

Review

The Structure, Property, and Ion Irradiation Effects of Pyrochlores: A Comprehensive Review

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Abstract: Since the beginning of the use of nuclear energy, humans have been faced with the problem of radionuclide disposal. At present, a large amount of waste is stored in pools or dry tanks at reactor sites. With the development of the nuclear power generation industry worldwide, the high storage cost (including building, maintaining, and operating storage pools) is overwhelming and serious, and urgent radionuclide disposal problems have become increasingly difficult. Safe and economical strategies are urgently needed for long-term storage and disposal of nuclear waste, which has become among the core issues in the utilization of nuclear energy. Pyrochlore ceramics are able to immobilize a variety of radionuclides and have excellent irradiation stability, so they have received extensive attention as hosts of radionuclides waste. This review summarizes the structure, composition, synthesis process, properties, and irradiation stability of pyrochlore ceramics, focusing on the ion irradiation effect of pyrochlore. In general, the cation radii ratio r_A/r_B is a key parameter related to various properties of pyrochlores. Zirconate pyrochlore is more easily transformed from pyrochlore to defective fluorite, and leads to better irradiation resistance.

Keywords: pyrochlore; irradiation; waste form; radiation model; radiation effect



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1. Overview

Throughout the world, there are currently 440 commercial nuclear power reactors in operation or suspension with ~390 GW(e) producing over 10% of the world's electricity and 56 reactors under construction with ~58 GW(e) (data from <https://pris.iaea.org/PRIS>, accessed on 15 September 2022). Greenhouse gas, which is the main pollution from fossil fuel burning, has been reduced substantially as a result of nuclear utilization. However, the radiative waste produced by the nuclear power plants in the form of spent nuclear fuel (SNF) is still a big issue [1]. SNF is generated by nuclear fuel, mainly uranium, thorium, and small amounts of plutonium, through fission reactions in the reactor core. Approximately 30 t of SNF is generated by a typical 1 GW(e) light-water reactor. That means that more than 12,000 t of SNF per annum are produced and a cumulative repository of 370,000 metric tons of heavy metal (MTHM) that have been stored either in pools or dry tanks at reactor sites [2,3]. The ultimate composition of SNF depends upon a lot of influencing factors, such as the reactor type, the neutron energy spectrum during the reaction and the burn-up (the degree of fission consumption of the fuel), as well as the origin fuel (type, chemical composition, and initial enrichment level ²³⁵U) [4]. Based on a general rule of thumb, in power generation, only approximately 5% of the uranium in the fuel is involved in fission, which also generates approximately 3–4 at.% fission products (¹³⁷Cs, ¹³¹I, ⁹⁰Sr,) and 1–2 at.% transmutation products such as ²⁴¹Am, ²³⁹Pu and ²³⁷Np, with typical burn-ups in the range of 35–45 MWd/kgU [1]. Hence, the high-level wastes must be converted into more stable solid forms by indispensable treatments, which are suitable for sequential

waste management, such as transportation, temporary storage, and geological disposal for long-term storage. This has become among the extremely crucial challenges for nuclear energy production.

Generally, the requirements for waste forms that are able to immobilize radionuclides are as follows [1,5–7]:

- Stable waste forms must exhibit high radiation stability and excellent tolerance to radiation effects, such as transmutation to new elements, ballistic effects, ionic and electronic excitation, gas bubble and volume swelling effect, depending on the types of high-level radionuclides.
- The immobilization system must have high waste loading for a sufficient amount of waste (typically 20–35%) to reduce volumes. Of course, higher waste loading is accompanied by higher irradiation damage, so a balance needs to be found between those.
- The waste forms must be chemically flexible and be able to accommodate a mixture of radionuclides and other contaminant species. It is possible to separate and immobilize mixed radionuclides into different substrates, but this means more complex processes and higher costs in terms of energy, money and time.
- The waste forms must be durable and resistant to aqueous dissolution to minimize the release of radiotoxic species, especially for those long half-life radionuclides such as ^{237}Np (2.1 million years) and ^{239}Pu (24,100 years).
- The fabrication process of waste forms must be simple and feasible under reasonable conditions, such as low temperatures and in an air atmosphere, by using well-established methods and avoiding vacuums and special atmospheres.
- The waste form are natural analogues. It is generally impossible to build confidence in predicted behavior from real and complete experiments of the waste forms in the laboratory directly (except some relatively short half-life nuclides, e.g., ^{244}Cm 18 years).
- The possibility of criticality for actinide waste forms must be carefully considered by reducing actinide concentrations or incorporating neutron absorbers, such as Gd and Hf, into the structure of the waste form.

Borosilicate glass has been comprehensively and thoroughly investigated as a waste form for the immobilization of high-level radionuclides [1,3,8–13]. However, borosilicate glass is not a universal waste form due to the restricted solubility of actinide oxides. Only approximately 3–10 wt.% actinide oxides can dissolve in the glass network [9–11]. Low solubility limits waste loadings to a relatively low level, which leads to large volumes of vitrified waste forms, and finally results in a significant increase in overall disposal costs. Glass-ceramics (GCs) with both crystalline and glass phases are a variation of a vitrified waste form, which is a chemically more flexible and less expensive compromise than the pure ceramic form. Generally, GCs can provide a higher chemical durability than glass, provided that the radionuclides are prevented from crystallizing into soluble species prior to incorporating into the matrix [14–17].

Based on a group of geochemically stable titanate minerals, synthetic rock (Synroc) was initially developed in the late 1970s in Australia for the immobilization of HLWs from Purex-type reprocessing of spent nuclear fuels [18]. Synroc is a polyphase ceramic waste form, which is composed of zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), and hollandite ($\text{Ba}(\text{Al,Ti})_2\text{Ti}_6\text{O}_{16}$), which demonstrates the ability to host thorium and uranium in the natural geological environment [18–24]. Apart from Synroc, many other ceramic waste forms were developed, such as pyrochlore [9,25–27]. For those ceramic waste forms, no matter single- or poly-phase ceramic, specific atomic sites in periodic structures of constituent crystalline phases may be occupied by radionuclides to form a dilute solid solution. Another form is to incorporate radionuclides through encapsulation, where the radionuclide-bearing phases, by simply drying the waste sludge, are encapsulated in another non-radionuclide-bearing material (e.g., ZrO_2 , TiO_2 and Al_2O_3) to form a composite waste form [19,28,29].

In nuclear waste glasses, rare earth titanates were discovered to incorporate actinide nuclides and further identified as a pyrochlore structure, which is the earliest evidence of

pyrochlore as a waste form [5,9,29]. Titanate wastes have been studied extensively since the 1980s, due to their high chemical durability [30,31]. Early research focused on monoclinic zirconolite, which is now regarded as a structural derivative of the isometric pyrochlore structure, and further studies reported a “cubic” zirconolite formed stably from higher actinide (or actinide analogue) concentrations, which is actually a disordered pyrochlore structure [32,33]. In addition, pyrochlore ceramics have excellent aqueous durability and irradiation resistance. Based on the available literature for various types of materials about radionuclide waste forms, we focus on an in-depth discussion of recent research on the pyrochlore waste forms. Although it is not possible for actual waste forms over the limited time scales by direct laboratory tests, ion irradiation experiments of the matrix with or without radionuclide analogues can provide important information for the long-term performance of waste forms. This comprehensive review will summarize the structure, the common synthesis processes and the main characteristics of pyrochlore in detail; introduce the main irradiation effect and damage model; and finally provide a summary of the irradiation resistance of pyrochlore ceramics.

2. Structure of Pyrochlore

Hitherto, pyrochlore phase materials encompass a wide range of chemical component that exists in over 500 naturally or artificially materials [34]. Pyrochlore structure is known as a derivative fluorite structure (CaF_2 , space No. 225, $Fm\bar{3}m$), which forms an isometric crystal system with the ideal structural formula $^{\text{VIII}}\text{A}_2^{\text{VI}}\text{B}_2^{\text{IV}}\text{X}_6^{\text{IV}}\text{Y}'$ (space No. 227, $Fd\bar{3}m$, $Z = 8$ and $a = 9\text{--}12 \text{ \AA}$), where A -sites and B -sites are occupied by metal cations, and X ($= \text{O}^{2-}$) and Y ($= \text{O}^{2-}, \text{OH}^-, \text{F}^-$) are anions [34–36]. The structure can be outlined in a simple and well-understood way by describing the shapes and topology of the coordination polyhedral (Figure 1a). All of the atoms in an ideal pyrochlore are on special positions, except the X -anion occupied 48f-site (X_{48f}). The larger A -site cations (mainly trivalent rare earth elements, usually $\sim 1 \text{ \AA}$ ionic radius) are eight coordinated (AX_6Y_2) and occupy 16d (0.5, 0.5, 0.5) sites. The smaller B -site cations ($\sim 0.6 \text{ \AA}$ ionic radius, mainly tetravalent cations including Ti, Zr, Hf, Sn, and etc.) are six coordinated (BX_6) which occupy 16c (0, 0, 0) sites. Herein, the X -anion occupies the 48f ($x_{48f}, 0.125, 0.125$) and the Y -anion locates at 8b (0.375, 0.375, 0.375). Thus, for the ideal structure, the X -anion and Y -anion are situated the tetrahedron XA_2B_2 and YA_4 , respectively. Note that the center of the tetrahedron consisting of four B -sites ($\square\text{B}_4$) is blank with a marked 8a position (0.125, 0.125, 0.125). The BX_6 octahedra are corner-linked with A -cations filling the interstices. Additionally, the structure can also be described as a structure in which the A -site and B -site coordinated polyhedral are connected with an edge sharing, as shown in Figure 1a. Moreover, the shapes of these polyhedrons are controlled by the position parameter x_{48f} which suggests that X_{48f} shifts towards the two of its B -cations. For $x_{48f} = 0.375$, the A -site coordination polyhedron AX_6Y_2 is a regular cube and the B -site polyhedron BX_6 is a trigonally-flattened octahedron (the topology of the fluorite structure). In this case, if A and B cations randomly occupy each other's positions, materials have a defective fluorite structure (space No. 225, $Fm\bar{3}m$), and the anions X and Y share the 7/8 of the 8c-site (0.125, 0.125, 0.125) in the new space group (Figure 1c). For $x_{48f} = 0.3125$, the B -site polyhedron BX_6 is a regular octahedron and the A -site coordination polyhedron AX_6Y_2 is a distorted trigonal scalenohedron, which is an ideal pyrochlore structure. Theory simulations of a wide range of pyrochlore compositions ($A = \text{Lu}^{3+}$ to La^{3+} ; $B = \text{Ti}^{4+}$ to Pb^{4+}) using energy minimization techniques suggest that the x_{48f} parameter also reflects some degree of disordering of the oxygen lattice for specific cation compositions [37–39]. Thus, the position parameter of X -anion, x_{48f} , between 0.3125 and 0.375, indicating the degree of distortion of the polyhedron and the degree of order in the structure. Generally, x_{48f} is nearly linearly associated with the cation radius ratios r_A/r_B [6,37,40]. So, the crystal structure of pyrochlore is mainly controlled by the cation radius ratios r_A/r_B , when r_A/r_B is between 1.46–1.78, it shows a pyrochlore structure, and when r_A/r_B is lower or higher than this range, showing defective fluorite structure and monoclinic structure, respectively [6,34,35].

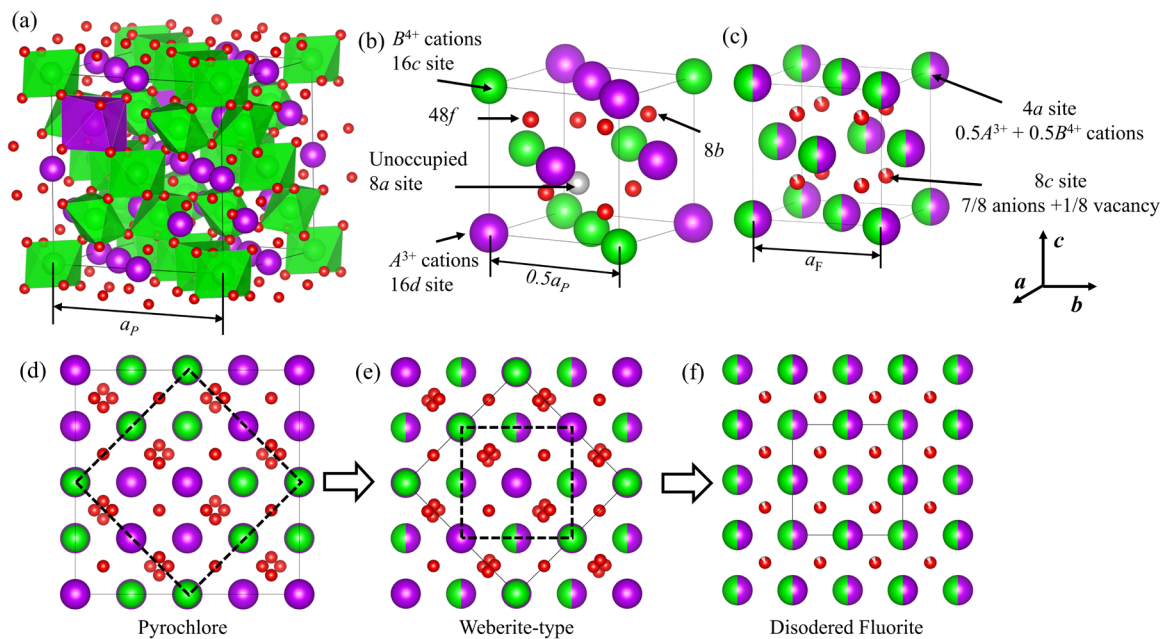


Figure 1. Pyrochlore structures described based on (a) the polyhedral network and (b) the derivative of fluorite structure, which is one eighth of the conventional unit cell of pyrochlore. Corresponding fluorite unit cells (c) are included for comparison. (d–f) Structural relations between the (d) pyrochlore, (e) weberite-type, and (f) disordered fluorite. Both the pyrochlore and weberite-type structures are supercells of disordered fluorite with unit cell parameters of $a_p = a_{WB} = 2a_F$ and $b_{WB} \approx c_{WB} \approx 2^{1/2}a_F$ (the subscripts refer to pyrochlore, weberite-type and disordered fluorite respectively). Red spheres represent oxygen sites that are fully occupied in the pyrochlore and weberite-type structures, and grey spheres represent oxygen vacancy. Purple and green spheres represent A-site (CN = 8) and B-site (CN = 6) cations, respectively. Half-purple and half-green spheres designate cation site mixing (CN = 7).

In recent years, weberite-type structure, another derivative structure of fluorite and pyrochlore, has been paid more and more attention. It is considered to be an intermediate phase of irradiated-induced ordered-disordered transition from pyrochlore to fluorite, which is obtained by pyrochlore loss over part of the long-range order [36,41–45]. The chemical formula of the orthorhombic weberite-type structure (space No. 63, $Ccmm$) can be written as ABC_2X_7 , where A and B are cations occupying 4a and 4b site, which are in octahedral (6-fold) and distorted cubic (8-fold) coordination, respectively. Whereas C is a random mixing of A and B atoms located at 8g site, which is distorted mono-capped octahedral (7-fold) coordination (Figure 1e). Anions X occupy 16h and three 4c sites, and there remains an ordered vacancy, as in the pyrochlore structure, but it is situated in another 4c site [46]. Figure 1d–f shows the structural relations between the pyrochlore, weberite-type, and disordered fluorite arrangement. Both pyrochlore and weberite-type structures are supercells of disordered fluorite with unit cell parameters of $a_p = a_{WB} = 2a_F$ and $b_{WB} \approx c_{WB} \approx 2^{1/2}a_F$. During the transition from pyrochlore to weberite-type, in pyrochlore, half of A and B atoms randomly exchange position, occupying the 8g site in weberite-type; in addition, two O_{48f} move to V_{8a} vacant site along the direction of $[1\ 0\ 0]$. Further, when the cations and anions are completely disordered respectively, the structure transforms to disordered fluorite.

In natural pyrochlore minerals, A-site can also be occupied by smaller radius cations such as alkali metal cations or alkaline-earth metal cations and molecular water and hydroxyl are potentially part of the structure. Stanek et al. [47,48] point out that a stable pyrochlore structure can be formed through A^{3+} vacancies to compensate for additional tetravalent B-site cations and interstitial oxygen atoms are also conducive to structural stability, especially near the defective fluorite structure. Due to a series of defects, structures can be formed by loss of cations and anions or inequivalence substitution, the general formula of pyrochlore is $A_{2-m}B_2X_{6-w}Y_{1-n} \cdot pH_2O$. The parameters m , w and

n are used to balance the charge generated by incomplete substitution or unequivalence replacement of the corresponding site: A , X , and Y . Based on the structural formula, several different ions can therefore be substituted into the pyrochlore structural sites as presented in Table 1 [6,34–36]. Due to the wide variety of combinations of A -site and B -site cations, as well as tunable oxygen vacancies, there is a possibility of the pyrochlores that can incorporate trivalent lanthanides and tri- and tetra-valent actinides which have great potential for nuclear waste forms and attracted the greatest interest [3,5,6,29].

Table 1. Ion substitute eligibility for the various sites of the pyrochlore supergroup [6,34–36].

Site	Ion
A	Rare-earth , U, Th, Na, Ca, Ag, Mn, Sr, Ba, Fe ²⁺ , Sn ²⁺ , Sb ³⁺ , □, ...
B	Ti , Sn ⁴⁺ , Zr, Hf, Ce, Ta, Nb, Sb ⁵⁺ , Mo, Cr, U, Pu, W, V, Fe ³⁺ , Mg, Al, Si, ...
X	O, OH [−] , F
Y	O, F, OH, □, H ₂ O, K, Cs, Rb, ...

Note: □ denotes a site vacancy. Bold indicates the most common substitutes.

