First principle study of the B-site doped double perovskite oxides LaMg_{0.5}M_{0.5}O_3 (M=Sc, Ti, Zr)

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Abstract. The stable configuration of double perovskite LaMgO_3 was constructed by CASTEP module in Materials Studio. How the B sites doping (Sc^{3+}, Ti^{4+}, Zr^{4+}) affect the structure and physical properties was theoretical investigated. Three configurations of doping are structural geometry and energy optimized by GGA+WC correlation function, according to the principle of minimum energy, the most stable geometry structure is obtained, based on this structure, the physical properties are calculated. The results show that: The energy of LaMg_{0.5}Ti_{0.5}O_3 is the lowest and it is deduced as semiconductor according to the band gap. In the vicinity of Fermi level, the interaction between p-electron and d-electron is obvious, which contributes the most to the density of states. By optical properties simulation, the frequency of absorption peaks of the three materials becomes lower and lower in low frequency range, while the absorption peaks of LaMg_{0.5}Sc_{0.5}O_3 and LaMg_{0.5}Zr_{0.5}O_3 appear earlier than LaMg_{0.5}Ti_{0.5}O_3 in high frequency range, but the peak intensity is lower.

1. Introduction
The nanostructured perovskite-type oxide with ABO_3 has received a lot of attention in the past few decades due to its high mobility in oxygen separation membranes [1-3], fuel cells [4-7], sensors [8], catalysts [9, 10] and other applications. In the structure of ABO_3 perovskite, the A-site cation can be rare earths such as La^{3+}, which will be suitable for the dodecahedron site of the skeleton, and the B-site cation can be 3d, 4d or 5d transition metal ions occupying the octahedron site. These oxides can tolerate partial substitution but still retain the perovskite structure [11], and are very stable in both oxidizing and reducing atmospheres. This kind of perovskite-type composite oxide has a variety of special physical and chemical properties, and its crystal structure is relatively stable, especially when the A-site or B-site ions are partially replaced, its crystal structure will not change fundamentally, while its performance can be improved. When doped with alkali (Mg^{2+}, Ca^{2+}, Sr^{2+}) , perovskite oxides as interconnections and/or cathodic components in solid oxide fuel cells and electrocatalysts have a great influence on conductivity, sinter and stability [12, 13].

General formula for A_2B'B''O_6 is coordinated by ABO_3 octahedron, depending on the difference in the ion radius and electric charge, the cations B' and B'' are used to occupy the site of the B site according to a certain size, to observe whether the crystal structure is arranged orderly between B' and B'' [14]. On
the other hand, the chemical substitution of B site element is a feasible method to optimize the energy band structure of perovskite. B-doped double perovskite has been proved to have excellent semiconductor properties and has been widely used in fuel cells and solar cells [15]. Initial studies of double perovskite oxides $A_2B'B''O_6$ focused on its structural characteristics and electromagnetic properties [16-20], while there are only a few studies have been done on lattice preparation conditions and structural characterization from the perspective of synthesis [21]. The double perovskite oxides $A_2B'B''O_6$ was usually used to synthesize many new compounds due to its diversity of crystal structure, such as $La_2Mg_0.5O_6$ [22].

Density functional theory (DFT) [23-24] is usually used to calculate the influence of B-doping on the structure and physical properties of double perovskite as well as the influence of band gap. In order to further study the influence on the structure and physical properties of double perovskite oxide $LaMg_0.5M_0.5O_3$ ($M=Sc, Ti, Zr$) by b-site doping, based on the first principle, this paper uses the CASTEP module in Materials Studio software to build the configurations of double perovskite $LaMg_0.5Sc_0.5O_3$, $LaMg_0.5Ti_0.5O_3$ and $LaMg_0.5Zr_0.5O_3$, combined with GGA+WC correlation function, the structure was geometrically optimized and energy optimized successively to find out its lowest energy structure and analyze its various physical properties, such as energy band structure, state density, fractal state density and optical properties.

