

Preparation, characterization and conductivity studies of AgI-Ag₂O-(TeO₂ + P₂O₅) fast ionic conducting glasses

S. JAYASEELAN, N. SATYANARAYANA*

Raman School of Physics, Pondicherry University, Pondicherry 605 014, India

E-mail: nallanis2000@yahoo.com

M. VENKATESWARLU†

Department of Physics, Eswari Engineering College, Chennai 600 089, India

Silverphosphotellurate (SPT) quaternary fast ionic conducting (FIC) glasses of compositions AgI-Ag₂O-[(1-x)P₂O₅ + xTeO₂], x = 0.0 to 1.0 in steps of 0.1, were prepared by melt quenching. All SPT compounds were characterized by X-ray diffraction and the amorphous nature of the samples was confirmed. The structure of all compositions was examined by Fourier Transform Infrared Spectroscopy. The glass transition temperature (T_g) was determined for all SPT samples, using differential scanning calorimetry. Complex impedance measurements were made on all glasses in the frequency range 40 Hz to 100 kHz. Impedance data were analyzed using Boukamp equivalent circuit software and the bulk conductivity was obtained. The highest conductivity ($\sigma = 1.59 \times 10^{-2}$ S/cm) was shown by the composition 60%AgI – 26.67%Ag₂O – 13.33% (0.3P₂O₅ + 0.7TeO₂). © 2004 Kluwer Academic Publishers

1. Introduction

A considerable amount of research has been dedicated in developing various types of new silver based fast ion conducting (FIC) compounds, since these FICs exhibit high conductivity, high stability, etc. at ambient temperatures and hence have potential applications as electrolyte materials in solid state ionic devices such as solid state batteries, capacitors, sensors and fuel cells [1, 2]. It is found that glassy silver fast ion conductors not only have high conductivity but also have other advantages such as ease of preparation over a wide range of compositions, isotropic properties, inertness and high stability compared with their respective crystalline counterparts [1–3]. Thus, many preparative methods such as melt quenching, sol-gel and evaporation have been employed to prepare a variety of silver based binary, ternary and quaternary glassy systems in bulk, powder and thin film forms to obtain high ion conductivity materials at ambient temperatures [1–6]. Recently, it has been found that by mixing two different types of glass formers, higher conductivities and wider glass forming regions could be achieved in silver based FIC glasses [7–9]. This is known as the ‘mixed former effect.’ Also, glasses containing tellurium dioxide (TeO₂) as a glassy network former have potential uses in optical applications because they have very high refractive indices and very good optical transmission from the ultraviolet to

the infrared region [10–12]. Hence, fast ion conducting silver based tellurate glasses not only have potential applications in ionic devices but also in optical devices such as optical switches, fibers and waveguides [10–15]. The present investigation describes the preparation of silverphosphotellurate (SPT) quaternary fast ion conducting glasses with compositions of AgI + Ag₂O + [(1-x)P₂O₅ + xTeO₂], x = 0.0 to 1.0 in steps of 0.1, using the melt quenching technique.

2. Experimental

2.1. Preparation of SPT samples by melt quenching

The melt quenching technique was employed to prepare SPT compounds with two different glass formers: (1-x)P₂O₅ + xTeO₂, x = from 0.0 to 1.0 in steps of 0.1, in the 60%AgI – 26.67 wt%Ag₂O – 13.33 wt% [(1-x)P₂O₅ + xTeO₂] system. For each composition, appropriate quantities of analar grade AgI, Ag₂O, TeO₂ and P₂O₅ chemicals were taken and mixed in an open platinum crucible. Each composition was melted at 600°C for 20 min. During this period, the melt was thoroughly stirred to ensure homogeneous mixing of the constituents. The molten liquid was then quenched into an aluminum vessel immersed in liquid nitrogen to form glass. Using an agate mortar and pestle, all the

*Author to whom all correspondence should be addressed.

† Present address: Department of Chemical Engineering, NTUST, Taipei, Taiwan.

prepared bulk SPT compounds were ground into fine powders, they were stored in a covered box to avoid atmospheric and light effects.

2.2. XRD, IR and DSC measurements

X-ray diffraction (XRD) measurements were carried out on all SPT samples using a Rigaku miniflex diffractometer with $\text{Cu K}\alpha$ radiation [wavelength, $\lambda = 1.5418 \text{ \AA}$] for 2θ values between $10\text{--}80^\circ$ at a scan rate of $20^\circ/\text{min}$. A sample of each composition of SPT was mixed with KBr powder, ground into fine powder under dry conditions and made into a thin transparent pellet using a KBr press. Fourier transform infrared (FTIR) spectra were recorded for all samples using a Shimadzu FTIR-8000 spectrometer in the frequency range $400\text{--}1200 \text{ cm}^{-1}$ with 4 cm^{-1} resolution, auto gain and 40 scans. Using a Mettler Toledo Star^e Differential scanning calorimeter (DSC), a sample of each composition of SPT was heated at $10^\circ\text{C}/\text{min}$ and the glass transition temperature (T_g) was identified.

