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FIC glasses based upon AgI-TlI eutectic

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Abstract.

New vitreous conductors, shown in the $\text{TeO}_2\text{-Tl}_2\text{O-AgI}$ system, are described. The ionic conductivity in these glasses increases with the AgI content. Structure consists of a covalent $\text{TeO}_2\text{-Tl}_2\text{O}$ network and a AgI sublattice with only a weak interaction between them.

The AgI-TlI system offers a deep eutectic for the $(\text{AgI})_{0.75}(\text{TlI})_{0.25}$ composition with a melting point at 220°C . This favourable medium has been selected to prepare new silver FIC glasses. So, glasses belonging to the pseudo quaternary $\text{TeO}_2\text{-Tl}_2\text{O-AgI-TlI}$ system have been elaborated : the study of transport properties of $[\text{TeO}_2\text{-TlO}_{0.5}]_{1-x} [(\text{AgI})_{0.75}(\text{TlI})_{0.25}]_x$ glasses has shown a very high ionic conductivity for $x \approx 0.82$: $\sigma_{25^\circ\text{C}} \approx 3.5 \cdot 10^{-2} (\Omega.\text{cm})^{-1}$. The influence of the Tl^+ ions presence on the Ag^+ ions mobility is discussed.

1-Introduction.

Since the discovery in 1973 of fast silver ionic conductivity in the $\text{SeO}_2\text{-Ag}_2\text{O-AgI}$ glasses by Kunze [1], many silver iodide - silver oxy-anions systems have been studied and have allowed to elaborate FIC Ag-glasses with a high electrical conductivity [2]. It has been found that in almost all systems studied the conductivity increases with the silver iodide content. Consequently, it is attracting to look for new means for synthesizing Ag-glasses containing the highest possible AgI content. One efficient process is the using of hyperquenching methods; FIC glasses have been so prepared in the $\text{M}_2\text{S}_3\text{-Ag}_2\text{S-AgI}$ ($\text{M} = \text{As}, \text{Sb}$) systems [3] : a conductivity of $2 \cdot 10^{-2} (\Omega.\text{cm})^{-1}$ is observed for the

material of composition close to $(As_2S_3)_3(Ag_3SI)_{97}$.

Another way consists in using the classical methods but with an eutectic iodide mixture instead of AgI. Indeed, it is well known that glasses are easily obtained by quenching liquid mixtures with a composition corresponding to a deep eutectic. Such an eutectic is formed between AgI ($T_m = 558^\circ C$) and TlI ($T_m = 440^\circ C$) for the composition $(AgI)_{0.75}(TlI)_{0.25}$ ($T_m = 202^\circ C$) [4]. Melting of this eutectic mixture with silver or thallium oxysalts (borate, phosphate, tungstate, molybdate, tellurate...) could allow to elaborate new FIC Ag-glasses. In this paper we describe some results obtained in the pseudo quaternary TeO_2 - Tl_2O -AgI-TlI system.

2-Experimental.

The glasses are prepared from mixtures of AgI, TlI, TeO_2 and Tl_2TeO_3 . AgI, TlI and TeO_2 are commercial products (Aldrich, 99% purity). Thallium tellurate is prepared by heating a stoichiometric mixture of TeO_2 and Tl_2CO_3 (Aldrich, 99% purity) at $450^\circ C$ under argon.

The appropriate mixtures of iodides and oxides are melted in an open silica tube at $400^\circ C$. The liquid is quickly quenched by using the "anvil and hammer" process in a cylindric mould. In these experimental conditions, glasses of ≈ 1.5 mm thickness have been obtained.

The specific mass of samples studied has been determined by Archimedes' method, the glass transition temperatures by differential scanning calorimetry with a DSC 92 Model Setaram instrument.

The conductivity measurements have been performed by the complex impedance method using a 1260 Solartron frequency response analyser, frequencies varying from 32 MHz to 10^{-2} Hz. Gold electrodes were deposited by evaporation on both sides of the pellets.

3-Results and Discussion.

The studied glasses in the quaternary TeO_2 - Tl_2O -AgI-TlI system corresponding to the $TeO_2/Tl_2O_{0.5}$ ratio equal to 1 can be formulated : $[TeO_2-Tl_2O_{0.5}]_{(1-x)}[(AgI)_\alpha(TlI)_{1-\alpha}]_x$. Fig.1 gives the glassy domains at room temperature corresponding to $\alpha = 1$ and $\alpha = 0.75$. Comparison of both domains shows that using of the eutectic $(AgI)_{0.75}(TlI)_{0.25}$ mixture involves the existence of a much wider glassy field and the formation of glasses with higher AgI contents.

Values of specific mass and T_g are gathered in Table 1. A large

$$\alpha = 1$$

$$\alpha = 0.75$$

Fig.1 -Limits at room temperature of glassy domains for the glasses of $[\text{TeO}_2\text{-TlO}_{0.5}]_{(1-x)}[(\text{AgI})_\alpha(\text{TlI})_{1-\alpha}]_x$ composition.

Table 1

Values of specific mass and T_g for some glasses.

