Structural Aspects and Ion Transport Properties of a New Mixed System BiI$_3$ - Ag$_2$WO$_4$

V. S. SHANKARAN[*] and S. AUSTIN SUTHANTHIRARAJ

Department of Energy, University of Madras,
Guindy Maraimalai Campus, Chennai 600 025, India
karanrrishabh@gmail.com

Abstract: An experimental attempt was made to analyze structural and ion transport properties in the case of a new mixed system *viz*., (BiI$_3$)$_y$ - (Ag$_2$WO$_4$)$_{100-y}$ where y = 10, 20, 30, 40, 50, 60, 70, 80 and 90 mol% respectively. The samples synthesized by the rapid melt-quenching technique were analyzed using Fourier Transform Infrared (FT–IR) spectroscopy, differential scanning calorimetric (DSC) analysis and silver ionic transport number studies. The results of FT–IR and DSC studies have revealed the formation of AgI and other phases in various compositions of the system. The transport number measurements carried out by Wagner's and EMF methods have indicated that silver ions may be responsible for the observed ionic transport in these newly formed solid electrolyte phases.

Introduction

Significant advances witnessed in the field of Solid State Ionics may be attributed to the devise and synthesize of new, useful and promising solid materials for the electrical power generation and storage system. Superionic conductors are expected to be among the fastest growing areas of solid state ionics over the next few decades and to offer materials for alternative energy sources often with the potential for immediate applications. A careful evaluation of the application prospects of solid electrolytes suggests an intensive search for better materials with improved ionic conductivity, thermal, chemical stability as well as processibility as these materials exhibit significant role in sustainable energy systems including advanced batteries, electrochemical capacitors, power sources, advanced sensors, electro chromic devices[1,2]. Investigations on several solid-state materials have contributed significantly to the advancement in the development of various devices with immediate applications in the recent years. In particular, silver ion conducting materials have shown interesting properties like high electrical conductivities, good electrochemical stability and consistency at high and room temperature as well. Hence, a variety of AgI – oxysalt superionic electrolytes have been widely studied[3]. A systematic study of their structural and electrical properties have demonstrated the feasibility of obtaining appreciably high silver

ionic conductivity values over a wide range of temperatures with improved stability[4]. More recently, development of a new solid system involving BiI_3 and silver oxyacid salt Ag_2CrO_4 was attempted by us through a systematic study of ion transport, structural, electrical and electrochemical properties and to demonstrate effective electrical conduction[5]. Stimulated by the success, we have extended our investigation to the new mixed system $BiI_3 - Ag_2WO_4$ through Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) and ion transport number studies by means of Wagner's polarization technique and EMF method.

Experimental

Powder specimens of the solid system $(BiI_3)_y - (Ag_2WO_4)_{100-y}$ ($10 \leq y \leq 90$) were prepared from analar grade chemicals of BiI_3 (Aldrich- Purity 99%) and Ag_2WO_4 (Aldrich- Purity 99%) by the rapid melt- quench method. Desired amounts of the starting materials namely BiI_3 and Ag_2WO_4 were annealed in quartz ampoules at 873 K for 6 h in a high temperature vertical tubular furnace before being quenched into liquid nitrogen. The obtained solid materials were crushed into fine powder and stored in darkened desiccators for further characterization studies.

Material characterization

The FT–IR spectra were recorded for all the samples of the mixed system $(BiI_3)_y - (Ag_2WO_4)_{100-y}$ ($10 \leq y \leq 90$) in the wave number region $4000 - 400$ cm^{-1} by the KBr pellet method at ambient temperature using a Perkin Elmer RX1 spectrometer.

Thermal analysis was carried out on all the synthesized samples using a NETZCH DSC – 204 differential scanning calorimeter over the temperature range 323-600 K at a heating rate of 10 K min^{-1} in order to determine the phase transition temperature of individual phases present in these compositions.

