



**HAL**  
open science

## Formation and properties of chalcogenide glasses based on GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-AgI system

Zhuobin Li, Changgui Lin, Guoshun Qu, Laurent Calvez, Shixun Dai, Xianghua Zhang, Tiefeng Xu, Qiuhua Nie

► **To cite this version:**

Zhuobin Li, Changgui Lin, Guoshun Qu, Laurent Calvez, Shixun Dai, et al.. Formation and properties of chalcogenide glasses based on GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-AgI system. *Materials Letters*, 2014, 132, pp.203-205. 10.1016/j.matlet.2014.06.083 . hal-01058370

**HAL Id: hal-01058370**

**<https://hal.science/hal-01058370>**

Submitted on 8 Oct 2014

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Formation and properties of chalcogenide glasses based on GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-AgI system**

Zhuobin Li<sup>a,b</sup>, Changgui Lin<sup>a,\*</sup>, Guoshun Qu<sup>a</sup>, Laurent Calvez<sup>c</sup>, Shixun Dai<sup>a</sup>, Xianghua Zhang<sup>c</sup>, Tiefeng Xu<sup>a</sup>, Qihua Nie<sup>a,b</sup>

<sup>a</sup> *Laboratory of Infrared Material and Devices, Advanced Technology Research Institute, Ningbo University, Ningbo 315211, China*

<sup>b</sup> *Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China*

<sup>c</sup> *Laboratoire des Verres et Céramiques, UMR-CNRS 6512, Campus de Beaulieu, Université de Rennes 1, 35042 Rennes Cedex, France*

**Abstract**

Novel glasses in GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-AgI system have been prepared by melt-quenching method. A large glass-forming region was found in the novel system, in which almost 60mol% AgI has been incorporated. The basic physiochemical properties of glass samples were investigated. With the addition of AgI, red shift of short-wavelength absorption edge indicates and distinct drop of the glass transition temperature ( $T_g$ ) were observed. In addition, a high Ag<sup>+</sup> ion conductivity of  $6.37 \times 10^{-4}$  S/cm at room temperature can be obtained in 55(0.6GeS<sub>2</sub>-0.4Sb<sub>2</sub>S<sub>3</sub>)-45AgI sample, indicating that these glasses have potential application as amorphous solid electrolytes.

**Keywords:** Amorphous materials, Electrical properties, Optical materials and properties.

**1. Introduction**

For several decades, chalcogenide glasses have attracted much attention due to their interesting properties: excellent IR transmittance, low phonon energy, high nonlinear refractive index, and good glass-forming abilities. Therefore, these materials present great potential for infrared optics applications

---

\* Corresponding author  
Changgui Lin, E-mail address: linchanggui@nbu.edu.cn

such as thermal imaging, laser power delivering, and ultrafast all optical switching [1-5]. Among numerous glasses, Ge-Sb-S has been well studied and has been shown to possess good thermal stability and high nonlinear optical properties.[6-8] Moreover, the large glass-forming region and the compositional dependencies of various properties make it possible to tailoring material for different applications. Previous research revealed that adding AgI into sulphide glass can greatly improve the nonlinear optical properties.[9] And the addition of haloid atom, iodine, would improve the glass-forming ability. In addition, superionic conducting chalcogenide glasses containing Ag ions have potential application in solid-state batteries.[10-12] Therefore, we choose  $\text{GeS}_2\text{-Sb}_2\text{S}_3\text{-AgI}$  glasses which was not investigated before as research subjects.

In this paper, we synthesized chalcogenide glasses in  $\text{GeS}_2\text{-Sb}_2\text{S}_3\text{-AgI}$  system and investigated their glass-forming ability, thermal, optical, and physicochemical properties.

