First-principles study of disordering tendencies in $Gd_2B_2O_7$ (B = Ti, Sn, Zr) compounds

Chen Zhong-Jun(陈中钧)[a)†], and Tian Dong-Bin(田东斌)[b)]

[a)] *Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*
[b)] *School of Microelectronic and Solid-state Electronics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*

(Received 9 May 2010; revised manuscript received 7 July 2010)

This paper performs the density functional theory calculations to obtain some factors influencing the response of pyrochlores $Gd_2B_2O_7$ (B = Ti, Sn, Zr) to ion irradiation-induced amorphization. The 48f oxygen position parameter x, cohesive energy, bond type and defect-formation energy are discussed. The results show that parameter x can be used to indicate the disordering tendencies within a given pyrochlore family. Bond type, cohesive energy and defect-formation energies can be used to explain some experimental observations, but they are not determined exclusively by radiation "resistance" for a different pyrochlore family.

Keywords: pyrochlores, density functional theory, disordering tendency, electronic properties
PACC: 7115H, 7280E, 7125T, 6170R

1. Introduction

Pyrochlore oxide materials have a general formula $A_2B_2O_7$, with large cations such as the actinides and lanthanides in the A site and smaller cations including most transition metal elements, typically such as Ti, Zr and Sn, in the B site. Thus, these pyrochlores have a wide variety of compositions (> 500) which lead to a wide range of technologically important properties, such as high ionic conductivity,[1] superconductivity,[2] luminescence[3] and ferromagnetism.[4] In pyrochlore structures, the A^{3+} and B^{4+} ions occupy the special sites of 16d (1/2,1/2,1/2) (A site) and 16c (0,0,0) (B site), respectively, and six equivalent O (denoted as O_{48f}) and the seventh O' (denoted as O_{8b}) oxygens are located at the 48f(x,1/8,1/8) and 8b(3/8,3/8,3/8) positions, respectively, so pyrochlore has a more descriptive formula of $A_2B_2O_6O'$ with four crystallographically nonequivalent types of atoms. The site of the missing oxygen which could complete the anion sublattice to form a fluorite structure is 8a(1/8,1/8,1/8) (denoted as O_{8a}). This structure can be visualized in a variety of ways, but it is often considered as an ordered defect fluorite structure, except that two cation sites and one-eighth of the anions are absent. The cations and oxygen vacancies are ordered. The system can be completely described in terms of the lattice constant a, and the parameter x defining the position of the O_{48f}. Recently, there has been a great interest in using pyrochlores materials with fluorite and fluorite-related structures, as potential host phases for the immobilization of actinides, particularly Pu.[5−15] The advantage of using these pyrochlore compositions is related to their remarkable compositional diversity and structural flexibility. Radiation damage from α-decay events of the incorporated radionuclides may result in their structural change, and consequently, affect the application of pyrochlores as potential waste forms. Up to now, many studies[5−17] simulated the α-decay damage in a variety of pyrochlore compositions using ion beam irradiation, particularly in the $Ln_2Ti_2O_7$ and $Ln_2Zr_2O_7$ systems.[5−8,11−17] These investigations suggest that the titanate pyrochlores $Ln_2Ti_2O_7$ readily undergo amorphization under irradiation,[5,16−18] while the zirconate pyrochlores $Ln_2Zr_2O_7$ have been identified to be particularly resistant to radiation damage with an exception of $La_2Zr_2O_7$.[6−9,15,18,19]

At the entire series of $Ln_2Ti_2O_7$ (Ln = Sm to Lu, and Y), it has been found that $Gd_2Ti_2O_7$ has an abnormally high susceptibility to ion beam damage with the highest T_c of ∼1120 K and a relatively low dose (∼0.18 dpa) by 1.0-MeV Kr^+ irradiation.[12,17,20] However, pyrochlore $Gd_2Zr_2O_7$ remained crystalline

