Investigation of ionic transport properties in the new mixed system BiI$_3$-Ag$_2$MoO$_4$

S. AUSTIN SUTHANTHIRARAJ[*], V. S. SHANKARAN
Department of Energy, University of Madras, Maraimalai Campus,Chennai 600 025, India

The phenomenon of ionic transport in the case of the new mixed system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$, prepared by rapid melt quenching method has been experimentally investigated in order to establish it as a silver ion-based fast ion conductor and reported in the present work. The relevant structural and thermal properties were evaluated by means of X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) and Differential scanning calorimetry (DSC) techniques. The electrical transport studies involving ionic transport number and temperature - dependent electrical conductivity measurements have been carried out in order to identify the various phases responsible for the conduction process. The electrical conductivity attains a maximum value of 1.9×10^{-3} Scm^{-1} for the typical composition $(BiI_3)_{0.2}–(Ag_2MoO_4)_{0.8}$ with an activation energy 0.26 eV for silver ionic transport at room temperature (298 K). The novel data obtained in terms of electrical transport studies have been discussed in the light of the observed structural characteristics.

1. Introduction

Fast ion 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 having appreciably high application potential. Such materials are likely to form the basis for all key technologies and, thus, the future of every modern society as well. A number of Ag$^+$, Na$^+$ and Li$^+$ ion based super ionic conductors which possess high ionic conductivity [1] have been examined and progress has been made towards understanding the relationship between the complex phenomenology of ionic transport and atomic structure in highly-disordered systems. These materials have attracted widespread attention mainly due to their high isotropic ionic conductivity as well as ease of material handling and synthesis. In particular, AgI–oxysalt glasses are known to show high ionic conductivity up to ~10^{-2} Scm^{-1} at room temperature [2-3]. In order to achieve further enhancement in the room temperature conductivity and increased stability, attempts have also been made using mixed glass formers [4-5] and mixed cations [6] systems. Similarly, combination of different dopants like, PbI$_2$, NaI and CdI$_2$ with the silver oxysalt matrix has also been developed [7-8]. Recent literature reports the class of silver oxysalt Ag$_2$MoO$_4$ - based electrolytes offering promising characteristics [9-11] and also an appropriate oxysalt component owing to its applications in ambient temperature oxygen sensor, chemical sensor and as electron beam recording material [12]. In view of this an attempt has been made to investigate ionic transport properties in a new pseudo binary system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$ which could be used for the fabrication of ionic devices, especially solid state batteries.

Our recent investigation concerning ion transport studies on a similar system BiI$_3$ – Ag$_2$CrO$_4$ [13] has indicated the formation of fast ionic solids. The present study is therefore aimed at the preparation by melt quenching technique, structural and thermal characterization through XRD and DSC, ionic transport by impedance measurement in order to explore the various ion conducting processes within the new mixed system namely BiI$_3$ – Ag$_2$MoO$_4$.

2. Experimental

2.1. Sample preparation

Commercially available analar grade Bismuth tri iodide, BiI$_3$ with 99.9% purity was purchased from Sigma-Aldrich Company (USA). The other starting material, namely silver molybdate, Ag$_2$MoO$_4$ was prepared by the co-precipitation method as suggested by Kawamura et al [14] using sodium molybdate Na$_2$MoO$_4$ and silver nitrate AgNO$_3$ as raw materials. The fresh precipitate prepared under safelight conditions was filtered and dried at 373 K in a vacuum oven. These chemicals were weighed according to their molecular weight percentage and mixed in various compositions conforming to the stoichometric formula of the mixed system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$,where x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mole fraction of BiI$_3$ respectively. The mixture was then placed in a quartz ampoule, vaccum sealed and annealed to 873 K for 6 h by suitably suspending the ampoule in a vertical tubular type high temperature furnace. The homogeneous melt obtained was rapidly quenched into liquid nitrogen. The series of solid materials

thus obtained were subsequently crushed into fine powder using pestle and mortar and stored in desiccators for further characterization studies.

2.2. X-ray diffraction (XRD) analysis

X-ray diffactograms were recorded for each of the prepared samples using a Bruker D8 Advanced model X-ray diffraction system with Cu-Kα1 (λ = 1.5406Å) radiation in the scanning angle (2θ) range between 10° and 70° at room temperature in order to identify various phases present within such samples.

