Physical properties of $\text{La}_2\text{B}_2\text{O}_7$ (B=Zr, Sn, Hf and Ge) pyrochlore: first-principles calculations

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Abstract

Using first-principles theory and further verified by the experimental results, we have studied the electronic structure, mechanical and thermal properties of $\text{La}_2\text{B}_2\text{O}_7$ (B=Zr, Sn, Hf and Ge) pyrochlore. It is shown that the $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore are charge-transfer-type insulators with the strong ionic bonding. The calculated band gap of $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Sn}_2\text{O}_7$, $\text{La}_2\text{Hf}_2\text{O}_7$, and $\text{La}_2\text{Ge}_2\text{O}_7$ are 4.01, 3.05, 3.13 and 2.42 eV, respectively. The elastic constants, hardness, shear modulus, bulk modulus, Young's modulus and Poisson's ratio of $\text{La}_2\text{B}_2\text{O}_7$ compounds were investigated systematically. Anisotropic elastic and thermal properties of $\text{La}_2\text{B}_2\text{O}_7$ compounds were discussed by using Zener's indexes (A^Z) and universal elastic anisotropic index (A^U). The sound velocities along [100], [110] and [111] directions were calculated for each $\text{La}_2\text{B}_2\text{O}_7$ compounds. Both Clark's model and Cahill's model were used to evaluate the minimum thermal conductivity of all compounds. According to the Clark's model, when the temperature is much higher than Debye temperature, the minimum thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Sn}_2\text{O}_7$, $\text{La}_2\text{Hf}_2\text{O}_7$, and $\text{La}_2\text{Ge}_2\text{O}_7$ are 1.27, 1.24, 1.09 and 1.41 W/m·K, respectively. According to the calculated results of these crystals, the

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$\text{La}_2\text{B}_2\text{O}_7$ compounds exhibit an extraordinary low thermal conductivity which can be used as thermal insulating materials.

Keywords: Pyrochlore; Ceramics; Minimum thermal conductivity; First-principles calculation.

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1. Introduction

Materials with the pyrochlore lattice structure have attracted much recent attention due to their wide applications in ceramic thermal barrier coatings[1,2], high-permittivity dielectrics[3], potential solid electrolytes in solid-oxide fuel cells[4], and immobilization hosts of actinides in nuclear waste[5]. Pyrochlore materials have the general formula $\text{A}_2\text{B}_2\text{O}_7$, where A and B are metallic cations that can be either trivalent and tetravalent or divalent and pentavalent, respectively. The structure of pyrochlore (space group $\text{Fd-}3\text{m}$, $Z=8$) can be described as an ordered defect fluorite structure, in which the cations form a face-centered cubic (fcc) array. To ensure charge neutrality, one-eighth of the anions are unoccupied. The general formula of pyrochlore can also be written as $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ with four crystallographic ally non-equivalent types of atoms. The loss of one-eighth of the anions reduces the coordination of the B-site cation from 8 to 6. As shown in Fig.1, Metal atoms in A and B positions occupy the $16\text{d}(1/2, 1/2, 1/2)$ and $16\text{c}(0, 0, 0)$ sites, respectively, and the oxygen of O and O' are in the $48\text{f}(x, 1/8, 1/8)$ and $8\text{b}(3/8, 3/8, 3/8)$ positions, respectively. In the perfect pyrochlore structure with $x = 0.3125$, the coordination of the B atoms and the RE(Rare metal) atoms are regular octahedral and distorted cubes, respectively. As x increases to

0.375, the B site polyhedral distort to trigonal ant prisms and the RE-site polyhedral changes to regular cubes.

For pyrochlore structure materials, unique structure leads to unique properties. However, some properties cannot be obtained from experiments. Therefore, simulations have become an ideal tool for systematic investigations of various properties of those compositions [6-9]. In this work, in order to investigate the intrinsic physical properties of the $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore systematically and to extend the range of applications of materials with the pyrochlore lattice structure, based on density functional theory (DFT), we present first-principles calculations of pyrochlore: $\text{La}_2\text{B}_2\text{O}_7$ with B= Zr, Sn, Hf , and Ge, respectively. The electronic structure, elastic coefficients, bulk modulus, shear modulus, Young's modulus, and thermal properties of $\text{La}_2\text{B}_2\text{O}_7$ crystals were studied systematically. The calculated results were compared with the available experimental results. Theoretical values of various properties obtained with these first-principles calculations can be used to improve mechanical, thermal and electrical properties available. We hope that the calculated results can contribute to the Materials Genome Initiative project which will accelerate the advanced materials discovery [10].

