JOURNAL OF SOLID STATE CHEMISTRY **70**, 141–150 (1987)

Physical and Chemical Characterization and Ionic Conductivity of Rapidly Quenched Glasses in the Sb_2S_3–Ag_2S–AgI System*

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Received December 1, 1986; in revised form February 2, 1987

The glass-forming regions in the Sb_2S_3–Ag_2S–AgI ternary system have been determined after rapid roller quenching. Some physical chemical properties including density, thermal behavior, transport number, ionic conductivity, electrochemical stability, and IR absorption spectra have been investigated. The best conductivity obtained is 0.06 $(\Omega\text{-cm})^{-1}$ for a molar composition: $0.03Sb_2S_3$–$0.57Ag_2S$–0.40AgI with an activation energy of 0.15 eV. The transport number measurements show that the glasses are essentially ionic conductors (0.991–0.998 as determined by an emf method). Using the triangular voltammetry method the redox stability domain has been determined; it is about 2 V for a current density of 0.1 mA/cm^2. A glass model structure has been proposed on the basis of the infrared spectra. © 1987 Academic Press, Inc.

1. Introduction

Since 1914, when Tubandt and Lorentz discovered the high conductivity of α-AgI (*1*), numerous silver ionic conductors have been studied. Recently a great deal of attention has been focused on ionic-conducting glasses because some of them present obvious advantages over crystalline solids: these are isotropic ionic conduction, absence of grain boundaries, mouldability, smaller composition constraints permitting an increase in the amount of mobile species, limited electronic conductivity, etc.

Ionic conductivity in a condensed phase is governed by the mobility and the concentration of charge carriers. The state of the art has not reached a point where it is easy to predict how to increase the ion mobility. Nevertheless it is a matter of fact that increasing the dielectric constant of a glass tends generally to increase the conductivity. Therefore sulfide glasses have generally higher conductivities than the corresponding oxides. In addition, it is well known that the presence of mixed anions improves cationic mobility. For these reasons we chose to investigate the glasses formed in the Sb_2S_3–Ag_2S–AgI system in order to compare their electrical characteristics to those of previously prepared materials based on P_2S_5 (*2*), GeS_2 (*3*), and As_2S_3 (*4*).

There is an empirical but not theoretical

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0022-4596/87 $3.00

correlation between the concentration of a mobile ion and the number of corresponding carriers. However, compositions which may be explored for superionic properties of glasses obtained by conventional methods are limited because many liquids tend to crystallize. Such a limitation has focused our attention on the rapid-quenching methods which prevent crystallization and, therefore, to enlarge the vitreous domains (5). In this work we have used the twin-roller quenching technique. This method had been successfully utilized by Pradel *et al.* especially for studying the GeS_2–Li_2S system (5).

We have already investigated glasses formed in the Sb_2S_3–Ag_2S system (6). An ionic conductivity of $\sigma_{25°C} = 5.6 \times 10^{-3}\ \Omega^{-1}$ cm^{-1} had been observed for the molar composition $0.10Sb_2S_3$–$0.90Ag_2S$. This conductivity was one of the best so far obtained for sulfide glasses. Mentus *et al.* (7) and Sun *et al.* also studied the system Sb_2S_3–AgI (8). Despite the fact that the maximum silver content was lower in the iodide glasses than in the sulfide glass ($0.33Sb_2S_3$–0.67AgI) the ionic conductivity was the same order of magnitude ($\sigma_{25°C}$ = $1.1 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$). The conclusion of these investigations was that the best Sb_2S_3-based materials should be obtained with silver sulfide for glass stability and high silver content and iodide for high silver mobility.

2. Experimental

The starting materials were sulfide Ag_2S (purity 99.9%), AgI (purity 99%, Aldrich Co.), and Sb_2S_3 (purity 99%, Ventron Co.).

Glass preparation using a rapid-quenching method was described in Ref. (6). Some glasses also have been prepared in sealed silica capsules quenched in water at 0°C (8). In both cases the temperature of the melt was 700°C. The thermal properties were studied with a Mettler TA2000 B apparatus using a sealed aluminum crucible with a heating rate of 5°C/mn. The other techniques utilized to determine density, chemical and electrochemical stability, electrical conductivity, transport number, and infrared spectroscopy have been described previously in Ref. (6).

