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► To cite this version:

Sun Hong Wei, Bernard Tanguy, Jean-Maurice Réau, Jean-Jacques Videau, Josik Portier. Investigations on glasses in the Sb₂S₃-Agl system. *Journal of Non-Crystalline Solids*, 1988, 99 (2-3), pp.222-232. 10.1016/0022-3093(88)90432-2 . hal-00260939

HAL Id: hal-00260939

<https://hal.science/hal-00260939>

Submitted on 9 Mar 2021

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INVESTIGATIONS ON GLASSES IN THE Sb_2S_3 -AgI SYSTEM

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New glasses have been prepared in the Sb_2S_3 -AgI system. A glass domain is observed from $0.90\text{Sb}_2\text{S}_3$ - 0.10AgI to $0.33\text{Sb}_2\text{S}_3$ - 0.67AgI .

A structural approach is proposed on the basis of infrared spectroscopy studies. It shows the presence of $\text{Sb}_2\text{S}_2\text{I}_4$ groups such as those observed in SbSI and SbS_3 pyramids like in Sb_2S_3 .

Thermal and chemical properties have been studied. Ionic conductivity has been determined. An Arrhenius behavior is verified between 25°C and T_g over the whole glass domain. A comparative study with glasses belonging to the Sb_2S_2 - Ag_2S system has been undertaken.

1. Introduction

In a previous study [1], we described the properties of glasses obtained by hyperquenching in the Sb_2S_3 - Ag_2S system. The ionic conductivity of these materials is relatively high $\sigma_{25^\circ\text{C}} = 5.6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for the composition $0.10\text{Sb}_2\text{S}_3$ - $0.90\text{Ag}_2\text{S}$ due to a glass structure analogous to that of silver sulfide). Taking into account the very similar structure of both silver sulfide and iodide, it was tempting to extend the previous work to the Sb_2S_3 -AgI system.

This system has already been investigated by Mentus et al. [2], and they found a glass for only one composition ($0.40\text{Sb}_2\text{S}_3$ - 0.60AgI).

2. Experimental

2.1. Glass preparation

The starting materials are silver iodide (purity 99%; Aldrich Co.) and Sb_2S_3 (purity 99%, Ventron Co.).

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Table 1

Results of the chemical analysis of the samples obtained by hyperquenching at 700 °C in the Sb₂S₃–AgI system

No.	Starting composition			Final composition		
	Atomic ratio and formula	mol%	wt. %	Atomic ratio and formula	mol%	wt. %
1	Ag 1	14.29	18.78	Ag 1	14.93	19.74
	Sb 2	28.57	42.39	Sb 1.9	28.36	42.34
	I 1	14.29	22.09	I 0.9	13.43	20.90
	S 3	42.86	16.74	S 2.9	43.28	17.02
	AgSb ₂ IS ₃			AgSb _{1.9} I _{0.9} S _{2.9}		(Δ = ± 5%)
2	Ag 3	27.27	30.99	Ag 3	28.43	32.28
	Sb 2	18.18	23.32	Sb 1.85	17.56	22.51
	I 3	27.27	36.46	I 2.85	27.00	36.09
	S 3	27.27	9.21	S 2.85	27.00	9.12
	Ag ₃ Sb ₂ I ₃ S ₃			Ag ₃ Sb _{1.85} I _{2.85} S _{2.85}		(Δ = ± 5%)

An attempt to prepare glasses by the hyperquenching method described in ref. [1] failed. Indeed, the mixtures of silver iodide and antimony sulfide give rise to volatile SbSI in agreement with the reaction

The obtained SbSI is condensed on the cold wall of the apparatus. Hence the composition of the obtained samples is different from that of the starting mixture as shown in table 1 which summarizes the results of the chemical analysis performed by the Service Central d'Analyse du CNRS.

As a consequence, glasses described in this research have been prepared in sealed tubes with a limited free volume. The mixtures of iodide and sulfide well homogenized and pressed into pellets of about 4 g are put into silica containers. Those are sealed under vacuum and heated to 700 °C. After 24 h the container is quenched in a mixture of liquid water and ice. The glassy state of the sample is confirmed by X-ray diffraction.

The other used techniques (thermal analysis, density, chemical and electro-chemical stability, electrical conductivity, transport number, infrared spectroscopy) have been previously described in ref. [1].

