

First-Principles Study on Cation-Antisite Defects of Stannate and Titanate Pyrochlores

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Abstract

The structure and formation energies of cation antisite defects for a series of stannate pyrochlores $A_2Sn_2O_7$ (A = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Lu, and Y) and titanate pyrochlores $A_2Ti_2O_7$ (A = La, Sm, Gd, Tb, Dy, Ho, Er, Lu, and Y) have been systematically investigated using the first-principles total energy calculations. The calculated results reveal that the lattice parameters increase and the oxygen positional parameters decrease with increasing ionic radii of the lanthanides in the stannate and titanate pyrochlore compounds, respectively. The results suggest that cation antisite defects in pyrochlore play an important role in determining their radiation-resistant properties. The present studies indicate formation energies of cation antisite defects are not simple functions of ionic radius, radius ratio, lattice parameters, and the oxygen positional parameters.

Keywords

Density Functional Theory, Pyrochlores, Cation-Antisite Defects, Total Energy

1. Introduction

The pyrochlore structure is closely related to the fluorite structure and can be considered as an ordered fluorite derivative. In recent years, pyrochlore has been used as one of numerous candidate materials proposed for the immobilization of actinide-rich wastes [1]-[6]. The advantages of using these pyrochlore compositions are related to their remarkable compositional diversity and structural flexibility. The pyrochlores under consideration typically exhibit $A_2B_2O_7$ stoichiometry, where actinides and lanthanides are incorporated on the A-site and Ti, Sn, Zr or Hf occupies the B-site. Radiation damage induced by α -decay events of the incorporated radionuclides

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may result in their structural change, consequently affecting the application of pyrochlores as potential forms to immobilize wastes [2] [7]-[9].

As host of nuclear wastes, the materials must be highly resistant to radiation damage. Ion-beam irradiation can possibly lead to amorphization or microcracking of the crystalline structure with accumulating of atomic scale defects in the materials [10]-[12]. The most important atomistic defects created in $A_2B_2O_7$ pyrochlore oxides when exposed to radiation damage conditions are cation antisite defects and anion Frenkel pairs [7] [13]-[15]. These defects are precisely the ones that are responsible for the pyrochlore to fluorite order-disorder transformation [10]. Many studies showed that a natural propensity to accommodate lattice disorder so that the materials will be less susceptible to detrimental radiation damage effects such as amorphization [13] [16] [17]. Therefore, many groups have researched in the order-disorder phase transition under equilibrium condition [10] [14]-[18]. Many experimental studies suggested that the titanate and stannate pyrochlore compounds readily undergo amorphization by using ion beam irradiation to simulate the α -decay damage [1] [7] [9] [19]-[22]. For example, Lian *et al.* [7] suggested experimentally that the resistance of the stannate pyrochlore structure to ion beam induced amorphization is affected not only by the relative sizes of the A-site and B-site cations, but also by the cation electronic configuration, the structural disorder and the bond type, particularly the covalence of the $\langle \text{Sn-O}_{48f} \rangle$ bond.

In an attempt to explain many of the experimental observations of order-disorder transitions in the pyrochlore system, as well as observed variations in radiation “tolerance”, many theoretical investigations had been performed to calculate the defect-formation energies of a large number of pyrochlore compositions [10] [13]-[18] [23] [24]. These studies suggested that the cation-antisite defects are relatively more important than the other defects. In order to better understand experimental observations and the importance of defects, we calculated the formation energies of cation antisite defects of $A_2\text{Sn}_2\text{O}_7$ (A = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, and Lu) and $A_2\text{Ti}_2\text{O}_7$ (A = La, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, and Lu) pyrochlore compositions systematically using *ab initio* pseudopotential plane-wave method.

2. Computational Method

The calculations were performed using the generalized gradient approximation (GGA) within density-functional theory, as implemented in Vienna *ab initio* simulation package (VASP) code [25]-[28]. The interaction between ions and electrons is described using the projector augmented wave (PAW) method [29]-[30], and the exchange correlation interaction is described by PW91 function [31]. The lattice parameters and internal atomic positions of all structures are fully relaxed using a conjugate gradient scheme. The convergence tests had been accomplished by using different k -point sampling and plane-wave cut-off energy, which results in performing the calculations with $4 \times 4 \times 4$ Monkhorst-Pack k -point mesh and a cutoff energy of 550 eV for the plane wave basis set. Calculating of structural parameters was based on the primitive unit cell (containing 22 atoms).

