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Molecular dynamics simulations of structural and melting properties of Li_2SiO_3

Shenggui Ma[a], Shichang Li[a], Tao Gao[a,c,*], Yanhong Shen[a], Xiaojun Chen[b], Chengjian Xiao[b], Tiecheng Lu[c]

[a] Institute of Atomic and Molecular Physics, Sichuan University, 610065 Chengdu, China
[b] Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China
[c] Key Laboratory of High Energy Density Physics and Technology of Ministry of Education, College of Physical Science and Technology, Sichuan University, Chengdu 610065, China

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ABSTRACT

Molecular dynamics simulations have been performed to investigate the structural and melting properties of single crystal and nanocrystal Li_2SiO_3. The simulated results of both lattice parameters and enthalpy as a function of temperature for single crystal are well consistent with the experimental values. The radial distribution functions and mean square displacement are utilized to analyze and characterize the structural evolution and melting behaviors in simulations. The models of nanocrystal Li_2SiO_3 are constructed by the Voronoi tessellation techniques. We predict that the melting temperature of single crystal Li_2SiO_3 is 1500 K, in close agreement with experiment. For nanocrystal Li_2SiO_3, the results indicate that the melting temperature decreases with the grain size decreasing, and drops to the range of 700–850 K.

1. Introduction

The crystalline lithium meta-silicate (Li_2SiO_3) has attracted more and more attention for their technological applications in several fields, such as cathode material in Li-ion batteries [1–3], tritium breeding material for nuclear fusion reactor [4,5], CO_2 sorbent to fight global warming [6–8], fast ion conductor [9,10], optical waveguides [11] and luminescent [12,13]. For example, the Li_2SiO_3, as a novel coating material, was applied for ameliorating the electrochemical properties of cathode or anode materials for high performance Li-ion batteries. The SiO_4 tetrahedra formed zigzag chains in Li_2SiO_3 can provide a three-dimension tunnel for Li^+ flowing which could greatly improve the Li^+ ion diffusion rate and enhance the electro-chemical performance [3]. Zhao et al. [3] have used Li_2SiO_3 as an electrode surface modification material to coat the Li-rich layered $Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ compound, and the results suggested that the Li_2SiO_3 coating layer effectively reduces the barrier for Li-ion transfer at the electrode–electrolyte interface. The Li_2SiO_3@$Li_4Ti_5O_{12}$ nanocomposites were synthesized by Wang et al. [14] via a hydrothermal route and sintering method, and the author suggested that the strategy with the Li_2SiO_3 supported structure was an effective way to improve the reversible capacity of anode materials for Li-ion batteries. Then, Bai et al. [15] used Li_2SiO_3 as an effective modifier to optimize the electrochemical performance of $Li_4Ti_5O_{12}$, and found that the Li_2SiO_3-coated $Li_4Ti_5O_{12}$ could be used as an anode material for high performance Li-ion batteries. In addition, the Li_2SiO_3 was considered as candidate tritium breeding material in the deuterium (D) - tritium (T) fusion reactor, and the ^6Li will be burnt-up by transmuting to tritium and helium though the reactions:

$$^6Li + n \rightarrow T + He$$

Nowadays, with the rapid development of nanotechnology, the nanostructured materials have received increased attention from academic to industrial research because of the unique properties which deviate from the ones of single crystal with the same chemical composition. The nanocrystals are based on the idea to introduce so many grain boundaries into a perfect crystal, and share increasing surface-to-volume ratio [16] and more pronounced size effects. Therefore, these nanocrystal materials may exhibit unusual physical and chemical properties endowed by confining the dimensions of such materials, and the overall behaviors of the combination of bulk and surface properties.

As a matter of fact, it is important to design and fabricate nanostructured electrode materials that provide high surface area and short diffusion paths for ionic transport and electronic conduction to overcome the resistance of the electrolyte when the charging-discharging rate is increased [17]. Meanwhile, the nanostructured ceramics may have effective thermal conductivity, excellent tritium release behavior

* Corresponding author at: Institute of Atomic and Molecular Physics, Sichuan University, 610065 Chengdu, China.
E-mail address: gaotao@scu.edu.cn (T. Gao).

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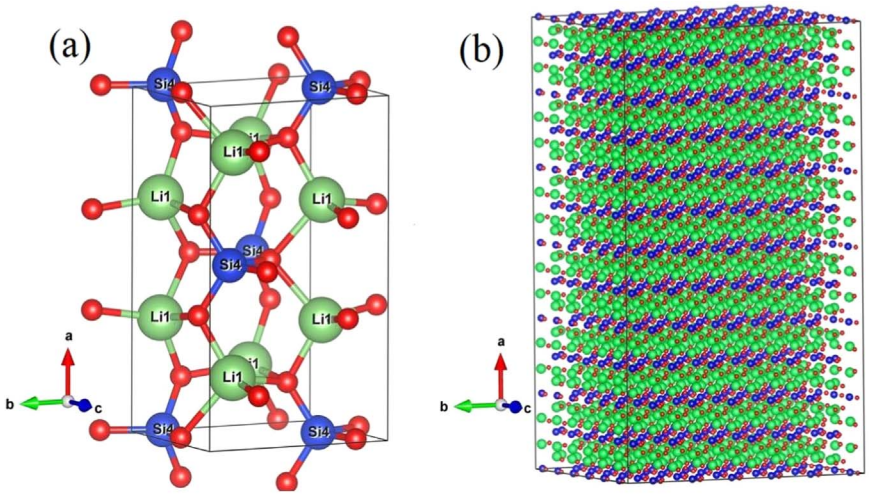