α	x	T_g ($^{\circ}\text{C}$)	ρ (g/cm^3)	α	x	T_g ($^{\circ}\text{C}$)	ρ (g/cm^3)
1	0	132	7.04	0.75	0.10	115	6.77
1	0.20	105	6.70	0.75	0.25	98	6.65
1	0.43	80	6.56	0.75	0.65	75	6.57
				0.75	0.82	50	6.38

decrease of T_g is observed when x increases for glasses relative to $\alpha = 0,75$ and a value of 50°C only is shown for the glass limit ($x = 0.82$). The samples corresponding to $x > 0.82$ have a paste state. One can hope that the ($x = 0.82$) limit reached at room temperature could be higher at lower temperature.

The transport number has been measured by an EMF method using the following electrochemical chain $(-)\text{Ag}/\text{Ag-glass electrolyte}/\text{C}, \text{I}_2(+)$. The thermodynamical potential of this cell is $E_{\text{th.}} = 0.687 \text{ V.}$ at 20°C and corresponds to the overall potential of $\text{Ag} + \frac{1}{2} \text{I}_2 \rightarrow \text{AgI}$. The results obtained for some compositions ($E_{\text{meas.}} = 0.682 \text{ V.}$) show that the transport number of the Ag^+ ions is close to 1.

Fig.2 gives the conductivity variation as a function of $(\alpha x)_{\text{AgI}}$ for the (1) and (2) series of materials relative to $\alpha = 1$ and $\alpha = 0.75$ respectively and, by title of comparison for the (3) series of $[\text{TeO}_2\text{-TlO}_{0.5}]_{0.57}[(\text{AgI})_\alpha(\text{TlI})_{1-\alpha}]_{0.43}$ ($0 \leq \alpha \leq 1$) composition.

Fig.2 -Variation of $\log \sigma_{25^{\circ}\text{C}}$ as a function of (αx)AgI content.

For $(\alpha x)_{\text{AgI}} \lesssim 0.18$, the curves relative to three series of materials are very close. For $(\alpha x)_{\text{AgI}} \gtrsim 0.18$, on the contrary, the TlI-glasses relative to a same $(x)_{\text{AgI}}$ value have a better conductivity.

An I.R. spectroscopy investigation of these glasses shows that the Te-O vibrational frequencies are identical to those of the $\text{Tl}_2\text{Te}_2\text{O}_5$ basic glass; consequently, the AgI or (AgI,TlI) iodides and the thallium tellurate (IV) seem to constitute both sublattices with weak interactions only between them. On the other hand, studies of glasses recrystallisation show always the presence of $\text{Tl}_2\text{Te}_2\text{O}_5$ and AgI (or AgI + TlI) and never the formation of silver tellurate.

The electrical properties of the (1) and (3) series glasses corresponding to $(\alpha x)_{\text{AgI}} \lesssim 0.18$ are very close. The replacement of tellurate sublattice by TlI has consequently no influence on conductivity in this composition domain involving small AgI amounts.

For $(\alpha x)_{\text{AgI}} \gtrsim 0.18$ ($\alpha \gtrsim 0.42$), conductivity is higher for the (3) serie glass than for the (1) serie glass and the ratio of conductivities $\sigma_{(3\text{-glass})} / \sigma_{(1\text{-glass})}$ is maximum when α is close to 0.75, value corresponding to the eutectic iodide mixture. The presence of the (AgI, TlI) sublattice could involve the existence of wider "bottlenecks" and a larger mobility for the Ag^+ ions, the more favourable conditions corresponding to $\alpha \approx 0.75$.

Let us compare now conductivities of glasses involving identical values of $(\alpha x)_{\text{AgI}}$ in three series of materials. For $(\alpha x)_{\text{AgI}} \lesssim 0.32$, compositions of the (2) series glasses are intermediate between these of the (1) and (3) series ones. The electrical properties of three series of materials are consequently very close in the composition domain relative to $(\alpha x)_{\text{AgI}} \lesssim 0.18$. For $0.18 \lesssim (\alpha x)_{\text{AgI}} \lesssim 0.32$, conductivities of the (2) and (3) series glasses are similar and higher than that of the (1) series glass. Consequently, the presence of a very small amount of TlI next to AgI is enough to enhance conductivity.

Beyond $(\alpha x)_{\text{AgI}}$ equal to 0.32, conductivity and TlI percentage are higher in glasses of the (2) series than in those of the (3) series : the replacement of thallium tellurate (IV) by TlI involves consequently an enhancement of conductivity, when the AgI percentage is high enough [$(\alpha x)_{\text{AgI}} \gtrsim 0.18$] (Fig.2).

On the other hand, using of the eutectic iodide mixture allows to un-
large the glass domain, to grow the $(\alpha x)_{\text{AgI}}$ content up to 0.62 and to obtain so materials with very high electrical performance :

$\sigma_{25^\circ\text{C}} \approx 3.5 \cdot 10^{-2} (\Omega.\text{cm})^{-1}$ for the $[\text{TeO}_2\text{-TlO}_{0.5}]_{0.18}[\text{AgI}]_{0.62}[\text{TlI}]_{0.20}$ glass.

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