3. Results

3.1. Glass-forming region and thermal properties

The glass forming region is shown in the diagram of fig. 1. Only one domain is observed from 0.90Sb₂S₃–0.10AgI to 0.33Sb₂S₃–0.67AgI. The color of the glasses changes from a bright black to a dark red when the silver

Fig. 1. Vitreous domain in the Sb_2S_3 -AgI system.

concentration increases. Figure 2 shows the variation of glass transition (T_g) and crystallisation (T_c) temperatures along the glass domain.

3.2. Chemical stability and density

Table 2 reports the chemical stability in water at different pH values. As previously observed for silver antimony sulfide glasses [1], the higher the silver content, the larger is the pH range where the glasses are stable.

Fig. 2. Variation of T_c and T_g vs. composition in the Sb_2S_3 -AgI glass system.

Table 2
Chemical stability of the $\text{Sb}_2\text{S}_3\text{-AgI}$ glasses

Composition (mol)	pH value of solution	Time (h)	AgCl ↓	Weight loss (%)	X-ray diffr. pattern
0.85 Sb_2S_3 -0.15AgI	0	24	no	~ 8.9	crystall.
	5.5	24	no	0	glassy
	8	24	no	+ 0.9	glassy
	11.5	24	no	+ 3.2	glassy
	14	24	no.	+ 9.1	crystall.
0.50 Sb_2S_3 -0.50AgI	0	24	no	~ 4.3	crystall.
	5.5	24	no	0	glassy
	8	24	no	0	glassy
	11.5	24	no	+ 2.5	glassy
	14	24	no	+ 7.2	crystall.

The density of the glasses increases linearly with the silver and iodide concentration (fig. 3).

3.3. Electrical properties

The transport number determined for the composition 0.33 Sb_2S_3 -0.67AgI is approximately 0.995, which shows that the electrical conductivity is mainly of ionic type due likely to silver mobility.

Fig. 3. Variation of the density vs. composition in the $\text{Sb}_2\text{S}_3\text{-AgI}$ system.

Fig. 4. Temperature dependence of the conductivity of glasses belonging to the $(1-x)\text{Sb}_2\text{S}_3-x\text{AgI}$ system.

Figure 4 gives the variation of the logarithm of the conductivity versus the reciprocal temperature for various compositions. An Arrhenius law is verified over the whole glass domain. Table 3 shows the values of the silver concentration, the ionic conductivity at 300 K, the activation energy and the pre-exponential term for various glasses.

Figure 5 gives the variation of the ionic conductivity and of the activation energy vs. atomic ratio, $r = \text{Ag}/(\text{Ag} + \text{Sb})$. The highest conductivity, i.e.,

Table 3

Values of Ag concentration, conductivity, activation energy and pre-exponential term in $\text{Sb}_2\text{S}_3-\text{AgI}$ glass system

Composition (mol)	$[\text{Ag}^+]$ (mol/cm ³)	$\sigma_{25^\circ\text{C}}$ ($\Omega \cdot \text{cm}$) ⁻¹	ΔE_a (eV)	$\log \sigma_0$
0.90Sb ₂ S ₃ -0.10AgI	1.37×10^{-3}	6.3×10^{-10}	0.50	0.7
0.80Sb ₂ S ₃ -0.20AgI	3.00×10^{-3}	4.8×10^{-7}	0.44	1.3
0.60Sb ₂ S ₃ -0.40AgI	7.31×10^{-3}	2.0×10^{-5}	0.36	1.2
0.50Sb ₂ S ₃ -0.50AgI	9.70×10^{-3}	5.0×10^{-5}	0.30	0.9
0.33Sb ₂ S ₃ -0.67AgI	1.49×10^{-2}	1.1×10^{-3}	0.25	1.3

Fig. 5. Variation of the conductivity and the activation energy vs. atomic ratio $r = \text{Ag}/(\text{Ag} + \text{Sb})$.

$\sigma_{25^\circ\text{C}} = 1.1 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$, together with the lowest activation energy ($\Delta E_a = 0.25 \text{ eV}$) has been obtained for the composition $0.33\text{Sb}_2\text{S}_3\text{--}0.67\text{AgI}$.

3.4. Electrochemical stability

The voltametric curve (fig. 6) has been determined for the glass corresponding to the upper limit of the observed existence range. It corresponds to the first cycle. The curve was plotted starting with an anodic sweep at B. A slight increase in current is observed. The cathodic sweep A' corresponds to silver reduction. The sharp current variation emphasizes that the silver ions are the majority carriers. During the A sweep, one observes the reoxidation of silver. The electrochemical stability is about 2 V with a current density of 0.1 mA/cm^2 . This value, higher than the theoretical decomposition voltage of Ag_2S (0.293 V) and that of AgI (0.689 V), shows that the mobility of S^{2-} or I^- anions is quite low.

