Review article

Electrical breakdown of insulating ceramics in a high-radiation field

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Abstract

This report addresses a recently reported phenomenon – that a simultaneous application of energetic particle radiation, electric field, and elevated temperature for an extended period of time has a permanent adverse effect on insulating ceramics, including electrical breakdown. This behavior poses a serious challenge for fusion devices, which require electrical insulators in several key components. The summary and recommendations developed here are based largely on the proceedings of a research assistance task force meeting entitled “Electrical Breakdown of Ceramics in a High-Radiation Field”. Since this is a rapidly expanding field, this report attempts to include highlights of pertinent studies reported at recent international meetings. In one recent meeting the fusion materials community recommended that this effect be referred to as radiation-induced electrical degradation (RIED).

1. Introduction

This report is based primarily on the proceedings and recommendations of a 1991 Research Assistance Task Force meeting on “Electrical Breakdown of Ceramics in a High Radiation Field” [1], sponsored by the US Department of Energy. It includes recent studies pertaining to this topic. This meeting was held in response to recent reports that a simultaneous application of energetic particle Radiation, Electric field, and elevated Temperature (to be referred to as Rad-E-T) for an extended period of time has an adverse effect on insulating ceramics and can lead to electrical breakdown [2–4]. These reports characterize the phenomenon as an unexpected increase in DC electrical conductivity, over and above that previously known. Above a critical dose the conductivity increases with irradiation. The previously known conductivity increase, Δσ, known as radiation-induced conductivity (RIC), was described by the phenomenological expression Δσ = kR where R is the ionizing radiation dose rate [5–7]. During the meeting, it was recommended that this new effect be generalized and termed radiation-enhanced electrical degradation, in order to distinguish it from RIC. It has since been accepted that the phenomenon be referred to as radiation-induced...
electrical degradation (RIED). The RIED acronym is used in this paper. It was reported at the meeting that RIED takes place after an incubation period with application of Rad-E-T. In contrast to RIC, removal of radiation does not return the conductivity to its pre-irradiation level. Furthermore, it was reported that the degraded ceramic insulator cannot be readily annealed or otherwise returned to its original low conductivity. This behavior poses a serious challenge for fusion devices, which require electrical insulators for several applications including diagnostic systems, radiofrequency and neutral beam heating systems, magnetic coil insulators, and toroidal current breaks.

The problem of selecting suitable electrical insulating materials for fusion applications may be far more complex than previously anticipated [8–10]. Selection criteria, in addition to resistance to radiation-induced swelling, changes in strength, resistance to thermal shock, thermal conductivity, electrical conductivity and dielectric loss tangent. In addition, chemi-physical near-surface alterations may have to be expanded to include more subtle synergistic effects due to combinations of environmental parameters such as electric field strength, temperature, and accumulated irradiation fluence measured as ionizing dose and displacements per atom (dpa). The observations reported at the meeting showed a large diversity, with conductivities for crystalline sapphire and polycrystalline alumina (α-Al₂O₃) samples having increased by several orders of magnitude from the reported pre-irradiation levels ranging from 10⁻¹⁴ to 10⁻¹⁰ (Ω m)⁻¹ to 10⁻³ to 10⁻⁵ (Ω m)⁻¹ under prolonged energetic electron irradiation near 750 K as the accumulated irradiation level approached 10⁻³ dpa [1–4,8]. Other results indicate conductivity reaching 10⁻⁵ (Ω m)⁻¹ as fission-spectrum neutron dpa approached unity, and total background gamma approached 2.4 x 10¹⁰ Gy at temperatures between 600 and 1000 K [1]. These conductivity values pose a challenge to reactor design and materials efforts. The meeting served two main purposes: (1) discussion of past and current results related to the extent of understanding of RIED; and (2) identification of opportunities and methodologies to serve as guidelines for research toward the understanding and solutions to this problem.

This report emphasizes the importance of in-situ studies. Traditionally, radiation damage to a material has been studied as a post-mortem event: the material is first subjected to irradiation and the resultant effect of the damage is later studied by experimental measurements and analyses, often in response to an applied external perturbation. The perturbation can be a beam of light, an electric field, or perhaps even the same type of beam that caused the damage in the first place, such as electrons, or neutrons. However, in certain situations the net effects of the perturbation applied during irradiation can be drastically different from those measured after irradiation. Specifically, the effects of Rad-E-T are not the same as those observed if the sample is first irradiated at an elevated temperature and then subjected to an electric field. One of the conclusions of the meeting is that there is a dearth of in-situ irradiation effects data base on dielectric materials, especially as it pertains to the use of these materials for fusion.

2. Characteristics of the fusion environment

The expected applications and operating conditions for ceramic insulators in fusion power systems [11,12] are as follows:

Insulators for lightly-shielded magnetic coils. Coils such as those used in divertors and for plasma stabilization may be located near the first wall. Insulators may be in either solid or powder form, depending on magnet design. Operating temperatures, will vary from slightly above to well above room temperature depending on extent of cooling supplied. First-wall-like radiation conditions (about 10¹³ n m⁻² s⁻¹ and 10⁴ Gy/s gamma) will be imposed on these insulators. The likely mode of failure is RIC, perhaps accompanied by RIED.

Windows for electron cyclotron resonant heating (ECRH) systems. ECRH windows must retain their transparency to electromagnetic beams of frequency about 100 GHz. Retention of high thermal conductivity is necessary to avoid thermal stress-induced mechanical failure resulting from absorption of energy from the beam. Attempts will be made to locate the windows well away from the first wall, but too remote a location will compromise operation of the ECRH system. The present expected dose rates for the ECRH windows are several orders of magnitude lower than that at the first wall (i.e. < 10¹⁰ n m⁻² s⁻¹).

Standoffs for ion cyclotron resonant heating antennas. These antennas will operate at about 100 MHz, and must be mounted inside the first wall. There will also be windows further along the coax lines behind the first wall. Thus radiation fields will be intense and operating temperatures will be high. In addition to radiation damage, the standoffs may be damaged by sputtering and/or by deposition of impurities.

