ABSTRACT: Several materials have or are currently being investigated for nuclear waste sequestration applications, including crystalline ceramic oxides, glasses, and glass–ceramic composites. Rare-earth phosphates have been investigated extensively for this application owing to the range of structures that the hydrous or anhydrous versions can adopt as well as the fact that naturally occurring rare-earth phosphates have been found to contain U or Th. The purpose of this mini-review is to discuss (generally) the properties that must be considered when identifying nuclear wasteform materials and (more specifically) the structure and properties of rare-earth phosphates with special attention being given to the resistance of these materials to radiation-induced structure damage. The last section of the mini-review contains an introduction to the development of glass–ceramic composite materials that contain rare-earth phosphate crystallites dispersed in a glass matrix. These composite materials have been suggested to be superior to using just glass or ceramic materials for nuclear waste sequestration applications owing to improved waste loading capabilities.

1. INTRODUCTION

Nuclear power is a major source of electricity worldwide. As of 2020, there were 449 operable reactors which were responsible for generating 10.6% of the world’s electricity. With 55 reactors under construction, 111 ordered, and 328 proposed, the global nuclear industry is expanding. In 2008, the International Energy Agency (IEA) projected that world energy requirements will nearly double by 2030. Various “green” energy sources such as wind, solar, and nuclear have been proposed to meet these energy demands while combating the prospect of climate change by producing little to no CO₂ emissions. Intermittent sources of energy, like solar and wind energy, would rely on backup sources approximately 80% of the time, whereas nuclear power is available on a consistent basis. Reliance on nuclear power provides energy security as the fuel is available from many politically stable countries, and the high energy density of uranium allows for easier storage of large energy reserves when compared to fossil fuels. One disadvantage of nuclear power is the generation of nuclear (radioactive) waste.

Radioactive waste in Canada (for example) is generated from uranium mining, milling, and refining; nuclear fuel fabrication; nuclear reactors; nuclear research; and radioisotope manufacturing and use. This waste is categorized depending on the level of radioactivity detected and/or the heat emitted by the material. Low-level radioactive waste (LLW) is those materials that are used in the workplace surrounding the use of radioactive materials (e.g., gloves, cloths, protective clothing). Intermediate-level radioactive waste (ILW) has had more direct contact with radioactive
materials, such as ion-exchange resins and reactor components. High-level radioactive waste (HLW) is defined as spent fuel and other materials emitting >2 kW/m³ of heat. A wasteform is defined as "waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging." The ultimate purpose of radioactive waste management is to immobilize radioactive elements in wasteforms to prevent the release of those radionuclides into the environment. Groundwater leaching has been identified as the most likely mechanism by which release of radionuclides may occur. Therefore, the most important requirement for a wasteform is to be chemically durable. Additionally, an ideal wasteform should be resistant to damage caused by radioactive decay processes, incorporate a wide range of elements with high loading, and be easy to fabricate with reasonable synthesis conditions. Several types of wasteforms have been studied to date including glasses, ceramics, and glass—ceramic composites. The purpose of this mini-review is to discuss some of the wasteform materials that have been proposed for nuclear waste sequestration with specific attention being given to rare-earth phosphate-based wasteform materials.

2. TYPES OF NUCLEAR WASTE FORM MATERIALS

2.1. Glasses. Radioactive glass wasteforms were first produced via vitrification on an industrial scale at the AVM (Atelier de Vitrification de Marcoule) plant in Marcoule, France in 1978. Since then, a global consensus has been reached on using glass materials, notably borosilicate glasses, as a host matrix for the immobilization of liquid HLW. Currently, glass vitrification technology has been used in most countries for the conversion of liquid HLW into durable solid wasteforms. The liquid HLWs which are compositionally similar (i.e., contain a wide range of radionuclides) are homogeneously distributed inside a glass matrix. Borosilicate glasses that are being used worldwide as a HLW matrix are generally prepared using varying mass percentages of chemicals such as SiO₂, B₂O₃, Al₂O₃, CaO, MgO, and Na₂O. The waste-loading capabilities of these glasses could range anywhere between 25% and 35% by mass. In addition to borosilicate glass materials, other materials such as aluminophosphate, silicate, rare-earth oxide, and iron-phosphate glasses are also being considered for the immobilization of HLW.