3. Results

3.1. Glass-Forming Regions

The glass-forming regions are shown in Fig. 1. In the vicinity of the Sb_2S_3–AgI line the rapid-quenching method has not been used due to the formation of volatile SbSI. When the silver-sulfide content in the starting mixture becomes high enough ($Ag_2S/(AgI + Sb_2S_3) > 0.1$) the formation of antimony thioiodide can be considered as negligible and a rapid roller-quenching method has been used without significant losses. A solid line is the limit of the glass domain obtained by rapid quenching, and the dashed line contains the glasses obtained in sealed tubes. Sb_2S_3 and Ag_3SbS_3 are amorphous. On the other hand, AgI, Ag_2S, and Ag_3SI cannot be obtained in the vitreous state with the quenching rate utilized (10^6 K/s). However, one obtains

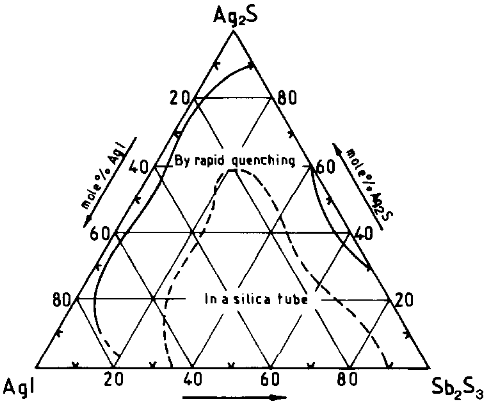

FIG. 1. Vitreous domains in the Sb_2S_3–Ag_2S–AgI system.

TABLE I

VALUES OF T_g, T_c, AND CRYSTALLIZATION ENTHALPY

No.	Composition (mole)	T_g (°C)	T_c (°C)	Cryst. enth. (J/g)
1	$0.33Sb_2S_3$–$0.67Ag_2S$	147	162	69.9
2	$0.22Sb_2S_3$–$0.42Ag_2S$–0.36AgI	144	180	47.9
3	$0.17Sb_2S_3$–$0.33Ag_2S$–0.50AgI	132	159	37.2
4	$0.10Sb_2S_3$–$0.20Ag_2S$–0.70AgI	86	112	23.3

TABLE III

TRANSPORT NUMBERS OF Ag^+ IONS IN THE Sb_2S_3–Ag_2S–AgI SYSTEM MEASURED BY emf (25°C)

No.	Composition (mole)	E_0	E_t	$t = E_0/E_t$
1	$0.17Sb_2S_3$–$0.33Ag_2S$–0.50AgI	0.685	0.687	0.997
2	$0.10Sb_2S_3$–$0.20Ag_2S$–0.70AgI	0.686	0.687	0.998
3	$0.06Sb_2S_3$–$0.24Ag_2S$–0.70AgI	0.686	0.687	0.998
4	$0.03Sb_2S_3$–$0.57Ag_2S$–0.40AgI	0.681	0.687	0.991

samples with a high $r = (Ag/Ag + Sb)$ ratio, i.e., close to 0.96.

3.2. *Thermal, Chemical Behavior and Density*

Table I gives, for example, the values of T_g, T_c, and of the crystallization enthalpy for some glasses with compositions located on the line joining AgI to $0.33Sb_2S_3$–$0.67Ag_2S$. The difference between T_g and T_c often given as characteristic of glass stability reaches a maximum when the AgI content is 36 mol%. This result is supported by the glass-making process: a glass with this composition can be prepared by classical method.

For the composition $0.03Sb_2S_3$–$0.57Ag_2S$–0.40AgI ($r = 0.96$), $T_g = 107$°C and $T_c = 141$°C have been obtained by a fluxmeter-microcalorimeter differential method.

Chemical stability in water already has been studied in the binary Sb_2S_3–Ag_2S and Sb_2S_3–AgI systems (*6*, *8*). The general tendency is that the smaller amount of antimony results in the more stable glass.

TABLE II

DENSITY OF SOME GLASSES IN THE Sb_2S_3–Ag_2S–AgI SYSTEM

Composition (mole)	Density
$0.65Sb_2S_3$–$0.23Ag_2S$–0.12AgI	4.96
$0.61Sb_2S_3$–$0.13Ag_2S$–0.26AgI	5.12
$0.33Sb_2S_3$–$0.33Ag_2S$–0.33AgI	5.34
$0.28Sb_2S_3$–$0.15Ag_2S$–0.57AgI	5.44
$0.12Sb_2S_3$–$0.48Ag_2S$–0.40AgI	5.96

Table II gives, for example, some values of glass density.

