1. Introduction

The lithium-ion battery (LIB) is the fastest growing and most promising battery for a broad range of applications, e.g. portable electronics, robotics and all-electric vehicles. Its most common design consists of a graphite anode, a Li metal oxide cathode and an electrolyte made of Li salt and an organic solvent. The electrolyte provides the conductive medium, in which the Li ions travel back and forth from one electrode to the other during discharge and charge. Presently, three types of LIBs are envisioned as the next generation Li-ion battery, namely, metal-air, multi-valent cation and all-solid state batteries [13]. The latter is a very promising battery that has many advantages [8, 6] and it is currently considered the next step on major OEM’s roadmaps[11]. Firstly, the all-solid-state battery can be made thinner and safer than conventional LIBs, because it does not need a separator and it does not use flammable liquid materials for the electrolyte that are susceptible to dangerous leaks. Secondly, the solid-state electrolyte can withstand voltages up to 10 V which can enable high voltage cathodes, and consequently increase the energy density capacity of the battery by 20-50%. Moreover, solid electrolytes usually show excellent storage stability and very long life[7].

The challenge of the all-solid-state battery is to increase ionic conductivity to be comparable or even better than that of conventional liquid electrolytes (typically around $10^{-3}$ S/cm at room temperature[8]). Solid electrolyte materials exhibit rather low ionic conductivity ranging from $10^{-8}$ to $10^{-5}$ S/cm (halides), $10^{-5}$ to $10^{-2}$ S/cm (oxides), $10^{-7}$ to $10^{-3}$ S/cm (sulfides) and $10^{-7}$ to $10^{-4}$ S/cm (hydrades) [6]. Currently, ceramics, sulfides, solid polymers, glasses and composites of ceramics or glasses are materials proposed for solid-state electrolyte technology. Glasses have been known for a while to be fast ionic conducting materials, however research efforts have been concentrated mostly on synthesis and optimization of the thermal properties [4].

Recently, Braga et al. proposed and patented a new all-solid state battery architecture based on Li+ or Na+ glassy electrolytes [13, 1, 2, 3]. One the major breakthroughs of this new battery is the fact that, it can be realized using Na which is abundant, inexpensive and capable of promoting sustainable use of raw materials. Furthermore, it may be made without cobalt in the cathode, which is an advantage because cobalt presents several unresolved issues regarding health [5, 19] and irresponsible mining practices [14]. This battery promises to provide 2-3 times the energy storage capacity of a comparable LIB and most importantly it appears not to form dendrites, which are associated to short circuits in LIBs.

In the present study we investigate the amorphous structure of Li$_3$ClO glass and its electronic structure and we compare with its crystalline counterpart. The paper is organized as following. In section 2 we discuss the methodology and computational methods used in this investigation. Section 3 presents the results and discussions. Finally in section 4 we present the conclusions of our study.
Electronic structure of glassy Li$_3$ClO

Figure 1: Antiperovskite Li$_3$ClO and Li$_3$ClO amorphous structures. The model of the amorphous structure of Li$_3$ClO was obtained using SQ method and cell of 500 atoms. Red, blue and green balls represent Cl, O and Li atoms respectively.

observed significant differences between the 250-atoms and 500-atoms cell. The equilibrium density of the glass was determined to be 1.63 g/cm$^3$ which is approximately 18% lower than the crystalline counterpart.

2.1. Computational details

The Vienna ab initio Simulation Package [26] (VASP) was used during the quenching. The Perdew-Burke-Ernzerhof (PBE) implementation of the exchange-correlation functional was used to generate the models of amorphous structures [25]. Due to the GGA’s well known failure to describe the band gap correctly, we also performed GW0 and HSE calculations. The eigenstates of the electron wave functions were expanded on a plane-waves basis set using pseudopotentials to describe the electron-ion interactions within the projector augmented waves approach (PAW) [12].

The convergence criterion for the electronic self-consistent cycle was fixed at 10$^{-7}$ eV per cell and for the relaxation of the forces on all ions, it was 10$^{-5}$ eV/Å. Calculations were performed at the Γ k-point with a cutoff energy of 350 eV. Calculations of antiperovskite structure were performed utilizing a k-point mesh of $12 \times 12 \times 12$, except when density of states (DOS) was calculated, in which case a $22 \times 22 \times 22$ was used. Structural optimizations were performed by using a standard conjugate gradient method during the stochastic quenching procedure.

