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NEW SILVER TELLURITE GLASSES

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The glass forming ranges in the TeO_2-$AgO_{0.5}$ and TeO_2-$AgO_{0.5}$-AgI systems have been assessed for two cooling rates; results based on heat capacity and electrical conductivity measurements as well as derived from infrared spectroscopy are presented. The ternary glasses are excellent conductors due to the presence of Ag^+ ions mainly supplied by AgI. The decrease in ΔC_p with increasing AgI-content suggests the presence of AgI microdomains which are finely distributed and do not contribute to the configurational heat capacity change. Fast motion of Ag^+ ions (low activation energy) occurs in the glassy matrix which shows slow structural relaxation (high activation barrier).

Keywords: silver tellurite glasses

Introduction

Tellurite glasses have interesting properties, such as low working temperature, high refractive index and optical transmission in the infrared (IR) region. The addition of Ag^+ may confer them also excellent electrical conductivities.

The existence of binary TeO_2-$AgO_{0.5}$ glasses has already been signaled [1, 2], but no ternary ones containing $AgO_{0.5}$ and AgI have yet been elaborated. In fact, α-AgI attains the highest conductivity value known to date ($1\Omega^{-1}$ cm^{-1}). It is the aim of the present investigation to elaborate new tellurite glasses displaying high conductivities.

Several models have already been proposed in order to explain the conduction processes in fast ion conducting glasses, either on a macroscopic or a microscopic level.

The diffusion-path model introduced by Minami [3] claims the presence of two types of Ag^+ ions in AgI-doped glasses, mobile ones essentially bound to I^-

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Table 1

Glass	$AgO_{0.5}$	Mole fraction			T_g/°C	T_f/°C	ΔH / eV	ΔE_σ / eV	Δc_p / J g^{-1}· K^{-1}	c_p / J g^{-1}· K^{-1}	
number	TeO_2	TeO_2	$AgO_{0.5}$	AgI						meas.	calc.
1	0.22	0.82	0.18	–	259						
					260.5						
2	0.35	0.74	0.26	–	237						
					238.5						
					239.5						
3	0.50	0.66	0.33	–	212.5			0.756			
					213						
4					198						
	0.66	0.60	0.40	–	201.5			0.635			
					203					110°C	
5	0.86	0.54	0.46	–	177	179.6	7.7	0.522	0.23	0.393	
					177						
6	1	0.50	0.50	–	160						
					162.5						
					163.5						

Table 1 (continued)

Glass	$AgO_{0.5}$	Mole fraction			T_g/°C	T_f/°C	ΔH / eV	ΔE_σ / eV	Δc_p / J g^{-1} K^{-1}	c_p / J g^{-1} K^{-1}	
number	TeO_2	TeO_2	$AgO_{0.5}$	AgI						meas.	calc.
7		0.486	0.414	0.10		163.6	7.0		0.215	0.380	0.376
						165.5			0.22		
8		0.430	0.370	0.20		141.7	6.5		0.19	0.353	0.362
						142.6			0.195		
9	0.86	0.378	0.322	0.30		130.1					
						132.5	5.9		0.165	0.347	0.348
						135.4			0.17	60°C	
10	0.86	0.324	0.276	0.40		91.2			0.15		
						95.4	4.7		0.15	0.320	0.315
11		0.322	0.428	0.25				0.420			
12		0.270	0.360	0.37				0.360			
13	1.33	0.240	0.320	0.44				0.354			
14		0.185	0.245	0.57				0.327			
15		0.146	0.194	0.66				0.295			

ions, and relatively immobile ones linked to the matrix. The high conductivity of AgI-$AgPO_3$ glasses, e.g., is attributed to the fast diffusion of Ag^+ ions via site percolation within microdomains of α-AgI approximately 2nm in size, distributed in a less conducting rigid matrix of $AgPO_3$ chains [4, 5]. The presence of amorphous AgI clusters embedded into voids of the host glass network was also suggested [6, 7].

