

Influence of the $S^{2-} = 2I^-$ Substitution on the Ionic Conduction Properties of the Ag^+ Glasses inside the $AgPO_3$ – Ag_2S – AgI System

J. M. REAU,* LIU JUN, B. TANGUY, J. J. VIDEAU, J. PORTIER,
AND P. HAGENMULLER

*Laboratoire de Chimie du Solide du CNRS Université de Bordeaux I, 351,
cours de la Libération, 33405 Talence Cedex, France*

Received July 17, 1989; in revised form November 17, 1989

The glass forming region in the $AgPO_3$ – Ag_2S – AgI system has been determined and some physical–chemical properties including thermal behavior, ionic conductivity, transport number, and infrared absorption have been investigated. The results of the electrical properties and the transport number measurements show that the conduction is essentially ionic in nature and due to silver ions alone. The study of the influence of the replacement of $2I^-$ by S^{2-} on the electrical properties of glasses of formulation $(AgS_{0.5})_\alpha(AgI)_\beta(AgPO_3)_\gamma$ ($\alpha + \beta + \gamma = 1$) exhibits a quasi-linear variation of $\log \sigma_{25^\circ C}$ with the ratio r [$r = AgS_{0.5}/(AgS_{0.5} + AgI) = \alpha/(\alpha + \beta)$] at fixed values of γ . A comparative investigation of the electrical properties of the glasses P_2O_5 – Ag_2O – AgI and P_2O_5 – Ag_2O – Ag_2S – AgI shows that these materials belong to the same family of glasses. An identical limit seems to be obtained when $y_{AgI} \approx 0.67$, independent of the nature of Ag_2X ($X = O, S$), either Ag_2O or $(Ag_2O + Ag_2S)$, and of the value of p , for the glasses of formulation $[P_2O_5 - p(Ag_2O + Ag_2S)]_{1-y}[AgI]_y$. © 1990 Academic Press, Inc.

I. Introduction

The study of electrical properties of glasses belonging to the Ag_2S – $AgPO_3$ system has shown that, as for AgI in the AgI – $AgPO_3$ glasses, the ionic conductivity increases and the activation energy decreases linearly with increasing Ag_2S mole fraction and that the values of $\log \sigma_{25^\circ C}$ and ΔE_σ obtained by extrapolation at $AgPO_3$ mole fraction $\rightarrow 0$ are close to those of α - Ag_2S . On the other hand, the infrared absorption investigations of the Ag_2S – $AgPO_3$ glasses have pointed out that these materials have features clearly different from those of the AgI – $AgPO_3$ system: whereas the $(PO_4)_n$ infi-

nite chains are not modified by introduction of AgI in the phosphate glass, Ag_2S is dissolved by an acid–base chemical ordering process, involving shorter phosphate chains, i.e., close to the pyrophosphate group at the glass forming boundary (1).

The existence domain of the Ag_2S – $AgPO_3$ glasses is clearly narrower than that of the AgI – $AgPO_3$ ones. Furthermore, whereas the electrical properties of α - Ag_2S and α - AgI are very close, those of the limit compositions, which can be formulated $Ag(PO_3)_{0.48}S_{0.26}$ and $Ag(PO_3)_{0.43}I_{0.57}$, are very different: $\sigma_{25^\circ C}(\text{sulfide glass}) \approx 10^{-3}\sigma_{25^\circ C}(\text{iodide glass})$. Such a representation shows, however, that these materials contain almost similar numbers of phosphate groups for the same amount of Ag^+ ions.

* To whom correspondence should be addressed.

As the series of AgI-AgPO_3 and $\text{Ag}_2\text{S-AgPO}_3$ glasses are characterized by different vitreous structures, we have carried out the research and the study of electrical properties of new glasses within the ternary $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system. Our aim was the determination of the influence of the replacement of 2I^- by S^{2-} on the electrical properties of glasses involving the same AgPO_3 content.

II. Experimental

Glasses are obtained from mixtures of AgI (purity 99%), Ag_2S (purity 99%), and AgPO_3 prepared by a wet method from AgNO_3 and NaPO_3 . The mixtures put into a sealed silica tube are melted at $500\text{-}700^\circ\text{C}$ and quenched in water at 0°C . The vitreous state is confirmed by absence of X-ray diffraction.