## 2. Experimental

Homogeneous  $\text{GeS}_2\text{-Sb}_2\text{S}_3\text{-AgI}$  glasses were obtained by melt-quenching method. High purity raw materials Ge, Sb, S (5N) and AgI (3N) were weighed in a glove box and mixed together. The mixtures were placed into pre-cleaned quartz ampoules and sealed under vacuum ( $\sim 10^{-3}$ Pa). Then, the ampoules were melted at  $950^\circ\text{C}$  for 12h in a rocking furnace and quenched in ice water to obtain bulk glasses. Subsequently, the glass samples were annealed at the temperature of  $T_g - 20^\circ\text{C}$  for 3h to remove inner constraints. Then the glass rods were cut and polished into disks of 10mm in diameter and 1mm in thickness.

Amorphous characteristics of the samples were confirmed by X-ray diffraction (Bruker D2 phaser,  $\lambda=0.15406$  nm, 30 kv, 10 mA,  $\text{CuK}\alpha$ ). Densities were measured in de-ionized water based on the

Archimedes principle. Vickers hardness values were obtained by Vickers microindenter (Everone MH-3, Everone Enterprises, Ltd., China) with a charge of 100g for 5s. The glass transition temperature ( $T_g$ ) and the onset of crystallization temperature ( $T_x$ ) were determined by DSC (TA Instruments Q2000, New Castle, DE) at a heating rate of 10 °C/min. The transmission spectra were recorded with a UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950, Waltham, MA) and FTIR spectrometer (Nicolet 381, USA). In addition, the conductivities were calculated from impedance spectra which were carried out using an impedance analyzer (Agilent 4294A, USA).

### 3. Results and Discussion

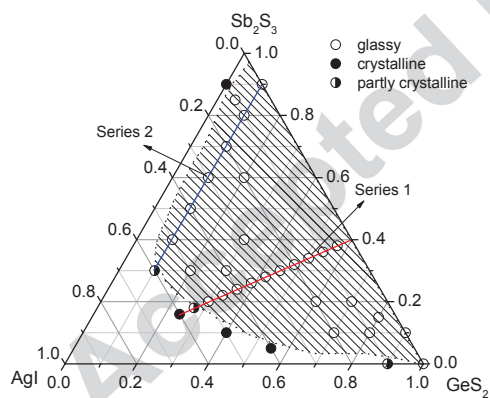


Fig. 1

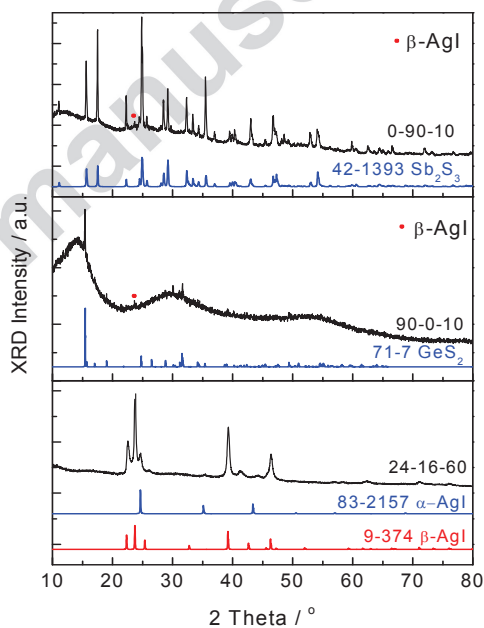


Fig. 2

A relatively wide glass-forming region was determined in the case of quenching 10g melts in water and shown in **Fig. 1**. It can be seen that the glass forming region is very large, and AgI can be largely incorporated into the  $\text{GeS}_2$ - $\text{Sb}_2\text{S}_3$  glasses. In the pseudo-ternary system, the amount of dissolved AgI can be reach to ~55mol% when the ratio of  $\text{GeS}_2$  to  $\text{Sb}_2\text{S}_3$  is 6/4 (series 1). With a constant of 10mol%  $\text{GeS}_2$

content (series 2), the glass-forming region reaches to ~60mol% amount of AgI. The large glass forming region is important because the large amount of AgI can enhance ionic conductivity and provides super-ionic glasses. **Fig. 2** shows the XRD patterns of some crystallized samples. Here the sample with the composition of  $x\text{GeS}_2\text{-}y\text{Sb}_2\text{S}_3\text{-}z\text{AgI}$  is named as  $x\text{-}y\text{-}z$ . It is obvious that no glass is obtained along the  $\text{Sb}_2\text{S}_3\text{-AgI}$  side. In the  $\text{GeS}_2\text{-AgI}$  system, sample with 10% AgI has  $\text{GeS}_2$  and  $\beta\text{-AgI}$  crystalline separate out. In the pseudo-ternary system, along the series 1, sample with 60% AgI (24-16-60) has the separation of crystalline  $\alpha\text{-AgI}$  and  $\beta\text{-AgI}$ .