According to a recent by-pass model [8], on the contrary, it is the residual liquid surrounding ordered microdomains that provides favoured pathways for ion migration. In the case of AgI-$AgPO_3$ glasses, a connective tissue made of essentially disordered amorphous AgI is supposed to surround $(PO_3)_{**}$ chain microdomains [9].

Experimental

Several glasses have been prepared using TeO_2, Ag_2TeO_3 and AgI as starting materials; Ag_2O must be avoided owing to its thermal instability. Paratellurite TeO_2 and β-AgI were of commercial purity (99.8%). Ag_2TeO_3 was obtained in aqueous solution according to the reaction

$$2AgNO_3+K_2TeO_3 \rightarrow Ag_2TeO_3+2KNO_3$$

The precipitate was washed, dried in vacuo at 200°C and analysed by X-rays.

After grinding, selected proportions of the powders were filled into an open silica tube and homogenised for 12 h at 800°C, which is at least 50°C above the liquidus for the whole system. Then the liquid was rapidly quenched by flattening it out between two blocks of copper which can be separated by rings. This technique yields either irregular plates 0.3 to 0.5 mm thick or short cylinders according to the ring dimensions. In the first case, the cooling rate is of the order of 10^4 deg/s, whereas in the second case, it diminishes with increasing thickness. In general, the ring dimension was chosen to be 15 mm in diameter and 1 mm high. Finally, the vitreous samples were annealed for 12 h 20°C below their respective glass transition temperatures.

Table 1 gives the mole fractions of some binary and ternary glasses investigated, as well as the ratio $R=AgO_{0.5}/TeO_2$. The compositions were ascertained by weighing before and after the fabrication. The samples were transparent and of yellow colour; they turned reddish with increasing $AgO_{0.5}$ content. In general glasses were prepared twice in order to test the reproducibility of the results. No crystalline phases could be detected by X-ray diffraction.

Specimens of less than 100 mg were used for DSC-measurments with the help of a Perkin-Elmer analyser, model 4; they were mainly prepared by slow quenching. They were first subjected to heating into the supercooled liquid region followed by cooling, both at 20 deg/min. During this cycle the sample adopted a firm position within the platinum crucible. Then its transition temperatures (glass transition T_g, crystallisation T_x) were determined during reheating at 20deg/min, from the intersection given by the steepest tangents on the curves recorded during the transition and the extrapolation of the curves before the transition.

In the case of ternary compositions, the fictive temperatures T_f and the heat capacities c_p were assessed; the uncertainty in c_p is of the order of 1–2%.

Following Moynihan *et al.* [10], the glasses were cooled at different rates (ranging from 0.5 to 20 deg/min), and the subsequent heating was recorded invariably at the same rate (20 deg/min) so that T_f is only dependent on cooling rate. The glasses were in general cycled in a temperature interval lying 50°C below and above T_f. A computer program allowed the calculation of T_f from the experimental curves considering that

$$\int_{T_1}^{T_2} (c_p - c_p^g)\,\mathrm{d}T = \int_{T_f}^{T_2} (c_p^l - c_p^g)\,\mathrm{d}T$$

T_1 is any temperature below and T_2, any temperature above the transition region for which the heat capacity values of the glasses (c_p^g) and the supercooled liquids (c_p^l) show no dependence on prior cooling rate.

The variation of T_f (in K) with cooling rate v permits the determination of a mean activation enthalpy ΔH for structural relaxation according to $\mathrm{d}\ln v/\mathrm{d}(1/T_f) = -\Delta H/R$. This Arrhenius equation is only valid for small temperature intervals and intermediate cooling rates [11, 12].

It was observed that the two AgI-richest compositions (glasses n°9 and 10) begin to crystallise at cooling rates less than 1 deg/min.

