Research paper

Investigations of crystal structures and the electronic structure changes of $Sr_3MgSi_2O_8$-$Sr_3MgSi_2O_{8-\delta}$ systems by first-principles calculation

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HIGHLIGHTS

- Computational model of $Sr_3MgSi_2O_{8-\delta}$ were built and investigated.
- The generated oxygen vacancies tended to be spreading among the lattice.
- The formation energy of oxygen vacancy when $\delta = 0.125$ is about 12.00 eV.
- This work is useful for understanding oxygen vacancy generation in $Sr_3MgSi_2O_{8-\delta}$.

ARTICLE INFO

ABSTRACT

The crystal structures, electronic structures and oxygen vacancy formation energy of $Sr_3MgSi_2O_8$-$Sr_3MgSi_2O_{8-\delta}$ materials were investigated by the first-principles calculations. For the $Sr_3MgSi_2O_8$, the band gap is calculated to be 4.99 eV. For the $Sr_3MgSi_2O_{8-\delta}$, a new band overlapping the Femi level appeared between the conduction band (CB) and valence band (VB). The oxygen vacancy formation energy of $Sr_3MgSi2O_{8-\delta}$ with $\delta = 0.125$ has been calculated. The value is ~12.00 eV. In addition, it can be found that the oxygen vacancies trended to be dispersing over the $Sr_3MgSi_2O_{8-\delta}$ lattice rather than getting together.

1. Introduction

Nowadays, materials containing oxygen vacancy are of great importance due to the fact that they can serve as oxygen ion conductor materials, host-materials for long-persistence luminescence, memristor materials and so on [1–10]. Therefore, the synthesis and design of novel materials containing oxygen vacancy always attract the researchers' attentions. For the past few years, due to the fact that novel long persistence luminescent materials in nanoscale have been developed, long persistence luminescence gradually catches the public's attentions due to its applications in fields such as bioimaging and biological temperature measurement [11–15]. For these materials, the amounts of oxygen vacancy is of great importance in determining their performances in the aforementioned fields [13,16,17].

Among the traditional phosphors, rare-earth ions (typically Eu^{2+} or Ce^{3+}) doped silicate-based materials have been explored due to their excellent performances. This is all because that they have advantages in aspects such as ease of synthesis, high fluorescence efficiency, excellent thermal quenching characteristics, chemical stability and environmentally friendly. Among the silicate-based materials, rare earth or transition metal ions doped $Sr_3MgSi_2O_8$, which could exhibit efficient emissions when excited by UV-light, have attracted much attention as a promising host material [18–25]. $Sr_3MgSi_2O_8$ has a monoclinic structure and crystallizes in the P 21/c space group. It possesses a lattice with $a = 13.8770$ Å, $b = 5.4577$ Å and $c = 9.4520$ Å while the β gets close to 90° [26]. There exist two cationic sites which can be substituted by rare earth ions or transition metal ions. Especially, long persistent luminescence can be observed for Eu^{2+} doped $Sr_3MgSi_2O_8$ due to the existing energy transfer process between the oxygen vacancy and the Eu^{2+} ions. Although there have been many literatures on reporting the luminescence properties of rare earth ion doped $Sr_3MgSi_2O_8$ phosphors, there has been no research concentrating on the analysis of the electronic band structures before and after the oxygen vacancy formed in its lattice. Therefore, a theoretical calculation is essential to give a
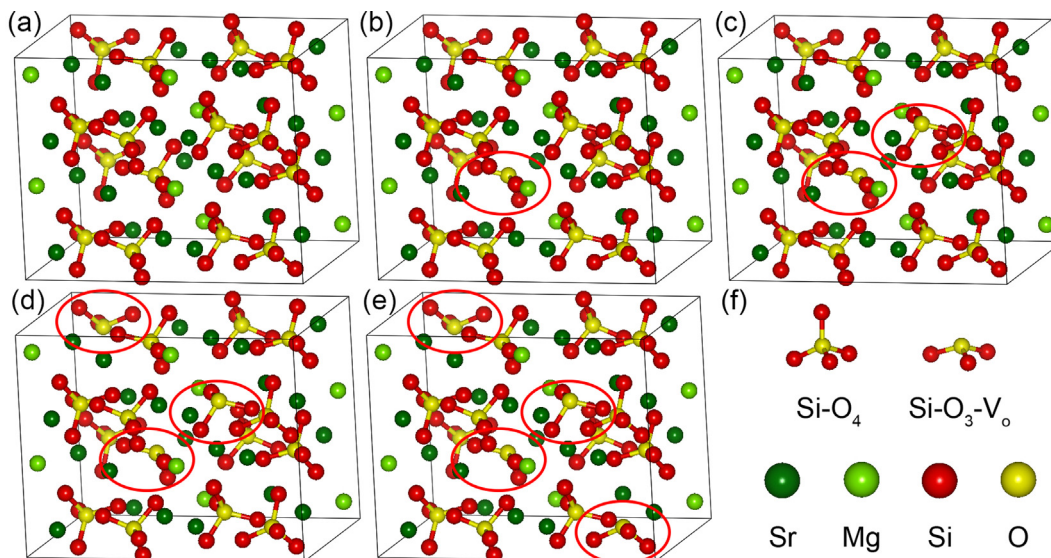
Fig. 1. (a)–(e) Crystal structure of $Sr_3MgSi_2O_{8-\delta}$ ($\delta = 0$, 0.125, 0.250, 0.500 and 1.000) materials with different oxygen vacancy concentrations. (f) An $Si-O_4$ group and an $Si-O_3-V_o$ group picked out from the lattice.

description on the changes of crystal structure and electron structure when oxygen vacancy formed in $Sr_3MgSi_2O_8$ lattice.