Insulators for neutral beam injectors (NBI). Although remote from the first wall, the massive insulators for the neutral beam injector sources will be exposed to low-level radiation resulting from streaming down the injector ducts. The insulators themselves may be made of lower grade ceramics in order to enable fabrication of the very large insulator/electrode stacks; if it is necessary to use radiation-sensitive silicate-based materials, then significant damage may occur.
Insulating coating for suppression of magnetohydrodynamic (MHD) forces. Liquid metal coolant pumped through the blanket will be impeded by MHD forces unless the metal pipes are lined with an insulating coating. Electrical requirements are modest, but cracking and spalling of the coating may occur if its bond is weakened by radiation. Differential swelling is a particular problem for this application. Radiation fields will be about an order of magnitude lower than those at the first wall, but will still be high enough to damage both metals and ceramics.

Toroidal current breaks. It may be necessary to divide the metal structure of the torus into electrically-isolated sections (in some designs) to minimize damage from disruptions. Insulating current breaks may take the form of thin ceramic layers or insulated bolts. Radiation fields will be as high as 10% of first wall level. The most serious problem is mechanical failure (flaking or fracture), which could lead to loss of electrical insulation.

Insulators and optical components for diagnostic systems. A number of dielectric materials are specified for use in diagnostic systems. Included are: probes to measure magnetic field intensity at the first wall, where temperatures may exceed 1000 K, windows and reflectors, likely located near the first wall; and optical fibers, used widely throughout the reactor. Of these, the most radiation-sensitive components are windows and fibers, where SiO$_2$-based materials are specified, and severe damage can be expected [13,14]. Remote ness from the first wall, frequent changeout, and periodic thermal annealing will be employed where possible to achieve viable performance. While more resistant to the effects of irradiation, ceramic insulators for other diagnostic systems will be less remote, and their performance is also a concern.

Insulators for superconducting toroidal field (TF) coils. Designs of TF coils usually specify polymer insulators. However, the known sensitivity of organic insulators to radiation damage, coupled with concern about generation of radiolytic gases, is increasingly directing attention to ceramic insulators. Radiation fields in these shielded magnets are low (about 10$^{15}$ n m$^{-2}$ s$^{-1}$ and 1 Gy/s), but their effect on conventional ceramics will be magnified by the greatly increased retention of displacement damage at 4 K. If construction requirements dictate that the insulator be injected into the TF coil structure, then inorganic cements can be considered; however, the relatively high radiation sensitivity of traditional water-bearing silicate-based cements must be taken into account.

3. Background studies and recent work

All solids conduct electricity to a greater or lesser extent, and all will suffer some form of electrical (or dielectric) breakdown in a sufficiently strong electric field [15]. In the case of insulators, such electrical breakdown is characterized by a rapid increase in the electrical conductivity [15–18]. In this section, we shall provide (a) the background information regarding electrical breakdown of oxides at high temperatures in the absence of irradiation; (b) a brief background of materials requirements for fusion devices; (c) electrical conductivity at high temperatures in the absence of radiation; and (d) a brief description of RIC.

3.1. Breakdown at high temperatures without irradiation

In the last two decades, the need for ceramics as insulators at high temperatures in a number of advanced energy systems has become very critical. Investigations of the electrical properties of several oxides [19–27], including MgO, Al$_2$O$_3$, MgAl$_2$O$_4$, Y$_2$O$_3$, TiO$_2$, CeO$_2$, MgSiO$_3$ and SiO$_2$, at high temperatures (1300–1500 K) have been reported. The results led to a new level of understanding of the fundamental mechanisms and phenomena that cause the breakdown of the insulating properties of oxide ceramics. In the breakdown process, the electrical current increases until the material evaporates along the path of least electrical resistance and leaves behind a large channeled gap. During the current increase the temperature of the sample was determined to rise above the ambient temperature. The observation and new understanding of the breakdown phenomena can be summarized as follows.

1) Formation of impurity precipitates and dislocations. The breakdown process frequently is preceded by the formation of a dark coloration in the crystal [19]. Fig. 1 shows a cross-sectional view of a MgO:Mn sample heat-treated at 1050°C for 2 h with a 1100 V potential applied between a point contact and a planar platinum electrode [21]. This figure illustrates the electric-field flux lines and the electrolytic-coloration effects observed in the crystal. The similarity between the shape of the altered region and the E-field distribution is noted. The narrow top portion of the 'volcano-shaped' dark region is located at the position where the cathode point contact was made. Near the broad bottom portion of the cone, where the coloration has not proceeded to the point of making the entire area completely opaque, the altered portion of the crystal was a dark brownish, amber color. Coloration generated in such manner has been shown to arise from Mie scattering from metallic precipitates that are produced by electrolytic reduction of impurities in the crystals.

In Fe-doped MgO (~ 1700 ppm) TEM micrographs revealed a variety of precipitates and dislocation tangles [19]. Analytical transmission electron microscopy (TEM) has provided an identification of the chemical composition and structure of the precipitates and has
demonstrated that they are formed coherently in the crystal lattice. Microdiffraction and X-ray fluorescence experiments indicated that the precipitates are body-centered iron primarily, and in some cases, FeO and MgFe$_2$O$_4$, all of which are coherent within the lattice. In undoped crystals, no Mie scattering was observed and the primary defects formed were dislocations.

There were discussions at the meeting as to whether the formation of metallic colloids is a necessary condition for breakdown. There was no uniform agreement. Most of the participants believed that it was not. It was then pointed out that there were counter-examples: in undoped high-purity MgO crystals, electrical breakdown did occur without the formation of metallic colloids [22].