2. Computational methods and details

The CASTEP code [11] was used in the present DFT calculations with plane-wave pseudopotential total energy scheme method. Local density approximation (LDA) [12] was used to describe the electronic exchange correlation interactions, and the average force acting on ions was reduced to 1.0×10^{-6} eV atom⁻¹. The mean

Hellmann–Feynman force acting on each atom was 0.01 eV.Å⁻¹. Valence electrons included in this paper were O 2s² 2p⁴, La 5s² 5p⁶ 5d¹ 6s², Zr 4s² 4p⁶ 4d² 5s², Sn 5s² 5p², Hf 5d² 6s², Ge 4s² 4p². Convergence tests with respect to k mesh point 10×10×10. We used a plane wave basis with a cut-off of 500 eV to expand the pseudo valence wave function. Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme was applied in geometry optimization. The lattice parameters were modified independently to minimize the free enthalpy, interatomic forces and unit-cell stresses. The present calculation scheme was successfully used to predict physical properties of materials in our previous work [7,13-14].

3. Results and discussions

3.1. Lattice constants and cell stability

The optimized lattice parameters and the experimental values of La₂B₂O₇ are shown in Table 1. Since the LDA method was applied, the calculated lattice parameters were little underestimated, and the average deviation between the experimental and theoretical value is less than 3%, so we concluded that the parameters used in this paper are suitable for all La₂B₂O₇ compounds calculations. As mentioned in the above, the range of x (O', 48f(x,1/8,1/8)) values is 0.3125 to 0.375 for materials with the pyrochlore structure. Distorted cubes appears when x equal to 0.3125 and crystal structure changes to regular cubes while x increases to 0.375. From the Table 1, it is shown that x equal to 0.331, 0.330, 0.328, and 0.319 for La₂Zr₂O₇, La₂Hf₂O₇, La₂Sn₂O₇ and La₂Ge₂O₇, respectively. Taking into account the ionic radii of

Zr, Hf, Sn and Ge are 72, 70, 69 and 53 *pm*, respectively, our calculated results predict an increase of x with the B cation radius increasing. However, this trend is not found in work of Pruneda *et al.*[9], but also observed in the some group's work [8,15]. The stability of $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore are identified by the formation enthalpy and cohesive energies, which are defined as following

$$\Delta H(\text{La}_2\text{B}_2\text{O}_7) = E_{\text{total}}(\text{La}_2\text{B}_2\text{O}_7, \text{cell}) - 2 \times E(\text{La}) - 2 \times E(\text{B}) - 7 \times \frac{1}{2} E(\text{O}_2) \quad (1)$$

$$E_{\text{coh}}(\text{La}_2\text{B}_2\text{O}_7) = E_{\text{total}}(\text{La}_2\text{B}_2\text{O}_7, \text{cell}) - 2 \times E_{\text{iso}}(\text{La, atom}) - 2 \times E_{\text{iso}}(\text{B, atom}) - 7 \times E_{\text{iso}}(\text{O, atom}) \quad (2)$$

In above Eq(1) and Eq(2), $\Delta H(\text{La}_2\text{B}_2\text{O}_7)$ and $E_{\text{coh}}(\text{La}_2\text{B}_2\text{O}_7)$ are the formation enthalpy and cohesive energy of $\text{La}_2\text{B}_2\text{O}_7$ compounds. $E_{\text{total}}(\text{La}_2\text{B}_2\text{O}_7, \text{cell})$ is the total energy per $\text{La}_2\text{B}_2\text{O}_7$ formula while $E(\text{La})$ and $E(\text{B})$ refer to the total energy of La and B crystal in the ground state. $E_{\text{iso}}(\text{La, atom})$ and ($E_{\text{iso}}(\text{B, atom})$) were calculated from isolated La and B atoms by using the supercell method. The results are shown in the Table 1. It is shown that the formation enthalpy of all $\text{La}_2\text{B}_2\text{O}_7$ formula is negative which indicates that these compositions are stable in the ground state. According to the value of formation enthalpy, the $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ge}_2\text{O}_7$ are more stable than the $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{La}_2\text{Hf}_2\text{O}_7$ in the ground state.

3.2. Electronic structure

Electronic structures will have impact on electronic transport properties of materials. We have calculated the band structures of $\text{La}_2\text{B}_2\text{O}_7$ compounds and the results are shown in Fig. 2. One can see that the $\text{La}_2\text{B}_2\text{O}_7$ compounds are charge-transfer-type insulators, and calculated band gap of $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Hf}_2\text{O}_7$,

$\text{La}_2\text{Sn}_2\text{O}_7$, and $\text{La}_2\text{Ge}_2\text{O}_7$, are 4.01, 3.05, 3.13 and 2.42 eV, respectively. According to the experimental values, the calculated band-gap value is smaller due to the insufficient description of the exchange correlation in the DFT calculations. A correction of the strong correlation effects is likely to increase the band gap. From Fig. 2, among the $\text{La}_2\text{B}_2\text{O}_7$ compounds, $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Hf}_2\text{O}_7$, and $\text{La}_2\text{Sn}_2\text{O}_7$, are direct band-gap insulators while $\text{La}_2\text{Ge}_2\text{O}_7$ are indirect band-gap insulators. Especially, $\text{La}_2\text{Ge}_2\text{O}_7$ has low band gap with 2.42 eV and corresponding absorption wavelength lies in the visible region. So $\text{La}_2\text{Ge}_2\text{O}_7$ may be used as potential photocatalytic and energy materials. As shown in Fig. 2, the electronic band dispersion curves for both the valence and conduction bands of four compounds are smooth and flat, implying the strong ionic bonding of these crystal structures.