3. Synthesis of Pyrochlore

Solid-state reaction is one of the most common methods for preparing polycrystalline pyrochlore ceramics. First, the metal oxide powders are preheated to remove any absorbed impurities, such as H₂O and CO₂, and then anhydrous ethanol or acetone is used as a mixing medium to mix the raw powder evenly. Finally, the dried mixture is pre-compressed for sintering. The residues of initial oxides can be avoided by choosing the appropriate synthesis sintering temperature, which can deteriorate the isolation properties of waste forms. The synthesis temperature required depends on the composition of the system, such as replacing Zr⁴⁺ with Ti⁴⁺, which can reduce the synthesis temperature [49]. In addition to heating by air furnaces, the energy required for the reaction can be provided by different heat sources. Guo et al. [50] use the nozzle of an aerodynamic levitator with oxygen flow to levitate the green pellet and heat the sample (~3023 K) by controlling the laser power. Zhang et al. [51–53] use the heat generated during the redox reaction between Ti and Fe₂O₃/CuO to provide the energy required for the reaction. Among them, heating by furnace and laser heating can precisely control the cooling rate. When heating by furnace (except for spark plasma sintering), a two-step [42,44,54–58] or three-step [59–64] sintering method is more commonly used compared with one-step [65–68] sintering, which is conducive to the uniform distribution of metallic cations in pyrochlore ceramics by being reground, pelletized, and heated. Although it needs to be held at a higher temperature for a long time, it is also conducive to the formation of the pyrochlore structure [69]. Pyrochlore ceramics prepared by reactive heating takes no longer than 5 min for the combustion and densification process [52,53], but this method will introduce metallic simple substance, and the distribution of metallic cation in the ceramic is not completely uniform. Spark plasma sintering (SPS) can rapid synthesis pyrochlore ceramics without introducing any impurities. Chen et al. [70] prepare Gd₂Zr_{2–x}Ce_xO₇ ($x = 0.0, 0.5, 1.0, 1.5$ and 2.0) pyrochlore ceramics with only three minutes of holding time via SPS and the single phase maintains until the value of x reaches 1.0, also the bulk density of the ceramics are more than 92%. It is worth noting that the relative density of the pyrochlore ceramics prepared under atmospheric pressure is only about 90% [58,71,72] unless used in conjunction with laser heating. Laser heating can prepare pyrochlore ceramics with a relative density of 96.3% under atmospheric pressure by solidification method [50]. Yet the relative density of the ceramic can be increased when a certain pressure is applied in the sintering step, such as SPS [70] and hot pressing. Brykała et al. [73] prepared Gd₂Zr₂O₇ pyrochlore ceramics with the relative density close to the theoretical value by HP under pressure of 30 MPa at 1723 K. At the same time, the increase in the density of the ceramic is beneficial to improve its radiation resistance ability [53].

The operation of the solid-state reaction is relatively simple. Since most rare earth and transition metal elements exist in the form of oxides, the raw materials required for

the preparation of various kinds of pyrochlore ceramics by the solid-state sinter are easy to obtain, which makes the solid-state sintering highly devisable. Due to the fact that of this, the high-entropy pyrochlore ceramics with complex compositions are mostly prepared by solid-state sintering [50,74–77]. Qi et al. [78–82] use oxides as raw materials to prepare single-phase ceramic powder by the above mentioned one-step method, the prepared powder is pressed into pellet to sinter at 2023 K for 8–10 h under vacuum and annealed at 1573 K in the air to prepare high entropy $(Y_{0.2}La_{0.2}Gd_{0.2}Yb_{0.2}Dy_{0.2})_2Zr_2O_7$ and different kinds of $A_2B_2O_7$ transparent ceramics, all the powders and ceramics have a defective fluorite structure. Additionally, Wang et al. [76] point that size disorder of about 5% is the boundary for the multi-component rare earth zirconate to form a single- or dual-phase region. The limitation of solid-state sintering is that it is difficult to achieve uniform distribution of cations and will introduce pollution during multiple steps of reground, pelletized, and heated.

The chemical-coprecipitation method is to react the mixed solution of the metal salt solution with a precipitant to obtain gel-like precipitates, and then the gel-like precipitates are washed, dried, calcined, ground, and the obtained powder is compacted and sintered to obtain the polycrystalline pyrochlore ceramics [83–90]. Compared with the solid-state sinter, the chemical-coprecipitation method has better dispersibility and uniformity, and the holding time required in the sintering process is also shortened.

The sol-gel method uses citric acid and ethylene glycol/anhydrous ethanol as chelator and solvent, respectively, and is mixed with the compound containing the desired cation (such as nitrate, etc.), and the mixture is evaporated to dryness to form the precursor. Pyrochlore ceramics powder can be prepared by calcining the precursor at a temperature of more than 1073 K, and the powder can be used to prepare polycrystalline pyrochlore ceramics through briquetting then sintering at about 1773 K [91–95]. Li et al. [96] modified sol-gel process by introducing NaCl and KCl, the salt addition is beneficial to control the abnormal particle growth, and the morphology of the $Lu_2Ti_2O_7$ powder is affected greatly by the salt amounts and types. The sol-gel method enables uniform mixing of cations at the atomic level, which facilitates the diffusion of components, so the reaction can be carried out at lower temperatures. Compared with the solid-state sintering, the chemical-coprecipitation method and the sol-gel method are more complicated to operate and will generate more chemical waste.

Hydrothermal method can prepare polycrystalline pyrochlore ceramics at the low temperature of no more than 513 K under autogenous pressure [97–101]. The reacting temperature, holding time, and reaction environment (pH value) are the key factors affecting the final product of hydrothermal method. Increasing the reaction temperature and prolonging the holding time is conducive to promoting the formation of the pyrochlore structure, also improving the crystallinity of the reaction products. The pH value required for each reaction system is different, and the pyrochlore ceramics phase cannot be formed unless the reaction environment is at the proper pH value [97,98,100]. When Trujillano et al. [99] prepare $Sm_2Sn_2O_7$ pyrochlore ceramics via hydrothermal method by microwave irradiation and compare this with the solid-state method, the results show that the reaction time (4h) can be greatly reduced by microwave irradiation compared with other heating methods, however, there are amorphous phase and hydrogen-carbonate impurities in the final product and the crystallinity is not as high as that of the solid-state method.

The single crystal titanate pyrochlore ceramics can be grown by flux technique [102,103]. A single crystal is grown at ~1508 K in a molten mixture consisting of oxides and PbF_2 as raw material and flux, respectively. Although the PbF_2 is an impurity and evaporates slowly during the synthesis period, but it will remain primarily superficially on the crystal and can be removed physically before analysis. The single crystal titanate pyrochlore ceramics can also be grown by floating zone technique [104–107].

In addition to the above bulk and powder pyrochlore ceramics, the molten salt and electrospinning method can be used to prepare nano pyrochlore ceramics. Li et al. have prepared nanowires [108], nanorods [109], and nanoplates [110] by molten salt method, and

the nanowires, nanotubes, and wire-in-tube architectures are prepared by Yu et al. [111] through single-nozzle electrospinning technique.

4. Property of Pyrochlore

Due to the flexible composition and unique structure, pyrochlore has a variety of outstanding properties including thermophysical properties, enhanced electrical properties, irradiation resistance and optical properties, and have potential applications for thermal barrier coatings material, solid electrolytes, radionuclide waste forms, etc. [40,75,76,83,84]. The irradiation resistance of pyrochlore will be introduced in detail in Section 5, and thermophysical properties and ionic conductivity will be summarized preliminarily in this section.

4.1. Thermophysical Properties

Most studies about thermophysical properties of pyrochlore are based on the application of thermal barrier coatings [112,113]. In fact, the irradiation resistance and the radiation damage process are inseparable from thermophysical properties of pyrochlore, especially, the transient thermal process and recrystallization after ion irradiation (described in the thermal spike model in Section 5.2.1) [114].

Liu et al. [83–88] have studied various thermophysical properties of rare earth zirconate ceramics ($A_2Zr_2O_7$), including heat capacity, thermal expansion and thermal conductivity, and reported that the thermal conductivities of rare earth zirconate ceramics first gradually decrease with increasing temperature, and then slightly increase above 1073 K due to the increased radiation contribution. The thermal conductivities of $(Yb_xSm_{1-x})_2Zr_2O_7$, $(Yb_xGd_{1-x})_2Zr_2O_7$, $(Sm_xGd_{1-x})_2Zr_2O_7$, $(Sm_xGd_{1-x})_2Zr_2O_7$, and $Sm_xZr_{2-x/2}O_2$ are located in the range of 1.40–1.99, 1.34–1.99, 1.20–1.99, 1.33–2.04, and 1.41–1.86 $W \cdot m^{-1} \cdot K^{-1}$, respectively [84–88]. The calculated minimum thermal conductivities of $A_2Zr_2O_7$ and A-site doped zirconate pyrochlores by Density functional theory are $\sim 1.2 W \cdot m^{-1} \cdot K^{-1}$ [40,112,113,115,116], while that of B-site doped zirconate pyrochlores shows a decreasing trend, except Ti [113,115–117]. Recently, high entropy pyrochlore exhibits lower thermal conductivity attracted attention [50,118–120]. Guo et al. [50] report that thermal conduction $0.947 W \cdot m^{-1} \cdot K^{-1}$ of $(Ho_{1/5}Y_{1/5}Dy_{1/5}Gd_{1/5}Eu_{1/5})_2Ti_2O_7$ at room temperature, which is lower than their single rare earth composition pyrochlore. Similarly, Li et al. [118] report that six species high entropy pyrochlores with thermal conductivities are lower than $1 W \cdot m^{-1} \cdot K^{-1}$.

4.2. Ionic Conductivity

The ionic conductivity of pyrochlore is linked to the migration ability of oxygen ions, which is mainly related to the concentration of oxygen vacancy and the activation energy of oxygen movement [75]. The ionic conductivity of pyrochlore shows a function of cation radius ratio r_A/r_B , and the total conductivity approaches its maximum value when the cation radius ratio is ~ 1.48 [75,89,121–125], as shown in Figure 2a. Due to the fact that as r_A/r_B decreases, the oxygen vacancy formation energy and migration energy barrier of oxygen decrease, that is, the migration ability of oxygen ions is enhanced, but at the same time, there is an order-disorder transition from pyrochlore to defective fluorite that causes the loss of the preferential migration path of oxygen ions [75,126]. Figure 2b shows the total conductivity of various pyrochlore including low/medium entropy and high entropy ceramics [75,122–125,127,128], suggesting that a high entropy strategy can effectively enhance the ionic conductivity of pyrochlores. Due to the fact that ionic conductivity is related to the disordered sensitivity of oxygen, to some extent, the high ionic conductivity suggests that the pyrochlore has a good anti-irradiation performance.

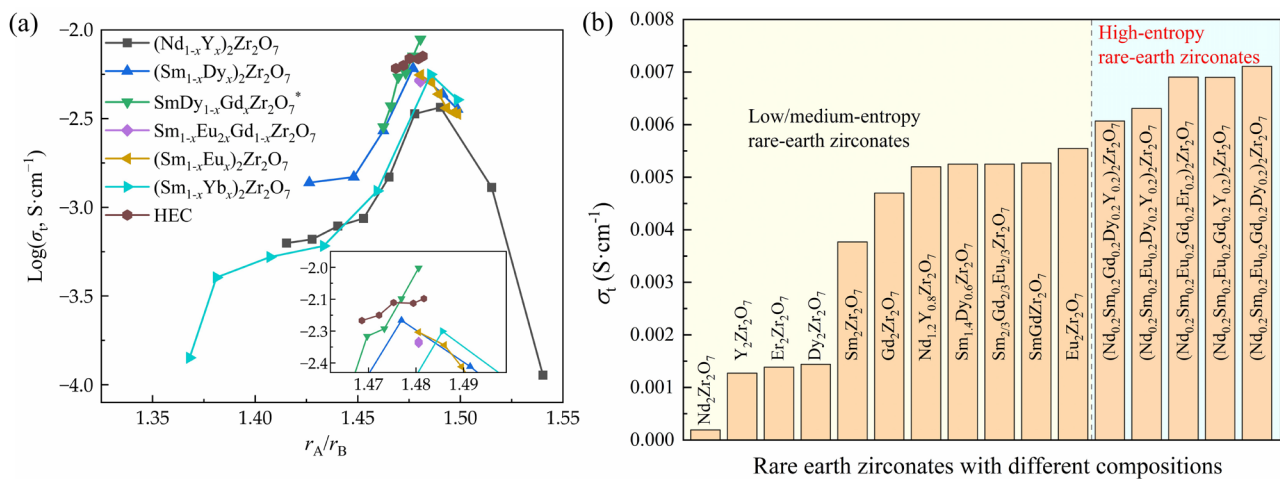


Figure 2. (a) The total conductivity of pyrochlores at 1073 K is a function of r_A/r_B . (b) Comparison of the total conductivity between high entropy rare-earth zirconates and other low/medium entropy rare-earth zirconates at 1073 K. Note, HEC from Ref. [75], (Sm_{1-x}Yb_x)₂Zr₂O₇ from Ref. [89], (Sm_{1-x}Eu_x)₂Zr₂O₇ from Ref. [122], Sm_{1-x}Eu_{2x}Gd_{1-x}Zr₂O₇ from Ref. [123], SmGd_{1-x}Dy_xZr₂O₇ from [121], (Sm_{1-x}Dy_x)₂Zr₂O₇ from Ref. [124], (Nd_{1-x}Y_x)₂Zr₂O₇ from Ref. [125], Gd₂Zr₂O₇ from Ref. [127], and Er₂Zr₂O₇ from Ref. [128]. * in (a) means the data of SmGd_{1-x}Dy_xZr₂O₇ is grain conductivity.

5. Radiation Stability

Radionuclides in HLW will undergo alpha (α) decay (e.g., Np, Am, Pu, and Cm) or beta (β) decay (e.g., ¹³⁷Cs and ⁹⁰Sr), or even both (e.g., U and Th), and release the energetic particles. β -decay produces high-energy β -particles (>0.5 MeV), very low energy β -recoil nuclei, and γ -rays, while, α -decay releases energetic α -particles (4.0–5.8 MeV), energetic α -recoil nuclei (70–100 keV), and some γ -rays. The energetic α -particle has a penetration depth of ~20 μ m and loses most of its energy through inelastic collisions (ionization and electronic excitations) with surrounding atoms within this path, and produces 100–200 atomic displacements near the end of its track. While an α -recoil atom shows predominately nuclear stopping (elastic collisions) and produces a dense collision cascade with 1000–2000 atomic displacements within a short range of ~0.02 μ m. However, β -decay causes on the average less than one atomic displacement per β -decay event hence only contributes a minor amount to radiation damage. There are also spontaneous fission and (α , n) reactions of some actinides but the rate of the reactions is very low, thus the contribution to the radiation field is small, and do not significantly contribute to the overall effect of radiation. In summary, >90 percent of the structural damage is caused by the alpha-recoil nucleus [7,26,129,130].

Generally, β -decay is the dominated radiation source in the first 500 years of storage, while α -decay is gradually dominant at longer time because of the long half-lives of the actinides and their daughter products. As shown in Figure 3a [8,29], for DOE (U.S. Department of Energy) high-level tank waste consisted of multiphase ceramics or glass-ceramics, the cumulative β -decay dose saturates at about 500 years, while the alpha decay dose is a near-linear function of storage time. For non-USA commercial HLW contained in ceramics endures doses of at least a time of 10 higher than those for DOE tank waste [8]. For several ²³⁹Pu concentrations in a ceramic waste form, the α -decay cumulative dose reaches a provisional plateau after 100,000 years, but increases over much longer time periods due to the ²³⁵U decay series, as shown in Figure 3b [7,8]. Additionally, the dose-time ranges for the contribution of self-irradiation damage in actinide-bearing glasses or ceramics are also shown in Figure 3b. The spontaneous fission half-life of ²³⁹Pu is 5.5×10^{15} years which is about 2×10^{11} times slower than the rate of α -decay (2.411×10^4 years). On the other hand, the spontaneous fission and α -decay half-lives of ²⁴⁴Cm are 1.35×10^7 and 18.10 years, respectively. This means that a rate of spontaneous fission for ²⁴⁴Cm is about 750 thousand times slower than that of α -decay [131]. Thus, spontaneous fission of ²³⁹Pu

or ^{244}Cm gives a negligible contribution to self-irradiation damage. Although in some materials, each spontaneous fission event can produce a significantly larger amorphous volume, and spontaneous fission can account for 2–3% of the amorphization rate [25]; however, the accumulation rate of radiation damage from spontaneous fission is a few orders of magnitude lower than that from α -decay, except ^{244}Cm . Therefore, radiation effects of spontaneous fission are generally ignored.

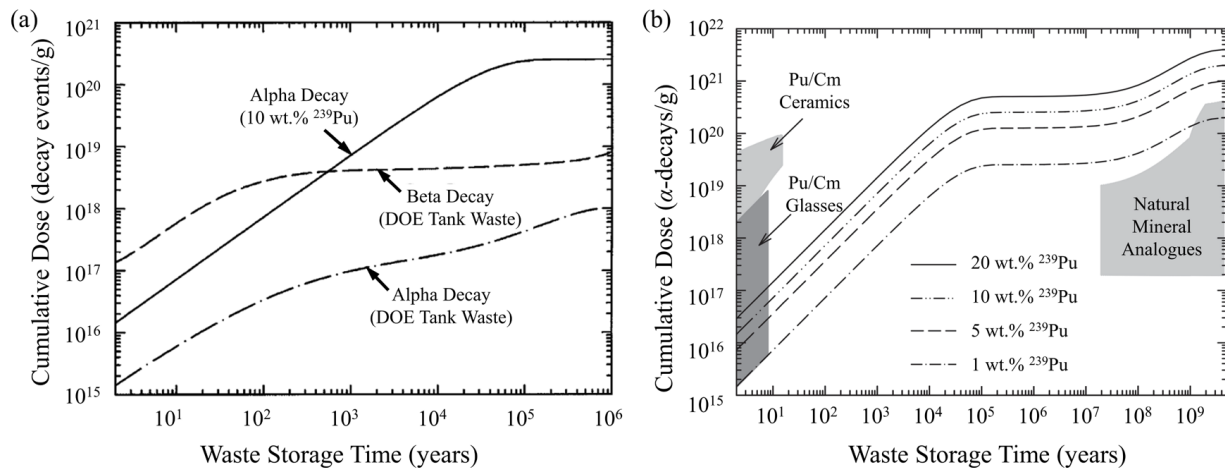


Figure 3. Cumulative Dose as a function of waste storage time. (a) β -decay and α -decay events per gram for a multiphase ceramics or glass-ceramics containing DOE high-level tank waste. Additionally shown is the cumulative number of α -decay events per gram for a ceramic containing 10 wt.% ^{239}Pu . (b) Cumulative α -decay dose as a function of time for different ^{239}Pu concentrations. Additionally, the dose-time ranges for available data from Pu/Cm containing glasses and ceramics, as well as for natural mineral analogues are also shown. (a) Reproduced with permission from Reference [29], Copyright © Springer Nature 2011; (b) Reproduced with permission from Reference [7], Copyright © Springer Nature 2010.