†Corresponding author. E-mail: zjchen@uestc.edu.cn
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at a relatively high dose of ∼36 dpa under 1.5-MeV Xe^+ irradiation even at $T = 25$ K.[11] At the same time $Gd_2Sn_2O_7$ experienced the radiation-induced transformation to the aperiodic state at the critical amorphization temperatures ∼350 K by 1.0-MeV Kr^+ irradiation.[21] So the radiation "resistance" to ion-beam-induced amorphization increased with the increase average B-site cation size from $Gd_2Ti_2O_7$ to $Gd_2Sn_2O_7$, and to the end member $Gd_2Zr_2O_7$. Lian *et al.*[12] have suggested experimentally that the resistance of the pyrochlore structure to ion beam-induced amorphization is not only affected by the relative sizes of the *Ln*- and *B*-site cations, but also by the cation electronic configuration, the structural disorder and the bond type. Recently, Chao *et al.*[22] have introduced the disordering energy—the energy cost required to fully disorder a pyrochlore into fluorite—as another important indicator of disordering tendency. Clearly, all of these concepts are related as they measure, in one way or another, the stability of the pyrochlore structure.

In an attempt to explain some experimental observed variations in radiation "resistance" and the effect of the *B*-site cation on the radiation "resistance", we will calculate the structural and electronic properties, cohesive energy and formation energies of point defects of pyrochlores $Gd_2B_2O_7$ (B = Ti, Sn, Zr) by using *ab initio* pseudopotential plane-wave method. So far, as far as we know, no theoretical radiation "resistance" investigations of $Gd_2B_2O_7$ (B = Ti, Sn, Zr) pyrochlore compounds have been reported.

2. Calculational method

This paper carries out the first-principles total energy calculations within the framework of density functional theory (DFT). The interaction between ions and electrons is described by using the projector augmented wave (PAW) method[23,24] and the exchange–correlation interaction is described by PW91 function[25] within DFT framework.[24,26] The influence of different k-point sampling and plane-wave cutoff energy was explored in a series of test calculations, leading to the calculations of electronic properties being performed with 6×6×6 k-point sampling and a cutoff energy of 400 eV containing 22 atoms. The defect-formation energy calculations were performed with 1×1×1 k-point sampling and a cutoff energy of 600 eV in a larger supercell containing 88 atoms. In our calculation, the 4f states of the Gd cation were treated as core-like states because the f-electrons are localized in the inner 4f levels.

3. Results and discussion

3.1. Structural properties

The static lattice parameters a, oxygen positional parameter x, the nearest bond length and bond angle are optimized at constant volume for the three cubic compounds $Gd_2B_2O_7$ (B = Ti, Sn, Zr) with ideal pyrochlore structures. The calculated results are presented in Table 1 along with comparison of available experimental and theoretical values. As can be seen from Table 1, our calculated lattice parameters are in good agreement with the experimental values[12,27−29] and other first-principles calculations.[29] Up to now, no information on the bulk modulus has been reported. Our calculated bulk moduli B_0 are 234.3 GPa, 314.7 GPa and 210.4 GPa for $Gd_2B_2O_7$ (B = Ti, Sn, Zr), respectively. The bulk modulus for $Gd_2Sn_2O_7$ is the largest among the three compounds investigated, suggesting that it may have higher rigidity.

The calculated cohesive energies are 7.224, 6.101 and 7.486 eV per atom for the three $Gd_2B_2O_7$ pyrochlores in the same order, as can be seen from Table 1. It is obvious that the cohesive energy of $Gd_2Zr_2O_7$ is the highest, indicating the strongest bonding in the electronic density of states, as will be discussed further in the next section. So we can deduce that $Gd_2Zr_2O_7$ is the most stable phase among the three compounds, which is consistent with the experimental observation.[11] We find that cohesive energy increases in the order Sn < Ti < Zr. Such a trend is not in agreement with their radiation "resistance". So it can be concluded that cohesive energy is not determined exclusively by radiation "resistance" for different pyrochlore families.