The T_G values have been determined by differential scanning calorimetry. The conductivity measurements are performed on samples annealed 30°C below T_G by the complex impedance method using a Solartron 1170 frequency analyzer. The glass samples are cylindrical (8 mm diameter, 1–2 mm thickness). On both sides the gold electrodes are deposited by evaporation. The measurements are carried out under argon atmosphere in the frequency range $10^{-2}\text{-}10^{+4}$ Hz and between 20°C and T_G .

Infrared absorption spectra in the range $200\text{-}1400\text{ cm}^{-1}$ were obtained using a double beam Perkin-Elmer 983 spectrometer. Samples are pellets (13 mm diameter, 1 mm thickness) constituted by a ground mixture of 1 part glass and 60 parts KBr pressed at 200 kg/cm^2 .

III. Glass Formation Domain and Thermal Properties

The glassy domain in the $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system is shown in Fig. 1. It is bounded by the lines connecting the point represent-

ing AgPO_3 to those of Ag_2S and AgI and by the full line inside the ternary diagram.

In a second domain located between the full line and the dashed line, hard materials appearing as aggregated small spheres are obtained. Though they are still amorphous, their glassy character is not obvious; consequently, the thermal and electrical properties have only been studied for the glasses belonging to the first domain.

The values of T_G have been reported in Fig. 1 and Table I for some glasses of the $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system. Whereas a slight increase of T_G is shown with the progressive introduction of Ag_2S into the AgPO_3 glass, a decrease of T_G is observed when x increases along the $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{Ag}_3\text{SI})_x(\text{AgPO}_3)_{1-x}$ lines.

To determine the influence of the anionic substitution $\text{S}^{2-} = 2\text{I}^-$ on the properties of glasses of the $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system, independently of the Ag^+ ions, the glassy compositions studied have been produced on the following form: $(\text{AgS}_{0.5})_\alpha(\text{AgI})_\beta(\text{AgPO}_3)_\gamma$ with $(\alpha + \beta + \gamma = 1)$.

The variation of T_G as a function of the ratio r [$r = \text{AgS}_{0.5}/(\text{AgS}_{0.5} + \text{AgI}) = \alpha/(\alpha + \beta)$] is given in Fig. 2 for some samples corresponding to different values of γ :

—for the very high values of γ ($\gamma = 0.70$ for instance), T_G increases quasi-linearly when r increases.

TABLE I

T_G , CONDUCTIVITY AT 25°C , ACTIVATION ENERGY, AND PREEXPONENTIAL TERM FOR SOME GLASSES OF THE $\text{Ag}_2\text{S-AgI-AgPO}_3$ SYSTEM

Compositions			T_G ($^\circ\text{C}$)	$\log \sigma_{25^\circ\text{C}}$ ($\Omega^{-1}\text{ cm}^{-1}$)	ΔE_σ (eV)	$\log \sigma_0$
Ag_2S	AgI	AgPO_3				
33.3	33.3	33.3	75	2.12	0.23	2.0
14.3	57.1	28.6	76	3.94	0.24	2.0
11.2	44.4	44.4	78	3.62	0.29	2.5
40	20	40	108	3.20	0.32	2.6
25	25	50	89	4.90	0.34	2.6
14.3	28.6	57.1	109	4.78	0.33	2.4
7.5	30.7	61.8	118	4.30	0.35	2.2
16.7	16.3	67	130	5.72	0.40	2.5
25	50	25		2.04	0.24	2.1

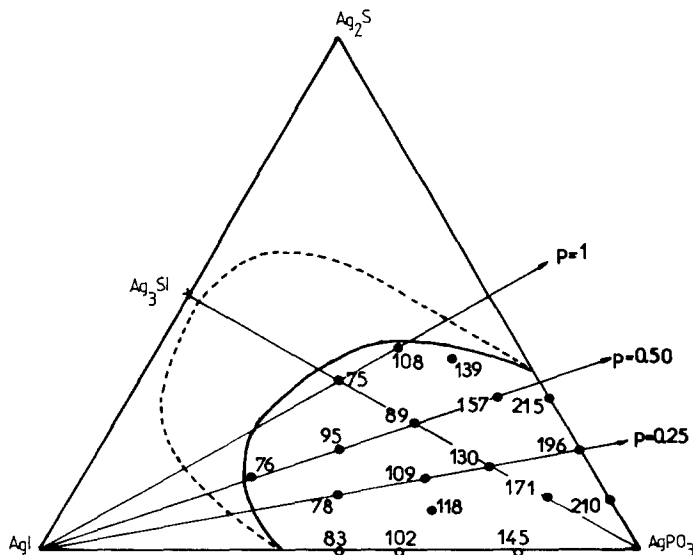


FIG. 1. Vitreous domains in the $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system (the numbers indicated in the figure represent the values of T_G).