5.1. Radiation Effects

The radiation effects of the interactions between ions and the structure, also called radiation damage, fall into two broad categories. The first one is the transfer of energy to electrons mainly by ionization and electronic excitations. The second one is the transfer of energy to atomic nuclei, primarily by a ballistic processes involving elastic (billiard-ball-like) collisions. Except for the transfer of energy, the particles from radioactive decay have a significant chemical effect on the host materials through deposition or incorporation into the host structure.

For ions, the mode of energy loss is controlled by the relative velocity of the incident ions and that of the orbital electrons of the target atoms. If the ion velocity is greater than that of the orbital electrons, ionization processes (also called electronic energy loss) will dominate. Otherwise, if the particle velocity is below, the proportion of ionization is small and most energy is lost by ballistic processes (also called nucleus energy loss). A widely accepted relationship between energy loss and incident particle energy is that if the energy of the incident particle is greater than 1 kV per nucleon (1 kV/u), ionization processes dominate; and if the energy of the ion falls below this limiting approximation elastic collisions with atomic nuclei are predominant; see Figure 4.

5.1.1. Ionization and Electronic Excitation

Energy loss by β -particles and α -particles is predominantly through Coulombic interactions. Interaction of γ -rays with matter is primarily through the photoelectric effect, Compton scattering, and electron-positron pair production. The high rate of energy absorption through ionization and electronic excitation in ceramics can result in self-heating. In the first few hundred years, the wastefoms were kept at temperatures of several hundred

degrees Celsius due to significant radiogenic self-heating [132]. In addition, a large number of electron-hole pairs were produced by ionization and electronic excitations. This resulted in covalent and ionic bond rupture, charged defects, enhanced self-ion and defect diffusion, and localized electronic excitations. In some ceramics, such as zirconolite, pyrochlore, and monazite, as well as most glasses, permanent defects were formed in the structure generated by localized electronic excitations [8,17,133,134].

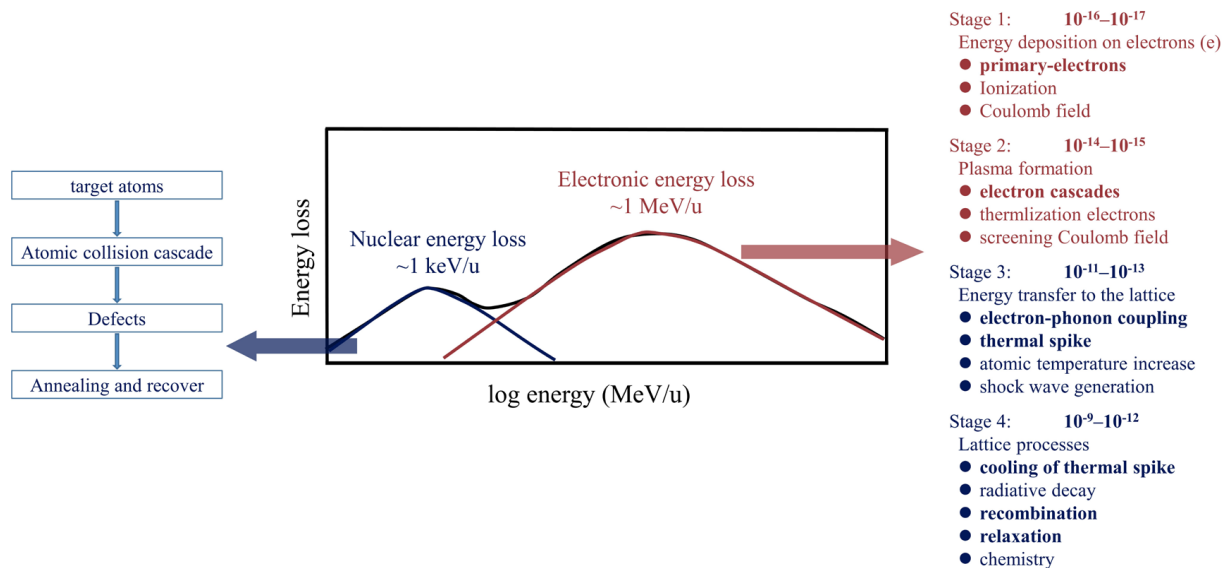


Figure 4. Schematic diagram of the relationship between energy loss and bombarding particle energy.

In recent years, swift heavy ions irradiation with ultra-high energy has been applied to study the effect of electron energy loss on the structure of materials. Lang et al. [135] performed ion irradiation experiments with a specific energy of 11.1 MeV/u (atomic mass unit u) on the $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ binary polycrystalline sample at room temperature and under vertical incidence, using ^{58}Ni , ^{101}Ru , ^{129}Xe , ^{181}Ta , ^{197}Au , ^{208}Pb , and ^{238}U ions. The electronic energy loss (dE/dx) of all ions was calculated by SRIM-2008 code [136] ranges from 10.9 keV/nm (^{58}Ni) to 49.7 keV/nm (^{238}U). Same as other $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ irradiation experiment results [60,137–141], as r_A/r_B increases (more Ti content), the irradiation damage track diameter is greater, which obeys a near-linear correlation. A concentric ring structure (also called core + shells) [141,142] was found as a representative morphology of damage of an individual ion tracks (cross-section); see Figure 5a. Generally, an ion track consists of an amorphous core surrounded by a disordered, defect-fluorite structured shell, and sometimes, a defect-rich pyrochlore halo would encircle the periphery as shown as Figure 5b. The total track size increases significantly over the energy-loss range studied, from ~5 nm for ^{101}Ru ions (21.7 keV/nm) to ~11 nm for ^{197}Au ions (40.1 keV/nm). Further, within the range of the ions studied, the intramural track structure changes noticeably: the small amorphous core gradually expands with the increase of dE/dx , and forming a predominantly amorphous tracks at high dE/dx [60,135,141]. The area ratio of amorphous core to the whole track r_a^2/r_{df+a}^2 is defined as the amorphous fraction f , and it has been plotted as a function of dE/dx in Figure 5b, which suggests an exponential growth. Ni tracks are intermittent, consisting of several relatively independent damage domains. That means that the critical energy loss for forming a track $(dE/dx)_c$ is very close to and only slightly higher than the energy loss of Ni ions of 10.9 keV/nm, which is in agreement with the result of $\text{Gd}_2\text{Ti}_2\text{O}_7$ at depth of ~5 μm [143]. What is more, the diameter of Ru ion tracks shows drastic change along their trajectory, which suggests that energy loss of Ru approaches to the track formation threshold [135]. Therefore, for the specific energy of ion beams ~11 MeV/u, in $\text{Gd}_2\text{Ti}_2\text{O}_7$, a consecutive tracks will arise when the energy loss surpasses $(dE/dx)_c$ ~11 keV/nm [135], which accords with experimental results

(11–13 keV/nm) obtained by Moll et al. [60] via heavy ions with slightly smaller specific energy (4.5–9.3 MeV/u).

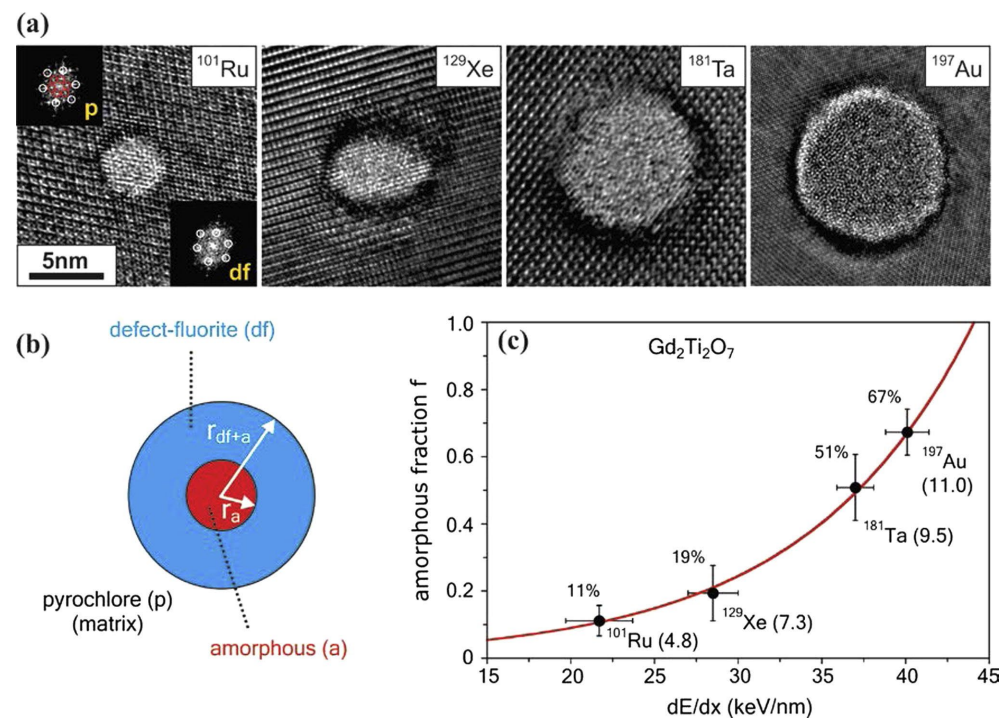


Figure 5. (a) High-resolution TEM images of individual tracks in $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore produced by 1.1 GeV Ru ions (21.7 keV/nm), 1.4 GeV Xe ions (28.5 keV/nm), 2.0 GeV Ta ions (37.0 keV/nm), and 2.2 GeV Au ions (40.1 keV/nm). The track diameters increase systematically with dE/dx as shown from left to right. (b) Schematic of track morphology showing the amorphous core (red) surrounded by a defect-fluorite structured shell (blue) embedded in the pyrochlore matrix. Fast Fourier transform (FFT) analysis of TEM images confirm the crystalline phase of matrix (pyrochlore, p) and track shells (defect-fluorite, df), displayed in (a) for the Ru ion track. The loss of the spots in the inner circles corresponds to the loss of the long-range ordered pyrochlore superstructure leading to the defect-fluorite structure. (c) The amorphous fraction within an ion track (normalized core-to-shell ratio) increases significantly as a function of dE/dx . The error bars represent the dE/dx variation over the entire sample thickness and the uncertainties of determining the area of amorphous core and entire track, respectively. The values in % represent the amorphous fraction, and the numbers in parenthesis are the total track diameters in nm (core + shell). The scale bar applies to all TEM images. Reproduced with permission from Reference [135], Copyright © Elsevier 2014.

The structure of ion tracks in multiple concentric phases is generally considered as a result of rapid deposition of high-density energy, which leads to melting or even vaporization of the material along the incident direction, followed by quenching and recrystallization during the rapid cooling of the matrix [137,144,145]. Firstly on atto-/femto-second time scales, the incident ion inelastic interacts with the target and primary collisions electron, ionization and a Coulomb field are generated thereby; secondly, electron cascades to form a plasma state with thermalization of electrons and screening of Coulomb field on femtosecond time scales; then, the excited electrons transfer their energy to atoms through electron-phonon coupling. In this process, the atoms are rapidly heated instantaneously, resulting in local melting and vaporization. A pressure wave to the surrounding area is generated by the synchronous volume change on pico-/femto-second scales. Subsequently the melted or vaporized material self-quenching, recrystallization, and defect recovery occur over nanoscale structures or phases during rapid cooling on nano-/pico-second time scales [137,146–148]; see Figure 4. The thermal spike models [114,143,145,149–153] to describe the track formation processes will be discussed in Section 5.2.1.

5.1.2. Ballistic Processes

Ballistic processes cause direct atomic displacements through elastic scattering collisions and are responsible for the atomic-scale rearrangement of the structure. The kinetic energies of recoils produced in β -decay and γ -decay are not sufficiently to form permanently displaced atoms. Likewise, due to their low mass, β -particles only induce well separated single displacement events at high energies, in general, only 0.1 atomic displacements per β -decay event [25,29]. In the 16 to 22 μm , α -particles dissipate most of their energy through ionization processes, but as the energy dissipates, nucleus energy loss (elastic collisions, also called nuclear stopping) begins to dominate, undergoing a lot of elastic collisions along their path to produce several hundred isolated atomic displacements [7,29]. A similar process can be found in ion irradiation, where the largest number of displacement atoms occurs near the end of the incident ion range. Compared with the aforementioned particles, α -recoil particles are heavier but exhibit lower energy. They can produce almost all the total number of displacement atoms by ballistic processes. The α -recoil loses 80% or more of its energy in elastic collisions over a very short range (20–30 nm) that produce energetic recoils, which in turn lose 60% or more of their energy in elastic collisions, resulting in cascading collision. As a result, about 50% of the energy of the recoils is deposited as “damage energy” in a highly localized displacement cascade, where 500–2000 atoms are energetically displaced by elastic collisions [8]. The displacement of atoms within a cascade primarily produces Frenkel pairs, but the cascade may also result in the direct formation of topologically disordered or amorphous state in the core of the cascade. The energy density deposited over the initial portion (~ 5 nm) of an α -recoil cascade can be very high (up to 1 eV/atom) and occurs over a very short time ($<10^{-12}$ s); this may lead to local melting in the cascade or additional atomic relaxations and rearrangements. Moll et al. [106] have compared the different damage processes between the electronic stopping at high energy and the nuclear stopping at low energy in $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystal. At high energy (irradiated by 870 MeV Xe, $S_e = 29$ keV/nm), amorphization occurs directly in individual ion tracks from the extreme electronic-energy deposition, and full amorphization results from the overlapping of these tracks as described by a direct impact model (cf. Section 5.2.2), while at low energy (irradiated by 4 MeV Au, $S_n = 5.2$ keV/nm), amorphization occurs via indirect processes and energy deposits by ballistic process. The amorphization accumulation process is described in the framework of both direct-impact/defect-stimulated model (cf. Section 5.2.3) and multi-step damage accumulation model (cf. Section 5.2.4) [106]. The above mentioned and other ion irradiation experience are summarized in Table A1 in Appendix A.

Both the partitioning of the energy loss by α -particles between ionization and elastic collisions and the distribution of displaced atoms can be determined by computational approaches based on the binary collision approximation (BCA), if the threshold displacement energies of atoms are known [154]. The scattering angle and energy transfer that results from each binary elastic collision computer can be determined by the SRIM codes [136] and a Monte Carlo approach, assuming a structureless medium (i.e., crystallinity is not considered). This method can also be used for charged-particle irradiation calculations. Molecular dynamics simulations have also been used to calculate radiation damage [137,155,156] and dislocation threshold energies [157–159]. Recently, ab-initio molecular dynamic (AIMD) has also been introduced into this field to obtain more accurate calculation results [160–164].

5.1.3. Transmutations and Gas Production

In addition to the energy transferred to the host, α -decay and β -decay also lead to the transmutation of radioactive parent nuclei into different chemical daughter elements. These elements must be accommodated into the structure and may tremendously impact the physicochemical properties of the host materials, especially ceramic waste forms. Being the mainly sources of transmutation in HLW, transmutation of ^{90}Sr and ^{137}Cs is accompanied by changes in both ionic radius and valence. ^{90}Sr has a half-life of 29.1 years and it decays to ^{90}Y by emission of a 546 keV β -particle without gamma photons. Additionally, ^{90}Y ,

which has a 64 h half-life, emits another high-energy β -particle with a maximum energy of 2.28 MeV and transmutes to ^{90}Zr which is stable (Figure 6a). Usually, the valence of Sr, Y, and Zr are +2, +3 and +4, respectively, and a final ionic radius decrease is 29% [165]. While the half-life of ^{137}Cs is 30.17 years, it emits high energy beta particle transmutes into stable ^{137}Ba in two ways, as shown in the Figure 6b and Cs^{1+} decays to Ba^{2+} with a decrease in ionic radius of 20%.

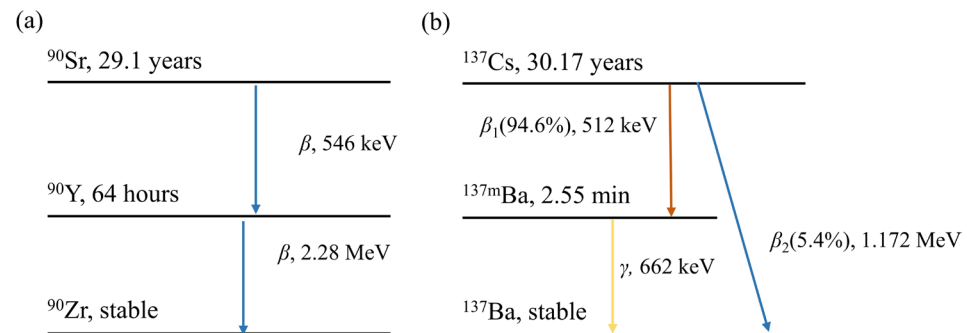


Figure 6. Schematic diagram of decay series for (a) ^{90}Sr , (b) ^{137}Cs .

The α -particles capture of two electrons to form helium atoms. Additionally, He atoms must (i) be accommodated in the interstitial position of lattices, (ii) be trapped at internal defects, (iii) aggregate to form bubbles, or (iv) be released via the ceramic surface. For HLW, most of the He will be generated over long time periods near ambient temperature, and the concentration should not exceed 100 atomic parts per million (appm), which should be easily accommodated. In the case of ceramic waste forms for Pu immobilization and disposal, concentrations of He can become quite high and difficult to accommodate within the structure, i.e., exceeding 2 at.% after 100,000 years for ceramics containing 20 wt.% ^{239}Pu [29]. For ion irradiation experiments using noble gas elements (He, Ne, Ar, Kr, Xe), bubbles formation is widely studied [58,166–170]. Taylor et al. [167] determined the critical He concentration (4.6 at.%) required to nucleate bubbles >1 nm in diameter in bulk $\text{Gd}_2\text{Zr}_2\text{O}_7$ by combined irradiation of Au and He ions. Additionally, bubbles distributed in the matrix alone, or formed 10–30 nm “long chains” parallel to the surface of the sample. In addition, the individual bubbles slightly increase lattice swelling, but the formation of bubble chains can reduce lattice strain. Huang et al. [170] further found that as the average grain size ranges from 221 to 55 nm, the He concentration thresholds for helium bubble nucleation along grain boundaries, formation of helium bubble chains within the grain, and intragranular ribbon helium bubbles are 1.7% to 2.8%, 5.9% to 15.2%, and 19.2% to more than 25.8%, respectively. The lattice swelling effect of $\text{Gd}_2\text{Zr}_2\text{O}_7$ is size-dependent, the smaller grain size has smaller lattice swelling. Holesinger et al. [58] concluded that the rapid amorphization of $\text{Gd}_2\text{Ti}_2\text{O}_7$ can accommodate more Kr large bubbles in the matrix without generating cracks, while $\text{Gd}_2\text{Zr}_2\text{O}_7$ maintains the crystalline structure under Kr irradiation but produces microcracks due to the accumulation of bubbles.