3.3. *Transport Number*

The silver transport number is measured by an emf method using the electrochemical cell

$$(-)\ Ag/Ag^+ \text{ glass electrolyte}/I_2 + C\ (+)$$

in which the overall cell reaction is

$$Ag(s) + \tfrac{1}{2}\, I_2(s) \rightarrow AgI(s).$$

The overall transport number of Ag^+ is given by the ratio $t = E_0/E_t$ where E_0 and E_t are the measured and the calculated emf of the cell, respectively.

Table III shows, for example, the results obtained for four compositions. The transport number ranges from 0.991 to 0.998 which means that the conductivity is mainly of the ionic type probably due to silver mobility.

3.4. *Ionic Conductivity*

The variation of conductivity vs reciprocal temperature is given in Fig. 2 for several glasses investigated in the ternary system. The Arrhenius law is verified for all studied samples below T_g. Electrical data are given in Table IV.

Figure 3a shows the variation of log $\sigma_{25°C}$ vs molar ratio $m = Ag_2S/(Ag_2S + 2AgI)$. Each curve corresponds to a constant atomic ratio $r = Ag/(Ag + Sb)$. Figure 3b shows the variation of activation energy for some typical compositions. Notice that the

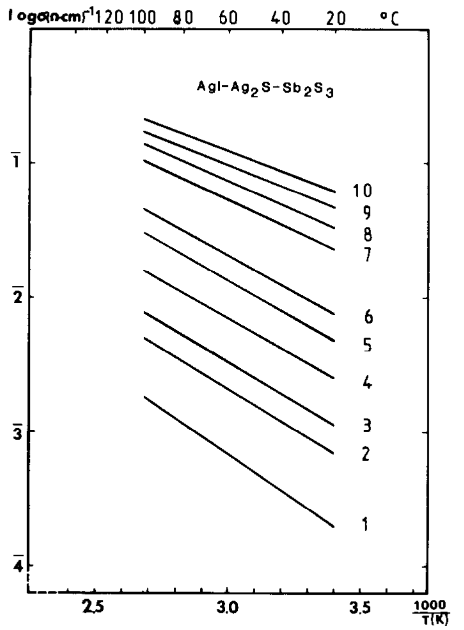

FIG. 2. (a) Variation of log σ vs reciprocal temperature for glasses belonging to the Sb_2S_3–Ag_2S–AgI system. (Glass compositions are given in Table IV.)

minimum value ($\Delta E_\sigma = 0.15$ eV) is very close to those of α-AgI ($\Delta E_\sigma = 0.10$ eV) (*9*) and α-Ag_2S ($\Delta E_\sigma = 0.11$ eV) (*10*).

It appears that two types of behavior are observed. The glasses with the largest antimony content ($r < 0.50$) have a high activation energy and their conductivity is relatively low. Furthermore a minimum for σ exists. On the other hand, glasses involving the highest silver content ($r > 0.50$) have the best conductivities and σ shows a maximum for a given value of m which increases with r. The maximum value corresponds to a S/I ratio close to 1. However, rapid-quenched Ag_3SI itself does not lead to a glass but dissociates to a sulfide and iodide in agreement with the phase diagram (*11*).

3.5. *Electrochemical Stability*

The voltammetric curves (Fig. 4) are obtained for two glasses with compositions $0.17Sb_2S_3$–$0.33Ag_2S$–0.50AgI and $0.20Sb_2S_3$–$0.60Ag_2S$–0.20AgI. They correspond to the first cycle. The curve has been plotted starting with an anodic sweep at B. A slight current increase is observed. The cathodic sweep A' corresponds to silver reduction. The sharp current variation indicates that the silver ions are the majority carriers. During the A sweep a reoxidation of silver metal is observed. The electrochemical stability domain 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) or AgI (0.689 V), shows that the anionic mobility is very low.

Figure 5 exhibits a discharge curve of

TABLE IV

VALUES OF CONDUCTIVITY AT 25°C, Ag MOLAR FRACTION, ACTIVATION ENERGY, AND PRE-EXPONENTIAL TERM OF Sb_2S_3–Ag_2S–AgI GLASSES