2.2. Ceramics. Naturally occurring crystalline minerals containing radionuclides are known to have been on Earth for millions of years and have been exposed to extreme environmental conditions. Some of the natural minerals have endured these extreme conditions and remained structurally stable on a geological time scale. This observation has inspired scientists to propose synthetic analogues of these crystalline minerals for HLW immobilization applications. Crystalline materials, unlike their amorphous counterparts (e.g., glasses), are thermodynamically stable and therefore should possess greater structural stability and chemical durability over the long periods of time required for HLW storage. In a crystalline wasteform, the radionuclides occupy specific atomic sites of the host matrix and become a part of the crystal structure. Since the atomic sites in a crystal structure have specific size, charge, and bonding requirements, the crystalline host matrix imposes restriction on the type of radioactive element that can be incorporated into the crystal structure. As a result, different crystalline materials are being developed or proposed to host specific types of radioactive elements (e.g., fission products; minor actinides) that are present in liquid HLW.

Among the various crystalline wasteforms that have been studied, multiphase wasteforms called SYNROC (synthetic rock) developed by Ringwood and co-workers have been investigated extensively in the literature. SYNROC is a polyphase assemblage of synthetic analogues of Ti-containing crystalline minerals and is generally comprised of hollanhdite (BaAl₂Ti₄O₁₂), perovskite (CaTiO₃), zirconolite (CaZrTi₂O₇), and rutile (TiO₂) phases. The minerals constituting the SYNROC wasteform have survived in various geological environments for millions of years, and therefore, SYNROC wasteforms possess higher chemical durability than glass-based wasteforms. In addition to high durability, the presence of multiple crystalline phases in SYNROC also allows for the incorporation of a wide variety of radionuclides resulting from the reprocessing of spent fuel. Single-phase wasteforms, on the other hand, are tailored for hosting specific radionuclides, and some of the proposed crystalline wasteforms include monazite (CePO₄), xenotime (YPO₄), brannerite (UTi₂O₇), pyrochlore (Gd₂Ti₂O₇), and zircon (ZrSiO₄). The leaching resistance of a material is one important property to consider when selecting materials as a nuclear wasteform. It has been demonstrated that several crystalline ceramic phases have significantly improved resistance to leaching, as shown in Figure 1, as well as other properties that are beneficial to the implementation of these materials as nuclear wasteforms.

![Figure 1. Comparison of the U leach rate from glass, brannerite, pyrochlore, and zirconolite materials, demonstrating the increased chemical durability of ceramic materials relative to glass. Reprinted with permission from Weber, W. J.; Navrotsky, A.; Stefanovsky, S.; Vance, E. R.; Vernaz, E. Material science of high-level nuclear waste immobilization. MRS Bull. 2009, 34 (1), 46–53. Copyright 2009 Materials Research Society.](image-url)

2.3. Glass—Ceramic Composites. Glass—ceramic composites, which may also be referred to as glass-ceramic materials or glass-composite materials, are heterogeneous materials that consist of ceramic crystallites dispersed in a glass matrix. By synthesizing a material that contains both crystalline ceramic and amorphous glass, the final material can possess properties that are greater than the sum of its parts. Various glass-ceramic composite materials have been investigated as wasteforms for nuclear waste sequestration. These materials have been studied for a variety of reasons including that (1) these materials have a higher waste loading of large elements (e.g., actinides) compared to glasses, as these elements can be incorporated into specific crystallographic sites that are large enough to accommodate them; (2) the
3. RADIATION EFFECTS IN NUCLEAR WASTEFORMS

