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Research Article

Electronic Structure Calculations of $A_2Ti_2O_7$ (A = Dy, Ho, and Y)

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Ab initio calculations have been performed on titanate pyrochlores $A_2Ti_2O_7$ (A = Dy, Ho, and Y) to investigate their electronic structures. The generalized gradient approximation (GGA) + U formalism has been used to correct the strong onsite Coulomb repulsion between the localized 4f electrons. The effects of effective U values on the structural and electronic properties of $A_2Ti_2O_7$ (A = Dy, Ho, and Y) have been discussed. It is shown that $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ exhibit different electronic structures from $Y_2Ti_2O_7$. The strong interaction between Dy and Ho 4f electrons and O 2p orbitals may increase the covalency of ⟨Dy–O⟩ and ⟨Ho–O⟩ bonds and decrease their irradiation resistance.

1. Introduction

Materials with the $A_2B_2O_7$ pyrochlore structure have wide ranges of composition that lead to remarkable properties and wide variations in ionic and electronic conductivity, catalytic activity, and electrooptic and piezoelectric behavior [1]. Because they can be used to immobilize actinides [2–5], the pyrochlores have attracted significant attention both theoretically and experimentally [6–21]. In $A_2B_2O_7$ pyrochlore structure, the A and B cations occupy the 16d (0.5, 0.5, 0.5) and 16c (0, 0, 0) sites, respectively, and the oxygens are in the 48f (x, 0125, 0.125) and 8b (0.375, 0.375, 0.375) positions (using the Wyckoff notation) [22]. Single crystals of the $A_2Ti_2O_7$ pyrochlores (A = Sm to Lu and Y) have been irradiated by 1 MeV Kr^+ ions, and their microstructural evolutions as a function of increasing radiation dose have been characterized [7]. A slight deviation from the monotonic trend of critical amorphization temperature T_c versus the ionic radius was observed for $Y_2Ti_2O_7$. T_c is frequently used as a measurement of the resistance of a material to amorphization, and lower values of T_c are the result of substantial dynamic annealing occurring during irradiation, which allows the materials to remain in the crystalline state. Generally, pyrochlores that are closer to the ideal fluorite structures are more susceptible to the radiation-induced pyrochlore-to-defect fluorite structural transition. The defect fluorite structure results from disordering of the A- and B-site cations, as well as the anion vacancies. Thus, pyrochlore compositions that are more easily disordered to the defect fluorite structure are more "resistant" to ion-beam-induced amorphization [7]. On the other hand, theoretical investigations reported by Sickafus et al. [18] have demonstrated that compounds with very dissimilar cationic radii (e.g., closer to the ideal pyrochlore structure, $x_{O48f} = 0.3125$) should exhibit the greatest susceptibility to structural destabilization (e.g., amorphization), whereas compounds with more similar radii (e.g., closer to the ideal fluorite structure) should behave more robustly in a radiation environment. For $A_2Ti_2O_7$ (A = Dy, Ho, and Y), the ionic radius ratio (r_A/r_{Ti}) decreases monotonically. According to Sickafus' point of view, the compounds should become more radiation resistant as the cation A varies from Dy to Ho. However, the critical amorphization temperatures were measured to be 910, 850, and 780 K for $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Y_2Ti_2O_7$ compounds, respectively [7], meaning that of these three compounds, $Y_2Ti_2O_7$ is the most radiation resistant. It is clear that cation radius ratio alone cannot be used to explain the different responses of these compositions to radiation.

To resolve the discrepancy between experimental observations and theoretical predictions, it is important to fundamentally understand the electronic structures of A-site elements and their effects on the stability of the pyrochlore

