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First-principles study of energetic and electronic properties of δ - $\text{Re}_6\text{MO}_{12}$ (Re = Ho, Gd, Y; M = U, W)

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First-principles calculations have been performed to study the structural, energetic, and electronic properties of δ - $\text{Re}_6\text{MO}_{12}$ (Re = Ho, Gd, Y; M = U, W). The calculated results indicated that the energetic tendencies for the formation of Frenkel-pair defects of δ - $\text{Re}_6\text{MO}_{12}$ are consistent with the experimental results, and the Frenkel-pair defects have a significant influence on radiation-induced phase transformation. Density of states (DOS) analysis showed hybridizations between W 5*d* and O 2*p* states in Y_6WO_{12} and between U 6*d* and O 2*p* states in $\text{Re}_6\text{UO}_{12}$ (Re = Ho, Gd, Y) are observed, but the interaction $\langle\text{M-O}\rangle$ orbital is much stronger in $\text{Re}_6\text{UO}_{12}$ (Re = Ho, Gd, Y) than that in Y_6WO_{12} . Bader charge analysis revealed that $\langle\text{U-O}\rangle$ bond in $\text{Re}_6\text{UO}_{12}$ (Re = Ho, Gd, Y) is more covalent than $\langle\text{W-O}\rangle$ bond in Y_6WO_{12} . It was proposed that $\langle\text{M-O}\rangle$ bond may play a more significant role in determining their radiation tolerance. © 2013 AIP Publishing LLC.

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I. INTRODUCTION

To develop advanced nuclear fuel forms or waste forms, crystalline oxides (δ)-phase compounds A_6BO_{12} with fluorite (CaF_2) derivative structures as radiation-tolerant materials have been received considerable attention in recent years.^{1–5} Experimentally, the tungsten-bearing compounds Y_6WO_{12} and $\text{Yb}_6\text{WO}_{12}$ were amorphized under the irradiation dose of 50 dpa (displacement per atom), while amorphization was not observed in the uranium-bearing A_6UO_{12} (A = Y, Gd, Ho, Yb, and Lu) at a higher dose of 65 dpa.⁵ In these compounds, $\text{Gd}_6\text{UO}_{12}$ and $\text{Yb}_6\text{UO}_{12}$ transformed to a fully fluorite phase, while no fully O-D transformation were found in Y_6UO_{12} , $\text{Ho}_6\text{UO}_{12}$, and $\text{Lu}_6\text{UO}_{12}$ under 2×10^{20} ions/m² fluence of Kr^{++} ions radiation.² As it is well known, several fluorite derivative compounds such as pyrochlores ($\text{A}_2\text{B}_2\text{O}_7$), γ - $\text{A}_2\text{B}_5\text{O}_{13}$, β - $\text{A}_2\text{B}_7\text{O}_{17}$, and δ - $\text{A}_4\text{B}_3\text{O}_{12}$ also undergo O-D phase transformation from an ordered fluorite derivative structure to a disordered fluorite phase under irradiation.^{6–9}

Great efforts have been devoted in investigating the factors influencing the response of δ - A_6BO_{12} to ion irradiation-induced O-D transformation. In δ - A_6BO_{12} , the radiation-induced O-D transformation involves cation antisite and anion Frenkel reactions.⁵ Several theoretical studies of δ - A_6BO_{12} compounds using density functional theory calculations have been performed and most of the calculations were focused on the effects of cation-antisite defect formation energy and O-D transformation energy on the stability of δ - A_6BO_{12} . Tang *et al.*⁵ demonstrated that δ - Y_6UO_{12} is the most difficult to undergo an ordered to disordered cubic fluorite transformation in the $\text{Yb}_6\text{WO}_{12}$, Y_6WO_{12} and Y_6UO_{12} , although the cation antisite formation energies of Y_6UO_{12} is the minimum. The results revealed that the cation-antisite defect formation energy cannot be a single interpretation to

O-D phase transition. They also investigated the O-D phase transformation energies in $\text{Re}_6\text{UO}_{12}$ (Re = Y, Lu, Ho, Gd, and Yb) using first-principles calculations with special quasi-random structure (SQS) approach.³ Their calculations indicated that $\text{Gd}_6\text{UO}_{12}$ and $\text{Yb}_6\text{UO}_{12}$ compounds have lower O-D transformation energies, and these two compounds are more readily undergo O-D phase transformation compared to other three compounds Y_6UO_{12} , $\text{Lu}_6\text{UO}_{12}$, and $\text{Ho}_6\text{UO}_{12}$. Obviously, from these calculations, which one of the cation antisite and anion Frenkel defects determining the radiation-induced O-D transformation tendencies of these δ - A_6BO_{12} compounds is uncertain.