The defect structures calculations were performed with $2 \times 2 \times 2$ Monkhorst-Pack k -point mesh and a cutoff energy of 550 eV in a unit cell containing 88 atoms. The cation-antisite defect structure models were established by exchanging A^{3+} cation and the B^{4+} cation. The cation-antisite defect formation energies were calculated by the difference between the total energy of the optimized stable structure and the relaxed defect structure. The $4f$ states of the lanthanide cations were treated as corelike states because the f -electrons are localized in the inner $4f$ levels [13].

3. Results and Discussion

3.1. Crystal Structure

The $A_2B_2O_7$ pyrochlore structure has the space group $Fd\bar{3}m$ that derives from the MO_2 fluorite like arrangement of atoms. The general formula of a pyrochlore can be written as $A_2B_2O_6O'$ with four crystallographically nonequivalent types of atoms. The A and B cations occupy the $16d$ (1/2, 1/2, 1/2) and $16c$ (0, 0, 0) sites, respectively, and the six equivalence O (denoted O_{48f}) and the seventh O' (denoted O_{8b}) oxygen are located at the $48f$ (x , 1/8, 1/8) and $8b$ (3/8, 3/8, 3/8) positions, respectively. An unoccupied interstitial site $8a$ (1/8, 1/8, 1/8) is surrounded by four B ions, and the “vacancies” at the $8a$ site are ordered on the anion sublattice [32] [33]. Geometrically, the B^{4+} cation is surrounded by six O_{48f} atoms in a distorted octahedron, and the A^{3+} cation is in a distorted cubic polyhedron formed by two O_{8b} and six O_{48f} atoms. The $48f$ oxygen atom is coordinated by two A^{3+} and two B^{4+} sites, and the $8b$ oxygen atom is inside a tetrahedron formed by A^{3+} cations. The cubic pyrochlore structure can

be completely determined by two independent parameters which are the internal parameter x for the O_{48f} positions and the lattice parameter a_0 . The fully-ordered lattice parameters a_0 and oxygen positional parameter x along with available cation ionic radii in this work for titanate and stannate pyrochlores had been demonstrated in **Figure 1**.

The results that the lattice parameters a_0 increase with increasing cation ionic radii of the lanthanides are showed in **Figure 1(a)**, which is in good agreement with experimental results [7] [9] [34] [35] and theoretical calculations [14]-[16] [36] [37].

For an ideal pyrochlore structure, $x = 0.3125$ such that each B^{4+} cation is surrounded by an ideal oxygen octahedron. The x parameter for a completely disordered defect-fluorite structure is 0.375 [16] [36]. It had been suggested that the positional parameter x of oxygen atoms occupying $48f$ site in pyrochlore structure could determine its radiation response behavior [7]. That indicated that pyrochlore compositions which have larger $48f$ oxygen positional parameter x , are more resistant to ion beam-induced amorphization [7]. The tendency of stannate pyrochlores positional parameters x in **Figure 1(b)** suggested that $Lu_2Sn_2O_7$ should be the most resistant to