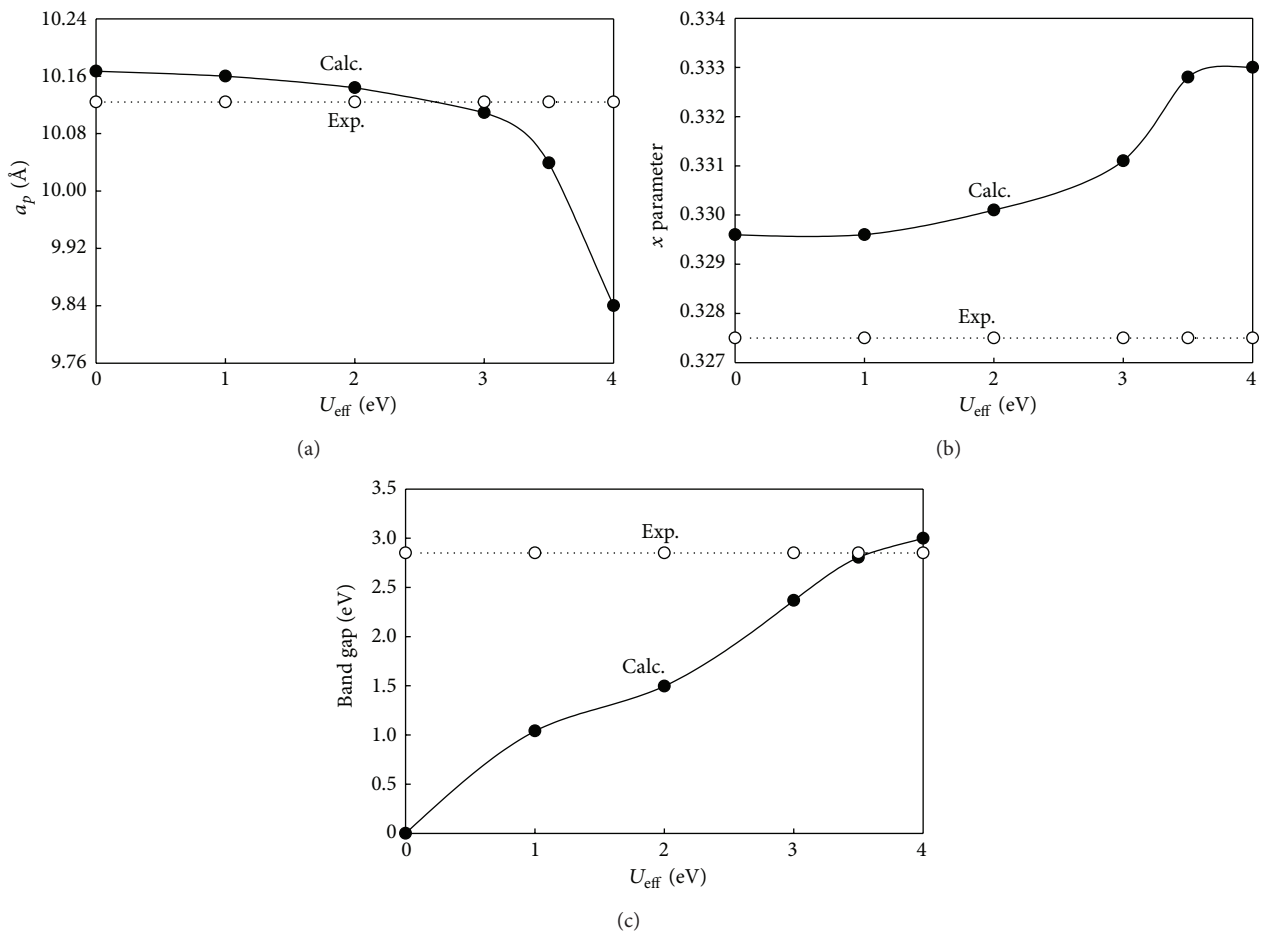


Figure 1: Dependence of the lattice parameter a_p (a), x (b), and band gap (c) of the $Dy_2Ti_2O_7$ on U_{eff}.

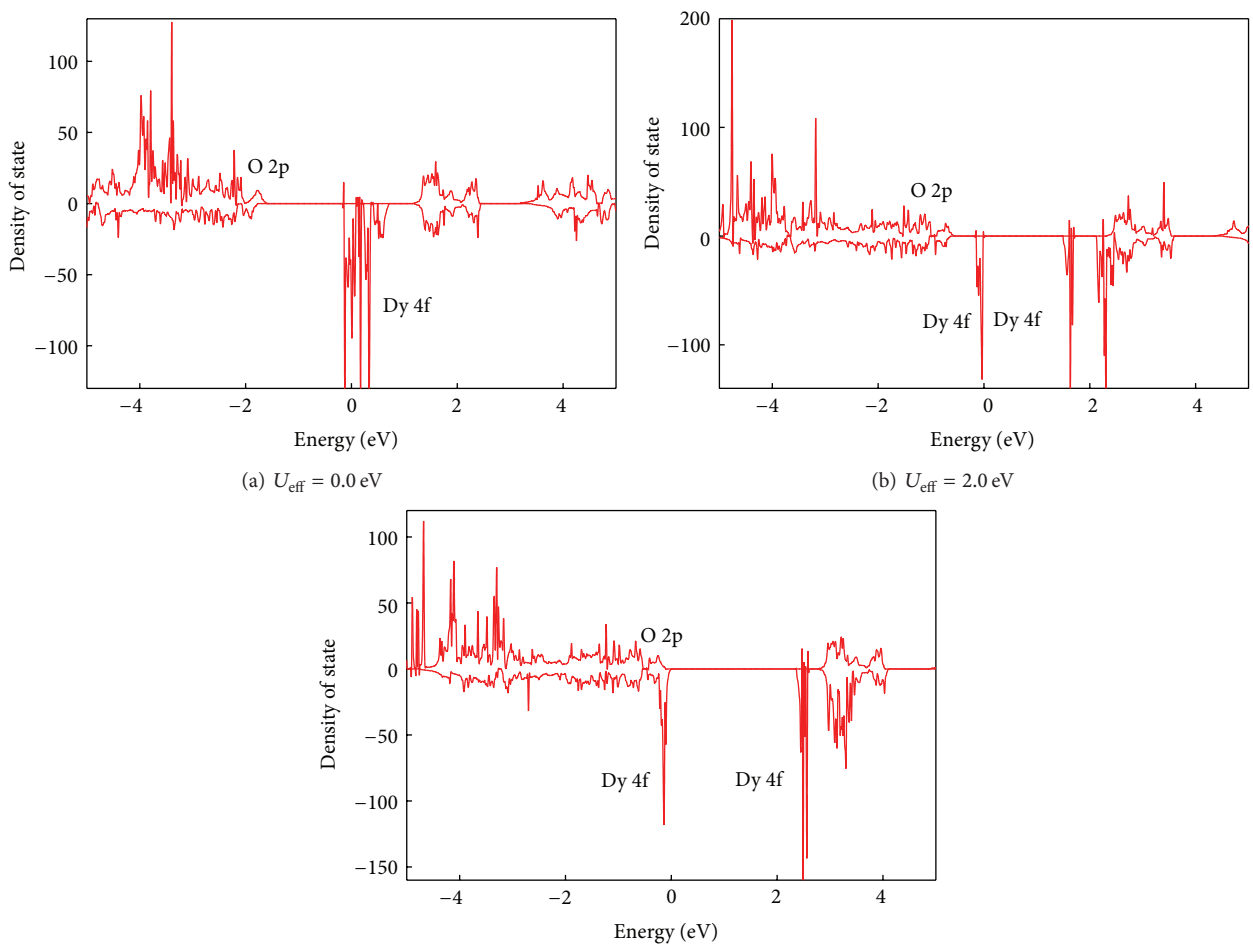
structure. In the present study, *ab initio* total energy calculations [17, 19, 23] based on density functional theory have been performed on $A_2Ti_2O_7$ (A = Dy, Ho, and Y) pyrochlores. GGA + U formalism has been used to account for the strong on-site Coulomb repulsion among the 4f electrons in $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$. How the structural and electronic properties of $A_2Ti_2O_7$ (A = Dy, Ho, and Y) pyrochlores are affected by the choice of U is discussed. These calculations will provide significant insight into the effects of electronic configuration on the thermochemical stability of pyrochlore of different compositions.

