***Ab initio* molecular dynamics simulations of ion-solid interactions in zirconate pyrochlores**

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Abstract

In this study, an *ab initio* molecular dynamics method is employed to study low energy recoil events in zirconate pyrochlores ($A_2Zr_2O_7$, $A=La, Nd$ and Sm). It shows that both cations and anions in $Nd_2Zr_2O_7$ and $Sm_2Zr_2O_7$ are generally more likely to be displaced than those in $La_2Zr_2O_7$. The damage end states mainly consist of Frenkel pair defects, and the Frenkel pair formation energies in $Nd_2Zr_2O_7$ and $Sm_2Zr_2O_7$ are lower than those in $La_2Zr_2O_7$. These results suggest that the order-disorder structural transition more easily occurs in $Nd_2Zr_2O_7$ and $Sm_2Zr_2O_7$ resulting in a defect-fluorite structure, which agrees well with experimental observations. Our calculations indicate that oxygen migration from $48f$ and $8b$ to $8a$ sites is dominant under low energy irradiation. A number of new defects, including four types of cation Frenkel pairs and six types of

anion Frenkel pairs, are revealed by *ab initio* molecular dynamics simulations. The present results may help to advance the fundamental understanding of the irradiation response behavior of zirconate pyrochlores.

Keywords: Computer simulation; Zirconate pyrochlores; Radiation effects; Charge transfer

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1. Introduction

Zirconate pyrochlores, with the chemical formula $A_2Zr_2O_7$ (where A is a rare earth element), have attracted considerable attention because of their potential use as solid oxide fuel cell electrode materials, fluorescence screens, thermal-barrier coatings, high-temperature heating elements, oxidation catalysts, and refractory ceramic materials for use in magnetohydrodynamic power generation.[1-8] Because they exhibit remarkable resistance to structural amorphization under ion-beam irradiation[6] and high chemical durability (release rates typically $<10^{-5}$ g.m⁻².d⁻¹ based on zirconium),[9] as well as the fact that zirconium has a low neutron absorption cross-section,[7] zirconate pyrochlores have also been proposed as inert matrix materials for actinide burning[7, 9] and host matrices for high level radioactive waste, especially for long half-life actinides.[10]

During the last few decades, a great number of investigations have been performed to understand the stability and response of pyrochlore oxides to irradiation.[4, 6, 11-15] The members of the isostructural pyrochlore family exhibit various responses to irradiation, depending on the chemical compositions. Generally, zirconate pyrochlores more readily accommodate structural disordering, and the disordered defect-fluorite structures are extremely stable under high dose irradiation. Wang et al. have reported that $Gd_2Zr_2O_7$ has a dramatically high radiation resistance to ion-beam-induced amorphization and remains crystalline at a dose of 5 dpa (1 MeV Kr⁺ at 25 K).[13] Sickafus et al. have found that $Er_2Zr_2O_7$ is radiation resistant and cannot be amorphized even at doses as high as 140 dpa by 350 keV Xe⁺ at room temperature.[14] Lian et al. investigated the radiation response of zirconate pyrochlores $A_2Zr_2O_7$ (A=La, Nd, Sm and Gd) under 1.5 MeV Xe⁺ irradiation, and found that $La_2Zr_2O_7$ was the only zirconate

pyrochlore that can be amorphized by these ion-beam irradiation conditions.[6] They suggested that the susceptibility to ion-beam damage for pyrochlore compounds was closely related to the deviation from the ideal fluorite structure, and pyrochlores that are structurally close to the fluorite structure have a greater tendency toward order-disorder transition and are more resistant to ion-beam-induced structural amorphization. Theoretically, Chartier et al. carried out molecular dynamics (MD) simulations of displacement cascades in $\text{La}_2\text{Zr}_2\text{O}_7$ using empirical fixed-charge potentials and suggested that point defect accumulation plays a major role in the amorphization process.[16] To explore the driving force for radiation-induced amorphization, Chartier et al. introduced different concentrations of antisites or Frenkel pairs (FPs) in $\text{La}_2\text{Zr}_2\text{O}_7$. They found that structural amorphization relies on the ability to reach a significantly high critical FP concentration before the crystalline structure collapses, and the accumulation of cation FPs is the main driving parameter for the amorphization.[4]