In order to provide more details about the composition of band structures from different atoms and orbitals of $\text{La}_2\text{B}_2\text{O}_7$ compounds, we have given the angular projected density of states (PDOS). It is shown in Fig. 3(a-d), for $\text{La}_2\text{Zr}_2\text{O}_7$ compound, that the bottom of the conduction band is dominated by the $5d$ orbital of the La atoms and the $4d$ orbital of Zr atoms, while the top of valence band mainly consists of $2p$ of O atoms orbital. According to the density of states (DOS) in lower energy, more sharp peaks can be seen in the range from -20 to -40 eV, and some of them are attributed to the semicore $4s$ and $4p$ orbital of Zr. For $\text{La}_2\text{Sn}_2\text{O}_7$, as shown in Fig. 3(b), the bottom of the conduction band is dominated by the $5d$ orbital of the La atoms, but the $5s$ and $5p$ orbital of Sn atoms also contribute to the conduction band. The top of valence band mainly consists of $2p$ of O atoms orbital combining with contribution of $5s$ and $5p$

orbital of Sn atoms. Different from the $\text{La}_2\text{Zr}_2\text{O}_7$, as shown in Fig. 3(c), the bottom of the conduction band of $\text{La}_2\text{Hf}_2\text{O}_7$ is dominated by the $5d$ orbital of both La and Hf atoms. Furthermore the contribution of $5d$ orbital of Hf atoms is larger than that of $5d$ orbital of Zr atoms. Especially, in Fig.3(d), it is shown that $\text{La}_2\text{Ge}_2\text{O}_7$ are indirect band-gap insulators with low band gap of 2.42 eV, and its low band gap comes from the oscillations of $4s$ orbital of Ge in the conduction band. Considering of the low band gap of 2.42 eV, $\text{La}_2\text{Ge}_2\text{O}_7$ has semiconductor properties.

3.3. Mulliken populations and intrinsic hardness

The bond length and orbital populations of $\text{La}_2\text{B}_2\text{O}_7$ compounds are shown in Table 2. It is shown that the calculated overlap populations of B–O and La–O bonds are positive in the range of 0 to 1, so that charge transfer has happened in these compounds and all crystals show ionic and covalent characters. For all $\text{La}_2\text{B}_2\text{O}_7$ compounds, there are two kinds of La–O bonds, and the length of O_{48f} –La bond is larger than that of O_{8b} –La bond. Overlap populations of O–B bond are larger than the O–La bond which indicates that O–B bond has stronger covalent characters. The relatively weak La–O bonds play a predominant role in determining the structural stability [8]. The calculated overlap populations for $\text{La}_2\text{B}_2\text{O}_7$ structures indicate that the chemical bonding is basically dominated by B–O bonds which possess larger bond order than La–O bonds. The B–O bonds in $\text{La}_2\text{B}_2\text{O}_7$ are mainly covalent, and La–O bonds are the mixture of covalent and ionic interactions. Based on the Gao's works [18], the intrinsic hardness of $\text{La}_2\text{B}_2\text{O}_7$ compounds can be quantitatively estimated by using the results of Mulliken population analysis for crystal. The expressions for hardness calculations

is given by Gao as

$$H_v^\mu (\text{GPa}) = 740 P^\mu (v_b^\mu)^{-5/3} \quad (3)$$

$$v_b^\mu = \frac{(d^\mu)^3 V_{cell}}{\sum_v [(d^v)^3 N^v]} \quad (4)$$

In Eq (3) P^μ is the Mulliken overlap population of the μ -type bond, and v_b^μ denotes the μ -type bond volume. In Eq (4), d^μ is the bond length of type μ , N^v the bond number of v -type, and V_{cell} the cell volume of each $\text{La}_2\text{B}_2\text{O}_7$ compound. According to the calculated chemical bond, the corresponding hardness of the crystals can be obtained by a geometric average of all the contributions

$$H(\text{La}_2\text{B}_2\text{O}_7) = [\text{H}_{\text{O}_{48f}-\text{La}}^{24} \text{H}_{\text{O}_{48f}-\text{B}}^{24} \text{H}_{\text{O}_{48b}-\text{La}}^8]^{1/56} \quad (5)$$

It is shown in Table 2, the calculated hardness of $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore with B= Zr, Sn, Hf, and Ge are 9.8, 14.9, 8.9 and 18.3 GPa respectively. The calculated hardness of $\text{La}_2\text{Zr}_2\text{O}_7$ is in good agreement with the experimental results while the value of the $\text{La}_2\text{Sn}_2\text{O}_7$ are slightly larger than the experimental results. From Table 2, one can see that the overlap populations of the O_{48f} -La of $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{La}_2\text{Ge}_2\text{O}_7$ are greater than that of $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Hf}_2\text{O}_7$ which lead to larger hardness. However, as far as we know, the experimental measured hardness of the $\text{La}_2\text{Hf}_2\text{O}_7$ and $\text{La}_2\text{Ge}_2\text{O}_7$ compounds is lack of reporting and the calculated value can provide reference. We can also evaluate the Vickers micro-hardness using the existing empirical rule between hardness and shear modulus $G = 6.78 H_v$ [19], and the estimated hardness of $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore with B= Zr, Sn, Hf, and Ge are 13.6, 14.1, 13.2 and 14.6 GPa, respectively. It is shown that the hardness evaluated by the empirical rule is larger than the Gao's method and experimental results.