No.	Composition (mole)	$\sigma_{25°C}$ (Ω^{-1} cm^{-1})	$\frac{Ag}{Ag + Sb}$	ΔE_σ (eV)	log σ_0
1	$0.33Sb_2S_3$–$0.33Ag_2S$–0.33AgI	1.9×10^{-4}	0.60	0.27	0.9
2	$0.22Sb_2S_3$–$0.42Ag_2S$–0.36AgI	6.8×10^{-4}	0.73	0.24	1.0
3	$0.17Sb_2S_3$–$0.33Ag_2S$–0.50AgI	1.1×10^{-3}	0.83	0.23	0.9
4	$0.10Sb_2S_3$–$0.20Ag_2S$–0.70AgI	2.6×10^{-3}	0.85	0.22	1.2
5	$0.11Sb_2S_3$–$0.32Ag_2S$–0.57AgI	4.8×10^{-3}	0.85	0.22	1.5
6	$0.12Sb_2S_3$–$0.48Ag_2S$–0.40AgI	7.4×10^{-3}	0.85	0.21	1.5
7	$0.05Sb_2S_3$–$0.85Ag_2S$–0.10AgI	2.2×10^{-2}	0.94	0.18	1.5
8	$0.04Sb_2S_3$–$0.26Ag_2S$–0.70AgI	3.2×10^{-2}	0.94	0.17	1.4
9	$0.05Sb_2S_3$–$0.55Ag_2S$–0.40AgI	4.5×10^{-2}	0.94	0.16	1.4
10	$0.03Sb_2S_3$–$0.57Ag_2S$–0.40AgI	6×10^{-2}	0.96	0.15	1.4

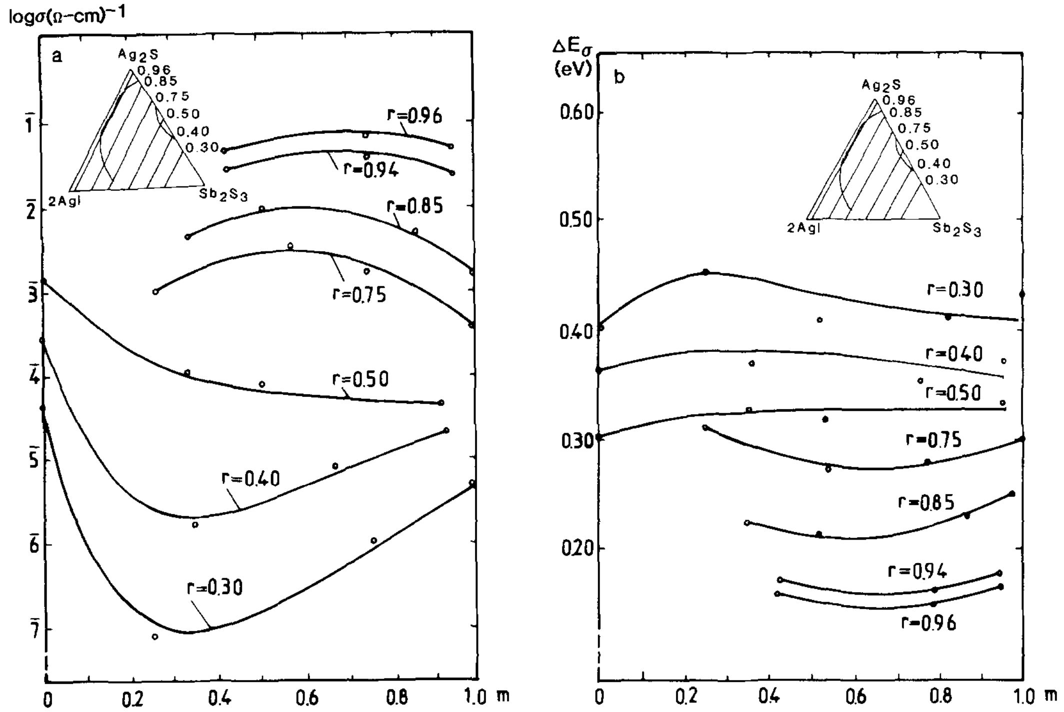

FIG. 3. (a) Variation of log $\sigma_{25°C}$ vs m = $Ag_2S/(Ag_2S + 2AgI)$ for glasses corresponding to a constant value of r = Ag/(Ag + Sb). (b) Variation of ΔE_σ vs m = $Ag_2S/(Ag_2S + 2AgI)$ for glasses corresponding to a constant value of r = Ag/(Ag + Sb).

two cells in series, each corresponding to the galvanic chain

(−) Ag/Ag + glass/glass + I_2/I_2 + C/C (+)

for a current density of 2 μA/cm^2 during 1000 hr. The internal resistance increase observed with time is due to the formation of poorly conducting γ-AgI at the cathode.