There are many factors that can influence the response of δ - A_6BO_{12} to radiation-induced O-D transformation, including cation antisite defects, Frenkel-pair defects, couple cation antisite/Frenkel-pair defects, ionic radius ratio, electronic and bonding properties. In this paper, we calculated the formation energies of cation antisite defects, anion Frenkel-pair defects, and coupled cation antisite/Frenkel-pair defect of δ - $\text{Re}_6\text{MO}_{12}$ (Re = Ho, Gd, Y; M = U, W) using first-principles calculations. The density of states and Bader charges were also provided and the effect of electronic structures and the bond properties on the stability of these compounds were analyzed.

II. CALCULATIONAL METHOD

First-principles calculations were performed using the all-electron projector augmented wave (PAW) method within the generalized gradient approximation (GGA), as implemented in the Vienna *ab initio* simulation package (VASP).^{10–15} The electronic exchange-correlation interactions were described by PW91 functional.¹⁶ The conjugate gradient scheme was used in relaxing lattice parameters and internal atomic positions of all the structures. The convergence tests were accomplished by using different k-point samplings and plane-wave cut-off energies. The testing results suggested that the total energies were calculated with

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$2 \times 2 \times 2$ Gamma centered k -point mesh and a cutoff energy of 500 eV, and a $5 \times 5 \times 5$ Gamma centered k -point mesh was used in the calculations of density of states and Bader charge. The electronic problem was in all calculations iterated until the changes in both the total energy were below 1×10^{-5} eV/atom. Ionic relaxation was stopped until the forces were less than 1×10^{-3} eV/Å. The ion-electron interaction was modeled by *Vanderbilt* ultrasoft pseudopotentials with the following atomic valence configurations: Y ($4s^2, 4p^6, 5s^2, 4d^1$), U ($6s^2, 7s^2, 6p^6, 6d^1, 5f^3$), and W ($6s^2, 5p^6, 5d^4$). Since the f -electrons of lanthanide cations are localized in the inner $4f$ levels, the $4f$ states of Gd and Ho were treated as the core states.¹⁷ Computations were based on the unit cell consisting of 76 atoms.

III. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structure of the compound δ -A₆BO₁₂ belongs to space group $R\bar{3}$ and is related to the fluorite phase (shown in Fig. 1). Different from δ -A₄B₃O₁₂ compounds, the δ -A₆BO₁₂ structure possesses ordering both the A and B cations on the cation sublattices, as well as the oxygen “vacancies” on the anion sublattices.^{3–5,18} The A³⁺ cations occupy the general 18*f* sites with VII-fold coordination relative to the surrounding O anions, while the B⁶⁺ cations occupy the 3*a* Wyckoff equipoint in VI-fold, distorted