The radiation emanating from HLW is a result of radioactive decay of fission products (e.g., $^{137}$Cs and $^{90}$Sr) and minor actinides (e.g., Np, Am, Cm) present in the HLW stream. The fission products decay via emission of β ($e^−$) particles, and in this process low-energy recoil nuclei, also called daughter products, are produced. The minor actinides, on the other hand, decay by producing energetic α ($^4$He$^+\$) particles and high-energy recoil nuclei. The fission products and minor actinides have shorter and longer half-lives, respectively. As a result, for the first ∼500 years of HLW storage, the radiation will predominantly arise from the β-decay of fission products after which the radiation will arise primarily from the α-decay of actinides. When these radionuclides are atomically confined within a solid matrix, the radioactive decay products dissipate their energy into the host matrix via ionization and elastic collision events. In the case of an ionization event, the energies of the decay products are used to excite and remove electrons from the atoms in the solid, whereas in an elastic collision event, the energies are transferred to atoms present in the host matrix. Both ionization and elastic collision events affect the structures and properties of nuclear wasteforms.

Among the decay products, α- and β-particles lose energy mainly by ionization processes, while the recoil nuclei resulting from α- and β-decay events transfer energy to atoms primarily via an elastic collision process. The decay products resulting from β-decay do not possess enough energy (e.g., energy of β-particle ∼0.5 MeV) to initiate atomic displacements in the host matrix. As a result, β-decay events do not cause significant damage to the structure of a nuclear wasteform. However, the α-decay event which produces high energy α-particles (4.5 to 5.8 MeV) and α-recoil atoms (70 to 100 keV) brings about the most structural damage in wasteforms. During an α-decay event, an α-particle can travel over a range of 16−22 μm and loses the majority of its energy to inducing ionization events. A portion of the energy of an α-particle is also used to produce a few hundred atomic displacements along its path with greater displacements occurring at the end of the particle trajectory. The heavier α-recoil atom, on the other hand, dissipates energy primarily via elastic collision processes over a very short range (30−40 nm) and causes 1000 to 2000 atomic displacements. Compared to α-recoil, the β-recoil atom only generates about 0.1 atomic displacements per β-decay event. As a result, several studies have focused on investigating the radiation damage in solid wasteforms due to α-recoil atoms.

The extent of structural damage due to α-decay events varies depending on the dose (i.e., number of α-decay events per gram of actinide) and type of nuclear wasteform that is being studied. Structurally, glass-based host matrices in which atoms are arranged in a random fashion are less affected by the atomic rearrangements that occur as a result of α-decay of actinides. The minor changes in the structure of a glass that accompanies the radioactive decay of actinides are usually manifested in a small increase or decrease in the volume of a glass wasteform. The maximum change in the volume of a glass wasteform after α-decay events is on the order of ∼1%.

As a result, significant changes in the chemical durability of glass wasteforms are not observed after α-decay. Crystalline wasteforms, on the other hand, are structurally more affected by radiation damage events. Crystalline wasteforms are characterized by long-range periodic arrangement of atoms, and in the event of an α-decay event, the high energy α-recoil atom tends to disrupt this periodic arrangement either partially or completely. In the former case, a disordered crystalline wasteform is produced, whereas in the latter the crystalline phase is completely transformed into an amorphous phase. These structural changes are accompanied by a swelling of the wasteform, and the change in volume of the crystalline wasteform can range between 5% and 18%. Swelling of a wasteform results in an increase in its surface area, thereby decreasing the chemical durability of the crystalline wasteform. The structural response of nuclear wasteforms to α-decay-induced radiation damage events has been studied in the literature either via incorporation of actinides in a wasteform (internal irradiation) and/or through simulation of damage by implanting high energy charged particles in a wasteform (external irradiation). A short account of internal and external irradiation methods is provided in the following section.