Atomistic simulations of ion-solid interaction have dramatically advanced the understanding of defect and defect processes in a number of nuclear materials, and the MD method using predefined atomic potentials has been well established as a powerful tool. However, most of the MD simulations employ empirical fixed-charge potentials, and the role of electrons and effects of variable charge states on defect production process cannot be described. While variable-charge potentials are of interest to simulate complex bonding and chemistry, particularly at interfaces, none have yet been developed or tested for the complex dynamics occurring during ion-solid interactions. In recent years, *ab initio* MD methods (AIMD), which offer a path that mixes the advantages of both MD and *ab initio* methods, have been employed to study low energy recoil events

in SiC, GaN, fluorite-structured oxides and pyrochlores.[17-21] In this method, the forces acting on the atomic nuclei are all computed on-the-fly based on electronic structure calculations. These studies demonstrated that the AIMD method can follow the electronic charge transfer during the collisions and predict new mechanism for defect generation as well as new defect states that are different from MD simulations employing empirical fixed-charge potentials, which has dramatically advanced the understanding of defect and defect processes in these materials.

In this study, the AIMD method is employed to investigate low energy recoil events in zirconate pyrochlores ($A_2Zr_2O_7$, $A=La, Nd$ and Sm). The threshold displacement energies, associated defects, stability of FPs, and role of charge transfer during the dynamic process are all determined. The radiation response of $La_2Zr_2O_7$ to low energy recoils is compared with that of $Nd_2Zr_2O_7$ and $Sm_2Zr_2O_7$, and the origin of the difference in radiation susceptibility is explored.

2. Computational details

The *ab initio* MD simulations were carried out using the modified SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code.[22] Norm conserving Troullier-Martins pseudopotentials[23] factorized in the Kleinman-Bylander form[24] were used to describe the interaction between ions and electrons, and the exchange-correlation functional was determined within the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof.[25] The reference electronic configurations employed for the La, Nd, Sm, Zr and O pseudopotentials and the pseudopotential core radii are provided in Table I. The valence

wavefunctions were expanded in a basis set of localized atomic orbitals, and single- ζ basis sets were used. All the simulations were conducted with a cell containing 176 atoms at a constant particle number and volume with periodic boundary conditions imposed along three directions. A cutoff energy of 150 Ry for the basis set and a K -point sampling of $1 \times 1 \times 1$ in the Brillouin zone were employed. A variable time step scheme was employed to avoid the instability of the simulations. An atom (La, Nd, Sm, Zr or O) was selected as the primary knock-on atom (PKA), and it was given a certain amount of kinetic energy, i.e., PKA energy, along a specific direction to initiate a recoil event. Under electron irradiation, the maximum energy transferred to an atom can be expressed as $T = 2E_e(E_e + 2m_e c^2) / M c^2$, where E_e is the incident energy, m_e is the electronic mass, M is the atomic mass and c is the velocity of light. Assuming 350 keV electrons incident on $\text{La}_2\text{Zr}_2\text{O}_7$, the maximum energy transfer to an oxygen atom is 64.4 eV. In this study, the PKA energy refers to the maximum transferred energy. For each PKA, recoils along three main crystallographic directions, i.e., $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$, as illustrated in Figure 1, were investigated.

3. Results and discussion

3.1. Structural and electronic properties of $\text{A}_2\text{Zr}_2\text{O}_7$ (A=La, Nd and Sm)

In $\text{A}_2\text{Zr}_2\text{O}_6\text{O}'$ pyrochlore structure, the A and Zr cations occupy $16d$ ($1/2, 1/2, 1/2$) and $16c$ ($0, 0, 0$) sites, respectively, and the oxygen anions are at the $48f$ ($x, 1/8, 1/8$) and O' $8b$ ($3/8, 3/8, 3/8$) positions (using Wyckoff notation), as presented in Fig. 1. The site of the missing oxygen that could complete the anion sublattice to form a fluorite structure is $8a$ ($1/8, 1/8, 1/8$). Geometrically, the A cations are coordinated to six $48f$

oxygen anions and two $8b$ oxygen anions, located within a distorted polyhedron; the Zr cations are six-coordinated to $48f$ oxygen anions in a distorted octahedron. The pyrochlore structure can be completely described by the cubic lattice constant a_0 and the $48f$ oxygen positional parameter x .

The optimized lattice parameters for $A_2Zr_2O_7$ ($A=La, Nd$ and Sm), as well as the bond distances between A and O_{48f} (d_{A-O48f}), A and O_{8b} (d_{A-O8b}), and Zr and O_{48f} ($d_{Zr-O48f}$), are summarized in Table II, together with available experimental and theoretical values. It is shown that our calculated structural parameters agree well with the experimental and theoretical values. Comparing the structural properties of $La_2Zr_2O_7$, $Nd_2Zr_2O_7$ and $Sm_2Zr_2O_7$, we find that there is a decrease in lattice constant and a slight increase in x_{O48f} with decreasing cation size, which is in good agreement with the experimental measurements reported by Lian et al. and Shimamura et al.[6, 7] As the cation varies from La to Sm, the d_{A-O48f} and d_{A-O8b} decrease by 0.06 and 0.03 Å, respectively, while the changes in $d_{Zr-O48f}$ are nearly negligible.

