, ibid Ref. [181], p. 387.