2.3. Pellet preparation and impedance measurements

By applying $5000 \text{ kg}/\text{cm}^2$ pressure, using a 10 mm die and plunger, all SPT samples were made in to pellets comprising: electrode (SPT 15% + Ag 85%)/SPT glassy electrolyte/electrode (SPT 15% + Ag 85%). The electrode material was made by adding a small quantity of solid electrolyte (15 wt%) to silver powder (85 wt%). The addition of SPT glass to the silver powder improves the interfacial properties [16–18]. Two probe impedance measurements were carried out at ambient temperature on each of the compositions using a Keithely 3330 LCZ meter with in the frequency range 40 Hz to 100 kHz. The electrical conductivity was calculated using the pellet dimensions and the bulk resistance of each SPT sample.

3. Results and discussion

3.1. XRD

Fig. 1 shows the X-ray diffractograms of various former compositions of SPT samples prepared by melt quenching. The XRD spectra show no sharp peaks confirming that all compositions are glassy in nature.

3.2. FTIR

Fig. 2 shows the FTIR spectra recorded at room temperature (300 K) for various compositions of SPT samples. For all the observed IR bands, assignments were made on the basis of reported values [19–25]. In Fig. 2, the FTIR spectrum for $x = 0.0$, i.e., $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$, showed band positions at 1118 , 908 , and 543 cm^{-1} . The IR peak observed at 1118 cm^{-1} is attributed to the non-bridging oxygen (NBO) symmetric stretching mode (ν_s) of the PO_3^- unit. The observed peak at 908 cm^{-1} is attributed to the asymmetric bending vibration mode of P-O-P in the PO_4^{3-} unit. The peak at 543 cm^{-1} band corresponds to the symmetric bending mode of the P=O-P unit.

The FTIR spectrum for $x = 1.0$, i.e., $\text{AgI-Ag}_2\text{O-TeO}_2$, shows band positions at 780 , 682 and 451 cm^{-1} .

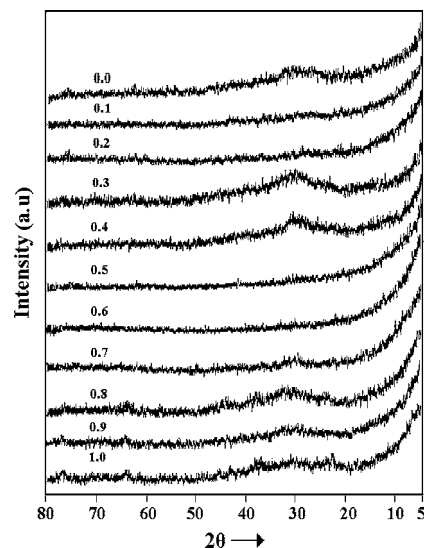


Figure 1 XRD spectra of compositions ($x = 0.0$ to 1.0 in steps of 0.1) of SPT compounds.

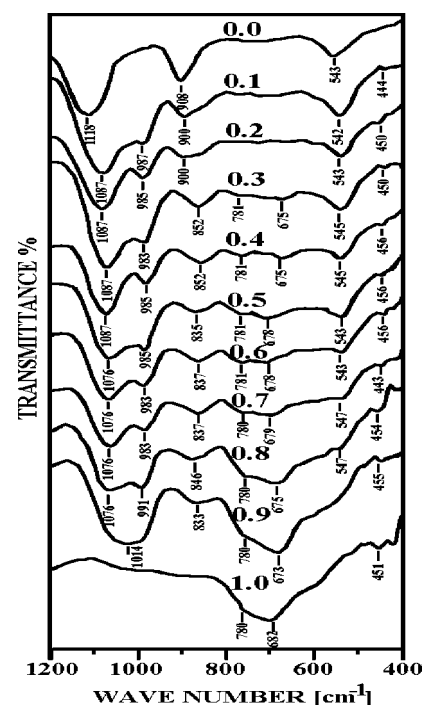


Figure 2 FTIR spectra of all SPT samples.