Sickafus et al. have predicted the radiation performance of a wide range of pyrochlore oxides based on a material's propensity to accommodate lattice point defects. They proposed that, with increasing cation radii ratio, the resistance to structural amorphization decreases, i.e., compounds with very dissimilar cation radii are more susceptible to lattice destabilization (and possible amorphization).[14] According to this criterion, zirconate pyrochlores with larger A radius, which exhibit larger cation radii ratio, are more likely to undergo amorphization. The radiation resistance of zirconate pyrochlores fortunately follows this criterion, whereas it is not applicable to titanate pyrochlores.[6, 26] Naguib and Kelly have discussed several criteria for resistance to

amorphization by radiation damage on the basis of experimental data on binary compounds.[27] In one criterion they have correlated the radiation tolerance of nonmetallic solids with the relative ionicity of the material, and suggested that materials with Pauling empirical ionicity lower than 0.47 are amorphized by irradiation, and those higher than 0.59 are not. Trachenko and co-workers have proposed that the radiation damage resistance of a complex nonmetallic material to amorphization is generally governed by the competition between the short-range covalent and long-range ionic forces, with covalency of bonding stabilizing the damage and making materials more amorphizable.[28, 29] In our calculations, the shorter $\langle\text{A-O}\rangle$ and $\langle\text{Zr-O}\rangle$ distances in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ suggest that these two zirconates are relatively more covalent materials than $\text{La}_2\text{Zr}_2\text{O}_7$, while $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ were observed to be more radiation resistant than $\text{La}_2\text{Zr}_2\text{O}_7$ experimentally,[6] indicating that the nature of the chemical bond is not the only factor determining the radiation resistance to amorphization.

To check the validity of the pseudopotentials employed in this study, the band gap for $\text{A}_2\text{Zr}_2\text{O}_7$ (A=La, Nd and Sm) are also calculated and compared with other calculations, as presented in Table II. The band gap values are predicted to be 3.33, 3.72 and 3.79 eV for $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, respectively. Uno et al. have investigated the band structure of zirconate pyrochlores based on density functional theory calculations using CASTEP code and reported the band gap values of 3.52 eV for $\text{La}_2\text{Zr}_2\text{O}_7$, 2.67 eV for $\text{Nd}_2\text{Zr}_2\text{O}_7$ and 2.86 eV for $\text{Sm}_2\text{Zr}_2\text{O}_7$. [8] Feng et al. considered Hubbard U corrections of the on-site Coulomb interactions in their calculations and suggested much larger band gap values, i.e., 4.1, 4.0 and 4.7 eV for $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and

$\text{Sm}_2\text{Zr}_2\text{O}_7$. [30] Unfortunately no experimental data are available for comparison and our results are purely predictive. Considering that standard density functional theory calculations usually underestimate the band gap, [20] our predictive results are expected to be smaller than experimental values.

3.2. Low energy recoil events in zirconate pyrochlores

One of the critical physical parameters for determining the primary state of radiation damage in a material and estimating the total number of defect states created under ion-irradiation is the threshold displacement energy (E_d). [31] This parameter is defined as the minimum amount of transferred kinetic energy necessary to permanently displace an atom from its original lattice site, thus forming a stable defect, such as a Frenkel pair. [20] In this study, the threshold displacement energies for A (A=La, Nd or Sm), Zr, O_{48f} and O_{8b} along the [100], [110] and [111] directions are determined. The details for determination of the threshold displacement energies have been described in our previous work. [19] The calculated values in each zirconate are summarized in Table III and are compared in Fig. 2.

Similar to $\text{Y}_2\text{Ti}_2\text{O}_7$, [32] $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$, [21] the threshold displacement energies are anisotropic, strongly dependent on the incidence direction. We find that, in each zirconate, the minimum E_d values are all along the [111] direction for A, O_{48f} and O_{8b} recoils. For Zr recoils, the minimum E_d values are along the [110], [111] and [100] for $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, respectively. Chartier *et al.* carried out MD simulations with empirical fixed-charge potentials on atomic displacement cascades in $\text{La}_2\text{Zr}_2\text{O}_7$ along fourteen different crystallographic directions. [16] It was suggested that the minimum values are 53 eV along the $[\bar{1}\bar{4}7]$, 68 eV along the [111], 6.7 eV along the