2. Calculational Method

All the calculations have been completed using the VASP code [24] with spin-polarized effects taken into account. A primitive unit cell containing 22 atoms was used for the present investigations, with a 4 × 4 × 4 Monkhorst-Pack k-point mesh. The ion-electron interaction was described by PAW pseudopotentials with the following atomic valence configurations: Ti ($3s^2$, $3p^6$, $3d^2$, and $4s^2$), Y ($4s^2$, $4p^6$, $4d^1$, and $5s^2$), Dy ($5s^2$, $5p^6$, $4f^{10}$, and $6s^2$), and Ho ($5s^2$, $5p^6$, $4f^{11}$, and $6s^2$). The PBE functional within the generalized gradient approximation was used to describe the exchange-correlation potential energy [25, 26], with the basis set for valence electrons consisting of plane waves with a cut-off energy of 400 eV. The calculations were performed based on ferromagnetic ordering of the magnetic moments and antiferromagnetic ordering, and spin ice model [27, 28] is not considered in the present work. The Hubbard U correction was introduced using the method proposed by Dudarev et al. [29], in which the Hubbard parameter U reflecting the strength of onsite Coulomb interaction and parameter J adjusting the strength of exchange interaction are combined into a single parameter $U_{\text{eff}} = U - J$.

3. Results and Discussion

3.1. Atomic and Electronic Structure of $Dy_2Ti_2O_7$. The pyrochlore structure can be completely described by the a-cell edge, a_p, and the 48 f oxygen positional parameter, x. The dependence of the lattice parameter a_p, x, and band gap of the $Dy_2Ti_2O_7$ on U_{eff} is shown in Figures 1(a), 1(b), and 1(c), respectively. As shown in Figure 1, the structural parameter a_p decreases slightly for $U_{\text{eff}} \leq 3.0$ eV. Above this value, the parameter changes more significantly. A U_{eff} of 2.6 eV



(a) $U_{\text{eff}} = 0.0$ eV

(b) $U_{\text{eff}} = 2.0$ eV

(c) $U_{\text{eff}} = 3.0$ eV

Figure 2: Total DOS distribution for $Dy_2Ti_2O_7$. (a) $U_{\text{eff}} = 0.0$ eV; (b) $U_{\text{eff}} = 2.0$ eV; and (c) $U_{\text{eff}} = 3.0$ eV. The upper and lower panels show the spin-up and spin-down channels, respectively.

yields a lattice constant of 10.12 Å, in excellent agreement with experiments [7]. For O_{48f} positional parameter x, it deviates from experimental value of 0.3275 with increasing U_{eff} values; that is, introducing $U_{\text{eff}} > 0$ makes the deviation from the experiment larger. Concerning the band structure of $Dy_2Ti_2O_7$, a sharp increase of band gap value with growing U_{eff} is observed. For a certain U_{eff} value of around 3.5 eV, the band gap value of 2.85 eV matches the calculated optical band gaps performed by Nemoshkalenko et al. [30]. It is shown that the band gap of $Dy_2Ti_2O_7$ presents stronger dependence on the U_{eff} value than lattice parameters.

Figure 2 displays the total density of state (DOS) distribution of $Dy_2Ti_2O_7$ at $U_{\text{eff}} = 0$, 2.0, and 3.0 eV. The Fermi level is set to 0 eV. At the pure GGA level, the f band does not split but shows a large peak around the Fermi level, leading to a metallic ground state, which disagrees with experiments [31]. Obviously, the pure GGA calculation without modifying the intra-atomic Coulomb interaction gives wrong results. It is suggested that introduction of a penalty function which corrects the intraband Coulomb interaction by the Hubbard U parameter is necessary for strongly correlated systems [32] such as $Dy_2Ti_2O_7$. If the U_{eff} is increased to 2 eV, the f bands undergo splitting, and a semiconducting solution with a finite separation of the occupied and unoccupied f band is found. The obtained band gap between the valence band edge (contributed by Dy 4f) and the bottom of the conduction band (contributed by Dy 4f) is 1.53 eV. In the case of $U_{\text{eff}} = 3$ eV, the unoccupied f bands shift toward higher energy level, resulting in a larger band gap value of 2.36 eV. A notable difference between the cases of $U_{\text{eff}} = 2.0$ eV and $U_{\text{eff}} = 3.0$ eV is that there is no mixture between the occupied f bands and the O 2p orbitals in the valence region at $U_{\text{eff}} = 2.0$ eV, whereas the occupied f bands become hybridized with the O 2p orbitals in the valence region at $U_{\text{eff}} = 3.0$ eV.