5.2. Damage Models

The irradiation-induced phase transformation in ceramics is of considerable interest, both in technological application and fundamental theory. Several phenomenological models were developed to decipher the damage accumulation induced by ion irradiation, as a function of temperature or flux. The amorphous fraction of $\text{Lu}_2\text{Ti}_2\text{O}_7$ which irradiated by 400 keV Ne at 77 K, 2.7 MeV Ar at RT, or 6.5 MeV Xe at RT increase with dose can be ascribed to defect-accumulation-like amorphization model (not introduce in this paper), direct-impact/defect-stimulated model (D-I/D-S) model and direct-impact model, respectively [57,171,172]. This suggests that different ion beam irradiation may apply different model. Common models are direct-impact model, cascade-overlap model, direct-impact/defect-stimulated model (D-I/D-S), the multi-step damage accumulation

model (MSDA) of Jagielski and Thome, the heterogeneous track overlap model (HTOM) and the thermal spike model (TS). The accumulated amorphous fraction derived from various models which widely used in the literature is compared in Figure 7.

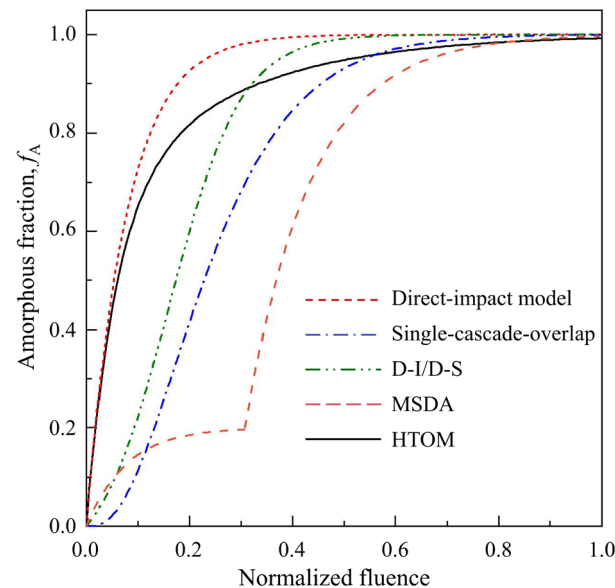


Figure 7. Amorphous fraction as a function of normalized ion fluence for direct-impact model, single-cascade-overlap, direct-impact/defect-stimulated (D-I/D-S), multiple step damage accumulation (MSDA), and heterogeneous track overlap model (HTOM). Reproduced with permission from Reference [142], Copyright © Elsevier 2012.

5.2.1. Thermal Spike Model

The thermal spike model has been applied to explain irradiation phenomena for a long time [173]. Many scholars have been instrumental in the development of this model, and now, it can be described the track formation in semiconductors and insulators [114,145,149,173]. The basic assumption of the model is that a high-temperature region (the thermal spike) is formed around the trajectory of a high-energy incident ion [145]. It is assumed that a melt is created when the temperature exceeds the melting point of the crystal. In a cylindrical region with a characteristic time of the order of 10^{-12} s, the energy deposited on the electronic system is transferred to the phonon system. Due to its small diameter, when the melt solidifies, the quenching rate of the molten cylinder may reach 10^{13} – 10^{14} K/s, which results in an amorphous structure. Szenes et al. [145] assumes that the variation of lattice temperature $\Delta T(r, t)$ has a radial Gaussian distribution which evolves with time as following equation:

$$\Delta T(r, t) = Q \left[\pi a^2(t) \right]^{-1} \exp \left[-r^2 / a^2(t) \right] \quad (1)$$

where $a^2(t)$ depends on the thermal diffusivity. Additionally, the value of Q can be obtained from the balance of energy $Q = (gS_e - L\rho\pi R^2)(\rho c)^{-1}$, where gS_e is the fraction of energy deposited in the thermal spike, $R = R(t)$ is the radius of the melted zone, and L , c and ρ are the latent heat of phase transition, the mean specific heat and the density, respectively. Another important assumption of the model is that the volume of the amorphous phase formed is proportional to the maximum volume of the melt region, and the proportionality factor taken is equal to 1 by the Szenes approach [145]. Yet as we all know now, the trajectory may be partially amorphous, or even with no amorphization, such as $\text{Gd}_2\text{Zr}_2\text{O}_7$. Therefore, this assumption should be revised to that track radius is equal to the maximum melt region [60]. The following equations are derived from the model:

$$R^2 = a_0^2 \ln \left(\frac{S_e}{S_{et}} \right), \text{ for } 1 \leq S_e / S_{et} \leq 2.7 \quad (2a)$$

$$R^2 = a_0^2 \frac{S_e}{2.7 S_{et}}, \text{ for } 2.7 \leq S_e/S_{et} \quad (2b)$$

$$S_{et} = \frac{\rho \pi c a_0^2 (T_m - T_{irr})}{g} \quad (3)$$

where a_0 is a parameter which characterizes the initial width of the temperature distribution in the spike, S_e and S_{et} are the electronic stopping power and the threshold of electronic stopping power respectively, and T_m and T_{irr} are the melting and irradiation temperatures. Moll et al. [60] used TS model to fit experiment data and provide that $a_0 = 5.8$ nm and $S_{et} = 13.2$ keV/nm for $\text{Gd}_2\text{Ti}_2\text{O}_7$; $a_0 = 4.9$ nm and $S_{et} = 13.2$ keV/nm for $\text{Gd}_2\text{TiZrO}_7$; and $a_0 = 4.1$ nm and $S_{et} = 13.8$ keV/nm for $\text{Gd}_2\text{Zr}_2\text{O}_7$.

The thermal spike model developed by Szenes [145] only considers the process starting when the energy is already transferred to the atoms. If the process of thermalization of the deposited energy on the electron system through electron-electron interaction is also considered [150]. A set of coupled nonlinear differential equations in cylindrical geometry were governed to describe the time and space evolutions of electronic system and lattice temperatures [114,150]:

$$C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} [r K_e(T_e) \frac{\partial T_e}{\partial r}] - g(T_e - T_a) + A(r) \quad (4a)$$

$$C_a(T_a) \frac{\partial T_a}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} [r K_a(T_a) \frac{\partial T_a}{\partial r}] + g(T_e - T_a) \quad (4b)$$

where $C_{e,a}(r,t)$, $T_{e,a}(r,t)$, and $K_{e,a}(r,t)$ are the heat capacity per unit volume (called specific heat), the temperature and the thermal conductivity of the electronic (e) and atomic (a) subsystem, respectively. $A(r)$ is the energy deposited into the electronic system, and g is the electron-phonon coupling strength.

The thermal spike proposed by Szenes [145], also called an analytical thermal spike (a -TS) model, provides an analytical solution to the differential equation for the atomic system (4b) ignoring the way the energy is transferred to the atoms. A complete numerical solution of the differential Equation (4) is determined by the inelastic thermal spike (i -TS) model [114,151]. The electronic thermal conductivity is linked to electron diffusivity by $D_e = K_e(T_e)/C_e(T_e)$, and the electron-phonon mean free time $\tau = C_e(T_e)/g$. So, the electron-phonon mean free path $\lambda^2 = D_e(T_e) \times \tau = K_e(T_e)/g$ and the λ will be the only free parameter in the solution of Equation (4) [151]. Yet a systematic study with several insulators has shown that λ decreases with the optical band gap, as shown in Figure 8a [174]. Based on such empirical correlation, λ has been determined for $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{TiZrO}_7$, and $\text{Gd}_2\text{Zr}_2\text{O}_7$ to be equal to 4.9, 4.3 and 3.8 nm, corresponding to a calculated band gap of 3.3, 7.4 and 11.5 eV, respectively [175]. For $\text{Gd}_2\text{Ti}_2\text{O}_7$, using $\lambda = 4.9$ nm, the energy $E_t = 0.8$ eV/at for creation of an ion track was determined [143]. Figure 8b presents i -TS calculations of Au ion (7 MeV/u), displaying the deposited energy density on the lattice as a function of (i) time after the ion impact (abscissa) and (ii) cylinder diameter (different lines) relative to the experiment data [135]. The horizontal lines correspond to the high-resolution TEM track diameters for Au (core 8.6 nm and core + shell 11.0 nm) and the energy densities to produce a molten track of given size is $E_t = 0.8$ eV/at for Au ion, while it is yielding an average $\langle E_t \rangle = 0.9$ eV/at for Ru, Xe, Ta, and Au [135]. Additionally, this $\langle E_t \rangle$ value agrees also with the results from other i -TS calculation for track formation in the same pyrochlore by U ions [143,176,177]. The variation of the calculated track diameters as functions of dE/dx based on $\langle E_t \rangle = 0.9$ eV/at is displayed in Figure 8c [135] (solid red curve) showing the great agreement with experimental results (round, red data points). The curve for $E_t = 0.56$ eV/at, which corresponds to the sum of the energy required to reach the melting temperature of $\text{Gd}_2\text{Ti}_2\text{O}_7$ (2123K), also plotted in Figure 8c via i -TS model (black dashed curve). The difference between 0.9 and 0.56 eV/at is about 360 kJ/mol supplying to melt latent heat, which is in good agreement with ~350 kJ/mol for the latent heat determined experimentally for $\text{La}_2\text{Zr}_2\text{O}_7$ [178]. Additionally, deposited energy of

formation amorphization E_a of $\text{Gd}_2\text{Ti}_2\text{O}_7$ irradiated by Au is plotted by dashed line in Figure 8b, and that from other ion irradiations is between 1.5 and 1.0 eV/at [135].

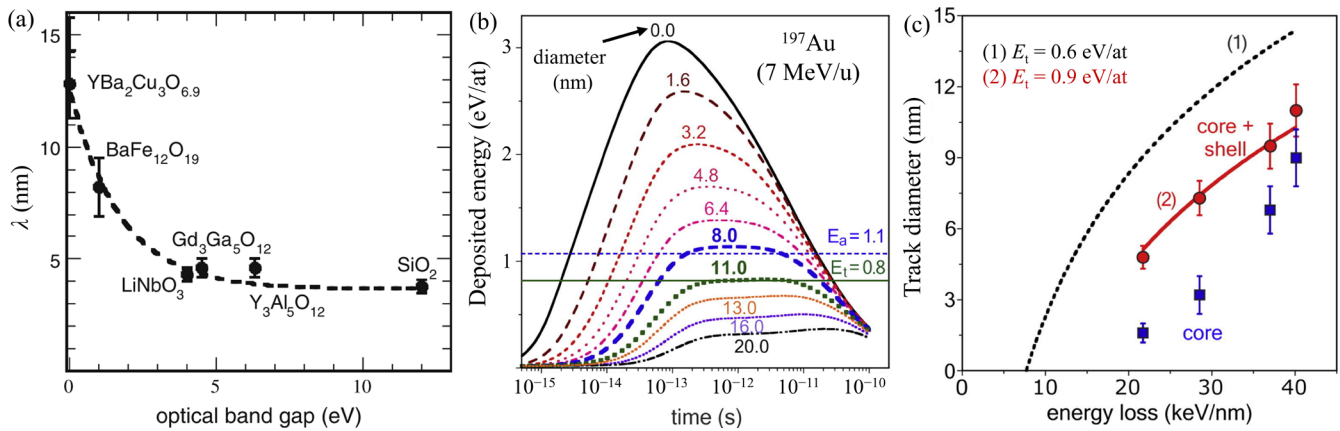


Figure 8. (a) Electron-phonon mean free path (λ) deduced from thermal spike fits versus optical band gap energy for different insulators [174]. (b) Inelastic thermal spike calculations of the evolution of the energy density deposited in $\text{Gd}_2\text{Ti}_2\text{O}_7$ vs. time for different diameters of the track cylinder (given in nm) for Au ion (7 MeV/u). Horizontal lines indicate the required energy density to obtain track diameters in agreement with experimental data from high-resolution TEM [135]. (c) Experimental track diameters for different ion beams in $\text{Gd}_2\text{Ti}_2\text{O}_7$ from high-resolution TEM measurements as a function of dE/dx : core-shell tracks (red circles) and amorphous track cores (blue squares). The solid red and dashed black curves are the results of thermal spike calculations based on $E_t = 0.90$ eV/at and $E_t = 0.56$ eV/at, respectively [135]. (a) Reproduced with permission from Reference [174], Copyright © Springer Nature 2009; (b,c) Reproduced with permission from Reference [135], Copyright © Elsevier 2014.

5.2.2. Direct-Impact Model and Cascade-Overlap Model

Direct-impact model has been completely analyzed and published by Gibbons [147]. Under the conditions of dose and temperature that ensure the production of an amorphous layer, assume that heavy ions create a sufficiently large defect density around the track of the ion to ensure that individual damage clusters are amorphous. For the idealized case, every implanted ion produces an amorphous cluster with a projected area A_i (each cluster is a right circular cylinder), and the total amorphous area A_A is the sum of the amorphous area of each implanted ion, which can be written as:

$$\frac{dA_A}{dN} = A_i \left(1 - \frac{A_A}{A_0} \right) \quad (5)$$

where N is the total number of implanted ion, the A_0 is the total area being implanted. The factor within parentheses is just the probability that a given ion will hit in the undamaged area. The solution of (5) is

$$A_A = A_0 \left(1 - e^{-A_i D} \right) \quad (6)$$

where D is the dose or ion fluence. Usually, we do not care about the real area but relative rate or called amorphous fraction f_a which represents the ratio of transformation to amorphous phase. Thus, the function (6) was rewritten as

$$f_a = 1 - \exp(-\sigma_a D) \quad (7)$$

where f_a is the amorphous fraction and σ_a is the amorphization cross-section.

For light ions, that cannot produce individual amorphous clusters without pre-damage, even though the approach to saturation is a function of dose. Thus another model cascade-overlap model was proposed. In this model, also assume that an implanted ion will create

a cylindrical cluster with a project area A_i , but that only overlap of clusters can produce an amorphous zone. There are serial equations describing the process of the production of amorphous:

$$\frac{dA_A}{dN} = A_i \frac{A_D}{A_0} \quad (8a)$$

$$\frac{dA_D}{dN} = A_i \left(\frac{A_u}{A_0} - \frac{A_D}{A_0} \right) \quad (8b)$$

$$\frac{dA_u}{dN} = -A_i \frac{A_u}{A_0} \quad (8c)$$

where A_A , A_D , and A_u represent the amorphous area, the damage area but not amorphous and the undamaged area. The solution for A_A is

$$A_A = A_0 \left[1 - (1 + A_i D) e^{-A_i D} \right] \quad (9)$$

An easy extension of this model can be developed for cases in which n -tuple cluster overlap is required for the production of amorphous zones and yields

$$A_A = A_0 \left[1 - \left(\sum_{k=0}^n \frac{(A_i D)^k}{k!} e^{-A_i D} \right) \right] \quad (10)$$

Obviously, when $n = 0$, Equation (10) is the same as Equation (6), and when $n = 1$, it is the same as Equation (9), which is called single-cascade-overlap model (also called double-impact model). Usually, only two damage overlaps are considered ($n = 2$), so it is called double-cascade-overlap model, and rewritten in the form of the commonly used amorphous fraction

$$f_a = 1 - \left[\left(1 + \sigma_t D + \sigma_t^2 D^2 / 2 \right) \exp(-\sigma_t D) \right] \quad (11)$$

where f_a is the amorphous fraction, σ_t is the total damage cross-section. The double-overlap model generally provides an excellent fit to data for a number of materials that exhibit a sigmoidal dependence of f_a on dose.

5.2.3. Direct-Impact/Defect-Stimulated Model

In this model [179], amorphous fractions mainly come from two ways, (i) direct-impact production $\sigma_a D$, and (ii) stimulated amorphization, which takes into account the defect-stimulated, cascade-stimulated, or implanted-ion-stimulated growth of the amorphous production at crystalline/amorphous (c/a) interfaces. The mathematical representation of this model is generally expressed as

$$\frac{df_a}{dD} = P_a(1 - f_a) + P_s f_a(1 - f_a) \quad (12)$$

where P_a and P_s are parameters for primary production of amorphous nuclei and stimulated amorphization. This model has been numerically fitted to results for semiconductor materials, such as Si [179,180], $\text{Si}_{1-x}\text{Ge}_x$ [181], and SiC [182,183]. Additionally, the solution of Equation (12) is given by the expression [144]

$$f_a = 1 - (\sigma_a + \sigma_s) / \{ \sigma_s + \sigma_a \exp[(\sigma_a + \sigma_s) D] \} \quad (13)$$

where σ_a and σ_s are cross-sections for primary amorphization and stimulated amorphization, respectively. Within this model, stimulated amorphization occurs at the c/a interfaces (the primary amorphization zone acts as the nucleus), so there must be some direct-impact amorphization ($\sigma_a > 0$) in order for continuous amorphization to “epitaxially” grow, since otherwise $f_a = 0$ if $\sigma_a = 0$. Yang et al. [171] used this model to fit the experimental data

for $\text{Lu}_2\text{Ti}_2\text{O}_7$ irradiated by 2.7 MeV Ar^{11+} ions, with great fitted results for $\sigma_s = 0.888 \pm 0.102 \text{ nm}^2$ and $\sigma_a = 0.008 \pm 0.003 \text{ nm}^2$. Zhang et al. successfully used this model to fit the single-crystal $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{O}_7$ irradiated by 1 MeV Au at room temperature (300 K), and the σ_a are both equal to 1.0 dpa^{-1} and σ_s are 56.8 and 66.0 dpa^{-1} , respectively [104,184].

The above models mainly consider the displacement cascades at low energy where the nuclear energy loss by ballistic collision is dominant and does not take into account simultaneous recovery processes. Furthermore, these models describe the change in amorphous fraction, f_a , with dose or time, and can be written in a unified form

$$\frac{df_a}{dD} = \sum_i P_{ai} g_i(f_a) \quad (14)$$

where P_{ai} is the amorphous production parameter for some i -th process and $g_i(f_a)$ is the probability of the process to take place for a given value of f_a . For example, for direct-impact model, parameter P_a is the represent the amorphization cross-section, σ_a , and the probability function $g_i(f_a)$ is given by the term $(1 - f_a)$, and the solution for f_a is given by Equation (7). If the recovery process is taken into account, the additional term should be added to the right of Equation (14) and the rate of amorphization is given by

$$\frac{df_a}{dD} = \sum_i P_{ai} g_i(f_a) - \sum_j K_j(T) h_j(f_a) \quad (15)$$

where $K_j(T)$ is the recovery rate at temperature T for some j -th process and $h_j(f_a)$ is the probability for that recovery process to occur for a given value of f_a . The different recovery mechanisms can have different forms. If the recovery process takes place in the bulk crystalline matrix, $h_j(f_a)$ is equal to $(1 - f_a)$, while at c/a interfaces, $h_j(f_a)$ is equal to $f_a(1 - f_a)$, similar D-I/D-S model. If the case of recovery processes in the bulk of amorphous regions, $h_j(f_a)$ is equal to f_a [144].