[012] and 7.0 eV along the [114] directions for La, Zr, O_{48f} and O_{8b}, respectively.[16] In this study, $[\bar{1}\bar{4}7]$, [012] and [114] are also considered for La, O_{48f} and O_{8b} in La₂Zr₂O₇, respectively. We find that the threshold displacement energies are 47 eV for La $[\bar{1}\bar{4}7]$, 36 eV for O_{48f}[012] and 23.5 eV for O_{8b}[114], which are larger than the minimum E_d values of 29.5 eV for La[111], 15.5 eV for O_{48f}[111] and 10.5eV for O_{8b}[111], respectively. The highest values in Nd₂Zr₂O₇ and Sm₂Zr₂O₇ are found to be along the [110] direction for cations and along the [100] direction for anions, while in La₂Zr₂O₇ the highest values are along the [110] and [111] direction for La and Zr, respectively, and along the [110] direction for anions. It is found that Sm₂Zr₂O₇ exhibits similar dependence on the incident direction as Gd₂Zr₂O₇. [21] Comparing the E_ds for cations and anions in zirconate pyrochlores, we find that generally considerably higher energies are needed for displacing the cations than for displacing the anions, similar to other oxides,[20, 21, 32] indicating that anion disorder is more easily involved in displacement events than cation disorder. It is notable that the E_d values for a certain species in Nd₂Zr₂O₇ and Sm₂Zr₂O₇ are nearly comparable to each other; however, the E_d values in La₂Zr₂O₇ are generally larger than those in Nd₂Zr₂O₇ and Sm₂Zr₂O₇. One exception is for A[110], in which case the E_d for Sm[110] is much larger than that for La[110] and Nd[110]. We find that the mechanism of defect generation for Sm[110] is more complex, as indicated by its damage end states summarized in Table IV. During the recoil event, Zr disorder is involved, and a Zr Frenkel pair defect is formed, which has not been observed for La[110] and Nd[110]. Furthermore, the number of anion disorder in Sm[110] is much greater than that in La[110] and Nd[110]. These results indicate that the energy barrier for defect generation in Sm [110] is much larger.

Our calculations show that the threshold displacement energies for cations and anions in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are generally smaller than those in $\text{La}_2\text{Zr}_2\text{O}_7$, and cation and anion disorder are induced, suggesting that $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are more likely to form defect-fluorite structures. Experimentally it has been observed that the defect-fluorite structure is radiation tolerant and structural amorphization does not occur. Our calculations thus indicate that $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are more resistant to ion-beam-induced amorphization than $\text{La}_2\text{Zr}_2\text{O}_7$, which agrees well with experimental observations.[6]

Table IV summarizes the defects created after displacement events. It appears that, for A and Zr recoils in different compositions, the defect end states exhibit much different character to each other, implying that the mechanism for defect generation are different. The created defects are mainly cation FPs and anion FPs. We note that antisite defects are also created in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, including Zr occupying the lattice Nd site, Nd occupying the lattice Zr or lattice O site in $\text{Nd}_2\text{Zr}_2\text{O}_7$ (in the case of Nd[100], Nd[110], Zr[100]), and Sm occupying the lattice Zr site or lattice O site in $\text{Sm}_2\text{Zr}_2\text{O}_7$ (in the case of Sm[111], Zr[100] and Zr[110]); however, antisite defects are not observed in $\text{La}_2\text{Zr}_2\text{O}_7$. This is somewhat different from the results of MD simulations performed by Chartier et al., who simulated single event displacement cascades in $\text{La}_2\text{Zr}_2\text{O}_7$ by a uranium PKA accelerated at 6 keV and found that the primary damage state consists of cation antisites and FPs.[16] Comparing the number of created defects in these three zirconates (see Fig. 3), we find that in most cases there are more defects created in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ than in $\text{La}_2\text{Zr}_2\text{O}_7$. The defects created after oxygen recoil events are also presented in Table IV. It is interesting to note that, except for the cases of

$O_{48f}[110]$ in $La_2Zr_2O_7$ and $O_{48f}[111]$ in $Nd_2Zr_2O_7$, the damage end states consist of only oxygen Frenkel pairs. It seems that the number of anion FPs created is smaller than that in $Gd_2Zr_2O_7$. [21]

