First-principles calculation of structural and electronic properties of pyrochlore $Lu_2Sn_2O_7$*

Chen Zhong-Jun(陈中钧)[a)†] and Chen Tai-Hong(陈太红)[b)]

[a)] *Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*
[b)] *College of Physical and Electronic Information, China West Normal University, Nanchong* 637002, *China*

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A Density functional theory method within generalized gradient approximation has been performed to obtain the static lattice parameters, oxygen positional parameter, bond length and bond angle and electronic properties of ideal $Lu_2Sn_2O_7$ pyrochlore. The results are in excellent agreement with available experimental measurements. Density of states (DOS) of this compound was presented and analysed. We also notice the presence of the hybridization between oxygen and Lu metal. The band structure calculations show that the compound has direct band gap of 2.67 eV at the Γ point in the Brillouin zone and this indicates that the material has a semi-conducting feature.

Keywords: stannate pyrochlores, density functional theory, pseudopotential approach, structure properties

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1. Introduction

Pyrochlore oxide materials have a general formula $A_2B_2O_7$, with larger cations such as the actinides and lanthanides occupying the A site and smaller cations including most transition metals, typically Ti, Zr and Sn, occupying the B site, so they have a wide variety of compositions (> 500) that lead to a wide range of technologically important properties, such as high ionic conductivity,[1] superconductivity,[2] luminescence,[3] and ferromagnetism.[4] Recently, there has been great interest in using pyrochlore oxide 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 pyrochlore as potential waste forms. $Lu_2Sn_2O_7$ pyrochlore, its structural parameters have been determined by Kennedy *et al.*[16] from experiment using Rietveld refinement based on powder neutron diffraction data. But up to now, as far as we know, there is few theoretical study on the structural and electronic properties for this compound. First principle methods have proved to be of considerable value in studies of a wide range of metal, insulator, and ceramic materials.[17−20] So, we will focus on investigating the effects of geometrical structures and electronic properties of stannate pyrochlore $Lu_2Sn_2O_7$ using *ab initio* pseudopotential plane wave method. The rest of the paper is organized as follows: in Sections 2 and 3, respectively, descriptions of the pyrochlore structure and the method of calculation are given. Section 4 contains our results and discussion, involving the equilibrium lattice constants, oxygen positional parameter, bond length and bond angle and density of states. Finally, the conclusion is given in Section 5.

2. Pyrochlore structure

The lanthanide stannate, $Lu_2Sn_2O_7$, has the isometric pyrochlore structure, with space group *Fd3m* and eight molecules in the unit cell. The general formula of pyrochlore can be written as $A_2B_2O_6O'$ with four crystallographically nonequivalent types of atoms. The Lu and Sn metal cations occupy the 16d(1/2, 1/2, 1/2) and 16c(0, 0, 0) sites, respectively and the O (denoted O_{48f}) and O′ (denoted O_{8b}) oxygens are located at the 48f(x, 1/8, 1/8) and 8b(3/8, 3/8, 3/8) positions, respectively. In $Lu_2Sn_2O_7$, Lu is formally

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†Corresponding author. E-mail: zjchen@uestc.edu.cn

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considered to adopt a +3 oxidation state, where localized 4f electrons were treated as core-like states; Sn is formally considered to adopt a +4 oxidation state, giving it an electronic configuration of $4d^{10}5s^0$.

This structure can be visualized in a variety of ways, but it is often considered as an ordered defect fluorite structure, except that there are two cation sites and one-eighth of the anions are absent. The cations and oxygen vacancies are ordered. The loss of one-eighth of the anions reduces the coordination of the Sn-site cation from 8 to 6. The anion sublattice can be completed by adding the missing oxygen in the 8a site to form the fluorite structure. The system can be completely described in terms of the lattice constant a and the x parameter defining the position of the O_{48f}. Geometrically, the smaller Sn^{4+} cation is surrounded by six O_{48f} atoms in a distorted octahedron and the larger Lu^{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 Lu^{3+} and two Sn^{4+} sites, and the 8b oxygen atom is inside a tetrahedron formed by Lu^{3+} cations.