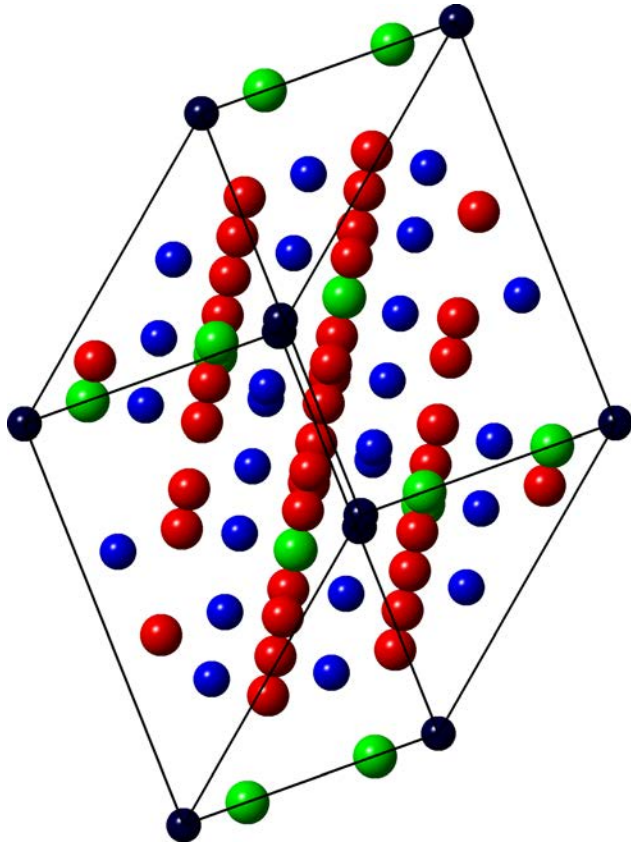


FIG. 1. Schematic diagram showing the idealized unit cell of δ -A₆BO₁₂ with B cation at the origin (black), and A cations (blue), and oxygen anions (red) in the cell interior. The green sphere represents “missing” O anions, compared to the ideal fluorite (CaF₂) crystal structure.

octahedral coordination relative to the nearest-neighbor oxygen anions.^{3–5,18} The O anions are placed in two sets of (18*f*) general positions O₁ and O₂ and occupy layers with the same x and y parameters as the metal ions. Relative to the ideal MO₂ fluorite phase, the formally vacant anion sites are located at the 6*c* equipoint positions on the triad axes and around by some relaxation of the O anions from their ideal fluorite positions.^{3–5,18}

Previous studies showed a trend toward delimiting the fluorite derivative structures stability field by a simple consideration of the cation radius ratio, and the radius ratio generally is chosen empirically to best fit the available experimental data.^{19,20} So the factor that may contribute to the O-D transformation in δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W) should take into account the cation radius ratio. The large size of radius ratio is not favorable to cation antisite reactions, which leads to restrict the atomic mechanisms available for lattice recovery from radiation damage.¹ According to this conclusion, Y₆WO₁₂ is more easily amorphized due to the maximum value of radius ratio in δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W) compounds from Table I, which is in good agreement with the experimental observations.^{2,4} Moreover, if the cation radius ratio is indeed an important parameter in determining susceptibility to radiation-induced damage, Yb₆UO₁₂ is also more radiation resistant than Y₆UO₁₂, since the radius ratio of Yb₆UO₁₂ ($r_{Yb}/r_U = 1.2671$) also is smaller than that of Y₆UO₁₂ ($r_Y/r_U = 1.3151$). However, experimentally, Tang *et al.* showed that Yb₆UO₁₂ and Gd₆UO₁₂ experienced a full O-D transformation but Ho₆UO₁₂, Y₆UO₁₂, and Lu₆UO₁₂ only partly underwent transformation.² Thus, the radius ratio alone cannot generally predict the O-D transformation or amorphization in δ -A₆BO₁₂. We propose alternative methods of determining pyrochlore stability of δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W) compounds, through energy-minimization calculations.

The optimized lattice parameters a and c are presented in Table I, which are in reasonable agreement with the experimental results.^{1–5,18} The bond lengths were obtained from the nearest distance between Re and O₁, Re and O₂, U and O₁, U and O₂ atoms (shown in Table I). The lengths of \langle Re-O₂ \rangle and \langle M-O₂ \rangle bonds increase with increasing lattice parameters c , but for \langle M-O₁ \rangle bond length, which only depends on the parameter of a . In addition, the interaction of \langle M-O₁ \rangle bond is relatively stronger than that of other bonds. It has been indicated that the \langle M-O₁ \rangle interaction may have more significant influence on the radiation resistance behavior of δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W).

TABLE I. The cation radius ratio r_{Re}/r_M , lattice parameters a and c (Å), and bond length d (Å) of δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W).

Composition	Radius		$d_{(Re-O_1)}$	$d_{(Re-O_2)}$	$d_{(M-O_1)}$	$d_{(M-O_2)}$	
	ratio	a					c
Ho ₆ UO ₁₂	—	9.9487	9.3734	2.3609	2.2546	2.0956	4.2567
Y ₆ UO ₁₂	1.3151	10.0712	9.4951	2.3924	2.2861	2.1091	4.3151
Gd ₆ UO ₁₂	1.3699	10.0998	9.5422	2.4181	2.2957	2.1114	4.3410
Y ₆ WO ₁₂	1.6000	9.8617	9.4039	2.3938	2.2813	1.9575	4.2876