5.2.4. Multi-Step Damage Accumulation Model

Based on the assumption that the damage accumulation is caused by multiple atomic recombination processes occurring in successive steps, a multi-step damage accumulation model (MSDA) is presented by Jagielski et al. [185]. In this model, each ion impact leads to the transformation of a given volume of the crystal into a new metastable atomic configuration which has the lowest free energy in the current conditions. Additionally, this metastable structure can be an intermediate structure or “nucleation site” in structural transformations during ion irradiation, so the direct amorphization process, the firstly disorder and then amorphization or other process containing intermediate phase transitions are all included. Although, the volume transformed by a single ion impact is comparable to that of a collision cascade for low-energy ion or to that of a damaged track for swift ion, short-range migration of defects and atoms (local atoms rearrangement) significantly affects the transition volume. That is, the previous ion impact will affect the next collision transition. This description is similar to the “overlap” and “stimulated effect” in the previous model, but the assumptions are totally different. The multi-step processes can be written in the following equations. Firstly, the perfectly crystal transforms to a partially damaged structure by a direct-impact mechanism, and therefore it can satisfy the following equation:

$$f_{d,1} = f_{d,1}^{\text{sat}} [1 - \exp(-\sigma_1 \Phi)] \text{ for } 0 < \Phi < \Phi_1 \quad (16a)$$

where $f_{d,1}^{\text{sat}}$ is the saturated damage accumulation in the first step, σ_1 is the cross-section of damage, and Φ is the irradiation fluence. Due to the destabilization of the crystal structure causing by implanted ions, a subsequent step of structural transformation occurs. The accumulated damage $f_{d,2}$ increase gradually from the saturation at the first step $f_{d,1}^{\text{sat}}$ to

that at the end of the second step $f_{d,2}^{\text{sat}}$. Additionally, the corresponding effective influence should be replaced $\Phi - \Phi_1$ rather than Φ . So, the equation of stage 2 can be written as

$$f_{d,2} = f_{d,1}^{\text{sat}} + \left(f_{d,2}^{\text{sat}} - f_{d,1}^{\text{sat}} \right) [1 - \exp(-\sigma_2(\Phi - \Phi_1))] \text{ for } \Phi_1 < \Phi < \Phi_2 \quad (16b)$$

According to the above considerations, the corresponding equation for stage i following

$$f_{d,i} = f_{d,i-1}^{\text{sat}} + \left(f_{d,i}^{\text{sat}} - f_{d,i-1}^{\text{sat}} \right) [1 - \exp(-\sigma_i(\Phi - \Phi_{i-1}))] \text{ for } \Phi_{i-1} < \Phi < \Phi_i \quad (16c)$$

The final equation which accounts for MSDA model is the sum of the individual steps m described by (16a–c):

$$f_d = \sum_{i=1}^m \left(f_{d,i}^{\text{sat}} - f_{d,i-1}^{\text{sat}} \right) G[1 - \exp(-\sigma_i(\Phi - \Phi_{i-1}))] \quad (17)$$

where G is a control function which keeps f_d nonnegative (converts negative values to 0 while positive values remain unchanged).

Comparing MSDA and the earlier model supported by Gibbons [147] (model in Section 5.2.2), the m and n parameters do not have the same meaning in both descriptions. In MSDA, m is the number of steps required for the development of the entire sequence of damage accumulation, whereas Gibbons n is the number of ion impacts needed to create a permanent disorder in a given region of the crystal. What is more, the function for MSDA is a piecewise function that is a continuous function of the Gibbons model. Specifically, when $m = 1$, the MSDA model has the exact same form as the direct-impact model ($n = 0$). Figure 9 [185] shows a three step MSDA model fit well with the low-energy Cs ions irradiation experimental date for yttria-stabilized zirconia (YSZ) and magnesium-aluminate spinel (MAS) [186,187]

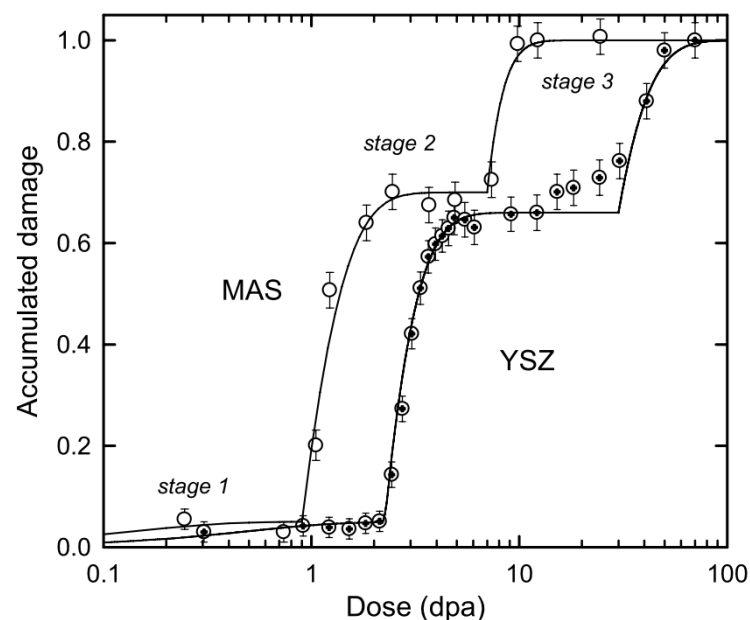


Figure 9. Accumulated damage (f_d) in YSZ and MAS crystals irradiated at RT with low-energy (160 keV) Cs ions. Solid lines are fits to RBS/C data using the MSDA model with $m = 3$ (three-step process). The conversion factors of fluence (expressed in 10^{15} cm^{-2}) to dpa scales are: 2.45 for MAS and 3.46 for YSZ crystals. Reproduced with permission from Reference [185], Copyright © Springer Nature 2009.

5.2.5. Heterogeneous Track Overlap Model

Due to the limitations of the direct-impact model in explaining the inhomogeneous ion tracks in $\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7$, which coexist a pyrochlore $\rightarrow$ amorphous ($\text{P} \rightarrow \text{A}$) transition, a pyrochlore $\rightarrow$ deficient fluorite ($\text{P} \rightarrow \text{F}$) transition and even a deficient fluorite $\rightarrow$ amorphization ($\text{F} \rightarrow \text{A}$) transition simultaneously. Sattonnay et al. [142] have developed a new phenomenological description, called the heterogeneous track overlap model (HTOM), to describe and explain the phase transformation accumulation (in fact, damage accumulation) when and where heterogeneous track formed.

In this model, an ion track is consisted of a mixture of an amorphous part and a defective-fluorite part, some of which may also have defective pyrochlore phase. The deficient fluorite part due to a $\text{P} \rightarrow \text{F}$ transition, but amorphization part comes from both $\text{P} \rightarrow \text{A}$ transition and $\text{F} \rightarrow \text{A}$ transition. The $\text{P} \rightarrow \text{A}$ transition occurs via directly in each individual ion impact, while a second impact into the previously transformed region ($\text{P} \rightarrow \text{F}$ region) will produce amorphization via $\text{F} \rightarrow \text{A}$ transition. In brief, the HTOM model can be regarded as the direct-impact mechanism coupled with a single-cascade-overlap process. Therefore, the variation in the transformed fraction with the ion fluence following the framework of the direct impact model, since one ion impact is most often sufficient to totally transform the matter inside a track,

$$f = f_{\text{sat}}[1 - \exp(-\sigma D)] \quad (18)$$

where f_{sat} is the saturated transformed fraction, σ is the section of the transformatal cylinder.

Figure 10 provides a schematic for the processes of the HTOM. It assumed that an ion injecting into a pyrochlore region of a sample (marked P) creates a track consisted of both defective fluorite (marked F) and amorphous (marked A) regions. According to this assumption, the variation in the fraction of pyrochlore structure (f_P) with the ion fluence follows the following equation:

$$\frac{df_P(D)}{dD} = -\sigma_{\text{PF}}f_P - \sigma_{\text{PA}}f_P \quad (19a)$$

where σ_{PF} and σ_{PA} are the cross sections of the cylinder directly transformed by each ion impinge into defective-fluorite or amorphous structures respectively.

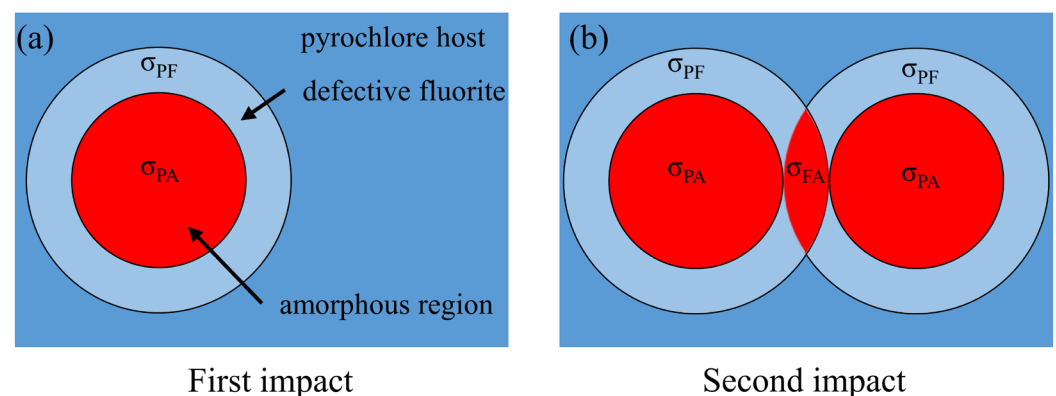


Figure 10. Schematic representations of the physical processes underlying the HTOM model with the cross sections of cylinders corresponding to swift heavy ion tracks: (a), first impact, (b) second impact. σ_{PA} and σ_{PF} are the areas directly converted by each ion impact into amorphous or disordered regions, and σ_{FA} is the area related to the transformation of a defective fluorite region into an amorphous one owing to a second ion impact.

Assumption two is that a second ion impact occurring in a disordered region will result in a transformation to an amorphous region. So the variation in the fraction of defective fluorite crystal (f_F) is given by:

$$\frac{df_F(D)}{dD} = \sigma_{PF}f_P - \sigma_{FA}f_F \quad (19b)$$

where the former term on the right-hand side of equation represents the transformation from pyrochlore to defective fluorite regions arising from a first ion impact, and the second term represents the transformation of the defective fluorite into amorphous regions which occurs in a second ion impact, and σ_{FA} is the cross sections of the $F \rightarrow A$ transition. Finally, the variation of amorphous fraction (f_A) equal to the sum of $P \rightarrow A$ transition and $F \rightarrow A$ transition and can be written as:

$$\frac{df_A(D)}{dD} = \sigma_{PA}f_P + \sigma_{FA}f_F \quad (19c)$$

Let the total transformation cross section be σ_t , with $\sigma_t = \sigma_{PF} + \sigma_{PA}$. The resolution of the system of differential equations (Equation (19a–c)) is thus given by the following expressions:

$$f_P(D) = \exp(-\sigma_t D) \quad (20a)$$

$$f_F(D) = \frac{\sigma_{PF} \exp(-\sigma_t D) [-1 + \exp(\sigma_t - \sigma_{FA}) D]}{\sigma_t - \sigma_{FA}} \quad (20b)$$

$$f_A(D) = 1 - \frac{\sigma_{PA} - \sigma_{FA}}{\sigma_t - \sigma_{FA}} \exp(-\sigma_t D) - \frac{\sigma_{PF}}{\sigma_t - \sigma_{FA}} \exp(-\sigma_{FA} D) \quad (20c)$$

It is worth noting that the direct-impact model can be regarded as the special case of HTOM model. When in Equation (20a–c), $\sigma_{PF} = \sigma_{FA} = 0$ and $\sigma_T = \sigma_{PA}$, that is, the tracks are totally amorphous, or $\sigma_{PA} = \sigma_{FA} = 0$ and $\sigma_T = \sigma_{PF}$, there is no amorphization occurs, the Equation (20a–c) are simplified to Gibbons equation form (Equation (7)).

Figure 11 [142] shows the experimental data and fitting line by Equation (20a–c) for phase transformation accumulation process for typical pyrochlore with irradiation under 120 MeV U ion, including $Gd_2Ti_2O_7$, Gd_2TiZrO_7 , $Gd_2Zr_2O_7$, and $Nd_2Zr_2O_7$. Among them, $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ are more special, the former only a pyrochlore (P) $\rightarrow$ amorphous (A) transformation is observed, and the latter only a pyrochlore (P) $\rightarrow$ defective fluorite (F) transformation occurs. The HTOM has also been successfully applied to $Y_2Ti_2O_7$ irradiated by 93 MeV Xe, and σ_{PA} , σ_{PF} , and σ_{FA} are 46.2 nm², 21.0 nm² and 67.2 nm², respectively [188].

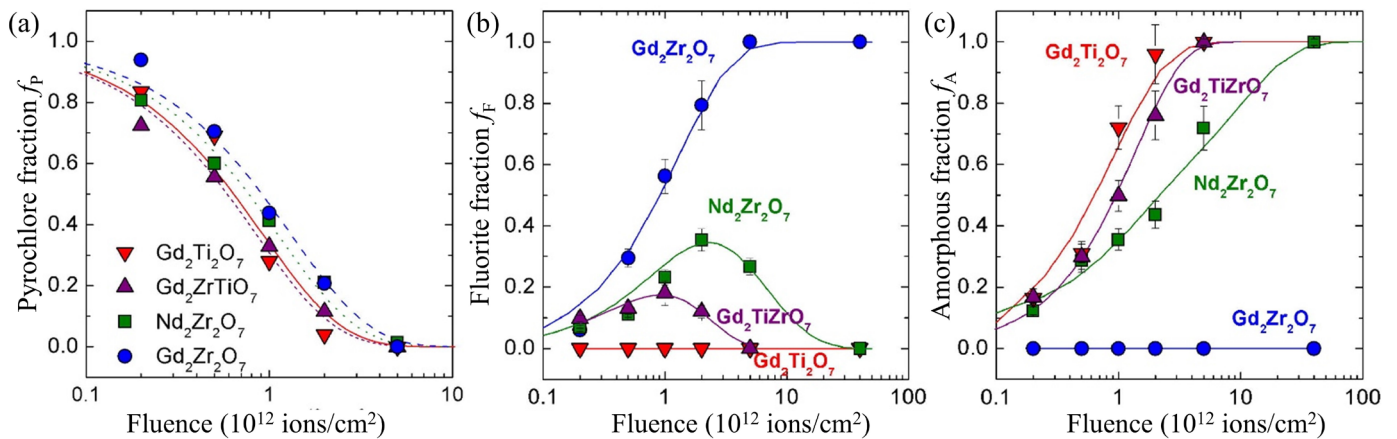


Figure 11. Variation of the fraction of (a) pyrochlore, (b) fluorite, and (c) amorphous phases vs the ion fluence for pyrochlores irradiated with 120 MeV U ions. Solid lines are fits to the data with HTOM (Equation (20a–c)). Reproduced with permission from Reference [142], Copyright © Elsevier 2012.

The HTOM fitting results σ_i of pyrochlores with chemical composition which irradiated by 119 MeV U are plotted in Figure 12a, marked by solid symbols [61,62,142]. Both σ_{PA} , σ_T , and σ_{FA} clearly increase with increasing r_A/r_B , whereas σ_{PF} globally decrease as r_A/r_B increasing with a relatively stable value $\sim 50 \text{ nm}^2$ for r_A/r_B between 1.5 to 1.6. The consequences of $\text{Nd}_2\text{Zr}_2\text{O}_7$ [62] and $\text{Y}_2\text{Ti}_2\text{O}_7$ [188] which irradiated by 93 MeV Xe ions are also shown in Figure 12, using hollow marks. For Figure 12b, using the σ_i/σ_T instead of σ_i as the ordinate, that is, normalized treatment of σ_i , which excludes the effect of variation of σ_T on σ_{PF} . It is clearly demonstrated that the susceptibility to amorphization by electronic excitation of pyrochlore and fluorite phases increases with increasing r_A/r_B . For 93 MeV Xe ions irradiation, due to the low S_e energy, the σ_i is smaller than that of corresponding pyrochlores irradiated by 119 MeV U ions, while the σ_{PF}/σ_T and σ_{FA}/σ_T are larger than that of ceramics irradiated by 119 MeV U ions. Due to the fact that the weaker electronic excitation (lower S_e) lead to smaller track cross-sections and make more fluorite fraction for single ion damage process. This phenomenon conforms to the laws of the TS model, and many pyrochlores show similar rules after being ion-irradiated in a broad energy range, including $\text{Nd}_2\text{Zr}_2\text{O}_7$ [62], $\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7$ [135]. Further, the diameter of ion tracks (d) may be deduced from the value for σ according $d = 2(\sigma/\pi)^{1/2}$. Thus, the total track diameters (d_T) and amorphous core diameter (d_A) are calculated and plotted vs. r_A/r_B in Figure 12c. Both d_T and d_A globally decrease as r_A/r_B decreases, but the variation rule of d_T is nearly linear, while d_A changes linearly with a greater slope during r_A/r_B from 1.75 to 1.5 and decreases rapidly below $r_A/r_B = 1.5$. The hollow marks in Figure 12c represent pyrochlores irradiated by 93 MeV Xe ion showing a similar rule. Moreover, these data also indicate that the radiation resistance of pyrochlores depends more on the cation radius ratio (r_A/r_B), both A and B cations play a significant role in the amorphization process, than on the B cation itself. Additionally, this rule is under a huge implication for the design of future matrices for waste forms. If the B cation is Zr and the A cation is Am, $r_A/r_B = 1.51$, so that the probability that $\text{Am}_2\text{Zr}_2\text{O}_7$ amorphizes upon electronic excitation is high. A similar conclusion is obtained with $A = \text{Np}$ ($r_{\text{Np}}/r_{\text{Zr}} = 1.60$) or $A = \text{Cm}$ ($r_{\text{Cm}}/r_{\text{Zr}} = 1.54$). In fact, $^{241}\text{Am}_2\text{Zr}_2\text{O}_7$ shows excellent resistance to amorphization during self-irradiation (alpha decay) for 40 days (0.02 dpa) and 370 days (0.21 dpa), respectively [189].

