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Frequency response analysis of $(BiI_3)_{0.3} – (Ag_2CrO_4)_{0.7}$ fast ion conducting glassy system

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A new pseudo binary mixed system $(BiI_3)_{0.3}$ – $(Ag_2CrO_4)_{0.7}$ prepared by melt quenching technique has already been identified as a fast ion conducting glassy system during an earlier investigations involving X-ray diffraction, FTIR and differential scanning calorimetry (DSC) studies, in conjunction with electrical conductivity analysis, exhibiting silver ionic conductivity (σ) of 7.1 x 10^{-3} Scm^{-1} at room temperature. This paper deals with frequency-dependent electrical data analysed in terms of conductivity spectra, dielectric loss and modulus formalisms, as a function of temperature over the domain 298 – 412 K. Whereas the observed frequency – dependent conductivity is found to obey Jonscher's universal law, the modulus spectra of the present system tend to suggest a distribution of the relaxation times, which is found to be temperature independent. The variation of dielectric constant and conductivity with frequency has been explained by correlating the microscopic nature of the ionic conduction process occurring within the choosen system.

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Keywords: Fast ionic conductor, Silver ionic conduction, Modulus spectra, Dielectric constant

1. Introduction

The ever- growing demand for global energy needs which is a major challenge in the progress of the modern day society, has brought increasing awareness of efficient, clean, and renewable energy sources. As many of the environment friendly sources of electrical energy cannot operate at all times, a thirst for electrical energy storage remains one of the primary concerns of new materials research. Consequently, efforts have been intensified in the search for electrochemical power sources that are eco-friendly. The development of new solid materials for both electrodes and electrolyte is creating opportunities for improved versions of electrical power generation and storage systems, which may themselves in turn revolutionize many industrial areas. Nowadays, significant advances witnessed in this field may be attributed to the rate at which such useful and promising materials are being devised and synthesized [1-5].

The rapid development of a new generation of electronic devices such as power sources, displays, and sensors requires intensive research on solid electrolytes in order to improve their ionic conductivity and thermal, chemical and dimensional stability as well as processability. In this context, studies pertaining to the design and development of fast ion conducting solids have been carried out extensively, as fast ion conducting solid electrolytes are known to exhibit a range of significant properties such as high ionic conductivity, high electronic resistivity, large electrochemical stability window, good mechanical strength and ability to form excellent interfacial contacts with suitable electrodes, ease of processing, good chemical and thermal stability and hazard – free operation at ambient conditions [6-7].

A number of fast ion conducting systems with various mobile ions like Li^+, Na^+, Ag^+, Cu^+, Pb^{2+}, etc. have been identified over the years and their electrical properties investigated widely. Though literature reports that the class of AgI – based electrolytes offer promising characteristics [8-9], further exploration in this field is still wide open. In recent years, several research groups have developed a new class of solid electrolytes exhibiting appreciably high silver ion conductivity values by the replacement of AgI with other metal halides such as PbI_2, CuI, CdI_2, etc., with silver oxyacid salts through a systematic study of their electrical and electrochemical properties [10-11]. More recently, development of a new solid electrolyte system involving BiI_3 and silveroxy salt Ag_2WO_4 was attempted by us through a systematic study of ion transport, electrical and electrochemical properties [12]. Encouraged by these studies, it was also demonstrated through similar work on the mixed system BiI_3–Ag_2CrO_4 that the effective electrical conduction in several compositions of such system may be correlated to constituent phases and their structural features as well [13]. Stimulated by this success, we have now extended our investigation to the fast ion conducting pseudobinary mixed system namely, $(BiI_3)_{0.3}$ – $(Ag_2CrO_4)_{0.7}$ involving detailed frequency – dependent conductivity, modulus and dielectric studies with a view to derive necessary and sufficient information about the bulk conductivity as well as the electrical behavior and transport process of the fast ion conductor.

2. Experimental

2.1 Sample preparation

Commercially available analar grade chemicals of BiI_3 (Aldrich - Purity 99%) and Ag_2CrO_4 (Aldrich - Purity 99%) were used as raw materials for the preparation of the new binary system$(BiI_3)_{0.3}$ - $(Ag_2CrO_4)_{0.7}$. The appropriate amounts of the starting materials were weighed out according to the stoichiometric composition $(BiI_3)_{0.3}$ - $(Ag_2CrO_4)_{0.7}$. The mixture was placed in a quartz ampoule, vacuum-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 thus obtained was rapidly quenched into liquid nitrogen temperature and the quenched sample was then finely powdered using an agate mortar, and stored in darkened desiccators in order to prevent any light-induced reactions prior to further electrical characterization.