3. Calculational method

In this work, first-principles total energy calculations within the density functional theory (DFT) framework are carried out. The interaction between ions and electrons is described using the projector augmented wave method[21,22] and the exchange–correlation interaction is described by PW91 function[23] within the density functional theory (DFT) framework.[22,24] The influence of different k-point sampling and plane-wave cut-off 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. In our calculation, the 4f states of the lanthanide cations were treated as core-like states due to the f-electrons being localized in the inner 4f levels.

4. Results and discussion

4.1. Structural properties

The static lattice parameters, oxygen positional parameter, bond length and bond angle are presented in Table 1 along with the comparison with available experimental data. Our calculated static lattice parameter agrees within 0.47% with the experimental value.[16] There are no other theoretical results which can be used to compare with our predictions. Our calculated variable oxygen positional parameter, x is 0.3424 for $Lu_2Sn_2O_7$. It agrees with experimental measurement to within 0.8%.[16] The Lu–O_{8b} distance, independent of oxygen x parameter, is always less than the Lu–O_{48f} distance. Our calculated Lu–O_{8b}, Lu–O_{48f} and Sn–O_{48f} distances and O_{48f}–Sn–O_{48f} and Sn–O_{48f}–Sn angles are in good agreement with the results obtained from the literature.[16]

Table 1. Calculated and experimental structural properties of stannate pyrochlores $Lu_2Sn_2O_7$.

Composition	$Lu_2Sn_2O_7$	
	This work	Experiment[16]
Lattice parameter a/Å	10.34	10.292
O_{48f} x parameter	0.3424	0.3397
⟨Lu–O_{8b}⟩ bond length/Å	2.239	2.2282
⟨Lu–O_{48f}⟩ bond length/Å	2.449	2.4559
⟨Sn–O_{48f}⟩ bond length/Å	2.063	2.040
Sn–O_{48f}–Sn bond angle/(°)	124.8	126.19
Lu–O_{48f}–Lu bond angle/(°)	96.6	95.60
O_{48f}–Sn–O_{48f} bond angle/(°)	100.8	99.96

4.2. Electronic structure

Lian *et al.*[25] have suggested that the resistance of the pyrochlore structure to ion beam-induced amorphization is affected by the cation electronic configuration. By investigating the electronic structure of this important class of materials, one can form the basic understanding of the physical properties of pyrochlores. In the present work, the total and partial density of states (DOS) and electronic energy band gap are presented.

The total DOS distribution consists of three regions (see Fig. 1). The lower part of the valence bands, ranging from −15 eV to −30 eV, is mainly dominated by Lu 6p and Sn 4d with small O 2s admixture and the upper part, ranging −10 eV to 0 eV, by O 2p with small O′ 2p admixture; the unoccupied conduction region, ranging from 0 eV to 10 eV, is predominantly contributed by Lu 5d and O 2p states and within 10 eV to 20 eV, it is derived from the admixture of the Lu 6p and O 2p states. Furthermore, there is an energy gap between the occupied O 2s states and the unoccupied Sn 5s states. Different from the upper valence band, the first conduction band is more sensitive to the type of the lanthanide elements, as can be seen from Fig. 1. Also, the lowest conduction band is

localized on Sn 5s state.

