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## The solubility of cerium in $\text{La}_2\text{Ti}_2\text{O}_7$ by DFT + U calculations



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### ARTICLE INFO

#### Article history:

Received 17 April 2015

Accepted 29 June 2015

Available online 6 July 2015

#### Keywords:

DFT + U

Solubility of cerium in  $\text{La}_2\text{Ti}_2\text{O}_7$

Radiation resistance

Charge state

### ABSTRACT

To investigate the solubility of cerium in  $\text{La}_2\text{Ti}_2\text{O}_7$ , the density functional theory plus Hubbard U correction (DFT + U) approach is employed. The geometrical structure, solution energy and electronic structure of  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $0 \leq y \leq 2$ ) have been analyzed. The results reveal that the  $\text{La}_2\text{Ti}_2\text{O}_7$ – $\text{Ce}_2\text{Ti}_2\text{O}_7$  solid solution exists over the entire range of cerium content. The calculated increase in the  $O_{48f}$  positional parameter,  $x$ , with increasing cerium content, may indicate the increased radiation resistance. The results of the density of states distribution and the Bader charge for each ion in  $\text{La}_2\text{Ti}_2\text{O}_7$ – $\text{Ce}_2\text{Ti}_2\text{O}_7$  solid solution suggest that cerium exhibits a reduced charge state in the solid solution.

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### 1. Introduction

The safe disposal of high level nuclear waste, especially the “minor” actinides ( $^{237}\text{Np}$ ,  $^{241}\text{Am}$  +  $^{243}\text{Am}$ , and  $^{244}\text{Cm}$ ) generated by the nuclear fuel cycle and the fissile Pu from dismantled nuclear weapons, remain major challenges in developing strategies for advanced fuel cycles [1–3]. In recent years, there has been great interest in using materials with fluorite-related structures as host phase for the immobilization of plutonium and “minor” actinides [2,4–12]. Pyrochlore compounds are closely related to the fluorite-structure ( $\text{AX}_2$ ), except that there are two cation sites and one-eighth of the anions are absent. They demonstrate an enormous range of physical, chemical, and electronic properties depending on the composition and the degree of disorder on the cation sites [13]. Therefore, they have been used as hosts for oxidation catalysts [14], ceramic thermal barrier coatings [15,16], and solid electrolytes in high temperature fuel cells [17]. In particular, these materials have long been considered as the potential host phases for the immobilization of the “minor” actinides and plutonium [2,18].

Titanate pyrochlores have been considered as the primary host phases of the high level nuclear waste for their chemical durability [2]. Numerous experimental and theoretical efforts have been made to investigate the properties and the radiation resistance of them [3,5,7,8,13,19–24]. Furthermore, the solubility of Pu in titanate pyrochlores has been studied by Shoup et al. [8]. They

prepared and identified  $\text{Pu}_2\text{Ti}_2\text{O}_7$  via X-ray diffraction and estimated the solubility limit of  $\text{Pu}_2\text{Ti}_2\text{O}_7$  in  $\text{A}_2\text{Ti}_2\text{O}_7$  ( $\text{A} = \text{Gd}, \text{Er}$  and  $\text{Lu}$ ). The results they obtained agree well with the solubility of  $\text{Ce}_2\text{Ti}_2\text{O}_7$  in the same cubic pyrochlore hosts [25]. As Pu is not easily studied experimentally, and Pu and Ce share many common chemical and crystallochemical properties, Ce has often been used as a nonradioactive surrogate for Pu [18,26–30]. Although the solubility limit of  $\text{Ce}_2\text{Ti}_2\text{O}_7$  in  $\text{A}_2\text{Ti}_2\text{O}_7$  ( $\text{A} = \text{Gd}, \text{Er}$  and  $\text{Lu}$ ) has been found by experiment [25], the solubility of Ce in  $\text{La}_2\text{Ti}_2\text{O}_7$  has not been investigated by now. Recently, density functional theory plus Hubbard U correction (DFT + U) have been applied to investigate the solubility of Ce in  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{Gd}_2\text{Zr}_2\text{O}_7$  by X. J. Wang et al. [18,31]. Their calculations indicated that cerium was soluble in  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{Gd}_2\text{Zr}_2\text{O}_7$ , which agreed well with the experiments conducted by Kulkarni et al. [32] and Lian et al. [33].