3.1. Internal Irradiation. Radiation-induced structural damage due to α-decay events is best studied through doping of short-lived actinides (e.g., Pu, Cm) in the wasteform of interest. In internal or self-irradiation methods, the radiation resulting from the α-decay of incorporated actinides varies gradually with time, and accordingly, the structural performance of nuclear wasteforms is monitored as a function of time. During an α-decay event, the wasteform is simultaneously exposed to radiation arising from both α-particles and α-recoil atoms. Therefore, the internal irradiation method enables determination of the structural stability of proposed wasteforms under conditions that are quite similar to those experienced by HLW incorporated wasteforms. However, the major disadvantages of employing an internal irradiation method to study radiation-induced damage processes in wasteforms are that it is time-consuming, and the radioactivity of the wasteform also places a limit on the access to various characterization techniques that could be used for examining the structure of the host matrix.

3.2. External Irradiation. The limitations faced by internal irradiation can be overcome using an external irradiation method in which the radiation events are simulated under laboratory conditions via high energy ion implantation. In this method, the radiation conditions representing different time periods of HLW storage are attained in a very short time by irradiating a thin region of the monolithic wasteform (e.g., pellet) with high-energy ion beams (e.g., He$^{2+}$, Ne$^+$, Kr$^{+}$, Au$^{+}$) of varying ion doses (i.e., number of ions/cm$^2$). The externally irradiated solids are also nonradioactive, which therefore allows the use of different experimental techniques to characterize the ion-implanted solids. Since α-decay is the major decay pathway for actinides present in HLW, the wasteforms are irradiated with high-energy light (e.g., He$^{2+}$) and/or heavy (e.g., Pb$^+$, Au$^+$) ions to simulate radiation effects due to α-particles and/or α-recoil atoms (i.e., daughter products), respectively.
4. RARE-EARTH PHOSPHATES AS NUCLEAR WASTEFORMS

In the search for a suitable crystalline wasteform, synthetic analogues of some of the naturally occurring rare-earth phosphate minerals have been identified as a potential host matrix for HLW storage. The rare-earth phosphate minerals are both compositionally and structurally diverse and can be found in nature as monazite [(Ce,La,Nd,Th,U)PO₄], xenotime [(Y,HREE,U,Th)PO₄; HREE = heavy rare-earth elements], fluorapatite [(Ca,Ce)₅(PO₄)₃F], vitusite [Na₃(Ce,La,Nd)- (PO₄)₃], rhabdophane [(Ce,La)PO₄·H₂O], churchite [YPO₄·2H₂O], and brockite [(Ca,Sn,Ce)PO₄·H₂O]. Of the various rare-earth phosphate minerals that exist in nature, the monazite and xenotime minerals contain the highest weight percent of rare-earth elements, and these minerals are used commercially for the extraction of rare-earth elements. Monazite and xenotime are abundant rare-earth minerals that exist as an accessory phase in rocks such as granitoids, pyroxenes, and gneisses. The mineral monazite is also found in alluvial deposits and beach sands as a result of the weathering of rocks. In addition to accommodating rare-earth elements, the monazite and xenotime minerals also contain varying amounts of Th and U, which makes these minerals slightly radioactive. Due to the presence of Th and U, these minerals have been exposed to radiation events over geological time scales, and yet the monazite mineral, in particular, has not been found completely in a metamict state (i.e., amorphous). This observation suggests that these minerals are structurally resistant to radiation damage events. However, radiation studies on synthetic and natural monazite samples have shown that these minerals are easily damaged by radiation events but could also recover from structural damage upon annealing at lower temperatures. Unlike the monazite mineral, radiation studies of xenotime minerals are not well documented in the literature. Monazite and xenotime minerals are also highly insoluble and possess high chemical durability in aqueous environments, and this is demonstrated by the fact that the monazite minerals are still present in beach sands and placer deposits wherein the minerals are frequently exposed to aqueous conditions. Based on this mineralogical evidence, synthetic analogues of monazite and xenotime minerals have been proposed as potential host candidates for nuclear waste sequestration applications.