3.4. Elastic constants and sound velocities

The mechanical properties of the materials are determined by the coefficient of elasticity. The second-order elastic constants were determined by means of linear fitting of the stress – strain curves. In our previous work [7], several different types of Lagrangian strains were applied on crystals and calculated Cauchy stress tensor for each strain after optimizing the internal degrees of freedom. The calculated elastic constants of $\text{La}_2\text{B}_2\text{O}_7$ compounds are summarized in Table 3. According to the calculated elastic constants, the corresponding mechanical properties such as shear modulus G , bulk modulus B , and Young's modulus E can be evaluated. For a cubic crystal $\text{La}_2\text{B}_2\text{O}_7$ compounds, C_{11} , C_{12} and C_{44} are three independent elastic constants. Elastic constant C_{11} refers to the uniaxial deformation along the $[001]$ direction, and C_{44} represents a pure shear deformation on (100) crystal plane. Elastic constant C_{12} is a mixture of σ_{11} and σ_{22} . In the cubic crystal, $C_{12} = C_{44}$ indicates that the interatomic force is central, and the anisotropic interactions appear between two atoms. As shown in Table 3, no $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore satisfies this criterion according to the calculated results, since $C_{12} > C_{44}$ for all $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Sn}_2\text{O}_7$, $\text{La}_2\text{Hf}_2\text{O}_7$, and $\text{La}_2\text{Ge}_2\text{O}_7$, respectively. On the other hand, the shear modulus of the cubic crystal is evaluated by C_{44} , and the smaller C_{44} , the smaller shear modulus.

The Voigt–Reuss–Hill (VRH) approximation is widely used to estimate the mechanical moduli of bulk polycrystalline materials [21]. Voigt and Reuss's schemes represent the upper and lower limits of the true elastic parameters, respectively. The mechanical moduli results are also listed in Table 3. The mechanical properties of

zirconia were also calculated for comparison. It is shown that the bulk modulus of $\text{La}_2\text{B}_2\text{O}_7$ compounds is not more than 200 GPa and it is larger than the experimental results because of the LDA applied. Generally speaking, LDA underestimated the lattice constant while overestimated the mechanical modulus. Another reason is that the experimental samples have all kinds of defects which lead to the underestimated value of the B and G. In this work, the deviations for Young's modulus between the calculated and measured values for some compounds are relatively small. For example, the deviations are 1.9 GPa for $\text{La}_2\text{Zr}_2\text{O}_7$ while 3.9 GPa for $\text{La}_2\text{Sn}_2\text{O}_7$. The Poisson's ratios (σ) of $\text{La}_2\text{B}_2\text{O}_7$ compounds are typical for ceramics in the range of 0.25–0.30. Two types of anisotropic indexes can be used to characterize the elastic anisotropy of cubic crystal: the first one is the widely used Zener's anisotropic indexes [22], and Zener's anisotropic parameters are calculated by Eqs. (6) and (7) for cubic crystal

$$A^Z = \frac{2C_{44}}{C_{11} - C_{12}} \quad (6)$$

$$A^E = \frac{C_{11} - C_{12} - 2C_{44}}{C_{11} - C_{44}} \quad (7)$$

and the second is universal elastic anisotropic index proposed by Ranganathan *et al.* is given by [23]

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0 \quad (8)$$

and

$$B^V = B^R = \frac{C_{11} + 2C_{12}}{3} \quad (9)$$

$$G^V = \frac{C_{11} - 2C_{12} + 3C_{44}}{5} \quad (10)$$

$$G^R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (11)$$

In the above Eq.(8), subscript V and R represent the Voigt and Reuss's estimations for B and G , respectively [21]. For a locally isotropic single crystal $A^U = 0$. The larger A^U means the more pronounced anisotropic materials, and the large deviation from unity indicates the anisotropic mechanical properties according to A^Z . From the calculated A^Z , A^E and A^U values listed in Table 3, the mechanical properties of $\text{La}_2\text{B}_2\text{O}_7$ compounds are all anisotropic. It is shown that anisotropic of $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{La}_2\text{Ge}_2\text{O}_7$ are more pronounced than that of $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Hf}_2\text{O}_7$. As mentioned above, $C_{44} \neq C_{12}$ indicates that the corresponding interatomic forces are not centrosymmetric in cubic crystals.