The 48f oxygen positional parameter x defines the deviation from the ideal fluorite structure and determines the order-disorder energetics[12] and is closely affected by the relative cations ionic size at A- and B-sites, electronic configuration, and structural disordering. Our calculated oxygen positional parameter, x, is in good agreement with experimental measurements for $Gd_2B_2O_7$ (B = Ti, Sn, Zr).[12,27,28] It is found that x increases with increasing ionic radii of the B^{4+} cations, which suggests the increasing radi-

ation "resistance" within a given Gd-pyrochlore family for the titanate, stannates, and zironates. Such a conclusion is in good agreement with previous experimental studies.[12] So parameter x is a very good indicator of disordering propensities between different pyrochlore families. To further reveal the calculated structures for the three pyrochlores, we show in Table 1 the most relevant bond distances. These results are also in good agreement with the experimental values.[12] The nearest-neighbouring distances for Gd–O_{8b}, Gd–O_{48f} and B–O_{48f} bonds (B = Ti, Sn, Zr) also increase with increasing ionic radii of the B^{4+} cations.

Summarizing the description of the structure, we find that the lattice constant a, oxygen positional parameter x, Gd–O_{8b} distance, Gd–O_{48f} distance and B–O_{48f} distance, all increase with the increasing ionic radii of the B^{4+} cations. The parameter x has an important effect on the resistance of the pyrochlore structure type to ion-beam-induced amorphization and can also be used to indicate the disordering tendencies within a given pyrochlore family. With increasing ionic radius from Ti (0.605 Å, 1 Å = 0.1 nm), Sn (0.690 Å) to Zr (0.720 Å), the parameter x increases from 0.3285, 0.3379 to 0.3389, suggesting an increasing radiation "resistance", which is in excellent agreement with previous experimental studies.[12]

3.2. Electronic properties

Lian *et al.*[12] have suggested that the resistance of the pyrochlore structure to ion beam-induced amorphization was affected by the cation electronic configuration. To further validate the relation between the radiation "resistance" and electronic structure and bond type, we calculated the total and partial density of states (DOS) and electronic band structure, which are shown in Figs. 1 and 2, Table 2 lists the band gap values. The Fermi level is set to 0 eV. As it can be seen, three compounds present an obvious different character.