In present work, the so-called DFT + U approach is also employed to study the solubility of cerium in  $\text{La}_2\text{Ti}_2\text{O}_7$ . The geometrical structure, solution energy and electronic structure of  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  have been analyzed. The main purpose of this paper is to provide an atomic level understanding of cerium incorporation in  $\text{La}_2\text{Ti}_2\text{O}_7$ , including a fundamental insight into the charge states and the energetics for Ce in  $\text{La}_2\text{Ti}_2\text{O}_7$ . For the pure end member,  $\text{La}_2\text{Ti}_2\text{O}_7$  pyrochlore has been investigated by Zhang et al. [19] and Xiao et al. [24], Pruneda et al. [43], and Chartier et al. [44]. Furthermore, the  $\text{Ce}_2\text{Ti}_2\text{O}_7$  pyrochlore structure has also been obtained by sol–gel methodology under reductive atmosphere by Mónica Martos et al. [57]. In a sense, this research will provide guidance for further researches in experiments.

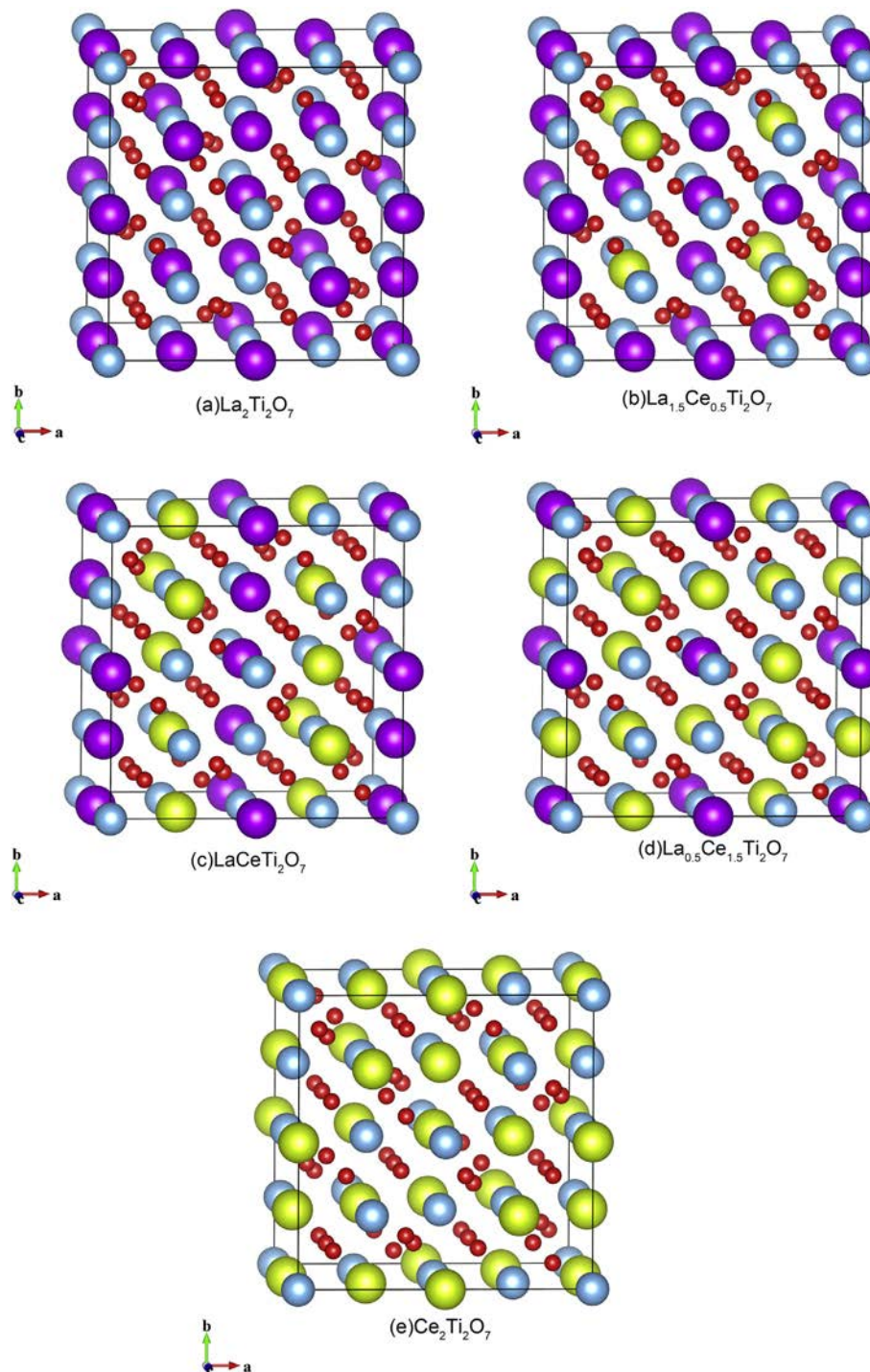
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## 2. Computational method

