

Available online at www.sciencedirect.com





Solid State Ionics 178 (2007) 779-783

www.elsevier.com/locate/ssi

# Preparation and characterization of CuI-doped silver borovanadate superionic system

S. Murugesan<sup>a,\*</sup>, A. Wijayasinghe<sup>a,b</sup>, B. Bergman<sup>a</sup>

<sup>a</sup> Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden <sup>b</sup> Institute of Fundamental Studies, Kandy, Sri Lanka

Received 26 May 2006; received in revised form 8 February 2007; accepted 9 February 2007

#### Abstract

A new cost effective glassy/crystalline superionic system xCuI–(100-x)[2Ag<sub>2</sub>O– $0.7V_2O_5$ – $0.3B_2O_3$ ], where x=30, 40, 45, 50 and 60, has been prepared by melt quenching technique and the ionic transport properties were studied. The phase analysis and thermal properties of the samples carried out using XRD, FTIR and DSC techniques confirmed the glassy-crystalline composite nature of the prepared materials. DSC analyses indicated the crystallization of some phases between 130 and 170 °C and the subsequent melting of these crystallized phases in the temperature range of 200-250 °C. The room temperature electrical conductivity studies were carried out by a.c. impedance analysis. High room temperature electrical conductivity of  $3.58 \times 10^{-3}$  S cm<sup>-1</sup> was obtained for the best conducting composition. These materials show high  $t_{Ag+}$  value of 0.997. The use of two glass formers helped to form materials with higher  $T_{\rm g}$ , higher thermal stability and better ionic transport properties. © 2007 Elsevier B.V. All rights reserved.

Keywords: Superionic; Impedance; Ionic transport; Solid electrolytes; Ionic conductivity

## 1. Introduction

In recent years, superion conducting glasses have gained considerable momentum in the application of solid state devices, since these materials have many advantages like higher room temperature electrical conductivity, absence of grain boundaries, isotropic properties, easy to prepare diversity of compositions, etc., when compared with their respective polycrystalline materials [1-6]. The main practical objective of the intensive research on these systems has been the maximization of their ionic conductivity, essential for potential applications in all-solid-state electrochemical devices, without a considerable loss of other properties. Electrolytes suitable for solid-state batteries are expected to show high ionic conductivities of the order of  $10^{-5}$ – $10^{-1}$  S cm<sup>-1</sup> and negligible electronic conductivity at their operating temperatures. A number of fast ionconducting glasses based on Ag<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, F<sup>-</sup>, O<sup>2-</sup> and Cu<sup>+</sup> have been reported [7,8]. Particularly, consistent attention is being paid to a family of materials obtained from the combination of AgI with silver oxysalts, which show interesting properties, the most important one being a glass-type structure with fast ionic behaviour [9-12]. Recently, silver ion conducting superionic materials have been developed by the combination of different dopants other than AgI, like, PbI<sub>2</sub>, CuI, and  $CdI_2$  in the silver oxysalt matrix [13–16]. It has also been found recently that the introduction of two glass formers increases glass transition temperature  $(T_g)$ , thermal stability and electrical conductivity as compared to those of single former glasses [17–19]. This paper is based on a study on the quaternary glassy/crystalline system  $xCuI - (100 - x)[2Ag_2O - x]$  $0.7V_2O_5-0.3B_2O_3$ ], where x=30, 40, 45, 50, and 60, which employs CuI as dopant salt to have a cost effective system. This paper essentially deals with the preparation, structural, thermal and ionic transport properties of the chosen system.

# 2. Experimental

# 2.1. Materials preparation

Analytical grade chemicals of Ag<sub>2</sub>O, V<sub>2</sub>O<sub>5</sub>, and B<sub>2</sub>O<sub>3</sub> as well as CuI, prepared in our laboratory by precipitation of CuI

<sup>\*</sup> Corresponding author. Tel.: +46 8 7908335; fax: +46 8 207681. E-mail address: smsan03@yahoo.co.uk (S. Murugesan).

