Fusion Engineering and Design xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Fusion Engineering and Design

journal homepage: www.elsevier.com/locate/fusengdes

First-principles study on the structural and electronic properties of Li_4SiO_4 and Al-doped Li_4SiO_4

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HIGHLIGHTS

- The structural and eletronic properties of Al-doped Li_4SiO_4 have been firstly studied by first-principles.
- The calculated results are well in agreement with the literature's experimental data.
- The band gap of Li_4SiO_4 can be reduced by Al-doped.

ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form 2 March 2016
Accepted 23 March 2016
Available online xxx

Keywords:
First-principles
Structural and electronic properties
Al-doped Li_4SiO_4
Tritium breeder

ABSTRACT

The structural and electronic properties of Li_4SiO_4 and Al-doped Li_4SiO_4 have been investigated using first-principles density functional theory. The crystal structure is fully relaxed. It can be concluded that the crystalline structure has been expanded as Al doped. The calculated total energies indicate that the Al atoms may occupy the Si 1, Si 2, Si 5 and Si 6 in preference to the other Si sits. The direct band gap of Li_4SiO_4 is 5.07 eV while Al-doped Li_4SiO_4 has a direct band gap of 4.78 eV. The values of the band gaps indicate that both of them are insulators. The value of the band gap reduces as Al-doped, which means that the conductivity could be improved as Al-doped.

1. Introduction

Lithium orthosilicate (Li_4SiO_4) has been recognized as the leading tritium breeding material in China, Europe and Korea [1–3], because of its low activation and favourable thermo-mechical properties. Recently, the Al-doped Li_4SiO_4 ($Li_{4+x}Si_{1-x}Al_xO_4$) solid solution has been designed as the advanced tritium breeding material, due to the improved Lithium atom density, mechanical property and thermal conductivity [4].

Theoretical studies on the Li_4SiO_4 are very few. Munakata and Yokoyama [5] calculated the crystal structures and electronic state of the Li_4SiO_4 based on the linear combination of atomic orbitals and Hartree-Fock (LCAO-HF) ab initio electron calculation. Duan [6] analyzed the structural, electronic, lattice dynamical, and thermodynamic properties of Li_4SiO_4 and its capability using Density functional theory (DFT). Tang [7,8] also studied the structural and electronic structures of Li_4SiO_4. To our knowledge, there is no comprehensive theoretical study on the Al-doped Li_4SiO_4.

In this work, the structural and electronic properties of Li_4SiO_4 and Al-doped Li_4SiO_4 were investigated using first-principes DFT.

2. Theoretical methods

The calculations of the structural and electronic properties in this study are carried with the Vienna ab initio simulation package [9,10] based first-principles DFT with plane-wave basis sets and the Projector augmented wave (PAW) pseudopotential [11,12] to describe the electron-ion interactions. From the experience in the literature [8,13], the generalized gradient approximation parameterized by Perdew-Burker-Ernzerhof [14] has been employed to evaluate the exchange-correlation functions. For some elements several PAW versions exist. The standard versions have been used for Al (s^2p^1) and O (s^2p^4) as recommended. Li_sv potential ($1s2s2p$) has been chosen since their transferability is much improved compared to the standard potential. For Si element, the Si_h potential (s^2p^2) has been employed. In the pseudopotentials that were utilized in this study, there are 3, 4, 3 and 6 electrons are treated as

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http://dx.doi.org/10.1016/j.fusengdes.2016.03.069
0920-3796/

Table 1
Experimental and optimized crystal structure parameters of Li_4SiO_4.

Crystal	Experimental	Optimized	deviations
Li_4SiO_4	a = 11.546	a = 11.6047	0.51%
$P2_1/m$	b = 6.090	b = 6.1270	0.61%
Z = 14	c = 16.645	c = 16.8102	0.99%
	β = 99.5°	β = 99.1378°	−0.36%
	V = 1154.34	V = 1180.07	2.2%

valence electrons for Li, Si, Al and O elements, respectively. The kinetic energy cut-off for the plane waves was set to 450 eV. The k-point sampling grids are achieved by using the Monkhorst–Pack [15] method set as $3 \times 5 \times 5$.

The crystal structure of Li_4SiO_4 was firstly reported by Vollekle [16], but this crystal structure is not suitable for ab initio studies since the location of Li atoms is not clear. Tranqui [17] redefined the structure by analyzing the electron diffraction patterns and X-ray diffraction data. Seven isolated SiO_4^{4-} tetrahedral are located in the mirror plane at y = 1/4, 3/4 and the Li atoms floating around them in this structure. Dejong [18] gave a similar structure, the differences between the structures are that some Li atoms are located in the different sites. In the structure reported by Tranqui, all Li atoms have fixed positions with full occupancy, whereas in the structure reported by Dejong four types of Li are half occupied and could form two sets in which the average position of each set is similar in position to the structure reported by Tranqui. Thus, the "super structure" reported by Tranqui was thought to be reasonable and taken into consideration in this work to simplify the calculations. Fig. 1 shows the unit cell mode (super structure).