All the calculations are performed with the Vienna Ab Initio Simulation Package (VASP) using the projector augmented wave method [34–37]. The generalized gradient approximation (GGA) parametrized by Perdew and Wang is adopted to treat the exchange–correlation effects [38]. The lattice parameters and internal atomic positions of all structures are fully relaxed using a conjugate gradient scheme. Computations are performed with

$4 \times 4 \times 4$   $k$ -point sampling in reciprocal space and a cutoff energy of 520 eV for the plane wave basis set, with spin-polarized effects considered. The Hubbard  $U$  correction is introduced using the method proposed by Dudarev et al. [39], in which the parameter  $U$ , reflecting the strength of on-site Coulomb interaction, and parameter  $J$ , adjusting the strength of exchange interaction, are combined into a single parameter  $U_{\text{eff}} = U - J$ . The value we employed is  $U_{\text{eff}}(\text{Ce}) = 5.0$  eV, as proposed by Andersson et al. and X. J. Wang et al. [18,31,40].



**Fig. 1.** The optimized structure of  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $y = 0, 0.5, 1.0, 1.5, 2.0$ ). The yellow, purple, sky-blue, and red spheres represent the cerium, lanthanum, titanium and oxygen, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Crystal structure refinement results for  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$ . The calculated lattice constant  $a_0$ (Å), the  $x$  positional parameter for 48f-site oxygen and bond distance (Å) are also shown.

	$a_0$	$x_{\text{O48f}}$	$d_{\langle\text{La-O48f}\rangle}$	$d_{\langle\text{La-O8b}\rangle}$	$d_{\langle\text{Ce-O48f}\rangle}$	$d_{\langle\text{Ce-O8b}\rangle}$	$d_{\langle\text{Ti-O48f}\rangle}$
$y = 0$	10.434	0.32255	2.614	2.259	–	–	1.994
<i>Theo.</i>	10.52 [24]	0.322 [24]	2.64 [24]	2.27 [24]	–	–	2.00 [24]
	10.541 [44]	0.323 [44]	2.63 [44]	2.28 [44]	–	–	2.02 [44]
	10.366 [43]	0.3227 [43]	2.59 [43]	2.24 [43]	–	–	1.98 [43]
$y = 0.5$	10.418	0.32270	2.608	2.263	2.595	2.233	1.994
$y = 1$	10.410	0.32286	2.607	2.262	2.604	2.246	1.990
$y = 1.5$	10.401	0.32313	2.610	2.268	2.587	2.247	1.992
$y = 2$	10.362	0.32478	–	–	2.579	2.244	1.989

**Table 2**

Incorporation and solution energies (eV) for Ce in  $\text{La}_2\text{Ti}_2\text{O}_7$  with the different pseudopotential of cerium<sup>a</sup>.