<sup>0167-2738/\$ -</sup> see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.ssi.2007.02.025

from aqueous solution of cupric nitrate with 5% excess KI at normal boiling point, were used as starting materials for the synthesis of various specimens. Solid samples of the mixed system  $xCuI-(100-x)[2Ag_2O-0.7V_2O_5-0.3B_2O_3]$ , where x=30, 40, 45, 50, and 60 were prepared by annealing appropriate mixtures of the starting materials in quartz boats at 923 K for 2 h and rapidly quenching the molten mixtures in liquid nitrogen. The quenched solid samples were ground into fine powders using an agate mortar and pestle, and used for further analyses.

## 2.2. Structural and thermal characterizations

X-ray diffraction (XRD) analysis is a powerful technique which, gives information about the amorphous or crystalline nature of the prepared samples and the different crystalline phases present in it. XRD analyses were carried out on powdered samples of the above system at room temperature (295 K) using a Siemens (model Kristalloflex) D5000 X-ray diffractometer system with Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$ =1.5418 Å) in the 2 $\theta$ range between 10 and 70°. Fourier transform infrared (FTIR) spectra were recorded for the various samples in the wave number region 4000–400 cm<sup>-1</sup> by the KBr pellet method at room temperature using a Perkin-Elmer model Spectrum RX1 FTIR Spectrometer. Differential scanning calorimetry is considered as a sensitive tool to examine the thermal stability of the prepared materials. Differential scanning calorimetric (DSC) studies were performed on powdered samples of the prepared system  $xCuI - (100 - x)[2Ag_2O - 0.7V_2O_5 - 0.3B_2O_3]$ , over the temperature range 298-573 K using a Modulated DSC 2920 model Differential scanning calorimeter (TA Instruments) at a heating rate of 5° min<sup>-1</sup> with platinum as the reference material and aluminium sample containers.

# 2.3. Electrical characterization

The room temperature (295 K) electrical conductivity of all the samples, which were made in to circular pellets of 11.2 mm dia at a pelletizing pressure of 400 MPa and placed between two silver electrodes, was measured by the complex impedance method using a PCI4 family EIS300 electrochemical impedance spectroscopy system (Gamry Instruments, Inc.) in the frequency range 1 Hz–300 kHz. The bulk resistance of the sample was obtained from Cole–Cole plots and used for the evaluation of conductivity. The silver ionic transport number ( $t_{Ag+}$ ) measurements were carried out using the galvanic cell technique. The details regarding the  $t_{Ag+}$  measurements are described elsewhere [20].

# 3. Results and discussion

#### 3.1. X-ray diffraction studies

X-ray diffractogram of all the compositions under study revealed the glass-like structure of the samples having x=30, 40, and 45 and also the crystal-glass composite nature of the other two compositions (having x=50 and 60). X-ray diffraction

patterns obtained for the different compositions of the system under study are given in Fig. 1. The XRD patterns show an amorphous background with some less intense peaks due to some crystallites dispersed in the glass matrix. By careful analvsis of these XRD peaks, it has been found that all the samples have CuO as one of the crystalline phase. While sample having x=30 shows peaks due to Ag<sub>3</sub>VO<sub>4</sub> phase, the sample with x=60exhibits peaks due to Cu<sub>5</sub>V<sub>2</sub>O<sub>10</sub> phase. The material compositions having x=45, 50 and 60 contain  $\gamma$ -AgI crystallites. The amount of AgI crystalline phase increases gradually with increasing CuI mol% (above 45 mol%) in the system, which is evident from the gradual increase of the height of the XRD peaks corresponding to AgI. The formation of AgI in these compositions as well as the increase in the amount of AgI crystals with increasing CuI mol% were confirmed in the DSC studies, which are presented in the Section 3.3 of this article. From these results it can be suggested that an ion exchange reaction taking place in the glassy matrix as per the following equation

$$2CuI + Ag_2O \rightarrow 2AgI + Cu_2O \tag{1}$$

This is in accordance with the Pearson's theory of hard and soft acids and bases [21]. This kind of ion exchange reactions was already reported by various workers in similar systems [22–24]. A portion of the Cu<sub>2</sub>O formed would have undergone aerial oxidation to form CuO and present in all the samples. In the sample with 60 mol% CuI, the above formed CuO may combine with  $V_2O_5$  to form  $Cu_5V_2O_{10}$  phase, as per the following equation.

$$5CuO + V_2O_5 \rightarrow Cu_5V_2O_{10} \tag{2}$$

Thus, the XRD studies showed the presence of more  $Ag^+$  ions in the iodide-ion environment and the copper ions (Cu<sup>+</sup> and Cu<sup>2+</sup>) in the oxide-ion environment of these materials, and the samples are expected to have high silver ionic conductivities.