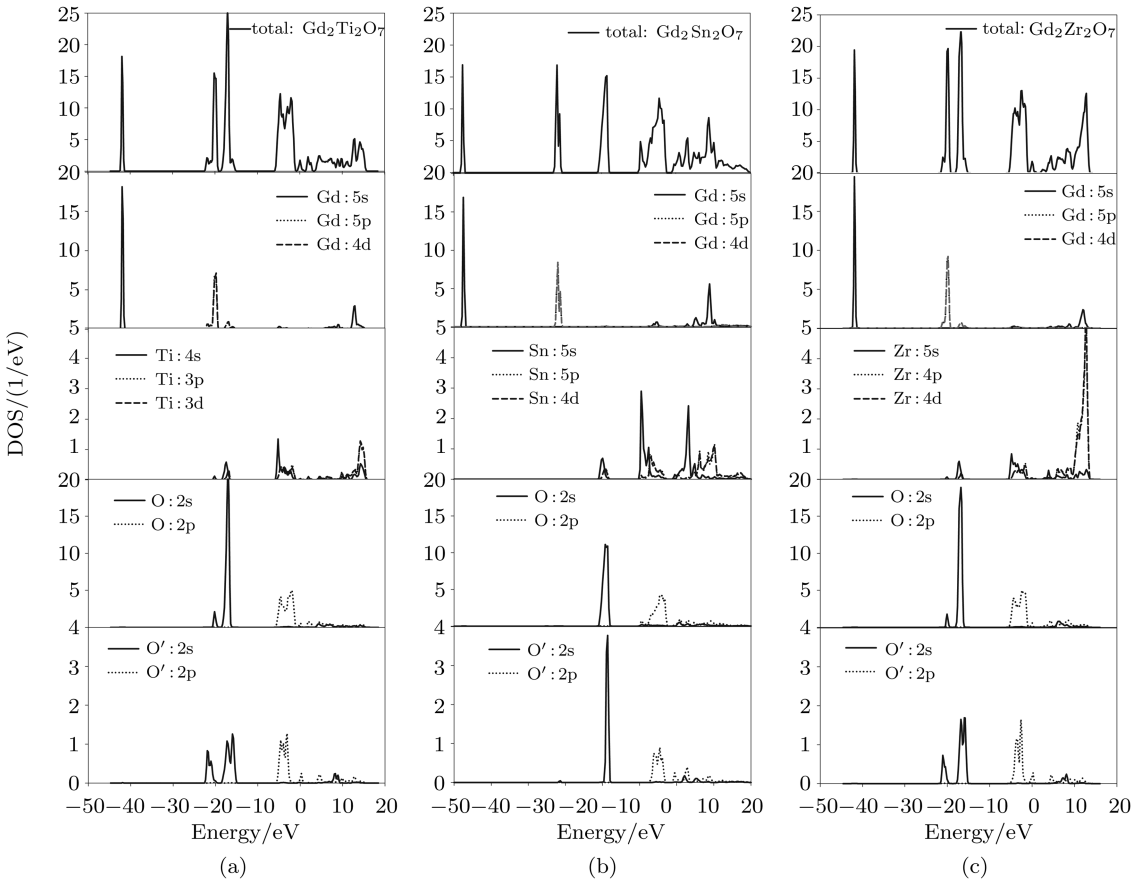


Fig. 1. The calculated total density of state (DOS) and atomic projected DOS (PDOSs) for (a) $Gd_2Ti_2O_7$, (b) $Gd_2Sn_2O_7$, and (c) $Gd_2Zr_2O_7$.

Table 1. Calculated structural properties of pyrochlores ($Gd_2B_2O_7$) along with comparison of experiments.

	R_B^{4+}/Å	cohesive energy /(eV/per atom)	B_0/GPa	lattice parameter/Å			x parameter/Å			⟨Gd–O_{8b}⟩ bond length/Å		⟨Gd–O_{48f}⟩ bond length/Å		⟨B–O_{48f}⟩ bond length/Å	
				Pre.	other calc.[28]	Exp.	Pre.	other calc.[28]	Exp.	Pre.	Exp.·[12]	Pre.	Exp.·[12]	Pre.	Exp. [23]
$Gd_2Ti_2O_7$	0.605	7.224	234.3	10.24	10.04	10.185[28] 10.186·[12]	0.3285	0.4233	0.4203[28] 0.3263·[12]	2.217	2.205	2.522	2.524	1.981	1.961
$Gd_2Sn_2O_7$	0.690	6.101	314.7	10.53		10.454[27]	0.3379		0.3348[27]	2.280		2.525		2.079	
$Gd_2Zr_2O_7$	0.720	7.486	210.4	10.66	10.58	10.51·[29] 10.54[28]	0.3389	0.4204	0.4263[28]	2.314		2.557		2.115	

Table 2. Calculated energy band gap values and the defect-formation energy of pyrochlores($Gd_2B_2O_7$) along with comparison of the other theoretical calculations.

composition	R_B^{4+}/R_{Gd}^{3+}	band gap value/eV	cation-antisite formation energy 1X/eV		Frenkel-pair formation energy O_{48f}–O_{8a}/eV	coupled cation-antisite/Frenkel-pair formation energy 1X+O_{48f}–O_{8a}/eV
			Pre.	other calc.	Pre.	Pre.
$Gd_2Ti_2O_7$	0.575	2.951	1.12	5.6∼6.0·[19]	7.84	1.27
$Gd_2Sn_2O_7$	0.655	2.760	2.52	4.4∼4.8·[19]	7.00	3.32
$Gd_2Zr_2O_7$	0.684	2.838	0.79	3.2∼3.6·[19] 3.6∼4.0·[19]	5.23	-3.36