Table 1 Density, hardness and characteristic temperature of the samples.

Compositions	Density, $\rho$	Hardness, $H_v$	$T_g$	$T_x$	$\Delta T$	
	( $\pm 0.002\text{g/cm}^3$ )	( $\pm 2\text{kg/mm}^2$ )	( $\pm 1^\circ\text{C}$ )	( $\pm 1^\circ\text{C}$ )	( $T_x - T_g$ )	
Series 1	90(0.6GeS <sub>2</sub> ·0.4Sb <sub>2</sub> S <sub>3</sub> )-10AgI	3.749	160	231	399	168
	80(0.6GeS <sub>2</sub> ·0.4Sb <sub>2</sub> S <sub>3</sub> )-20AgI	3.952	142	213	400	187
	70(0.6GeS <sub>2</sub> ·0.4Sb <sub>2</sub> S <sub>3</sub> )-30AgI	4.192	130	187	401	214
	60(0.6GeS <sub>2</sub> ·0.4Sb <sub>2</sub> S <sub>3</sub> )-40AgI	4.441	114	182	402	220
	55(0.6GeS <sub>2</sub> ·0.4Sb <sub>2</sub> S <sub>3</sub> )-45AgI	4.481	104	155	402	247
Series 2	10GeS <sub>2</sub> -80Sb <sub>2</sub> S <sub>3</sub> -10AgI	4.245	143	215	286	71
	10GeS <sub>2</sub> -70Sb <sub>2</sub> S <sub>3</sub> -20AgI	4.346	141	203	298	95
	10GeS <sub>2</sub> -60Sb <sub>2</sub> S <sub>3</sub> -30AgI	4.397	136	187	305	118
	10GeS <sub>2</sub> -50Sb <sub>2</sub> S <sub>3</sub> -40AgI	4.616	120	178	305	127
	10GeS <sub>2</sub> -40Sb <sub>2</sub> S <sub>3</sub> -50AgI	4.762	107	162	313	151

The detailed parameters of samples are provided in **Table 1**. It is obviously that, with increasing contents of AgI, the density increases and the hardness decreases. The evolution of density is easy to understand because of the heavy mass of AgI. The variation of hardness is also due to the addition of iodine atoms. As a non-bridging atom, iodine plays the role as the glass network terminator and breaks M-S-M (M=Ge or Sb) bonds to form M-I bonds. Thus, the addition of AgI decreases the dimensionality of structural network and makes the network more opened, and consequently resulting in the decrease of hardness. Previous research found that the  $T_g$  have an intimate relationship with the crosslink density and

the network connectivity of the glasses.[13] As discussed above, iodine atom is a glass network terminator, and the addition of iodine will induce the descending of network connectivity. Thus, the value of  $T_g$  will decrease with the addition of AgI gradually.

