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MR. XINYU HUANG (Orcid ID : 0000-0001-7112-8106)

DR QING JIAO (Orcid ID : 0000-0003-1482-6981)

DR CHANGGUI LIN (Orcid ID : 0000-0002-0574-6296)

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## Effect of heat treatment on AgI-rich chalcogenide glasses with enhanced ionic conductivity

Corresponding author mail id :- 1175032149@qq.com

Xinyu Huang<sup>1</sup> | Qing Jiao<sup>1\*</sup> | Changgui Lin<sup>1</sup> | Yeting Zhang<sup>1</sup> | Zhen Yang<sup>1</sup> | Tiefeng Xu<sup>1</sup> | Xianghua Zhang<sup>2</sup> | Hongli Ma<sup>2</sup> | Xueyun Liu<sup>1</sup> | Shixun Dai<sup>1</sup>

<sup>1</sup>Key Laboratory of Photoelectric Detection Materials and Devices of Zhejiang Province, Ningbo University, 315211, Ningbo, China

<sup>2</sup>Laboratory of Glasses and Ceramics, Institute of Chemical Science UMR CNRS 6226, University of Rennes 1, 35042, Rennes, France

### Abstract

The glass ceramics of AgI-based electroconductive chalcogenide system was realized by using an appropriate heat treatment at a fairly high temperature ( $T_g + 40$  °C) and different times ranging from 4 h to 20 h. The crystallization behavior and electroconductive properties of the heat-treated samples were studied in detail. Transmission study was performed, and the results show that the cut-off edge of the short wavelength is red-shifted at prolonged

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annealing time but remains an excellent transmittance in the mid-infrared (IR) region. XRD and SEM results indicated that the precipitated crystalline phases are mainly  $\beta$ -/ $\gamma$ -AgI. Moreover, a small amount of  $\alpha$ -AgI, which is rarely existed at room temperature, is precipitated in the AgI-rich chalcogenide glass-ceramics. The ionic conductivity of all glass-ceramics was enhanced by heat treatment in contrast to that of base glass. Raman analysis exhibited the structure variation of the glass sample after heat treatments. This study provided an observation of crystallization in chalcogenide glass containing large amounts of AgI and be of good guidance to fabricate novel AgI-based chalcogenide glass-ceramics that can be candidates in infrared optics and solid electrolyte applications.

## 1 | INTRODUCTION

Alkali-doped chalcogenide glasses have attracted much attention because of their good glass-forming ability, low phonon energy, extended infrared transparency,<sup>1,2</sup> and because of their potential applications in optical fibers, chemical sensors, and solid-state electrolytes<sup>3-5</sup>.

However, their application scope is often limited owing to their weak mechanical properties and poor thermal stability. Crystallization process on glasses after heat treatment is one of the approaches enhancing their stability for satisfying applications. This approach improves the thermo-mechanical properties, particularly thermal expansion, thermal shock sensitivity, and resistance to crack propagation of chalcogenide glasses<sup>6</sup>. Notably, microcrystals of AgI contained chalcogenide glass-ceramic have become a focus research because of their potential application in solid-state batteries<sup>7-9</sup>, in which  $\text{Ag}^+$  ions exhibit high ionic conductivity exceeding  $10^{-3}$  S/cm at room temperature. Superionic conductor  $\alpha$ -AgI has a

high ionic conductivity of 1 S/cm when it is thermodynamically stable above 147 °C. Phase transformation from  $\alpha$ -AgI to a low-temperature phase,  $\beta$ -/ $\gamma$ -AgI, usually occurs at 147 °C, which is still difficult to inhibit this transformation and stabilizing the superionic conductor  $\alpha$ -AgI in glasses and ceramics. High-temperature phase  $\alpha$ -AgI can be stabilized at room temperature, although only in oxide glasses<sup>10</sup>. For example, Tatsumisago successfully stabilized  $\alpha$ -AgI in AgI–Ag<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> glass-ceramic at room temperature through a twin-roller rapid quenching technique<sup>11,12</sup>. Meanwhile, conductivity of AgI-based phosphate glasses can be enhanced after appropriate crystallization process<sup>13</sup>. Compared with glassy oxides, chalcogenide glassy electrolytes are particularly promising for the high ionic conductivity and superior ductility allowing for room temperature processing, which makes them more suitable for use in all-solid-state batteries<sup>14</sup>. Therefore, exploring novel chalcogenide glass solid electrolytes with optimum combination of high room-temperature conductivity ( $10^{-4}$  S/cm) and chemical stability has become a focus of substantial research.