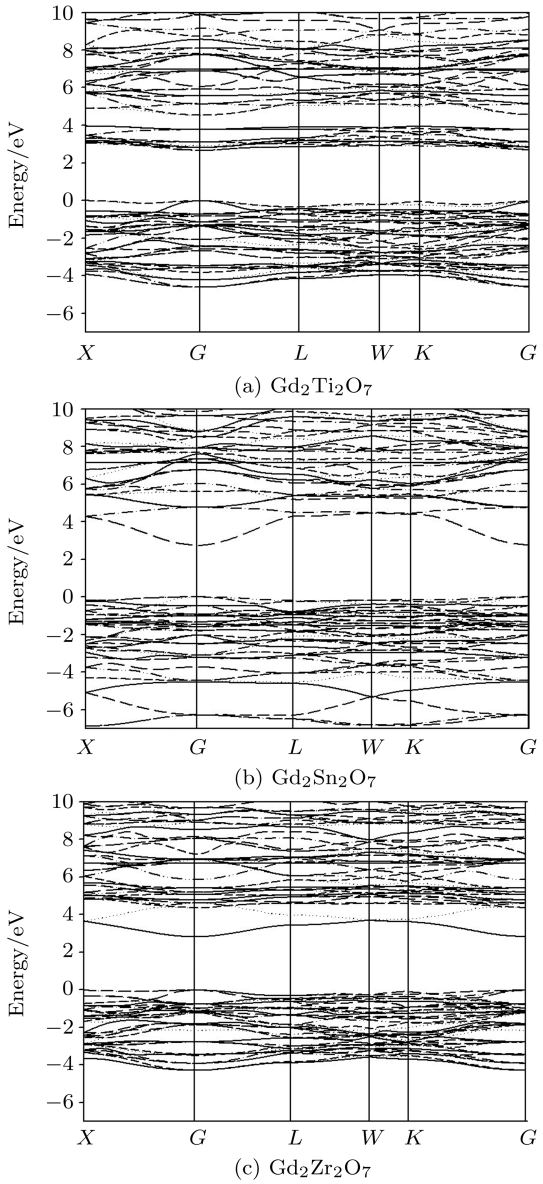


Fig. 2. The calculated electronic band structures for (a) $Gd_2Ti_2O_7$, (b) $Gd_2Sn_2O_7$, and (c) $Gd_2Zr_2O_7$.

The lowest valence band, ranging from –40 eV to –50 eV, is formed by Gd 5s states, while there exists a slight difference that the energy peaks of $Gd_2Sn_2O_7$ generally shift downwards in energy relative to the corresponding orbital peaks of $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$, meaning that stronger interaction exists between Gd and oxygen in $Gd_2Sn_2O_7$. The upper valence band, ranging from –19 eV to –35 eV, is mainly composed of Gd 5p and 4d states and O 2s state, we also notice a strong hybridization between Gd 5p and 4d states for these compounds, at the same time there exists a stronger O′ 2s energy peaks of $Gd_2Sn_2O_7$ corresponding orbital peaks of $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$. The top part, ranging from –10 eV to 0 eV, is dominated by O 2p and a minor O′ 2p states with a small admixture of the B p and d states (B = Ti, Sn, Zr) due to the hybridization between these states and the O 2p states. It is obvious that the covalency of B–O bonds decreases in the order Sn > Ti > Zr. Such a trend is in agreement with Mulliken overlap population analysis by Lumpkin *et al.*[18] and electronic structure analysis by Panero *et al.*[30] The stronger ⟨Sn–O⟩ covalent bond is also observed by Kennedy *et al.*[27] that the covalent character of the ⟨Sn–O⟩ bond of stannate pyrochlores implies a less degree of distortion of the SnO_6 coordination octahedron, resulting in a structure more compatible with the ordered pyrochlore superstructure. This leads to a greater susceptibility of stannate pyrochlore to ion beam irradiation induced amorphization, as compared with the titanate and zirconate pyrochlores. However, $Gd_2Ti_2O_7$ has the highest critical amorphization temperature (above which no amorphization occurs regardless of radiation dose) at ∼1120 K,[12] $Gd_2Sn_2O_7$ becomes aperiodic state at ∼350 K.[21] $Gd_2Zr_2O_7$ is stable even at ∼2 K.[11] Clearly, such phenomena cannot be simply explained by the covalency of B–O bonds, and other effects may play an important role here.

