

## RAPID FABRICATION AND THERMAL PERFORMANCE OF Ag<sub>3</sub>SI SUPER-IONIC CONDUCTOR

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Compared to the reported method, relatively high pure silver sulfide iodide (Ag<sub>3</sub>SI) crystal, a kind of super-ionic conductor, was synthesized in a more facile procedure through the designed melt-cooling technique followed by a heat-treatment at 160°C for half an hour, which is confirmed by the corresponding X-ray Diffraction patterns. Utilizing the designed differential thermal analyzer method, we investigated the dynamic mechanism of forming process of Ag<sub>3</sub>SI crystal phase after experiencing the heat-treatment, which shows that relatively high pure Ag<sub>3</sub>SI crystals are easily deposited in the melt-cooled Ag<sub>3</sub>SI sample when heat-treatment.

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### 1. Introduction

Chalcogenide glasses have the excellent optical properties such as high refractive index and large optical transmission ranges extending in the mid-infrared region. The properties found in chalcogenide glasses make them very interesting for technological applications, such as optoelectronics and chemical sensors, which leading to a very broad prospects for development in thermal imager, information storage, national defense, military, biological engineering and medical fields<sup>[1-9]</sup>. Here we focus on the fabrication of a kind of fast ionic conductor, i.e. Ag<sub>3</sub>SI super-ionic conductor.

Super-ionic conductor materials are solid state systems that display ionic conductivities<sup>[10]</sup>. There exist many solid materials with high ionic conductivity, such as a class of lithium compounds, silver compounds etc. It's acknowledged that AgI is a prototype high ionic conductor material, it has three phases α-AgI, β-AgI and γ-AgI, and α-AgI-type has highest ionic conductivity<sup>[11-15]</sup>(10<sup>0</sup>S/cm). Another well-known class of silver compound super-ionic conductor is Ag<sub>3</sub>SI, Ag<sub>3</sub>SI is one of such materials and has been the subject of numerous studies<sup>[16-20]</sup>. It belongs to the Ag-base super-ionic conductors, it also has three phases α, β and γ. The high temperature α-phase has the same structure like α-AgI with a disordered distribution of both anions and cations in bcc lattice. The ionic conductivity of α-Ag<sub>3</sub>SI also can up to 10<sup>-1</sup>S/cm. Ag<sub>3</sub>SI has two phase structure transition. At 520K, the phase structure transition happens between β and α phase, the anions in α phase becomes disordered but still ordered in β phase. At the γ-β transition (T=157K), the phase lattice becomes different. The β phase structure is still bcc as α-AgI-type lattice with the a disordering of Ag ions and a ordering of S and I ions. But in the γ phase both anions and cations becomes ordered which is characterized by a rhombohedra distortion of the anion sublattice within space group R<sub>3</sub><sup>[21-24]</sup>.

For the preparation of the fast ionic conductor materials, there exist several traditional methods. Such as the solid phase sintering method, hydrothermal method, precipitation-calcination method, sol-gel method and so on. Among them, the solid phase sintering method is a common

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method, because the high temperature can provide the energy for solid phase reaction. It makes it easier to get the synthesized materials. The purity of the production depends on the temperature and the time of the reaction. For some materials, it's difficult to synthesize, so we need to improve the reaction temperature or prolong the reaction time.