The ionic transport studies were carried out for all the samples within the present system by Wagner's polarization technique[6] wherein a polarization cell was made in the form of a pellet from the powdered sample forming the electrolytic phase sandwiched between a non-blocking electrode consisting of a mixture of silver metal powder and electrolyte and an ion blocking electrode, carbon. On the application of a small dc potential (~200 mV) across the cell with polarity (-) (Ag, electrolyte) / electrolyte / carbon (+), the current and potential difference are noted simultaneously as a function of time using a Keithley model 6157A electrometer. Subsequently, the value for output current at time t = 0s corresponds to total electrical conductivity due to ions and electrons. After 6-7 h, a steady state output corresponding to just the electronic conduction was noted. From the above measured values, the total ion transport number was evaluated using the relation $t_{ion} = 1 - t_e$, where t_{ion} and t_e respectively correspond to the total ion transport number and

the electronic transport number[7]. The electronic transport number is given by $t_e = \dfrac{I_e}{I_t}$

where I_t is the initial total current due to all the mobile species *i.e.*, ions and electrons and I_e is the electronic current which is the steady residual current indicating the fully depleted situation of the blocking electrode. Furthermore, the silver ionic transport number values have also been determined in order to find out the extent of contribution of silver ions to the electrical transport in the present system, by employing the EMF technique[8]. Accordingly, open circuit voltage (OCV) values of the electrochemical cells, with a configuration (-) Ag,

electrolyte / electrolyte / I_2 (+), fabricated from the powdered sample forming the electrolytic phase where the anode consists of a mixture of silver metal powder and electrolyte in the weight ratio 2:1 and the cathode from iodine were measured. The open circuit voltage of individual cells were then compared with the thermodynamically calculated value (687mV) at room temperature reported[9] for the typical solid state electrochemical cell (-) Ag / AgI / I_2 (+).

Results and Discussion

FT–IR analysis

The FT–IR spectral patterns recorded for nine different compositions of the mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$ $(10 \leq y \leq 90)$, corresponding to y = 10, 20, 30, 40, 50, 60, 70, 80 and 90 mol % BiI_3 are shown in Figure 1.
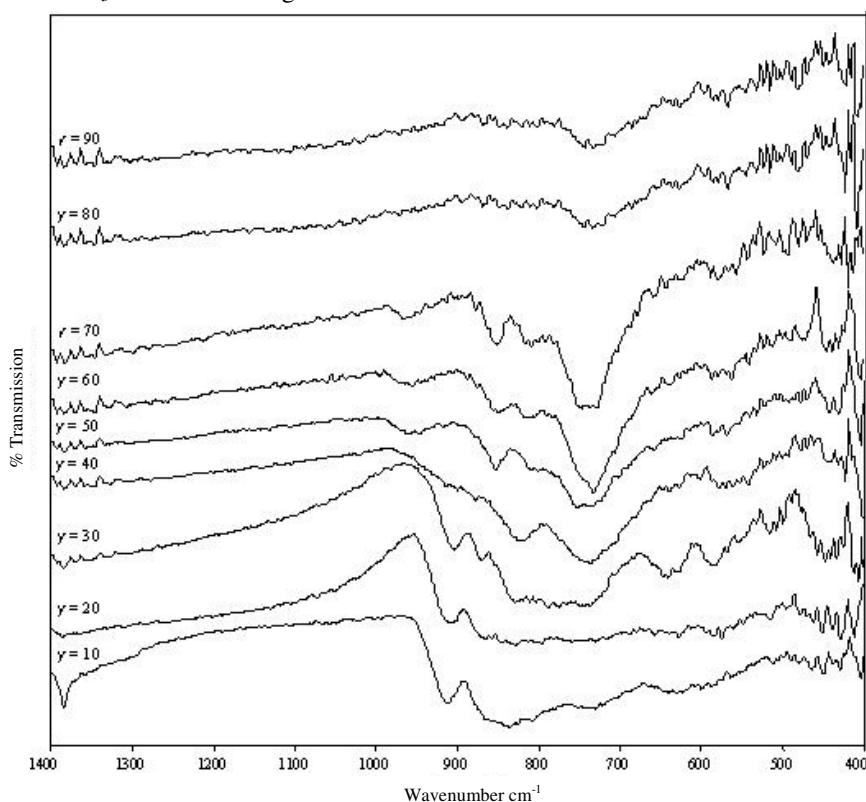