—for the lower values of γ ($\gamma \approx 0.60$), a slope change, which becomes sharper when γ decreases, takes place for $r \approx 0.67$, i.e., for the glasses located close to the line connecting AgPO_3 to Ag_3SI in Fig. 1. T_G in-

creases slowly at rising r in the region $r \approx 0.67$, but quickly for $r \geq 0.67$.

IV. Ionic Conductivity

The electrical properties of glasses belonging to the $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system have been determined as a function of temperature and composition. An Arrhenius behavior is shown for all investigated samples below T_G . Some electrical data are gathered in Table I.

The transport number has been measured by an EMF method using the electrochemical chain: $(-)\text{Ag}/\text{Ag glass electrolyte}/\text{C}, \text{I}_2(+)$. The thermodynamic potential of the cell is $E_{\text{th}} = 0.687$ V at 20°C and corresponds to the overall potential of the following reaction: $\text{Ag} + \frac{1}{2} \text{I}_2 \rightarrow \text{AgI}$. The results obtained for some compositions (Table II) show that the transport number is close to 1 and that the conductivity is mainly of the ionic type probably due to silver mobility.

Influence on the transport properties of

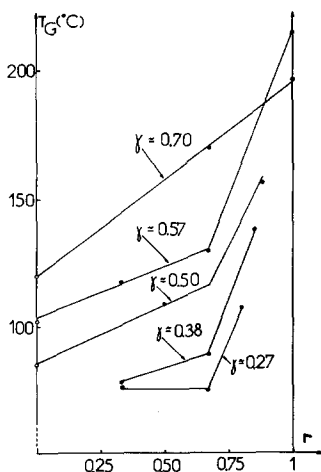


FIG. 2. Variation of T_G as a function of $r = \text{AgS}_{0.5}/(\text{AgS}_{0.5} + \text{AgI})$ in the $(\text{AgS}_{0.5})_\alpha(\text{AgI})_\beta(\text{AgPO}_3)_\gamma$ glasses ($\alpha + \beta + \gamma = 1$).

TABLE II
TRANSPORT NUMBER OF Ag^+ IONS IN SOME
GLASSES (25°C)

Compositions			E_0	E_t	$t = E_0/E_t$
Ag_2S	AgI	AgPO_3	(V)	(V)	
7.5	30.7	61.8	0.686	0.687	0.998
11.2	44.4	44.4	0.686	0.687	0.998
14.3	28.6	57.1	0.684	0.687	0.995
20	40	40	0.684	0.687	0.995
25	25	50	0.682	0.687	0.993

the introduction of AgI into sulfide glasses has been studied for different glasses corresponding to a constant value of ratio $p = \text{Ag}_2\text{S}/\text{AgPO}_3$. The composition of the glasses can then be represented by the general formula $(\text{AgPO}_3 - p\text{Ag}_2\text{S})_{1-y}(\text{AgI})_y$.

Figure 3 gives the variation of $\log \sigma_{25^\circ\text{C}}$ as a function of y (p being fixed) for the $(\text{AgPO}_3 - p\text{Ag}_2\text{S})_{1-y}(\text{AgI})_y$ glasses. We have reported the values previously obtained relative to the $\text{AgPO}_3\text{-AgI}$ system ($p = 0$) (2).

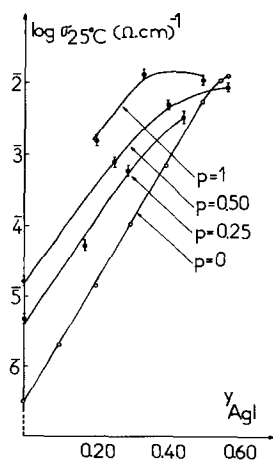


FIG. 3. Variation of $\log \sigma_{25^\circ\text{C}}$ vs y for the $(\text{AgPO}_3 - p\text{Ag}_2\text{S})_{1-y}(\text{AgI})_y$ glasses corresponding to constant p values.