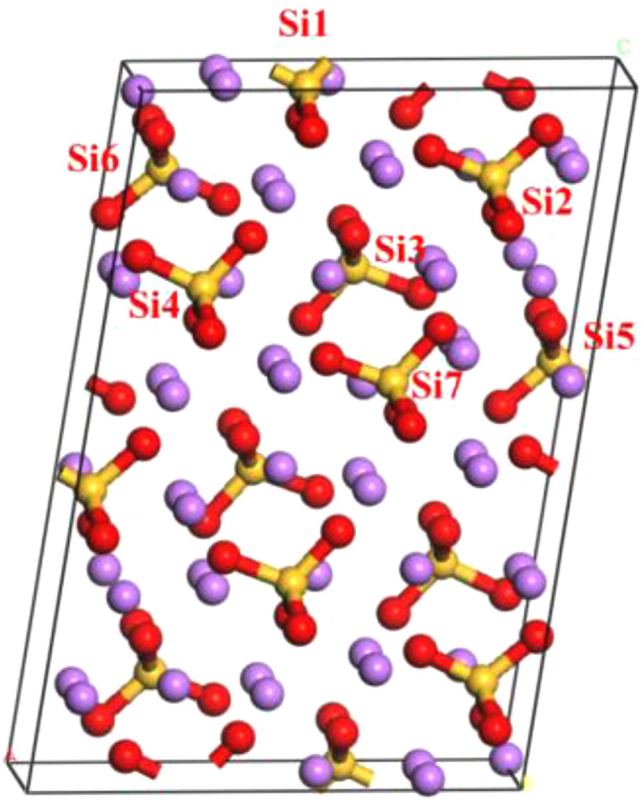

Fig. 1. Crystal structure of Li_4SiO_4. The purple balls stand for Li, red balls stand for O, the yellow balls stand for Si. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Equations and figures

3.1. Structural properties

Table 1 compares the experimental measurements [17] with our theoretical calculations of Li_4SiO_4. After optimization, crystal constants a, b and c are all elongated parallel to x, y, z axis, while β is slightly reduced. The optimized structural parameters have <1% deviation. It is consistent with the literature's results [7,8]. Table 2 shows the Si—O bond distance and O—Si—O bond angle for every SiO_4 tetrahedron, it is indicated that Si—O bond length ranges from 1.6081 to 1.6926 Å, which are slightly longer than the experimental values, and the O—Si—O bond angle varies from 105.30° to 114.71°. The similar results had been found in the Duan and Parlinski [6] and Tang et al.'s reports [8]. All the Si atoms occupy the 2e site in the Li_4SiO_4, but only two Si—O bond lengths are equal in one SiO_4

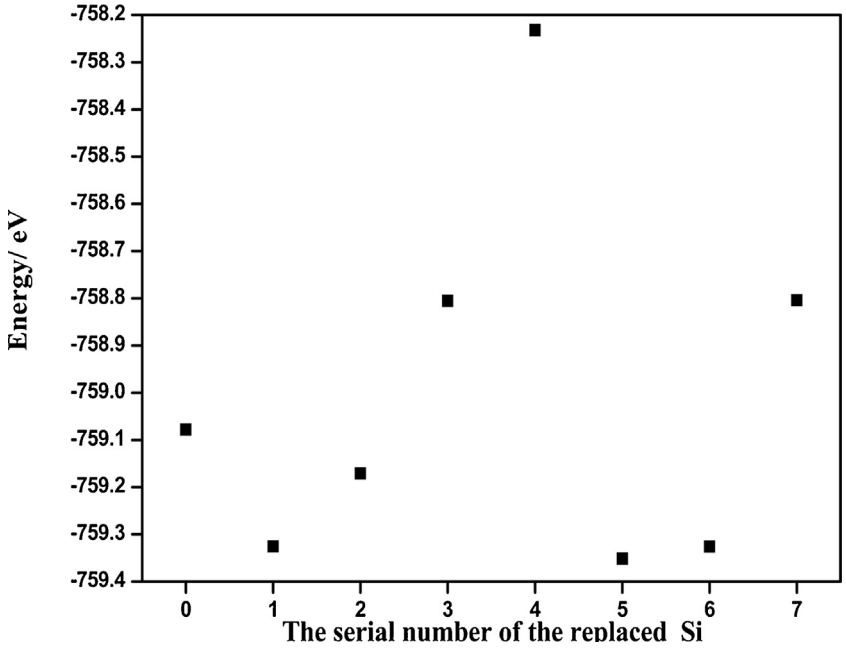

Fig. 2. The calculated total energies of $Li_{4+x}Si_{1-x}Al_xO_4$ (x = 1/14).

Please cite this article in press as: L. Zhao, et al., First-principles study on the structural and electronic properties of Li_4SiO_4 and Al-doped Li_4SiO_4, Fusion Eng. Des. (2016), http://dx.doi.org/10.1016/j.fusengdes.2016.03.069