(2) Physical parameters affecting electrical breakdown. Several parameters were found to affect the electrical characteristics and influence the electrical breakdown process of MgO and other oxide crystals [24]. They are temperature, surface preparation, electric field, field reversal, ac and dc, ambient atmosphere, electrode material, and impurity content in the sample. Some parameters are more critical than others. Parameters such as surface preparation are obvious villains. It has been shown that chemically etched surfaces are much more resistant to electrical breakdown than mechanically polished surfaces [22–26]. At elevated temperatures dislocations generated by mechanical polishing in the surface region of MgO crystals propagate into the bulk material [28,29] and can therefore provide the conditions conducive to electrical breakdown.

These studies on electrical breakdown were primarily confined to dc conditions. Application of ac did not produce breakdown. This observation was not surprising, in view of the model that was deduced. The breakdown was clearly demonstrated to be a space charge problem, as shown in the following segment.

(3) A space charge problem. In view of the production of precipitates, it was tempting to interpret the increase in conductivity as due to the inter-twinning of precipitates. It is realized that the population of the precipitates, if any, is low – typically no more than $10^{13}$ cm$^{-2}$. Furthermore, a simple experiment appears to discard this likelihood. When the conductivity begins to increase rapidly, the polarity of the electric field is reversed [22]. The result is that the electrical conductivity decreases instead of continuing to increase, as would be expected if the current increase is due to the creation of a conducting path, due to metallic precipitates. Reversal can be administered as many times as desired with the same general result. The results are shown in Figs. 2 and 3.

When a moderate dc electric field was applied to a nickel-doped MgO crystal at 1473 K, a slight decrease in current was observed initially. Then the current increased slowly at first and subsequently exponentially until the sample experienced electrical breakdown and could no longer be used as an electrical insulator. However, in the experiment shown in Fig. 2 the sample
was not allowed to proceed to breakdown since this would have destroyed it. When the current reached a certain level, in this case 18 mA, the applied field was reversed, because at this current the breakdown was imminent and the sample temperature began to significantly exceed the ambient temperature. The time required for the current to reach 18 mA was considered to be the characteristic time for breakdown. Fig. 2 illustrates the current behavior of several field reversals. Fig. 3 is a plot of the characteristic time for breakdown as a function of chronological field reversals. The initial decreasing time trend is evident. After the fifth reversal, the characteristic time remains constant. These results suggest that the breakdown is not due to creation of conducting paths via precipitates, but is a manifestation of creation of space charge.

Other features of conductivity increase at high temperatures are consistent with a double-injection model [25] in which hole injection at the anode is augmented by the accumulation of negative charge through some form of ion or vacancy migration. The resultant increase in hole concentration demands an equal increase in electron concentration from the cathode. Hence, there is creation of an exponentially increasing current which, unchecked, will lead to electrical breakdown.

**Suppression and enhancement of breakdown by impurity doping.** A study on the effect of impurities on the characteristic time for electrical breakdown was performed in MgO crystals [23]. This host was chosen because of its high melting temperature, simple crystalline structure, high purity, and availability as a high-quality refractory crystal. Crystals doped individually with H, Cu, Co, Fe, Ni, Cr, and V were used. The source of the material, the crystal-growth conditions, and the experimental conditions were identical. The results are shown in Fig. 4. Crystals doped with V, Cr, Fe, or Ni were more susceptible to breakdown. Doping with Co, H, or Cu suppressed breakdown. Doping with Cu provided the most dramatic effect; Cu suppressed the breakdown characteristic time by a factor of about 20.

### 3.2. Insulating materials for fusion power systems

The dielectric materials requirements for fusion systems have been summarized in several publications in which both the general and more specific aspects were treated [30–33]. These devices require electrical insulators in diagnostic systems, radiofrequency and neutral beam systems, and in magnetic assemblies. During the operation of such devices, the insulating systems are bombarded by neutrons and gamma rays (which result in Compton electrons) resulting directly or indirectly from the D–T fusion reaction. Alpha particles from the D–T reaction are stopped in the plasma or at the first wall of the reactor and will not generally bombard the ceramic insulators.

One of the important findings in the study of the high-temperature electrical breakdown without irradiation is that of all the oxides studied, sapphire (crystalline alumina) is the only material immune to electrical breakdown, within the experimental time scale [26]. Therefore, alumina is a leading material candidate for sub-systems in fusion devices.

### 3.3. Conductivity at high temperatures (without irradiation)

Experimental studies of electrical conduction in insulators at elevated temperatures is important for many
modern energy and electronic systems, and has received much attention for many years. Theoretical descriptions often deviate significantly from experimental measurements, especially in the wider band gap materials, because of the presence of atomic and structural defects which are ill-characterized and can give rise to donors, acceptors, and charge trapping levels within the band gap. Fig. 5 shows the spread of conductivity versus temperature curves reported for sapphire [34], compared to results obtained by Will-deLorenzi-Janora [35]. For example, at 1000 K the conductivity ranges over six orders of magnitudes, varying from \(10^{-13}\) to \(10^{-6}\) \((\Omega \cdot m)^{-1}\). A similarly wide range of conductivities has been reported for other insulators, such as MgO, BeO, Y\(_2\)O\(_3\), AlN, BN, and Si\(_3\)N\(_4\) [36]. This range of experimental variations appears to be due to different material purities, preparation procedures, material forms (single crystal, polycrystalline, sintered, fused, etc.), thermochemical history, and experimental techniques. The latter may depend on the number of contacts, with or without guard ring, AC or DC, atmosphere, or vacuum. Therefore one of the key characteristics of electrical measurements has been the large variability.

There were several reports at the meeting on conductivity versus temperature measurements, shown in Fig. 6. Also shown is the recent curve by Will et al. made on high-purity sapphire crystal, employing experimental techniques along the lines suggested by Frederikse and Hosler [37] to eliminate surface and gas leakage conduction. These crystals were taken from boules grown by the Schmid–Viechnicki technique and obtained from Crystal Systems, Newton, MA. Using high-purity samples and paying careful attention to parasitic leakage paths, they obtained conductivity values lower than those previously reported; above 1000 K the electronic conduction mechanisms dominate over ionic conduction and the activation energy approaches \(E_u/2\), as suggested by theory. This value is higher than previously reported values. Other studies report higher conductivities for both high-purity single crystals as well as commercial polycrystalline alumina. Therefore it may not be surprising that variability in conductivities can prevail when the materials are placed in a high radiation field, even apart from the RIC dose-rate dependent conductivity. This, in fact, was a major concern at the meeting.