3.2. Atomic and Electronic Structure of $Ho_2Ti_2O_7$. Figure 3 shows the lattice parameters and band gaps of the $Ho_2Ti_2O_7$ as a function of U_{eff}. Generally, $Ho_2Ti_2O_7$ shows similar dependence on the effective U values to the case of $Dy_2Ti_2O_7$. The lattice constants decrease with increasing U_{eff}, and the reason for this behavior is a slight hybridization of Ho 4f and

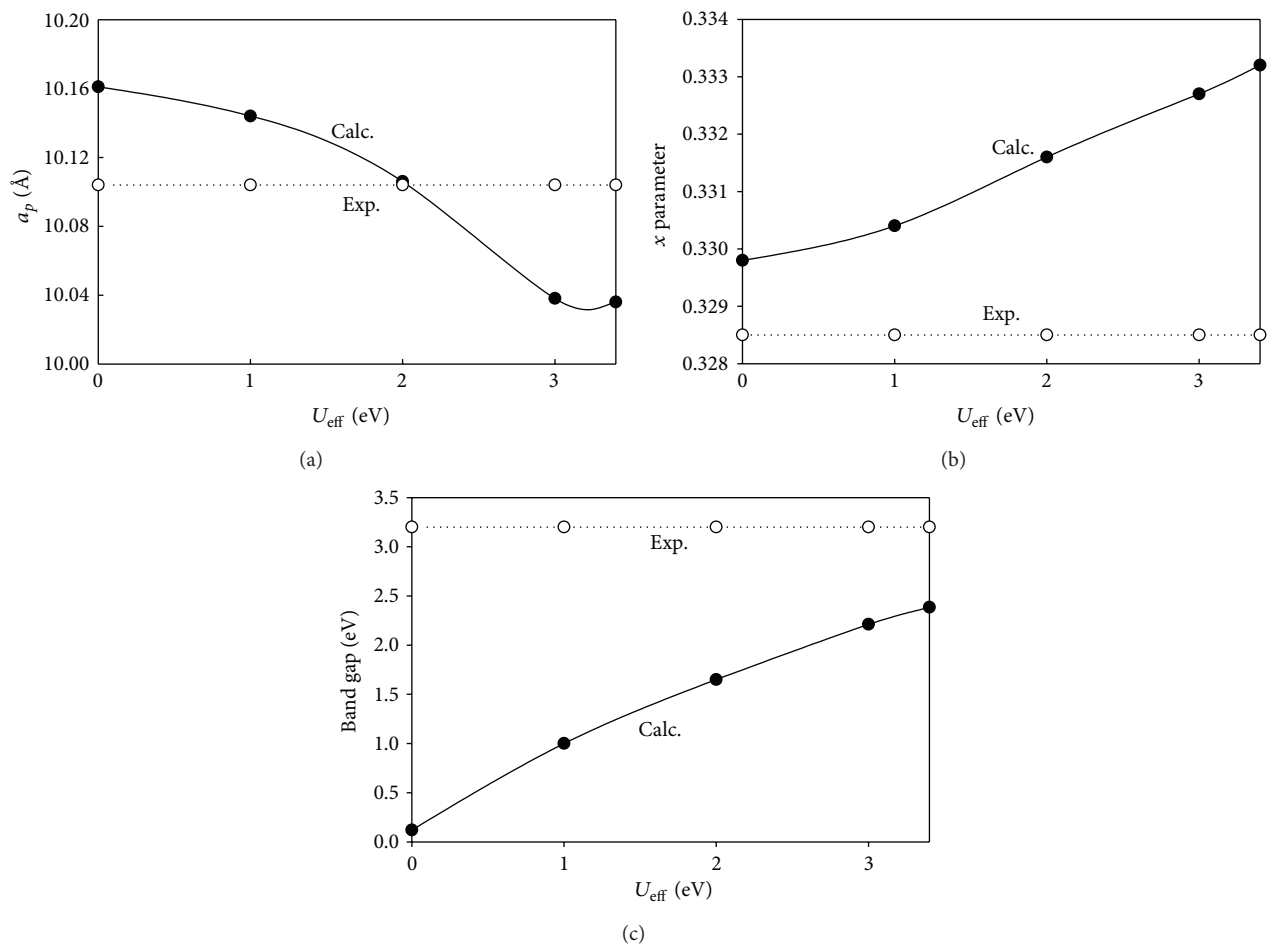


Figure 3: Dependence of the lattice parameter a_p (a), x (b), and band gap (c) of the $Ho_2Ti_2O_7$ on U_{eff}.