Whatever the value of p provided $p \leq 0.50$, $\log \sigma_{25^\circ\text{C}}$ increases at rising y and a maximum of conductivity, to which is associated a minimum of activation energy, seems to be observed for glasses with a AgI mole concentration close to 0.57. When $p = 1$, $\log \sigma_{25^\circ\text{C}}$ is maximum already for $y = 0.33$. A similar result has been obtained for the $(\text{As}_2\text{S}_3 - p\text{Ag}_2\text{S})_{1-y}(\text{AgI})_y$ and $(\text{Sb}_2\text{S}_3 - p\text{Ag}_2\text{S})_{1-y}(\text{AgI})_y$ glasses (3).

On the other hand, one can note that variations of transport properties are lower and become lower as p and y increase and that the width of the domain characterized by a linear composition dependence of $\log \sigma_{25^\circ\text{C}}$ becomes smaller when p increases: $p = 0$, $y \leq 0.50$; $p = 0.50$, $y \leq 0.25$.

The influence of the introduction of Ag_2S can be investigated by plotting $\log \sigma_{25^\circ\text{C}}$ for different glasses of compositions $(\text{AgPO}_3 - q\text{AgI})_{1-z}(\text{Ag}_2\text{S})_z$ as a function of z ($q = \text{fixed}$) (Fig. 4). Whatever the value of q , it seems that $\log \sigma_{25^\circ\text{C}}$ increases quasi-linearly with z . However, it may be noted that the glasses contain only low Ag_2S mole concentrations ($z_{\text{Ag}_2\text{S}} \leq 0.40$).

As the introduction of Ag_2S and AgI into an AgPO_3 glass involves an enhancement of the electrical properties, we were interested to study the series $(\text{AgPO}_3)_{1-x}(\text{Ag}_3\text{SI})_x$. Figure 5 gives the variation of $\log \sigma_{25^\circ\text{C}}$ as a function of x for the $(\text{AgPO}_3)_{1-x}(\text{AgI})_x$, $(\text{AgPO}_3)_{1-x}(\text{Ag}_2\text{S})_x$, and $(\text{AgPO}_3)_{1-x}(\text{Ag}_3\text{SI})_x$ glasses. At a given value of x , the $(\text{AgPO}_3)_{1-x}(\text{Ag}_3\text{SI})_x$ glasses have the highest conductivity. On the other hand, contrary to $(\text{AgPO}_3)_{1-x}(\text{AgI})_x$ and $(\text{AgPO}_3)_{1-x}(\text{Ag}_2\text{S})_x$, the $(\text{AgPO}_3)_{1-x}(\text{Ag}_3\text{SI})_x$ glasses do not seem to show a linear dependence of $\log \sigma_{25^\circ\text{C}}$ with x when x increases.

It must be pointed out, however, that the introduction of x_{AgI} , $x_{\text{Ag}_2\text{S}}$, and $x_{\text{Ag}_3\text{SI}}$ into AgPO_3 involves, respectively, the contribution of x_{Ag^+} , $2x_{\text{Ag}^+}$, and $3x_{\text{Ag}^+}$ ions. We have plotted in Fig. 5 the variation of $\log \sigma_{25^\circ\text{C}}$ as a function of $x_{\text{AgS}_{0.5}}$ and $x_{\text{AgS}_{0.33}\text{I}_{0.33}}$, respectively, for the glasses $(\text{AgPO}_3)_{1-x}(\text{AgS}_{0.5})_x$