Fig. 6 also shows the data from Klaffky et al. on the temperature-dependent conductivity of undoped Czochralski-grown Al\(_2\)O\(_3\) single crystals measured in the presence of irradiation with 1.5 MeV electrons, albeit restricting the accumulated electron fluence to low values, i.e. \(< 1 \times 10^{16} \text{e/cm}^2\). The salient feature is that in the presence of ionizing radiation at a dose

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Fig. 5. Conductivity versus temperature for past measurements of \(\alpha\)-Al\(_2\)O\(_3\) (Ref. [36]) compared to the recent measurements of Will, deLorenzi and Janora (Ref. [35]), performed on a single crystal at \(10^{-7}\) Torr vacuum (\(< 40\) ppm impurities); and Pells on Vitox alumina (99.9\% pure polycrystalline, less than 2 \(\mu\)m grain size (major impurity 500 wppm MgO) under unspecified vacuum (Ref. [94]).

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Fig. 6. Conductivity versus temperature for alumina, after Will et al. (Ref. [35]), Pells (Ref. [32]), Hodgson (Ref. [2]), and Klaffky et al. (Ref. [7]).
rate of $6.6 \times 10^3$ Gy/s, the conductivity is increased about eight orders of magnitude.

3.4. Radiation-induced conductivity (RIC)

In earlier measurements, insulators were subjected to high-temperature and high-radiation exposure, to be followed by subsequent measurements of the electrical conductivity. This procedure, known as post-irradiation conductivity measurement, was recognized at an early stage in the fusion program to lead to erroneous conclusions. It was also recognized that there would be substantial changes in the insulating properties of dielectrics during operation in the elevated-temperature, high-radiation environment of a fusion reactor. Experiments using electron accelerators were performed on sapphire to study RIC effects [7]. The enhancement of the dc electrical conductivity in insulators during irradiation was recognized as a potential problem fairly early in the design of fusion systems. RIC is a direct result of the creation of electron–hole pairs by ionizing radiation. The total electron dose for these experiments was relatively low, however, and the experiments were confined primarily to studies of the RIC dependence on the temperature and beam intensity [7]. From these studies, values of the constants $\kappa$ and $\delta$ near 750 K for undoped crystalline sapphire were determined; $\kappa \approx 8 \times 10^{-13}$ and $\delta = 0.85$, when the dose rate, $R$, is expressed in units of rad/s and conductivity in $(\Omega \cdot cm)^{-1}$. Pells [1] has reported that $\delta$ for $\text{Al}_2\text{O}_3$ can vary between 0.5 and 1.3. The RIC effect reaches equilibrium rapidly, either increasing or decreasing and does not seem to present great challenge to reactor designers.

3.5. Radiation-induced conductivity by proton irradiations

Farnum et al. [38] measured RIC in sapphire from 100 to 10 MHz during irradiation with 3 MeV protons. A thin sample was employed, so that the protons passed through the material. In one series of experiments, the beam was repeatedly cycled on and off while the conductivity was monitored, with the result shown in Fig. 7. Conductivity increased sharply at the beginning of the irradiation, but then decayed exponentially with time. When the beam was turned off, conductivity returned to its near-zero starting value. As the experiment progressed, RIC dropped well below the initial value, but remained above the beam-off reading. These results were interpreted in terms of a balance between the generation of electrons and holes, and their trapping and recombination at displacement-type defects, which built up as the radiation dose increased.

Proton irradiation caused an immediate increase of the loss tangent from about $10^{-4}$ to more than 1.0. As was the case for the resistivity component of loss, the increase in loss tangent lessened at longer times. Such a large increase in loss tangent could cause unacceptable degradation in performance of insulators used for high-frequency applications.

3.6. Radiation-induced conductivity in a reactor

Insulating windows to a fusion reactor chamber must transmit radio frequency energy at a loss that does not become excessive. Stoller et al. [39] measured the change in dielectric loss tangent of alumina at 100 MHz during irradiation in the gamma irradiation facility at the Oak Ridge National Laboratory and in the mixed gamma and neutron environment of a TRIGA fission reactor. Under gamma irradiation alone, there was no significant increase in the loss tangent; however, the mixed gamma–neutron irradiation field produced an increase in the loss tangent by a factor of about 15 to a final value of about $10^{-4}$. This loss-tangent degradation is high enough to cause concern for the design of radio frequency windows.

4. Effects due to simultaneous application of Rad-E-T

In this section we shall provide a brief overview of recent studies on the effects of combined Rad-E-T in ceramics, with emphasis on electron and neutron irradiations. For a full account of this work, the reader should consult the original papers where details are available. Nevertheless, even the abbreviated accounts given here illustrate that the knowledge of Rad-E-T effects on the insulating property of dielectrics is scant.
Fig. 8. Current versus time for a single-crystal alumina sample obtained from Roditi-Union Carbide ur grade during electron irradiation at 773 K with 1.8 MeV electrons with an applied field of 130 kV/m (Ref. [2]).