3.3. Stability of Frenkel pair defects in zirconate pyrochlores

Our calculations suggest that the defects created by low energy recoils are mainly cation FPs and anion FPs. The A cation FPs (A=La, Nd and Sm) consist of an A vacancy and an A interstitial occupying the bridge site between A and Zr atoms, as illustrated in Figs. 4(a) and (b). Figures 4(c) and (d) provide the defect configurations for Zr cation FPs, in which the Zr interstitial occupies $8a$ or bridge sites. These four types of cation FPs are denoted as FP1, FP2, FP3 and FP4, respectively. The calculated formation energies, which are defined as the difference in the total energies between the ideal system and the defective system containing one FP pair, are listed in Table V, along with the FP separation. It is shown that in all cases FP1 is more stable than other cation FPs. Six types of anion FPs (see Fig. 5), which are denoted as FP1 to FP6, are also revealed from our AIMD simulations. It is noted that the oxygen interstitial in the anion FPs occupies the vacant $8a$ sites in most cases and oxygen migration from $48f$ or $8b$ to $8a$ sites are dominant under low energy recoil events. The stability of anion FPs has been investigated by Panero et al. using an *ab initio* method, in which the Frenkel pairs are formed by the reactions of $O_{48f} \rightarrow V_{48f} + O_{8a}$ and $O_{8b} \rightarrow V_{8b} + O_{8a}$. [33] They proposed that such defect structures were not stable in the absence of cation antisite defects, and the structure relaxation will cause oxygen to return to its initial position, which is in contrast with our results. This is because Panero et al. only considered a limited number

of anion FP configurations, and the anion FP configurations revealed in the present study were not taken into account. We calculate the formation energies for FP1 to FP6 and find that all these defects are energetically stable, as shown in Table VI. The FP3 defect is the most favorable in the three zirconates, and defect formation in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ is predicted to occur easily. It is noted that the formation energy in $\text{Sm}_2\text{Zr}_2\text{O}_7$ is negative, indicating that defect formation is an exothermic process and the defect structure is even more stable than the pristine pyrochlore structure. Further study is needed to explain the higher stability of the structure with FP defects. Comparing the FP formation energies in zirconate pyrochlores, it is interesting to find that both the cation and anion FP formation energies in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are smaller than those in $\text{La}_2\text{Zr}_2\text{O}_7$, suggesting that $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are more easily disordered to the defect-fluorite structure.

3.4. Charge transfer during dynamical processes

The partial charge transfer, i.e., sharing of some valence electrons instead of full transfer of the valence electrons, between the PKA and its neighboring atoms is expected due to overlapping of outer electron orbitals during close approach, which affects the interatomic interactions. Compared with the MD method employing empirical fixed-charge potentials, the most striking feature of AIMD simulation of displacement events is that the role of charge transfer during the dynamic process can be explored. Gao et al. have investigated the ion–solid interactions in SiC using AIMD method and revealed that the dynamic evolution is a charge-transfer assisted process, and charge transfer to and from recoiling atoms can alter the energy barriers and dynamics for stable defect formation.[18] The AIMD simulations of recoil events in $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$

carried out by Wang et al. have revealed the average transferred charge from the PKAs to their neighbors for developing a suitable charge-transfer potential in MD.[21] In this study, the role of charge transfer in the displacement events in zirconate pyrochlores is also investigated. Considering that the smallest threshold displacement energies are along the [111] direction for A (A=La, Nd or Sm), O_{48f} and O_{8b} PKAs, we only study the charge transfer of recoil events along this direction. The results in Fig. 6 present the variation of the effective charges with time for cation PKAs at 30 eV and anion PKAs at 20 eV in zirconate pyrochlores. The charges are relative to their respective effective charges in an ideal state and are obtained from Mulliken charge analysis. The Mulliken Charges are defined as $N_A = \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} S_{\mu\nu}$ with density matrix P , overlap matrix S , and A the set of basis functions for which the population is computed.[34] It should be pointed out that the calculated Mulliken charge is strongly dependent on both the basis set and the length of chemical bond. Although the absolute value has little physical meaning, the relative trends like the changes in the charges of the primary-knock-on atom during the recoil events, as revealed in this study, are still insightful. Similarly in other oxides,[20, 21] charge gain and loss occurs over the whole dynamic process. As compared with the charge of the atom in the ideal state, the A PKAs mainly lose electrons to other atoms, and the O PKAs mainly gain electrons from other atoms, because the changes in the effective charges are positive and negative for A and O PKAs, respectively. In the literature, the Pauling electronegativity for La, Nd and Sm has been reported to be 1.1, 1.14 and 1.17, respectively.[35] These values are small and very similar to each other, suggesting that the ability for A-site cations to lose electrons is similar. This is consistent with our results that there are relatively small differences in