Fig. 1. X-ray diffraction patterns obtained for the different compositions of the system  $xCuI-(100-x)[2Ag_2O-0.7V_2O_5-0.3B_2O_3]$ .

#### 3.2. FTIR spectral analyses

Fig. 2 reports the IR absorbance spectra recorded at room temperature for the different compositions of the present superionic system. The spectra contain absorption bands near 500, 690, 855, 920 and 965  $\text{cm}^{-1}$  in all the compositions. The observed IR bands in the sample compositions of the present system are assigned by careful comparison of these bands with the IR bands reported in ternary vanadate [22,25], boarate [26,27] and quaternary borovanadate systems [12]. The absorption bands at 500  $\text{cm}^{-1}$  (week) and 690  $\text{cm}^{-1}$  (strong) are, respectively, assigned to  $v_{sym}$  and  $v_{asym}$  stretching vibrations of V–O–V bridge of  $V_2O_7^{4-}$  groups. The observed IR bands at 965 and 920 cm<sup>-1</sup> are attributed to the symmetric and anti-symmetric stretching vibrations of the VO<sub>3</sub> terminal groups of the pyrovanadate ions which are formed by the condensation of VO<sub>4</sub><sup>3-</sup> tetrahedra. Dimitriev et al. [28] reported that the band at 1020 cm<sup>-1</sup> in glassy  $V_2O_5$  shifts to 960 cm<sup>-1</sup> in  $Ag_2O-V_2O_5$  glass due to bonding of  $Ag^+$  ions with the unbridged double bonded oxygen thus shifting the frequency to lower values. They have also explained that, the symmetry of  $V_2 O_7^{4-}$  and  $V O_4^{3-}$  groups in these compounds decreases due to condensation effects which result in an increase in the number of absorption bands in the spectra. The samples having 30 and 40 mol% of CuI show a broad medium absorption band at 1370–1420 cm<sup>-1</sup> which is attributed to the  $v_3$  mode of BO<sub>3</sub> groups. The band observed at  $855 \text{ cm}^{-1}$  in all the compositions corresponds to BO<sub>4</sub> groups. Thus, the IR results indicated the formation of  $V_2 O_7^{4-}$  and  $V O_4^{3-}$  groups in these compounds and the presence of interaction between the Ag<sup>+</sup> ions and the nonbridging oxygens.



Fig. 2. FT-IR spectra recorded for the different glassy/crystalline compositions of the system xCuI–(100-x)[2Ag<sub>2</sub>O– $0.7V_2O_5-0.3B_2O_3$ ].



Fig. 3. DSC heating curves obtained for the different glassy/crystalline compositions of the system  $xCuI-(100-x)[2Ag_2O-0.7V_2O_5-0.3B_2O_3]$ .

# 3.3. DSC analyses

The DSC traces of the samples under study provide abundant information on thermodynamic transitions occurring during heating of initially amorphous samples. DSC heating curves obtained for the different glassy/crystalline compositions of the present system are shown in Fig. 3. The characteristic endothermic shifts of the base lines are due to the glass transition processes. The glass transition temperatures  $T_g$  are about 95 °C (for x=30 glass), 68 °C (for x=40 glass), 94 °C (for x=45 glass), 96 °C (for x=50 glass) and 96 °C (for x=60 glass). The endothermic peaks observed at 141, 143 and 146 °C for the compositions with x=45, 50 and 60, respectively, are due to the  $\beta \rightarrow \alpha$  phase transition of AgI [29,30] and reveal the formation of  $\gamma$ -AgI as one of the phases in these compositions. The height of these endothermic peaks (around 143 °C) increases from x=45 to 60 (nearly same weight of sample  $\approx 40$  mg used in all measurements), which suggests that the amount of AgI increases with increasing amount of CuI (i.e., x) in the system and this has already been observed in XRD studies. The crystallization temperatures  $T_{\rm c}$ are observed at around 135, 142 and 154 °C (for x=30), 98 and 121 °C (for x=40), 171 °C (for x=45) and 179 °C (for x=50). Triple and double exothermic peaks present in the compositions with 30 and 40 mol% CuI, respectively, represent three and two different crystalline phases appearing during heating up. Consequently, three and two endothermic peaks (between 180 and 250 °C) corresponding to the melting of these crystallized phases appear in the respective DSC