O 2p orbitals. The experimental lattice constant [7] of 10.104 Å is obtained for $U_{\text{eff}} = 2$ eV. For the O_{48f} positional parameter, it deviates from experimental value of 0.3285 with increasing U_{eff} values. As compared with $Dy_2Ti_2O_7$, the band gap value increases less significantly with U_{eff}. At $U_{\text{eff}} = 3$ eV, the band gap of $Ho_2Ti_2O_7$ is still 0.82 eV smaller than experimental measurement of 3.2 eV [33].

Figure 4 presents the total DOS of $Ho_2Ti_2O_7$ at $U_{\text{eff}} = 0$, 2.0, and 3.0 eV. At $U_{\text{eff}} = 0$ eV, the pure GGA calculation without modifying the intra-atomic Coulomb interaction yields a metallic ground state, in contrast to experiments [33]. As the U_{eff} is increased to 2 eV, the f bands splits, and the occupied and unoccupied f band contributes significantly to the valence bands and conduction bands, respectively. The corresponding band gap between the valence band edge and the bottom of the conduction band is 1.65 eV. Different from the total DOS distribution of $Dy_2Ti_2O_7$ at $U_{\text{eff}} = 2$ eV, the occupied f bands hybridize with O 2p orbitals in the valence region. At $U_{\text{eff}} = 3$ eV, it is noted that the main effect of increasing U_{eff} value is to push the unoccupied f bands toward higher energy level, resulting in a larger band gap value of 2.38 eV.

3.3. Atomic and Electronic Structure of $Y_2Ti_2O_7$. Yttrium titanate pyrochlore is an important member of pyrochlore family, and it is often served as a model system for pyrochlores because of its simple electronic structure [12]; that is, no f electrons exist in $Y_2Ti_2O_7$. For this composition, GGA + U method has also been employed to study if the intra-atomic electron correlations are important for Y-4d states. In Figure 5, we plot the equilibrium lattice parameters and band gap value of $Y_2Ti_2O_7$ as functions of U_{eff}. As shown in the figure, the lattice constant a_p and O_{48f} positional parameter deviate from experimental values of 10.1 Å and 0.33 [7] with increasing U_{eff} values. Specially, the choice of U_{eff} values has almost no effects on the band gap values. It is indicated that the intra-atomic electron correlations are negligible for Y-4d states in $Y_2Ti_2O_7$.

The total DOS distribution of $Y_2Ti_2O_7$ at $U_{\text{eff}} = 0.0$ eV is presented in Figure 6. The valence bands mainly consist of O 2p orbitals with small contribution from Ti 3d states, and the conduction bands are mainly composed of Ti 3d states hybridized with O 2p orbitals. The corresponding band gap is 2.82 eV, in excellent agreement with the calculated value of 2.84 eV reported by Jiang et al. [34]. This value is 0.32 eV

