Microstructural evolution of solution-processed Li–Ge–Ga–S chalcogenide powders for Li$^+$ ion battery applications

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ARTICLE INFO

ABSTRACT

Sulfur-based chalcogenide Li–Ge–Ga–S powders for use in solid electrolyte of Li$^+$ ion batteries have been successfully synthesized via a low-temperature solution-based process. Their Li$^+$ ion conductivity turns out to be ~7 × 10^{-4} S/cm at room temperature which is quite comparable with that of melt-quenched or mechanically-alloyed analogues. It is revealed that their microstructure becomes amorphized appropriately at a specific Ga/Ge ratio where the ionic conductivity is maximized. A structural model is proposed, which emphasizes correlations between gallium and lithium inside the amorphous structures.

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1. Introduction

Some Li$^+$ conducting chalcogenide materials that are categorized as fast ion conductors (FICs) normally exhibit conductivity greater than 10^{-4} S/cm at room temperature, which is far superior to that of the conventional oxide-based counterparts [1–3]. This improved lithium ion conduction in such chalcogenide matrices is mainly attributed to much enhanced covalence of chemical bonds among constituent atoms [4]. To be more specific, decrease in the Coulombic interactions between the mobile positive ions and surrounding chalcogen atoms that tend to be charged less negatively in this case is known to contribute to such a significant increase of Li$^+$ ion conductivity. In addition, as for FICs based on amorphous chalcogenide, the dimensionality of their backbone structure would be controlled relatively easily via compositional adjustments, which results from characteristic features of amorphous chalcogenide materials, i.e., presence of homopolar bonds and thus formation of amorphous phases in a wide compositional range including far off-stoichiometric compositions [5]. This flexibility in controlling the backbone structure would facilitate providing larger free volume and so percolation channels to some desired chalcogenide matrices, which then results in such a superior Li$^+$ ion conduction. The enhanced ionic conductivity observed from thio-LISICON seems to be quite reasonable in this regard [6]. It is worth mentioning from the structural viewpoint of chalcogenide FICs that either amorphous or glass-ceramic phase is normally preferable to crystalline phase with exception of a few superionic crystalline compounds with quite complicated stoichiometric compositions in which constituent atoms are well arranged to render the fast ion transport feasible [7].

Among a few fast-ion-conducting sulfur-based chalcogenides, Li–Ge–S system is known to form a stable amorphous state but its Li$^+$ ion solubility is limited [8–10]. Effects of GeO$_2$ introduced to this Li–Ge–S material have been investigated in terms of structural stability and ionic conductivity [11,12]. It has been known that its lithium solubility as well as ionic conductivity is further increased through the addition of Ga [13–15]. Lithium conductivity of Li–Ge–Ga–S electrolyte typically exceeds 10^{-4} S/cm at room temperature, which seems to be good enough for practical applications. Here, it is noteworthy that melt quenching (MQ) or mechanical alloying (MA) technique has been almost exclusively applied so far in order to produce sulfide FICs [10–15], and in this case highly pure starting materials such as Li$_2$S and GeS$_2$ are used [8–10]. In this respect, besides these typical processing routes, a new viable processing technique is needed which can be more cost-effective and/or more energy-efficient. Based on this consideration, we have aimed to develop a low-temperature solution-based process for preparation of (amorphous) Li-containing Ge–Ga–S powders. Ionic conductivity of our solution-processed Li–Ge–Ga–S powders is described in connection with compositional variations, Ga/Ge ratio in particular, and other processing conditions. Their microstructural evolution is then explained mainly in terms of Ga/Ge ratio.

2. Experimental

In our solution-based process to synthesize Li–Ge–Ga–S powders, thioacetamide (TAA), $GeCl_4$ and $GaCl_3$, all of which were purer than 99.9%, were used as precursors of sulfur, germanium and gallium, respectively. According to our routine procedures, TAA was first dissolved into absolute ethanol in order to create a solution to which $GeCl_4$ and $GaCl_3$ were further introduced on a drop-by-drop basis. Lithium in the form of either Li_2S or LiCl was subsequently added. After introducing each precursor, the solution was subjected to stirring for 10 min, and thus prepared solution containing all the precursors was kept at 100 °C for 48 h for aging. All the processes were performed in a glove box filled with nitrogen in order to prevent oxygen contamination. The aged samples were thermally treated at 250 °C for 1 h inside a nitrogen-filled chamber in order to minimize volatile impurities. Note that processing parameters such as temperature, duration and mixing sequence were set to vary in an effort to optimize our solution-based synthesis route. However, it is worthwhile to mention that the processing conditions detailed above resulted in better ionic conductivities in most cases.

In order to prepare specimens for impedance measurements, the synthesized powders were pelletized into a disk, under a uniaxial pressure applied at room temperature, using a steel mold with inner diameter of 16 mm. To form electrodes, indium foils (or graphite powders in some cases) were placed at both sides of the disk, which were then pressed again [1]. All of the procedures were carried out inside a glove box to prevent oxygen contamination. Impedance measurements were performed using an impedance analyzer (SI-1260, Solatron) in the frequency range of 0.1 Hz–1 MHz. The ionic conductivity was calculated with the real part value of the impedance where an arc and a straight tail meet together as shown in Fig. 1.