4.1. RIED by electron irradiation

Hodgson first extended the earlier studies to higher doses and demonstrated that the problem of electrical insulation for fusion power systems extends beyond the RIC effects [2–4]. Sapphire crystals were subjected to simultaneous application of Rad-E-T in order to simulate fusion reactor conditions. It was something of a surprise to the ceramics and fusion community when the failure of sapphire insulation under bombardment by high-energy electrons was announced [2,33]. The sample was held at 773 K at a field strength of 130 kV/m and subjected to irradiation with 1.8 MeV electrons from a HVEC Van de Graaff accelerator. Initially, the simultaneous application of Rad-E-T generates a RIC which remains constant for a long period of time. Based upon previous experimentally determined [7] values of $K$ and $\delta$, the value of RIC at the dose rate employed ($R = 1 \times 10^8$ Gy/h) was expected to be $\sim 1 \times 10^{-6}$ (\(\Omega\) m)$^{-1}$. This value was approximately the RIC level observed. At some critical dose corresponding to about 30 h of irradiation, shown in Fig. 8, the electrical conductivity began to increase, signaling the onset of what was reported to be an electrical breakdown process. At about 70 h the conductivity had increased to $8 \times 10^{-5}$ (\(\Omega\) m)$^{-1}$. The increase appeared to be in the base conductivity and not an increase in RIC, since post-irradiation measurements give a conductivity that was reduced only by the RIC. It was reported that the increase in conductivity was attended by a dark coloration, which Hodgson associated with the presence of colloids [40]. He suggested that the colloid production plays an important role in the RIED. The RIED was found to be a strong function of the applied electric field. Under identical conditions, but without the electron irradiation, there would be no increase in the electrical conductivity for the duration of the experiment [26]; therefore, no degradation would occur. Thus the RIED is linked to bombardment with energetic electrons.

Hodgson [2–4] also reported the same effect in single-crystal MgO and in single-crystal and polycrystalline spinel. In addition, similar results were obtained for conductivities measured by ac voltages up to 126 MHz. However, RIED was not reported during irradiations with 0.3 MeV electrons, which is below the reported $\alpha_{0}$ displacement damage threshold for energetic electrons, $0.40 \pm 0.04$ MeV [41,42]. Therefore, on the basis of this energy dependence, Hodgson concluded that both elastic collision and ionization events are necessary for electrical breakdown.

Recently Zong et al. [43] subjected single crystals of sapphire to electron Rad-E-T under experimental conditions similar to Hodgson’s investigations [2–4], but not identical. The samples were irradiated in air, instead of vacuum. The energy of the electrons was 1.8 MeV. The dose rate and the fluence were higher than those of the previous study, and only the center portion of the sample disk was irradiated. Fig. 9 illustrates a semi-log plot of the dc conductivity of a sapphire crystal at various stages of electron irradiation. The $c$
axis of the crystal was perpendicular to the sample surface, and parallel to the applied electric field and the incoming electron beam. During irradiation the temperature of the sample was held at 773 K and an electric field of 2120 V/cm was maintained. The beam current was about 4 µA/cm², or $2.5 \times 10^{13}$ e cm⁻² s⁻¹. The top curve illustrates the conductivity during irradiation, represented by $\sigma$. Obviously these values, which include RIC, depend on the intensity of the beam current, which was maintained at a constant level. No data were taken initially during irradiation, but the conductivity was projected by the dotted line. The beam current was intense, reflected by the nearly flat curve throughout; clearly the conductivity was dominated by RIC. These results confirmed that at some critical electron fluence during Rad-E-T, the post-irradiation electrical conductivity increased rapidly, albeit the critical dose was a factor of 10 higher than that observed by Hodgson. The conductivity did not increase indefinitely but saturated at $\sim 2 \times 10^{-7}$ (Ω m)⁻¹. Two main conclusions emerged from this study: First, the mechanism for RIED was attributed to the charge of electrons and holes created during irradiation, rather than due to displacements of indigenous ions by elastic collisions with the energetic bombarding electrons. Second, the primary defect which leads to RIED was deduced to be dislocations produced during Rad-E-T. TEM revealed a large average dislocation density, non-uniformity distributed throughout the degraded area, with an overall density of $\sim 10^6$ cm⁻², as opposed to $\sim 10^4$ cm⁻² at the periphery of the sample which was not subjected to electron bombardment or to an electric field. No second phase was observed. The concentration of point defects, as characterized by optical absorption and electron paramagnetic resonance, was not detectable in this crystal.

Furthermore they pointed out two serious flaws in Hodgson's experiments. First, no meaningful conclusions can be obtained from his energy dependence experiment, because the sample he used for the 0.3 MeV electrons was too thick – much thicker than the range of the electrons. Second, the spectrum he attributed to the optical absorption of the F⁺ center (anion vacancy with one-electron) was erroneously identified. The full-width-at-half-maximum of the absorption band was far too large. In addition, no anion vacancies were observed after RIED in Zong's samples, nor in the work in Refs. [56,57]. Zong et al. [43] pointed out that there should be negligible anion-vacancy concentration after RIED at 773 K, because oxygen interstitials at that temperature are highly mobile. In brief, the production rate of anion vacancies was much smaller than the thermal annihilation rate.

4.2. RIED by neutron irradiation

In-situ electrical conductivity measurements were also performed in fission reactors and in a spallation neutron source. Shikama et al. performed Rad-E-T experiments on alumina crystal, Kyocera SA 100 (99.9% pure), in the JMTR water-cooled fission reactor at the Oarai Establishment of Japan Atomic Energy Research Institute [44-49]. The neutron flux at the specimens with JMTR operating at full power (50 MW) was estimated to be $3.4 \times 10^{17}$ and $1.8 \times 10^{16}$ n m⁻² s⁻¹ for the fast ($E > 1.0$ MeV) and thermal ($E < 0.63$ eV) neutrons respectively. The flux for $E > 0.1$ MeV was about a factor of 10 higher. The gamma dose rates at the position used in this facility were estimated to be about $2.8 \times 10^3$ Gy/s at reactor full power. The sample temperature was 600–630 K and the applied electric field was 500 kV/m. The results are shown in Fig. 10. Initially the electrical conductivity was due primarily to RIC. The conductivity was essentially constant at about $6 \times 10^{-6} \Omega$ m⁻¹ up to about 5 days at full reactor power. This RIC value agrees with the phenomenological $KR^6$ expression with known values of $K$ and $\delta$ [7]. During this period the specimen had accumulated $2 \times 10^{23}$ n/m² fast neutrons ($E > 1.0$ MeV) and ($2-6) \times 10^9$ Gy of gamma rays. However, the conductivity began to increase after 10 reactor full-power days, and continues to increase even after 44 days at full power. At a neutron dose of $2 \times 10^{24}$ n/m² and a gamma dose of ($2-6) \times 10^{10}$ Gy, the conductivity had increased to $2 \times 10^{-5}$ (Ω m⁻¹).