Figure 1. FT–IR spectra recorded for nine different compositions of the mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$, $(10 \leq y \leq 90)$

The absorption band noticed around 830 ± 5 cm^{-1} in the case of four different compositions with y = 10, 20, 30 and 40 mol % BiI_3 may be ascribed to the γ_3 vibration mode of tetrahedral WO_4^{2-} species[10,11]. Interestingly, the absorption maximum noticed around 830 cm^{-1} has also been reported for the vibrational frequency of the A_{1g} mode of WO_6 octahedral units for AgI – Ag_2WO_4 glasses[12,13]. The observed absorption peak around 912 ± 5 cm^{-1} for the samples with composition y = 10, 20, 30 and 40 mol% may be assigned to the terminal WO bonds γ_1 arising as a result of formation of WO_4^{2-} group[14]. The γ_2 (e) vibration mode of the anionic WO_4^{2-} group is evident from the presence of medium

absorption band around 405 ± 2 cm^{-1} in all the compositions[15]. The absorption band noticed around 732 ± 3 cm^{-1} in all the samples is similar to the absorption band at 735 cm^{-1} reported for minerals of russelite structure, classified as one of the complex oxides in which an anionic WO_4^{2-} group is bonded to bismuth as the cation. The observed absorption bands around 456 ± 3 cm^{-1} in the case of the nine different compositions may be ascribed to γ_2 stretching mode of octahedral WO_6^{6-} ions[16,17]. Similarly the absorption band appearing at 623 ± 3 cm^{-1} for the compositions with y varying from 10 to 50 mol% BiI_3 are assigned to the vibrational frequency of γ_3 stretching mode of WO_6^{6-} ions[16,17]. Thus FT–IR data of the present mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$ $(10 \leq y \leq 90)$ suggest the formation of polyanions such as tetrahedral WO_4^{2-} ions and octahedral WO_6^{6-} ions units may characterize the oxyanion framework in these samples[18]. Moreover, FT–IR data of the present mixed system was found to be in good agreement with XRD results of the present system reported elsewhere[19].

DSC results

The typical DSC curves obtained for various compositions in the mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$, where y = 10, 20, 30, 40, 50, 60, 70, 80 and 90 mol % respectively are shown in Figure 2.

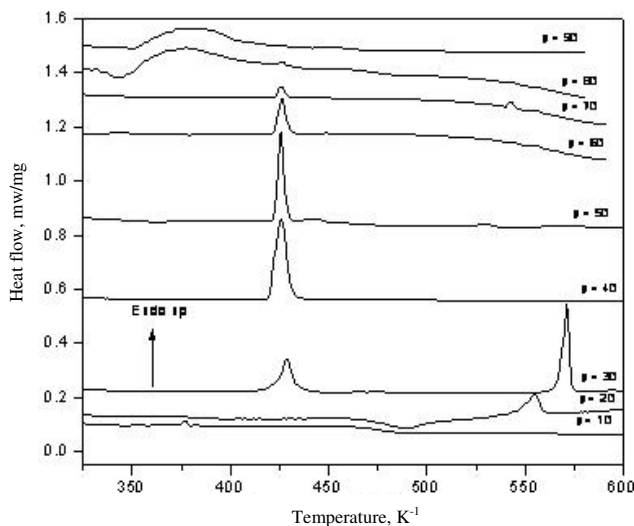**Figure 2.** DSC traces observed for mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$, $(10 \leq y \leq 90)$