3.6. Infrared Spectroscopy

Figure 6 gives the IR absorption spectrum of two glasses relatively rich in antimony and corresponding to the same $r \simeq 0.4$ ratio but with different iodide concentrations. Both spectra show the vibrations which characterize Sb_2S_3 (270 and 150 cm^{-1}) and Ag_2S (190 and 100 cm^{-1}) *(12–14)*. In addition, on the spectrum corresponding to higher iodine content a band located around 180 cm^{-1} is observed, which could be assigned to the ν(Sb–I) vibrations *(15, 16)* as in previously investigated Sb_2S_3-AgI glasses *(8)*. A new band below 100 cm^{-1} appears. Such a band has been reported for SbI_3 and attributed to the ν(SbI_3) vibrations *(17)*. The corresponding ν(Sb–I) stretching vibrations expected around 150 cm^{-1} are probably hidden by the δ(SbS_3) bending vibration band. The presence of SbI_3 itself is very uncertain. This iodide is very volatile with a boiling point of 401°C. However, iodine-rich entities such as (Sb_2SI_6) intermediate between SbI_3 pyramids found in the iodide and $Sb_2S_2I_4$ groups found in SbSI could exist in the glass.

Figure 7 shows three spectra of silver-rich glasses. As in Fig. 6a and b, the SbS_3 vibrations are observed but with a lower intensity. The band below 100 cm^{-1} already existing in Fig. 6a is enhanced with iodine

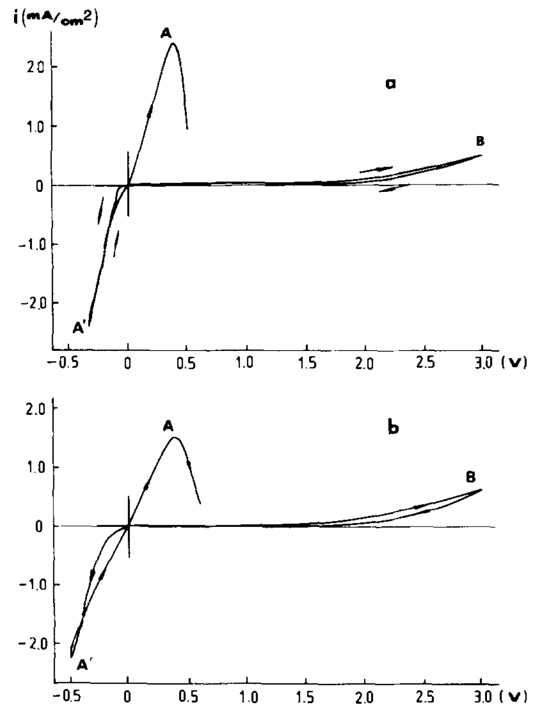

FIG. 4. Triangular voltammetric curves for the glasses (a) $0.17Sb_2S_3$–$0.33Ag_2S$–$0.50AgI$ and (b) $0.20Sb_2S_3$–$0.60Ag_2S$–$0.20AgI$ (35 mV/s, 25°C).

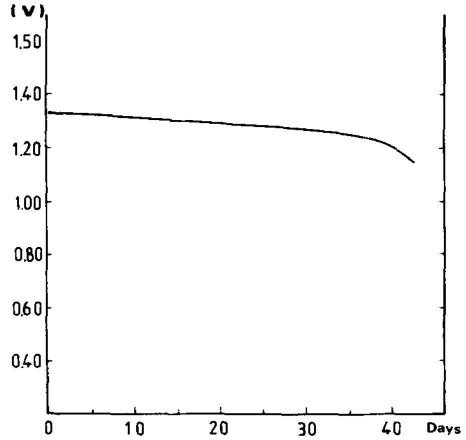

FIG. 5. Discharge curve using a glass ($0.03Sb_2S_3$–$0.57Ag_2S$–$0.40AgI$) in a galvanic chain t = 25°C, I = 2 μA/cm^2.

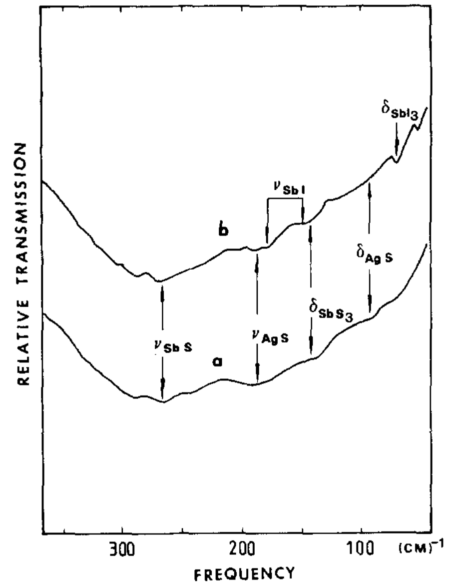

FIG. 6. Far-infrared spectra of compositions (a) $0.55Sb_2S_3$–$0.40Ag_2S$–$0.05AgI$ and (b) $0.48Sb_2S_3$–$0.11Ag_2S$–$0.41AgI$ (r = Ag/(Ag + Sb) ≈ 0.4).