2.3. Differential scanning calorimetry (DSC) analysis

To examine the thermal stability of those freshly - prepared samples, DSC analysis was performed on all the samples of the system $(BiI_3)_x − (Ag_2MoO_4)_{1-x}$ (0.1≤ x ≤ 0.9) over the temperature range 293–573 K using a NETZSCH DSC 204 instrument, at the scanning rate of 10 K min⁻¹.

2.4. FTIR Spectra

Fourier transform infrared (FTIR) spectra were recorded for all the samples of the mixed system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$, (0.1≤ x ≤ 0.9) taken in the form of pellets pressed at a pressure of 500 kgcm⁻² with KBr using a Perkin Elmer RX1 spectrophotometer in the wave number region 4000 – 400 cm⁻¹ at room temperature with a resolution of 4cm⁻¹.

2.5. Electrical conductivity studies

The electrical conductivity measurements were carried out by complex impedance method on all the compositions of the system under investigation. For this, all the synthesized solid samples were ground into fine powder and pressed into circular pellets of 8mm diameter at an optimum pressure of 5000 kgcm⁻² with silver electrodes on both sides having the configuration Ag/electrolyte/Ag. The complex impedance measurements were carried out using a computer-controlled Hewlett-Packard HP 4284A model Precision LCR Meter in the frequency range 20 Hz - 1 MHz and in the temperature range 298–433 K. The value of the bulk resistance of the sample was obtained from the analysis of the observed complex impedance data using the Boukamp equivalent circuit formalism and hence the conductivity values were estimated.

2.6. Ionic transport number measurements

The ionic transference number (t_{ion}) was measured for each composition of the present mixed system by Wagner's dc polarization method [15]. In this technique, 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. Subsequently, a constant dc potential of 100 mV was applied across the cell with polarity (-) (Ag, electrolyte) / electrolyte / carbon (+). The current was measured as a function of time using a Keithley Electrometer Model 6517A till the current becomes constant indicating the fully depleted condition of the blocking electrode. The total ion transport number (t_{ion}) of the sample was evaluated using the relation $t_{ion} = 1 − t_e$ where t_e denotes the electronic transport number. The electronic transport number is given by $t_e = \frac{I_e}{I_t}$ where I_t 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.

The extent of contribution of silver ions to the electrical transport in the present system in terms of silver ion transport number t_{Ag+} data was evaluated by employing the EMF method. A galvanic cell with a configuration (-) Ag, electrolyte / electrolyte /I_2 (+), was accordingly 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. The cell was made in the form of a pellet by pressing the cell components under a pressure of 5000 kg cm⁻². The open circuit voltage of individual cells were measured and compared with the thermodynamically calculated value (687mV) at room temperature reported for the typical solid state electrochemical cell (-)Ag / AgI /I_2(+) [16].

3. Results and discussion

3.1. Powder XRD results

The X-ray diffractograms for various compositions of the electrolyte system $(BiI_3)_x − (Ag_2MoO_4)_{1-x}$ (0.1≤ x ≤ 0.9), where x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mole fraction BiI_3 are shown in Figure 1. The JCPDS data were used as the standard criteria to carefully analyze the diffraction peaks of various phases obtained for all the prepared samples constituting the rapidly quenched system.

In the case of the typical composition having x = 0.1 mole fraction BiI_3, the two XRD peaks appearing at 2θ = 28.3 and 57.3° may be attributed to the presence of tetragonal body centered silver bismuth molybdenum oxide $AgBi(MoO_4)_2$ compound [17] whereas those set of XRD peaks noticed at scanning angles 2θ = 27.1, 31.8, 33.3 and 50.9° correspond to the existence of unreacted Ag_2MoO_4 phase [9,18].

The presence of tetragonal body centered silver bismuth molybdenum oxide $AgBi(MoO_4)_2$ as one of the constituent phases in the case of the composition with x = 0.2 and 0.4 is evident from the occurrence of XRD peaks around 2θ = 28.3, 33.9, 46.4, and 57.3° with (hkl) planes of (112), (200), (204) and (312) respectively [17], whereas for the composition with x = 0.2 those XRD peaks occurring at scanning angles 2θ = 27.1, 31.9, 33.3 and

$50.9°$ respectively may be ascribed to the unreacted Ag_2MoO_4 phase.