Another important mineral that is chemically related to monazite is rhabdophane. Rhabdophane is a naturally occurring hydrous rare-earth phosphate mineral (REPO₄·nH₂O; RE = La to Dy) that is formed during the aqueous alteration of monazite minerals and could play a role in controlling the solubility of actinides. A few studies have shown the formation of rhabdophane on the surface of synthetic phosphate ceramics as a result of chemical alteration and have proposed that rhabdophane could act as a protective barrier by either delaying or stopping the release of actinides to the environment. In terms of structural stability, the rhabdophane phase is considered to be stable at lower temperatures and can undergo structural transformations to the monazite- or xenotime-type structure at higher temperatures. It is for this reason that the synthetic analogues of the rhabdophane mineral have not received attention as a potential nuclear wasteform in the literature.

A fourth polymorph of rare-earth phosphates referred to as churcheite is also found in nature, and like rhabdophane, churcheite is also a hydrous rare-earth phosphate mineral (REPO₄·2H₂O; RE = Gd to Lu and Y). Churchite-type materials lose water upon heating and eventually undergo a structural transformation to the xenotime-type structure. It has been proposed that the churcheite phase could precipitate on the surface of the xenotime mineral during the low-temperature aqueous alteration of the latter, and as a result, the churcheite phase could play an important role in delaying or stopping the migration of actinides from the xenotime mineral to the biosphere.

4.1. Crystal Structures of Monazite and Xenotime.

Monazite (REPO₄; RE = La to Gd) and xenotime (REPO₄; RE = Tb to Lu and Y) type structures crystallize in monoclinic (P2₁/n) and tetragonal (I₄₁/amd) crystal systems, respectively. In the monazite structure, the RE ions are coordinated to nine oxygen atoms, and the arrangement of oxygen atoms interpenetrated by a tetrahedron of oxygen atoms is shown in Figure 2a). The REO₄ polyhedra in the monazite structure consist of nine unique REO₄ polyhedra (shown in Figure 2a). The REO₄ polyhedra consist of two unique RE octahedra (Figure 2a) and as a result are significantly distorted. As a result of this distortion, the monazite structure offers greater structural flexibility and can accommodate cations of differing sizes and charges. Chains of alternating REO₄ polyhedra and PO₄ tetrahedra connected via edge sharing are present along the c-axis, and these chains are connected to each other via edge sharing of REO₄ polyhedra (Figure 2a).

In the xenotime-type structure (e.g., YPO₄), the RE ions are coordinated to eight oxygen atoms, and the resulting REO₄ polyhedra consist of two unique RE–O bond distances (e.g., Ce–O = 2.460–2.776 Å in CePO₄) and as a result are significantly distorted. As a result of this distortion, the xenotime structure offers greater structural flexibility and can accommodate cations of differing sizes and charges. Chains of alternating REO₄ polyhedra and PO₄ tetrahedra connected via edge sharing are present along the c-axis, and these chains are connected to each other via edge sharing of REO₄ polyhedra (Figure 2b).

4.2. Crystal Structure of Rhabdophane.

Rhabdophane (SmPO₄·2H₂O) materials crystallize in a monoclinic crystal system (space group: C2), and the crystal structure consists of two chains (Ch1 and Ch2) of alternating Sm–O polyhedra and PO₄ tetrahedra (Figure 3a). The PO₄ tetrahedra in Ch1 (Figure 3b) are distorted to the same extent and have four unique P–O bond distances and P–O–P bond angles, whereas in Ch2, the symmetry of the alternating PO₄ tetrahedra are not the same (i.e., four unique P–O bond
and the Y atoms are provided by the water molecules. The atoms of which six oxygen atoms are provided by the polyhedra, the central yttrium atom is bonded to eight oxygen tetrahedra, and these 1D chains are in turn connected to each other through the formation of hydrogen bonds (H-bonds) between the layers, and this results in the formation of a 3D network. In addition to the interlayer H-bonds, intralayer H-bonds are also present in the churchite-type structure.