2.2 Characterization studies

Electrical conductivity spectra, dielectric loss and modulus formalisms were employed for the analysis of the complex impedance data obtained for powdered samples, of the fast ionic composition $(BiI_3)_{0.3}$ - $(Ag_2CrO_4)_{0.7}$ made into pellets of 8 mm diameter and 3 mm thickness under a pelletizing pressure of 5 ton/cm^2, using an Hewlett - Packard HP 4284A Precision LCR meter in the frequency window 20 Hz- 1MHz and over the temperature range 298 – 412 K.

The formation of certain glassy phases mixed with other polycrystalline materials was illustrated from our earlier work concerning structural and thermal features of the mixed system BiI_3-Ag_2CrO_4 [13]. The complex impedance measurements were also carried out on five different compositions of the mixed system $(BiI_3)_x$–$(Ag_2CrO_4)_{1-x}$, where x = 0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction of BiI_3 wherein the impedance data were analyzed by means of the Boukamp equivalent circuit software in order to obtain the electrical conductivity, σ using the formula $\sigma = \frac{t}{A \times R_b}$ where t denotes the thickness of the sample pellet and A its area of cross section. It is interesting to note that the electrical conductivities of the five different compositions of the above mixed system were in the range 10^{-6} to 10^{-3} Scm^{-1} at room temperature (298 K). The best conducting sample of this system viz., x = 0.3 mole fraction of BiI_3 was found to have an electrical conductivity as high as 7.1×10^{-3} Scm^{-1} at 298 K.

3. Results and discussion

The Arrhenius plots of log(σT) versus 1000/T obtained for the best conducting composition $(BiI_3)_{0.3}$ – $(Ag_2CrO_4)_{0.7}$ over the temperature range 298 – 412 K at various frequencies are shown in Fig. 1. The values of activation energy (E_a*) at different frequencies as calculated from the slope of the observed linear plot drawn by the least square method along with the value of activation energy (E_a) evaluated by complex impedance analysis for comparison are displayed in Table 1. It is interesting to note that a constancy of activation energy (E_a^*) at all frequencies has been observed.

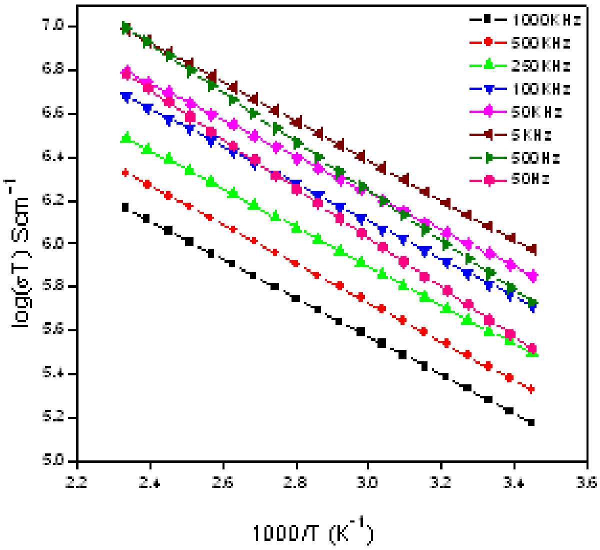

Fig. 1. Plots of log(σT) versus 1000/T obtained at different frequencies for the best conducting composition $(BiI_3)_{0.3}$ – $(Ag_2CrO_4)_{0.7}$.

Table 1. Frequency dependent conductivity results for the best conducting composition $(BiI_3)_{0.3}$ – $(Ag_2CrO_4)_{0.7}$.

Frequency kHz	Frequency-dependent conductivity equation $\log_{10}(\sigma T) = \log_{10}\sigma_0 - E_a^*/2.303kT$	Frequency - dependent activation energy E_a^* (eV)	Activation energy calculated from dc conductivity E_a (eV)
1000	$\log_{10}\sigma T = 5.022 - 1.827(10^3/T)$	0.12	0.12
500	$\log_{10}\sigma T = 6.105 - 1.417(10^3/T)$	0.12	
250	$\log_{10}\sigma T = 4.345 - 0.591(10^3/T)$	0.12	
100	$\log_{10}\sigma T = 4.18 - 0.827(10^3/T)$	0.12	
50	$\log_{10}\sigma T = 5.478 - 1.362(10^3/T)$	0.12	
5	$\log_{10}\sigma T = 6.733 - 1.75(10^3/T)$	0.12	
0.5	$\log_{10}\sigma T = 6.585 - 1.766(10^3/T)$	0.12	
0.05	$\log_{10}\sigma T = 7.785 - 2.317(10^3/T)$	0.12	

3.1 Conductivity spectra

Recently a number of attempts have been made to investigate the behavior of frequency - dependent conductivity of fast ionic solids using complex impedance analysis. During the present study the frequency response analysis has been carried out in terms of conductivity (σ), dielectric (ε) and modulus (M) formalisms for the best conducting composition containing x = 0.3 mole fraction of BiI_3.