Fig. 4. Complex impedance plots obtained at room temperature for the samples having x=30, 45 and 60 in the system  $xCuI-(100-x)[2Ag_2O-0.7V_2O_5-0.3B_2O_3]$ .

traces. Similar results were reported by Krasowski et al. [31,32] for AgI–Ag<sub>2</sub>O–V<sub>2</sub>O<sub>5</sub> system. The melting peaks are feeble in the composition with 60 mol% CuI and it suggested that those crystalline phases are formed in very low amounts in this sample. The DSC results complemented the XRD results. The phases crystallizing out in these transitions are not identified at this stage and this work is in progress in our lab.

#### 3.4. Conductivity studies

X-ray diffraction and differential scanning calorimetric studies confirmed the glass-like (glassy materials with small amount crystalline phases) nature of the samples of compositions having x=30, 40, and 45 and also the crystal-glass composite (glasses with more amount of crystalline phases) nature of the other two compositions. The complex impedance plots observed for the three different material compositions, namely, x=30, 45, and 60 at room temperature are given in Fig. 4. There is one depressed semicircle corresponding to grain boundary effects and a part of another semicircle corresponding to bulk resistance are seen for the compositions x=30 and 60 whereas only the depressed semicircle (grain boundary) is present for x=45 composition. Due to the high conducting nature of this sample the relaxation frequencies of bulk property are expected to be very high, so the bulk resistance effects would be observed at very high frequencies only. It can also be noted from Fig. 4 that, the grain boundary resistance is very small ( $\sim 15\%$  of total) compared to the bulk resistance, confirming the glass-like nature of these materials. The electrical conductivity values obtained from the complex impedance plots showed that all these samples have electrical conductivities in the range of  $10^{-3}$ - $10^{-4}$  S cm<sup>-1</sup> at room temperature (295 K). Interestingly, the composition 45CuI-36.67Ag<sub>2</sub>O-12.83V<sub>2</sub>O<sub>5</sub>-5.5B<sub>2</sub>O<sub>3</sub> exhibits electrical conductivity as high as  $3.58\pm0.01\times10^{-3}$  S  $cm^{-1}$  at room temperature. This high value of electrical conductivity is five times larger than the electrical conductivity observed for the similar system which uses CdI<sub>2</sub> as dopant salt, namely, 30CdI<sub>2</sub>-46.67Ag<sub>2</sub>O-16.33V<sub>2</sub>O<sub>5</sub>-7B<sub>2</sub>O<sub>3</sub> [14] and is comparable with the electrical conductivities reported for the similar systems with AgI as dopant salt. The room temperature

electrical conductivity increases from x=30 to 45 due to the increased formation of Ag<sup>+</sup> ions with iodide ion environment which contribute to the conduction. But, though more increased Ag<sup>+</sup> ions with iodide ion environment is expected in the compositions x=50 and 60, the  $\sigma_{RT}$  decreases because of the formation of more amount of crystalline phases. The observed high values of room temperature electrical conductivity suggest the suitability of these materials for solid state electrochemical device applications.