B. Defect formation energy

In fluorite derivative structures compounds, the O-D transformation necessarily involves disordering of both cation and anion sublattices. On the other hand, the radiation-induced O-D transformation is caused by cation antisite reactions and anion Frenkel-pair reactions. For example, many theoretical researches indicated that the pyrochlore compositions with lower cation-antisite defect energies are more easily disordered to the defect fluorite structure and more “resistant” to ion beam-induced amorphization.^{17,21–25} In addition, great efforts have also been devoted to investigating the factors influencing the response of A_6BO_{12} to ion irradiation-induced O-D transformation, especially defect formation energy. Tang *et al.*³ have studied the radiation tolerance of complex oxides Re_6MO_{12} ($Re = Lu, Yb, Ho, Gd$ and Y). It was suggested that the compounds with lower O-D transformation energies are more likely to form disordered fluorite and behave more robustly in a radiation environment. Furthermore, they also indicated that cation antisite defect is less susceptible to O-D transformation in Y_6WO_{12} , Yb_6WO_{12} , and Y_6UO_{12} .⁵ However, it is still not clear which one of the cation antisite reactions and anion Frenkel-pair reactions controls the ion-irradiation-induced amorphization process in δ - A_6BO_{12} . In an attempt to explain the disordering process under irradiation, we calculated the formation energies of the cation antisites, Frenkel-pair, and coupled cation antisite/Frenkel-pair defects for δ - Re_6MO_{12} ($Re = Ho, Gd, Y; M = U, W$).

The antisite formation energy was calculated by the difference between the total energy of the optimized stable structure and the relaxed defect structure by using one Re cation exchanges with the nearest M cation in δ - Re_6MO_{12} ($Re = Ho, Gd, Y; M = U, W$). Two oxygen migration paths have been taken into account: $O_1 \rightarrow V_{6c}$ (from O_1 18f site to 6c site oxygen vacancies) and $O_2 \rightarrow V_{6c}$ (O_2 migrate to oxygen vacancies). It was found that the Frenkel-pair with $O_1 \rightarrow V_{6c}$ (NN-Frenkel) defect structure is not stable and the relaxed structure leads oxygen to return to its initial position. So the Frenkel-pair defect formation energy is defined by the energy difference between the optimized stable structure and the unrelaxed NN-Frenkel defect structure. The other formation energy of Frenkel-pair with oxygen migration via $O_2 \rightarrow V_{6c}$ (2NN-Frenkel) was calculated by the difference between the total energy of the optimized stable structure and the fully relaxed defect structure. The coupled cation antisite/Frenkel-pair defect energy was obtained from the fully relaxed structure containing a cation antisite and a Frenkel-pair defect. The calculated results are shown in Table II.

In the calculations presented here, the Frenkel-pair defect formation energies are larger than that of cation antisites for all compounds, implying that cation antisite disorder may precede oxygen disorder. The NN-Frenkel defect was not found to be stable upon relaxation without the presence of associated cation defects. Together with the fact that the NN-Frenkel formation energies are larger than those of cation antisites and coupled cation antisite/NN-Frenkel defects, it indicates that oxygen defect formation independent of cation defects is unlikely. The NN-Frenkel formation energy is substantially lowered in the presence of a cation antisite defect. The results may suggest that the energetics of NN-Frenkel formation become much more favorable in the presence of a cation antisite defect.^{23,26,27} However, the phenomenon was not observed in the 2NN-Frenkel defects reaction. It may be due to locating interstitial and vacancy at a large distance for Frenkel-pair with oxygen migration via $O_2 \rightarrow V_{6c}$.

For a cation antisite defect, the formation energies increase along with variation of the cation radius ratio. The result agrees well with the observation from Tang *et al.* that the cation antisite formation energies of Y_6UO_{12} are smaller than that of Y_6WO_{12} and Yb_6WO_{12} .⁵ At the same time, Tang *et al.*² demonstrated that Y_6WO_{12} and Gd_6UO_{12} are more readily disordered than Ho_6UO_{12} and Y_6UO_{12} . It is suggested that the O-D transformation in δ - Re_6MO_{12} is not entirely controlled by the cation antisite defects, since the compounds with lower formation energies of cation antisite are more easily disordered to defect fluorite structure.