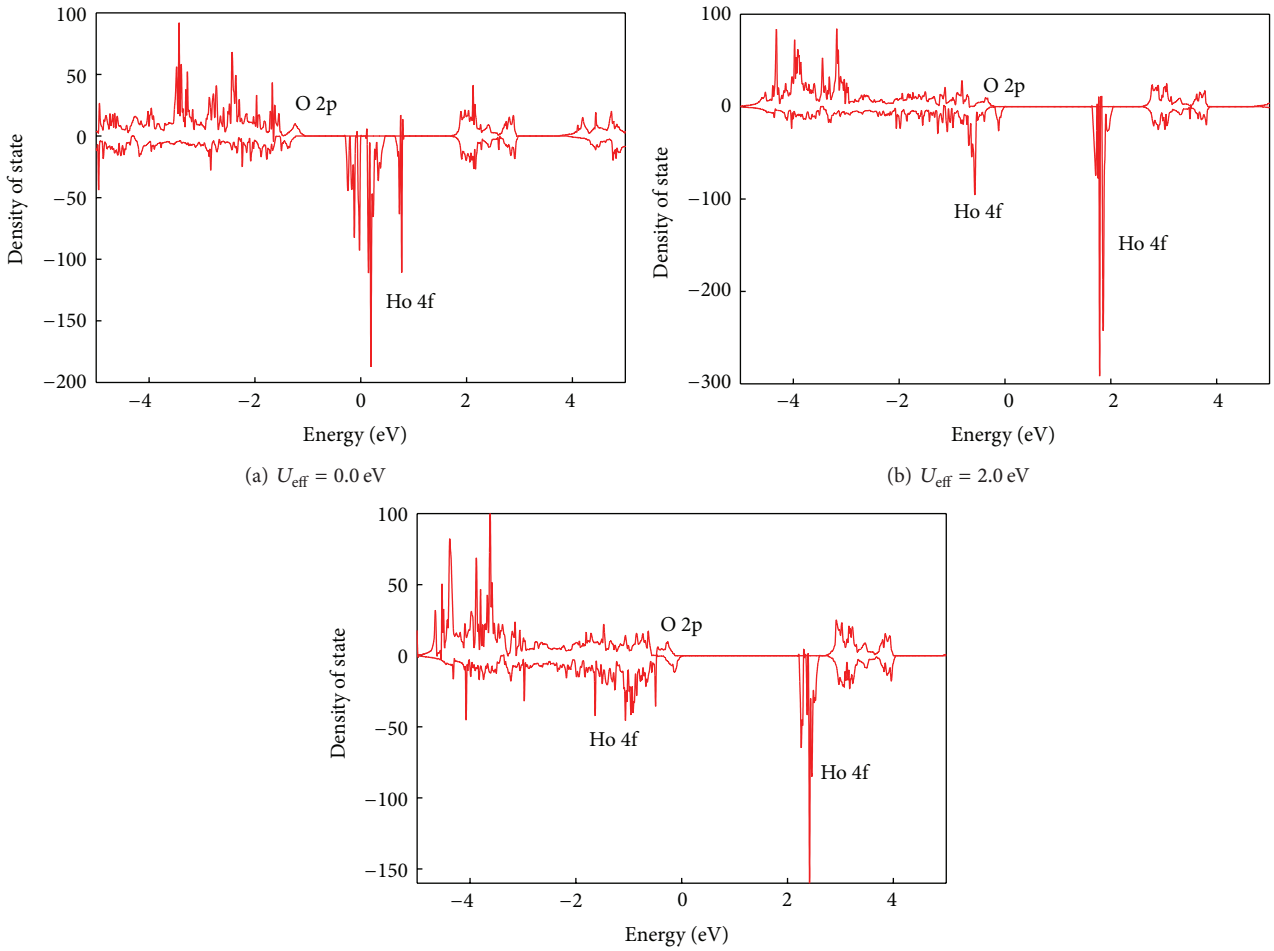


FIGURE 4: Total DOS distribution for $Ho_2Ti_2O_7$. (a) U_{eff} = 0.0 eV; (b) U_{eff} = 2.0 eV; and (c) U_{eff} = 3.0 eV. The upper and lower panels show the spin-up and spin-down channels, respectively.

larger than our previous work on $Y_2Ti_2O_7$ [10], as a result of different pseudopotential of Y employed.

3.4. Comparison of the Electronic Properties of $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Y_2Ti_2O_7$. The following discussions are based on the results obtained by U_{eff} = 3.5 eV for Dy, U_{eff} = 3.4 eV for Ho, and U_{eff} = 0.0 eV for Y. Comparison of the partial DOS distribution of these three compositions is presented in Figure 7. It is noted that the $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ have similar DOS results; in contrast, $Y_2Ti_2O_7$ shows a very different character. This is probably due to the fact that 4f electrons play an important role in $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$. The electronic structures of a series of titanate oxides $A_2Ti_2O_7$ (A = Sm-Er, Yb, and Lu) have been studied by Nemoshkalenko et al. [30] using X-ray photoelectron, emission spectroscopy, as well as the first-principles band structure calculations, where the lanthanide 4f states are assumed not to be hybridized with the other states. The calculations in the present work show that A-site 4f electrons do take part in the chemical bonding. For $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$, the most striking features are the hybridization of Dy 4f and Ho 4f orbitals with O 2p orbitals, as shown in Figure 7. Especially, a strong hybridization occurs for $Dy_2Ti_2O_7$ in its upper valence region. The 4f electrons also contribute greatly to the lower conduction bands of $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$. Unlike $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$, ⟨Ti–O⟩ interaction is more significant in $Y_2Ti_2O_7$, since its valence and conduction bands are mainly contributed by O 2p states hybridized with Ti 3d states and Ti 3d orbitals hybridized with O 2p orbitals, respectively.

Under irradiation, $Y_2Ti_2O_7$ is the most radiation resistant and $Dy_2Ti_2O_7$ is the least [7]. Since the pyrochlore compositions that are more easily disordered to the defect fluorite structure are more "resistant" to ion-beam-induced amorphization [18], $Dy_2Ti_2O_7$ is the least probable to transform into defect-fluorite structure and $Y_2Ti_2O_7$ is the most. This means that of the three compositions investigated, $Dy_2Ti_2O_7$ is the most stable thermodynamically and $Y_2Ti_2O_7$ is the least. The cation radius ratio criteria, as proposed by Sickafus et al. [18], clearly cannot be used to explain the different responses of these compositions to radiation. The radiation tolerance of nonmetallic solids has been correlated with the