The presence of $AgBi(MoO_4)_2$ as one of the constituent in the case of the composition with x = 0.3 is evident from the occurrence of XRD peaks around 2θ = 28.4 and $46.3°$. Also the formation of a new product is seen from the existence of the diffraction peak at the scanning angle 2θ of $49.2°$.
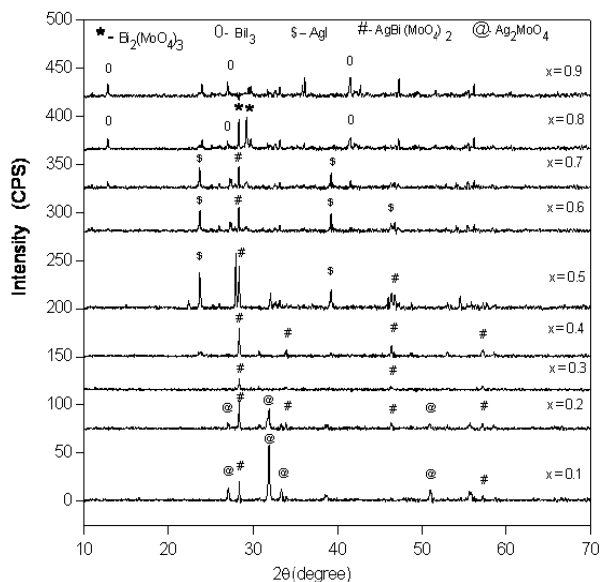

Fig. 1 X-ray diffractograms obtained for various compositions of the mixed system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}(0.1 \leq x \leq 0.9)$.

Considering the observed XRD patterns pertaining to the higher order concentration of BiI_3 viz., from x = 0.5 to 0.7 mole fraction, the formation of face centered cubic lattice of room temperature AgI phase is evident from those characteristic peaks at scanning angles 2θ = 23.7, 39.2 & 46.4^0, corresponding to evaluated d-spacing values of 3.75, 2.29 & 1.96 Å owing to three specific lattice planes (111), (220) and (311) respectively [19]. Furthermore, the formation of $AgBi(MoO_4)_2$ phase along with some unidentified new phases is also seen in the case of the composition with x = 0.5, 0.6 and 0.7 mole fraction BiI_3.

Furthermore, the set of diffraction peaks corresponding to d-spacing values of 3.15 & 3.05Å observed at scanning angles 2θ = 28.3 and $29.2°$ respectively may be assigned to the new phase viz., bismuth molybdenum oxide $Bi_2(MoO_4)_3$ [20], in case of the composition with x = 0.8 mole fraction BiI_3. On the other hand, those XRD peaks noticed at 2θ = 12.8, 26.9 and $41.5°$ in case of the typical composition x = 0.8 and 0.9 mole fraction indicate the presence of traces of the starting material BiI_3 [21].

Thus, the observed XRD patterns for the mixed system under study, depict the formation certain polycrystalline materials in addition to AgI as a result of probable solid state exchange reaction presumably occurring between BiI_3 and Ag_2MoO_4.