5.3. Temperature Dependence

As previously stated, the processes of ion irradiation involve transient thermal process, quenching and self-annealing process. Each step involves heat diffusion, especially during self-annealing process which significantly affects the rearrangement of atoms and the restoration of structures. This also means that the ion irradiation damage process shows a strong temperature dependence.

5.3.1. The Critical Amorphous Temperature

Ordinarily, for ion-irradiation experiments of this special material, the higher the temperature is, a higher the ion dose required for the material to be completely amorphous. Even when the temperature arrives at a certain degree, the recrystallization rate is higher than the damage rate, thus, the complete amorphous cannot be approved even if the dose is higher. So, the critical amorphization fluence F_C (or called critical amorphous dose D_C) is defined as the ion fluence (dose) required for full amorphization at a special temperature [91,190,191]. Additionally, the critical amorphous temperature T_C is defined as the lowest temperature above which no full amorphization occurs in the materials under ion-irradiation. In other words, at the critical amorphous temperature, the critical amorphous dose tends to infinity. $\text{Gd}_2\text{Ti}_2\text{O}_7$ will occur fully amorphous transform by 1 MeV Kr at low dose, about 0.2 dpa during 320 to 500 K [139] which is similar to the dose for Cm-doped $\text{Gd}_2\text{Ti}_2\text{O}_7$ [25], and this dose is equivalent to $4 \times 10^{18} \alpha$ decays per gram or 600 years of storage for a waste form containing 10 wt% ^{239}Pu . However, the critical amorphous fluence F_C increase with the increase of temperature, for $\text{Gd}_2\text{Ti}_2\text{O}_7$, the F_C increase sharply above 800 K, and the upper temperature limit for amorphization is about 1100 K. While for $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$, with Ti

substituted by Zr, the F_C increase and the T_C decrease. For Zr-rich composition ($x = 0.5$), there is no amorphization above 380 K, whereas highly enriched in Zr, for $x > 0.75$, amorphization is extremely difficult to achieve at ultra-low temperature (cryogenic temperatures), and only partial amorphization was observed (30% amorphous for $x = 0.75$) [139]. For end member, $\text{Gd}_2\text{Zr}_2\text{O}_7$, irradiation to extremely high ion fluences, 1.5 MeV Xe at 25 K with equivalent dose 7 dpa or at room temperature with 15 dpa, showed no evidence of amorphous regions in the crystalline matrix [138,139,192]. For comparison, the dose of 15 dpa is equivalent to 3×10^{20} α decays per gram or the accumulated dose for a waste form containing 10 wt% ^{239}Pu storing over 30 million years. It confirms that compositions in this regime will be extremely durable and radiation resistance to amorphization under repository conditions. In Zr-rich pyrochlores (e.g., $\text{Gd}_2\text{Zr}_2\text{O}_7$, $\text{Gd}_2\text{Zr}_{1.8}\text{Mg}_{0.2}\text{O}_{6.8}$, $\text{Gd}_{1.9}\text{Sr}_{0.1}\text{Zr}_{1.9}\text{Mg}_{0.1}\text{O}_{6.85}$, and $\text{Gd}_{1.9}\text{Sr}_{0.1}\text{Zr}_{1.8}\text{Mg}_{0.2}\text{O}_{6.75}$, the pyrochlore-to-fluorite structure transformation at low temperatures is complete after a dose of about 0.4 dpa, whereas could not be amorphized even at temperature as low as 25 K [139]. Up to now, there are few reports of complete amorphization of rare earth zirconated pyrochlores, e.g., $\text{La}_2\text{Zr}_2\text{O}_7$ with $T_C = 310$ K under 1.5 MeV Xe irradiated and critical amorphous dose 1.19, 3.55, and 5.20 dpa for $(\text{La}_{1-x}\text{Ce}_x)_2\text{Zr}_2\text{O}_7$ ($x = 0, 0.1$ and 0.2) with 1 MeV Kr at 25 K, respectively [65,91].

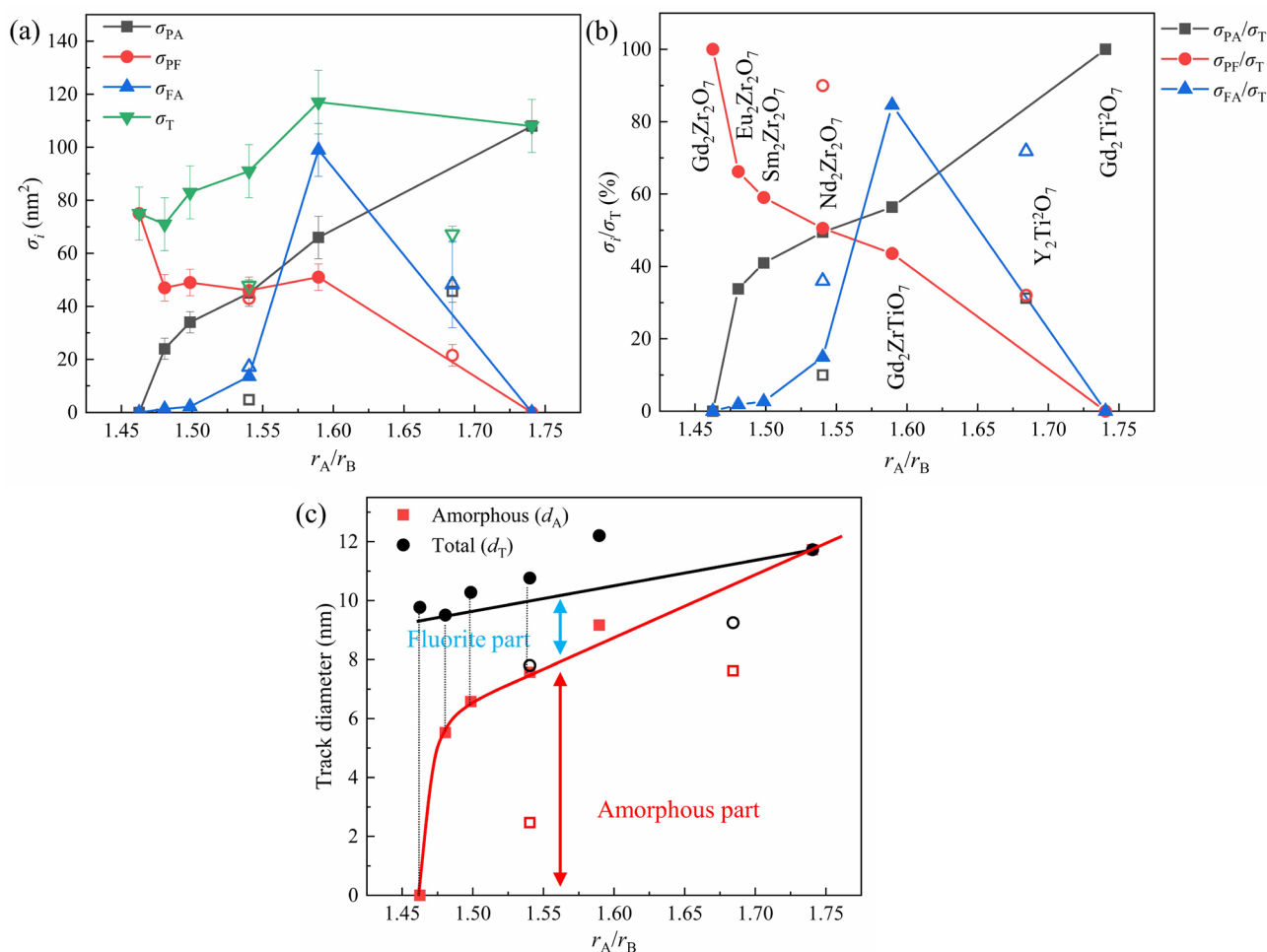


Figure 12. Variation in of (a) cross-section σ_i , (b) σ_i/σ_T , (c) the total track diameter (d_T), and the amorphous track core diameter (d_A) as a function of the cation radius ratio for pyrochlore ceramics. The solid marks are $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{TiZrO}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$, $\text{Sm}_2\text{Zr}_2\text{O}_7$, $\text{Eu}_2\text{Zr}_2\text{O}_7$, and $\text{Nd}_2\text{Zr}_2\text{O}_7$ irradiated with 119 MeV U ions [61,62,142], while the hollow marks represent $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$ irradiated with 93 MeV Xe ions from Refs. [62,188]. The lines are guides for the eye.

Wang et al. [193] developed an empirical model based on cascade “quenching” and epitaxial recrystallization to describe the temperature effect of the accumulation of the amorphous fraction during ion beam irradiation experiments. Weber also deduces the expression of the critical temperature, T_C . The critical fluence (F_C) versus temperature data are fitted to follow equation [193]:

$$F_C = \frac{F_{C0}}{1 - \exp\left[\frac{E_a}{k_b} \times \left(\frac{1}{T_C} - \frac{1}{T}\right)\right]} \quad (21)$$

$$T_C = \frac{E_a}{k_b \ln\left(\frac{v F_{C0}}{\Phi}\right)} \quad (22)$$

where F_{C0} is the critical fluence at 0 K, E_a is the activation energy for recovery process, k_b is the Boltzmann constant, T is the temperature of the irradiation experiment, Φ is the ion flux of ion irradiation and v is the effective attempt frequency.

The critical temperature of a serial of pyrochlores was fitted by Equation (21) and plotted as a function of cation radii ratio in Figure 13 [55,66,68,91,93,133,139,190–192,194–196]. The triangle represents the data fitted from pyrochlores which are irradiated by 1 MeV Kr, while square, circle and rhombus represent that irradiated by 1.5 MeV Xe, 0.6 MeV Ar and 0.6 MeV Bi, respectively. A series of colors are used to distinguish the types of pyrochlores, including grey for actinide doped pyrochlores [66], red for rare earth titanate pyrochlores [68,93,133,190–192,195], green for $A_2(Ti_{1-x}Zr_x)_2O_7$ [55,139], purple for rare earth stannate pyrochlores [55,194], yellow for $Y_2(Ti_{1-x}Sn_x)_2O_7$ [55], orange for rare earth hafnate pyrochlores [55], and blue for $La_2Zr_2O_7$ [91], respectively. The triangles with black edge are calculated by Lumpkin et al. [55] from the model (Equation (2) in Ref. [196]) which obtain by multiple linear regression method fitting data from ab-initio calculation. It is clear from Figure 13 that there is a certain correlation between the critical temperature (T_C) and the ratio of cation radius (r_A/r_B), so the data obtained by 1 MeV Kr ion irradiation, except the three points with black arrow (Y_2TiO_5 , Yb_2TiO_5 and $YbYTiO_5$), are linearly fitted and drawn by a red solid line in the Figure 13. The fitting equation is following $T_C = 3335.9 r_A/r_B - 4792.7$, and coefficient of determination R^2 is equal to 0.85. The T_C increases with the increase of r_A/r_B , obviously. However the r_A/r_B of data for fitting is located between 1.51 and 1.78, so the fitting formula is not suitable for r_A/r_B lower than 1.51. When the r_A/r_B of pyrochlores is lower than 1.52, the critical temperature decreases rapidly and approaches 0 K. At an ultra-low temperature, the pyrochlores with a small cationic radius ratio will not be completely amorphous and even does not appear amorphous at a larger irradiation dose with low-energy ions. For example, no amorphization occurred for $Y_2Sn_2O_7$ ($r_A/r_B = 1.48$), $Er_2Sn_2O_7$ ($r_A/r_B = 1.46$), $Gd_2Zr_2O_7$ ($r_A/r_B = 1.46$), and $Gd_2Hf_2O_7$ ($r_A/r_B = 1.48$), under 1 MeV Kr ion irradiation at 25 K at a dose of ~ 5.18 , ~ 5.94 , ~ 5 , and ~ 4.54 dpa, respectively [194,197]. Moreover, under 1.5 MeV Xe ion-irradiation at 25 K, only disordered fluorite transform occurs for $Gd_2Zr_2O_7$ ($r_A/r_B = 1.46$), $Sm_2Zr_2O_7$ ($r_A/r_B = 1.50$), $Nd_2Zr_2O_7$ ($r_A/r_B = 1.54$) at a dose of ~ 36 , ~ 7.3 , and ~ 7 dpa [91]. $Ce_2Zr_2O_7$ ($r_A/r_B = 1.58$) is a special one; there is no amorphous for it under MeV Kr ion irradiation at 25 K at a dose of ~ 7.08 dpa [65], which also suggests that zirconated pyrochlores have better irradiation resistance.

What is more, except for r_A/r_B , the composition of B-site also influences the critical temperature. The critical amorphization temperatures of stannate pyrochlores are much higher than those of titanate, hafnate, and zirconated pyrochlores having similar ionic radius ratios, $T_C(A_2Sn_2O_7) > T_C(A_2Ti_2O_7) > T_C(A_2Hf_2O_7) > T_C(A_2Zr_2O_7)$, even stannate pyrochlores have a smaller r_A/r_B and higher T_C than those of titanate pyrochlores. For example, the r_A/r_B of $La_2Sn_2O_7$ and $Y_2Ti_2O_7$ are both 1.68, however, the critical amorphization temperatures of $La_2Sn_2O_7$ and $Y_2Ti_2O_7$ with 1 MeV Kr irradiations are 960 and 780 K, respectively [194,195]. Additionally, the T_C of $La_2Sn_2O_7$ is higher than that of $A_2Ti_2O_7$ ($A = Ho, Er, Yb, Lu$) whose r_A/r_B are from 1.677 to 1.615 and T_C are from 850 K to 480 K [194,195]. The critical amorphization temperature of $Nd_2Sn_2O_7$ is 700 K is signifi-

cantly higher than that of $\text{Lu}_2\text{Ti}_2\text{O}_7$ (480 K) and $\text{Y}_2\text{Ti}_{1.2}\text{Sn}_{0.8}\text{O}_7$ (335 K), although the ionic radius ratio of $\text{Nd}_2\text{Sn}_2\text{O}_7$ ($r_A/r_B = 1.607$) is slightly less than that of $\text{Lu}_2\text{Ti}_2\text{O}_7$ ($r_A/r_B = 1.61$) and is slightly larger than that of $\text{Y}_2\text{Ti}_{1.2}\text{Sn}_{0.8}\text{O}_7$ ($r_A/r_B = 1.595$) [55,194,195]. In addition, although the r_A/r_B of $\text{Gd}_2\text{Sn}_2\text{O}_7$ (1.526) is similar to that of $\text{Gd}_2(\text{Zr}_{0.75}\text{Ti}_{0.25})_2\text{O}_7$ (1.523), complete amorphization cannot be approached in $\text{Gd}_2(\text{Zr}_{0.75}\text{Ti}_{0.25})_2\text{O}_7$ with 1 MeV Kr irradiation at 25 K while the critical amorphization doses are ~ 0.81 dpa for $\text{Gd}_2\text{Sn}_2\text{O}_7$ [139,197]. Furthermore, $\text{La}_2\text{Zr}_2\text{O}_7$ has a larger cation radius ratio ($r_A/r_B = 1.61$) than $\text{Gd}_2\text{Sn}_2\text{O}_7$ ($r_A/r_B = 1.526$), the amorphization doses (D_C) for $\text{La}_2\text{Zr}_2\text{O}_7$ irradiated by 1 MeV Kr at 25 K and room temperature are ~ 1.19 dpa and ~ 3.42 dpa, respectively, whereas D_C for $\text{Gd}_2\text{Sn}_2\text{O}_7$ at 25 K and room temperature are ~ 0.81 dpa and ~ 3.4 dpa, respectively [65,194,197]. The r_A/r_B of $\text{La}_2\text{Hf}_2\text{O}_7$ (1.633) is slight higher to that of $\text{Yb}_2\text{Ti}_2\text{O}_7$ (1.628), while the T_C of $\text{La}_2\text{Hf}_2\text{O}_7$ is 563 K, which is significantly less than that of $\text{Yb}_2\text{Ti}_2\text{O}_7$ (594 K (poly-crystal) or 611 K (single-crystal)) [195,196], and the similar rule for $\text{La}_{1.6}\text{Y}_{0.4}\text{Hf}_2\text{O}_7$ ($r_A/r_B = 1.594$, $T_C = 473$ K) and $\text{Nd}_2\text{Sn}_2\text{O}_7$ ($r_A/r_B = 1.607$, $T_C = 700$ K). It is of note that although Y^{3+} (0.1019 nm) is slightly larger than Ho^{3+} (0.1015 nm), $\text{Y}_2\text{Sn}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$ have a higher irradiation resistance (i.e., a higher critical dose for amorphization or lower critical amorphous temperature) to ion beam induced amorphization than $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, respectively. This deviation for yttrium pyrochlores is consistent with the mass of yttrium (88.906 g/mol) which almost half of that of holmium (164.93 g/mol). Which will lead to low density, small energy deposition (both electronic and nuclear), the deeper ion range and more easily transform to fluorite structure than holmium pyrochlores [194,195].