It is evident in Table II the NN-Frenkel defect energy is much larger than the 2NN-Frenkel defect energy because the NN-Frenkel defect structure is unrelaxed. The NN-Frenkel defect and 2NN-Frenkel defect energies of Gd_6UO_{12} are significantly less than that of Ho_6UO_{12} and slightly less than that of Y_6UO_{12} . The demonstrations are virtually identical with the experimental phenomena that Gd_6UO_{12} will more readily undergo O-D transformation than Y_6UO_{12} and Ho_6UO_{12} , because a fully O-D phase transformation was observed in the irradiated Gd_6UO_{12} , while Y_6UO_{12} and Ho_6UO_{12} occurred partly O-D phase transformation under 300 keV Kr^{++} ion irradiation to a fluence of 2×10^{20} ions/m².^{2,3} For Y_6WO_{12} compound, the NN-Frenkel formation energies similar to that of Y_6UO_{12} and Gd_6UO_{12} may be overestimates. However, the 2NN-Frenkel formation energies of Y_6WO_{12} are much lower than that of δ - Re_6UO_{12} ($Re = Ho, Gd, Y$) compounds, which may suggest that Y_6WO_{12} is more likely to form the defect fluorite structure upon ion beam irradiation. The result is in accordance with experimental observation that O-D phase transformation may occur more readily in compound Y_6WO_{12} .

TABLE II. Calculated defect formation energies (eV) of δ - Re_6MO_{12} ($Re = Ho, Gd, Y; M = U, W$). NN-F = NN-Frenkel.

Composition	Radius ratio	Cation antisite	NN-F	2NN-F	Coupled cation-antisite/NN-F	Coupled cation-antisite/2NN-F
Ho_6UO_{12}	—	1.2853	6.0416	2.4962	1.2567	2.7204
Y_6UO_{12}	1.3151	1.3019	5.6776	2.3968	1.2053	2.6728
Gd_6UO_{12}	1.3699	1.3419	5.6456	2.3557	1.3065	2.6250
Y_6WO_{12}	1.6000	1.8423	5.6335	1.8852	1.8009	3.4437

From the present calculations, it is interesting to note that Frenkel-pair formation energies of δ - A_6BO_{12} have more significant influence on radiation-induced phase transformation than other type defects, and the compounds with lower value of Frenkel-pair defect formation energies are energetically more susceptible to radiation-induced O–D transformation in δ - Re_6MO_{12} ($Re = Ho, Gd, Y; M = U, W$). Furthermore, the defect formation energies obtained in the present studies can be used to explain some experimental observations.

C. Electronic and bonding properties

In this work, all of these compounds present similar total density of states. As a typical example, the total DOS and partial DOS (PDOS) for every atom distribution of Y_6UO_{12} , Gd_6UO_{12} and Y_6WO_{12} are shown in the Fig. 2. The Fermi level is set to 0 eV.

For Y_6UO_{12} compound, the hybridization interaction exists among the Y 4*d*, U 5*f*, and 2*p* states of oxygen in the conduction bands from Fig. 2(a). The lower part of the valence band is mainly dominated by O 2*s*, but the upper part mainly by O 2*p* states. The band peaks in the energy range from -21.3 eV to -19.6 eV are mainly composed of Y 4*p*, U 6*p* and O 2*s* orbitals. The bands ranging from -17.3 eV to -14.4 eV are contributed from U 6*p* and O 2*s* states with small admixtures of U 6*d* orbitals. The upper part of the valence bands is mainly composed of Y 4*d*, 4*p*, U 6*d*, 6*p*, and O 2*p* orbitals. The DOS of Gd_6UO_{12} is similar to Y_6UO_{12} , except the Gd atomic partial DOS of valence bands and conduction bands are donated by Gd 5*p* and 5*d* states.

The disparities between Y_6UO_{12} and Gd_6UO_{12} are that the width of the PDOS of U 6*p* and O 2*s* states in Gd_6UO_{12} is clearly narrower than that in Y_6UO_{12} , and the number of peaks is also less than those in Y_6UO_{12} at the energy range from -21.3 eV to -19.6 eV (shown in Fig. 2(b)). These indicate that the hybridization between U 6*p* and O 2*s* states in Gd_6UO_{12} is stronger than that in Y_6UO_{12} . In addition, the intensities of O 2*s* or 2*p* in Gd_6UO_{12} are relatively weaker than the corresponding peaks in Y_6UO_{12} , meaning the smaller electron distribution on O 2*s* or 2*p* in Gd_6UO_{12} and the weaker interaction between O and U in Gd_6UO_{12} . It is proposed that $\langle U-O \rangle$ bond of Y_6UO_{12} is more covalent than that of Gd_6UO_{12} .