3.2. Differential scanning calorimetric analysis

Fig. 2 depicts those DSC traces recorded for various compositions in the mixed system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}$, where x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mole fraction BiI_3 and Table 1 presents the relevant DSC results obtained for such compositions of the mixed system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$. Interestingly, in the DSC curve observed for the sample having the composition corresponding to x = 0.1 mole fraction, a broad exothermic peak noticed around 406 K may be attributed to the crystalline phase transition occurring in the sample [9]. In the case of those compositions with x = 0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction the appearance of an endothermic peak around 343 - 353 K may be related to the physical change of melting whereas an exothermic peak appearing around the 373-383 K temperature range may be due to the crystallization process which would have occurred within the system. The formation of a metastable crystalline compound with the composition $(AgI)_{0.67} – (Ag_2MoO_4)_{0.33}$ nucleating at $\approx$ 383K over the entire composition range of the system $(AgI)_{1-x} – (Ag_2MoO_4)_x$ has been reported [22-24]. Evidently, the endothermic peak noticed near 423 K may be due to the characteristic $\beta\rightarrow\alpha$ phase transition in AgI as observed in those samples with x varying from 0.4 to 0.8 mole fraction of BiI_3 [11].
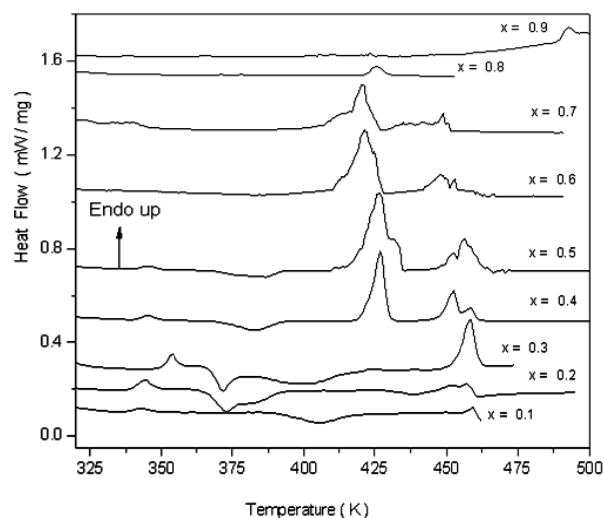

Fig. 2 DSC traces recorded for various compositions in the mixed system $(BiI_3)_x – (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$.

The absence of diffraction peaks corresponding to AgI in the observed XRD patterns for the compositions containing 0.4 and 0.8 mole fraction of BiI_3, may be attributed to the fact that the content of AgI in these particular compositions is so small that it could not influence any appreciable change in the observed XRD patterns. The additional endothermic around 458 K in case of those compositions with x = 0.2, 0.3, 0.4, 0.5 and 0.6 mole fraction may be attributed to the presence of a new phase. It is worthwhile to mention here that the

eutectic temperature was also found at 453 K for x =0.25, which corresponds to the formation of $(AgI)_{0.75}$ – $(Ag_2MoO_4)_{0.25}$ (3:1 composition compound) as observed from the equilibrium phase diagram for the system $(AgI)_{1-x}$-$(Ag_2MoO_4)_x$ [23-24]. In the case of the composition having x = 0.9 mole fraction BiI_3 certain endothermic peak due to melting of an unknown phase was observed around 492 K. Thus the present XRD data in conjunction with DSC data suggest that AgI and some polycrystalline phases may be formed during melting of BiI_3 and Ag_2MoO_4 together.

Table 1 Results of DSC obtained for the various compositions of the mixed system
$(BiI_3)_x$-$(Ag_2MoO_4)_{1-x}$,($0.1 \le x \le 0.9$).

Composition (x)	Endothermic peak position (K)	Exothermic peak position (K)
0.1	342, 459	406
0.2	344, 457	372
0.3	353, 458	372, 400
0.4	345,427, 453, 459	382
0.5	347, 426, 451, 456	383
0.6	421, 448, 452	-
0.7	421, 441, 449	-
0.8	425	-
0.9	492	-

3.3. FTIR spectra

The FTIR spectra recorded at room temperature in the range 400 – 1200 cm^{-1} for nine different compositions of the pseudo binary mixed system $(BiI_3)_x$ - $(Ag_2MoO_4)_{1-x}$, ($0.1 \le x \le 0.9$) where x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mole fraction respectively are shown in Fig. 3.

It is evident from Fig. 3 that no characteristic absorption bands were observed beyond 1200 cm^{-1}. All the spectra presented in Fig. 3 are found to show the absorption band at around 830 ± 4 cm^{-1} which may be assigned to the υ_3 mode of vibration of the monomeric tetrahedral orthomolybdate ions MoO_4^{2-} [25], whereas the absorption band noticed at 880 ± 2 cm^{-1} in the case of those compositions with x = 0.5, 0.6 and 0.7mole fraction of BiI_3 corresponds to υ_1 mode of the monomeric tetrahedral orthomolybdate MoO_4^{2-} ions [26].