The band at 780 cm^{-1} is attributed to ν_1 normal vibrational mode of TeO_4 polyhedra. The 682 cm^{-1} band corresponds to the symmetric stretching vibrational mode of the Te-O bond in the TeO_4 group [25–27]. The 451 cm^{-1} band is attributed to Te-O-Te bridging of TeO_4 polyhedra. Hence, the FTIR spectra of compositions $x = 0.0$ and $x = 1.0$ are due to the formation of phosphate and tellurate networks respectively. The observed FTIR bands positions and their assignments for all compositions are shown in Table I, showing that all bands can be referenced to either phosphate or tellurate networks.

3.3. DSC

Fig. 3 shows the DSC curves measured for various SPT samples. The glass transition temperature (T_g) for each composition is shown in Fig. 4. It is found that the glass

TABLE I FTIR bands positions and their assignments for SPT glasses

No. of bands	FTIR bands positions in cm^{-1} for $x = 0.0$ to 1.0 in steps of 0.1 of SPT glasses											Assignments	Reference no.
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0		
1	1118	1087	1087	1077	1087	1076	1076	1076	1076	1014	–	NBO stretching mode (ν_s) of PO^- unit	[20, 21]
2	–	987	985	983	985	985	983	983	991	–	–	Asymmetric bending vibration mode of P-O-P in PO_4^{3-} unit	[20, 21]
3	908	900	900	852	852	852	835	837	846	833	–	Asymmetric bending vibration of P-O-P in PO_4^{3-}	[20, 21]
4	–	–	–	781	781	781	781	780	780	780	780	ν_1 normal vibrational mode of TeO_4 polyhedra	[25, 26]
5	–	–	–	675	675	678	678	679	675	673	682	Symmetric stretching vibration (broad band) Te-O	[25, 26]
6	543	542	543	545	545	543	543	547	547	–	–	Stretching mode of P=O-P unit	[24–26]
7	–	444	450	450	456	456	456	443	454	455	451	Te-O-Te	[25, 26]

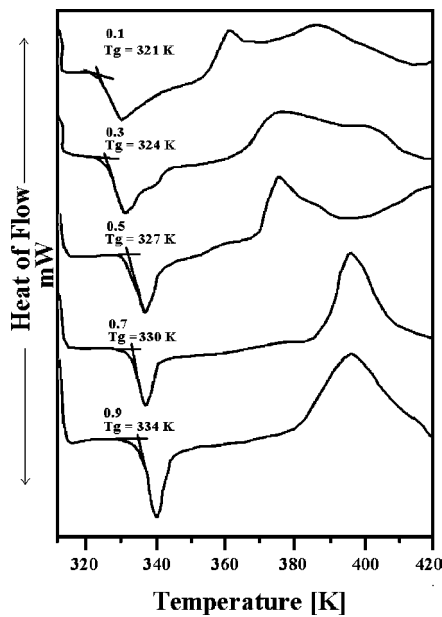


Figure 3 DSC thermograms of various compositions of SPT compounds.

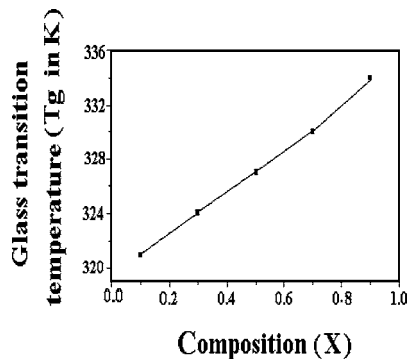


Figure 4 The variation of glass transition temperature (T_g) with composition.

transition temperature (T_g) increases with increase in TeO_2 content. The glass transition temperature (T_g) is a measure of the strength of a material [28]. Hence, from the Figs 3 and 4, it is concluded that the strength of $\text{AgI-Ag}_2\text{O-TeO}_2\text{-P}_2\text{O}_5$ glasses increases with TeO_2 content.

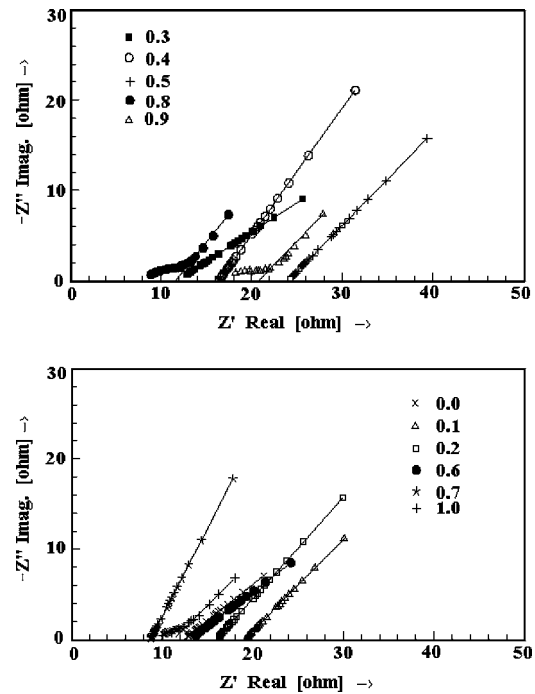


Figure 5 Impedance spectra obtained at room temperature for all SPT samples.