$\text{Ag}_3\text{SI}$  was discovered in 1960s by Takahashi and Yamamoto, it's reported that  $\text{Ag}_3\text{SI}$  was a high ionic conductor, and the crystal of  $\text{Ag}_3\text{SI}$  was prepared by solid phase reaction methods. Putting an equal mole fractions of  $\text{AgI}$  and  $\text{Ag}_2\text{S}$  into a sealed evacuated glass tube heating at  $550^\circ\text{C}$  for 17h, but because of the  $\text{Ag}_2\text{S}$  decomposed into  $\text{Ag}$  and  $\text{S}$  in vacuum at  $550^\circ\text{C}$ , so we need to prevent the decomposition to control the sulphur vapour at about 1 atm<sup>[25]</sup>. Another synthesize method was reported by Sadao Hosahino, the power specimen of  $\text{Ag}_3\text{SI}$  was prepared by the solid state reaction of a stoichiometric mixture of  $\text{AgI}$  and  $\text{Ag}_2\text{S}$  at about  $550^\circ\text{C}$  for 5 days and was annealed at about  $220^\circ\text{C}$  for another two days. The process of annealing at about  $220^\circ\text{C}$  was necessary, because it's easy for  $\alpha$ - $\text{Ag}_3\text{SI}$  to quench to room temperature and produced the crystal of  $\alpha^*\text{-Ag}_3\text{SI}$ <sup>[26]</sup>. Without using melt-cooling methods there also has another way to prepare  $\text{Ag}_3\text{SI}$  crystal. Preparing 100 ml solutions of 1mol/L  $\text{Na}_2\text{S}$  and 1mol/L  $\text{KI}$  and pouring them together, after which 100 ml of 3mol/L  $\text{AgNO}_3$  was added, the precipitate formed was digested near the boiling point and then allowed to stand for 3h. After filtration it was dried at  $200^\circ\text{C}$  for 60h. The entire procedure was carried out in a darkened room to minimize any photo decomposition.

From those methods above, it can be seen that using the solid phase sintering method to prepare the sample should control the specific conditions or prolong the reaction time to complete the formation of the  $\text{Ag}_3\text{SI}$ . Finding some other ways to short the preparation time and obtain the high-pure  $\text{Ag}_3\text{SI}$  crystal is the point of this paper.

## 2. Experimental

### (1) Q0 sample preparation

The Q0 sample was obtained by a melt-cooling process, the reagent-grade  $\text{Ag}_2\text{S}$  (Aladdin) and  $\text{AgI}$  (Aladdin) crystalline powders were weighted in an equal molar. Then transferring them into a silica ampoule and sealed under the vacuum of  $10^{-4}$  Torr. After that, the silica ampoule was put into a rocking furnace melting at  $850^\circ\text{C}$  for 20h and annealing at  $300^\circ\text{C}$  for 10h during the melt-cooling process. When cooling to room temperature, removing the Q0 sample from the ampoule and reground it into the powder

### (2) Q0-heat treatment sample preparation

Putting the Q0 sample into a drying oven. Controlling the temperature at  $160^\circ\text{C}$ , and heat treat for 0.5h.

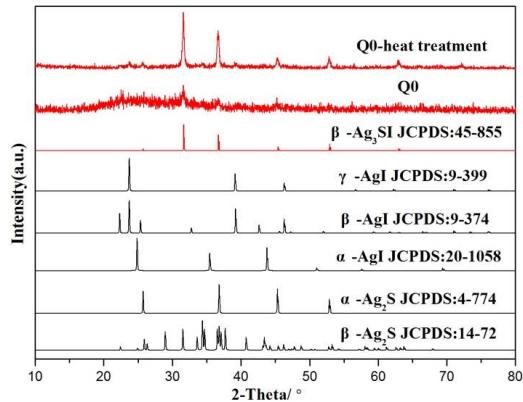
### (3) Characterization

Crystal phase analysis was conducted by the x-ray diffraction method (Rigaku, RU-200B) with  $\text{Cu K}_\alpha$  radiation. Three types of powder samples (the Q0 sample, the Q0-heat-treatment sample and the raw materials samples) were measured using the DSC to detect their crystallization behaviors. The samples were placed in a aluminum crucible at room temperature and kept for 5 min at  $40^\circ\text{C}$  then heated at 10 K/min to the maximum scanning temperature of  $270^\circ\text{C}$ , and cooling to room temperature at the same rate (10 K/min) to obtain the DSC curves of the samples.

