

Solution-based fabrication of germanium sulphide doped with or without Li ions for solid electrolyte applications

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Ge-S and Li-Ge-S powders were synthesized via solution-based process in order to employ chalcogenide-based solid electrolyte for use in Li secondary batteries. GeCl₄ and thioacetamide in combination result in Ge-S powders of which major crystalline phase becomes GeS₂ where the tetragonal and orthorhombic phases coexist after heat treatment. A chemical treatment using NaOH brings about the reduction of chlorine in the powders obtained. However, the heat treatment at 300 °C is more effective in minimizing the chlorine content. When lithium chloride is used as the precursor of Li ions, the LiCl powders are agglomerated with an inhomogeneous distribution. When Li₂S is used, the Li-Ge-S powders are distributed more uniformly and the orthorhombic GeS₂ phase dominates in the powders.

Key words: Solid electrolyte, Li secondary battery, Chalcogenide, Germanium sulfide, Solution-based process.

Introduction

It has been experimentally demonstrated that sulfur-based chalcogenide is quite promising as a solid electrolyte for Li secondary batteries. The ionic conduction of Li⁺ ions can be conspicuously facilitated in a chalcogenide matrix mainly due to its enhanced covalence in the chemical bonds among constituent atoms compared to conventional oxide counterpart. Specifically, the decrease in the Coulombic interactions between the mobile positive ions and the surrounding chalcogen atoms that are likely to be charged less negatively in this case, is known to contribute to the significant increase in the conductivity of Li⁺ ions. On the other hand, the dimensionality of the backbone structure of a chalcogenide can be controlled relatively easily via compositional adjustment, which is attributed to the characteristic features of chalcogenide system, i.e., the presence of homopolar bonds between chalcogen atoms and Mott's 8-*N* rule [1]. This flexibility in controlling dimensionality would provide a larger free volume to some desired chalcogenide matrices, resulting in the superior ionic conduction. Therefore, the enhanced conductivity observed from thio-LISICON seems to be quite reasonable [2]. More recently, it was reported that a new stoichiometric composition in quaternary Li-Ge-P-S system, i.e., Li₁₀GeP₂S₁₂, exhibits a highly appreciable Li conductivity comparable to that of an organic liquid

[3], thus exemplifying the significance of the chemical bonds and structural dimensionality inherent in chalcogenide systems.

It is worthwhile to note that among a multitude of chalcogenide systems germanium and sulfur form very stable amorphous or crystalline structures, together with the case of arsenic and sulfur. Therefore, it would be anticipated that any practical chalcogenide solid electrolytes incorporate Ge and S as major constituent atoms. In fact, it was experimentally verified that amorphous structures can be formed out of Li₂S-GeS₂ [4, 5]. In addition, a metastable crystalline phase, Li₄GeS₄, can also be present [6]. Effects of GeO₂ introduced to this Li-Ge-S material have been investigated in terms of the structural stability and ionic conductivity [7-10]. Up to now, the melt-quenching or mechanical milling has been applied for fabrication of Li-containing chalcogenides, and in this case highly pure Li₂S and GeS₂ are used as starting materials. In this regard, besides the typical fabrication methods, it is quite important to explore a new fabrication route for Li-Ge-S that would be more cost-effective or energy-efficient. Based on these considerations, this work is aimed at fabricating germanium sulfide with or without Li ions via a solution process. Microstructures of the samples prepared are evaluated in connection with the precursors used or the amount of impurities such as chlorine in particular.

Experiments

For synthesis of thio-germanate powders via a solution process, 99.999% pure GeCl₄ (Alfa Aesar) and 99% pure thioacetamide (TAA, Alfa Aesar) were used

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as precursors of germanium and sulfur, respectively. TAA was firstly dissolved into absolute ethanol to make a solution, and then GeCl_4 was introduced on a drop-by-drop basis rather than just added all at once in order to secure a better reaction between the two solutes. The resulting solution was dried for 48 hours at 100°C . All the steps were carried out in a glove box filled with nitrogen to prevent any contamination.