Two sorts of electrical measurements were performed on the glasses. The cation transport number was determined from the e.m.f. of the following electrochemical cell

$$^{-}\mathrm{Ag/Ag^+}\ \text{conducting glass}/\mathrm{I_2+C^+}$$

involving the reaction $\mathrm{Ag_{(s)}+1/2I_{2(s)} \rightarrow AgI_{(s)}}$ whose theorectical e.m.f. is equal to 0.687 V at 25°C. The transport number is simply the ratio of the experimental e.m.f. to the theorectical one. A Keithley multimeter having an impedance of $10^{14}\ \Omega$ was employed. Besides, electrical conductivity studies were carried out using complex impedance measurements after having deposited gold electrodes using complex impedance measurements after having deposited gold electrodes onto the sample surfaces. A Solartron apparatus was used in the frequency range 10^{-2}–10^{4} Hz.

The infrared absorption spectra were recorded between 1500 and 800 cm^{-1} with the help of a Perkin-Elmer spectrophotometer. The specimens prepared by rapid quenching were in suspension in nujol and placed between two CsI disks.

Results

1. Glass formation ranges

Figure 1 shows the ratios R=$AgO_{0.5}$/TeO_2 of the glasses investigated and delimits the vitreous domains in the $AgO_{0.5}$-TeO_2-AgI system according to the two quenching techniques. Only the formation of AgI-rich glasses does not depend sensibly on the cooling rates employed. In the binary system $AgO_{0.5}$–TeO_2, glasses appear at either side of the eutectic formed between Ag_2TeO_3 ($xAgO_{0.5}$=0.66) and TeO_2, and over a much larger range than was signaled previously by Mochida [1]. Pure paratellurite could not be obtained in a vitreous state up to rates of 10^4 deg/s, contrary to Lambson *et al.* [13] who used alumina crucibles.

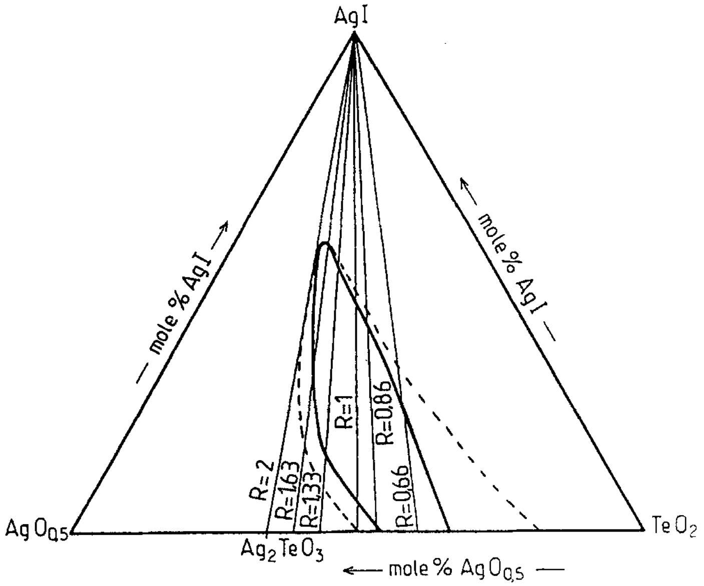

Fig. 1 The glass forming region in the system TeO_2–$AgO_{0.5}$–AgI

2. *DSC studies*

All binary glasses were heated to 420°C, the eutectic temperature being 437°C. Figure 2 represents the heat flow curve obtained on the $0.66TeO_2$–$0.33AgO_{0.5}$ composition: the glass transition is followed by crystallisation and by two small, non identified effects. Reheating of the crystallised sample shows normal behaviour. A rise of the $AgO_{0.5}$ content leads to more complicated curves with two crystallisation peaks; the glass transition temperatures drop as indicated in Table 1.