$x$		0.5	1	1.5	2
Defect formation energy	PW91(Ce)	2.857	7.148	12.113	16.299
	PW91(Ce_3)	2.858	7.149	9.814	16.299
Incorporation energy	PW91(Ce)	–3.160	–10.113	–15.601	–17.812
	PW91(Ce_3)	–3.633	–8.694	–12.126	–19.373
Solution energy	PW91(Ce)	–0.303	–2.965	–3.488	–1.513
	PW91(Ce_3)	–0.775	–1.545	–2.312	–3.074

<sup>a</sup> PW91(Ce), Ce 4f electron is considered as the valence electron in this pseudopotential; PW91(Ce\_3), Ce 4f electron is not considered as the valence electron in this pseudopotential.

### 3. Results and discussion

#### 3.1. Crystal structure and structural properties of $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$ ( $0 \leq y \leq 2$ )

The ideal pyrochlore structure has the space group  $Fd3m$  that derives from the  $\text{MO}_2$  fluorite like arrangement of atoms. There are eight molecules of the general formula  $\text{A}_2\text{B}_2\text{O}_6\text{O}'$  in the unit cell. The A and B metal cations occupy the 16d (0.5, 0.5, 0.5) and 16c (0, 0, 0) sites, respectively, and the oxygen is in the 48f ( $x$ , 0.125, 0.125) and 8b (0.375, 0.375, 0.375) positions (using Wyckoff notation). An unoccupied interstitial site 8a (0.125, 0.125, 0.125) is surrounded by four B ions, and the “vacancies” at 8a site are ordered on the anion sublattice [41,42]. The cubic pyrochlore structure can be completely determined by two independent parameters which are the internal parameter  $x$  for the O<sub>48f</sub> positions and the lattice parameter  $a_0$ . In order to study the solubility of Ce in  $\text{La}_2\text{Ti}_2\text{O}_7$ , La is replaced with Ce at different concentrations, resulting in  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $y = 0, 0.5, 1.0, 1.5, 2.0$ ). The configurations of these compositions are illustrated in Fig. 1. A full structural relaxation for  $\text{La}_2\text{Ti}_2\text{O}_7$  containing different Ce content was performed. Each composition is found to be energetically stable. The relaxed lattice sizes and the internal positional parameter  $x_{\text{O48f}}$  for Ce substituted  $\text{La}_2\text{Ti}_2\text{O}_7$  together with available theoretical results are given in Table 1 [24,43,44]. It is found that there is a slight increase in  $x_{\text{O48f}}$  and decrease in lattice constant with increasing cerium content. Generally, the  $x$  parameter has been used as an indicator of the degree of disorder in pyrochlore structures. For an ideal pyrochlore structure, the value of  $x$  would be 0.3125 and 0.375 for the disordered defect-

fluorite structure. Experimentally, it has been reported that pyrochlore compositions with larger 48f oxygen positional parameter  $x$  are more resistant to ion beam-induced amorphization [4,44–46]. This study indicates that the substitution of Ce for La in  $\text{La}_2\text{Ti}_2\text{O}_7$  decreases the stability of  $\text{La}_2\text{Ti}_2\text{O}_7$  and may result in increased radiation resistance. The ionic radii of  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  are 1.16 Å (in eightfold coordination) and 1.14 Å (in eightfold coordination), respectively [47]. The ionic radius of  $\text{Ce}^{3+}$  is slightly smaller than that of  $\text{La}^{3+}$ , which may lead to a slight decrease in lattice constant with increasing Ce content.