It is known that the mechanical properties of materials are dependent on the crystal orientations. We set $G_{100} = C_{44}$ and $G_{110} = (C_{11} - C_{12})/2$, where G_{100} and G_{110} represent the shear modulus along the $[100]$ and $[110]$ directions, respectively. The anisotropic property of shear modulus (G) for cubic crystal can be measured by calculating the difference between G_{100} and G_{110} . There is a relationship of $G_{100} = G_{110}$ for an isotropic crystal. The average shear modulus $G' = (C_{100} + C_{110})/2$ is compared with the value calculated using the Voigt–Reuss–Hill approximation (G_{VRH}). Polar coordinates of the shear modulus in $\text{La}_2\text{B}_2\text{O}_7$ compounds are shown in Fig. 4. The horizontal and vertical coordinates are along the $[100]$ and $[110]$ crystal orientations. The diagonal line represents the $[111]$ direction. The angle θ refers to the difference between G_{111} and G' . The deviations are shown in Fig. 4, especially for $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{La}_2\text{Ge}_2\text{O}_7$ which are also verified by anisotropic index A^U as given in Table 3.

The velocity of sound is closely related to the thermal properties of materials. It is known that there are one longitudinal mode and two transverse modes for each direction. The longitudinal mode corresponding to the longitudinal acoustic (LA) branch in the phonon spectrum while the two transverse modes are correlated to the transverse acoustic (TA) branches. The sound velocities of both longitudinal and transverse waves along three different crystal directions were studied for $\text{La}_2\text{B}_2\text{O}_7$ cubic crystals including [100], [110] and [111] in this paper. The calculated sound velocities for the $\text{La}_2\text{B}_2\text{O}_7$ compounds are shown in Table 4. For [100] and [111] direction, it is found that the sound velocities of longitudinal waves are significantly greater than transverse waves for all compounds. Along the [110] direction, two sound velocities of transverse waves have two different values which also can be confirmed by the non-degenerated phonon dispersion curves. Because it is known that the thermal conductivity is determined by the sound velocity and density, so the anisotropy of the sound velocity will lead to the anisotropy of the thermal conductivity. By comparison, the sound velocities of cubic ZrO_2 are also calculated and it is shown that the average sound velocity of $\text{La}_2\text{B}_2\text{O}_7$ compounds is lower than cubic ZrO_2 and the thermal conductivity of $\text{La}_2\text{B}_2\text{O}_7$ is lower than the cubic ZrO_2 .

3.5. Thermal conductivity

The Debye temperature is an important physical parameter and it can be estimated by the following expression [27,28]

$$\Theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (12)$$

where k_B is Boltzmann's constant, M the molecular mass, N_A the Avogadro's number, ρ the density, and n the number of atoms in molecular. The average sound velocity v_m is given as

$$v_m = \left(\frac{3(v_l v_t)^3}{2v_l^3 + v_t^3} \right)^{1/3} \quad (13)$$

where in the above equation

$$v_l = \left(\frac{B + \frac{4}{3}G}{\rho} \right)^{1/2} \quad (14)$$

and

$$v_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (15)$$

The calculated Debye temperature of $\text{La}_2\text{B}_2\text{O}_7$ crystals are listed in Table 4, it is shown that the values are around 500 K for most $\text{La}_2\text{B}_2\text{O}_7$ crystals except $\text{La}_2\text{Hf}_2\text{O}_7$ with 421.7 K. The thermal conductivity of an insulator describes the diffusivity of heat flow by phonon transport in a temperature gradient. There are two theoretical methods to evaluate the limit of the thermal conductivity: Clark's model [1] and Cahill's model [29]. According to the Clark's model, when the temperature is much higher than Debye temperature, phonon mean free path tends to the lattice parameters, and the minimum thermal conductivity becomes independent of temperature which is given by [1]

$$\kappa_{\min, \text{Clark}} = 0.87 k_B \Omega^{-2/3} (E / \rho)^{1/2} \quad (16)$$

where in the above equation

$$\Omega = \frac{M}{n\rho N_A} \quad (17)$$

Which M is molar mass, n the total number of atoms per formula and ρ the density. Cahill proposed a model based on Einstein's model, to predict the thermal conductivity of a wide range of amorphous solids and highly disordered crystals[29]

$$\kappa = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} k_B n^{\frac{2}{3}} \sum_i v_i \left(\frac{T}{\theta_{Di}}\right)^2 \int_0^{\theta_{Di}/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \quad (18)$$

where subscript i refers to the type of sound velocity, and v_i including one longitudinal mode and two transverse modes. The minimum thermal conductivity of Cahill's model at high temperature limit is given by

$$\kappa_{\min, \text{Cahill}} = \frac{k_B}{2.48} n^{\frac{2}{3}} (2v_t + v_l) \quad (19)$$

where n is the density of number of atoms per volume, v_t and v_l the sound velocity of transverse wave and longitudinal wave.