3. Results and Discussion

3.1. Amorphous structure

Fig. 2 shows selected radial distribution functions (RDFs) for crystalline and amorphous Li$_3$ClO. In all cases, the first peak of the RDFs of the amorphous structure are shifted towards lower values than those of the crystalline structure. These is clearly reflected in the bond distances. Table 2 lists the bond distances for both crystalline and amorphous structures. In all cases this distance is shorter in the glass. In particular, the main peak of $g_{O-O}$ moves from 3.9 Å in the crystalline structure to 3.1 Å in the glass and a small peak develops at 1.5 Å. This small peak has been associated to oxygen molecules impurities and have been observed before in other amorphous materials such as amorphous alumina [10].

![Graph showing RDFs of crystal and amorphous structures of Li$_3$ClO.](image)

**Figure 2:** Radial distribution function of crystal and amorphous structure of Li$_3$ClO. (a) denote Li-Li, Cl-Li, Cl-Cl, and Cl-Li pairs and (b) O-O and Cl-O pairs.

Table 1

| Bond | Shortest Distance (Å) |
|------|----------------------|
|      | Crystalline | Amorphous |
| O-O  | 3.91       | 1.54      |
| O-Li | 1.96       | 1.79      |
| O-Cl | 3.39       | 3.25      |
| Li-Li| 2.76       | 2.18      |
| Li-Cl| 2.76       | 2.31      |
| Cl-Cl| 3.91       | 3.41      |

Coordination numbers are listed in Table 1. It is shown that most of pairs have smaller coordination number in amorphous state compared to crystalline one. For example, the coordination number of O-O pair is reduced from 6 into 4.4 by amorphization. However, O-Li coordination number increases from 6 to 10.25, which means O atom went to Li atom from O atom.

Fig. 3 displays the angular distribution function (ADFs) of crystal and amorphous state of Li$_3$ClO. It is shown that the O-O-Li angle which is originally located at 0° in the crystalline structure changes into 32° and the O-Li-Li angle
Table 2

| Bond   | Crystalline | Amorphous |
|--------|-------------|------------|
| O-O    | 6           | 4.4        |
| O-Li   | 6           | 10.25      |
| O-Cl   | 8           | 4.6        |
| Li-Li  | 14          | 10.57      |
| Li-Cl  | 4           | 2.95       |
| Cl-Cl  | 6           | 3.4        |

Figure 3: Selected angular distribution function of crystal and amorphous structure of Li$_3$ClO. Full- and dashed-lines represent amorphous and crystalline structure, respectively.

which is positioned at $0^\circ$, $45^\circ$, and $90^\circ$ changes into $32^\circ$ and $42^\circ$. Therefore, their angle becomes smaller into an acute angle. On the other hand, the O-Cl-Li angle which is located at $36^\circ$ in crystalline state becomes $31^\circ$, and thus its change is small compared to other angles presented in the figure.

3.2. Electronic structure

Fig. 4 shows the density of states (DOS) of crystalline and glassy Li$_3$ClO. From top to bottom the figure displays DOS for: anti-perovskite Li$_3$ClO as calculated by PBE, GW0 and HSE and glassy Li$_3$ClO PBE and HSE. The calculated band gap of crystalline Li$_3$ClO as obtained by PBE, GW0 and HSE is 4.84 eV, 6.9 eV and 6.48 eV, respectively. These results are in good agreement with other values found in the literature; 6.44 [13] and 5 eV [24]. The band gap of the amorphous system is in comparison relatively smaller, 3.55 eV for PBE and 5.03 for HSE. However we observe that the valence band shifts to higher energy levels.

4. Conclusions

We have investigated Li$_3$ClO in the amorphous and crystalline state by means of ab initio calculations. Models of the amorphous structure of Li$_3$ClO glass were generated by the stochastic quenching method. The amorphous structures were characterized by means of radial distributions functions and angle distribution functions. Coordination numbers and bond lengths were also obtained from the simulations. These materials are insulators in both the crystalline state and as a glass. The density of states was investigated using PBE, GW0 and the hybrid HSE functionals. As expected the band gap obtained by PBE is smaller than both GW0 and HSE results.

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