5. EFFECT OF ION IRRADIATION ON THE STRUCTURE OF REPO$_4$

Numerous studies have employed an external irradiation method to investigate the effect of radiation on the structures of REPO$_4$ materials. In the external irradiation method, single or dual ion-beam irradiation of REPO$_4$ has been performed followed by analysis using a variety of techniques. In single ion-beam irradiation mode, heavy or light ion beams such as Au or He are typically used for ion irradiation and simulate the structural changes due to either an α-recoil atom or an α-particle. In the dual ion-beam irradiation mode, heavy and light ion beams such as Au and He are used in tandem, respectively. Dual ion-beam irradiation simulates the combined effects of the α-recoil atom and α-particle on the structure of REPO$_4$. The structural response of REPO$_4$ ceramics to ion irradiation has been studied using various structural characterization techniques such as in situ transmission electron microscopy (TEM), glancing angle X-ray absorption near-edge spectroscopy (GA-XANES), photoluminescence spectroscopy, etc. Two independent studies investigating the effect of ion irradiation on the structure of REPO$_4$ using ex situ GA-XANES and in situ TEM techniques will be discussed in the following sections.

5.1. GA-XANES Investigation of Ion-Irradiated REPO$_4$ Ceramics

Rafiuddin and Grosvenor investigated the structural response of Au$^+$ ion irradiated La$_{1-x}$Yb$_x$PO$_4$ ceramics using GA-XANES. The La$_{1-x}$Yb$_x$PO$_4$ (x = 0.0, 0.3, 0.7, and 1.0) ceramics were synthesized by conventional solid-state methods, and sintered pellets were produced prior to Au$^+$ ion implantation. In that study, high energy Au$^+$ ions (2 MeV) of varying ion doses ($1 \times 10^{14}$, $5 \times 10^{14}$, and $1 \times 10^{15}$ ions/cm$^2$) were implanted into La$_{1-x}$Yb$_x$PO$_4$ pellets. A Stopping and Range of Ions in Matter (SRIM-2013) software package was used in this study to generate the Au$^+$ ion implantation depth profile in La$_{1-x}$Yb$_x$PO$_4$. SRIM calculations have shown that the Au$^+$ ions were implanted to a depth ranging between 50 and 450 nm and that the maximum number of Au$^+$ ions was found at a depth of ~275 nm. Since the ions are implanted in the near-surface region of the pellet, a surface-sensitive GA-XANES technique was used in this study to monitor the changes in the local structure of the material due to ion implantation. The local structure around the P atom in ion-irradiated La$_{1-x}$Yb$_x$PO$_4$ ceramics was investigated using P K-edge GA-XANES. The P K-edge GA-XANES spectra of ion-irradiated LaPO$_4$ (monazite-type) and YbPO$_4$ (xenotime-type) ceramics are shown in Figure 5 and Figure 6. In comparison to the pristine as-synthesized material, the P K-edge GA-XANES spectra of ion-irradiated LaPO$_4$ and YbPO$_4$ exhibited significant changes in the near-edge line shape, thus indicating a change in the local structure of P due to ion implantation. In this study, the change in the local structure of P was attributed to a distortion of the PO$_4$ tetrahedra caused by ion.
implantation. It was observed in this study that for YbPO$_4$ ceramics implanted to a dose of $1 \times 10^{15}$ ions/cm$^2$ the spectral line shape of the ion-irradiated material showed similarities to the pristine material, thus indicating a partial recrystallization of the structure (Figure 6).

It was proposed in this study that the partial recrystallization could be a result of the high dose of Au$^-$ ions causing a local heating of the sample and, thus, providing the necessary impetus for the movement of some of the displaced atoms to their original lattice sites.