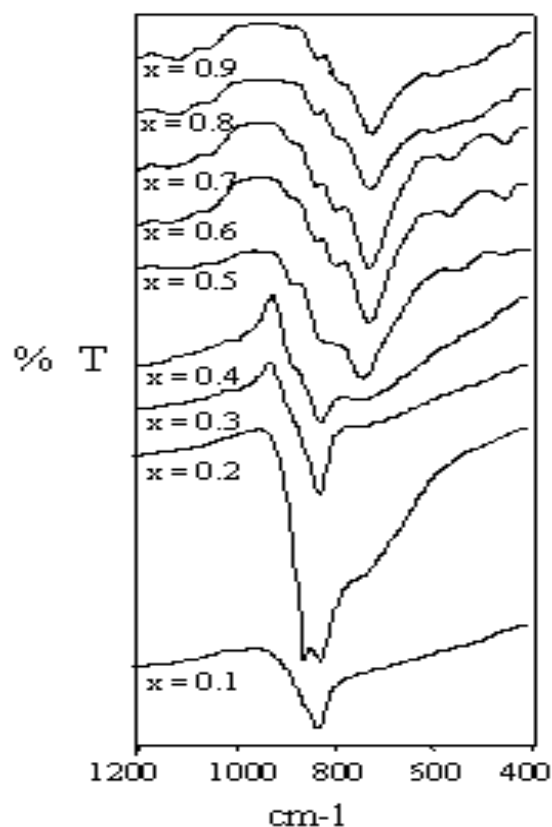*Fig. 3 The FTIR spectra recorded for nine different compositions of the pseudo binary mixed system $(BiI_3)_x$ - $(Ag_2MoO_4)_{1-x}$, ($0.1 \le x \le 0.9$).*

The absorption band appearing at 790 ± 2 cm^{-1} for the set of four different compositions containing x = 0.6, 0.7, 0.8 and 0.9 mole fraction BiI_3 may be attributed to the formation of dimeric bitetrahedral anions $Mo_2O_7^{2-}$. Besides, the additional band observed around 595± 2 cm^{-1} in case of those compositions with x= 0.8 and 0.9 and the band around 452 ± 2 cm^{-1}, for those compositions with x= 0.5, 0.6, 0.7, 0.8 and 0.9 may be assigned to asymmetric υ_{as} and symmetric υ_s modes of Mo – O – Mo bonds in $Mo_2O_7^{2-}$ [27] respectively. These asymmetric and symmetric bands result from condensation of MoO_4 tetrahedral into $Mo_2O_7^{2-}$ ions. The absorption band noticed around 725 ± 2 cm^{-1} in those samples with x = 0.6, 0.7, 0.8 and 0.9 mole fraction lies in the vicinity of Mo – O – Mo vibrations present in $K_2Mo_2O_7$ crystalline [25]. Moreover, the introduction of BiI_3 into the lattice of silver oxy salt leads to the appearance of a new vibration band at 745 ± 2 cm^{-1} for those compositions with x = 0.2, 0.3, 0.4 and 0.5 mole fraction BiI_3 .Thus, the present FTIR studies tend to reveal the presence of anionic species such as MoO_4^{2-} and $Mo_2O_7^{2-}$ in the multi-phase network of BiI_3 - Ag_2MoO_4.

3.4. Electrical conductivity results

The ac response of a variety of compositions in the mixed system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$, where $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 mole fraction of BiI_3 has been measured in terms of real(Z') and imaginary parts(Z'') of complex impedance(Z^*) at different temperatures. The complex impedance plots observed at room temperature (298 K) for various compositions in the mixed system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$ $(0.1 \leq x \leq 0.9)$ consist of semi-circles in the high frequency region coupled with spikes in the low frequency region. The observed depressed arcs appear to suggest the non-Debye behavior of the present system similar to solid electrolytes [28]. The spike may be attributed to the polarization effect at the electrode/sample interfaces. The value of bulk resistance of the sample under test has been obtained from the point of intersection of the impedance plot on the real axis [29]. Figure 4 depicts the set of typical complex impedance plots obtained for composition $(BiI_3)_{0.2} - (Ag_2MoO_4)_{0.8}$ at six different temperatures viz., 298, 303, 313, 323, 333 and 353 K respectively.
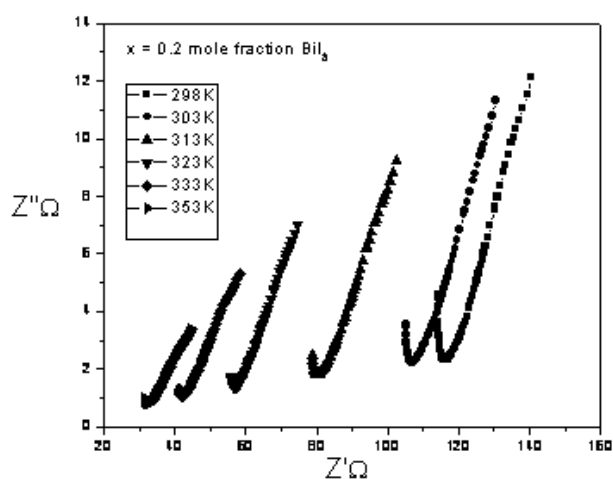