Seen from Fig. 2(c), the conduction bands are mainly composed of Y 4*d*, W 5*d*, and O 2*p* orbitals. Compared to DOS of Y_6UO_{12} , there are less hybridization between W 5*d* and O 2*p* states than that of U 6*d* and O 2*p* states in the valence bands. Especially, the hybridization phenomenon is not observed in the energy range from -21.3 eV to -19.6 eV. The results suggest that the covalent interaction of the $\langle U-O \rangle$ bond of Y_6UO_{12} is stronger than that of the $\langle W-O \rangle$ bond in Y_6WO_{12} . Experimentally, it was observed that Y_6WO_{12} can be more readily disordered and amorphized than Y_6UO_{12} .⁵ Combined with the relation between $\langle U-O \rangle$ bond and O–D transformation in Re_6UO_{12} ($Re = Ho, Gd, Y$), it is clear that the covalent interaction of the $\langle M-O \rangle$ bond may play more significant role in determining the set of irradiation damage in δ - Re_6MO_{12} ($Re = Ho, Gd, Y; M = U, W$).

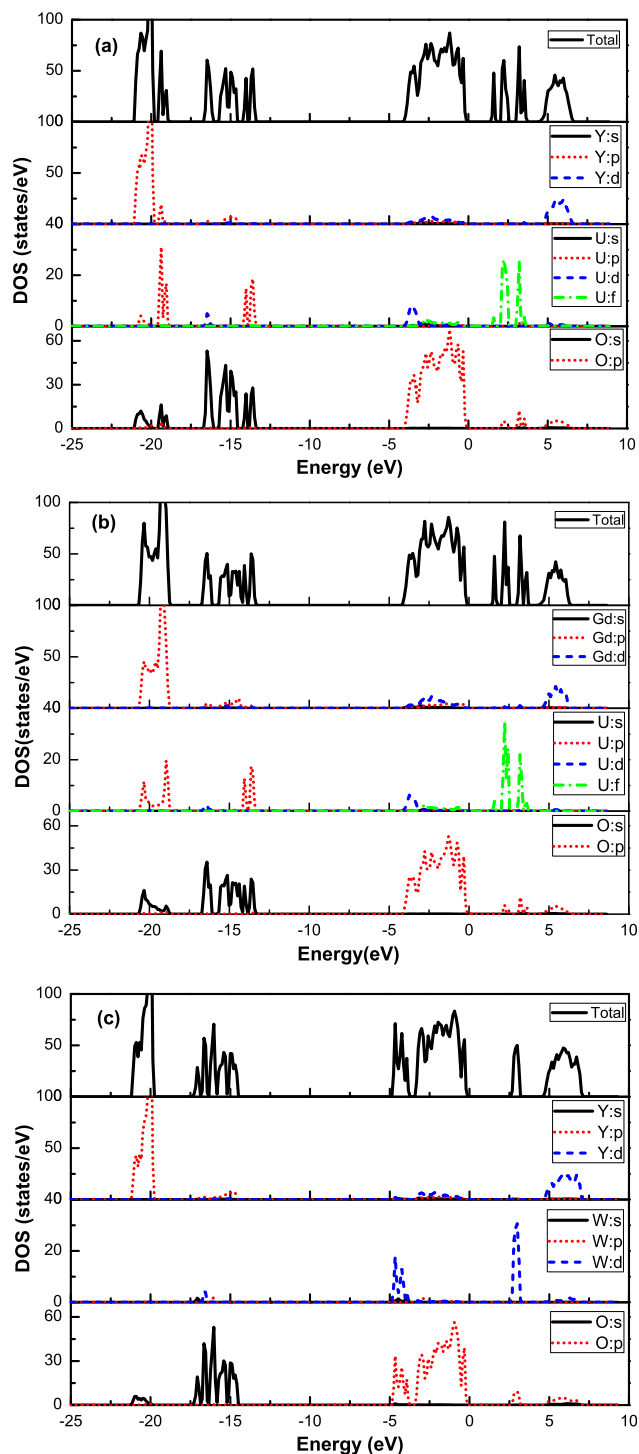


FIG. 2. (a) Total and partial DOS curves for Y_6UO_{12} ; (b) Total and partial DOS curves for Gd_6UO_{12} ; (c) Total and partial DOS curves for Y_6WO_{12} .