In order to minimize impurities, in particular chlorine, two additional routes of chemical treatment and thermal treatment were employed. The chemical treatment with mixed solution of NaOH and butylamine induces a preferred chemical reaction between Na and Cl through which NaCl particles are precipitated [11-12]. Specifically, these chemicals were added into the germanium sulfide solution, which were subsequently filtered after the precipitation of NaCl particles. On the other hand, for the thermal treatment, the dried germanium sulfide powders were heat-treated for one hour at 300°C under nitrogen atmosphere.

In this work, LiCl (99.9998%, Sigma Aldrich) and Li_2S (99%, Sigma Aldrich) were used as a precursor of lithium. Upon the introduction of each Li precursor, the ratio of Li to Ge was changed to Ge : Li = 1 : 2. This solution was then subjected to the thermal treatment for purification. X-ray diffractometer (XRD, Ultima IV, Rigaku) was used for the identification of crystalline phases of the resulting powders. To observe their morphology and compositions, scanning electron microscope (SEM, JSM-6700F, JEOL) equipped with an energy dispersive X-ray spectrometer (EDS) was utilized.

Results and Discussion

The chemical interactions between TAA and GeCl_4 rendered the solution colored to yellowish immediately after adding the germanium precursor. For further increase of GeCl_4 , Ge-S particles began to precipitate

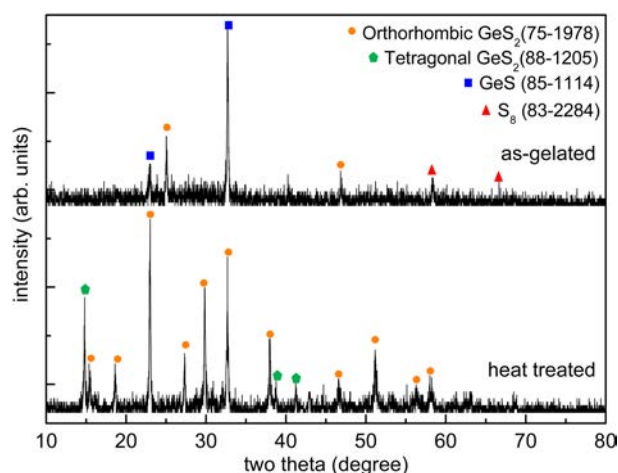


Fig. 1. X-ray diffraction patterns of as-gelated and heat treated germanium sulfide powders. Note that the numeral in each parenthesis corresponds to JCPDS Card No. for each crystalline phase identified.

inside the solution. Fig. 1 shows the X-ray diffraction patterns of as-gelated and heat-treated germanium sulfide powders. It is seen that the resulting powders after drying consist of various crystalline phases such as GeS and S_8 as well as GeS_2 . However, after the heat-treatment at 300°C , GeS_2 phase becomes to dominate without GeS or S_8 phases. It should be noted that the GeS_2 powders synthesized consist of either tetragonal or orthorhombic phases.

The chemical treatment was employed in order to reduce the chlorine residues in Ge-S powders. The addition of NaOH and butylamine in combination is expected to induce the formation of NaCl [11-12]. Upon the addition of NaOH, the solution was changed to milky in its color due to the desired chemical reaction, and then white particles started to be precipitated. Fig. 2 reveals that the separated and dried precipitates turned out to be NaCl as expected, thus effectively eliminating chlorine phases associated with the Ge-S powders. On the other hand, the dried filtrate was amorphous. As far as amount of chlorine is concerned, this chemical treatment was effective as shown in Table 1. However, it is seen that the heat-treatment is more effective in removing the chlorine-related impurities caused by the precursors. Based on these experimental results, only the thermal treatment was employed to Li-containing Ge-S powders for impurity reduction.