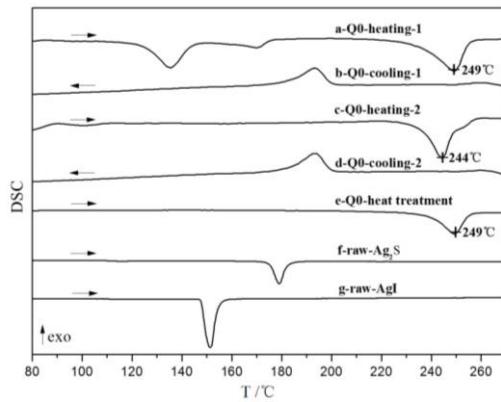
## 3. Results

As shown in Fig.1, according to the XRD pattern of the  $\text{Ag}_3\text{SI}$  sample (Q0) prepared by the traditional melt-cooling method, the peaks of the crystal  $\text{Ag}_3\text{SI}$  are not so obvious. In addition, some weak peaks ascribed to  $\text{AgI}$  crystal phase appears, which indicate that the melt-cooling sample contains a small fraction of  $\text{AgI}$  crystal. But, when subjected to heat treatment, the diffraction peaks of the  $\text{Ag}_3\text{SI}$  crystal phase show up more clearly in the XRD pattern. Furthermore, the diffraction peaks, which belong to  $\text{AgI}$  crystal phase, disappear completely.

Therefore, through this method, we can obtain highly pure  $\text{Ag}_3\text{SI}$  crystals.



*Fig.1 XRD patterns of the samples together with the crystal phases of  $\text{AgI}$ ,  $\text{Ag}_2\text{S}$  and  $\text{Ag}_3\text{SI}$ .  
 $Q_0$ : the sample prepared by melt-cooling method according to the batch  $\text{Ag}_3\text{SI}$ .  $Q_0$ -heat treatment: the sample heat treated at 160 °C for 0.5 hrs after obtaining  $Q_0$ .*



*Fig.2 DSC upscans and downscans of the sample ( $Q_0$ ) prepared by the melt-cooling method and the sample ( $Q_0$ -heat treatment) heat treated at 160 °C for 0.5 hrs after obtaining  $Q_0$  sample. All curves were recorded on subsequent heating or cooling at 10K/min. Curves a-d: firstly up-scanning the sample  $Q_0$  from 80-270°C followed by down-scanning from 270 - 80°C, then repeating it. Noted the variation of the effect of a dynamic heating process for  $Q_0$  sample. Curves e-g: up-scanning curves for the  $Q_0$ -heat treatment sample, the  $\text{Ag}_2\text{S}$  and  $\text{AgI}$  crystal phases which we used as raw materials in the preparation of the  $Q_0$  samples. For clarity, the curves are shifted in parallel.*

Fig. 2 shows DSC curves of the three types of powder samples (the  $Q_0$  sample, the  $Q_0$ -heat-treatment sample and the raw materials samples). Only three kind of endothermic peaks can be detected at around 137°C, 175°C and 250°C, they are ascribed to the phase change peaks of the crystal  $\text{AgI}$ ,  $\text{Ag}_2\text{S}$  and  $\text{Ag}_3\text{SI}$ , respectively. In the Fig.2 (a), there exists three endothermic peaks, but it only remains the transformation peak of the  $\text{Ag}_3\text{SI}$  crystal in the second up-scanning curve as Fig.2(c) shows. This is due to the possible scenario that the  $\text{AgI}$  and  $\text{Ag}_2\text{S}$  have reacted in the first dynamic heating process. Furthermore, the  $Q_0$ -heat-treatment sample also has one endothermic peak, which is similar to the curve Fig.2(c) shows. But we can clearly find that in these two curves the transformation temperature of  $\text{Ag}_3\text{SI}$  crystal is different. This implies that the dynamic heating process and heat treatment process have different influence on the obtained  $\text{Ag}_3\text{SI}$  crystal phase. In addition, compared with the curves f and g, both of the transformation peaks of

the AgI and Ag<sub>2</sub>S offset to the left in the curve a. It's closely related to the chemical condition around the AgI and Ag<sub>2</sub>S crystal phase.