The unoccupied conduction region, ranging from 0 to 10 eV, is essentially derived from the admixture of the p and d states of B atoms for the three compounds. It is noticeable that Gd 5s states is contributed to the conduction bands for $Gd_2Sn_2O_7$, whereas such contribution is not observed for $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$. Also, it is obvious that the conduction bands of Zr differ greatly from those of Ti and Sn. A strong peak representing Zr 4p and 4d orbitals is observed for $Gd_2Zr_2O_7$, suggesting a strong hybridization between Zr 4p and 4d states, whereas such a strong peak does not exist for Ti and Sn, as shown in Fig. 1.

The DOS curves at oxygen O and O′ atoms show similar characters for $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$. On the other hand, the two nonequivalent oxygen sites O and O′ have noticeably different features. Moreover, it can be seen that the PDOS of the first site of oxygen O atoms has higher values than that of the second site O′. Such difference may be due to their different surroundings. Indeed, the first site of oxygen atoms O is coordinated by B and Gd atoms while the second site O′ is coordinated only by Gd atoms.

The calculated electronic band structures of $Gd_2B_2O_7$ (B = Ti, Sn, Zr) pyrochlore compounds are given in Fig. 2. It can be seen that all of them have a direct band gap at the $G(000)$ point in the Brillouin zone. The band gaps of $Gd_2Ti_2O_7$, $Gd_2Sn_2O_7$

and $Gd_2Zr_2O_7$ are estimated to be 2.951, 2.760 and 2.838 eV, respectively. These results indicate that the three compounds are of semiconducting character. Since there are no data of literatures for comparison, the values of these band gaps are purely predictive.

3.3. Defect formation energies

Under irradiation, two most important point defects created in $A_2B_2O_7$ pyrochlore oxides when exposed to displacive radiation damage conditions are cation-antisite defects and anion Frenkel-pairs defects.[28,30] Minervini and Grimes[31] and Pirzada[32] also suggested that in pyrochlore materials, cation Frenkel reactions are much higher energy processes than their corresponding anion Frenkel or Schottky reactions. Sickafus *et al.*[19] proposed that the disorder process could be used to explain defect formation during irradiation. Under ion beam irradiation, pyrochlore compositions which are more easily order–disordered to the disordered defect fluorite structure are more "resistant" to ion-beam-induced amorphization. Wilde and Catlow[28,33] employed pair potentials to calculate defect properties in $Gd_2Zr_2O_7$, and suggested that the disorder mechanism in pyrochlore is a concerted-exchange process involving both anion and cation-antisite defects. Our earlier studies[34] found that defect formation energies can be used to explain some experimental observations. So, to provide valuable insights into the possible radiation effects of pyrochlores, we calculated the formation energies of defects in $Gd_2B_2O_7$ (B = Ti, Sn, Zr) pyrochlore based on a larger cell containing 88 atoms, considering the cation-antisite defects, Frenkel-pair defects, and coupled cation-antisite/Frenkel-pair defects. The formation energy of a cation-antisite defect was calculated by the difference between the total energy of the optimized stable structure and the relaxed defect structure with one Gd^{3+} cation exchange with the nearest B^{4+} cation. And the formation energy of a Frenkel-pair defect was calculated by the difference between the total energy of the optimized stable structure and the unrelaxed defect structure with oxygen migration via 48f–8a, since this defect structure is not stable and the relaxed structure will lead oxygen to return to its initial position. For the coupled cation-antisite/Frenkel-pair defect structure, its energy was obtained from the fully relaxed structure containing a cation-antisite defect and a Frenkel-pair defect. The calculated results are presented in Table 2, along with available theoretical values for comparison.