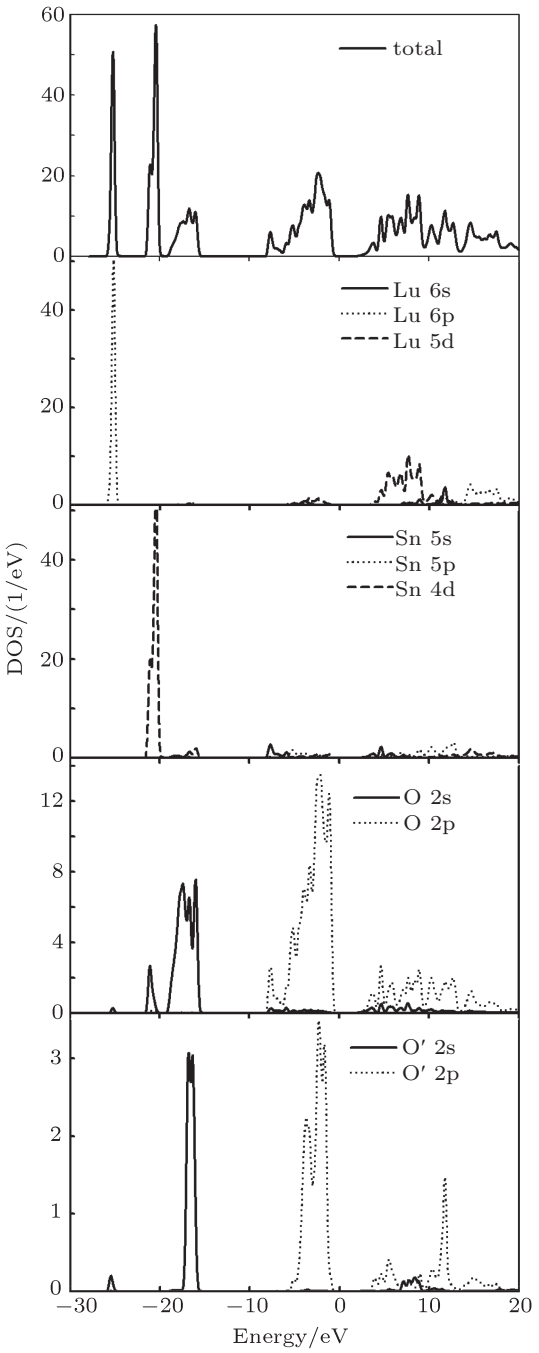


Fig. 1. The calculated total DOS and atomic projected DOS (PDOS) of $Lu_2Sn_2O_7$ at the predicted equilibrium lattice constant.

On the other hand, the PDOS of the two nonequivalent oxygen atoms are noticeably different from each other. It can be seen that the intensities of the O atom peak are stronger than that of the O′ atom peak. Such a difference can be due to the differences in their local molecular environment: O is surrounded by two Lu^{3+} and two Sn^{4+} cations and O′ is surrounded by four Lu^{3+} cations. Hence, the difference in the electronic structures of the O and O′ oxygens is expected.

The electronic band structures of the $Lu_2Sn_2O_7$ compound also present in Fig. 2. It shows the compound has a direct band gap at the Γ point in the Brillouin zone, which is dominated by O 2p and Sn 5s states. Also, the band gap is narrow with value of 2.67 eV, indicative of the presence of a semiconducting feature for the materials.

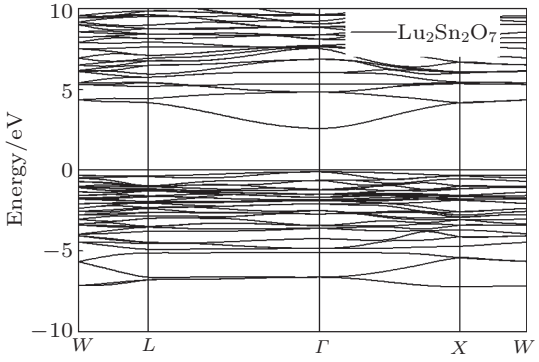


Fig. 2. The calculated electronic band structure of $Lu_2Sn_2O_7$. The position of the Fermi level is set at 0 eV.

5. Conclusion

In this work we have investigated stannates pyrochlore $Lu_2Sn_2O_7$ employing a plane wave pseudopotential method based on DFT. A detailed analysis of structural and electronic properties has been presented. The computed structural parameters are in excellent agreement with the experimental measurements. Electronic structure calculations predict a direct band gaps of 2.67 eV at the Γ point, indicating that the material has a semi-conducting feature.

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