Point defects in garnet-type solid electrolyte (c-$Li_7La_3Zr_2O_{12}$) for Li-ion batteries

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ABSTRACT

Using *ab-initio* density-functional theory (DFT) methods, the atomic structure and electronic properties of one of the most promising family of solid electrolytes for Li-ion battery applications, lanthanum oxides with a garnet-type structure (c-$Li_7La_3Zr_2O_{12}$) are studied. The Li-ion (Li^+) defects including Li/Li^+ vacancies, interstitials, and vacancy–interstitial pair defect formation energy within the $Li_7La_3Zr_2O_{12}$ supercell are systematically investigated. This study is essential to understand the defect chemistry and the Li^+ conductivity mechanisms. Our results indicate that the Li^+ vacancy defects are thermodynamically more favorable than interstitial Li^+ defects. This work will therefore be helpful to elucidate the atomic level mechanisms of Li defect formation in order to improve the ionic conductivity for future Li-ion battery applications.

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1. Introduction

During the past few years, a lot of research activities have been focused on improving the energy, power density and cycle life of Li-ion batteries for providing reliable power sources to various technological future devices including biomedical, hybrid motor vehicles and micro devices [1,2]. Among the different parts of the battery, inorganic solid electrolytes have attracted much attention because of safety concerns and reliability of currently used organic electrolytes [3]. The main advantages of solid electrolytes over conventional organic liquid electrolytes are: resistance to shocks and vibrations, absence of self-discharge, better cycle life, better safety, better chemical stability and convenience to integrate and scale down the size over the traditional liquid electrolytes [3,4]. These properties have attracted much attention of the battery scientists and engineers in order to develop all solid state Li-ion batteries. However, due to the significantly lower ionic conductivity of the currently available solid electrolytes, their practical use in Li ion batteries is hindered. Therefore, there is an intensive effort to develop fast Li-ion-conducting inorganic materials for their use as solid-state electrolytes. Several theoretical and experimental works have been published about some of the most popular solid electrolytes, including *Lithium Phosphorus Oxynitride*, LiPON [4–9], $LiTi_2(PO_4)_3$ (LTP) [10,11], Sodium (Na) Super Ionic Conductor of the NASICON family [12–14], Lithium lanthanum titanates (*LLTO*) [15–17], and Lithium

super-ionic conductors, $Li_{10}GeP_2S_{12}$ [18]. All of them suffer from their own limitations such as poor ionic conductivity or instability at interfaces with electrodes. Anode materials with a lower redox potential than 1.8 V vs Li/Li^+ cannot be used in LLTO and LTP materials due to the redox reaction of titanium which limits the energy and power densities of all-solid-state rechargeable lithium-ion batteries [19].

Recently, garnet-type materials have been proposed as promising candidates for solid electrolytes of Li-ion batteries because of their high ionic conductivity, wide potential window and high electrochemical stability [20]. Their structures are of the form $A_7B_3C_2O_{12}$, containing a $B_3C_2O_{12}$ framework substructure with B cations in 8-coordination sites and C cations in octahedral sites (see Fig. 1). The framework contains a 3D-connected interstitial space consisting of tetrahedral 24d-A sites bridged by a single octahedron and sharing opposite sides a common face with each of the two neighboring A sites, while the bridging octahedral sites share common edges. The existence of 3 tetrahedral-A and 6 bridging-octahedral sites for a total of 9 sites per formula unit is supposed to provide low activation energy barriers for the motion of guest lithium ions if they are disordered and with a partial occupancy of both types of sites [21,22].

Garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte is commonly observed in two phases (tetragonal and cubic). In particular, the Li-rich garnet-type cubic $Li_7La_3Zr_2O_{12}$ [21–23] has shown one of the highest Li-ion conductivities (5×10^{-4} S cm^{-1} at room temperature) among the crystalline Li-ion-conducting oxides. In addition, this material has shown an excellent thermal performance and chemical stability against air, moisture and at the interface with electrodes, including molten lithium [24]. Ohta *et al.* have shown a chemically stable interface with

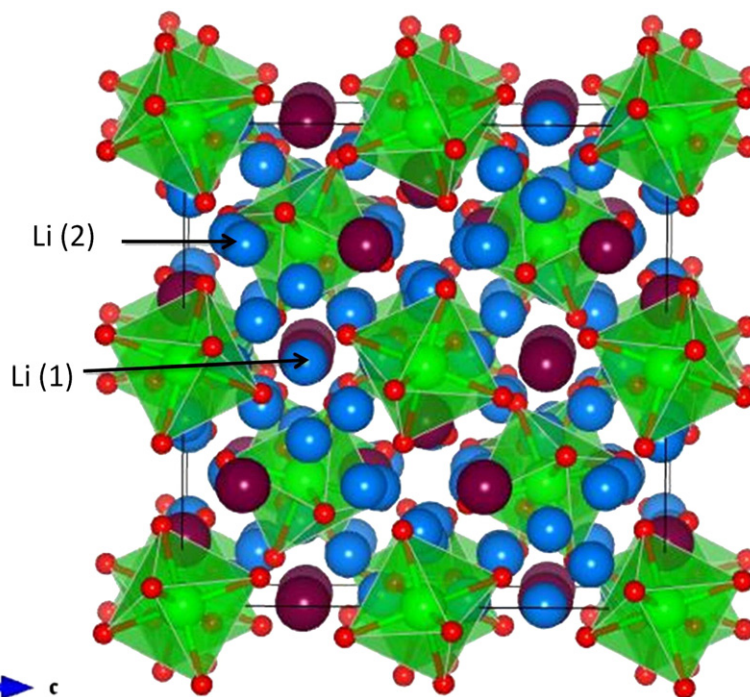**Fig. 1.** Atomic structure of cubic $Li_7La_3Zr_2O_{12}$. Blue balls represent Li atoms, purple balls Zr atoms, green balls La and red balls oxygen atoms.