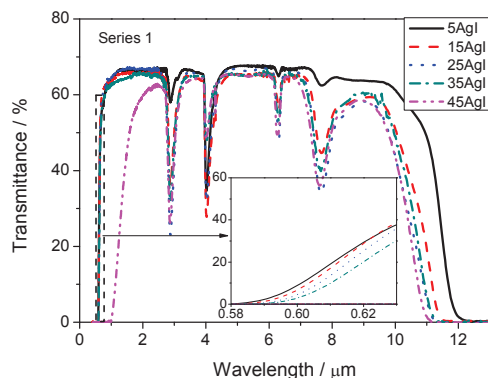


Fig.3

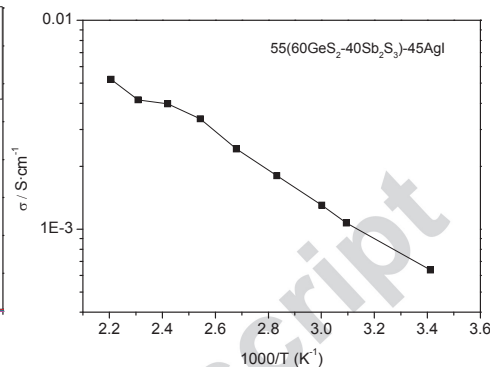


Fig. 4

**Fig. 3** shows the Vis-IR transmission spectra of  $\text{GeS}_2\text{-Sb}_2\text{S}_3\text{-AgI}$  glasses. Most of these glasses have good transparency in IR region, but the transmission region becomes narrow with the addition of AgI. According to previous researches[14, 15], the addition of halides in chalcogenide glass would usually induce the blue shift of the cut-off edge of short wavelength ( $\lambda_{\text{vis}}$ ) due to the lower polarizability of haloid ions compared with  $\text{S}^{2-}$  ions. Herein, on the contrary,  $\lambda_{\text{vis}}$  shifts toward the long wavelength with the addition of AgI. This is probably because of the high polarizability of  $\text{Ag}^+$  ions. Furthermore, the absorption bands at  $2.9\mu\text{m}$ ,  $6.3\mu\text{m}$ , and  $7.7\mu\text{m}$  can be attributed to the  $-\text{OH}$ ,  $\text{H}_2\text{O}$ , and  $-\text{S}-\text{O}-$ , respectively. These IR impurity absorption bands are enhanced with the addition of AgI because of its hygroscopic property.

As discussed above, the large amount of AgI may provide superionic glasses. To identify whether these glasses have superionic conducting characteristic, we employed impedance spectra to calculate the conductivity. The total conductivity contains ionic and electronic contribution. Here the electronic conductivity is negligibly small compared to the ionic one. The calculated results were plotted in **Fig. 4**.

The results showed that the conductivity at room temperature for 55(0.6GeS<sub>2</sub>-0.4Sb<sub>2</sub>S<sub>3</sub>)-45AgI is  $6.37 \times 10^{-4}$  S/cm. The high conductivity can be attributed to the mobile Ag ions in glass matrix.

#### 4. Conclusion

In this work, we prepared GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-AgI chalcogenide glasses and determined the glass-forming region. Up to almost 60mol% AgI can be dissolved in this glass system. The glasses have excellent IR transmittance which makes them good materials for application in IR optics. In addition, the high Ag<sup>+</sup> ion conductivity of  $6.37 \times 10^{-4}$  S/cm at room temperature can be obtained for 55(0.6GeS<sub>2</sub>-0.4Sb<sub>2</sub>S<sub>3</sub>)-45AgI sample. This results indicating that this glass system has a potential application in amorphous solid electrolytes.

#### Acknowledgements

This work was partially supported by the International Science & Technology Cooperation Program of China (Grant No. 2011DFA12040), 973 Program (Grant No. 2012CB722703), the NSFC (Grant No. 61108057), the Zhejiang Provincial Natural Science Foundation of China (Grant No. LY14E020001), and State Key Laboratory of Silicate Materials for Architectures (Wuhan University of Technology) (Grant No. SYSJJ2013-03). It was also sponsored by K.C. Wong Magna Fund in Ningbo University.

#### References

- [1] X.H. Zhang, Y. Guimond, Y. Bellec. *Production of complex chalcogenide glass optics by molding for thermal imaging*. J. Non-Cryst. Solids 2003; 326: 519-523.
- [2] A. Zakery, S.R. Elliott. *Optical properties and applications of chalcogenide glasses: a review*. J. Non-Cryst. Solids 2003; 330: 1-12.
- [3] G. Delaizir, P. Lucas, X. Zhang, H. Ma, B. Bureau, J. Lucas. *Infrared glass-ceramics with fine porous surfaces for optical sensor applications*. J. Am. Ceram. Soc. 2007; 90: 2073-2077.
- [4] K. Abe, H. Takebe, K. Morinaga, *Preparation and properties of Ge-Ga-S glasses for laser hosts*. J. Non-Cryst. Solids 1997; 212: 143-150.
- [5] X.F. Wang, Z.W. Wang, J.G. Yu, C.L. Liu, X.J. Zhao, Q.H. Gong. *Large and ultrafast third-order optical nonlinearity of GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-CdS chalcogenide glass*. Chem. Phys. Lett. 2004; 399: 230-233.
- [6] H. Takebe, T. Hirakawa, T. Ichiki, K. Morinaga. *Thermal stability and structure of Ge-Sb-S glasses*. J.