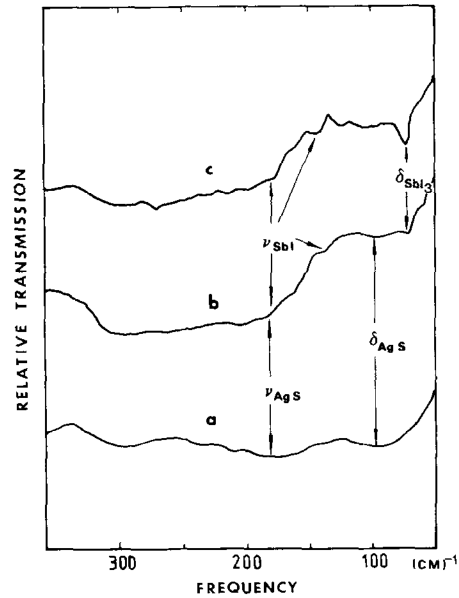

FIG. 7. Far-infrared spectra of compositions (a) $0.13Sb_2S_3$–$0.87Ag_2S$, (b) $0.15Sb_2S_3$–$0.60Ag_2S$–$0.25AgI$, and (c) $0.10Sb_2S_3$–$0.20Ag_2S$–$0.70AgI$ (r = Ag/(Ag + Sb) ≈ 0.85).

content (Fig. 7b and c). Due to lower Sb_2S_3 rate, the (Sb–I) band of SbI_3 species appears close to 150 cm^{-1} (Fig. 7c). The presence of Ag–I stretching vibrations cannot be excluded. However, they would be hidden by the band corresponding to the (Ag–S) vibrations.

4. Discussion

The variation of the ionic conductivity (Fig. 3a, b) shows the influence of total percentage of Ag atoms. The respective influence of the introduction of AgI and Ag_2S can be studied by plotting log $\sigma_{25°C}$ and ΔE_σ for different glasses $(Sb_2S_3\text{-}pAg_2S)_{1-y}(AgI)_y$ and $(Sb_2S_3\text{-}qAgI)_{1-z}(Ag_2S)_z$ as a function of y (p = const) and z (q = const), respectively (Fig. 8a, b) and Fig. 9a, b).

(*a*) $(Sb_2S_3\text{-}pAg_2S)_{1-y}(AgI)_y$ *glasses*. The variation with y of transport properties is strongly dependent on p:

for the very low values of p ($p = \frac{1}{4}$, for instance), a maximum of ΔE_σ and a minimum of log σ is observed for a particular value y_m which decreases when p increases,

for higher values of p ($1 < p < 2$), log σ increases and ΔE_σ decreases linearly when y increases, and

for the highest values of p, ΔE_σ decreases rapidly and log σ increases for the low y values. Then when y increases, the variations of log σ and ΔE_σ become small.

(*b*) $(Sb_2S_3\text{-}qAgI)_{1-z}(Ag_2S)_z$ *glasses*. For the low q values ($q = \frac{3}{7}$, for instance), a minimum of conductivity associated with a maximum of ΔE_σ is found for a particular z value as previously observed for p in case (a);

for the high q values (q = 1.8, for instance), log σ and ΔE_σ depend only slightly on z when it is small ($z < 0.40$). Then log σ increases with z when ΔE_σ decreases.

These results show that the introduction of AgI into (Sb_2S_3–pAg_2S) and of Ag_2S into (Sb_2S_3–qAgI) glasses lead to a decrease in electrical properties when p and q are low.

It must be noted that the variation of log σ and ΔE_σ with y for the $(Sb_2S_3\text{-}pAg_2S)_{1-y}(AgI)_y$ glasses is linear only for some particular values of p ($1 \leq p \leq 2$).