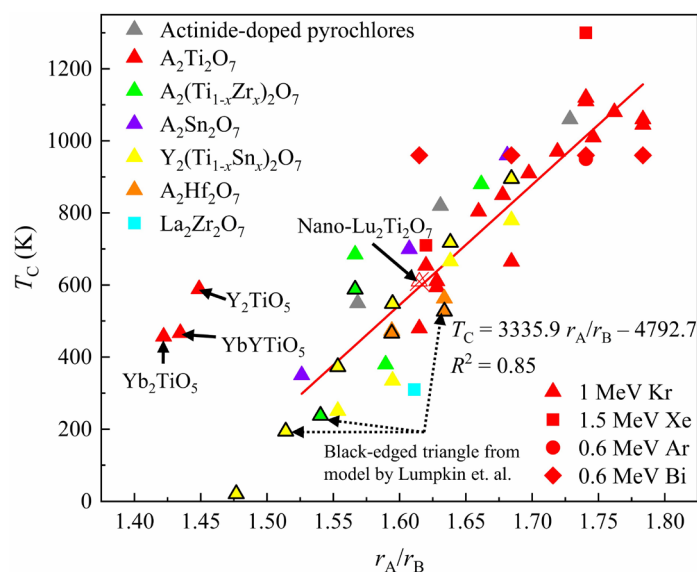


Figure 13. The critical amorphization temperature T_C of pyrochlores irradiated by ions as a function of the cation ionic radius ratio r_A/r_B . The triangle, square, circle, and rhombus represent irradiated ions 1 MeV Kr, 1.5 MeV Xe, 0.6 MeV Ar, and 0.6 MeV Bi, respectively. Grey, red, green, purple, yellow, orange, and blue represent actinide doped pyrochlores [66], titanate pyrochlores ($\text{A}_2\text{Ti}_2\text{O}_7$) [68,93,133,190–192,195], Zr-doped titanate pyrochlores ($\text{A}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$) [55,139], stannate pyrochlores ($\text{A}_2\text{Sn}_2\text{O}_7$) [55,194], Sn-doped yttrium titanate pyrochlores ($\text{Y}_2(\text{Ti}_{1-x}\text{Sn}_x)_2\text{O}_7$) [55], hafnate pyrochlores ($\text{A}_2\text{Hf}_2\text{O}_7$) [55], and lanthanide zirconate pyrochlores ($\text{La}_2\text{Zr}_2\text{O}_7$) [91], respectively. Additionally, the triangles with black edges represent data [55] calculated from the model proposed by Lumpkin et al. (Equation (2) in Ref. [196]). The red solid line is obtained by linear fitting all data points irradiated by 1 MeV Kr ion, except the three points with black arrows (Y_2TiO_5 , Yb_2TiO_5 and YbYTiO_5) and the data marked by black-edged triangles.

This more complex behavior of different types of pyrochlores may reflect different cation electronic configurations in bond type. The stronger covalent character of the $\langle \text{Sn-O} \rangle$ bond of stannate pyrochlores implies a lesser degree of distortion of the SnO_6

coordination octahedron which result in a structure more close to the ordered pyrochlore superstructure [198]. For example, the $\langle \text{Sn-O} \rangle$ bond length in $\text{Gd}_2\text{Sn}_2\text{O}_7$ is approximately 0.2048 nm, which is smaller than the sum of the effective ionic radii of O^{2-} (0.138 nm for CN = 4) and Sn^{4+} (0.069 nm for CN = 6), implying the more covalent for the $\langle \text{Sn-O} \rangle$ bond. Thus, the position parameter of O_{48f} (x_{48f}) reported for $\text{Gd}_2\text{Sn}_2\text{O}_7$ (0.3348) is slightly lower than $\text{Nd}_2\text{Zr}_2\text{O}_7$ (0.335) although that the cation radius ratio of $\text{Nd}_2\text{Zr}_2\text{O}_7$ (1.540) is greater than that of $\text{Gd}_2\text{Sn}_2\text{O}_7$ (1.526) [35]. Additionally, it lead to a greater susceptibility of stannate pyrochlore to ion irradiation induced amorphization, comparing with the titanate, hafnate, and zirconate pyrochlores with similar r_A/r_B .

First-principle calculations based density-functional theory (DFT) point that a conspicuous covalency for the $\langle \text{Sn-O} \rangle$ bond and mainly ionic character for the $\langle \text{Ti-O} \rangle$, $\langle \text{Hf-O} \rangle$ and $\langle \text{Zr-O} \rangle$ bonds [117,196,199]. Depending on the Mulliken overlap population analysis [196], the covalency of $\langle \text{B-O} \rangle$ bonds increases in the order $\text{Sn} > \text{Ti} > \text{Hf} > \text{Zr}$ and this trend roughly follows that of Pauling's electronegativity. Additionally, the disordering energies (the energy difference between the fully ordered pyrochlore and the fully disordered defect-fluorite structures) of $\text{A}_2\text{B}_2\text{O}_7$ were calculated and result implies that for zirconate, hafnate, and stannate pyrochlores, disordering energy approximately linear increases with increasing A^{3+} size [37]. However, the titanate pyrochlore series have a maximum disordering energy at $\text{Gd}_2\text{Ti}_2\text{O}_7$ [37] which has the highest critical amorphization temperature among all titanate pyrochlores [195]. Other theoretical calculation based empirical potentials [38,47,48] or DFT [200], showing agreement with these results. Disordering energies of stannate pyrochlores are significantly higher than corresponding titanate pyrochlores, although the ionic radius of Sn^{4+} (0.069 nm) is much larger than that of Ti^{4+} (0.0605 nm). Furthermore, it is obvious that the disordering energy of a given hafnate pyrochlore is always larger than that of its corresponding zirconate substitution, despite the very similar ionic radius of Zr^{4+} (0.072 nm) and Hf^{4+} (0.071 nm) [37]. Such phenomena also can be revealed that the covalency of $\langle \text{B-O} \rangle$ increases in order of $\text{Sn} > \text{Ti} > \text{Hf} > \text{Zr}$, which cannot be simply explained by the r_A/r_B . The phase transform temperature of the order-disorder transition also proves above conclusion [201,202].

5.3.2. Recover Process

Re-crystallization process of fully amorphous pyrochlores has also been investigated. Firstly, amorphous materials crystallize to form a disorder fluorite structure; then, the stable pyrochlore phase is recovered. Temperatures of forming defective fluorite structure and pyrochlore structure are related to the irradiation resistance. For example, for $\text{Nd}_2\text{Zr}_2\text{O}_7$, the formation of fluorite structure occurred at 598 K [62], while the temperature of crystallization of $\text{Gd}_2\text{TiZrO}_7$ is 948 K [153], indicating that the amorphous phase is less stable in $\text{Nd}_2\text{Zr}_2\text{O}_7$ than in $\text{Gd}_2\text{TiZrO}_7$, and, as we all knew, $\text{Nd}_2\text{Zr}_2\text{O}_7$ has better irradiation resistance than $\text{Gd}_2\text{TiZrO}_7$. The annealing process is different for $\text{Gd}_2\text{Ti}_2\text{O}_7$, which shows that the recrystallization of amorphization towards its pyrochlore structure occurs directly at 1073 K [153]. It is due to the extortionate formation energy of cation antisite defects to no thermal cation disordering could occur [39,203]. Park et al. [204] pointed that the recrystallization process depends on the energy difference between the amorphous and possible crystalline structures, because of the different driven force of the atomic rearrangements to recover the structures. $\text{La}_2\text{Ti}_2\text{O}_7$ has a higher structural freedom degree, fewer structural constraints, than $\text{Gd}_2\text{Ti}_2\text{O}_7$, hence, a lower energetic barrier to rearrangement is, which lead to a lower onset crystallization temperature than that of $\text{Gd}_2\text{Ti}_2\text{O}_7$ [204]. The formation enthalpies of those compounds could be another piece of evidence. $\text{Gd}_2\text{Ti}_2\text{O}_7$ has a formation enthalpy of -3822.5 kJ/mol which is 33 kJ/mol higher than that of $\text{La}_2\text{Ti}_2\text{O}_7$ [205]. Chung et al. [41,42] suggest that use amorphization enthalpy accounting for all the factors that affect the amorphization resistance as a more effective parameter to predict the irradiation toleration of a given chemical composition pyrochlore. Additionally, this method can also be used for other potential waste form material research [206]. Combing high temperature differential scanning calorimetry (DSC)

and neutron total scattering experiments, the damage recovery process of pyrochlore is shown a complex multistep processes with decoupled long-range recrystallization and short-range defect recovery operation at different temperature and time scales [41,42]. The disorderd and the amorphous pyrochlores have a similar local atomic arrangements described as weberite-like [36,44,46], which explains the onset temperatures for the second event of $\text{Dy}_2\text{Ti}_2\text{O}_7$ [42], $\text{Dy}_2\text{Sn}_2\text{O}_7$ [41], $\text{Er}_2\text{Ti}_2\text{O}_7$ [45], and $\text{Gd}_2\text{Ti}_2\text{O}_7$ [204] are all close to 1148 K (the thermal energies required to trigger the effective atomic movements for the local structural re-arrangement for different compositions are nearly identical). Yet the initial long-range recrystallization temperatures are compositionally dependent, which is conformity to the experimental results mentioned above. Although the re-crystallization processes are multifaceted, the initial crystalline temperature increase with the increasing of r_A/r_B , globally [41,42,45,62,153,204,207]. Atom-scale simulations based on density functional theory have revealed that differences between the formation enthalpies or disordering enthalpies of weberite-type and defect fluorite for $\text{A}_2\text{Sn}_2\text{O}_7$ and $\text{A}_2\text{Ti}_2\text{O}_7$ are nearly constants, respectively, while the formation enthalpy of pyrochlore is composition dependent [208,209]. Additionally, those DFT simulations also suggest that the weberite-type structure is more energetically stable than the fully ordered pyrochlore structure for most zirconate and hafnate pyrochlores while almost the whole titanate and stannate pyrochlores prefer ordered pyrochlore structure [208,209]. Janish et al. [105] show the re-crystallization process of $\text{Gd}_2\text{Ti}_2\text{O}_7$ amorphized by He ion irradiation. The results show that at lower temperature (1098 K), the initial recrystallization starts at the interface between the irradiated and unirradiated material, where the primary pyrochlore acts as a center of nucleation, but the new crystal grain grown is quickly hindered by the porous network of the He implanted region. At higher temperature (1148 K), the recrystallization front occurs at the top of the porous zone, which the He bubbles act as the nucleation center [105].

5.4. Size Dependence

It is worth mentioning that the critical amorphous dose of material and critical amorphous temperature of the material are also affected by the grain size. Zhang et al. [210] have systematically studied the Kr irradiation induced amorphous response to $\text{Gd}_2(\text{Ti}_{0.65}\text{Zr}_{0.35})_2\text{O}_7$ with different processing temperature and corresponding crystal size. $\text{Gd}_2(\text{Ti}_{0.65}\text{Zr}_{0.35})_2\text{O}_7$ powders maintain nanocrystal (~18 nm) annealing at less than 1000 °C, and are not completely amorphous under 1MeV Kr irradiation at room temperature (partially amorphous with ~1.72 dpa for 1000 °C), whereas the critical amorphous dose of larger-grained crystals (more than 100 nm) is ~0.73 dpa [210], which is similar to Wang's result ($D_C = 0.66$ dpa) [139]. Wen et al. [93] have reported that the grain nanomatization improves the critical amorphous dose at room temperature and the critical amorphous temperature of titanate pyrochlores. On the one hand, the defect formation energy is reduced as the defect is formed closer to the surface, which indicates that, at the same defect concentration, the larger specific surface areas, the lower average defect formation energy is [93]. Which also explains the variation of the degree of disordering as grain size, e.g., occupancy of Gd in 16c changes from 0.57 to 0.87 as the crystal size changing 17 to 380 nm, although most variation occurs at annealing temperatures during 1273 K (~18 nm, occupancy 0.57) and 1473 K (~100 nm, occupancy 0.8) [210,211]. Furthermore, susceptibility of pyrochlores to amorphization has been proved to be related to the energetics of disordering [39]. Thus, nanomaterials can able to tolerate disorder defects in the structure than coarse crystal materials, that is, higher radiation-induced amorphous resistance. Similarly, enhanced irradiation resistance has been shown in other nanomaterials including alloys and ceramics, e.g., Au (~23 nm) [212], Pd (<30 nm) [213,214], TiNi alloy (23–31 nm) [215], MgGa_2O_4 (4–12 nm) [216], CePO_4 (20 nm or 40 nm) [134] and ZrO_2 (<15 nm) [213,214]. On the other hand, MD simulations have shown that the interfaces especially, grain boundary, act a sink to effectively annihilate defects, facilitating the self-healing of the radiation-induced damage [217,218]. The cell volume expansion, the amorphization fraction and the threshold He or Xe concentrations of bubble formation are size dependent for $\text{Gd}_2\text{Zr}_2\text{O}_7$ [94,170]. For example, as the average grain size ranges from 221 to 55 nm, the

He concentration thresholds for helium bubble nucleation along grain boundaries, formation of helium bubble chains within the grain, and intragranular ribbon helium bubbles are 1.7% to 2.8%, 5.9% to 15.2%, and 19.2% to more than 25.8%, respectively [170]. However, nano-crystalline materials are not intrinsically radiation-tolerant, and an optimized size regime may exist that displays the greatest radiation tolerance against amorphization [134,210]. Meldrum et al. [219] found that nano-crystalline ZrO_2 (~3 nm) embedded in an amorphous SiO_2 matrix is completely amorphous with a dose of 0.9 dpa at ambient temperature, while bulk pure ZrO_2 cannot be amorphized even at very high ion doses of 680 dpa [220]. Similarly, for monazite CePO_4 , nanoparticles show lower critical temperature and higher critical dose than their bulk counterpart (~450 K), whereas, ~20 nm size CePO_4 nanoparticles shows a higher critical temperature (~435 K) and lower critical dose (~0.35 dpa) than the 40 nm sized monazite (~413 K, ~0.47 dpa) [134,221]. This phenomenon has been attributed to the delicate balance between the bulk free energy and surface free energy of polymorphs and the defect free energy introduced by energetic ions [219]. A small grain size has two opposing effects on the energy of an irradiated material: (i) a smaller grain size hinders the accumulation of vacancies in the grain interior, which decreases the free energy resulting from irradiation-induced defects; and (ii) a smaller grain size increases the free energy resulting from the grain boundary [222]. The higher density defect and the higher surface free energy of ultrafine materials provide additional energy for the amorphous process. Thus, the grain size must be optimized.

6. Conclusions

6.1. Summary

During irradiation, pyrochlore ceramics lose their long-range order gradually, transform to defect fluorite structure, and eventually convert into amorphization. For swift ion irradiation, the morphology of ion track is core (amorphous) + shell (defect fluorite) ion track in pyrochlore, while for low energy implanted ion, loss their crystal structure through defect accumulation without obvious ion track. In addition, the cation radii ratio r_A/r_B is a key parameter of pyrochlore $A_2B_2O_7$, which is related to the lattice parameter, phase structure, properties, especially radiation resistance. Generally, cation radii ratio r_A/r_B plays a dominant role of the radiation response of different pyrochlore compositions, but the B site ionic species also shows significant influence of the radiation tolerance. The irradiation resistances of zirconate and hafnate pyrochlore are much stronger than that of titanate and stannate pyrochlore, which is mainly related to disordering energy. The weak covalency of $\langle \text{Zr-O} \rangle$ in zirconate pyrochlore enables to accommodate more defects and has lower disordering energy, which is the fundamental reason for the excellent irradiation resistance performance of zirconate pyrochlore. It is of great significance for the design of waste form for different waste streams.

6.2. Outlook

Although the research so far on pyrochlore ceramics has demonstrated their excellent radiation resistance and great potential as a candidate waste form for radioactive waste, further effort on some fundamental and processing aspects is still necessary. The areas identified for further investigation include but are not limited to the following.

Matrices with Zr, being the dominant B site metal hosted, are preferred as these materials offer great irradiation resistance. Doped Ti or other element on B site should also be investigated to further decreased leach rates or improve synthesis process on an industrial scale to find a balance between cost and performance. In recent years, high entropy materials have attracted a lot of attention. High entropy alloys show excellent properties in anti-irradiation applications [223–228], while high entropy ceramics as potential waste forms are rarely studied [77,107,229,230] and need to be comprehensive and in-depth research. The maximum amount of radionuclide solidification needs to be accurately studied, which is essential for industrial applications and the development of safety guidelines. Additional methods such as glass-ceramic should be investigated. This would result in further increased stability but also limit the load density of radionuclides.

The ion irradiation experiment is an accelerated simulation test of radionuclides self-irradiation in waste forms. There is a distinct lack of literature comparing the ion irradiation test to actual radionuclides self-irradiation. Additionally, for long term geological disposition, a long-term ion irradiation test, and an industrial scale synthesis and irradiation study are necessary. This review mainly focuses on the irradiation damage on pyrochlores, but the leaching studies of pyrochlores are equally important, especially the long-term leaching research and irradiation damage coupled leaching study which are heavily lacking.

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Appendix A

The ion irradiation experiences mentioned and other reported in literature are summarized in Table A1, including composition, irradiation ion, the range of flux or fluence, critical amorphization dose or fluence and corresponding reference.

Table A1. Summary of publications of pyrochlore ion-irradiation.

Composition	Irradiation Ion	Range of Flux or Fluence	D_C or F_C	Ref.
Gd ₂ Ti ₂ O ₇	3 MeV Ar	5×10^{13} – 3×10^{16} ions/cm ²		[231]
Gd ₂ Ti ₂ O ₇ Er ₂ Ti ₂ O ₇ Lu ₂ Ti ₂ O ₇ CaZrTi ₂ O ₇	1.5 MeV Xe, 1 MeV Kr, 0.6 MeV Ar 20–1073K	8.5×10^{11} ions/cm ² /s	0.23 dpa (RT) 0.25 dpa (RT) 0.51 dpa (RT)	[102,133]
Gd ₂ Ti ₂ O ₇ Sm ₂ Ti ₂ O ₇ Eu ₂ Ti ₂ O ₇ Y ₂ Ti ₂ O ₇	1 MeV Kr 25–1023 K	8.5×10^{11} ions/cm ² /s	~0.5 dpa (RT) 0.8 dpa (RT)	[190]
Gd ₂ (Ti _{2-x} Zr _x)O ₇ ($x = 0, 0.5, 1, 1.5, 2$)	1 MeV Kr 20–1100 K		0.2 dpa (320–500 K) for $x = 0$	[139]
Gd ₂ (Ti _{2-x} Zr _x)O ₇ ($x = 0, 0.5, 1, 1.5, 2$)	2 MeV Au RT	5×10^{14} ions/cm ²	3×10^{14} ions/cm ² for $x = 0$	[138]
Gd ₂ (Ti _{0.65} Zr _{0.35})O ₇	1 MeV Kr	2.5×10^{15} ions/cm ²	0.73 dpa (FA, coarse-grained, >100 nm) 1.75 dpa (PA, nanocrystal, <20 nm)	[210]
A ₂ Ti ₂ O ₇ (A = Y, Sm, Gd, Lu)	2 MeV Au RT		0.18 ± 0.01 dpa (RT)	[191]
Sm ₂ Ti ₂ O ₇	1 MeV Au (170, 300, 700 K)	1×10^{12} – 8×10^{13} ions/cm ²	0.14, 0.14, 0.22 dpa for 170, 300, 700 K	[184]

Table A1. Cont.