As shown in Table 5, the calculated thermal conductivity of compounds decreased with Ma (the average mass per atom) increasing, and the $\text{La}_2\text{Hf}_2\text{O}_7$ has lowest minimum thermal conductivity with 1.09 W/m·K according to the Clark's model. It is also shown that the values obtained by Cahill's model are slightly larger than Clark's model. However, for the $\text{La}_2\text{Sn}_2\text{O}_7$, both of the two methods give too small values as compared with the measured value. The reason is that the experimental minimum thermal conductivity of $\text{La}_2\text{Sn}_2\text{O}_7$ is given at 1273K while the mean free length of phonon did not reach the limit value. Actually, $\text{La}_2\text{B}_2\text{O}_7$ has a lower elastic modulus and minimum thermal conductivity than its binary BO_2 counterpart. For example, the

thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ compounds is smaller than that of cubic ZrO_2 which is attributed to the effects of the weak La–O bonds presented in the ternary pyrochlore. According to the Cahill's model combining with Eq(18), as shown in Fig. 5, the minimum thermal conductivity of $\text{La}_2\text{B}_2\text{O}_7$ is increased with the temperature increasing, and reached a constant value at high temperature. It is also shown that the thermal conductivity decreased with the larger atomic number at given temperature. According to the calculated results of thermal conductivity, the $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore exhibit relatively low thermal conductivities and these compounds are suitable to be used as thermal insulating materials.

4. Conclusions

In summary, by using the DFT with plane-wave pseudopotential total energy scheme method, we have studied the electronic structure, mechanical and thermal properties of $\text{La}_2\text{B}_2\text{O}_7$ (B=Zr, Sn, Hf, and Ge) pyrochlore. The electronic structure, elastic coefficients, bulk modulus, shear modulus and Young's modulus of $\text{La}_2\text{B}_2\text{O}_7$ have been investigated systematically. It has been shown that the $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore are charge-transfer-type insulators with the strong ionic bonding of these crystal structures. For all $\text{La}_2\text{B}_2\text{O}_7$ crystals, there are two kinds of La–O bonds, and the length of O_{48f} –La bond is larger than the length of O_{8b} –La bond. The calculated overlap populations for $\text{La}_2\text{B}_2\text{O}_7$ structures indicated that the chemical bonding is basically dominated by B–O bonds which possess larger bond order than La–O bonds. Based on the Gao's works, the intrinsic hardness of $\text{La}_2\text{B}_2\text{O}_7$ compounds are quantitatively estimated by using the results of Mulliken population analysis for crystals. The

calculated hardness of $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore with $\text{B} = \text{Zr}, \text{Sn}, \text{Hf}$, and Ge are 9.8, 14.9, 8.9 and 18.3 GPa, respectively. Both Clark's model and Cahill's model were used to evaluate the limit of the thermal conductivity: According to the Clark's model, the minimum thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Hf}_2\text{O}_7$, $\text{La}_2\text{Sn}_2\text{O}_7$, and $\text{La}_2\text{Ge}_2\text{O}_7$, are 1.27, 1.09, 1.24 and 1.41 eV, respectively. It is shown that $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore exhibit relatively low thermal conductivities, indicating that these compounds may find important applications in the thermal insulating materials.

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Fig.1

Fig. 2

Fig. 3

Fig. 4

Fig 5

Table 1 Lattice parameters, cohesive energy and formation enthalpy of $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore (B=Zr, Sn, Hf, and Ge).

Methods	$\text{La}_2\text{Zr}_2\text{O}_7$		$\text{La}_2\text{Sn}_2\text{O}_7$		$\text{La}_2\text{Hf}_2\text{O}_7$		$\text{La}_2\text{Ge}_2\text{O}_7$	
	Cal ^a	Exp ^b	Cal ^a	Exp ^c	Cal ^a	Exp ^b	Cal ^a	Cal ^d
x	0.331	0.331	0.328	0.329	0.330	0.331	0.319	0.319
a(Å)	10.73	10.77	10.630	10.70	10.91	10.75	10.19	10.19
V(Å ³)	1236.8	1249.2	1200.1	1225.1	1298.9	1242.3	1058.90	1058.9
ρ (g m ⁻³)	6.14	-	6.94	-	7.64	-	6.71	-
Ec(eV/atom)	-9.60	-	-8.18	-	-9.29	-	-8.18	-
ΔH (kJ/mol)	-5091.5	-	-4242.8	-	-4651.8	-	-5132.2	-

^a This work; ^b Ref [16]; ^c Ref [17]; ^d Ref [8]

Table 2 Population analysis and hardness of $\text{La}_2\text{B}_2\text{O}_7$ (B=Zr, Sn, Hf, and Ge) pyrochlore.