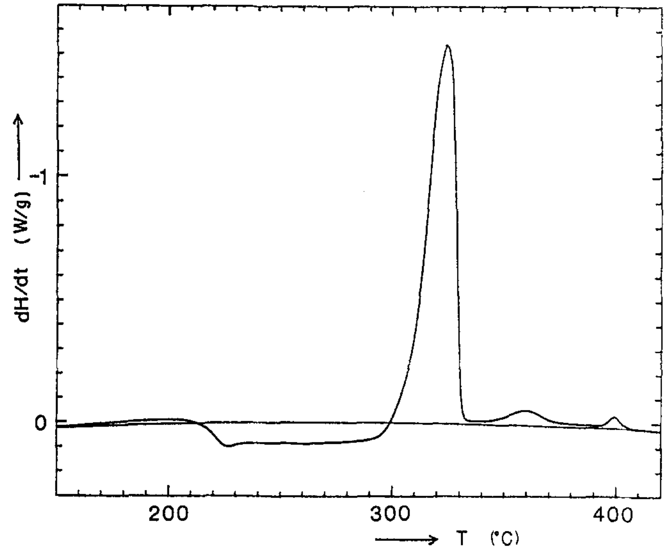

Fig. 2 DSC curves, at 20 deg/min, of vitreous and crystallised sample n°3

The ternary glasses undergo several transformations during heating up to the liquid state at 600°C. The β-α transition of AgI around 147°C is absent (Figs 3 and 4, e.g.).

Heating and cooling cycles were performed in order to derive values for the mean activation enthalpy accompanying structural relaxation. Examples are given in Figs 3–5 for the $(0.54TeO_2$–$0.46AgO_{0.5})_{1-x}AgI_x$ glasses, x being 0, 0.2 and 0.4, respectively. The fictive temperatures obtained after cooling at 20 deg/min are listed in Table 1 along with the activation enthalpies and the heat capacity differences between the vitreous and supercooled liquid states taken at the fictive temperature. T_f (±2°C), ΔH (±0.5 eV) and Δc_p (±0.005 J/gK) are seen to decrease with rise in AgI. A comparison of the curves recorded after cooling at the same rates (1, 5 or 20 deg/min) shows that the overshoot in the Δc_p-values diminishes strongly with increasing AgI content c_p-values measured experimentally and calculated by use of the additivity rule are also given in Table 1, they differ by 1–2%. The value for the binary glass (n°5) was determined precisely, as it entered the calculation along with the literature value for AgI [14]. Any differences in c_p due to the quenching method were not significant.

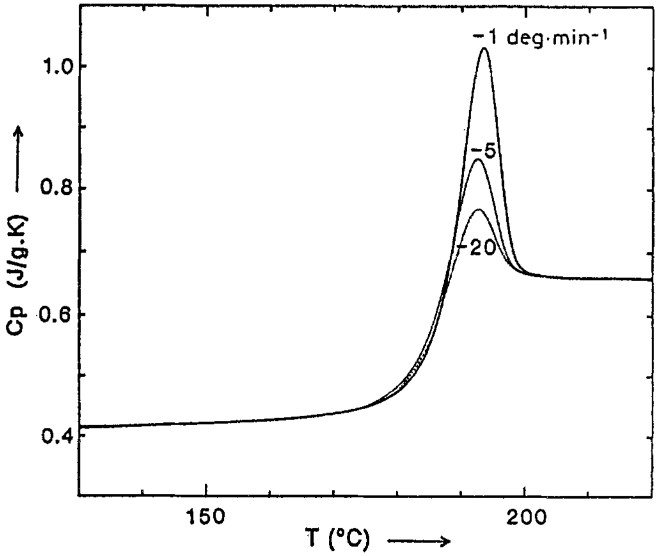

Fig. 3 DSC curves obtained during heating, at 20 deg/min, glass n°5 after cooling at the rates indicated