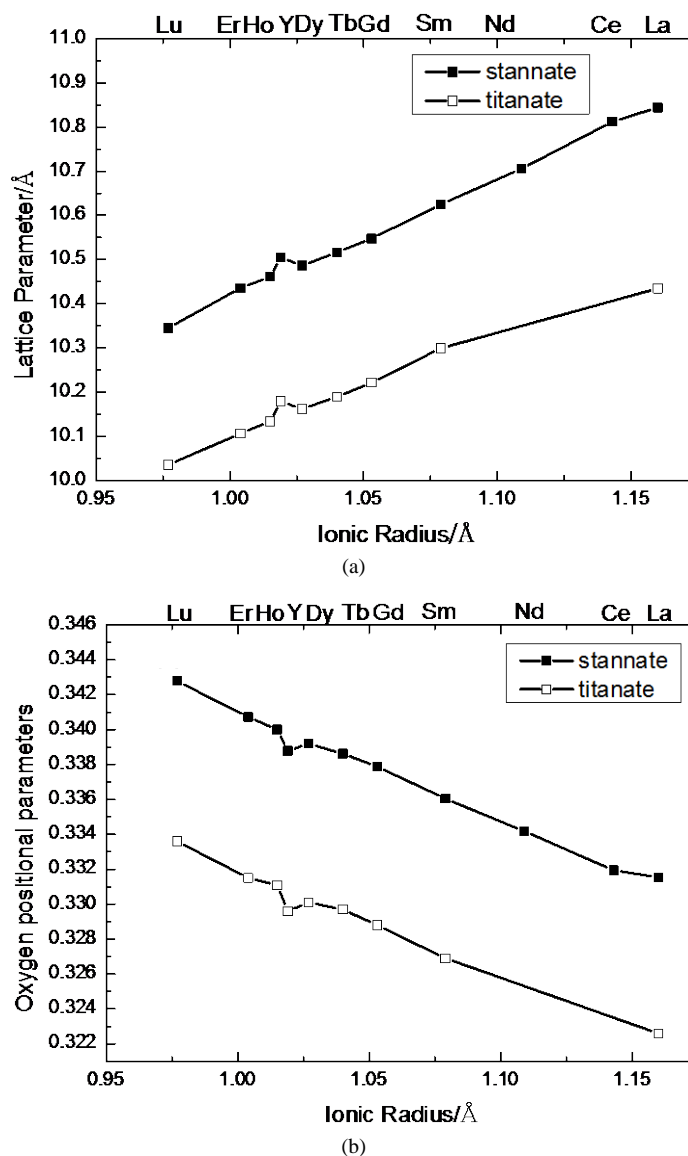


Figure 1. The function of the calculated structures parameters: (a) Lattice parameters a_0 ; and (b) O_{48f} positions parameter x of titanate and stannate pyrochlore along with cation ionic radii.

ion beam-induced amorphization and $\text{La}_2\text{Sn}_2\text{O}_7$ should be the most readily amorphized under irradiation. These results were confirmed by the experiments [9] and other theoretical calculations [36].

The calculated 48 f oxygen positional parameters x for titanate pyrochlores are also shown in **Figure 1(b)**. The results indicate that the parameters x almost reduce linearly with increasing ionic radii of the lanthanides, which is in contrary to the results reported by Lian *et al.* [7], in which $\text{Gd}_2\text{Ti}_2\text{O}_7$ has the smallest x value and the least radiation resistance, however, which is consistent with the theoretical calculation [14] [15]. These results indicate that the positional parameter x is not the only indicator that determines the radiation-resistant properties of pyrochlores.

3.2. Cation-Antisite Defect Formation Energies

The formation energy of a cation-antisite is calculated by the difference between the total energy of the optimized stable structure and the relaxed defect structure with one A^{3+} cation exchanged with the nearest neighbor Sn^{4+} cation or Ti^{4+} cation.

The calculated cation-antisite defect formation energies for $\text{A}_2\text{Sn}_2\text{O}_7$ are shown in **Figure 2(a)**. The results indicate that the defect formation energies show almost a linear reduce with increasing ionic radius of the lanthanides. The results reveal a significantly reduced capability of radiation resistance as the cation ionic radius ratio (r_A/r_B), which was confirmed the experimental observations that La, Nd, and Gd stannates were sensitive to ion beam induced amorphization, and the critical amorphization temperature reached 960 K, while other stannate pyrochlores formed the disordered fluorite structure even at the lower temperature under ion irradiations. However these results are different from the paper published by Chen *et al.* [13], in which they had shown that the formation energies of the cation-antisite defects did not increase continuously from Lu^{3+} to La^{3+} . This difference may be due to different calculation accuracy and the choice of pseudopotential. At the same time, all calculations including this calculation indicate that $\text{Lu}_2\text{Sn}_2\text{O}_7$ has the lowest cation-antisite defect formation energy [13] [18]. This suggests that $\text{Lu}_2\text{Sn}_2\text{O}_7$ is the most resistant to ion beam-induced amorphization since pyrochlore compositions that are more easily disordered to the defect fluorite structure are more “resistant” to ion beam-induced amorphization, which was also observed in the previous irradiation experiments [9].