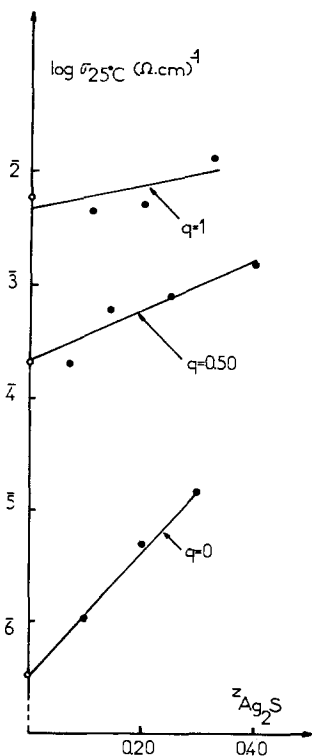


FIG. 4. Variation of $\log \sigma_{25^\circ\text{C}}$ vs z for the $(\text{AgPO}_3 - q \text{AgI})_{1-x}(\text{Ag}_2\text{S})_x$ glasses corresponding to constant q values.

and $(\text{AgPO}_3)_{1-x}(\text{AgS}_{0.33}\text{I}_{0.33})_x$: for the same amount of Ag^+ ions introduced into AgPO_3 , the $(\text{AgPO}_3)_{1-x}(\text{AgI})_x$ glasses display the best conductivity.

The influence of the anionic substitution $\text{S}^{2-} = 2\text{I}^-$ on the electrical properties of glasses of the $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ system has been determined by plotting $\log \sigma_{25^\circ\text{C}}$ as a function of the ratio $r = \text{AgS}_{0.5}/(\text{AgS}_{0.5} + \text{AgI}) = \alpha/(\alpha + \beta)$ in the glasses $(\text{AgS}_{0.5})_\alpha(\text{AgI})_\beta(\text{AgPO}_3)_\gamma$ ($\alpha + \beta + \gamma = 1$) corresponding to different fixed values of γ (Fig. 6). Whatever the value of γ , the variation of $\log \sigma_{25^\circ\text{C}}$ as a function of r is quasi-linear. For high AgPO_3 rates ($\gamma \geq 0.40$), $\log \sigma_{25^\circ\text{C}}$ decreases when r increases; the experimental points for given γ values are located on

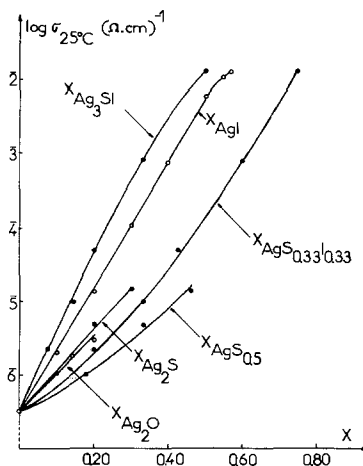


FIG. 5. Variation of $\log \sigma_{25^\circ\text{C}}$ as a function of x for the $(\text{AgPO}_3)_{1-x}(\text{AgI})_x$ [2], $(\text{AgPO}_3)_{1-x}(\text{Ag}_2\text{S})_x$ [1], $(\text{AgPO}_3)_{1-x}(\text{Ag}_3\text{SI})_x$, $(\text{AgPO}_3)_{1-x}(\text{AgS}_{0.5})_x$, $(\text{AgPO}_3)_{1-x}(\text{AgS}_{0.33}\text{I}_{0.33})_x$, and $(\text{AgPO}_3)_{1-x}(\text{Ag}_2\text{O})_x$ [4] glasses.

quasi-parallel lines. For low AgPO_3 mole concentrations ($\gamma \leq 0.40$) the electrical properties of glasses are independent of the value of r .

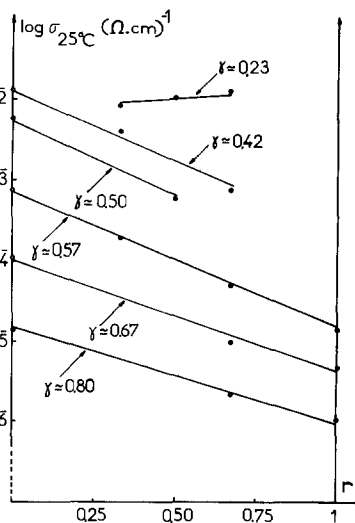


FIG. 6. Variation of $\log \sigma_{25^\circ\text{C}}$ as a function of $r = \text{AgS}_{0.5}/(\text{AgS}_{0.5} + \text{AgI})$ for the $(\text{AgS}_{0.5})_\alpha(\text{AgI})_\beta(\text{AgPO}_3)_\gamma$ glasses.