the charge transfer in the three zirconates for the A[111] recoil events. However, large discrepancies exist for the Zr[111] and O[111] displacement events. In the case of Zr[111], the Zr PKAs in $\text{La}_2\text{Zr}_2\text{O}_7$ mainly lose electrons to other ions, as compared to lattice Zr ions; in contrast, the Zr PKAs in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ also gain electrons from other ions, resulting in a maximum electron gain of $\sim 0.12 |e|$ in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\sim 0.16 |e|$ in $\text{Sm}_2\text{Zr}_2\text{O}_7$. For O_{48f} [111] and O_{8b} [111] recoil events, the changes in the Mulliken charges in $\text{La}_2\text{Zr}_2\text{O}_7$ are much different from those in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$. It appears that the oxygen PKAs in $\text{La}_2\text{Zr}_2\text{O}_7$ do not gain electrons as much as those in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$. In the case of O_{48f} [111], the maximum electron gain are $\sim 0.24 |e|$ for $\text{La}_2\text{Zr}_2\text{O}_7$ and $\sim 0.52 |e|$ for $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$. For O_{8b} [111], the maximum electron gains are 0.20 , 0.78 and $0.74 |e|$ for $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, respectively. During each displacement event, we find that the system potential energy increases, and the maximum increased potential energies for $\text{La}_2\text{Zr}_2\text{O}_7$ are generally larger than those for $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, as shown in Fig. 7. The maximum potential energy represents the maximum in screened-Coulomb interactions between the PKA and one or more atomic nuclei on lattice or defect sites, similar to classical two-body interaction.[36] Our calculations show that more significant charge transfer in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ results in less potential energy increase, i.e., smaller interactions due to more effective screening of the Coulomb force between the PKA and its neighbors, which may decrease the energy barrier for defect generation. Consequently, the ions in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are more likely to be displaced to form defect-fluorite structure that are resistant to irradiation-induced amorphization. These results indicate that charge transfer may contribute effectively to the different radiation response

behavior of $\text{La}_2\text{Zr}_2\text{O}_7$, and $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$.

4. Conclusions

The displacement events in zirconate pyrochlores ($\text{A}_2\text{Zr}_2\text{O}_7$, A=La, Nd and Sm) have been studied using *ab initio* molecular dynamics methods. It is found that the threshold displacement energies for both cations and anions in $\text{La}_2\text{Zr}_2\text{O}_7$ are generally larger than those in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$. In each zirconate, the minimum E_d values are all along the [111] direction for A, O_{48f} and O_{8b} recoils; for Zr recoils, the minimum E_d values are along the [110], [111] and [100] for $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, respectively. The defects created are mainly cation and (or) anion Frenkel pairs. Antisite defects are also created in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$, while they are not observed in $\text{La}_2\text{Zr}_2\text{O}_7$. Both cation and anion Frenkel pair formation energies in $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are smaller than those in $\text{La}_2\text{Zr}_2\text{O}_7$. These results indicate that $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are more likely to undergo order-disorder transition to form a defect-fluorite structure. Since the defect-fluorite structure is extremely stable under ion-irradiation and structural amorphization cannot be induced, our calculations suggest that $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ are more radiation resistant than $\text{La}_2\text{Zr}_2\text{O}_7$, which is in good agreement with the experiments.

Four types of cation FPs and six types of anion FPs with high stability have been revealed by our AIMD simulations. The oxygen interstitial for the anion FPs occupies the vacant $8a$ sites in most cases, and the structure relaxation will not cause the oxygen to return to its initial position. This contradicts with previous theoretical studies that only considered a limited number of anion FP configurations. Our calculations also suggest

that oxygen migrations from *48f* or *8b* to *8a* sites rather than from *48f* to *48f* sites are dominant under low energy irradiation. Charge transfer is found to occur in the recoil events of zirconate pyrochlores, and more significant charge transfer results in less system potential energy increase, which may decrease the energy barrier for defect generation and assist in the formation of defect-fluorite structure. These results indicate that the role of charge transfer in the radiation response of $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ is not negligible.

Acknowledgements

H.Y. Xiao was supported by the scientific research starting funding of University of Electronic Science and Technology of China (Grant No. Y02002010401085) and by the NSAF Joint Foundation of China (Grant No. U1330103). W.J. Weber and Y. Zhang were supported by the U.S. Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering Division. The theoretical calculations were performed using the supercomputer resources at TianHe-1 located at National Supercomputer Center in Tianjin.

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Table I. The reference electronic configurations for the La, Nd, Sm, Zr and O pseudopotentials and the pseudopotential core radii (Bohr).