#### 3.2. Incorporation and solution energy of cerium in $\text{La}_2\text{Ti}_2\text{O}_7$

To investigate Ce solubility in  $\text{La}_2\text{Ti}_2\text{O}_7$  pyrochlore, the solution energy is calculated. It can be obtained by the incorporation energy and defect formation energy [18,30,31]:

$$E^{\text{Sol}} \approx E^{\text{InC}} + E^{\text{F}}$$

The defect formation energy  $E^{\text{F}}$  is determined by total energy calculation of supercells with and without the La vacancy [18,23,31]:

$$E^{\text{F}}(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7) = E(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7) - E(\text{La}_{2-y'}\text{Ce}_y\text{Ti}_2\text{O}_7) + \mu(\text{La})$$

We removed one La vacancy from  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$ , resulting in  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$ , where  $E(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7)$  and  $E(\text{La}_{2-y'}\text{Ce}_y\text{Ti}_2\text{O}_7)$  are the total energy of  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  and  $\text{La}_{2-y'}\text{Ce}_y\text{Ti}_2\text{O}_7$  respectively.  $\mu(\text{La})$  is the chemical potential of La, which is obtained under the  $\text{La}_2\text{O}_3$ -rich and O-rich condition [48].

$$\mu(\text{La}_2\text{O}_3) = 2\mu(\text{La}) + 3\mu(\text{O});$$

$$\mu(\text{O}) = 0.5\mu(\text{O}_2)$$

Here,  $\mu(\text{La}_2\text{O}_3)$  and  $\mu(\text{O}_2)$  are the total energies of bulk  $\text{La}_2\text{O}_3$  and free  $\text{O}_2$  molecule, which are calculated to be –42.26 eV and –9.13 eV, respectively [31]. The vacancy formation energies are listed in Table 2.

The incorporation energy  $E^{\text{InC}}$  is defined as the energy required

**Table 3**

Bader charge ( $|e|$ ) for each ion in  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $y = 0, 0.5, 1.0, 1.5, 2.0$ ).

$y$	Ce	La	Ti	O <sub>48f</sub>	O <sub>8b</sub>
0	–	2.0826	2.2419	1.2163	1.3415
0.5	2.1555	2.0738	2.2312	1.2192	1.3256
1	2.1336	2.0759	2.2439	1.2176	1.3418
1.5	2.1142	2.0725	2.2441	1.2190	1.3249
2	2.1030	–	2.2434	1.2252	1.3591

to incorporate a cerium in a pre-existing vacant lanthanum lattice site [18,31,49]:

$$E^{\text{Inc}}(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7) = E(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7) - E(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7) - \mu(\text{Ce})$$

where  $E(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7)$  is the total energy of the system with Ce occupying a La lattice site.  $E(\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7)$  is the total energy of the system containing a vacancy defect without Ce incorporation. The same method we used to calculate  $\mu(\text{La})$  can be adopted to obtain  $\mu(\text{Ce})$ .  $\mu(\text{Ce}_2\text{O}_3)$  has been calculated to be  $-39.78$  eV [18,31]. The calculated incorporation energies are reported in Table 2. They are negative, meaning that Ce becomes more stable than its free state when it is incorporated in the La vacant site [18,31,50]. According to  $E^{\text{Sol}} \approx E^{\text{Inc}} + E^{\text{F}}$ , the solution energies are also determined and the results are showed in Table 2. It is found that all the values are negative, independent of cerium concentration, suggesting that cerium solution is an exothermic reaction and cerium is soluble in  $\text{La}_2\text{Ti}_2\text{O}_7$ . The very similar ionic radii of  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  may result in the solubility of Ce in  $\text{La}_2\text{Ti}_2\text{O}_7$ .