In their second experiment the temperature and the electric field more closely approximated those of the electron irradiations. The fluxes were $3.4 \times 10^{17}$ and $1.8 \times 10^{18}$ n m⁻² s⁻¹ for fast ($E > 1.0$ MeV) and thermal ($E < 0.6286$ MeV) neutrons respectively. The ionizing dose rate (gamma rays) was estimated to be $5 \times 10^3$ Gy/s. The specimen was, however, polycrys-

![Fig. 10](image-url)
capsule. Farnum et al. pointed out that this effect served. The sapphire was irradiated in an evacuated could have been caused by degradation of the vacuum measurements would be necessary to verify these re-

The results are shown in Fig. 11. The conductivity began to increase at about 3 days, and continued to increase throughout the experiment, which lasted at least 40 days. This second experiment confirmed the conductivity increase observed in the first experiment.

On the other hand, in a much earlier study, Ranken and Veca [50] found no conductivity increase when they irradiated plasma arc sprayed ceramic test specimens of alumina and yttria with a fast neutron dose at 6 x 10^-24 n m^-2 at irradiation temperatures of about 1000 K and an applied field of 40 kV/m. Rather, they observed a general decrease in conductivity as a function of irradiation time, or dose.

Recently Farnum et al. [51] measured electrical conductivity of alumina and sapphire under applied fields of up to 185 kV/m during elevated-temperature irradiation with spallation neutrons and accompanying ionizing radiation. Up to a level of 2 x 10^23 n/m^2 no RIED was observed in alumina irradiated in argon at 668, 888, and 928 K with an applied DC voltage of 50 and 150 kV/m; in fact, conductivity decreased with time in a manner reminiscent of that observed in sapphire during irradiation with 3 MeV protons [38]. However, in sapphire irradiated at the same temperatures with an applied AC voltage of 185 kV/m at 20 kHz, a RIED-like increase in conductivity was observed. The sapphire was irradiated in an evacuated capsule. Farnum et al. pointed out that this effect could have been caused by degradation of the vacuum in the capsule and that post-irradiation conductivity measurements would be necessary to verify these results.

4.3. Other studies

Measurements by Shikama and Pells [52–54] reported the formation of aluminum colloids in α-alumina by 1.0 MeV electron irradiation in a high-voltage electron microscope. Pells [55] used 18 MeV protons to irradiate alumina and spinel. For irradiation temperatures above 673 K and proton doses up to 7.5 x 10^22 m^-2, there were large increases in the intrinsic conductivity that were not reduced by annealing at 923 K.

More recently Kesternich et al. [56] have proposed an alternative interpretation for the previously reported anomalous conductivity increase. In their experiment, pulsed 28 MeV alpha particles were used to irradiate ~150 𝜇m thick polycrystalline alumina and silicon nitride in vacuum at 773 K with an electric field of 350 kV/m. An increase of 10^4 in conductivity was observed in the alumina sample and 10^3 in the silicon nitride specimen under certain experimental conditions. However, the conductivity of the alumina saturated thereafter. The authors concluded that the increase in conductivity was not due to degradation of the bulk material, but was a result of radiation-induced surface contamination. In a similar study by Jung et al. [57], a polycrystalline alumina with a thickness of 250 𝜇m was irradiated with 10.7 MeV protons at 800 K with an electric field of 320 kV/m. Again an increase in conductivity was reported. They attributed the increased conductivity to radiation-induced surface contamination consisting of carbon. To demonstrate this point, they (1) deposited carbon films on their samples with and without electric field and (2) performed RIED experiments at 523 and 723 K. The results were optical absorption spectra similar to that obtained by Hodgson [40]; in fact, the RIED performed at 523 K was practically identical. Therefore, Jung et al. [57] strongly suggested that the RIED observed by Hodgson was due to surface contaminations during irradiation. Regardless whether the increased electrical conductivity is due to RIED or surface contamination, the implication of their conclusions in these studies is likely to add another dimension to ceramic degradation under irradiations: surface conductivity resulting from gas-environment impurity contamination.

At the sixth International Conference on Fusion Reactor Materials (ICFRM-6) Hodgson proposed an explanation as to why in certain cases RIED was not observed. He proposed that dose rates and irradiation temperature play an important role [58]. He reported that for higher dose rates, as typically encountered in pulsed accelerators, equivalent damage requires higher dose, thereby accounting for the report that RIED was not observed in some accelerator experiments. In addition, Zinkle and Hodgson [59] reported that for irradiation-temperature dependence a high temperature cutoff at ~823 K was observed. The updated curve is shown in Fig. 12.

4.4. Other meetings

Recently a joint USDOE–Japan Monbusho meeting entitled “Dynamic Effects of Irradiation in Ceramics”
Fig. 12. The total dose required to degrade samples of single (SC) and polycrystalline (PC) alumina to $10^{-6} \, (\Omega \text{ m})^{-1}$ as a function of irradiation temperature at $10^{-10} \, \text{dpa s}^{-1}$.

Fig. 13. Electrical conductivity versus equivalent neutron fluence for several investigations. (After Ref. [60].)
participants at the workshop announced plans to conduct such a round robin experiment during the coming year.