	Electronic configuration
La	$6s^2 (4.35) 6p^0 (5.40) 5d^1 (4.35) 4f^0 (4.35)$
Nd	$6s^2 (3.05) 6p^0 (4.15) 5d^0 (3.05) 4f^4 (3.05)$
Sm	$6s^2 (3.08) 6p^0 (4.10) 5d^0 (3.08) 4f^6 (3.08)$
Zr	$5s^2 (3.05) 5p^0 (3.20) 4d^2 (2.68) 4f^0 (2.68)$
O	$2s^2 (1.45) 2p^4 (1.45) 3d^0 (1.45) 4f^0 (1.45)$

Table II. Calculated and experimental structural parameters and band gap for $A_2Zr_2O_7$ (A=La, Nd, Sm). a_0 : lattice constant; x_{O48f} : positional parameter for O_{48f} ; d_{A-O48f} : bond distance between A and O_{48f} ; d_{A-O8b} : bond distance between A and O_{8b} ; $d_{Zr-O48f}$: bond distance between Zr and O_{48f} .

		a_0 (Å)	x_{O48f}	d_{A-O48f} (Å)	d_{A-O8b} (Å)	$d_{Zr-O48f}$ (Å)	Band gap (eV)
$La_2Zr_2O_7$	Our Calc.	10.837	0.3211	2.726	2.346	2.065	3.33
	Other Calc.	10.848 ^a	0.333 ^a	2.645 ^a	2.348 ^a	2.114 ^a	3.52 ^b , 4.1 ^c
	Exp. ^d	10.805	0.332	2.635	2.339	2.105	
$Nd_2Zr_2O_7$	Our Calc.	10.746	0.3226	2.691	2.326	2.054	3.72
	Other Calc.						2.67 ^b , 4.0 ^c
	Exp.	10.678 ^e	0.335 ^f				
$Sm_2Zr_2O_7$	Our Calc.	10.704	0.3245	2.666	2.318	2.053	3.79
	Other Calc.						2.86 ^b , 4.7 ^c
	Exp.	10.594 ^e	0.342 ^f				

^aReference[37].

^bReference[8].

^cReference[30].

^dReference[38].

^eReference[7].

^fReference[6].

Table III. Calculated threshold displacement energies (eV) for each recoil in $A_2Zr_2O_7$ (A=La, Nd and Sm). The minimum threshold displacement energies for each species are indicated in bold.

	$La_2Zr_2O_7$	$Nd_2Zr_2O_7$	$Sm_2Zr_2O_7$
A[100]	30	26	25.5
A[110]	33	38	60.0
A[111]	29.5	21.5	21.5
Zr[100]	41	29.5	26.5
Zr[110]	39.5	40	39.5
Zr[111]	49.5	27	27.5
O_{48f} [100]	20.5	17.5	18.5
O_{48f} [110]	29.5	14	15
O_{48f} [111]	15.5	6.5	7.0
O_{8b} [100]	11	7.0	8.0
O_{8b} [110]	14.5	4.0	4.0
O_{8b} [111]	10.5	3.0	3.0

Table IV. Defect configurations for each recoil in $A_2Zr_2O_7$ (A=La, Nd and Sm). X_{vac} : vacancy of X-type atoms; X_{8a} : X interstitial occupying the $8a$ site. In this work, X_{int} indicates X interstitial occupying a site other than $8a$.

	$La_2Zr_2O_7$	$Nd_2Zr_2O_7$	$Sm_2Zr_2O_7$
A[100]	$3La_{vac}+3La_{int}+O_{vac}+O_{int}$	$Nd_{vac}+Nd_{Zr} \text{ antisite}+Zr_{int}$	$Sm_{vac}+Sm_{int}+Zr_{vac}+Zr_{8a}+6O_{vac}+6O_{int}$
A[110]	$2La_{vac}+2La_{int}+2O_{vac}+2O_{int}$	$Nd_{vac}+Nd_O \text{ antisite}+3O_{vac}+4O_{int}$	$Sm_{vac}+Sm_{int}+Zr_{vac}+Zr_{8a}+Zr_{vac}+Zr_{int}+9O_{vac}+9O_{int}$
A[111]	$La_{vac}+La_{int}+O_{vac}+O_{int}$	$2Nd_{vac}+2Nd_{int}+O_{vac}+O_{int}$	$2Sm_{vac}+Sm_{int}+Sm_O \text{ anitiseite}+2O_{vac}+3O_{int}$
Zr[100]	$Zr_{vac}+Zr_{int}+O_{vac}+O_{int}$	$Zr_{vac}+Zr_{Nd} \text{ anitiseite}+Nd_O \text{ antisite}+O_{8a}+2O_{vac}+2O_{int}$	$Zr_{vac}+Zr_{int}+Sm_{vac}+Sm_O \text{ antisite}+O_{8a}$
Zr[110]	$2Zr_{vac}+2Zr_{int}+2O_{vac}+2O_{int}$	$2Zr_{vac}+2Zr_{int}+6O_{vac}+6O_{int}$	$Sm_{vac}+Sm_{Zr} \text{ antisite}+Zr_{int}+6O_{vac}+6O_{int}$
Zr[111]	$Zr_{vac}+Zr_{int}$	$2Zr_{vac}+2Zr_{int}+2O_{vac}+2O_{int}$	$Zr_{vac}+Zr_{int}+2O_{vac}+2O_{int}$
$O_{48f}[100]$	$O_{vac}+O_{8a}$	$O_{vac}+O_{int}$	$O_{vac}+O_{8a}$
$O_{48f}[110]$	Anion disorder between O_{48f}	$O_{vac}+O_{int}$	$O_{vac}+O_{int}$
$O_{48f}[111]$	$O_{vac}+O_{8a}$	$2O_{vac}+O_{int}+O_{8a}$	$O_{vac}+O_{8a}$
$O_{8b}[100]$	$O_{vac}+O_{8a}$	$O_{vac}+O_{8a}$	$O_{vac}+O_{8a}$
$O_{8b}[110]$	$O_{vac}+O_{8a}$	$O_{vac}+O_{int}$	$O_{vac}+O_{int}$
$O_{8b}[111]$	$O_{vac}+O_{8a}$	$O_{vac}+O_{8a}$	$O_{vac}+O_{8a}$