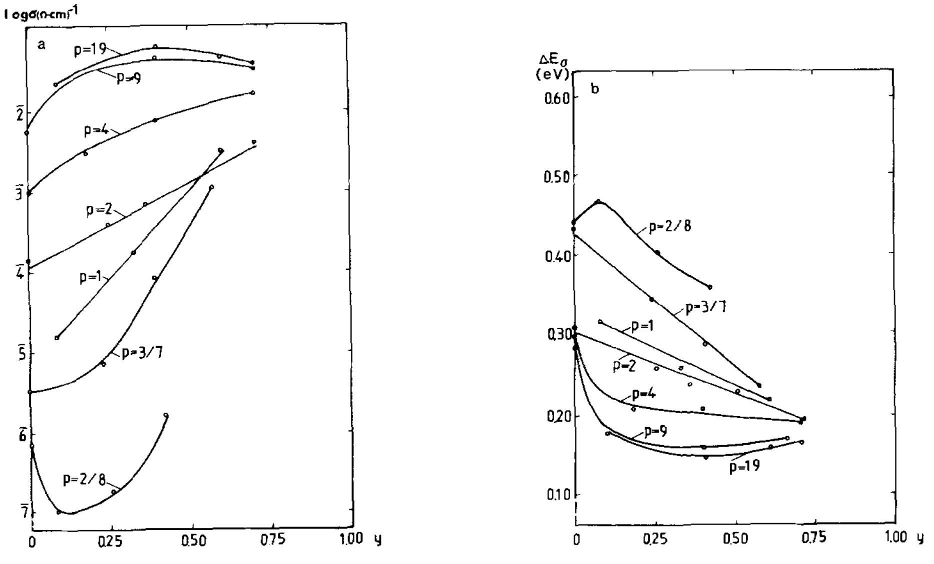

FIG. 8. (a) Variation of log $\sigma_{25°C}$ vs y for glasses $(Sb_2S_3\text{-}pAg_2S)_{1-y}(AgI)_y$ corresponding to constant p value. (b) Variation of ΔE_σ vs y for glasses $(Sb_2S_3\text{-}pAg_2S)_{1-y}(AgI)_y$ corresponding to constant p value.

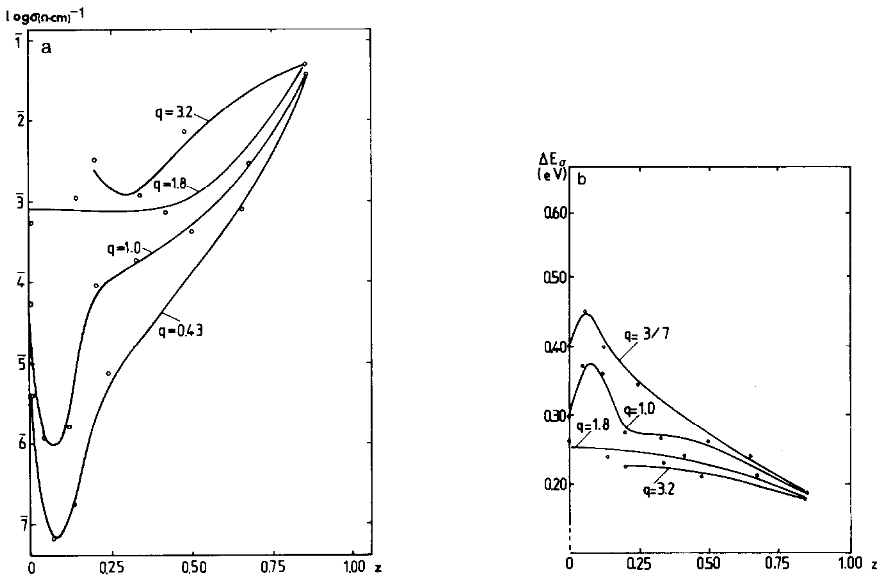

FIG. 9. (a) Variation of log $\sigma_{25°C}$ vs z for glasses $(Sb_2S_3–qAgI)_{1-z}(Ag_2S)_z$ corresponding to constant q value. (b) Variation of ΔE vs z for glasses $(Sb_2S_3–qAgI)_{1-z}(Ag_2S)_z$ corresponding to constant q value.

Similar results have been obtained for other glasses as $(Ag_2S–GeS_2)_{1-y}(AgI)_y$ (*3*), $(Ag_2S–P_2S_5)_{1-y}(AgI)_y$ (*2*), and $(Ag_2S–pAs_2S_3)_{1-y}(AgI)_y(p = 1, 2)$ (*4*). Results obtained for low and high values of p ($p < 1$ and $p > 2$) in $(Sb_2S_3–pAg_2S)_{1-y}(AgI)_y$ show that such a behavior depends on p.