Ga-Sb-S glass is a recent novel Ge-free system that has a broader transmission range and lower cost than Ge-based chalcogenide glasses. In our previous work<sup>15</sup>, we successfully introduced a large amount of AgI in a Ga-Sb-S glass matrix, which subsequently exhibited good glass-forming ability, transparency, and heat stability. To fabricate chalcogenide glass-ceramics used in solid batteries, we investigated glass composition of 40(0.8Sb<sub>2</sub>S<sub>3</sub>-0.2Ga<sub>2</sub>S<sub>3</sub>)-60AgI containing large amounts of AgI. The effect of heat treatment on crystallization behavior is important to the electroconductive properties of the chalcogenide glasses, especially to AgI phase transformation associated with high conductivity. Therefore, elaborating the crystalline mechanism and phase transformation of

AgI-based chalcogenide glasses for opt-electric applications is necessary, especially for the establishment of high-conductivity AgI phase containing chalcogenide solid electrolyte materials.

## 2 | EXPERIMENTAL PROCEDURES

Bulk glass (20 g) with a composition of 40(0.8Sb<sub>2</sub>S<sub>3</sub>–0.2Ga<sub>2</sub>S<sub>3</sub>)–60AgI was prepared by the conventional melt-quenching technique. The weighed highly pure gallium (6N), antimony (5N), sulfur (5N), and silver iodide (4N) were weighted and placed into separate cleaned quartz glass ampoules, which were then sealed under a vacuum of 10<sup>-3</sup> Pa. A sealed ampoule with an inner diameter of 10 mm was placed in a rocking furnace. The raw materials were heated from 25 °C to 850 °C at a 2 °C/min heating rate, maintained at this temperature for 12

h in the rocking furnace, further equilibrated at 700 °C, and finally quenched in cold water.

To remove the inner constraints during rapid quenching, we swiftly transferred the alloys to a preheated furnace and annealed them at  $T_g$  of –30 °C for 5 h. The bulk glasses were obtained

by removing them from the ampoules, and the glass rods were finally cut and polished into disks of 10 mm in diameter and 2 mm in thickness. Glass-ceramics were obtained in the same

annealing furnace after heat treatments at a fixed temperature of 40 °C above  $T_g$  for different durations (4h, 8h, 12h and 20h) in air condition. Glass characteristic temperatures, including

glass transition temperature ( $T_g$ ) and onset temperature of crystallization ( $T_x$ ), were identified

by heating 10 mg of the samples in a hermetic aluminum pan at a 10 °C/min rate under N<sub>2</sub> atmosphere in a differential scanning calorimeter (TA Instruments Q2000, New Castle, DE).

Then, we heat-treated the obtained disks at 2°C/min to a designed temperature and held for different durations to obtain glass ceramics.