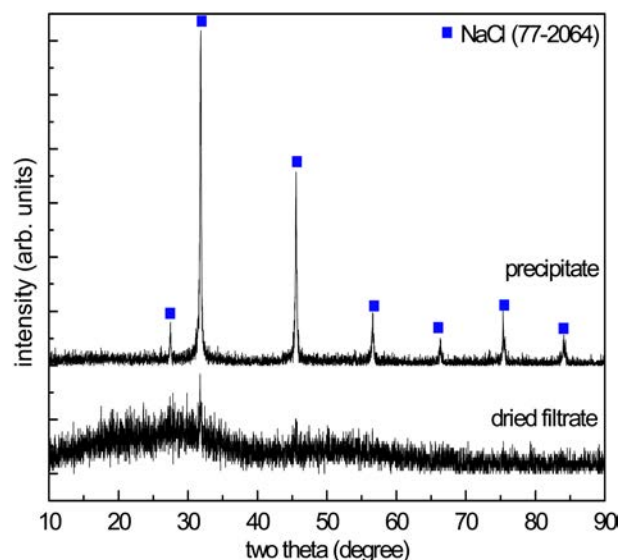


Fig. 2. X-ray diffraction patterns of the white precipitate and the dried filtrate separated after the chemical treatment.

Table 1. EDS analysis results of the germanium sulfide samples

element	relative amount (mol%)		
	as-gelated	chemically treated	thermally treated
Ge	14.5	25.7	28.6
S	27.6	58.1	63.8
Cl	57.9	16.2	7.6

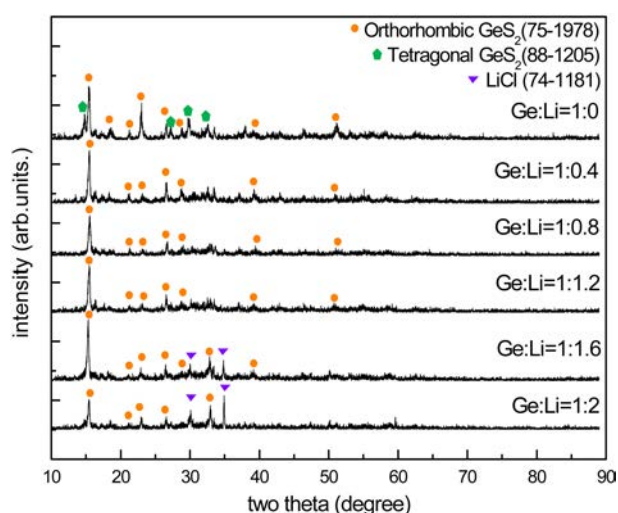


Fig. 3. X-ray diffraction patterns of Li containing Ge-S powders with varying Ge : Li ratio up to 1 : 2. Note that LiCl was used as precursor of Li for these powder samples to which an identical thermal treatment was applied.

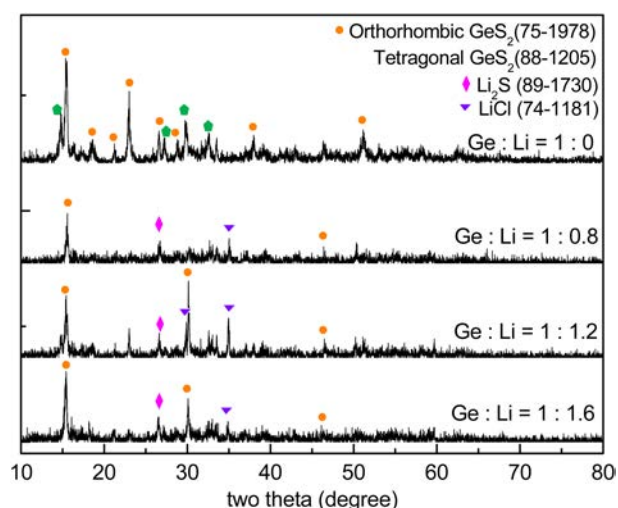


Fig. 4. X-ray diffraction patterns of Li containing Ge-S powders with varying Ge : Li ratio. Note that for these sample Li_2S was used as precursor, and all the powder samples were thermally treated under the same condition.