### 3.3. Electronic properties of $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$ ( $0 \leq y \leq 2$ )

A number of studies have been carried out to study the charge state of Ce (or Pu) in pyrochlores doped with Ce (or Pu) [33,51–53]. In this paper, the Bader charge for each ion in  $\text{La}_2\text{Ti}_2\text{O}_7$ – $\text{Ce}_2\text{Ti}_2\text{O}_7$  solid solution was calculated to verify the charge state of Ce in  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$ . The results are summarized in Table 3. It is found that the charge state of cerium decreases from 2.16 |e| to 2.10 |e| with increasing cerium content. These values are considerably smaller than the Bader charge of 2.40 |e| for  $\text{CeO}_2$  [31,54], and are comparable to the Bader charge of 2.01 |e| for  $\text{CeO}_{1.96875}$  [31,54]. These results suggest that the cerium in  $\text{Ce}_2\text{Ti}_2\text{O}_7$ – $\text{La}_2\text{Ti}_2\text{O}_7$  solid solution exhibits a reduced charge state. Mónica Martos et al. [57] also suggested that the reduction state of cerium ions exists in  $\text{Ce}_2\text{Ti}_2\text{O}_7$  pyrochlore. As the classical model of an ionic material with nominal charges is oversimplified, the charge state is not the nominal +3 |e|. Calculations in this study also show that the Bader charge for Ti ions is larger than that for La and Ce ions, meaning that the  $\langle \text{Ti}-\text{O} \rangle$  bond is more covalent than  $\langle \text{La}-\text{O} \rangle$  and  $\langle \text{Ce}-\text{O} \rangle$  bonds. The Bader charge for Ce is slightly larger than that for La, implying that the cerium content has an effect on the charge