Based on the optimized geometries, we calculated the Bader charge to provide some fundamental understanding for the nature of the chemical bond. In Table III, we showed the calculated Bader charges for the cations of Re^{3+} and M^{6+} , and O at two anion sites. The charge state is not the nominal $+3 |e|$, $+6 |e|$, or $-2 |e|$ because the classical model of an ionic material with nominal charges is oversimplified.²⁸ Although the Bader charge for M ions is much larger than those for Re ions, the $\langle M-O \rangle$ bond is more covalent than $\langle Re-O \rangle$ bond, since the charge state for M ions

TABLE III. Calculated Bader charges (|e|) for each ion in δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W).

Composition	Radius		Re	M	O ₁	O ₂	
	ratio	<i>a</i>					<i>c</i>
Ho ₆ UO ₁₂	—	9.9487	9.3734	2.0473	2.8053	-1.1899	-1.3249
Y ₆ UO ₁₂	1.3151	10.0712	9.4951	2.1723	2.791	-1.2289	-1.4085
Gd ₆ UO ₁₂	1.3699	10.0998	9.5422	2.044	2.7963	-1.1898	-1.3202
Y ₆ WO ₁₂	1.6000	9.8617	9.4039	2.1725	2.9073	-1.2563	-1.4007

corresponds to a nominal +6 |e| state.²⁹ The Re³⁺ charges of Ho₆UO₁₂ and Gd₆UO₁₂ are less than that of Y₆UO₁₂, which showed that ⟨Re-O⟩ bond for Y₆UO₁₂ is less covalent character than those of Ho₆UO₁₂ and Gd₆UO₁₂. The ⟨Y-O⟩ of Y₆WO₁₂ has similar character to that of Y₆UO₁₂. This indicates that the radiation tolerance is not sensitive to the ⟨Re-O⟩ bond in these compounds. The charges of U are similar in the Re₆UO₁₂ (Re = Ho, Gd, Y). However, the ⟨W-O⟩ bond of Y₆WO₁₂ is obviously different from ⟨U-O⟩ of Re₆UO₁₂ (Re = Ho, Gd, Y), which is due to the charges of W are larger than that of U. It suggests that the ⟨U-O⟩ bond of Re₆UO₁₂ is more covalent than that of ⟨W-O⟩ bond in Y₆WO₁₂. The uranate compounds Ho₆UO₁₂ and Gd₆UO₁₂ were more difficult to be amorphized than the tungstate Y₆WO₁₂ from the experiment.⁵ A close correlation was found between ⟨M-O⟩ bond and the susceptibility of δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W) to ion-beam-induced amorphization. The inference is similar to the DOS analysis.

IV. CONCLUSION

In this work, we have investigated the energetics of defects and characterized electronic the properties of δ -Re₆MO₁₂ (Re = Ho, Gd, Y; M = U, W) using first-principles calculations based on density functional theory. A detailed analysis of the structural parameters, the defect formation energies, and electronic properties are presented. The results indicate that the lattice parameters and cation radius ratio cannot be used to fully explain the O-D transformation or amorphization in these compounds. The calculated defect formation energies reveal that the radiation damage in δ -Re₆MO₁₂, including O-D transformation and amorphization, is closely associated with the defect formation energy. Moreover, it is anticipated that the compounds with lower Frenkel-pair defect formation energies may be more readily undergo ion beam-induced O-D transformation and amorphization, which may explain some experimental observations.

The analysis of DOS and Bader charges shows that the covalent interaction of the ⟨U-O⟩ bond in Y₆UO₁₂ is stronger than that of the ⟨W-O⟩ bond in Y₆WO₁₂. The ⟨U-O⟩ bond in Gd₆UO₁₂ is less covalent than that in Y₆UO₁₂ because of the hybridization of U 5*f* electrons with O 2*p* orbital. Based on the experiment observations and present calculations, it is proposed that the ⟨M-O⟩ bond in δ -Re₆MO₁₂ (Re = Ho, Gd,

Y; M = U, W) is susceptible to O-D transformation and radiation-induced amorphization.

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