5. Scientific issues and opportunities

The fusion power plant environment commands one of the most demanding sets of materials requirements of any advanced technology involving ceramics. In support of various critical components in the reactor, the ceramics must overcome a combination of hostile environmental conditions. Their successful application requires materials integrity to extend over the life of the reactor. Therefore an understanding of the critical scientific issues in conjunction with the fusion operating conditions is essential in order to advance the materials technology to meet these demands. We shall address several of these key issues below:

5.1. Radiation damage

During the operation of the fusion reactor, the insulating ceramics are bombarded by neutrons and gamma rays (which result in Compton electrons) resulting directly or indirectly from the D–T fusion reaction. Alpha particles from the D–T reaction are stopped in the plasma or at the system first wall and will not make contact with the ceramic insulators. At this time, it appears likely that in a fusion chamber RIED would be induced by either the neutrons, or the gamma rays, or the synergism with both radiation fields. Is the RIED due to a radiation damage mechanism? There are other conductivity processes operating in insulators such as space charge limited conductivity, Frenckel–Poole emission, tunnel or field emission [61]. If it is a result of the radiation, then one may focus on the mechanisms and the corresponding cross sections in producing defects in insulating crystals by neutrons and gamma rays. Therefore one of the important issues is: Is RIED a result of an elastic collision between an incoming energetic particle and a lattice ion, or caused by an ionization process? In the Hodgson experiment, 1.8 MeV electrons were used. These electrons have enough energy to displace lattice ions by elastic collisions [62, 63]. On the other hand, the ionization-loss mechanism of charged particles may also cause displacements of indigenous ions, as is well-known in the alkali halides and many silica-based compounds [64–67]. Indeed, electron–hole pairs are created in abundance. Determination of the triggering mechanism would shed light on whether the neutrons, gamma rays, or both, are detrimental to RIED in ceramics.

In Rad-E-T experiments using electrons, such as performed by Klaffky et al. [7] and by Hodgson [2–4], the RIC remains essentially constant when experimental conditions, such as the temperature and dose rates, are unchanged. However, as pointed out in an earlier section, when the electron irradiation extends to a (critical) dose substantially beyond that used by Klaffky et al. [7], the electrical conductivity begins to increase. This sequence indicates that there exists an incubation period during which the electrical conductivity remains constant, or may even decrease. It is therefore essential to know: What defects (point and/or extended), if any, are formed during the incubation period? Hodgson suggested that aluminum colloids play an important role in the RIED. Is the formation of metallic precipitates during Rad-E-T a necessary condition for electrical breakdown? What are the dynamical processes involving these defects that trigger the increase in the electrical conductivity? Can doping with impurities lead to suppression of the RIED mechanism? These are fundamental issues which will provide a basis for an understanding of the RIC-RIED mechanisms.

5.2. Temperature dependence of RIC-RIED

The temperature of application for the ceramic materials in fusion devices is expected to be between room temperature and 1100 K, although in some situations, cryogenic temperatures will be used. This moderate temperature range may actually be an impediment in several ways. First, these temperatures may be sufficiently high to generate thermally activated defects at a rate which is more prominent than at lower temperatures. Secondly, many thermally activated processes, such as atomic diffusion, which can lead to dynamic repair of damage at the atomic level, may not be sufficiently prominent at these temperatures. In fact, it appears that the defect production in the 800 K regime overshadows the annealing mechanism. Thirdly, the strength of alumina, for example, may actually undergo a minimum at ~ 800 K because it occurs before the onset of appreciable radiation heat transfer which serves to diminish thermal gradients and therefore stresses in the materials. Indeed there are indications that degradation of physical properties in insulating ceramics may be avoided by the judicious choice of the ambient temperature. Operating at lower or higher temperatures may provide better performance with respect to RIED [59].

5.3. Mechanical stresses

The ability of a ceramic to maintain structural integrity under the swelling and applied loads is very important to the application [68]. As noted in Section 3.2, α-alumina is the only ceramic investigated which does not suffer electrical breakdown at high temperatures in the absence of radiation. It is likely that α-Al₂O₃ is also more resistant to electrical breakdown
in a radiation field than other oxides. However, the shortcoming of this material is that it swells under irradiation. Conversely, MgAl₂O₄ spinel is resistant to radiation-induced swelling, but the characteristic time for elevated temperature electrical breakdown, even in a radiation-free environment, is very short [26]. It is encouraging that certain additives in α-alumina can serve to suppress swelling [50].

5.4. Impurities and transmutation effects

Since the largest body of knowledge exists for the traditional high-temperature ceramic materials, α-Al₂O₃, MgAl₂O₄, and MgO, these materials warrant new research on their processing to improve their RIED performance. There have been suggestions that the onset of colloid formation is associated with certain trace element impurities. There has been previous work on ultra-high purity synthesis and processing of α-alumina in attempts to define the current limits on the extrinsic and intrinsic nature of its properties [69,70]. Currently all nominally pure α-Al₂O₃ has approximately 100 ppm total impurity content [71], while from estimates of defect formation energies, the onset of intrinsic behavior should occur at trace impurity contents below 1 ppm. With the routine achievement of ppb levels of contamination in silicon, an intrinsic α-alumina is not obtainable. This material may show a greater stability and delayed onset of the colloidal precipitation process. In addition to a better understanding of the role of trace impurities in the RIED process, the possibility exists that intentionally doping α-alumina with impurities may achieve a fully compensated material which may neutralize the onset of RIED.

The role of impurities in RIED has yet to be investigated. Traditionally impurities (or dopants) have always played a major role not only in the radiation damage of solids, but also in the electrical characteristics of insulators [23,72–83]. There is no reason to believe that in RIC-RIED, the situation would be any different. Indeed, in the case of electrical breakdown of ceramics, it has been shown that the positive effect of impurities in MgO crystals is dramatic (Fig. 4). Doping the crystals with copper impurities improved the breakdown longevity by a factor of 20. In a real situation, this magnitude of improvement can often translate from a failing to a passing grade. The understanding of the mechanism of any enhancement (or suppression) of RIED could be elusive, but nevertheless essential. From a technological point of view, an understanding of the mechanisms of RIED will serve to guide the usage (or non-usage) of impurities pertaining to possible suppression of RIED.