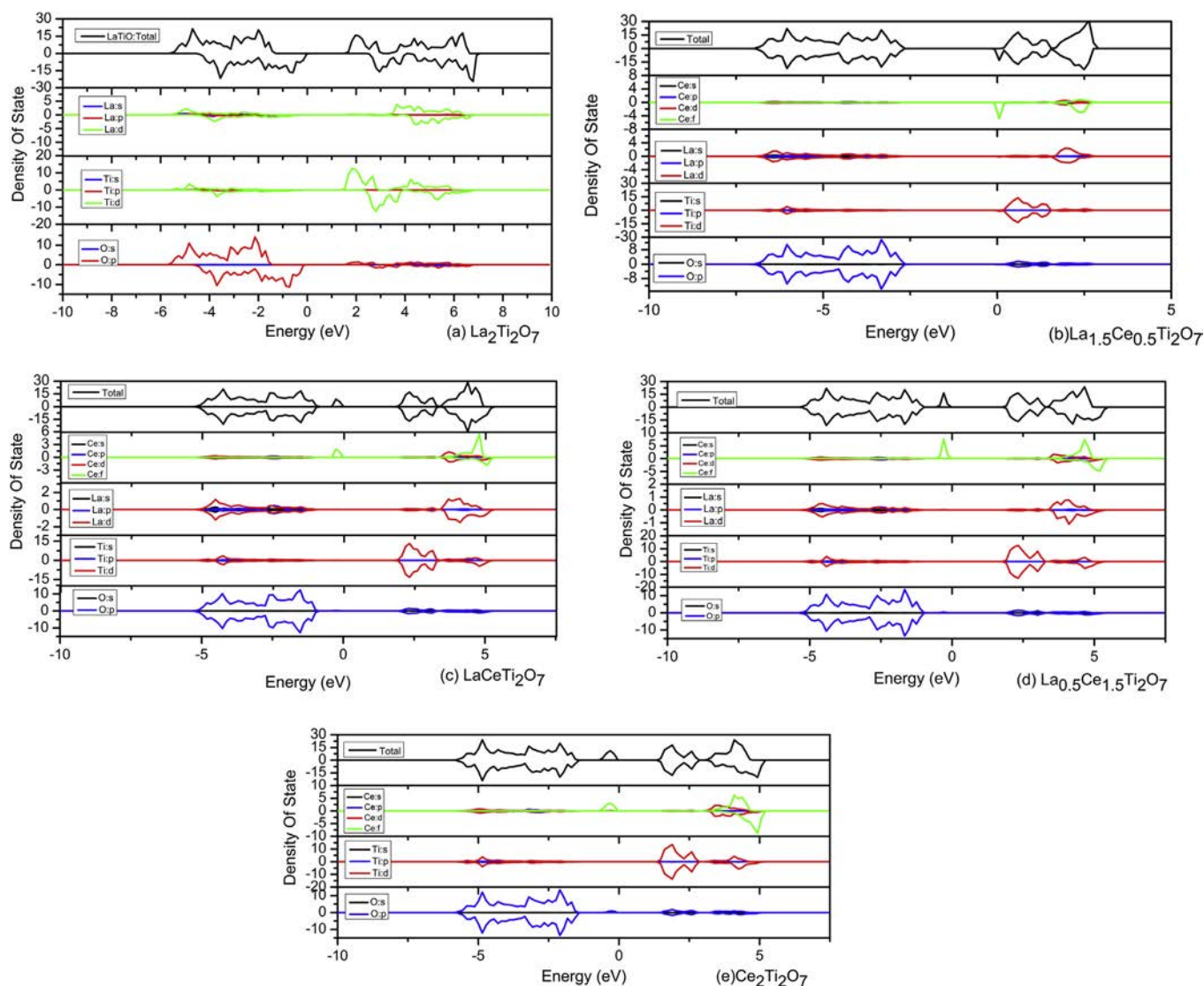


Fig. 2. DOS distribution for (a)  $\text{La}_2\text{Ti}_2\text{O}_7$ , (b)  $\text{La}_{1.5}\text{Ce}_{0.5}\text{Ti}_2\text{O}_7$ , (c)  $\text{LaCeTi}_2\text{O}_7$ , (d)  $\text{La}_{0.5}\text{Ce}_{1.5}\text{Ti}_2\text{O}_7$ , (e)  $\text{Ce}_2\text{Ti}_2\text{O}_7$ .

distribution of this material.

Fig. 2 shows the total and partial DOS for  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $0 \leq y \leq 2$ ). The Fermi level is set 0 eV. After cerium doping, one striking feature for the DOS distribution is that a small Ce 4f peak appears near the Fermi level. It reveals that the Ce 4f orbitals in  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $0 < y \leq 2$ ) are partially occupied and localized and it shows a similar character to  $\text{Ce}_2\text{O}_3$  and Ce-doped  $\text{La}_2\text{Zr}_2\text{O}_7$  pyrochlores and Ce-doped  $\text{Gd}_2\text{Zr}_2\text{O}_7$  pyrochlores [18,31]. In addition, numerous studies [30,40,55,56] have demonstrated that Ce 4f orbitals are not occupied in  $\text{CeO}_2$  and they are partially occupied and localized in defective  $\text{CeO}_2$ . Obviously, cerium exhibits a reduced charge state in this solid solution.

#### 4. Conclusion

In this study, the geometrical structure, solution energy, and electronic structure of  $\text{La}_{2-y}\text{Ce}_y\text{Ti}_2\text{O}_7$  ( $0 \leq y \leq 2$ ) have been investigated by DFT + U approach. The value of the  $O_{48f}$  positional parameter increases with the rising of cerium content, which suggests that cerium incorporation in  $\text{La}_2\text{Ti}_2\text{O}_7$  may lead to increased radiation resistance. Calculations also reveal that the  $\text{Ce}_2\text{Ti}_2\text{O}_7$ – $\text{La}_2\text{Ti}_2\text{O}_7$  solid solution exists over the entire range of cerium content and cerium in the solid solution exhibits a reduced charge state.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (No.11475076 and 11175076).

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