For $Gd_2B_2O_7$ (B = Ti, Sn, Zr), the formation energies of cation-antisite defects are 1.12, 2.52, and 0.79 eV, obviously, the defect formation energy in $Gd_2Sn_2O_7$ is larger than that in the other two investigated compounds, which is due to the greater degree of covalent bonding between ⟨Sn–O⟩ in comparison with ⟨Ti–O⟩ or ⟨Zr–O⟩. The formation energies of Frenkel-pair defect are 7.84, 7.00, and 5.23 eV, respectively. It can be seen that Frenkel-pair defect formation energies are significantly larger than the cation-antisite defect formation energies. However, it can be observed that the Frenkel-pair formation energy is substantially lowered in the presence of a cation-antisite defect, indicating that cation disorder causes the disorder of local oxygen, which is consistent with the results obtained from $A_2Ti_2O_7$[30] and $A_2Sn_2O_7$ pyrochlores.[34] The calculated cation-antisite defect formation energies are 0.15 eV and 0.8 eV lower than those of the coupled cation-antisite/Frenkel-pair defect energies in $Gd_2Ti_2O_7$ and $Gd_2Sn_2O_7$, respectively, suggesting that $Gd_2Ti_2O_7$ and $Gd_2Sn_2O_7$ pyrochlores are more likely to form the cation-antisite defect fluorite structure upon ion beam irradiation. It is interesting to note that the coupled cation-antisite/Frenkel-pair defect energy of $Gd_2Zr_2O_7$ is negative, with a value of –3.36 eV, indicating that it may easily form the defect fluorite structure. Also, we have also noticed that our calculated three forms of defect formation energies in $Gd_2Zr_2O_7$ is lower than those in $Gd_2Ti_2O_7$ and $Gd_2Sn_2O_7$, this fact suggests that the compound may easily form defect fluorite structures and may have higher possibility to resist amorphization due to irradiation, which is consistent with earlier investigations.[11] In a word, the defect formation energies can be used to explain some experimental observations, but it is not determined exclusively by the radiation "resistance".

In conclusion, the calculated defect-formation energies and covalency of ⟨B–O⟩ bonds decreases, but the cohesive energy increases in the same order as Sn→Ti→Zr, this fact is not consistent with the degree of radiation "resistance". Chao *et al.*[22] have also pointed out for the same A^{3+} cation, it is more difficult to disorder stannate pyrochlores than titanate pyrochlores. In our calculation, we also find that Gd-titanate pyrochlore is clearly an exception, our calculated covalency of ⟨B–O⟩ bonds, the cohesive energy and defect-formation energies all indicate that $Gd_2Sn_2O_7$ has lowest "resistance" to ion-beam-induced amorphization.

4. Conclusion

First principles calculations based on a DFT/PAW method have been carried out on $Gd_2B_2O_7$ (B = Ti, Sn, Zr) compounds to investigate their radiation response behaviour. The effects of the properties of the material (e.g., the 48f oxygen parameter x, cohesive energy, bond type, and defect-formation energy) on the resistance of Gd-pyrochlores to ion-beam-induced amorphization have been discussed. Our results suggested that the parameter x can be used to indicate the disordering tendencies within a given pyrochlore family; bond type, cohesive energy and defect–formation energies can also be used to explain some experimental observations, but they do not determine exclusively the radiation "resistance" for different pyrochlore families. Our considered defect–formation energies of $Gd_2Zr_2O_7$ is lower than those of $Gd_2Ti_2O_7$ and $Gd_2Sn_2O_7$, this fact suggests that the compound may easily form defect fluorite structures and may have high possibility to resist amorphization due to irradiation. Up to now, it is still necessary to search into better factors to explain completely the experimental response of pyrochlores to ion beam-induced amorphization.

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