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Density functional theory study of electronic structures in lithium silicates: Li_2SiO_3 and Li_4SiO_4

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Abstract. Lithium silicates, such as Li_2SiO_3 and Li_4SiO_4, are considered as favorable candidates for the tritium breeding materials of a nuclear fusion reactor. Their bulk electronic properties and mechanics are important for the tritium behavior and tritium breeding blanket designs. We have studied the structural and electronic properties of Li_2SiO_3 and Li_4SiO_4 bulks using density functional theory (DFT) within generalized gradient approximation (GGA). The calculated crystal parameters are well consistent with the experimental results. The electronic band energy calculations show that Li_2SiO_3 and Li_4SiO_4 are insulators with a band gap of about 5.36 and 5.53 eV, respectively. Their valence band properties are mainly determined by the oxygen $2p$ orbital electrons. The two types of oxygen atoms, nonbridging oxygen (NBO) atoms and bridging oxygen (BO) atoms, in Li_2SiO_3 reveal significantly different electron distribution of oxygen $2p$ orbital. The Si $3s$ and $3p$ hybridization is observed in Li_2SiO_3, but not in Li_4SiO_4. In both lithium silicates, the electronic density increases more steeply around Li and Si atom sites compared with that around O atoms. Additionally, the mechanical properties of both lithium silicates were calculated and discussed first time.

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Key words: electronic structure, density functional theory, lithium silicates, fusion

1 Introduction

The breeding blanket material is the key of a fusion reactor because of the production of tritium which is required by fusion reactors of the deuterium-tritium type [1–3]. This material should have a number of properties, such as (a) low electric conductivity, (b) high

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mechanical resistance, (c) high thermal stability, (d) potentially high tritium generation and (e) fast tritium release [2], to be considered as a possible candidate for the tritium breeding blanket. Keeping these properties in mind, some lithium-containing ceramics, including Li_2O, $LiAlO_2$, Li_4SiO_4, Li_2SiO_3, Li_2ZrO_3, Li_2SnO_3 and more recently Li_2TiO_3, have been proposed [4–17]. Each of these materials has advantages and disadvantages that should be kept in mind towards choosing a material to use. Among these ceramics, lithium silicates, Li_4SiO_4 and Li_2SiO_3, have attractive natures for lithium density, compatibility with the structure materials, release performance of bred tritium and so forth. However, there are many characteristics still not determined, like diffusion constants of tritium in the bulk and on the surface, determination of precise parameters defining adsorption and desorption, identification of mechanism of tritium release and how the generation and tritium release is affected by the defects of the crystalline structure.

Recent advance in the computer performance and computer codes makes it possible to study the chemical nature of condensed materials, such as metal, alloy, ceramics and others, by *ab initio* calculation that is a powerful tool to know how the electrons affect the property of substance. Actually, in order to understand the natural properties of lithium-based ceramics, the tritium localization in and the interaction mechanism with the surface and defects of lithium-based ceramics, especially for Li_2O, a lot of theoretical investigations based on the quantum chemistry calculation had been performed soon after solid tritium breeding concept emerging in fusion energy development [18–27]. Among these investigations, a lot of works were carried out for the bulk ground state properties, various defects formations and migrations, and the hydrogen isotopes absorption and desorption behaviors on the surface of lithium oxide (Li_2O) [18–25].

Nevertheless, only a few theoretical studies are available regarding the ground state properties and dynamics of the tritium in ternary lithium-containing ceramics due to their structural complications. For example, Campos studied two possible substitutional sites in the positions occupied by lithium atoms [26] and two octahedral sites [27] for tritium atoms in the Li_2TiO_3 structure using a quantum chemistry approach. It was found that the tritium atoms in lithium titanate preferably occupied in octahedral sites near lithium layers and followed by substitutional sites in lithium layers and titanium layers, respectively. These studies can give clues for understanding of behavior of tritium bred in the crystals or on the surface of breeder materials.

Although some efforts [28–30] had been made to study the hydrogen isotopes or water molecular adsorption on and desorption from lithium silicates surface based on the cluster model using quantum chemistry method, few studies have been done regarding the tritium behavior or ground state properties in Li_2SiO_3 and Li_4SiO_4 bulks. Ching *et al*. [31] studied the electronic structures of Li_2SiO_3 and $Li_2Si_2O_5$ and examined their electronic density of state (DOS) by density functional calculations in a periodic system based on the experimental crystal structure. Munakata *et al*. [32], probably the first one, studied the electron state in Li_4SiO_4 crystal using *ab initio* calculation implemented in the CRYSTAL98 code, and reported the charge Mulliken population analysis and the electron density of state (DOS). However, the further investigation has not been reported as for