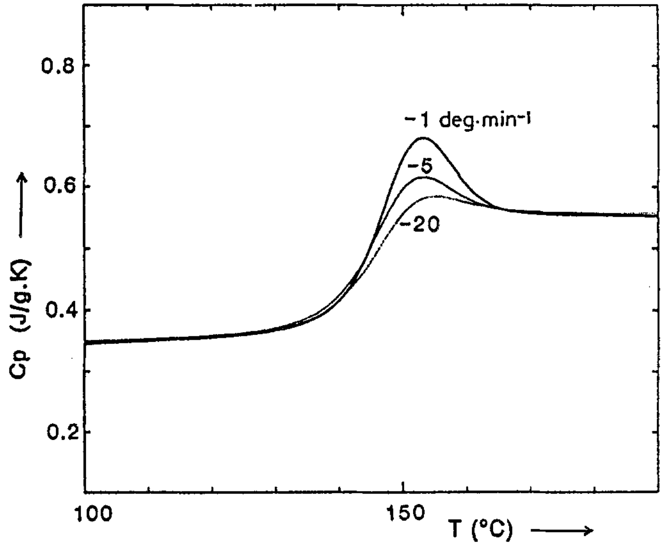

Fig. 4 DSC curves obtained during heating, at 20 deg/min, glass n°8 after cooling at the rates indicated

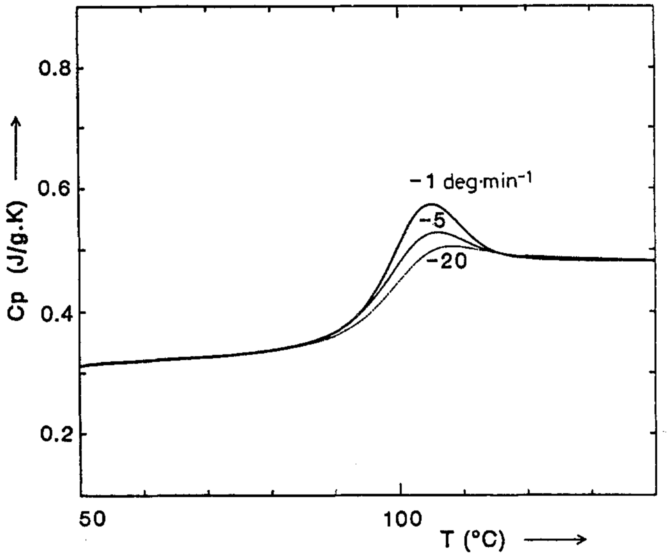

Fig. 5 DSC curves obtained during heating, at 20 deg/min, glass n°10 after cooling at the rates indicated

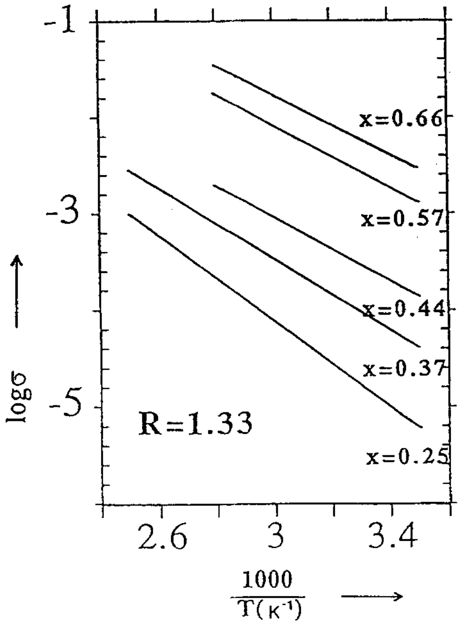

Fig. 6 Plot of electrical conductivity *vs.* inverse of temperature for the glasses n°11–15

3. Electrical measurements

Determinations of the transport numbers confirms that the electrical conductivity in the ternary glasses is essentially due to the Ag^+ ion.

Below T_g, the variation of the logarithm of electrical conductivity with inverse of absolute temperature yields straight lines like those in Fig. 6 for the $(0.43TeO_2–0.57AgO_{0.5})_{1-x}$ AgI_x glasses (n°11–15). They may be represented by an Arrhenius relationship $\sigma = \sigma_o \exp(-\Delta E_\sigma / kT)$, ΔE_σ being the activation energy for the motion of the Ag^+ ions. This energy decreases with increasing AgI content (Table 1), parallel to the strong increase of the σ-values.

4. Infrared spectroscopy

Detailed spectra will be published elsewhere and only the most important results are related.