Optical transmission spectra ranging from 0.25  $\mu\text{m}$  to 16  $\mu\text{m}$  were recorded by using a PerkinElmer Lambda 950 spectrophotometer and a Nicolet 380 FT-IR spectrometer. Elemental analysis and crystalline morphology in the glass-ceramic was observed with a scanning electron microscope (Hitachi S-4800, Japan) with an accelerating voltage of 15 kV. Observation was performed on freshly glass surface. The crystalline phase precipitated in heat treatment samples were identified by using X-Ray diffraction (XRD) and compared with JCPDF cards. Room temperature XRD was performed with a Bruker D2 diffractometer (Bruker D2 Phaser,  $\lambda = 0.15406$  nm, 30 kV, 10 mA,  $\text{CuK}\alpha$ ) in a reflection mode at room temperature in a  $2\theta$  range of  $10^\circ$ – $70^\circ$ . Raman spectra were obtained at room temperature by using the back-scattering configuration of a laser confocal Raman spectrometer (type: Renishaw inVia, Gloucestershire, UK) with an excitation wavelength at 785 nm. The resolution of the Raman spectrum was  $1\text{ cm}^{-1}$ . For electrical measurements, gold electrodes with a diameter of 8 mm were sputtered on the parallel surfaces of the as-prepared samples. Using a frequency response analyzer (CHI 660e), we measured electrical conductivity through a complex impedance technique over a wide range of frequencies from 1 Hz to 1 MHz. Ac impedance was measured at room temperature and all performed measurements were found to be well reproducible. In addition, several precautions to prepare the uniform and homogenous samples during preparation were taken like that all glass samples were stuck in the same mold polished to keep the same in thickness and smoothness

### 3 | RESULTS AND DISCUSSION

DSC trace of the as-quenched precursor glass with the labeled characteristic temperatures ( $T_g$ ,  $T_{x1}$ ,  $T_{x2}$ ) is presented in Figure 1. The  $\Delta T$  ( $\Delta T = T_{x1} - T_g$ ) value, which indicates the devitrification tendency of a glass when heated above  $T_g$ , is determined to be 155 °C. The  $\Delta T$  value of ~142 °C means the mechanical and thermal stability of the samples during heating.

The small exothermic peak locating at 297 °C is originated from the crystallization in the glass matrix. According to previous research<sup>6,16,17</sup>, a suitable heat treatment temperature usually ranges from 10 °C to 30 °C above  $T_g$ . In this work, considering the high  $\Delta T$ , we selected a high  $T_{HT}$  ( $T_g + 40$  °C) to render the crystallization process controllable. We placed the base glasses in a ventilated furnace at 195 °C from 4 h to 20 h to obtain crystallized samples. The Vis-NIR transmission spectra of the glass samples are presented in Figure 2.

The absorption bands at 2.9  $\mu\text{m}$ , 4.1  $\mu\text{m}$ , 6.3  $\mu\text{m}$ , and 9.6  $\mu\text{m}$  can be attributed to –OH, –SH, H<sub>2</sub>O, and Sb–O, respectively. These IR impurity absorption peaks are due to the hygroscopic property of AgI. The optical transmission of glass-ceramics usually decrease as the size of precipitated crystals become close to the incident wavelength owing to the increase of scattering loss in the UV-NIR light region<sup>18</sup>. Thus, heat treatment must be performed in such manner that the crystals precipitated from the glass matrix are small enough for good optical transmittance in the required IR region. As shown in Figure 2a, the Vis-NIR transmittance of the samples is extremely sensitive to the precipitation of crystals. The sample heat-treated for 4, 8, and 12 h showed decline in transmission from 650 nm to 2500 nm but had good transparency levels in the mid-IR region. The cut-off edge of short wavelength red-shifted at prolonged heat-treatment time (4 h to 20 h), indicating the nucleation and growth of the

crystals in the glassy matrix. Moreover, a large drop in maximum transmittance was observed when the heat-treatment duration was prolonged to 20 h. The possible reason is the growth and agglomeration of the precipitated crystallites. The agglomeration of the precipitated crystals is shown in the scanning electron microscopy (SEM) micrographs.