The transmutation of host nuclei (or even impurities) under particle bombardment may produce daughters, which are highly radioactive (long decay lifetimes) or serve to enhance RIED. These conditions would tend to rule out certain types of ceramic hosts, or impurities.

5.5. Atomic and electronic structures

Extensive work is needed to determine the atomic structure of the materials at all stages in the RIC/RIED process, covering the role of extrinsic impurities and intrinsic atomic defects, to the nucleation and growth processes of RIC/RIED. This will require high sensitivity experimental techniques that may include magnetic resonance, electron microscopy, EXAFS, X-ray diffraction, optical spectroscopy, and positron annihilation spectroscopy, to study the atomic structure of materials. In addition, modeling including atomistic simulations of defect interactions, and quantum-based calculations of defect formation and radiation damage in a highly ionizing and displacive radiation field, is desirable. This work should apply to both in-situ and ex-situ studies and encompass pulse techniques to understand the myriad of atomic structural phenomena which are occurring in the fusion reactor environment. An understanding of this sort will also illuminate the possible recovery processes which are competing to reduce the RIED sensitivity of ceramics and which can be advantageously tailored in the final materials.

The fusion environment involves moderately high temperatures and high levels of particle and ionizing radiation. The conductivity behavior of ceramics is impurity/defect dependent, and temperature dependent. In addition to the normal thermal carrier excitation across a band gap, increase in temperature decreases the band gap in ceramics. This temperature-dependent change in the electronic structure, arising from thermal lattice expansion and electron–phonon interaction, plays an important role in the intrinsic high-temperature electronic conductivity of ceramics [84,85]. This is an example where more understanding of the electronic structure is needed. The first-order effect, more thermal creation of carriers, supplies an incomplete picture. Besides the temperature dependence of the intrinsic and extrinsic electronic structure of materials, the high level of ionizing radiation leads to high levels of radiation-induced electron–hole pairs in the electronic structure of the materials.

The electronic structure is closely coupled to the atomic structure. As atomic defects accrue, their bonding can be substantially different from the equilibrium room-temperature material, opening up more avenues for new electronic processes to occur. Expanding our understanding of the electronic properties will involve both theoretical calculations of the temperature-dependent equilibrium and non-equilibrium structure of ceramics [86], and experimental determinations of the
be coupled to understanding the effects of other stresses on the material, such as radiation-induced swelling. Important issues will be: What are the electronic carriers? Are they polaronic, large or small? What is the role of the lattice stabilization of the electronic (polaronic) carriers in initiating other processes which distort the atomic structure? Insight into the degradation of the insulator to a metallic state, in terms of changes in the atomic bonding and electronic structure will be the context for understanding the myriad of competing processes in fusion reactor ceramics.

5.6. Defect chemistry

Defect chemistry of ceramics corresponds to the intermediate stage at which thermally created (or radiation-induced) defects and defect clusters react en route to either annihilation or agglomeration to form precursors or nuclei for precipitates. Defect chemistry studies supply information on the behavior and of defect processes in ceramics under a large variety of conditions, for example, temperature, oxidizing or reducing atmosphere, and irradiation. Therefore these studies can play a very strong role in determining the nature of the processes occurring in ceramics during RIC/RIED. The methods of defect chemistry involve in-situ conductivity measurements or variants thereof. Defect chemistry supplies information on: (1) defect dependence on temperature and oxygen partial pressure, (2) interaction of defects and impurities, and (3) dopant effects. Furthermore, defect chemistry can help to understand the precursors to colloid formation, or defect annihilation and colloid disappearance. Aside from the measurement of electrical conductivity at various temperatures, defect chemistry has not been applied to fusion system materials. Therefore this area provides many fruitful opportunities.

6. Recommendations

6.1. Standardization

A wide range of conductivity values were obtained under very diverse experimental conditions (see Fig. 13). In addition, a review of the literature has revealed how difficult these measurements in ceramics can be, even without an impressed radiation field. For these reasons it is recommended that the RIC/RIED observations in insulating materials be performed and repeated, focusing on three elements: (1) standardization of measurement technique, (2) standardization and reproducibility of samples, and (3) parallel multiple laboratory/investigator participation, with at least one set of measurements, for interlaboratory comparison, under similar parameters.

6.2. New materials with minimal RIC-RIED

Previous studies have shown that oxide ceramics subjected to moderate electric fields at high temperatures, but in the absence of radiation, are susceptible to electrical breakdown [19-27]. It is believed that the addition of radiation would serve to accelerate the breakdown process. Therefore it is essential to select for fusion candidates which are least susceptible to electrical breakdown in the absence of radiation. α-Al₂O₃ (alumina) is such a material. Even though the conductivity of alumina was found to degrade under extended electron irradiation, it is still likely to be more resistant to RIED than other oxides which readily breakdown without radiation, such as MgO (magnesia) and MgAl₂O₄ (spinel). Therefore alumina is still a candidate for fusion applications, notwithstanding its undesirable characteristic of anisotropic swelling and strength loss under prolonged neutron irradiation.

In order to pursue materials which are least susceptible to RIED, it is necessary to understand the cause of the phenomenon. Therefore it is recommended that different materials be studied, in order to establish a database for categorizing and understanding those materials which are resilient to RIED and those which are not. Various materials have been suggested, Si₃N₄, SiC, AlN, Sc₂O₃, Ta₂O₅, and La₂O₃ [87,88]. The area of new materials is a fertile one from a solid-state chemistry approach, to establish a data base for establishing structural families which are susceptible to RIED, and to establish structure-property relationships in order to target certain structural families for Rad-E-T for application.

The second area of new materials research involves developments in materials processing. For example new forms of materials preparation such as spray deposition [89], the formation of gradient materials or the development of thin film forms of materials which have novel and non-equilibrium structures may hold promise. Some of these microstructurally distinct materials may show enhanced resistance to RIED. These materials might be re-engineered for their radiolytic properties.

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