both Li metal [25] and the standard layered oxide cathode material $LiCoO_2$ showing good charge–discharge performances [26]. The tetragonal $Li_7La_3Zr_2O_{12}$ phase [27,28] shows lower Li ionic conductivity compared to the cubic morphology, where the Li sites are fully occupied. Other experimental works on different garnet-related oxides and their derivatives like $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ $(0 \leq x \leq 1)$ showed a room-temperature ionic conductivity of $\sigma_{Li} \approx 1.0 \times 10^{-3}$ S cm^{-1} for $x = 0.6$ with an activation energy of 0.35 eV, making this family of Li-ion solid electrolytes a very interesting possibility for enabling a new generation of Li-ion rechargeable batteries. It has been argued that the Li ion conductivity can be further enhanced by substitutional doping of Li and La^{+3} ions by alkaline earth atoms in the host structures [30].

Recently, Bernstein et al. have investigated the phase stability of the high conducting cubic phase and its phase transition to a tetragonal structure by using DFT and molecular dynamic (MD) simulations, to show that the transition depends on the vacancy concentration [31]. Al substitution for Li is found to stabilize the cubic phase [29,32], without hampering the ionic conductivity. The effect of ionic substitution (Ta, Al, Ga) on the conductivity has been studied in detail by Allen et al. [33]. Some experimental groups assume that the presence of Al or Ga on Li sites will be detrimental to the Li ionic conductivity, and that the impurities therefore need to be concentrated on substitutions that are not part of the Li conduction pathway [32]. However, a detailed modeling study of Li ion defects at the atomic level and the ionic conductivity mechanism on Garnet-type solid electrolytes is still lacking in the literature. Since, the nature of defects in solid electrolytes has a crucial role in determining Li ionic conductivity, in this modeling work we primarily focus on the Li defect formation on the cubic $Li_7La_3Zr_2O_{12}$.

In this paper, we report our *ab initio* DFT calculations on the atomic structure and Li defects in the fast ion conducting Garnet-type solid electrolyte, comparing our results with the available experimental data.

2. Methodology

We performed *ab initio* DFT calculations [34–36], with plane wave basis sets and projector augmented wave (PAW) [37,39] pseudo-potentials, as implemented in the Vienna *Ab-initio* Simulation Package

(VASP) [35,37–42]. The electronic wave functions are represented by plane wave basis with a cutoff energy of 450 eV. The exchange and correlation interactions were incorporated through the generalized gradient approximation functional (GGA) [43]. A supercell containing 192 atoms with 8 formula units were used in our model. In the defect calculations, the atomic positions were allowed to relax while the cell size and angles were kept fixed. The energy and forces were converged up to 10^{-4} eV and 0.01 eV/Å, respectively. A Monkhorst–Pack [44] $2 \times 2 \times 2$ k-point mesh was used for the self-consistent calculations whereas a $4 \times 4 \times 4$ k-point mesh was used for the density of state (DOS) calculations. We have also used the GGA + U approximation [45–47] to describe the 3d electron–electron correlation interaction. In the DFT + U approximation, a Hubbard (the U) term is added to the conventional Kohn–Sham Hamiltonian to treat more accurately the localization of strongly correlated electrons, and also to reduce the self-interaction errors present in the standard DFT. A single effective coulomb energy parameter $Ú$ $(= U - J)$ with the on-site coulomb energy U and the exchange interaction J is included in the Hamiltonian. The $Ú$ parameters used in our system are 2.3 and 3.5 eV for La and Zr, respectively. We have also used larger U values up to 5 eV which are used for other transition metal-oxides [48,49].

We consider the Li defects in the dilute limit, with a low defect concentration and negligible defect–defect interaction. The concentration of Li defects in the materials is controlled by equilibrium condition under which they are formed and, in an approximate way, its dependence on formation energy is given by the following expression:

$$C = N \, \exp\left[\frac{-E_f}{kT}\right] \tag{1}$$

where C is the defect concentration, N is the number of available defect sites in the system, k is the Boltzmann constant, E_f is the formation energy of the defect and T is the temperature. Thus, the formation energy can give us an insight about the availability of defects for ionic conduction. A lower defect formation energy will result in higher Li^+ defect concentration in the solid electrolyte.