To evaluate the size and distribution of the crystalline particles, we performed SEM analysis on the fresh surface of the base glass and glass-ceramic specimens crystallized at 195 °C at various time. Figure 3(a) shows the initial stage of the base glass, while Figure 3(b) and 3(c) show the well-defined growing crystals. The grains of specimens crystallized at 195 °C for 4 h were small (~200 nm). As shown in the distribution of the precipitated crystallites in the image, the grains and grain boundaries became distinct. After the heat treatment time increased to 8 h, the sizes of most of the crystallized grains increased to 500 nm, as shown in Figure 3(c). As the crystallization time reached 20 h, a wide distribution of grain shape and size (2 μm) was observed (Figure 3(d)). An increase in grain size at crystallization time of 4–20 h was more evident, and grain size distribution remained fairly uniform, although some irregular and large grains were noted in the micrograph (Figure 3(d)). At prolonged heat treatment time, the size of the crystals increased further, and the Mie diffusion shifted the cut-off edge to the short wavelength. This shift was in good agreement with Vis-IR spectra. Notably, it should be clear that the crystalline is located on the bulk surface about 10 μm according to our further cross-section SEM measurement. As can be seen the EDS results in Table 1, the weight percentage of Ag increased from 18.87% to 27 %, while the base glass and I atomic weight percentage increased from 21.19% to 28.45% in the marked region. Meanwhile, Ga, Sb, and S contents decreased, suggesting that the precipitated

crystalline phase is assigned to the AgI phase. Although O was found in the base glass and glass-ceramic, however, the oxides ratio is rarely small and the influence of oxides in this research will be neglected in the ionic conductivity study.

As depicted in Figure 4, the XRD patterns of the samples heat-treated for different durations were collected by detecting the base glass and glass-ceramics. First, the XRD of the base glass exhibited a broad hump without any detectable sharp peak in the same manner as amorphous materials. When the heat treatment time was increased from 4 h to 20 h, three different crystal phases were precipitated in these samples. Several peaks appeared at the following locations: 22.4°, 23.8°, 24.7°, 39.2°, and 46.3°, which agree well with that of standard  $\alpha$ -AgI (JCPDF card of no. 70-1022),  $\beta$ -AgI ((JCPDF card of no. 78-1655) and  $\gamma$ -AgI (JCPDF card of no. 9-399). The precipitated crystals were mainly  $\gamma$ -AgI and  $\beta$ -AgI phases, and a small amount of  $\alpha$ -AgI phase was observed in the AgI-riched chalcogenide glass-ceramics. As the heat treatment time increased to 20 h, the diffraction peak became significant, and the amplitude of the peak assigned to  $\alpha$ -AgI increased, suggesting increase in the size and magnitude of the crystallites. The results indicated that the number of  $\alpha$ -AgI nuclei was saturated in the glass matrix during the quenching process and most of the precipitation crystals were still the low temperature phase of AgI. For the high conductive chalcogenide glass and ceramics, large superior conductors of  $\alpha$ -AgI phase is a pursuit in research hoping effective solid electronic materials.

We detected the Raman spectra of the samples with laser confocal Raman spectrometer to trace the structural evolution of crystallization. As shown in Figure 5, the Raman spectra were dominated by the bands between 50 and 400  $\text{cm}^{-1}$ , which are composed of several overlapped

bands. The Raman bands and their corresponding assignments for base glass and glass-ceramic are summarized in Table 2. Two main changes were observed when heat treatment time was increased. The first was the increased amplitude of  $107\text{ cm}^{-1}$  and decreased amplitude of the shoulder peak at  $138\text{ cm}^{-1}$ . According to many research<sup>7,19,22</sup>, the shoulder peak around  $107\text{ cm}^{-1}$  is corresponding to [SbSI] and  $\beta$ -AgI, and that at  $138\text{ cm}^{-1}$  corresponds to [SbI<sub>3</sub>] unit. The crystallization of AgI decreased I<sup>-</sup> concentration in the glass matrix and converted the [SbI<sub>3</sub>] structural units to [SbSI]. The second change was that the Raman band around  $275\text{ cm}^{-1}$  shifted to  $265\text{ cm}^{-1}$ . Considering the previous studies on chalcogenide glass containing AgI and the vibration theory<sup>15</sup>, we surmised that the peak at  $275\text{ cm}^{-1}$  is caused by the formation of the [SbS<sub>3-x</sub>I<sub>x</sub>] mixed structure<sup>23</sup>. Owing to the precipitation of AgI, [SbS<sub>3-x</sub>I<sub>x</sub>] and [GaS<sub>4-x</sub>I<sub>x</sub>] units decreased in amount and decomposed to the [SbSI], [SbS<sub>3</sub>], and [GaS<sub>3</sub>-S<sub>3</sub>Ga] units to compensate the loss of I<sup>-</sup> in the network structure. With referenced to the Raman vibrations of SbSI and SbI<sub>3</sub> crystals, the transformation of [SbI<sub>3</sub>] structural units to [SbSI] with increased heating time further implied the precipitation of AgI microcrystals.