2. Configuration construction and calculation methods

At room temperature of 300 K, double perovskite oxides $LaMg_0.5M_0.5O_6$ ($M=Sc, Ti, Zr$) has a cubic symmetrical structure. The spatial groups are P2 1/ C, and the spatial group code 14, the cation at site B is $Mg^{2+}$, and the anion occupying the corner is $O^{2-}$. The initial values of lattice constants $a$, $b$ and $c$ are set as $a=5.50$ Å, $b=5.50$ Å, $c=8.00$ Å respectively. According to the high symmetry of its structure, cationic $Sc^{3+}$, $Ti^{4+}$, $Zr^{4+}$ was used to partially replace the $Mg^{2+}$ ion in B site, the replacement proportion is $Mg_0.5M_0.5$. Figure 1 shows the optimized configuration structure of $LaMg_0.5Ti_0.5O_3$. Since the cellular structure of $Sc^{3+}$ and $Zr^{4+}$ substituted B site is similar to that of $Ti^{4+}$ substituted, the cell structure diagram of $LaMg_0.5Ti_0.5O_3$ is provided only. As can be seen from Figure 1, one cell contains four $ABO_3$ molecules, including four $La^{2+}$, two $Mg^{2+}$, two $Ti^{4+}$, and twelve $O^{2-}$.

![Figure 1. The configuration structure of LaMg0.5Ti0.5O3](image)

3. Geometry energy optimization

The structural geometry and energy optimized of B-doped cells of $LaMg_0.5M_0.5O_6$ ($M=Sc, Ti, Zr$) was carried out by the CASTEP module in Materials Studio combined with GGA+WC as related functions, the optimized results are shown in Table 1.

| Geometric structure | $a$/Å | $b$/Å | $c$/Å | $V$(Å$^3$) | $E$/eV | $E_g$/eV |
|---------------------|-------|-------|-------|-----------|--------|----------|
| $LaMg_0.5Sc_0.5O_3$ | 5.603156 | 5.757090 | 7.968716 | 257.021655 | -13230.27585 | 0 |

Table 1. The geometric structure lattice constant, total energy change and band gap of the optimized $LaMg_0.5MO_3$ ($M=Sc, Ti, Zr$)
LaMg_{0.5}Ti_{0.5}O_{3}  

\begin{tabular}{llllll}
5.559491 & 5.578987 & 7.851478 & 243.523913 & -13875.77924 & 3.743 \\
LaMg_{0.5}Zr_{0.5}O_{3}  

\begin{tabular}{llllll}
5.640815 & 5.762782 & 8.027946 & 260.958850 & -13247.801497 & 4.344 \\
\end{tabular}

It can be seen that the cell volume and energy obtained by different doping elements have obvious changes. Where, a, b and c respectively represent the lattice constants of the configuration structure after geometric optimization, V represents the optimized volume, and E represents the value of the optimized energy. In all configuration structures, the cell volume is at the lowest configuration corresponding to the lowest energy. The energy from low to high is LaMg_{0.5}Ti_{0.5}O_{3} (-13875.77924 eV), LaMg_{0.5}Zr_{0.5}O_{3} (-13247.801497 eV), LaMg_{0.5}Sc_{0.5}O_{3} (-13230.27585 eV). It can also be found that the optimal LaMg_{0.5}Ti_{0.5}O_{3} cell volume is the smallest. Therefore, compared with Sc^{3+} and Zr^{4+}, the cell geometry is the most stable when B-doped LaMg_{0.5}M_{0.5}O_{6} ion with Ti^{4+}.