3.5. IR spectroscopy

Figure 7 shows the infrared absorption spectra of the vitreous Sb_2S_3 , $0.75\text{Sb}_2\text{S}_3\text{--}0.25\text{AgI}$ and $0.40\text{Sb}_2\text{S}_3\text{--}0.60\text{AgI}$ samples, together with that of crystallized AgI [5]. Pure Sb_2S_3 is characterized by a strong band at about 275

Fig. 6. Triangular voltammetric curve for the glass $0.33\text{Sb}_2\text{S}_3-0.67\text{AgI}$ plotted at 35 mV/s and 25°C .

Fig. 7. Far IR absorption spectra of the glasses Sb_2S_3 , $0.75\text{Sb}_2\text{S}_3-0.25\text{AgI}$, $0.40\text{Sb}_2\text{S}_3-0.60\text{AgI}$ and of crystallized AgI .

Fig. 8. IR absorption spectrum of SbSI.

cm^{-1} and a weaker one at about 150 cm^{-1} corresponding respectively to stretching and bending Sb–S vibrations [3,4]. In the spectra of the chalcogenide glasses, those two bands are still present. In addition, one observes a weaker band at 180 cm^{-1} . Its intensity increases with AgI content. It can be attributed by comparison with the SbSI spectrum (fig. 8) that presents a similar band. Starting from the results of the symmetry mode analysis of Petzelt [6] and Balkanski et al. [7], one may assign this band to B_{1u} and B_{3u} modes corresponding to the Sb–I stretching vibrations in SbSI (table 4). It should be observed that the stretching vibrations in SbI_3 occur at approximately the same frequency [8]. One may pay attention to the fact that the bands present in the AgI spectrum do not appear in glass spectra.

4. Discussion

In a previous paper, Mentus et al. found only a $0.40\text{Sb}_2\text{S}_3\text{--}0.60\text{AgI}$ glass composition in the system whereas we detected a large domain of glass [2]. The more extended domain observed by us is probably due to a higher rate of quenching. We may notice that the glass obtained by the authors corresponds to the silver-rich limit of the glass domain. The ionic conductivities measured in both investigations are of the same order of magnitude.

Taking into account the results of the IR absorption studies, it is quite likely that $\text{Sb}_2\text{S}_2\text{I}_4$ groups such as those observed in SbSI and SbS_3 pyramids like in Sb_2S_3 are present in our glasses (fig. 9). The substitution in the lattice of sulfur by iodine leads to partial depolymerization of the $(\text{Sb}_4\text{S}_6)_n$ chains which characterize the Sb_2S_3 lattice [9]. Silver ions are probably randomly located between those groups.

Table 4

Normal modes of vibrational frequencies of SbSI with D_{2h} symmetry.

Normal mode of active infrared vibration		Frequencies (cm^{-1})	Vibrations of $\text{Sb}_2\text{S}_2\text{I}_4$ units
B_{1u}	ν (SbI)	180	
	ρ_r (SbI_2)	67	
	Ring deformation (Sb_2S_2)	248	
B_{2u}	ν (SbS)	139	
	ρ_w (SbI_2)	80	
B_{3u}	ν (SbI)	170	
	ν (SbS)	322	
	δ (ISbI)	60	

It is worthwhile to compare the ionic conductivities in the pure sulfide glasses and in thioiodide glasses in order to understand the respective influence of iodine and sulfur. We can notice that the present glasses, like those found in the first domain of the $\text{Sb}_2\text{S}_3\text{-Ag}_2\text{S}$ system, have probably a similar structure [1]. However, fig. 10 shows that at equal silver concentration the conductivity is higher and the activation energy lower in the iodide case. This

Fig. 9. Projections of the Sb_2S_3 (a) and SbSI (b) type structures in the (001) and after [10].

Fig. 10. Variation of $\log \sigma_{25^\circ\text{C}}$ and ΔE as a function of the Ag concentration for the Sb_2S_3 -AgI and Sb_2S_3 -Ag₂S glass systems.

property should be due either to weakening of the silver–lattice bond resulting from replacement of sulfur by iodine, the charge of which is lower, or to a steric effect due to large size of iodine involving an easier displacement of the Ag^+ ions.

We can conclude from this discussion that the best system that can be designed for a given glass former is that built up with silver sulfide which gives rise to both glass stability and high silver ion concentration and silver iodide which leads to weak silver–lattice bonding. Such superionic glasses can be expected in the Ag–Sb–S–I system and will be described in a next paper [11].

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