The Nyquist plots of impedance obtained at  $25\text{ }^{\circ}\text{C}$  for the glass-ceramics crystallized at  $195\text{ }^{\circ}\text{C}$  for different durations are shown in Figure 6. In the spectra,  $Z_{re}'$  and  $-Z_{im}''$  are the real and imaginary components of the impedance  $Z(\omega)$ , respectively. The sample resistance was determined from the best fit of the semicircular arcs by using an equivalent model consisting of two parallel RQ circuits (where R is a resistance and Q is a constant phase element) in series<sup>24</sup>. The intercept point of linear tail in low frequency range with real axis nearly corresponds to the total (bulk and grain-boundary) resistance  $Z_0$ . All the glass-ceramics

had much lower  $Z_0$  than the base glass. The ionic conductivity ( $\sigma$ ) calculated from total resistance was  $1.49 \times 10^{-4}$  S/cm for the base glass. The  $\text{Ag}^+$  ionic conductivity of glass-ceramics increased at the initial crystallization time from 4 h ( $4.68 \times 10^{-4}$  S/cm) to 8 h ( $4.91 \times 10^{-4}$  S/cm), reached a maximum at 12 h heat treatment ( $5.68 \times 10^{-4}$  S/cm), and decreased after 20 h heat treatment ( $4.97 \times 10^{-4}$  S/cm). According to the research of Ong SP<sup>25</sup>, oxygen-substituted compound has much lower ionic conductivity than sulfides compound, because the much smaller anion radius and polarizability of the oxide anion compared to the sulfide anion leading to the lower diffusivity (two orders of magnitude). Thus, combined with the above results, the increased oxygen content of glass-ceramic in this research is not the key for the higher conductivity of glass-ceramics. The relationship between the ionic conductivity of the sample and heat-treatment time can be explained as follows: First, the grain boundary resistance may be reduced by heat treatment because grain boundary resistance is inversely proportional to ionic conductivity<sup>26</sup>. Second, increase in the amount of precipitated AgI crystals, especially the superionic conductor  $\alpha$ -AgI phase, partly improves ionic conductivity at prolonged heat treatment time. In fact, the formed structure of SbSI units in a network can present a ribbon framework and forms an effective ionic transport channel for  $\text{Ag}^+$  ions benefiting for the raise of the ionic conductivity<sup>7</sup>. Similar structure units were constructed in the present work, as indicated by the Raman results, for the transport of the  $\text{Ag}^+$  ions. At 20 h heat treatment, the resultant ionic conductivity decreased as calculated. According to the XRD and Raman results,  $\alpha$ -AgI phase was partially crystallized, and the precipitates were mainly  $\beta$ -AgI and  $\gamma$ -AgI crystalline phases. The poorly conducting crystalline<sup>27,28</sup> ( $\beta$ -AgI and  $\gamma$ -AgI) grew and increased continuously, leading to a large crystallinity degree, as shown in

Figure 3(d). Consequently, the precipitated AgI crystalline decreased the amounts of  $\text{Ag}^+$  transported across the SbSI channel. The drop in  $\text{Ag}^+$  ionic conductivity was caused by disrupted movement of  $\text{Ag}^+$  ions when  $\beta/\gamma$ -AgI crystals increased. These results showed the crucial role of controlled microcrystal growth to the transport of conductive ions. The growing of superionic conductor and large amounts of stable  $\alpha$ -AgI in chalcogenide glass is still a continuous hard work for a higher ionic conductivity, leading to the practical value of amorphous solid electrolytes applications.