#### **4. Discussion**

According to the traditional fabrication method of Ag<sub>3</sub>SI crystals reported in the references<sup>[25-26]</sup>, the preparation temperature was below the melting point of AgI and Ag<sub>2</sub>S. But in order to get the highly pure crystal, these methods need longer duration than 3 weeks. Considering the closed surroundings of the chemical reaction for AgI and Ag<sub>2</sub>S in a silica ampoule, we can enhance the reaction rate through increasing the temperature. Surely, when conducting the melt-cooling method, we find that the silica ampoule wall is very clean when melting at 850°C for 20hrs followed by annealing at 300°C for 10h during the melt-cooling process. Therefore, it is practicable to enhance the temperature to 850°C and this will shorten the reactive duration.

The XRD pattern in Fig.1 shows that the Q0 sample has some peaks for Ag<sub>3</sub>SI crystal phase, which is not so clear. Combining with the DSC curves, we find that there are several transformation peaks of Ag<sub>3</sub>SI, Ag<sub>2</sub>S and AgI phase change. Compared with the DSC curves between Q0 and Q0-heat-treatment sample, the extinction of the transformation peaks of AgI and Ag<sub>2</sub>S phase change further indicate that the residual AgI and Ag<sub>2</sub>S react and the new phase Ag<sub>3</sub>SI will form after the heat treatment procedure. The second up-scanning curve of the Q0 sample is similar with that of the Q0-heat treatment sample, which means that both the dynamic heating process and the heat treatment process can obtain relative pure Ag<sub>3</sub>SI crystal phase. But the transformation temperature of the Ag<sub>3</sub>SI phase change for the sample obtained by the dynamic heating process is lower than the transformation temperature of Ag<sub>3</sub>SI phase change for the sample obtained by the above-mentioned heat treatment process. It might because of the change of the crystal structure; more experiments should be done in the next step.

Compared to that of AgI and Ag<sub>2</sub>S crystal, the transformation peak of AgI and Ag<sub>2</sub>S crystal phase in the sample obtained by the melt-cooling has a small offset toward the lower temperature and a broadened width of half-height. In our opinion, this phenomenon can be explained as follows. Among the samples obtained by the melt-cooling method, there should contain many nanoparticles. On the one hand, the larger nanoparticles can be divided roughly into two parts, i.e., the surface and an inner core parts. The surface region is affected strongly by the generation of defects, whereas the core part behaves more like bulk AgI or Ag<sub>2</sub>S crystal. Therefore, the phase transition was initiated at the inner part and then shifts gradually to the surface part, resulting in the observed broad DSC peaks. On the other hand, some smaller nano-size AgI and Ag<sub>2</sub>S, the whole part of the nanoparticle is subject to the interfacial effects, leading to a sudden transition at the lower temperature. So the transition peak of AgI and Ag<sub>2</sub>S in fig.2(a) shows a broad peak and an offset toward the lower temperature compared with the normal AgI and Ag<sub>2</sub>S crystals as corroborated by the references<sup>[27-28]</sup>.

#### **5. Conclusions**

In summary, using melt-cooling method followed by a heat-treatment, we really can fabricate the highly pure Ag<sub>3</sub>SI crystals, which can shorten the fabricating period compared to the reported method. Using the designed differential thermal analyzer method, we analyze the dynamic mechanism of forming process of Ag<sub>3</sub>SI crystal phase. It indicates that the Q0 sample and Q0-heat-treatment sample both have the transformation peaks of the Ag<sub>3</sub>SI (at 249°C), which is also confirmed by the X-ray Diffraction patterns.

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