4. Energy band structure

Figure 2 gives the energy band structure of B-doped LaMg_{0.5}M_{0.5}O_{6} (M=Sc, Ti, Zr), and the band gap values were calculated in Table 1. It can be seen from the figure that the band gap changes significantly with different doped elements. From Figure 1 and Table1, in the configuration of LaMg_{0.5}Sc_{0.5}O_{3} inexistence band gap around the Fermi level \( E_g = 0 \text{ eV} \), so it belongs to conductor material. However, there exist significant band in the configuration of LaMg_{0.5}Sc_{0.5}O_{3} and LaMg_{0.5}Zr_{0.5}O_{3}, the band gap is 3.743 eV and 4.344 eV respectively, both the valence-band top and conduction band bottom are located at Γ point, therefore, the materials of these two structures are semiconductor materials. It can also be seen from Figure 2 that the energy band structures corresponding to the spin up and down of all structures completely coincide, indicating that all the three materials are antiferromagnetic structures.

5. State density analysis

Figure 3 shows comparison diagram of total state density of LaMg_{0.5}Sc_{0.5}O_{3}, LaMg_{0.5}Ti_{0.5}O_{3} and LaMg_{0.5}Zr_{0.5}O_{3}. It can be seen from the figure that the total state density peaks of B-doped
LaMg_{0.5}M_{0.5}O_{6} (M=Sc, Ti, Zr) under Fermi energy level are almost unchanged, all of which are 7 peaks. However, a wide delocalized distribution is formed above the Fermi level. Unlike LaMg_{0.5}Sc_{0.5}O_{3} and LaMg_{0.5}Zr_{0.5}O_{3}, LaMg_{0.5}Ti_{0.5}O_{3} appear extra peak in the vicinity of 4.0 eV. What’s more, Figure 4 shows partial density of states of B-doped LaMg_{0.5}M_{0.5}O_{6} (M=Sc, Ti, Zr). It can be seen that the three B-doped structures have a similar distribution of fractal wave state density in the vicinity of Fermi level, s electron obviously interacts with p electron, which makes great contribution to DOS, this is probably due to the interaction between the 2p orbital of oxygen and the 3d orbital of Ti, thereby \( \sigma \) bond formed.
6. Reflectivity
Figure 5 shows the optical properties of the configuration of LaMg0.5M0.5O3 (M=Sc, Ti, Zr). The three B-doped structures exhibit similar optical properties, the frequency at which an absorption peak occurs becomes lower and lower in low frequency range. Among them, LaMg0.5Sc0.5O3 and LaMg0.5Zr0.5O3 has an almost identical peak reflectivity, however LaMg0.5Ti0.5O3 and LaMg0.5Sc0.5O3 showed a higher absorption peak compared with LaMg0.5Zr0.5O3 in the high frequency range, and it moves to a higher frequency range, in this frequency range it can be used as a high energy laser.

7. Conclusion
Based on the first principle, the configuration of double perovskite LaMg0.5Sc0.5O3, LaMg0.5Ti0.5O3 and LaMg0.5Zr0.5O3 was constructed by CASTEP module in Materials Studio, the structure was geometrically optimized and energy optimized successively combined with GGA+WC correlation function. Finally, the optimized geometry is obtained and its physical properties are analyzed.

1) The energy of LaMg0.5Ti0.5O3 is the lowest and it is deduced as semiconductor according to the band gap.

2) In the vicinity of Fermi level, the interaction between d-electron and p-electron of three investigated B-doped materials is obvious, which contributes the most to the density of states.

3) In the reflectivity simulation, the frequency at which an absorption peak occurs of the three investigated materials becomes lower and lower in low frequency range, while the absorption peaks of LaMg0.5Sc0.5O3 and LaMg0.5Zr0.5O3 appear earlier than LaMg0.5Ti0.5O3 in high frequency range, but the absorption peak intensity is low.
Acknowledgments

Financial support for this work was provided by the Guizhou Provincial Education Department Foundation Project: Application study on High Temperature Air Combustion Technology in Low Calorific Value Coalbed Methane in Liupanshui Area (No. Qianjiaohi KY Zi [2018]373), Research Initiation Fund of Liupanshui Normal University: Study on combustion performance response and emission of natural gas mixed with coalbed methane (No.LPSSYKYJJ201815).

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