Fig. 1. (a) The unitcell of Li_2SiO_3. (b) The single crystal (6 × 6 × 6 supercell) of Li_2SiO_3.

and good irradiation resistance in the D-T fusion reactor [18,19]. Several works have been published about the syntheses and structural analysis for nanocrystal Li_2SiO_3. Khomane et al. have firstly reported the synthesis of nanoparticles of Li_2SiO_3 by coupling of sol–gel method in reverse micro-emulsion [20]. Then, nanocrystal Li_2SiO_3 particles have been synthesized by Zhang et al. [21] using a sol-gel process and investigated by XRD and differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA), Fourier-transform infrared (FTIR), and NMR analysis. Recently, the nanostructure Li_2SiO_3 powders were successfully synthesized by Alemi et al. [22] via a hydrothermal route, and found that the Li/Si molar ratio has a major effect on the size, morphology and optical properties. As the width and length of the nanostructures will affect physical–chemical properties, the morphology of Li_2SiO_3 nanostructures has been effectively controlled via adjusting the hydrothermal temperature and Li/Si molar ratio by Li and Yang [23].

Atomistic modelling techniques such as molecular dynamics (MD) simulations have emerged as a powerful tool to provide a physical insight into understanding various phenomena and have been widely employed to characterize the structural, mechanical and thermodynamic properties of metals and ceramics. The classical MD simulations employing classical interatomic potentials are an important computational technique and build a bridge between purely theoretical studies and experimental research. The computational cost is largely reduced, and the length and time scales are larger compared with first principle calculations. Moreover, the information of temperature and pressure can be freely chosen and output in the MD simulations.

Numerous works have been conducted to study the melting properties of metal nanocrystals by MD simulations, and found that the melting temperature is significantly reduced by a decrease in the average grain size. For example, the melting temperature of the Fe nanoparticles decreased with particle radius [24]. The melting temperature of W [25], Au [26], Ag [26], Cu [26], and Al [26,27] nanoparticles are also decreased with the size of the particles decreases. The melting process of Sn nanoparticles at different size has been simulated by Dalgic and Domekeli [28], the results indicated that the melting temperature of Sn nanoparticles depends nonlinearly on particle radius. The melting point of fcc-metal (Ni, Cu, Au) nanoparticles with respect to particle size was investigated by Shibuta [29], and the results shown that the melting point do not decrease monotonically but have some fluctuation with decreasing particle radius. Therefore, much research attention for nanomaterials was been focused on the metal, because of its simple structure, single element and accurate interatomic potential. Nevertheless, the information for melting properties on nanocrystals ceramics is still lack, especially for single crystal and nanocrystal Li_2SiO_3.

The present work aims to perform MD simulations to investigate the physical properties (lattice parameters and enthalpy) of single crystal Li_2SiO_3 firstly, these results can provide a validation of methodology and interatomic potential used in current study. The melting temperature is also predicted and validated against experimental data. The mean square displacement and radial distribution functions are utilized to analyze and characterize the structural evolution and melting behaviors. Finally, the nanocrystals of Li_2SiO_3 are constructed by the Voronoi tessellation techniques, then the melting behavior of the nanocrystal Li_2SiO_3 are also discussed.

The work is organized in the following manner: in the next section, a brief but important description of computational methodology is given. Then the detailed results and discussions are presented in Section 3. Finally, the main conclusions are summarized in Section 4.

2. Computational methodology

2.1. Structures of single crystal and nanocrystal

The unitcell of Li_2SiO_3 with space group $Cmc2_1$ (No. 36) [30] has 4 formula units (24 atoms) which is depicted in Fig. 1(a). The lattice constants of *a*, *b* and *c* are 9.396 Å, 5.390 Å and 4.661 Å, respectively. The Li_2SiO_3 structure is comprised of corner sharing [SiO_4] tetrahedra forming parallel chains along the c-axis with decorating lithium ions between the chains [31]. The single crystal of Li_2SiO_3 is carried out on a 6 × 6 × 6 supercell (5184 atoms), and the system consisted of 1728 Li atoms, 2592 O atoms and 864 Si atoms. The constructed single crystal structure can be seen in Fig. 1(b). The nanocrystals of Li_2SiO_3 are created by the Voronoi tessellation techniques [32–36] and visualized by *OVITO* program (Open Visualization Tool) [37]. In our previous work, the nanocrystals of Li_4SiO_4 are also constructed in this method [32]. A Voronoi tessellation is made by partitioning a plane with *n* points into *n* convex polygons such that each polygon contains one point. Among the numerical techniques developed to generate representative models of nanocrystal, the Voronoi tessellation techniques are widely accepted methods for construct nanocrystal of metals [38,39] and ceramic materials [40,41]. Therefore, the initial structures of the nanocrystal Li_2SiO_3 are constructed using the Voronoi tessellation methods in the present work, and some of them that the cell dimensions are 100 × 100 × 100 $Å^3$ are presented in Fig. 2(a-f).

2.2. Molecular dynamics (MD) simulations

In all simulations, the empirical potentials of Coulomb-Buckingham potentials are used to describe the interatomic interactions. Details about the pair potentials have been reported in our previous study [42].