The evolution of the IR spectra characterising the binary glasses shows that the introduction of $AgO_{0.5}$ perturbs the network of pure TeO_2, the coordination number of Te passing progressively from 4 to 3+1 and finally to 3 in case of Ag_2TeO_3. Nonbridging oxygen atoms appear simultaneously. AgI-additions modify only slightly the Te–O network of the binary glasses.

Conclusions

The extension of the glass forming ranges in the TeO_2-$AgO_{0.5}$-AgI system depends on the cooling rate and the $AgO_{0.5}/TeO_2$ ratio. The coordination number of tellurium changes continuously from 4 to 3 by incorporation of silver oxide into the paratellurite network, parallel to the decrease of the glass transition temperature and the increase in the number of nonbridging oxygen atoms. Vitrification becomes more difficult when this last number is either too small or too high. The presence of TeO_3^{2-} ions favorises the apparition of iodide rich glasses which are rather unstable; the glass transition temperatures decrease with increasing AgI and TeO_3^{2-} contents.

According to the IR spectra, the introduction of I-ions does not modify sensibly the Te–O network; there are no important interactions between AgI and the glassy matrix.

DSC measurements show that the heat capacity difference between the vitreous and supercooled liquid states decreases with rise in AgI; a priori this may be caused by an increasing amount of a crystalline phase which does not contribute to the structural relaxation phenomenon. Its distribution must be extremely fine in order to escape detection by X-rays. The neutron diffraction studies of Rousselot *et al.* point to the presence of amorphous clusters containing at least 5-formula AgI-units with a tetracoordination of Ag by halide anions.

Hallbrucker and Johari [5] have already observed that T_g and Δc_p decrease upon addition of AgI to $AgPO_3$ glasses and concluded that configurationally fixed microdomains of α-AgI exist within random chains of $AgPO_3$. As a matter of fact, no β → α transition is observable in DSC-runs.

The activation enthalpies for structural relaxation derived from the DSC measurements are surprisingly high and may not be significative, as the temperature and cooling rate intervals studied are rather restricted. Their trend seems to be correct: ΔE as well as the overshoot in Δc_p decrease with increasing AgI concentration.

The heat capacities of the glasses could not be determined to better than 2% due to a certain instability of the apparatus. If the c_p values are considered to be equal to the molar fraction weighted average of those of the constituents, the differences between experimental and calculated values are also of the order of 1–2%. Estimates based on the Neumann-Kopp rule seem to be quite satifactory for glasses.

The electrical measurements indicate that these new tellurite glasses are fast ion conducting ones due to the Ag^+ ions bound to AgI. The activation energy decreases with increasing AgI content in accord with higher conductivities. The very different activation enthalpy values derived from DSC studies confirm the decoupling of the motion of the conducting ions from those determining the amorphous matrix relaxation. Further studies are in progress in order to elucidate the nature of the AgI microclusters.

* * *

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Zusammenfassung — Für zwei Abkühlgeschwindigkeiten wurden die Glasbildungsintervalle in den zwei Systemen TeO_2-$AgO_{0,5}$ und TeO_2-$AgO_{0,5}$-AgI geschätzt; es werden sowohl die auf der Basis von Messungen der Wärmekapazität und elektrischen Leitfähigkeit als auch die auf der Basis von Infrarotspektroskopie ermittelten Ergebnisse dargelegt. Die ternären Gläser sind wegen der hauptsächlich durch die Anwendung von AgI gegenwärtigen Ag^+-Ionen ausgezeichnete Leiter. Bei zunehmenden AgI-Gehalt weist die sinkende c_p auf die Existenz von fein verteilten AgI-Mikrobereichen hin, die nicht zur konfigurativen Wärmekapazitätsänderung beitragen. In der Glasmatrix mit langsamer Strukturrelaxation (hohe Aktivierungsbarriere) erfolgt eine schnelle Bewegung der Ag^+-Ionen (niedrige Aktivierungsenergie).