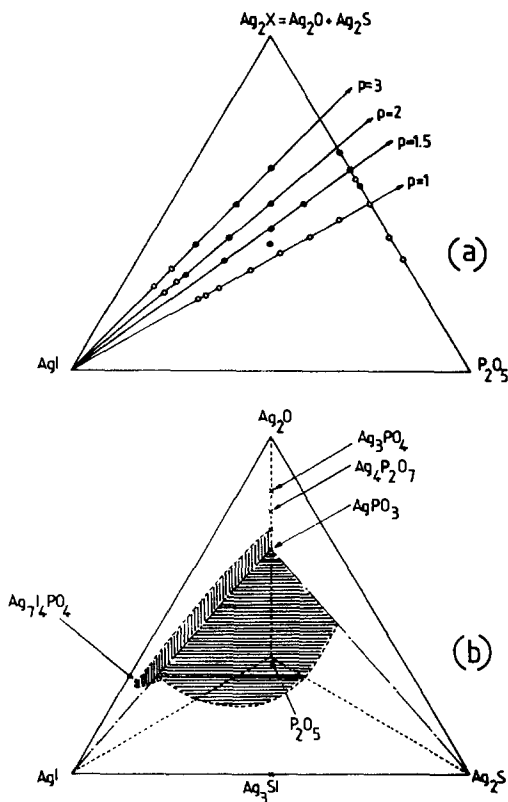


FIG. 7. (a) Points representative of the $\text{P}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$ and $\text{P}_2\text{O}_5\text{-(Ag}_2\text{O + Ag}_2\text{S)-AgI}$ glasses in the equilateral triangle whose apexes correspond to P_2O_5 , Ag_2X ($\text{X} = \text{O, S}$), and AgI . (b) Spatial view of the vitreous domain shown in the quaternary $\text{P}_2\text{O}_5\text{-Ag}_2\text{O-Ag}_2\text{S-AgI}$ system.

V. Comparison of the Electrical Properties of the $\text{AgPO}_3\text{-Ag}_2\text{O-AgI}$ and $\text{AgPO}_3\text{-Ag}_2\text{S-AgI}$ Glasses

Infrared absorption investigations of the $\text{Ag}_2\text{S-AgPO}_3$ glasses have shown the large structural analogy of these materials with the $\text{Ag}_2\text{O-AgPO}_3$ glasses (1). On the other hand, the composition dependence of $\log \sigma_{25^\circ\text{C}}$ for the glasses $(\text{AgPO}_3)_{1-x}(\text{Ag}_2\text{S})_x$ and $(\text{AgPO}_3)_{1-x}(\text{Ag}_2\text{O})_x$ (4), given in Fig. 5, shows that the electrical performance of both series are very close. Such a result can be extended to glasses involving a high content of AgI .

Let us compare, for instance, $\log \sigma_{25^\circ\text{C}}$ for both glasses:

(i) $(\text{AgPO}_3)_{28.6}(\text{Ag}_2\text{S})_{14.3}(\text{AgI})_{57.1}$, the composition of which can be written:

$$(\text{P}_2\text{O}_5)_{14.3}(\text{Ag}_2\text{O})_{14.3}(\text{Ag}_2\text{S})_{14.3}(\text{AgI})_{57.1}$$

$$[\log \sigma_{25^\circ\text{C}} = \bar{3}.94 \Omega^{-1} \text{cm}^{-1}].$$

(ii) $(\text{P}_2\text{O}_5)_{14.3}(\text{Ag}_2\text{O})_{28.6}(\text{AgI})_{57.1}$ [$\log \sigma_{25^\circ\text{C}} = \bar{3}.89 \Omega^{-1} \text{cm}^{-1}$].

These materials which involve the same AgI mole concentration and the same P_2O_5 mole concentration have very close values of $\log \sigma_{25^\circ\text{C}}$.