5. Conclusions

In previous publications we have studied sulfide glasses (*6*) and thioiodide glasses (*8*) corresponding to both $Sb_2S_3–Ag_2S$ and $Sb_2S_3–AgI$ binary systems. In sulfide glasses, when the silver content is low, we have assumed that the structure of the glass is based on polymerized SbS_3 pyramids. As the silver content increases the structure could be related to that of α-Ag_2S. In the thioiodide glasses we have concluded that SbS_3 pyramids and $Sb_2S_2I_4$ groups are both present.

The variation of the ionic conductivity within the ternary system seems to characterize two types of behavior.

For glasses rich in antimony (e.g., $r \lesssim 0.5$) the conductivity is relatively low. On the basis of the infrared spectra, one can assume that the structure is based on polymerized SbS_3 pyramids and $Sb_2S_2I_4$ groups. Silver ions are probably located in the vacancies of the lattice.

For silver-rich glasses ($r > 0.75$), on the other hand, the conductivity is very high. The infrared spectroscopy does not allow the determination of an accurate structural approach of the silver environment. However, it can be observed that the same sulfide and thioiodide groups surround antimony and that the main absorption is due to the Ag–S vibrations. One has to point out that the activation energy ($\Delta E_\sigma = 0.15$ eV) observed for the $0.03Sb_2S_3–0.57Ag_2S–0.40AgI$ glass is very close to that of α-Ag_2S ($\Delta E_\sigma = 0.11$ eV) and α-AgI ($\Delta E_\sigma = 0.10$ eV). At least for the border composition ($r = 0.96$), the results suggest that the struc-

TABLE V

CONDUCTION PROPERTIES OF SOME SILVER ELECTROLYTES AT 25°C

No.	Composition (mole)	$\sigma_{25°C}$ (Ω^{-1} cm^{-1})	ΔE_{σ} (eV)	Ref.
1	$0.75AgI–0.25Ag_2MoO_4$	1.1×10^{-2}	0.22	(*19*)
2	$0.575AgI–0.425AgPO_3$	1.5×10^{-2}	0.25	(*20*)
3	$0.333Ag_2S_3–0.667Ag_2S$	1×10^{-4}	0.35	(*21*)
4	$0.45P_2S_5–0.55Ag_2S$	2.7×10^{-5}	0.38	(*21*)
5	$0.45GeS_2–0.55Ag_2S$	1.4×10^{-3}	0.33	(*21*)
6	$0.45GeS_2–0.05GeS0.45Ag_2S$	3.5×10^{-4}	0.34	(*21*)
7	$0.477(GeS_2–Ag_2S)–0.523AgI$	6.0×10^{-3}	0.28	(*3*)
8	$0.35(P_2S_5–Ag_2S)–0.65AgI$	1.6×10^{-2}	0.20	(*2*)
9	$0.45(AS_2S_3–Ag_2S)–0.55AgI$	8×10^{-3}	0.22	(*4*)
10	$0.10Sb_2S_3–0.90Ag_2S$	5.6×10^{-3}	0.28	(*6*)
11	$0.33Sb_2S_3–0.67AgI$	1.1×10^{-3}	0.25	(*8*)
12	$0.03Sb_2S_3–0.57Ag_2S–0.40AgI$	6.0×10^{-2}	0.15	This work
13	5% $AgNO_3$ aqueous solution	2.0×10^{-2}	—	(*22*)

ture of the glass is related to the high temperature forms of the iodide and the sulfide which have the same anionic arrangement and which give solid solution on the sulfide side (90). The thio- and thioiodoantimony polyhedra should be dispersed in the matrix. Adding Sb_2S_3 to AgI and Ag_2S mixtures for making glasses results in the proper thermal properties in the melt. Antimony sulfide could probably be replaced by any chalcogenide (GeS_2, Ag_2S_3, etc.) able to play a similar role.

Table V allows a comparison of the performance of some silver-conducting glasses and of an aqueous solution at room temperature. The silver antimony thioiodide glasses are among the best ionic conductors. The conductivity is comparable to that of solution of silver nitrate. The activation energy is the lowest ever observed in a glass. It is very close to that of the high-temperature forms of AgI and Ag_2S. Rapid-quenching preparation methods do not allow the quenching of these compounds down to room temperature in the vitreous state but lead to glasses with similar compositions, related structures, and comparable ionic conductivities.

Acknowledgments

The authors express their sincere thanks to Dr. Claudy for thermal analysis and to Dr. Derouault for technical support in far-IR absorption measurements.

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