The effect of annealing on the structure of ion-irradiated La$_{1-x}$Yb$_x$PO$_4$ was also investigated in this study to determine if the materials could recover from the structural damage via thermal annealing. Ion-irradiated La$_{1-x}$Yb$_x$PO$_4$ samples were heated to 300 and 900 °C, and the structural response was monitored using P K-edge GA-XANES (Figure 7). Evidence of partial structure recovery was observed for all samples annealed to 300 °C as indicated by the similarities in the spectral line shape of the ion-irradiated sample to those of the pristine material. Similar observations were made in this study for LaPO$_4$, La$_{0.7}$Yb$_{0.3}$PO$_4$, and La$_{0.3}$Yb$_{0.7}$PO$_4$ annealed to 900 °C, although complete structural recovery was only observed for the YbPO$_4$ sample annealed to 900 °C.

### 5.2. In Situ TEM Investigation of Dual-Ion-Beam-Irradiated REPO$_4$ Ceramics

Rafiuddin et al. investigated the effect of dual ion beam irradiation on the structure of xenotime-type ErPO$_4$ ceramics using in situ TEM. In this study, the ErPO$_4$ powders were synthesized via a hydrothermal method, and the resulting powders were pressed into pellets of 5 mm diameter and sintered at 1600 °C in air for 3 h. Prior to ion irradiation, a focused ion beam (FIB) technique was used to prepare thin lamellas of ErPO$_4$ (dimension $\sim$10.30 × 5.40 μm; thickness $\sim$60–83 nm). In this study, the dual ion beam irradiation was performed under in situ conditions inside a 200 keV TEM vacuum chamber, and the structural response was monitored using in situ TEM. The ErPO$_4$ lamellas were

Figure 5. P K-edge GA-XANES spectra of LaPO$_4$ implanted with Au$^-$ ions to doses of (a) $5 \times 10^{14}$ ions/cm$^2$ and (b) $1 \times 10^{15}$ ions/cm$^2$. Reprinted with permission from Rafiuddin, M. R.; Grosvenor, A. P. Probing the effect of radiation damage on the structure of rare-earth phosphates. J. Alloys Compd. 2015, 653. Copyright 2015 Elsevier B.V.

Figure 6. P K-edge GA-XANES spectra of YbPO$_4$ implanted with Au$^-$ ions to doses of (a) $1 \times 10^{14}$ ions/cm$^2$, (b) $5 \times 10^{14}$ ions/cm$^2$, and (c) $1 \times 10^{15}$ ions/cm$^2$. Reprinted with permission from Rafiuddin, M. R.; Grosvenor, A. P. Probing the effect of radiation damage on the structure of rare-earth phosphates. J. Alloys Compd. 2015, 653. Copyright 2015 Elsevier B.V.

Figure 7. P K-edge GA-XANES spectra of Au$^-$ ion implanted (a) LaPO$_4$, (b) YbPO$_4$, (c) La$_{0.7}$Yb$_{0.3}$PO$_4$, and (d) La$_{0.3}$Yb$_{0.7}$PO$_4$ annealed to 300 and 900 °C. Reprinted with permission from Rafiuddin, M. R.; Grosvenor, A. P. Probing the effect of radiation damage on the structure of rare-earth phosphates. J. Alloys Compd. 2015, 653. Copyright 2015 Elsevier B.V.
irradiated using 1.5 MeV Au\(^{2+}\) and 160 keV He\(^+\) ions in sequential and simultaneous irradiation modes. In the sequential mode, the lamellas were first irradiated using Au\(^{2+}\) ions followed by irradiation using He\(^+\) ions, whereas in the simultaneous mode the lamellas were irradiated simultaneously using both Au\(^{2+}\) and He\(^+\) ions.

It was shown in this study that the xenotime-type ErPO\(_4\) material turned amorphous upon irradiation with Au\(^{2+}\) ions at a fluence of \(5 \times 10^{13}\) ions/cm\(^2\) (Figure 8). Sequential irradiation of the amorphous lamella with He\(^+\) ions (\(1 \times 10^{17}\) ions/cm\(^2\)) did not result in the recrystallization of the sample. However, simultaneous irradiation (Au\(^{2+}\) + He\(^+\)) of the ErPO\(_4\) material did not result in radiation-induced amorphization of the sample at all the ion fluences studied, and the material continued to remain crystalline (Figure 9).