Table 1 gives the summary of the relevant DSC results observed for the individual samples of the system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$, $(10 \leq y \leq 90)$. It is quiet evident from Table 1 that endothermic peaks observed at 426 ± 1 K for the samples with y varying from 30 to 80 mol% are comparable to the characteristic phase transition temperature of AgI[20], and tend to indicate their presence as one of the constituents. In case of the composition with y = 20 mol % BiI_3 the broad exothermic peak at temperature 490 K followed by an endothermic peak at temperature 555 K may be related to the crystalline phase transition which would have occurred within the system followed by the melting of the above mentioned crystalline phase appearing during heating. The endothermic peak that appears at 571 K in the case of the composition with y = 30 mol % is found to be in consistent with the melting temperature of AgI-Ag_2WO_4 glasses[18,21]. The formation of a new phase in those composition with y = 50

mol% BiI_3 is evident from the two endothermic dips at 443 K and 529 K in addition to the characteristic endothermic peak at 426 K. Further, the two endothermic events occurring around 543 K and 554 K in the case of those compositions with y = 60 and 70 mol % may be associated with the formation of new phases. Thus, these results appear to confirm the presence of new phases in the mixed system under study as confirmed from the XRD results observed for the present system and reported elsewhere[19]. Thus, the present structural and thermal features are found to be in conformity with each other. The formation of AgI and other silver ionic phases may be explained on the basis of the hard and soft acids and bases (HSAB) principle proposed by Pearson[22]. The HSAB rule states that soft acids would prefer to bind to soft or polarizable bases and that hard acids would prefer to bind to hard or non-polarizable bases as a result of various degrees of ionic and covalent bonding. It is, therefore, possible that silver iodide may be formed during the ion exchange reaction between BiI_3 and the silver oxysalt *i.e.* (Ag_2WO_4) in the molten state due to the softness of silver ions and I^- ions. Similar ion exchange reactions were also reported by many workers[23,24].

Table 1. Results of DSC obtained for the various compositions of the mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$ ($10 \leq y \leq 90$)

Composition (y)	Endothermic peak position (K)	Exothermic peak position (K)
10	377, 383	-
20	555	490
30	427, 571	-
40	425	-
50	426, 443, 529	-
60	426, 543, 554	-
70	426, 543, 554	-
80	377, 426	-
90	377	-

Ionic transport number data

Table 2 presents the values of ion transport number (t_{ion}) evaluated by Wagner's direct current polarization method as well as the silver ion transport number (t_{Ag+}) data evaluated by emf method for the various compositions in the mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$ ($10 \leq y \leq 90$) at room temperature.

Table 2. Ionic transport number (t_{ion}) and silver ionic transport number (t_{Ag+}) data obtained by Wagner's and EMF method respectively for the mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$ ($10 \leq y \leq 90$)

Composition (y)	Ionic transport number (t_{ion})	Silver ion transport number (t_{Ag+})
10	0.98	0.95
20	0.99	0.96
30	0.99	0.99
40	0.99	0.97
50	0.97	0.95
60	0.95	0.92
70	0.92	0.91
80	0.9	0.9
90	0.89	0.9

It is evident from Table 2 that the ionic transport number (t_{ion}) values vary from 0.89 to 0.98 for all the nine compositions of the present system. Further, the measured silver ionic transport number (t_{Ag+}) values are approximately equal to the corresponding t_{ion} values. This feature suggests that the ionic conductivity is apparently due to the migration of silver ions (Ag^+) only and it may be argued that the electronic/hole contribution to the total conductivity would be negligible as compared to the ionic contribution to the total conductivity in these compositions, which are superionic in nature[25]. These results are similar to those reported in the case of AgI-doped with similar oxysalt matrices[26].

Conclusion

Detailed investigation concerning spectroscopic and thermal characterizations of a series of compositions of the new mixed system $(BiI_3)_y$ - $(Ag_2WO_4)_{100-y}$ ($10 \leq y \leq 90$) has revealed the formation of Ag^+- based fast ionic conductors. The feasibility of obtaining these materials has been explained on the basis of ion exchange chemical reactions occurring between the cations namely Ag^+ and Bi^+ ions and anions involving I^- and WO_4^{2-} ions. The detailed analysis of ion transport number data are found to be in excellent agreement with the above proposition thus exhibiting fast ionic conduction due to silver ion transport at ambient conditions.

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