As Ag_2S and Ag_2O seem to play similar roles in the P_2O_5 -based glasses, we have located within the equilateral triangle, the apexes of which represent P_2O_5 , Ag_2X ($\text{X} = \text{O, S}$), and AgI (Fig. 7a), points representing a large number of glasses belonging to the

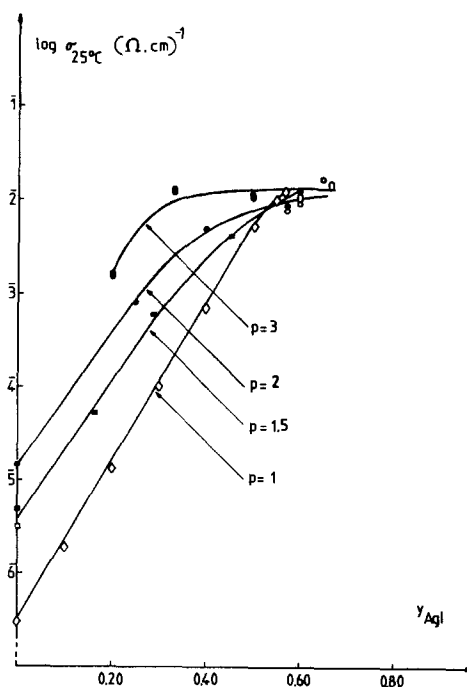


FIG. 8. Variation of $\log \sigma_{25^\circ\text{C}}$ vs y for the $[\text{P}_2\text{O}_5 - p(\text{Ag}_2\text{O} + \text{Ag}_2\text{S})]_{1-y}[\text{AgI}]_y$ glasses corresponding to constant p values. (The points noted \diamond , \square , \circ , \emptyset correspond to oxide glasses ($\text{X} = \text{O}$); the points noted \blacklozenge , \blacksquare , \bullet , \bullet correspond to sulfoxide glasses ($\text{X} = \text{O, S}$)).

P_2O_5 - Ag_2O - AgI (2, 4, 5) or P_2O_5 -(Ag_2O + Ag_2S)- AgI systems. All these materials seem to belong to the same family of glasses whose spatial view is given in Fig. 7b.

Figure 8 gives the variation of $\log \sigma_{25^\circ C}$ as a function of y (with p fixed) for the $[P_2O_5 - p(Ag_2O + Ag_2S)]_{1-y}[AgI]_y$ glasses. Whatever the value of p , $\log \sigma_{25^\circ C}$ increases when y increases and an identical upper limit value, $(\log \sigma_{25^\circ C})_{lim} \approx 2.10 \Omega^{-1} cm^{-1}$, seems to be observed when $y = 0.67$, independently of the nature of the additive Ag_2X , Ag_2O , or $(Ag_2O + Ag_2S)$. This conductivity maximum is very close to that of the crystallized material $Ag_7I_4PO_4$ (6) ($\log \sigma_{25^\circ C} \approx 2.28 \Omega^{-1} cm^{-1}$) which contains the same AgI rate: $(P_2O_5)_{8.33}(Ag_2O)_{25}(AgI)_{66.67}$.

On the other hand, the variations of $\log \sigma_{25^\circ C}$ become weaker as the p and y parameters increase. It may be pointed out that the variation of $\log \sigma_{25^\circ C}$ is linear only for some

particular values of p ($1 \approx p \approx 2$) and for $y < y_1$; y_1 becomes smaller and smaller when p increases: $p = 1$, $y_1 \approx 0.50$; $p = 2$, $y_1 \approx 0.25$. An analogous result had been obtained for the glasses $(As_2S_3 - pAg_2S)_{1-y}(AgI)_y$ and $(Sb_2S_3 - pAg_2S)_{1-y}(AgI)_y$ (3).

References

1. LIU JUN, J. PORTIER, B. TANGUY, J. J. VIDEAU, AND C. A. ANGELL, *Solid State Ionics* **34**, 87 (1989).
2. J. P. MALUGANI, G. ROBERT, AND R. MERCIER, *Mater. Res. Bull.* **15**, 715 (1980).
3. J. M. REAU, B. TANGUY, J. J. VIDEAU, J. PORTIER, AND P. HAGENMULLER, *Solid State Ionics* **28-30**, 792 (1988).
4. A. MAGISTRIS, G. CHIODELLI, AND M. DUCLOT, *Solid State Ionics* **9-10**, 611 (1983).
5. T. MINAMI AND M. TANAKA, *Rev. Chim. Miner.* **16**, 283 (1979).
6. T. TAKAHASHI, S. IKEDA, AND O. YAMAMOTO, *J. Electrochem. Soc.* **119**, 477 (1972).