Fig. 4 Complex impedance plots obtained for the composition $(BiI_3)_{0.2} - (Ag_2MoO_4)_{0.8}$ at six different temperatures viz., 298, 303, 313, 323, 333 and 353 K.

It is observed in Figure 4 that as the temperature increases, the point of intersection is shifted towards the origin i.e., towards the high frequency side. Hence, it is quite evident that the bulk resistance of the sample decreases with increase in temperature, resulting in an enhancement of electrical conductivity at higher temperature as in the case of ionic solids. Similar results have been observed in the case of all the remaining compositions too.

It is worthwhile to mention the values of room temperature electrical conductivity (σ_{298K}) of the mixed system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$ for the various compositions with x= 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 are 2.7×10^{-4}, 1.9×10^{-3}, 1.2×10^{-3}, 1.2×10^{-3}, 1.8×10^{-4}, 1.3×10^{-4}, 9.1×10^{-5}, 3.3×10^{-5} and 1.5×10^{-5} Scm⁻¹

respectively. The observed electrical conductivity values are found to be of the order of $10^{-5} - 10^{-3}$ Scm⁻¹ at 298K. It is evident that the best conducting composition in the system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$ having x= 0.2 would possess an electrical conductivity value of 1.9×10^{-3} Scm⁻¹ at 298K. Also, the conductivity values for compositions with x= 0.2, 0.3 and 0.4 mole fraction BiI_3 of the present system are comparable to the conductivity data reported [30] for the AgI-Ag₂MoO₄ system. The present results suggest that a new phase with an electrical conductivity value higher than that of AgI may be formed during this investigation thus revealing the superionic nature of the chosen mixed system as well. Further, the room temperature electrical conductivity values of those compositions having x= 0.5 and 0.6 mole fraction BiI_3 have been found to be of the order of10^{-4} Scm⁻¹ and comparable to that of AgI. DSC results discussed earlier have also suggested the formation of AgI traces, in these compositions as revealed by the characteristic $\beta - \alpha$ phase transition peak observed at 426 and 421 K respectively. In the case of compositions with x= 0.7, 0.8 and 0.9 mole fraction of BiI_3 the relatively low conductivity values of the order of 10^{-5} Scm⁻¹ at ambient temperature may be due to the formation of other reaction products.

3.5. Temperature-dependent conductivity and transport number data

The variation of $\log(\sigma T)$ as a function of inverse of absolute temperature (1000/T) for the nine different compositions of the mixed system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$, over the temperature range 298 – 443 K is presented in Fig. 5.
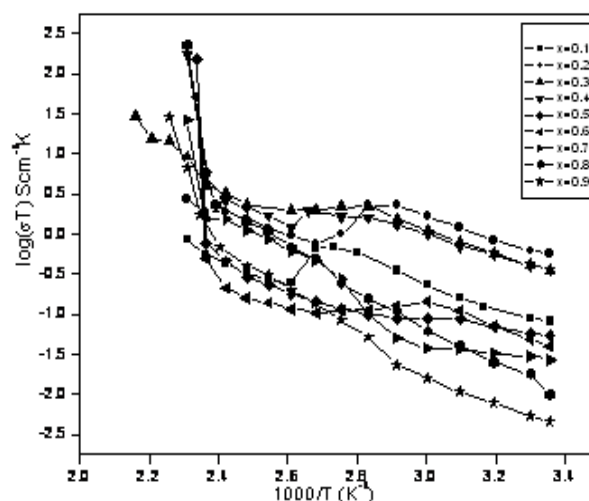