On the contrary, the $\text{La}_2\text{Ti}_2\text{O}_7$ has the lowest formation energy, while $\text{Gd}_2\text{Ti}_2\text{O}_7$ has the highest one as in **Figure 2(b)**. In addition, an inflection point was found at the $\text{Y}_2\text{Ti}_2\text{O}_7$ in the titanate pyrochlore. The results indicate that the formation energies of cation antisite do not linearly depend on the cation radii and the internal parameter x of the O_{48f} positions in the titanate pyrochlore compositions, which also was found in the other calculation [15]. However the results are in contrary to the results reported by Minervini *et al.* [18]. The present results in the titanate pyrochlore are confirmed the experimental observation performed by Lian *et al.* [7], where the $\text{Gd}_2\text{Ti}_2\text{O}_7$ had the highest critical temperature and the least radiation resistance and the critical temperature at the $\text{Y}_2\text{Ti}_2\text{O}_7$ had a trough point along with the cation radius. These results also explain why $\text{Gd}_2\text{Ti}_2\text{O}_7$ has the least resistance to radiation-induced amorphization since it is the least likely form a defect fluorite structure in the titanate pyrochlore compositions. Moreover, the formation energies of cation-antisite pairs for $\text{Y}_2\text{Ti}_2\text{O}_7$ are also more than its adjacent compounds $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$, which consistent with the experimental observation [7], where critical temperature for $\text{Y}_2\text{Ti}_2\text{O}_7$ is lower than $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$.

Comparing **Figure 2(a)** with **Figure 2(b)**, it shows that for the same A^{3+} cation, the formation energies of cation antisite defects for stannate pyrochlores is higher than those of titanate pyrochlores, which suggests that stannate pyrochlores is more difficult to disorder than titanate pyrochlores. It is quite surprising since the ionic radius of Sn^{4+} (0.69 Å) is much larger than that of Ti^{4+} (0.605 Å). The results are in contrary with the conclusion in the literatures [7] [18], which showed that the lowest cation-antisite defect energies are associated with the compounds where cation ionic radius ratio (r_A/r_B) is the smallest.

Figure 3 summarizes the defect formation energies of cation-antisite for stannate and titanate pyrochlores as a function of the cation ionic radius ratio (r_A/r_B). Defect formation energies of cation-antisite for stannate pyrochlores are much higher than those of titanate pyrochlores having similar ionic radius ratios (r_A/r_B). For example, the cation ionic radius ratio (r_A/r_B) of $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$ is 1.68; however, the defect formation energies of $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$ are 3.5855 eV and 2.5854 eV, respectively. The defect formation energy of $\text{Nd}_2\text{Sn}_2\text{O}_7$ is 3.3153 eV, significantly higher than that of $\text{Lu}_2\text{Ti}_2\text{O}_7$ (2.0591 eV), although the ionic radius ratio (r_A/r_B) of $\text{Nd}_2\text{Sn}_2\text{O}_7$ ($r_{\text{Nd}^{3+}}/r_{\text{Sn}^{4+}} = 1.607$) is slightly less than that of $\text{Lu}_2\text{Ti}_2\text{O}_7$ ($r_{\text{Lu}^{3+}}/r_{\text{Ti}^{4+}} = 1.61$). These results confirm the experimental observation that the critical amorphization temperatures of stannate pyrochlores are much higher than those of titanate and zirconate pyrochlores having similar ionic radius ratios (r_A/r_B) [9]. The trends of