We attempted to incorporate Li to the Ge-S powders via our solution process. With increasing LiCl amount, the orthorhombic GeS_2 phase becomes dominant over the tetragonal phase and the results are demonstrated in Fig. 3. Any diffraction peaks corresponding to the crystalline Li_2S phase are not detected, but the peaks of LiCl start to appear from the Ge : Li ratio of 1 : 1.6. On the other hand, Fig. 4 shows that, as Li_2S was introduced as a precursor, the GeS_2 phase became orthorhombic without any clear peaks indicating its tetragonal structure. It is seen that Li_2S phase is evident together with LiCl phase. It is inferred that Li provided from the Li_2S precursor reacts with Cl from the germanium precursor, indicating that minimization of chlorine is needed before the addition of Li_2S . Here, it is worthwhile to mention that the GeS_2 phase is

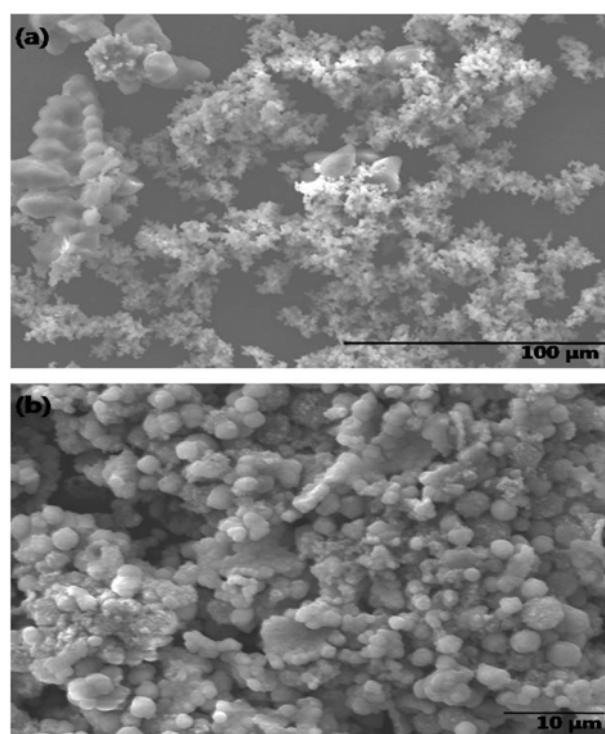


Fig. 5. SEM micrographs of the Li containing Ge-S powders, synthesized via the solution-based process and thermally treated at 300 °C, where the precursor used was (a) LiCl or (b) Li_2S .

transformed into more distorted orthorhombic structure regardless of the Li precursors used in this work. It could be assumed that Li ions are able to be incorporated into the interstitial sites available inside the GeS_2 lattice, and as a result its structure becomes more distorted.

SEM observation confirms that abundance of LiCl phase in the Li-Ge-S powders results in a distinct morphology. There are two conspicuously different types of particles mixed together when LiCl was used as a precursor (Fig. 5 (a)). The EDS analysis suggests that the relatively bigger and more irregular particles are close to the LiCl phase, whereas the smaller and more spherical particles are GeS_2 phase. It is known that solubility of LiCl against ethanol is low and therefore LiCl tends to be agglomerated to form such large particles rather than being dispersed [13]. In the mean time, when Li_2S is used, the resulting powders become finer and more spherical with negligible LiCl agglomeration (Fig. 5 (b)). It was already confirmed that Li-Ge-S films feature electrical conductivity due to Li^+ ions better than that of LIPON, even though the films are fabricated via a sputtering process and have Li_2S phase inside [6]. It is worthwhile to note that the present Li-Ge-S powders prepared via a solution-based process also contain Li_2S phase.

Conclusions

Ge-S and Li-Ge-S powders were synthesized via a

solution-based process for use them as solid electrolyte of Li secondary batteries. TAA and GeCl_4 are used to form Ge-S powders of which major crystalline phase becomes GeS_2 where the tetragonal and orthorhombic coexist after heat treatment. As for the reduction of chlorine, a chemical treatment based on NaOH addition turns out to be less effective than a simple thermal treatment carried out at 300 °C. When LiCl is used as the precursor of Li ions, LiCl phase agglomerates instead of being dispersed. Li_2S is thus a better starting material, and in this case the structure of GeS_2 in our Li-Ge-S powders becomes more distorted.

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