3. Results and discussion

Shown in the inset of Fig. 1 is a representative Nyquist plot of impedance data obtained from our solution-processed Li–Ge–Ga–S powders. This complex impedance spectrum reveals the typical fingerprint of an ionic conductor, i.e., an arc in high frequencies followed by a spike in a low frequency region [16]. Taking a look at the Ga/Ge ratio dependence
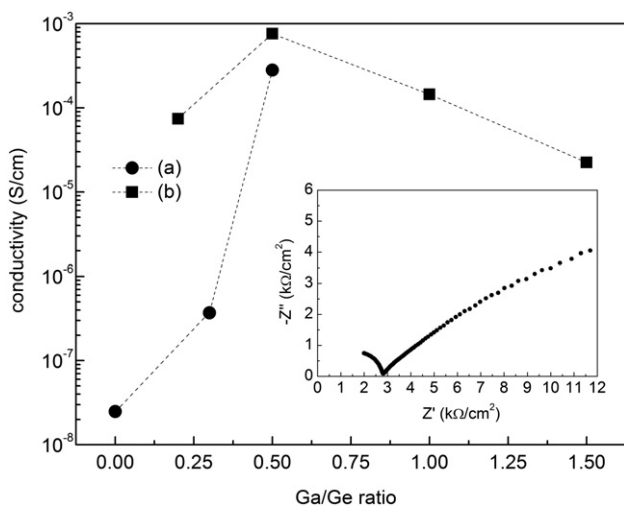

Fig. 1. Ionic conductivity of solution-processed Li–Ge–Ga–S powders plotted as a function of nominal Ga/Ge ratio. Duration for heat treatment at 250 °C was set to be (a) 10 min or (b) 60 min, but the other processing conditions were set to identical. Note that Li/(Ga + Ge) ratio was kept identical to be 3.3 for all of the samples. The inset displays a representative example of Nyquist plots of impedance data which in this case was obtained from a pelletized specimen with Ga/Ge ratio of 0.5 in the frequency range from 0.1 Hz to 10^6 Hz.
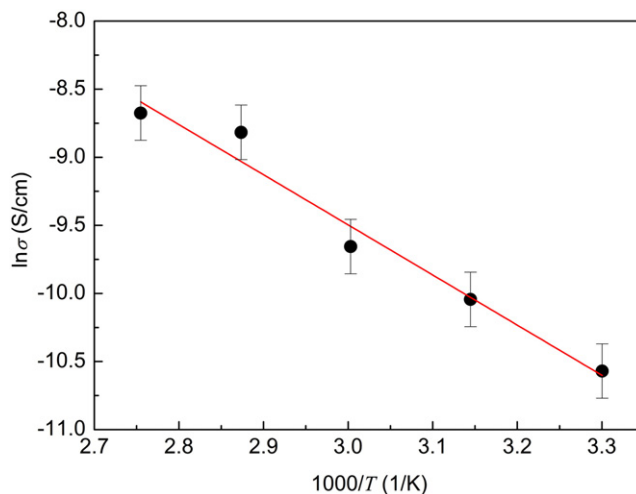

Fig. 2. Temperature-dependent conductivity of a solution-processed sample with Ga/Ge and Li/(Ga + Ge) ratios of 0.5 and 3.3, respectively. The straight line is obtained through a least-squares linear fit to the measured data.

of ionic conductivity shown in Fig. 1, one can see first that it increases remarkably upon the introduction of Ga. Taking into consideration two samples with different Ga/Ge ratios but identically processed, increase of conductivity tantamount to approximately one order of magnitude is achieved in powders with nominal Ga/Ge ratio of 0.3 compared with powders without Ga. Interestingly, the ionic conductivity is maximized at nominal Ga/Ge ratio of 0.5, which then starts to decrease for further increase of the relative amount of Ga. The ionic conductivity turns out to be dependent on processing conditions as well. For example, differing duration time of heat treatment results in variation of ionic conductivity, as is usually found from other solution-based processes [17]. Notably, in the case of heat treatment at 250 °C, duration of 1 h gives rise to such a significant enhancement of ionic conductivity as compared with duration of 10 min (see Fig. 1). Nevertheless, it is reasonably inferred that the amount of Ga relative to that of Ge in our solution-processed Li–Ge–Ga–S powders exerts a definite influence on their ionic conductivity.

The maximum room temperature conductivity we have obtained so far is ~7×10^{-4} S/cm, which was measured from the specimen with the Li/(Ga + Ge) ratio of 3.3 (see Fig. 1 again). This value is quite comparable with previously reported values; Li_2S–GeS_2–Ga_2S_3 glasses prepared via melt-quenching technique have been reported to exhibit ionic conductivity ranging from 10^{-6} to 10^{-4} S/cm [13–15]. In addition, this ionic conductivity was reported to be further improved up to ~10^{-3} S/cm with the addition of LiI [18]. In comparison with these previously reported conductivities, the ionic conductivity of the present Li–Ga–Ge–S powders is remarkable in that these materials are synthesized via a low-temperature solution process. On the other hand, conductivities measured at several different temperatures reveal an Arrhenius behavior as displayed in Fig. 2, and in this case the least-squares fit to a straight line that is corresponding to activation energy for the ionic conduction turns out to be 0.31 eV. We recognize that this activation energy belongs well to the typical range that the Li^+-conducting chalcogenide electrolytes exhibit [11,19].

Shown in Fig. 3 are X-ray diffraction (XRD) patterns of our solution-processed sulfide powders from which one can get information on their structural changes accompanied with varying nominal Ga/Ge ratio. When Ga is absent, i.e., Ge/Ga ratio of 1/0, the major crystalline phase identified in the XRD pattern is assigned as orthorhombic GeS_2. However, in the case of powders with nominal Ge/Ga ratio of 1/0.1, tetragonal GeS_2 phase appears to dominate. We thus rationalize from this observation that the presence of relatively small amount Ga stabilizes tetragonal GeS_2 phase rather than orthorhombic GeS_2. For further increase of Ga content, amorphization seems to take place in