An \(\alpha\)-healing mechanism (i.e., healing of structural defects due to the rise in the local temperature of the material occurring as a result of \(\alpha\)-particle irradiation, ionization-driven diffusion of point defects, and recombination of vacancy and interstitial sites) was proposed in this study to explain the absence of radiation-induced amorphization.

### 6. GLASS–REPO\(_4\) COMPOSITES

As indicated earlier, glass–ceramic composites have been proposed as next-generation materials for nuclear waste sequestration applications. Glass–ceramic composite materials are normally synthesized using a two-step process where the ceramic and glass phases are synthesized separately before being mixed and then annealed to form a composite material.

A one-step method has been investigated where all precursors are mixed from the beginning followed by annealing. A one-step method would save on fabrication costs and would be compatible with already existing glass-producing infrastructure and would also be safer since the HLW would not need to be handled for as long a period compared to the two-step method.

Glass–ceramic composites containing LaPO\(_4\) (monazite-type), YPO\(_4\) (xenotime-type), or CePO\(_4\) (xenotime-type) crystallites dispersed in a borosilicate glass (BG) matrix have been synthesized by both one- and two-step methods using either solid-state or coprecipitation methods. It was observed that glass–ceramic composites containing rare-earth phosphates dispersed in a borosilicate glass matrix could be formed using either one- or two-step methods and exhibit similar properties (e.g., morphology, crystal structures, etc.). However, when comparing the solid-state vs coprecipitation
methods, it was observed that these glass—ceramic composite materials could be formed at significantly lower temperatures when using the coprecipitation method (e.g., 700 °C) compared to the solid-state method (e.g., 1100 °C). Further, it was also demonstrated that the glass composition can affect the formation of secondary (i.e., unwanted) crystalline phases when lower annealing temperatures are used. An example SEM image and corresponding EDX maps from a glass—ceramic composite material containing CePO₄ crystallites formed by a one-step coprecipitation method are shown in Figure 10.

Figure 10. (a) SEM image of a 40 wt % CePO₄–BG composite material synthesized with a Ce⁴⁺ precursor and annealed at 1100 °C. EDX maps of (b) Ce, (c) Si, and (d) Na. Reprinted with permission from Donato, G.; Grosvenor, A. P. Crystallization of rare-earth phosphate-borosilicate glass composites synthesized by a one-step coprecipitation method. Cryst. Growth Des. 2020, 20 (4), 2217–2231. Copyright 2020 American Chemical Society.

7. SUMMARY AND CONCLUSIONS
Several strategies have been proposed for the safe sequestration of nuclear waste, which is important for the continued expansion of nuclear power plants to help combat climate change. While this mini-review has focused on rare-earth phosphate materials, it should be noted that many solid-state materials having different structures and compositions have been proposed for the sequestration of nuclear waste. Rare-earth phosphates are an interesting class of solid-state materials owing to the variety of structures that can be adopted and various compositions. These materials are promising nuclear wasteforms owing to their ability to accommodate a range of rare-earth and actinide ions; however, further work is required. This includes studying the corrosion resistance of these materials, which has already begun, and studying their ability to accommodate HLW elements such as minor actinides. It is also believed that composite materials will be important wasteform materials owing to the ability of these materials to incorporate a broad range of nuclear waste elements.

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Notes
The authors declare no competing financial interest.

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Giovanni Donato earned his B.Sc. degree from Toronto Memorial University (formally Ryerson University) and his M.Sc. degree from the University of Saskatchewan. The focus of Mr. Donato’s M.Sc. thesis research was on the synthesis and characterization of rare-earth phosphate-containing glass-ceramic composite materials.

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