Table V. Calculated formation energies (E_f) for a cation Frenkel pair and the Frenkel pair separation (d_{FP}). The Frenkel pair configurations are illustrated in Fig. 4. The minimum formation energies are indicated in bold.

Defect	La ₂ Zr ₂ O ₇		Nd ₂ Zr ₂ O ₇		Sm ₂ Zr ₂ O ₇	
	E_f (eV)	d_{FP} (Å)	E_f (eV)	d_{FP} (Å)	E_f (eV)	d_{FP} (Å)
FP1	4.68	6.05	4.19	6.00	3.82	6.05
FP2	6.23	4.84	5.83	4.76	5.30	4.73
FP3	8.55	5.86	8.52	5.76	7.59	6.27
FP4	7.01	4.97	6.58	4.88	6.19	4.85

Table VI. Calculated formation energies (E_f) for an anion Frenkel pair and the Frenkel pair separation (d_{FP}). The Frenkel pair configurations are illustrated in Fig. 5. The minimum formation energies are indicated in bold.

Defect	$\text{La}_2\text{Zr}_2\text{O}_7$		$\text{Nd}_2\text{Zr}_2\text{O}_7$		$\text{Sm}_2\text{Zr}_2\text{O}_7$	
	E_f (eV)	$d_{FP}(\text{\AA})$	E_f (eV)	$d_{FP}(\text{\AA})$	E_f (eV)	$d_{FP}(\text{\AA})$
FP1	1.69	13.16	1.11	13.08	0.66	13.01
FP2	1.59	6.31	1.07	6.28	0.67	6.26
FP3	0.52	1.82	0.01	1.89	-0.43	1.94
FP4	1.19	3.93	0.69	3.88	0.29	3.84
FP5	2.64	5.39	2.19	5.35	1.73	5.31
FP6	2.93	4.69	2.59	4.65	2.16	4.61

Figure captions

Figure 1. Schematic view for a pyrochlore structure.

Figure 2. Threshold displacement energies for different recoils in $A_2Zr_2O_7$ (A=La, Nd and Sm).

Figure 3. Defect numbers for cation recoils in $A_2Zr_2O_7$ (A=La, Nd and Sm).

Figure 4. Schematics of the cation Frenkel pair (FP) configuration. (a) FP1; (b) FP2; (c) FP3; (d) FP4. La_{bri} denotes La interstitial occupying the bridge site between La and Zr.

Figure 5. Schematics of the anion Frenkel pair (FP) configuration. (a) FP1; (b) FP2; (c) FP3; (d) FP4; (e) FP5; (f) FP6.

Figure 6. Variation of the effective Mulliken charges with time for (a) A[111] (A=La, Nd and Sm) at an energy of 30 eV; (b) Zr [111] at an energy of 30 eV; (c) O_{48f} [111] at an energy of 20 eV; (d) O_{8b} [111] at an energy of 20 eV.

Figure 7. Potential energy increase for (a) A[111] (A=La, Nd and Sm) at an energy of 30 eV; (b) Zr [111] at an energy of 30 eV; (c) O_{48f} [111] at an energy of 20 eV; (d) O_{8b} [111] at an energy of 20 eV.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.