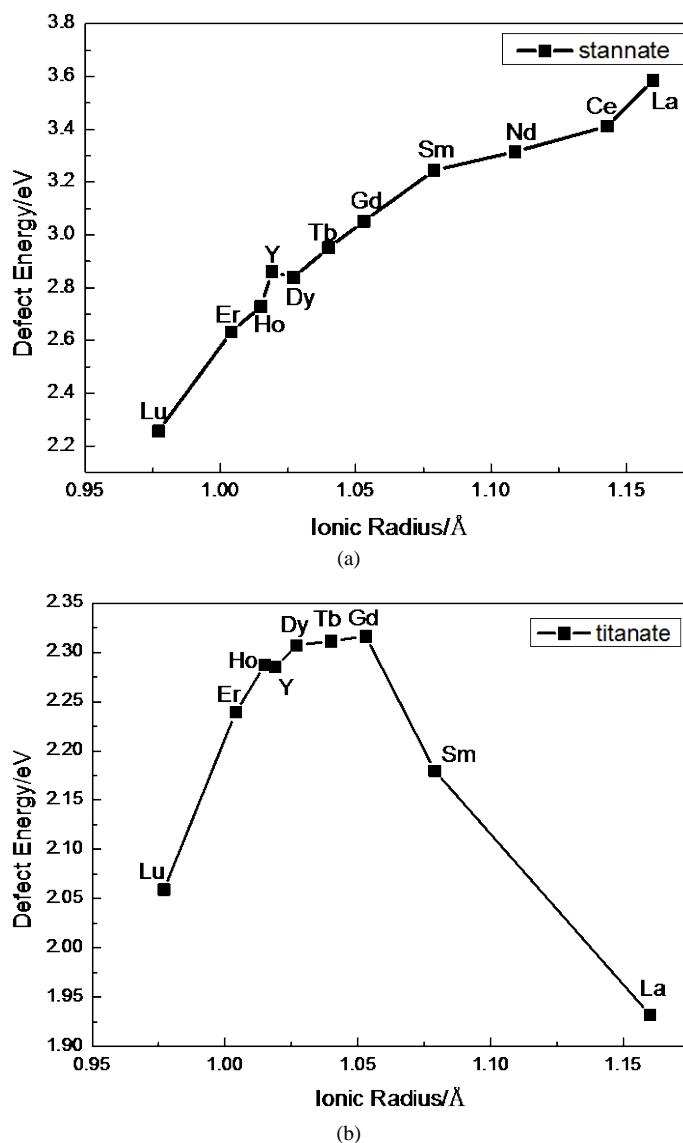


Figure 2. The function of the calculated cation-antisite defect formation energies of pyrochlores with their cation ionic radii. (a) The formation energies of stannate pyrochlores; and (b) The formation energies of titanate pyrochlores.

cation-antisite defect formation energies for stannate and titanate pyrochlores suggest that cation-antisite defect formation energies are not the simple function of ionic radius or radius ratios (r_A/r_B).

4. Conclusion

In this work, we have performed a systematic first-principles study of the tendency for formation energies of cation-antisite defects in a wide range of stannate and titanate pyrochlores to investigate cation-antisite defect formation energies in determining their radiation resistance behavior to amorphization. The lattice parameters a_0 increase with increasing ionic radii of the lanthanides as well as positional parameters x reduce in the stannate and titanate pyrochlore compound. The calculated cation-antisite defect formation energies being consistent with experimental observations are found to be linearly dependent upon the cation radius ratio (r_A/r_B) in the stannate pyrochlore. However, there are a maximum value for $Gd_2Ti_2O_7$ and an inflection point for $Y_2Ti_2O_7$ in the titanate pyrochlores. These results also suggest that the strong correlation between defect formation energies of cation-

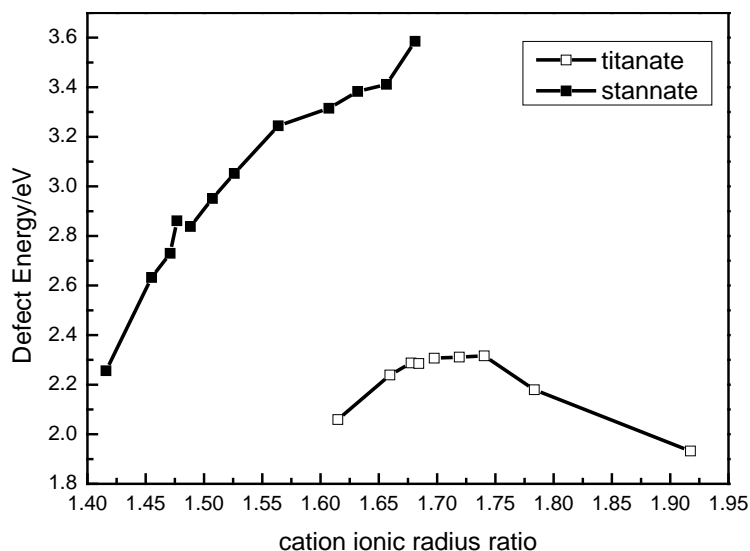


Figure 3. The cation-antisite defect formation energies of both stannate and titanate pyrochlores as a function of their cation ionic radius ratio (r_A/r_B).

antisite and radiation-resistant properties, but the radiation-resistant properties and formation energies of cation-antisite defects are not the simple function of ionic radius, radius ratios (r_A/r_B), lattice parameters a_0 , and the 48f oxygen positional parameter x .

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