In this work, the crystal structures and electronic structures of $Sr_3MgSi_2O_8$-$Sr_3MgSi_2O_{8-\delta}$ ($\delta = 0.125$, 0.250, 0.500 and 1.000) were investigated by the first-principles calculations. Their band structures, total density of states (TDOS) and partial density of states (PDOS) were obtained. For the initial $Sr_3MgSi_2O_8$ lattice, the band gap is ~4.99 eV. For the $Sr_3MgSi_2O_{8-\delta}$ lattice, a new band overlapping the Femi level appeared between the conduction band (CB) and valence band (VB). It locates at ~1.66 eV above the top of VB and ~3.34 eV below the bottom of CB. The newly-presented band indicated that the formed oxygen vacancy would induce trap-state in the band gap. This would facilitate the electron hopping process. In addition, the formation energy of $Sr_3MgSi_2O_{8-\delta}$ with $\delta = 0.125$ has been calculated. The value is ~12.00 eV. On the other hand, it has been found that the elimination of the oxygen atoms located in different $Si-O_4$ tetrahedrons occurred more easily than that of the $Si-O_3$ tetrahedron that already disposed of one oxygen atom in the crystal. This investigation is helpful for better understanding oxygen vacancy formation process and the formation energy of $Sr_3MgSi_2O_8$-$Sr_3MgSi_2O_{8-\delta}$ systems.

2. Theoretical calculations

The theoretical calculations reported in this paper were based on density functional theory (DFT) and carried out by ABINIT package [27–32]. GGA-PEB functional combined with Nom-conserving pseudo potential were employed [33]. It has been reported that the $Sr_3MgSi_2O_8$ had a monoclinic structure and crystallizes in the P 21/c space group. It possesses a lattice with $a = 13.88$ Å, $b = 5.46$ Å and $c = 9.45$ Å while the β gets close to 90°. In order to investigate the influence of oxygen vacancy formation on the electronic band structure, a $1 \times 2 \times 1$ $Sr_3MgSi_2O_8$ supercell containing 24 Sr atoms, 8 Mg atoms, 16 Si atoms and 64 O atoms was created. From one to four oxygen atoms are removed from different $Si-O_4$ groups of the initial structure one by one to construct the $Sr_3MgSi_2O_{8-\delta}$ structure and $\delta = 0.125$, 0.250, 0.500 and 1.000, respectively. When δ reached 0.250, a computational model with two oxygen atoms removed from the one $Si-O_4$ group was constructed and calculated. The energy cut-offs of plane waves were set as 900 eV and the tolerance of self-consistent field calculations (SCF) was 1.0e−6 eV/atom. The k-point samplings were $1 \times 1 \times 1$ for geometry optimization.

The oxygen vacancy formation energy can be expressed as follows

[34,35]:

$$E_f^v(T) = E_{tol}^v(T) - E_{tol}^p(T) + E_o(T) \tag{1}$$

$$E_{tol}^v(T) = E_{tol}^v(0) + C_V^v T \tag{2}$$

$$E_{tol}^p(T) = E_{tol}^p(0) + C_V^p T \tag{3}$$

$$E_o(T) = G_O^0(0) + \Delta G_O^0(T) \tag{4}$$

$E_f^v(T)$, $E_{tol}^v(T)$, $E_{tol}^p(T)$ and $E_o(T)$ are the oxygen vacancy formation energy, the total energy of the structure after removing one O atom, the total energy of the initial complete structure and the energy of a single oxygen atom at T K, respectively. Meanwhile, $E_{tol}^v(0)$ and $E_{tol}^p(0)$ are the total energy of the structure after removing one O atom and the total energy of the initial complete structure at 0 K, respectively. $G_O^0(0)$ is the Gibbs free energy of O atom at T K and 1 atm. All the parameters needed in Eq. (1) have been obtained from the calculations. The $\Delta G_O^0(T)$ can be obtained through consulting the manual of industry chemistry and the value is −0.432 eV at 300 K. $C_V^v T$ and $C_V^p T$ are the heat capacity of structures with and without oxygen vacancy. Usually, for solid state materials, the $C_V^v T$ value is close to that of $C_V^p T$. Therefore, Eq. (1) can be written as

$$E_f^v(T) = E_{tol}^v(0) - E_{tol}^p(0) + G_O^0(0) - 0.432 \tag{5}$$

3. Results and discussion

Fig. 1(a) gives the initial crystal structure of $Sr_3MgSi_2O_8$. It possesses a monoclinic structure and crystallizes in the P 21/c space group. For the Sr atoms, there exist two distinct crystallographic sites for the alkali earth metal atoms: the Sr1 atom is twelve-fold coordinated by six O1 and six O2 atoms, and the Sr2 atom is seven-fold coordinated by oxygen atoms. Therefore, SrO_{12} and SrO_7 polyhedrons appear in the $Sr_3MgSi_2O_8$ crystal lattice. Meanwhile, for the Mg atom, only one distinct crystallographic site is available and the Mg atom is six-fold coordinated by oxygen atoms forming MgO_6 octahedron. The Si atom is four-fold coordinated by oxygen atoms and forms SiO_4 tetrahedron. In addition, the O atoms of a SiO_4 tetrahedron would connect with SrO_{12}, SrO_7 and MgO_6 polyhedrons. Fig. 1(b)–(e) gave the $Sr_3MgSi_2O_{8-\delta}$ crystal structures with different oxygen vacancy concentrations and the SiO_4 groups with removed oxygen atoms have been marked with red circles. The aforementioned crystal structures were obtained through

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