Fig. 5 Log(σT) as versus (1000/T) plots for nine different compositions of the mixed system $(BiI_3)_x - (Ag_2MoO_4)_{1-x}$

It is seen from Fig. 5 that in the case of those compositions with x= 0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction of BiI_3 the conductivity increases with temperature but decreases in the region 343 – 383 K and

then it shows an increasing trend with temperature. This feature may be due to the formation of an ordered structure probably due to the crystallization of one of the phases present as evident from the corresponding DSC curves. Furthermore in the case of those compositions with x=0.1, 0.2 and 0.3 mole fraction of BiI₃ the fact that no abrupt change is seen around 420 K, in the temperature-dependent electrical conductivity plots indicates the absence of AgI as a possible product in the system as also evident from XRD and DSC results. Similar trend has been reported [31-32] for those superionic systems of AgI – Ag₃SO₄ and (Cu₁₋ₓAgₓI)-(Ag₂O)-(MoO₃) respectively. Apart from their Arrhenius behavior with temperature, a phase transition at around 420 K is also evident from Figure 4 for those compositions with x = 0.4, 0.5, 0.6, 0.7and 0.8 in the case of the mixed system (BiI₃)ₓ – (Ag₂MoO₄)₁₋ₓ.

Table 2. Activation energies (E_a) for electrical conduction and associated ionic transport t_{ion} and silver ion transport number t_{Ag+} data for the mixed system $(BiI_3)_x$-$(Ag_2MoO_4)_{1-x}$, $(0.1 \leq x \leq 0.9)$.

Composition (x)	Activation energy E_a (eV)	Ionic transport number t_{ion}	Silver ion transport number t_{Ag+}
0.1	0.31	0.97	0.96
0.2	0.26	0.99	0.98
0.3	0.30	0.99	0.98
0.4	0.22	0.98	0.99
0.5	0.24	0.97	0.96
0.6	0.26	0.96	0.96
0.7	0.41	0.95	0.94
0.8	0.47	0.93	0.93
0.9	0.44	0.91	0.9

The set of activation energies (E_a) for various compositions of the mixed system (BiI₃)ₓ – (Ag₂MoO₄)₁₋ₓ estimated from the relationship $\sigma T = \sigma_0 \, exp\left(\frac{-E_a}{kT}\right)$ (where

k denotes Boltzmann's constant, T the absolute temperature and σ_0 the 'pre-exponential factor') are presented in Table 2 together with the corresponding room temperature ion transport number (t_{ion}) as well as the silver ion transport number (t_{Ag+}) data obtained during the present investigation. It is clear from Table 2 that the activation energies of these material are of the order of 0.22 – 0.47 eV in the temperature region 298 – 383 K. Also, It is evident from Table 2, that the best conducting composition x = 0.2 in the present system with electrical conductivity 1.9 x 10⁻³ Scm⁻¹ has a low activation energy of 0.26 eV in the lower temperature range (298 – 353 K) and is comparable to those reported [9] for the similar superionic conducting system AgI-Ag₂O-MoO₃.

It is clear from Table 2 that all the nine different compositions are ionic in nature, exhibiting ionic transport number t_{ion} and silver ion transport number t_{Ag+} values of 0.91- 0.99 and 0.90 – 0.99 respectively at ambient temperature. The fact that the high electrical conductivity of 1.9x10⁻³ Scm⁻¹ at 298 K in the case of x = 0.2 mole fraction BiI₃ and the corresponding silver ion transport number t_{Ag+} of 0.98 are realized suggests that the ionic conductivity is apparently due to the migration of silver ions (Ag^+) only and that electronic/hole contribution to the total conductivity would be negligible as compared to the ionic contribution to the total conductivity. These results appear to reveal the feasibility of obtaining highly conducting silver ion conductors formed due to ion exchange chemical reaction between BiI₃ and Ag₂MoO₄ during the melting process in the chosen system.

4. Conclusions

The present XRD, DSC and FT-IR results obtained for the new mixed system (BiI₃)ₓ-(Ag₂MoO₄)₁₋ₓ, (0.1≤ x ≤ 0.9) have revealed the formation of new fast ionic materials in addition to AgI. Further investigations concerning complex impedance analysis and transport measurements have suggested that the composition having x= 0.2 mole fraction BiI₃ would show the maximum conductivity of 1.9 x10⁻³ Scm⁻¹ at 298 K coupled with the activation energy of 0.26 eV due to silver ion transport.