# 3.5. Ionic transport number studies

Table 1 presents the silver ionic transport number  $(t_{Ag+})$ values obtained by EMF method for the various compositions of the system at room temperature along with their room temperature electrical conductivities. From Table 1, it is evident that the silver ionic transport number of these materials is nearly unity. It is generally expected that both Ag<sup>+</sup> and Cu<sup>+</sup> ions are conductive in such mixed systems. However, it is obvious from Table 1 that the values of silver ionic transport number obtained through EMF technique are greater than 0.993 for all the compositions and thus appears to exclude the contribution of Cu<sup>+</sup> ions to the conductivity of these specimens as explained elsewhere [33]. Already it has also been observed from the XRD studies that, the Ag<sup>+</sup> ions are present in the more iodide-ion environment and the Cu<sup>+</sup> ions are present in the more oxide-ion environment. So, the Ag<sup>+</sup> ions interacting with iodide-ions contribute to the conduction and the Cu<sup>+</sup> ions which are interacting with oxide-ions do not contribute to the conduction as explained by Minami [11]. These  $t_{Ag^+}$  values are also found to be greater than those of 16.33V<sub>2</sub>O<sub>5</sub>-7B<sub>2</sub>O<sub>3</sub> [14] and 40CuI-40Ag<sub>2</sub>O-20V<sub>2</sub>O<sub>5</sub> [34] systems. Thus, these materials would have negligible electronic contributions to the total conductivity as compared with the ionic transport and that the ionic conductivity is apparently due to  $Ag^+$  ions only [11,23,25]. The absence of any appreciable electronic conductivity would be attributed to the suppression of the formation of the reduced transition metal ions namely V<sup>4+</sup> ions as discussed elsewhere [35]. Therefore, the present  $t_{Ag+}$  data are found to be in good agreement with the conductivity results thus confirming the superionic nature of these materials and their suitability to solid state devices.

Table 1

Electrical conductivity and  $t_{Ag^+}$  data for the system  $xCuI-(100-x)[2Ag_2O-0.7V_2O_5-0.3B_2O_3]$ 

Composition ( <i>x</i> )	Electrical conductivity at 295 K, $\sigma_{295 \text{ K}}$ (S cm <sup>-1</sup> )	Open circuit voltage of the cell (-) Ag+SE// SE//I <sub>2</sub> (+) (mV)	Silver ionic transport number $(t_{Ag+})$ at 295 K
30	$1.18\!\pm\!0.01\!\times\!10^{-4}$	682	0.993
40	$2.41\!\pm\!0.01\!\times\!10^{-3}$	683	0.994
45	$3.58\!\pm\!0.01\!\times\!10^{\!-3}$	685	0.997
50	$2.28\!\pm\!0.01\!\times\!10^{-3}$	682	0.993
60	$2.82 {\pm} 0.01 {\times} 10^{-4}$	683	0.994

## 4. Conclusions

Silver ion conducting glassy/crystalline solid electrolyte materials were prepared in a new cost-effective system xCuI- $(100-x)[2Ag_2O-0.7V_2O_5-0.3B_2O_3]$  by melt quenching technique. The structural and thermal characterizations carried out on the prepared samples indicated the glassy/crystalline composite nature of these materials. Due to the ion exchange reactions which are occurring in the glass matrix, Ag<sup>+</sup> ions are present in the more iodide-ion environment and the Cu<sup>+</sup> ions are present in the more oxide-ion environment. The best conducting composition of this new superionic system exhibited electrical conductivity as high as  $3.58 \times 10^{-3}$  S cm<sup>-1</sup> at 295 K. These materials show high  $t_{Ag+}$  values, viz., greater than 0.993 for all the investigated compositions. So, the Ag<sup>+</sup> ions interacting with iodide-ions contribute to the conduction and the Cu<sup>+</sup> ions which are interacting with oxide-ions do not contribute to the conduction. The use of two glass formers helped to have materials with higher  $T_{g}$ , thermal stability and better ionic transport properties. The observed high value of ionic conductivity at 295 K suggests that these materials would be suitable for solid state electrochemical device applications.

#### References

- [1] D. Kunze, in: W. Van Gool (Ed.), Fast Ionic Transport in Solids, North Holland, Amsterdam, 1973.
- [2] B.V.R. Chowdari, S. Radhakrishna, Material for Solid State Batteries, World Scientific, Singapore, 1986.
- [3] H. Takahashi, K. Shishitsuka, T. Sakuma, Y. Shimojo, Y. Ishii, Solid State Ionics 113–115 (1998) 685.
- [4] J.E. Garbarczyk, P. Machowski, M. Wasiucionek, W. Jakubowski, Solid State Ionics 157 (2003) 269.
- [5] A.K. Arof, Phys. Status Solidi, A Appl. Res. 140 (1993) 491.
- [6] M. Tacher, R. Mercier, J.P. Malugani, P. Chieux, Solid State Ionics 25 (1987) 263.
- [7] N. Machida, T. Shigematsu, N. Nakanishi, S. Tsuchida, T. Minami, J. Chem. Soc. Faraday Trans. 88 (1992) 3059.