3.4. Impedance results

The measured imaginary (Z'') and real (Z') parts of impedance (Z) data for all compositions of SPT glasses are shown in Fig. 5. Using Boukamp equivalent circuit software, the impedance data were analyzed with the non-linear least square fitting procedure. The best bulk resistance (R_b) of each composition is obtained from the intercept of the straight line with the real axis of impedance plots [29]. The bulk conductivity, σ , was calculated using $\sigma = (t/\pi r^2) (1/R_b)$ where, t is the thickness and r is the radius of the pellet. Fig. 6 shows the conductivity variation with composition. Conductivity varies randomly with composition and the highest conductivity ($\sigma = 1.59 \times 10^{-2} \text{ S/cm}$) is found for $60\% \text{ AgI} - 26.67\% \text{ Ag}_2\text{O} - 13.33\% [0.3\text{P}_2\text{O}_5 + 0.7\text{TeO}_2]$. Table II gives the compositions and conductivity for all the SPT samples.

TABLE II Compositions and conductivity of SPT glasses

Former variation	Weight percentage				Conductivity (σ Scm ⁻¹)
	AgI	Ag ₂ O	TeO ₂	P ₂ O ₅	
0.0	60	26.67	0.0	13.33	9.26 (± 0.03) $\times 10^{-3}$
0.1	60	26.67	1.33	12.00	1.07 (± 0.04) $\times 10^{-2}$
0.2	60	26.67	2.66	10.66	1.12 (± 0.04) $\times 10^{-2}$
0.3	60	26.67	4.00	9.33	1.44 (± 0.02) $\times 10^{-2}$
0.4	60	26.67	5.33	7.99	1.06 (± 0.03) $\times 10^{-2}$
0.5	60	26.67	6.66	6.66	6.25 (± 0.03) $\times 10^{-3}$
0.6	60	26.67	7.99	5.33	1.03 (± 0.02) $\times 10^{-2}$
0.7	60	26.67	9.331	4.00	1.59 (± 0.03) $\times 10^{-2}$
0.8	60	26.67	10.66	2.66	1.34 (± 0.03) $\times 10^{-2}$
0.9	60	26.67	11.99	1.33	9.76 (± 0.05) $\times 10^{-3}$
1.0	60	26.67	13.33	0.0	1.21 (± 0.03) $\times 10^{-2}$

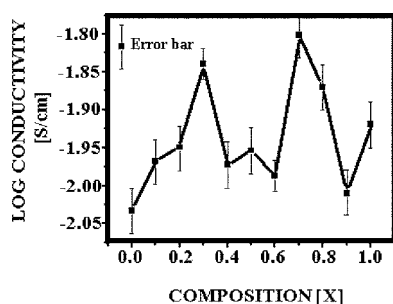


Figure 6 Conductivity as a function of composition of SPT glasses.

The conductivity (σ) is given by

$$\sigma = n\mu e \quad (1)$$

where, n is the number of carrier ions, μ is the mobility of the carrier ions and e is the charge of the carrier ions. In the 60%AgI–26.67%Ag₂O–13.33% [(1– x)P₂O₅ + x TeO₂] system, by fixing the AgI and Ag₂O contents, only the amounts of P₂O₅ and TeO₂ were varied, such that the concentration of Ag⁺ ions from AgI and Ag₂O remained constant. Hence, the variation of conductivity with composition must be due to a change in mobility (μ) of the charge carrier (Ag⁺) as a result of changes in the SPT glassy structure.

4. Conclusions

XRD results confirmed that all of the compositions of SPT samples prepared by melt quenching were amorphous. The FTIR spectra revealed that the structure of the SPT glasses changed with former composition and also confirmed that the SPT glassy matrix is composed of a tellurate and phosphate network. The observed random variation of conductivity with composition in the SPT glasses may be attributed to the mixed former effect and the highest conductivity ($\sigma = 1.59 \times 10^{-2}$ S/cm) composition was found to be 60%AgI–26.67%Ag₂O–13.33% [0.3P₂O₅ + 0.7TeO₂].

Acknowledgments

The authors acknowledge DRDO, AICTE & UGC, Govt. of India, for financial support in the form of major research projects. MV gratefully acknowledges CSIR,

Govt. of India, for financial support in the form of a major research project (No. 03/(0925)/01/EMR-II).