Ceram. Soc. Jpn 2003; 111: 572-575.

[7] K. Fedus, G. Boudebs, Q. Coulombier, J. Troles, X.H. Zhang. *Nonlinear characterization of  $GeS_2-Sb_2S_3-CsI$  glass system*. J. Appl. Phys. 2010; 107: 023108.

[8] L. Petit, N. Carlie, F. Adamietz, M. Couzi, V. Rodriguez, K.C. Richardson. *Correlation between physical, optical and structural properties of sulfide glasses in the system  $Ge-Sb-S$* . Mater. Chem. Phys. 2006; 97: 64-70.

[9] K. Iliopoulos, G. Hatzikyriakos, S. Couris, J. Ren, T. Wagner, M. Frumar, F. Kyriazis, S.N. Yannopoulos.  *$GeS_2-Ga_2S_3-AgI$  glasses with high nonlinear optical properties*. Transparent Optical Networks (ICTON), 2011 13th International Conference on.

[10] M. Kassem, D. Le Coq, R. Boidin, E. Bychkov. *New chalcogenide glasses in the  $CdTe-AgI-As_2Te_3$  system*. Mater. Res. Bull. 2012; 47: 193-198.

[11] S. Stehlik, J. Kolar, M. Bartos, Mil. Vlcek, M. Frumar, V. Zima, T. Wagner. *Conductivity in  $Ag-As-S$  ( $Se, Te$ ) chalcogenide glasses*. Solid state ionics 2010; 181: 1625-1630.

[12] M.A. Ureña, A.A. Piarristeguy, M. Fontana, B. Arcondo. *Ionic conductivity ( $Ag^+$ ) in  $AgGeSe$  glasses*. Solid state ionics 2005; 176: 505-512.

[13] J. Heo, J.D. Mackenzie. *Chalcohalide glasses: I. Synthesis and properties of  $Ge-S-Br$  and  $Ge-S-I$  glasses*. J. Non-Cryst. Solids 1989; 111: 29-35.

[14] H. Tao, S. Mao, W. Tong, X. Zhao. *Formation and properties of the  $GeS_2-In_2S_3-KCl$  new chalcohalide glassy system*. Mater. Lett. 2006; 60: 741-745.

[15] Z. Yang, G. Tang, L. Luo, W. Chen. *Glass formation and properties of  $GeSe_2-Ga_2Se_3-MX$  ( $MX$  is alkali halide) chalcohalide glasses*. Mater. Res. Bull. 2008; 43: 3596-3600.

#### Figure captions

Fig. 1 Glass-forming region of  $GeS_2-Sb_2S_3-AgI$  system.

Fig. 2 XRD patterns of some crystallized samples and the JCPDF cards of no. 83-2157  $\alpha$ - $AgI$  and no.

9-374  $\beta$ - $AgI$ .

Fig. 3 Vis-IR transmission spectra of glass samples in series 1.

Fig. 4 Temperature dependence of the conductivity for 55(0.6 $GeS_2$ -0.4 $Sb_2S_3$ )-45 $AgI$  glass.



### Highlights

1. The first research about the novel GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-AgI system.
2. The glass-forming region is very large in this system, and large amount of AgI can dissolved in this system.
3. The ionic conductivity at room temperature of 55(60GeS<sub>2</sub>-40Sb<sub>2</sub>S<sub>3</sub>)-45AgI can reach to  $6.37 \times 10^{-4}$  S/cm, indicating that this glass system has a potential application in amorphous solid electrolytes.

Accepted manuscript