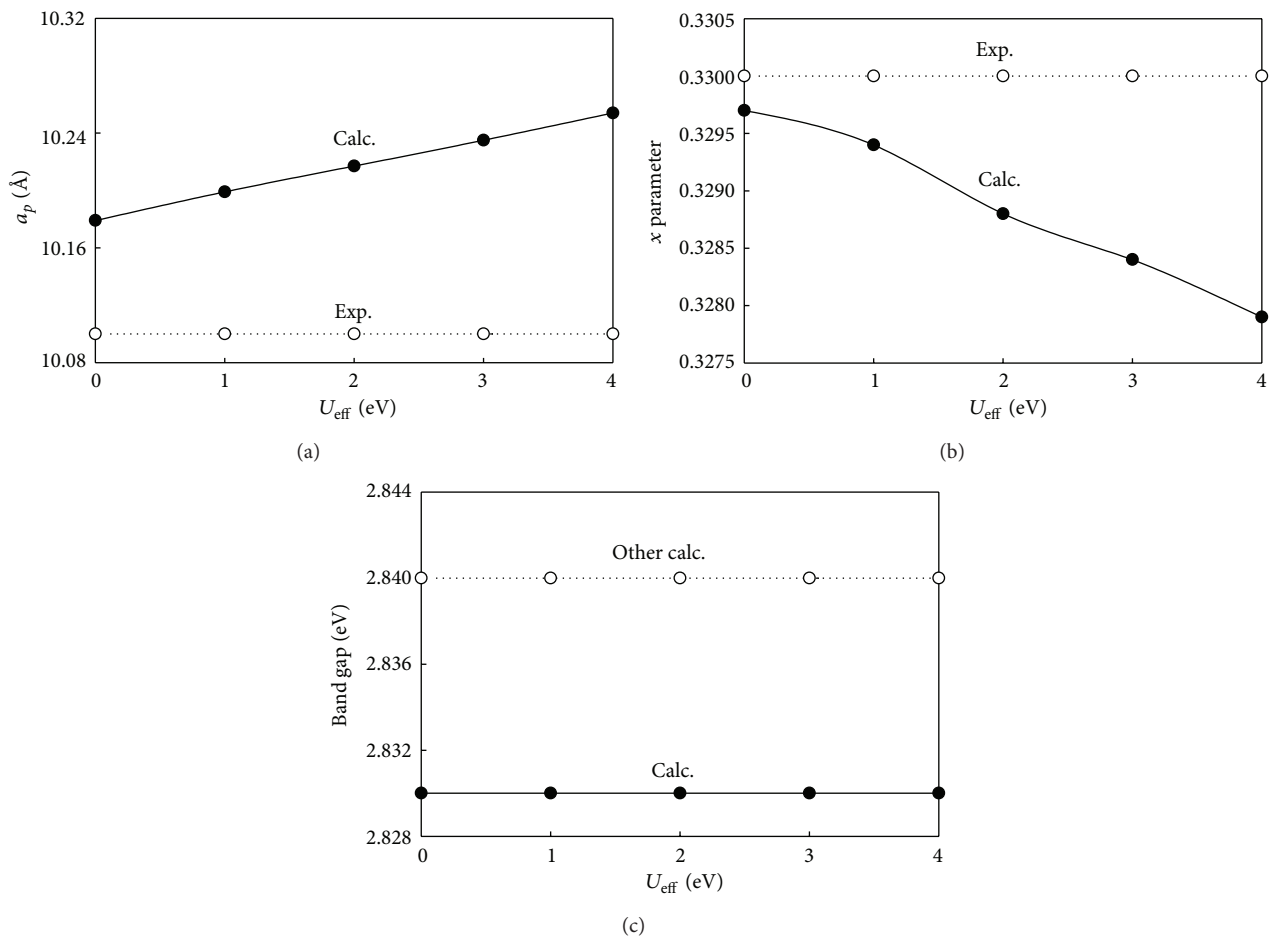


Figure 5: Dependence of the lattice parameter a_p (a), x (b), and band gap (c) of the $Y_2Ti_2O_7$ on U_{eff}.

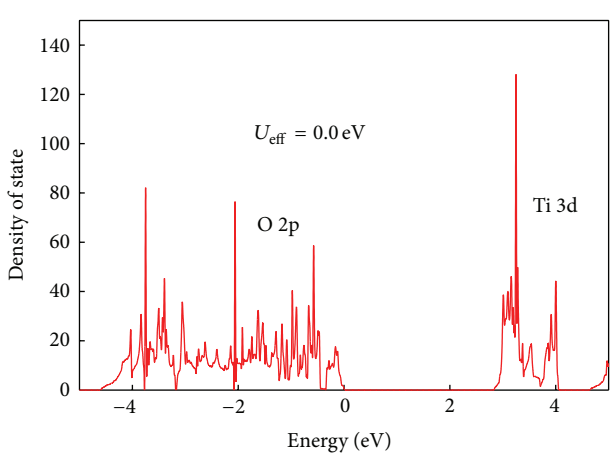


Figure 6: Total DOS distribution for $Y_2Ti_2O_7$ at U_{eff} = 0.0 eV.

nature of the chemical bond in earlier work [35–38]. They demonstrated that the more covalently bonded materials are more readily amorphized at lower temperatures under heavy ion irradiation. For pyrochlores, the less covalently bonded compositions are more easily disordered to defect-fluorite structures [7], which are highly radiation resistant and remain crystalline at extreme radiation dose. In the present work, the strong interaction between Dy and Ho 4f electrons and O 2p orbitals may increase the covalency of ⟨Dy–O⟩ and ⟨Ho–O⟩ bonds and decrease the irradiation resistance of $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$.

4. Conclusions

The electronic structures of $A_2Ti_2O_7$ (A = Dy, Ho, and Y) have been investigated using GGA + U method. The effects of effective U values on the structural and electronic properties of pyrochlores have been studied. It is shown that for strongly correlated systems such as $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$, it is necessary to correct the intraband Coulomb interaction by the Hubbard U parameter. We suggest that the electronic structure can be reasonably described with U_{eff} of 3 ∼ 4 eV for $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$.

$Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ have similar DOS distribution; in contrast, $Y_2Ti_2O_7$ shows a very different character. The DOS distributions of $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ show that A-site 4f electrons hybridize significantly with O 2p orbitals in the valence region. Since $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ are

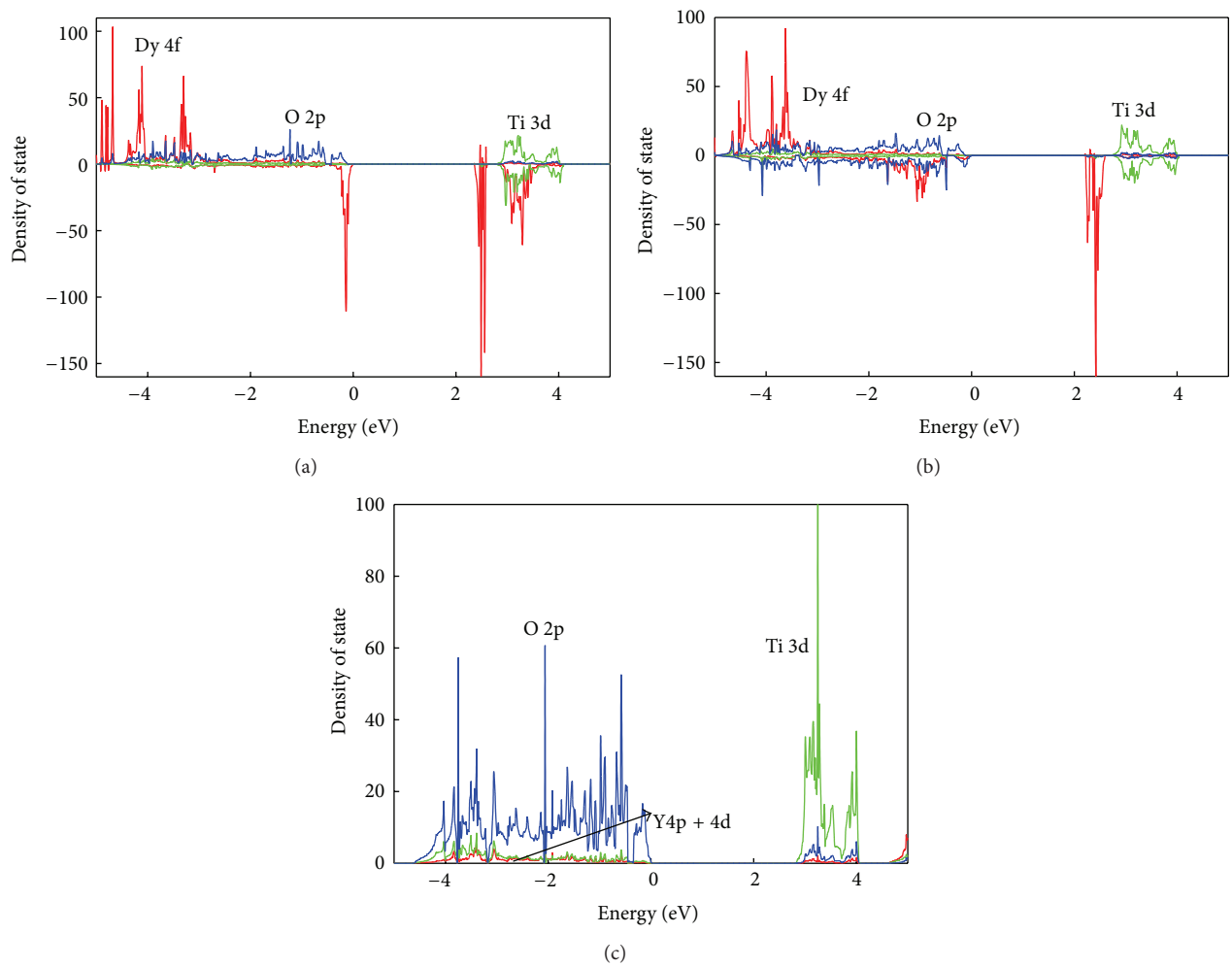


Figure 7: Partial DOS distributions of (a) $Dy_2Ti_2O_7$; (b) $Ho_2Ti_2O_7$; and (c) $Y_2Ti_2O_7$.

less radiation resistant than $Y_2Ti_2O_7$, it is suggested that the strong interaction between Dy and Ho 4f electrons and O 2p electrons may increase the covalency of ⟨Dy–O⟩ and ⟨Ho–O⟩ bonds and decrease the irradiation resistance of $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$.

Acknowledgments

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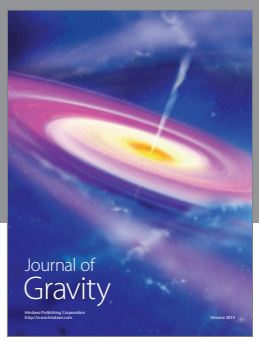

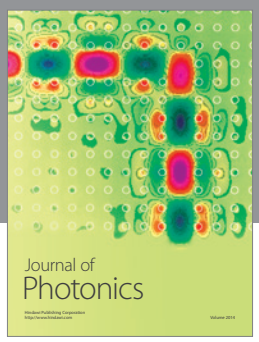

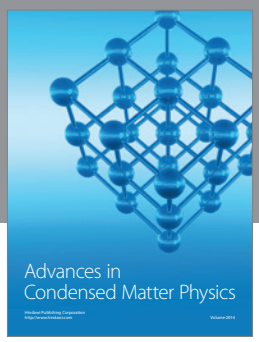

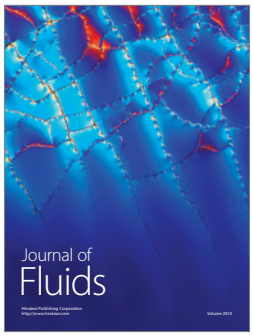

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