	Atom	s	p	d	f	Total	Charge(e)	Bond	Population	Length(Å)	N ^u	Ω (Å ³)	V _b ^u	H ^u	Hv	
															Cal	Exp
$\text{La}_2\text{Zr}_2\text{O}_7$	O _{8b}	1.85	4.91	0.00	0.00	6.76	-0.76	O _{48f} -La	0.10	2.63	24	309.2	7.48	2.59	9.8 ^a	9.9 ^b
	O _{48f}	1.86	4.96	0.00	0.00	6.82	-0.82	O _{48f} -Zr	0.45	2.08	24		3.69	37.69		
	Zr	2.39	6.49	1.99	0.00	10.87	1.13	O _{8b} -La	0.19	2.32	8		5.12	9.22		
	La	2.05	6.13	1.26	0.00	9.44	1.56	O _{8b} - Zr	0	>4.00	0					
$\text{La}_2\text{Sn}_2\text{O}_7$	O _{8b}	1.86	4.99	0.00	0.00	6.86	-0.86	O _{48f} -La	0.22	2.62	24	300.0	7.03	6.32	14.9 ^a	10.6 ^c
	O _{48f}	1.86	4.97	0.00	0.00	6.83	-0.83	O _{48f} -Sn	0.56	2.15	24		3.89	43.29	14.0 ^c	
	Sn	1.11	1.45	0.00	0.00	2.56	1.44	O _{8b} -La	0.15	2.30	8		4.79	8.17		
	La	1.98	6.21	1.27	0.00	9.46	1.54	O _{8b} - Sn	0	>4.00	0					
$\text{La}_2\text{Hf}_2\text{O}_7$	O _{8b}	1.86	4.88	0.00	0.00	6.74	-0.74	O _{48f} -La	0.08	2.63	24	324.7	7.59	2.03	8.9 ^a	
	O _{48f}	1.87	4.96	0.00	0.00	6.82	-0.82	O _{48f} -Hf	0.56	2.12	24		4.12	39.26		
	Hf	0.47	0.52	2.09	0.00	3.08	0.92	O _{8b} -La	0.21	2.36	8		5.50	9.09		
	La	1.98	6.08	1.23	0.00	9.29	1.71	O _{8b} -Hf	0	>4.00	0					
$\text{La}_2\text{Ge}_2\text{O}_7$	O _{8b}	1.85	4.94	0.00	0.00	6.79	-0.79	O _{48f} -La	0.29	2.58	24	264.7	6.76	8.89	18.3 ^a	
	O _{48f}	1.86	4.96	0.00	0.00	6.82	-0.82	O _{48f} -Ge	0.44	1.93	24		2.86	56.50		
	Ge	0.89	1.59	0.00	0.00	2.48	1.52	O _{8b} -La	0.08	2.21	8		4.24	5.33		
	La	2.16	6.23	1.35	0.00	9.74	1.26	O _{8b} -Zr	0	>4.00	0		0			

^a This work; ^b Ref[20]; ^c Ref[14]

Table 3 Elastic coefficients (GPa), bulk modulus (GPa), shear modulus (GPa), Yong's modulus (GPa), Poisson's ratio (σ), anisotropic properties (A^Z , A^E and A^U), longitudinal (v_l), transverse (v_t) and average (v_m) sound wave velocity (m s^{-1}), Debye temperature (K) Θ_D of $\text{La}_2\text{B}_2\text{O}_7$ (B=Zr,Sn,Hf, and Ge) pyrochlore.

	Method	C_{11}	C_{44}	C_{12}	B_V	B_R	B	G_V	G_R	G	E	σ	B/G	A^Z	A^E	A^U	v_l	v_t	v_m	Θ_D
$\text{La}_2\text{Zr}_2\text{O}_7$	Cal ^a	291.6	99.6	126.3	181.4	181.4	181.4	92.8	92.0	92.4	237.1	0.28	1.96	1.17	0.17	0.04	7126.1	3925.1	4374.5	486.6
	Cal ^b	282.0	92.0	122.0	-	-	176.0	-	-	87.0	208.0	0.30	2.02	-	-	-	6960.6	3802.2	4240.2	518.1
	Exp ^c	-	-	-	-	-	157.0	-	-	84.0	239.0	0.27	1.87	-	-	-	6695.5	3741.1	4164.8	508.8
$\text{La}_2\text{Sn}_2\text{O}_7$	Cal ^a	298.4	106.7	135.4	189.7	189.7	189.7	96.6	94.9	95.8	245.9	0.28	1.98	1.31	0.26	0.08	6972.6	3830.2	4269.6	473.9
	Cal ^d	297.0	97.0	124.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Exp ^d	314.9	94.5	125.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Exp ^e	-	-	-	-	-	190.0	-	-	94.0	242.0	-	2.02	-	-	-	-	-	-	-
$\text{La}_2\text{Hf}_2\text{O}_7$	Cal ^a	286.5	96.5	126.2	179.6	179.6	179.6	89.9	89.2	89.7	230.4	0.29	2.00	1.21	0.17	0.04	6257.5	3424.6	3818.6	421.7
	Cal ^f	286.0	94.0	126.0	-	-	180.0	-	-	88.0	228.0	0.29	2.05	-	-	-	-	-	-	-
$\text{La}_2\text{Ge}_2\text{O}_7$	Cal ^a	314.4	109.6	142.8	200.0	200.0	200.0	100.1	98.6	99.3	255.7	0.29	2.0	1.28	0.23	0.07	7038.3	3847.3	4290.3	506.5
	Cal ^f	315.0	111.0	143.0	-	-	200.0	-	-	100.0	258.0	0.29	2.0	-	-	-	-	-	-	-
$\text{ZrO}_2(\text{cubic})$	Cal ^a	580.9	79.8	115.8	270.9	270.9	270.9	140.9	108.3	124.6	542.4	0.30	2.1	0.34	0.61	1.5	8221.9	4390.5	4904.4	605.25
	Exp ^g	474.0	-	95.0	-	-	268.0	-	-	136.0	442.0	0.23	1.97	-	-	-	8554.2	4706.4	5245.7	698.6