- [8] A.L. Laskar, S. Chandra, Superionic Solids and Solid Electrolytes: Recent Trends, Academic Press, San Diego, 1989.
- [9] M. Lazzari, B. Scrosati, C.A. Vincent, J. Amer. Ceram. Soc. 61 (1978) 451.
- [10] S.S. Sekhon, Indian J. Pure Appl. Phys. 37 (1999) 282.
- [11] T. Minami, J. Non-Cryst. Solids 56 (1983) 15.
- [12] A.K. Arof, J. Power Sources 52 (1994) 129.
- [13] B. Rivolta, F. Bonino, B. Scrosati, Mater. Chem. Phys. 19 (1988) 557.
- [14] K.P. Padmasree, D.K. Kanchan, H.R. Panchal, A.M. Awasthi, S. Bharadwaj, Solid State Commun. 136 (2005) 102.
- [15] K. Hariharan, R. Suresh Kumar, Bull. Electrochem. 12 (1996) 665.
- [16] S.A. Suthanthiraraj, P.R. Umarani, Mater. Sci. Eng., B, Solid-State Mater. Adv. Technol. 96 (2002) 226.
- [17] B.V.R. Chowdari, P. Pramodakumari, J. Non-Cryst. Solids 197 (1996) 31.
- [18] B.V.R. Chowdari, R. Gopalakrishnan, S.H. Goh, K.L. Tan, J. Mater. Sci. 23 (1988) 1248.
- [19] N. Satyanarayana, R. Patcheammalle, P. Muralidharan, M. Venkateswarlu, B. Rambabu, Solid State Ionics 136–137 (2000) 1097.
- [20] S.A. Suthanthiraraj, S. Murugesan, P. Maruthamuthu, Solid State Ionics 143 (2001) 413.
- [21] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
- [22] K. Hariharan, R. Suresh Kumar, Solid State Ionics 104 (1997) 227.
- [23] V.G. Chandrasekhar, S.A. Suthanthiraraj, Solid State Ionics 62 (1993) 61.
- [24] K.P. Padmasree, D.K. Kanchan, A.R. Kulkarni, Solid State Ionics 177 (2006) 475.
- [25] T. Minami, K. Imazawa, M. Tanaka, J. Non-Cryst. Solids 42 (1980) 469.
- [26] T. Minami, Y. Ikeda, M. Tanaka, J. Non-Cryst. Solids 52 (1982) 159.
- [27] K.M. Shaju, S. Chandra, Phys. Status Solidi, B Basic Res. 181 (1994) 301.
- [28] Y. Dimitriev, V. Dimitrov, M. Arnaudov, D. Topalov, J. Non-Cryst. Solids 57 (1983) 147.
- [29] S. Chandra, Superionic Solids—Principles and Applications, North-Holland, Amsterdam, 1981.
- [30] M. Tatsumisago, T. Saito, T. Minami, J. Non-Cryst. Solids 293–295 (2001) 10.
- [31] K. Krasowski, J.E. Garbarczyk, M. Wasiucionek, Phys. Status Solidi, A Appl. Res. 183 (2001) 381.
- [32] K. Krasowski, J.E. Garbarczyk, Phys. Status Solidi, A Appl. Res. 158 (1996) K13.
- [33] S. Murugesan, S.A. Suthanthiraraj, P. Maruthamuthu, Solid State Ionics 154–155 (2002) 621.
- [34] V.G. Chandrasekhar, S.A. Suthanthiraraj, J. Mater. Sci. 28 (1993) 4043.
- [35] S.A. Suthanthiraraj, S. Murugesan, P. Maruthamuthu, Mater. Res. Bull. 37 (2002) 2145.