#### 4 | CONCLUSIONS

A series of AgI-rich  $40(0.8\text{Sb}_2\text{S}_3-0.2\text{Ga}_2\text{S}_3)-60\text{AgI}$  electroconductive chalcogenide glass and glass-ceramics were prepared and investigated. The obtained glass-ceramics were highly transparent in the mid-IR region (2–14  $\mu\text{m}$ ). The XRD results indicated that the precipitated crystalline phase was mainly  $\beta/\gamma$ -AgI, and a small amount of  $\alpha$ -AgI was detected in AgI-rich chalcogenide glass-ceramics at room temperature. After the precipitation of AgI, the  $[\text{SbI}_3]$  units decomposed and the  $[\text{SbSI}]$   $[\text{SbS}_3]$ , and  $[\text{GaS}_3-\text{S}_3\text{Ga}]$  units formed to compensate the loss of  $\Gamma$ . The progressive modification of the glass network enhanced the ionic conductivity of the glass-ceramics. The novel AgI-based chalcogenide glass-ceramics is potential for infrared optics and solid electrolyte applications.

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### Figure Captions

**Figure 1.** DSC curve for bulk glass of  $40(0.8\text{Sb}_2\text{S}_3-0.2\text{Ga}_2\text{S}_3)-60\text{AgI}$  at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$

**Figure 2.** Transmission curves of (a) Vis-NIR and (b) IR spectra for base glass and the corresponding samples crystallized at  $195\text{ }^\circ\text{C}$  for 4, 8, 12 and 20 h. The inset of (a) shows the photographs of base glass and glass-ceramic under digital microscope ( $\lambda = 980\text{nm}$ )

**Figure 3.** SEM micrographs of specimens crystallized at  $195\text{ }^\circ\text{C}$  for (a) 0 h, (b) 4 h, (c) 8 h, and (d) 20 h.

**Figure 4.** XRD patterns of  $40(0.8\text{Sb}_2\text{S}_3-0.2\text{Ga}_2\text{S}_3)-60\text{AgI}$  base glass and glasses heat-treated at  $195\text{ }^\circ\text{C}$  for 4, 8, 12, and 20 h. The JCPDF cards 70-1022 ( $\alpha$ -AgI), 78-1655 ( $\beta$ -AgI), and 9-399 ( $\gamma$ -AgI) are also presented.

**Figure 5.** Raman spectra of  $40(0.8\text{Sb}_2\text{S}_3-0.2\text{Ga}_2\text{S}_3)-60\text{AgI}$  base glass and glasses heat-treated at 195 °C for 4 h, 8 h, 12 h, and 20 h, respectively, including reference of the SbSI and SbI<sub>3</sub> crystals.

**Figure 6.** AC impedance of  $40(0.8\text{Sb}_2\text{S}_3-0.2\text{Ga}_2\text{S}_3)-60\text{AgI}$  base glass and glasses heat-treated at 195 °C for 4 h, 8 h, 12 h and 20 h, respectively.

### Table

**Table 1.** Atomic weight percentage of base glass and the precipitated crystalline phase at 195 °C for 20 h.

Element	Atom/% (Base)	Atom/% (20 h)
Ga	5.24	4.52
Sb	31.38	22.18
S	23.00	13.86
Ag	18.87	27.00
I	21.19	28.45
O	0.32	3.99

**Table 2.** Assignments of Raman shift ( $\text{cm}^{-1}$ ) of the  $40(0.8\text{Sb}_2\text{S}_3-0.2\text{Ga}_2\text{S}_3)-60\text{AgI}$  glass-ceramics.

Raman shift ( $\text{cm}^{-1}$ )	Assignments	Refs.
107	[SbSI]	7,19
138	[SbI <sub>3</sub> ]	7
265	[GaS <sub>3</sub> -S <sub>3</sub> Ga]	20
290, 314	[SbS <sub>3</sub> ]	20,21