References

1. B. V. V. CHOWDARI and S. RADHAKRISHNA (eds.), Solid State Batteries, World Scientific, Singapore, 1986.
2. T. MINAMI, K. IMAZUANA and M. TANAKA, *J. Non-Cryst. Solids* **42** (1980) 469.
3. W. VANGOOL (ed.), Fast Ionic Transport in Solids, North-Holland, Amsterdam, 1973.
4. T. MINAMI, Y. JAKUMA and M. TANKA, *J. Electrochem. Soc.* **124** (1977) 1659.
5. M. VENKATESWARLU, K. NARASIMHA REDDY, B. RAMBABU and N. SATYANARAYANA, *Solid State Ion.* **127** (2000) 147.
6. N. SATYANARAYANA, XIAOGANG XIE and B. RAMBABU, *J. Mater. Sci. & Engg. B* **2** (2000) 7.
7. A. MAGISTRIS, G. CHIODELLI and M. DUCLOT, *Solid State Ion.* **9/10** (1983) 611.
8. N. SATYANARAYANA and S. RADHAKRISHNA, *ibid.* **28–30** (1988) 811.
9. N. SATYANARAYANA, A. KARTHIKEYAN and M. VENKATESWARLU, *J. Mater. Sci.* **31** (1996) 5174.
10. H. YAMAMOTO, H. NASU, J. MUSTOKA and K. KAMORA, *J. Non-Cryst. Solids* **170** (1994) 87.
11. H. BURGER, V. VOGEL and V. KOZHUKHAROV, *Infrared Phys.* **25** (1985) 395.
12. H. MORE, T. KITAMI and H. SAKATA, *J. Non-Cryst. Solids* **168** (1994) 157.
13. A. J. IKUSHIMA, *ibid.* **178** (1994) 1.
14. E. M. VOGEL, M. J. WEBER and D. M. KORL, *Phys. Chem. Glass.* **32** (1991) 231.
15. A. B. SEDDON, *J. Non-Cryst. Solids* **184** (1995) 44.
16. M. VENKATESWARLU and N. SATYANARAYANA, *J. Mater. Sci. Eng. B* **54** (1998) 189.
17. N. SATYANARAYANA, R. PATCHEAMALLE, P. MURALIDHARAN, M. VENKATESWARLU and B. RAMBABU, *Solid State Ion.* **136/137** (2000) 1047.
18. N. SATYANARAYANA, A. KARTHIKEYAN, M. VENKATESWARLU and B. RAMBABU, *Phys. Chem. Glass.* **42** (2001) 67.
19. KAZUO NAKAMOTO, "Infrared and Raman spectra of Inorganic and Coordination Compounds," 4th ed. (John Wiley & Sons, New York, part-II, 1986).
20. C. DAYANAND, G. BHIKSHAMAIAH, V. JAYATYAGARAGU, M. SALGRAM and A. S. R. KRISHNA MURTHY, *J. Mater. Sci.* **31** (1996) 1945.
21. M. K. P. SEYDEI and S. A. SUTHANTHIRARAJ, *Bull. Electrochem.* **12**(11/12) (1996) 683.
22. Y. DIMITRIEV, V. DIMITRIEV, M. ARNAUDOV and D. TOPALOV, *J. Non. Cryst. Solids* **57** (1983) 47.
23. KAMITSOS, M. A. KARAKASSIDES, G. D. CHRYSOSIKOS, J. M. HUTCHINSON, A. J. POPPIN, M. D. INGRAM and J. A. DUFFY, *Phys. Chem. Glass.* **36** (1995) 141.
24. Y. DIMITRIEV, V. DIMITRIEV and L. LAKOV, *ibid.* **29** (1988) 45.
25. L. LAKOV, V. DIMITRIEV, Y. DIMITRIEV, G. BOGACHEV and V. KRASSTEV, *ibid.* **39** (1998) 241.
26. D. ILIEVA, V. DIMITRIEV, Y. DIMITRIEV, G. BOGACHEV and V. KRASSTEV, *ibid.* **39**(4) (1988)
27. M. M. EL-SAMANOUDY, A. I. SABRY, E. E. SHAISHA and A. A. BAGHAT, *ibid.* **32**(3) (1991).
28. S. R. ELLIOTT, Physics of Amorphous Materials, Longman Scientific & Technical, London, 1990.
29. J. ROSS MACDONALD (ed.) "Impedance Spectroscopy" (John Wiley & Sons, New York, 1987).

Received 4 February

and accepted 10 October 2003