References

[1] A. L. Laskar, S. Chandra, Super Ionic Solids and Solid Electrolytes, Recent Trends, Academic Press, San Diego (1989).
[2] K. Shahi, J. B. JR. Wagner, J. Phys. Chem. Solids, **43**,713 (1982).
[3] R. K Gupta, R. C. Agrawal, Solid State Ionics, **72**, 314 (1994).

[4] M. Hosono, J. Kawamura, H. Itoigawa, N. Kuwata, T. Kamiyama, Y. Nakamura, J. Non-Cryst. Solids, **244**, 81 (1999).

[5] R. C. Agrawal, M. L. Verma, R. K. Gupta, Solid State Ionics, **171**, 199 (2004).

[6] P. S. Kumar, P. Balaya, P.S. Goyal, C. S. Sunandana, J. Phys. Chem. Solids, **64**, 961 (2003).

[7] K. P. Padmasree, D. K. Kanchan, H. R. Panchal, A.M. Awasthi, S. Bharadwaj, Solid State Commun., **136**, 102 (2005).

[8] K. Hariharan, R. Suresh Kumar, Solid State Ionics, **104**, 227 (1997).

[9] A. Dalvi, K. Shahi, J. Phys. Chem. Solids, **64**, 813 (2003).

[10] S. Bhattacharya, A. Ghosh, Solid State Ionics, **176**, 1243 (2005).

[11] A. Dalvi, A. M. Awasthi, S. Bharadwaj, K. Shahi, J. Phys. Chem. Solids, **66**, 783 (2005).

[12] J. Kuwano, Solid State Ionics, **40/41**, 696 (1990).

[13] S. Austin Suthanthiraraj, V. S. Shankaran, Ionics, **19**, 787 (2013).

[14] J. Kawamura, M. Shimoji, J. Non-Cryst. Solids, **88**, 281 (1986).

[15] S. Chandra, S. K. Tolpadi, S. A. Hashmi, Solid State Ionics, **651**, 28 (1988).

[16] B. B. Owens, A. R. Argue, J Electrochem. Soc. **117**, 898 (1970).

[17] Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Powder Diffraction File, ID no: 32-0999.

[18] Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Powder Diffraction File, ID no: 08-0473.

[19] Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Powder Diffraction File, ID no: 78-0641.

[20] Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Powder Diffraction File, ID no: 70-1396.

[21] Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Powder Diffraction File, ID no: 89-0307.

[22] C. Tomasi, P. Mustarelli, A. Magistris, J. Solid State Chem. **140**, 91 (1998).

[23] A. Magistris, G. Chiodelli, G. Vigana, Z. Campari, Natur forsch, **A31**, 974 (1976).

[24] F. Rocca, A. Kuzmin, P. Mustarelli, C. Tomasi, A. Magistris, Solid State Ionics, **121**, 189 (1999).

[25] N. Machida, H. Eckert, Solid State Ionics, **107**, 255 (1998).

[26] T. Minami, T. Katsuda, M. Tanaka, J. Non-Cryst. Solids, **29**, 389 (1978).

[27] T. Minami, M. Tanaka, J. Non-Cryst. Solids, **38/39**, 289 (1980).

[28] J. O. Isard, D. Kruschike, W. Miller, J. Non-Cryst. Solids, **157**, 131 (1991).

[29] J. R. Macdonald, Impedance Spectroscopy, Emphasizing Solid Materials and Systems. Wiley, New York (1987).

[30] A. Schiraldi, G. Chiodelli, A. Magistris, J. Appl. Electrochem. **6**, 251 (1976).

[31] K. A. Murugesamoorthi, K. Hariharan, S. RadhaKrishna Solid State Ionics, **21**, 327 (1986).

[32] S. Austin Suthanthiraraj, S. Murugesan, P. Maruthamuthu in: A. R. Kulkarni, P. Gopalan (Eds.), Ion Conducting Materials – Theory and Applications, Narosa Publishing House, New Delhi, 2001, pp. 155-158 (2001).

*Corresponding author: suthan98@gmail.com