^a This work; ^b Ref[7]; ^c Ref[[24]; ^d Ref[14]; ^eRef[25]; ^f Ref [8]; ^g Ref [26]

Table 4 The anisotropic sound velocities of $\text{La}_2\text{B}_2\text{O}_7$ (B =Zr, Sn, Hf and Ge) pyrochlore, and the unit of velocity (v) is $\text{m}\cdot\text{s}^{-1}$.

	[100]		[110]			[111]	
	$[100]v_l$	$[001]v_{ll,2}$	$[110]v_l$	$[1-10]v_l$	$[001]v_l$	$[111]v_l$	$[11-2]v_{ll,2}$
$\text{La}_2\text{Zr}_2\text{O}_7$	6970.8	3739.7	7171.9	5246.7	4075.5	7237.8	3835.7
$\text{La}_2\text{Sn}_2\text{O}_7$	6760.3	3911.9	7039.8	4996.7	4042.2	7130.5	3710.66
$\text{La}_2\text{Hf}_2\text{O}_7$	6124.4	3926.2	6296.6	4851.4	3553.8	6352.8	3347.6
$\text{La}_2\text{Ge}_2\text{O}_7$	6843.7	3946.1	7098.6	5054.9	4041.1	7181.6	3736.4
$\text{ZrO}_2(\text{cubic})$	9479.1	3117.1	8138.8	8481.2	3514.8	7640.1	5300.5

Table 5. Calculated sound velocity, Debye temperature and minimum thermal conductivity of $\text{La}_2\text{B}_2\text{O}_7$ (B =Zr, Sn, Hf and Ge) pyrochlore. M_a is the average mass per atom.

	$M_a(10^{-26}\text{Kg})$	$\kappa_{\min}(\text{Clark})(\text{W}/\text{m}\cdot\text{K})$	$\kappa_{\min}(\text{Cahill})(\text{W}/\text{m}\cdot\text{K})$	$\kappa_{\text{exp}}(\text{W}/\text{m}\cdot\text{K})$
$\text{La}_2\text{Zr}_2\text{O}_7$	8.64	1.27	1.41	1.5 ^a
$\text{La}_2\text{Sn}_2\text{O}_7$	9.47	1.24	1.37	2.0 ^b
$\text{La}_2\text{Hf}_2\text{O}_7$	11.24	1.09	1.21	-
$\text{La}_2\text{Ge}_2\text{O}_7$	8.08	1.41	1.56	-
$\text{ZrO}_2(\text{cubic})$	6.82	2.28	2.39	2.5 ^c

^a Ref[7];^bRef[25];^cRef[30]

Figure Legends:

Fig.1 Crystal structure of $\text{La}_2\text{B}_2\text{O}_7$ (B= Zr, Sn, Hf , and Ge) pyrochlore. Atomic positions are described in detail in the paper.

Fig. 2. The calculated band structures of $\text{La}_2\text{B}_2\text{O}_7$ pyrochlore (B=Zr, Sn, Hf, and Ge) near the Fermi level. The dashed line is the Fermi energy.

Fig. 3. The calculated angular projected density of states (PDOS) and total density of states (TDOS) of $\text{La}_2\text{B}_2\text{O}_7$ (B=Zr, Sn, Hf, and Ge) pyrochlore within LDA. The dashed line is the Fermi energy.

Fig. 4. Anisotropic shear modulus of $\text{La}_2\text{B}_2\text{O}_7$ (B= Zr, Sn,Hf, and Ge) pyrochlore. G_{VRH} represents the VRH approximation results and G' is the average of shear modulus along [100] and [110] crystal directions.

Fig 5 The thermal conductivity of $\text{La}_2\text{B}_2\text{O}_7$ (B= Zr, Sn, Hf , and Ge) pyrochlore vs temperature according to the Cahill's model.

Graphical Abstract:

According to the Cahill's model, $\text{La}_2\text{B}_2\text{O}_7$ (B= Zr, Sn, Hf , and Ge) pyrochlore exhibit relatively low thermal conductivities, indicating that these compounds may find important applications in the thermal insulating materials.