Composition	Irradiation Ion	Rang of Flux or Fluence	D_C or F_C	Ref.
$A_2Zr_2O_7$ ($A = La, Nd, Sm, Gd$)	1.5 MeV Xe 25–300 K	8.6×10^{11} ions/cm ² /s	5.5 dpa (RT) and 0.65 dpa (25 K) for $La_2Zr_2O_7$	[91]
$Gd_2Zr_2O_7$	200 keV Ti RT	10^{17} ions/cm ²		
Single crystal $Er_2Ti_2O_7$ Single crystal $Er_2Zr_2O_7$	350 KeV Xe ⁺⁺ 120 K	1×10^{15} – 5×10^{16} ions/cm ²	1×10^{15} ions/cm ²	[39,232]
$(La_{1-x}Ce_x)_2Zr_2O_7$ ($x = 0, 0.1, 0.2, 1$)	1 MeV Kr 25 K and RT	1.25×10^{12} ions/cm ² /s	3.42 dpa (RT) and 1.19 dpa (25 K) for $x = 0$; 3.55, 5.20, 7.08 dpa (25 K) for $x = 0.1, 0.2, 1$	[65]
$An_2Zr_2O_7$ $An = Am, Cm, Bk, Cf$	Self-irradiation			[233,234]
Single crystal $A_2Ti_2O_7$ ($A = Sm, Eu, Gd, Dy$ and Er)	1 MeV Kr (RT)	5×10^{14} ions/cm ² (1.74×10^{14} ions/cm ² for Er)	0.11, 0.138, 0.143, 0.160, 0.229 dpa (RT) respectively	[103]
Single crystal $A_2Ti_2O_7$ ($A = Sm-Lu, Y$)	1 MeV Kr (RT–1073 K)	6.25×10^{11} ions/cm ² /s	0.25, 0.23, 0.18, 0.11, 0.25, 0.27, 0.25, 0.45, 0.55, 0.37 dpa (RT) for $A = Sm-Lu, Y$	[195]
$A_2Sn_2O_7$ ($A = La-Lu, Y$)	1 MeV Kr (25–973 K)	6.25×10^{11} ions/cm ² /s	0.32, 0.61, 1.41, 3.40 dpa (RT) for $A = La, Nd, Eu, Gd$; 0.37, 0.81, 2.57, 4.36 dpa (25 K) for $A = Nd, Gd, Dy, Ho$.	[194]
$Gd_2Sn_2O_7$ $Gd_2Hf_2O_7$	1 MeV Kr (25–300 K)	1.25×10^{12} ions/cm ² /s	3.4 dpa (RT) 4.54 dpa (RT), NA	[197]
$Ca_{1.04}Ce_{0.97}Ti_{1.99}O_{6.96}$, $Ca_{0.62}Gd_{0.97}U_{0.23}(Zr_{0.84}Ti_{1.34})O_{6.90}$ $Ca_{0.47}Gd_{0.95}Th_{0.40}Zr_{1.29}Ti_{0.89}O_{7.05}$, ($Ca_{0.44}GdTh_{0.42}Zr_{2.13}O_{7.05}$, $Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09}$,	1 MeV Kr (293–1173 K)		2.0×10^{14} ions/cm ² (RT) 3.75×10^{14} ions/cm ² (RT) 5.62×10^{14} ions/cm ² (RT) NA NA	[66]
$Nd_2Zr_2O_7$ $Gd_2Zr_2O_7$ $Gd_2Ti_2O_7$	120MeV Au 90MeV I 70MeV Ni	1×10^{12} – 1×10^{14} ions/cm ² 3×10^{10} ions/cm ² /s		[67]
$Gd_2Ti_2O_7$ Gd_2ZrTiO_7 $Gd_2Zr_2O_7$	4 MeV Au 1.5 GeV Xe 2.6 GeV U	1×10^{12} – 1×10^{16} ions/cm ² 1×10^{11} – 5×10^{12} ions/cm ²	0.4 dpa 0.8 dpa	[54]
$Gd_2Zr_{2-x}Ti_xO_7$ ($x = 0, 0.5, 1, 1.5, 2$)	1.43 GeV Xe; 4 GeV Xe 7 GeV U (10, 20, 40 GPa)	1×10^{10} – 1×10^{13} ions/cm ² $\sim 3 \times 10^{12}$ ions/cm ²		[140,141]
$Y_2Ti_{2-x}Sn_xO_7$ ($x = 0, 0.4, 0.8, 1.2, 1.6, 0$) $La_2Hf_2O_7$, $La_{1.6}Y_{0.4}Hf_2O_7$ $Nd_2Zr_2O_7$, $Nd_2Ti_{0.8}Zr_{1.2}O_7$	1 MeV Kr (50–650 K)	6.25×10^{11} ions/cm ² /s	6.4, 23.4, 26.6, 5.3×10^{14} ions/cm ² (RT) for $x = 0.4, 0.8$, and $La_{1.6}Y_{0.4}Hf_2O_7$, $Nd_2Ti_{0.8}Zr_{1.2}O_7$	[55]
$Am_2Zr_2O_7$	Self-irradiation (α -decay)	40 days (0.02 dpa) 370 days (0.21 dpa)		[189]
100-oriented single crystals YSZ	940 MeV Pb 850 MeV Xe 2.6 GeV U	1×10^{10} – 1×10^{13} ions/cm ² 1×10^8 ions/cm ² /s		[152]

Table A1. Cont.

Composition	Irradiation Ion	Rang of Flux or Fluence	D_C or F_C	Ref.
$\text{REE}_2(\text{U}_{0.06}\text{Sn}_{1.94})\text{O}_7$ $\text{REE}_2(\text{U}_{0.06}\text{SnZr}_{0.94})\text{O}_7$ $\text{REE}_2(\text{U}_{0.06}\text{Zr}_{1.94})\text{O}_7$ $\text{REE} = 0.12\text{La} + 0.24\text{Ce} + 0.10\text{Pr}$ $+ 0.38\text{Nd} + 0.08\text{Sm} + 0.05\text{Eu} + 0.03\text{Gd}$	1 MeV Kr	1×10^{14} ions/cm ² /s		[235]
$\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ $(x = 0, 1, 2)$	870 MeV Xe 780 MeV Kr (RT)	1×10^{10} – 1×10^{13} ions/cm ² 1×10^8 ions/cm ² /s		[60]
$\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ ($x = 1, 2$)	870 MeV Xe	2×10^{11} – 1×10^{13} ions/cm ²		[236]
Single crystal $\text{Ho}_2\text{Ti}_2\text{O}_7$	1.0 MeV Au (300 K, 7° off <001> direction)	2×10^{12} – 3.1×10^{13} ions/cm ²	0.12 dpa	[104]
$\text{Lu}_2(\text{Ti}_{2-x}\text{Lu}_x)\text{O}_{7-x/2}$ $(x = 0, 0.4, 0.67)$	400 keV Ne (77 K)	1×10^{15} – 1×10^{16} ions/cm ² 1×10^{12} ions/cm ² /s		[56]
$\text{Y}_2\text{Ti}_2\text{O}_7$ $\text{Yb}_2\text{Ti}_2\text{O}_7$ Y_2TiO_7 YbYTi_2O_7 $\text{Yb}_2\text{Ti}_2\text{O}_7$	1 MeV Kr (50–650 K)	6.25×10^{11} ions/cm ² /s		[68]
Gd_2TiO_5 , $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{TiZrO}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$ $\text{REE}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$, $x = 0$ – 1 $\text{REE} = 0.24\text{La} + 0.46\text{Ce} + 0.21\text{Pr}$ $+ 0.75\text{Nd} + 0.15\text{Sm} + 0.02\text{Eu} + 0.03\text{Gd} + 0.14\text{Y}$	1.1 GeV Ru 2.2 GeV Au (8 K or 300 K) 1 MeV Kr (RT)	5×10^{10} – 1×10^{11} ions/cm ² 1×10^8 ions/cm ² /s	0.3 dpa for $\text{REE}_2\text{Ti}_2\text{O}_7$	[137] [237,238]
$\text{Er}_2\text{Ti}_2\text{O}_7$	400 keV Ne (77 K)	2×10^{18} – 2×10^{19} ions/cm ² 1×10^{16} ions/cm ² /s		[71]
$\text{Y}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Hf}_2\text{O}_7$	400 keV Ne (77 K)	5×10^{14} – 6×10^{16} ions/cm ² 1×10^{12} ions/cm ² /s		[72,239]
$\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{ZrTiO}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$, $\text{Eu}_2\text{Zr}_2\text{O}_7$, $\text{Sm}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$	120MeV U RT	2×10^{11} – 4×10^{13} ions/cm ² 2×10^9 ions/cm ² /s		[142]
$\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$, $\text{Eu}_2\text{Zr}_2\text{O}_7$, $\text{Sm}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$	119MeV U RT	2×10^{11} – 4×10^{13} ions/cm ² 1×10^8 ions/cm ² /s		[61]
A_2TiO_5 $\text{A} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}$	1.47 GeV Xe (RT)			[240]
Nd_2TiO_5 Gd_2TiO_5 Yb_2TiO_5	2.2 GeV Au (RT)	-3×10^{13} ions/cm ²	$\sim 7.5 \times 10^{12}$ ions/cm ² $\sim 1.5 \times 10^{13}$ ions/cm ² $\sim 3 \times 10^{13}$ ions/cm ²	[207]

Table A1. Cont.

Composition	Irradiation Ion	Rang of Flux or Fluence	D_C or F_C	Ref.
Nd ₂ Zr ₂ O ₇	4 MeV Au	1×10^{12} – 1×10^{16} ions/cm ²		[62]
	74 MeV Kr 92 MeV Xe 119 MeV U 900 MeV U 940 MeV Pb	2×10^{11} – 2×10^{14} ions/cm ² 2×10^9 ions/cm ² /s		
Gd ₂ Zr _{2-x} Ti _x O ₇ ($x = 0, 0.5, 1, 1.5, 2$)	⁵⁸ Ni, ¹⁰¹ Ru, ¹²⁹ Xe, ¹⁸¹ Ta, ¹⁹⁷ Au, ²⁰⁸ Pb, ²³⁸ U 11.1MeV/u RT	5×10^9 – 2×10^{14} ions/cm ² 1×10^8 ions/cm ² /s		[135]
Gd ₂ Ti ₂ O ₇ , La ₂ Ti ₂ O ₇	2.0 GeV Ta (RT)	1×10^{10} – 1×10^{13} ions/cm ²		[204]
A ₂ Ti ₂ O ₇ A = Gd, Y	92 MeV Xe (RT) 109 MeV U (RT)	2×10^{11} – 2×10^{16} ions/cm ² 5×10^{12} ions/cm ²	5, 10 $\times 10^{12}$ ions/cm ² for A ₂ Ti ₂ O ₇	[63]
Lu ₂ Ti ₂ O ₇	600 keV Kr (RT, 723 K)	4×10^{15} ions/cm ² 1×10^{12} ions/cm ² /s		[241]
Lu ₂ (Ti _{2-x} Lu _x)O _{7-x/2} $x = 0$ – 0.667	2.7 MeV Ar	2×10^{14} – 8×10^{14} ions/cm ²		[171]
Gd ₂ Zr ₂ O ₇	12 MeV C ₆₀ 2.6 GeV U	1×10^{11} ions/cm ² 5×10^{11} ions/cm ²		[242]
	30 MeV C ₆₀ 1.5 GeV U	5×10^{10} – 1×10^{11} ions/cm ²		[177]
Lu ₂ Ti ₂ O ₇	200 keV He	2×10^{15} – 2×10^{17} ions/cm ²		[166]
Gd ₂ Zr ₂ O ₇	120MeV Au RT	3×10^{11} – 1×10^{14} ions/cm ²		[69]
Gd ₂ Zr ₂ O ₇	320 MeV Ar	2×10^{14} – 1×10^{16} ions/cm ²		[243]
A ₂ Ti ₂ O ₇ (A = Yb, Er, Y, Gd, Sm)	2.2GeV Au	5×10^{10} – 3×10^{13} ions/cm ²		[244]
Er ₂ Sn ₂ O ₇ Dy ₂ Sn ₂ O ₇ Dy ₂ Ti ₂ O ₇	2.2 GeV ¹⁹⁷ Au RT (2.1GeV, after Al foil)	8×10^{12} ions/cm ²		[41,42,44,46]
Er ₂ Ti ₂ O ₇	2.2 GeV Au RT	5×10^{12} ions/cm ²		[45]
Y ₂ Ti ₂ O ₇	93 MeV Xe	2×10^{11} – 1×10^{13} ions/cm ²		[188]
Gd ₂ Zr ₂ O ₇	7 MeV Au + 200 keV He or 65 keV He	2.2×10^{15} 2×10^{15} – 2×10^{16} 2×10^{17} ions/cm ²		[167]
	1 MeV Kr (RT–600 K)	6.25×10^{11} ions/cm ² /s	0.36, 0.53, 0.81 dpa (RT), respectively	[93]
Nd ₂ Zr ₂ O ₇	0.5 MeV He	1×10^{14} – 1×10^{17} ions/cm ²		[245]
(Gd _{1-4x} U _{2x}) ₂ (Zr _{1-x} U _x) ₂ O ₇ ($x = 0, 0.1, 0.14$)	1.5 MeV Xe	1×10^{12} – 1×10^{15} ions/cm ² 5×10^{11} ions/cm ² /s		[246,247]

Table A1. Cont.

Composition	Irradiation Ion	Rang of Flux or Fluence	D_C or F_C	Ref.
$\text{Lu}_{2-x}\text{Ce}_x\text{Ti}_2\text{O}_7$ $x = 0-0.7$	400 keV Ne	$1 \times 10^{14}-2 \times 10^{15}$ ions/cm ²		[248]
$\text{Gd}_{1.891}\text{}^{244}\text{Cm}_{0.091}\text{Pu}_{0.013}\text{Sn}_2\text{O}_7$	Self-irradiation		1.52 dpa (RT)	[249]
$\text{La}_2\text{Zr}_2\text{O}_7$	1 MeV Zr	$3.98 \times 10^{13}-7.96 \times 10^{14}$ ions/cm ²		[250]
$\text{Gd}_2\text{Zr}_2\text{O}_7+x\text{TRPO}$ $x = 0, 25, 40\text{wt}\%$	0.5 MeV He	$1 \times 10^{14}-1 \times 10^{17}$ ions/cm ² /s		[168]
$\text{Lu}_2\text{Ti}_2\text{O}_7$	0.4 MeV Ne (77 K) 2.7 MeV Ar, 6.5 MeV Xe (RT)	1×10^{12} ions/cm ² /s		[57]
$(\text{Gd}_{1-x}\text{Nd}_x)_2(\text{Zr}_{1-y}\text{Ce}_y)_2\text{O}_7$ ($0 \leq x, y \leq 1$)	0.5 MeV He	$1 \times 10^{15}-1 \times 10^{17}$ ions/cm ² /s		[169,251]
$\text{Gd}_2\text{Zr}_2\text{O}_7, \text{Nd}_2\text{Zr}_2\text{O}_7,$ $\text{Nd}_2\text{Ce}_2\text{O}_7$	2.0 MeV Xe	$4.08 \times 10^{13}-5.28 \times 10^{16}$ ions/cm ² /s		[252,253]
$\text{Nd}_2\text{Zr}_2\text{O}_7, \text{Sm}_2\text{Zr}_2\text{O}_7,$ $\text{Er}_2\text{Zr}_2\text{O}_7$	2.2 GeV Au	$5 \times 10^{10}-3 \times 10^{13}$ ions/cm ²		[254]
$\text{Gd}_2\text{Ti}_2\text{O}_7, \text{Sm}_2\text{Ti}_2\text{O}_7,$ $\text{Yb}_2\text{Ti}_2\text{O}_7, \text{Gd}_2\text{ZrTiO}_7$	55 MeV I	5×10^{10} ions/cm ²		[255]
$\text{Nd}_2\text{Zr}_2\text{O}_7$ $\text{Nd}_{1.9}\text{U}_{0.1}\text{Zr}_2\text{O}_7$	2 MeV Kr	$6 \times 10^{15}, 2 \times 10^{16}$ ions/cm ²		[256]
$\text{Gd}_2\text{Ti}_2\text{O}_7, \text{Gd}_2\text{Zr}_2\text{O}_7$	400 keV Kr	5.36×10^{16} ions/cm ²		[58]
$\text{Gd}_2\text{Zr}_2\text{O}_7$	190 keV He	5×10^{17} ions/cm ²		[170]
$\text{Nd}_2\text{Zr}_2\text{O}_7$	100 MeV Ag (RT, 1000 K)	$3 \times 10^{11}-2 \times 10^{13}$ ions/cm ²		[257]
$\text{Gd}_2\text{Zr}_2\text{O}_7 + 35\text{wt}\%\text{TRPO}$	0.5 MeV He	$1 \times 10^{15}-1 \times 10^{17}$ ions/cm ²		[258]
Single-crystal $\text{Gd}_2\text{Ti}_2\text{O}_7$	190 keV He	1×10^{17} ions/cm ² /s	Re-crystallization	[105]
$\text{Gd}_2\text{Zr}_2\text{O}_7$	5 MeV Xe	$5 \times 10^{14}-4 \times 10^{15}$ ions/cm ²		[94]
$\text{Y}_{2-x}\text{A}_x\text{Ti}_2\text{O}_7 \pm \delta$ ($A = \text{U, Ce}; x =$ $0.05, 0.075, 0.10, 0.20, 0.30$)	^{60}Co (γ -source.)	1000 kGy 5.8 kGy/h		[95]
$\text{La}_2\text{Zr}_2\text{O}_7$	500 keV Kr 1 MeV Xe (88 K or 300 K)	$1 \times 10^{13}-1 \times 10^{14}$ ions/cm ²		[259,260]
$\text{Gd}_2(\text{Ti}_{2-y}\text{Zr}_y)\text{O}_7,$ ($y = 0, 0.4, 0.8, 1.2, 1.6, 2$)	120 MeV Au RT	$1 \times 10^{13}-1 \times 10^{14}$ ions/cm ²		[64]
Single crystal ($\text{Yb}_{0.2}\text{TM}_{0.2}\text{Lu}_{0.2}\text{Ho}_{0.2}\text{Er}_{0.2}$) ₂ Ti_2O_7	4 MeV Au RT (4° off normal surface)	$5 \times 10^{12}-6 \times 10^{14}$ ions/cm ² 4.2×10^{11} ions/cm ² /s	0.13 dpa	[107]
$(\text{La}_{0.2}\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$	9 MeV Au RT	4.5×10^{15} ions/cm ² /s		[77]
$(\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2})_2\text{Ti}_2\text{O}_7$	800 keV Kr RT		0.27 dpa	[230]

Note, NA, PA and FA means no amorphization, partial amorphization and fully amorphization, respectively.

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