The observed conductivity spectra (logσ versus logω) for the present fast ion conducting composition with x = 0.3 mole fraction of BiI_3 at five different temperatures 298, 324, 353, 393 and 412 K are shown in Fig. 2.

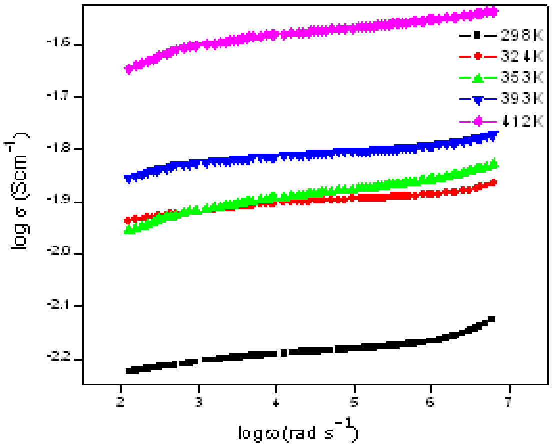

Fig. 2. Conductivity spectra for the best-conducting sample $(BiI_3)_{0.3}– (Ag_2CrO_4)_{0.7}$ at different temperatures.

These spectra may be explained well by considering three distinct frequency domains namely the low frequency region, mid frequency region and high frequency region. The variation of conductivity in the low frequency region is attributed to the various polarization effects at the electrode and electrolyte interface. In the mid frequency plateau region, conductivity is found to be almost independent of frequency from which dc conductivity of the sample, σ(0) could be evaluated [14]. In the high frequency region closer to relaxation times, the mobility of the charge carriers is high and hence the conductivity increases with frequency obeying the Jonscher's universal law. The high frequency region shows an increase in conductivity with increasing frequency obeying the Jonscher's universal law [15].

$$\sigma(\omega) = \sigma(0) + A\omega^n \tag{2}$$

where σ(0) is identified as dc conductivity. n and A are temperature - dependant constants.

Table 2 gives the values of fitting parameters A, n and σ(0) evaluated at five different temperatures viz., 298, 324, 353, 393 and 412K along with their hopping rate ω_p. In this system the values of σ(0) and A increase with increase in temperature whereas n decreases with increase in temperature. This type of variation is as expected in the case of silver ion conducting systems [16].

Table 2. Values of electrical conductivity parameters derived for the sample $(BiI_3)_{0.3} – (Ag_2CrO_4)_{0.7}$.

T (K)	A	n	σ(o) Scm-1	$\omega_p=\{\sigma(o)/A\}^{1/n}$ rad s^{-1}
298	2×10^{-9}	0.8	6.6×10^{-3}	8.3×10^{7}
324	6×10^{-9}	0.8	1.3×10^{-2}	2×10^{8}
353	1×10^{-7}	0.6	1.3×10^{-2}	3.1×10^{8}
393	3×10^{-7}	0.5	1.6×10^{-2}	7.1×10^{8}
412	9×10^{-5}	0.2	2.6×10^{-2}	3.9×10^{10}

3.2 Dielectric results

Complex permittivity (ε*) of a system having ε' and ε" as real and imaginary components is related to impedance data by the following equation

$$\varepsilon * = \frac{1}{j\omega C Z^*} = \varepsilon' - j\varepsilon" \tag{3}$$

where Z^* is complex impedance, ω = 2πf is the angular frequency and C, the vaccum capacitance of the cell is given by $\frac{\varepsilon_0 A}{t}$ in which t is the thickness of the sample and A is the effective area of electrodes.

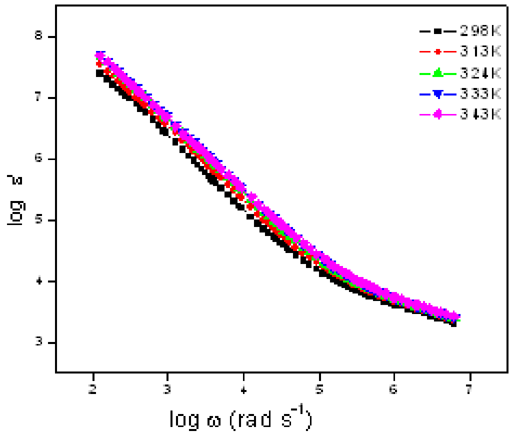

Fig. 3. Dielectric constant ε' versus logω for $(BiI_3)_{0.3}$*–* $(Ag_2CrO_4)_{0.7}$ *at different temperatures.*

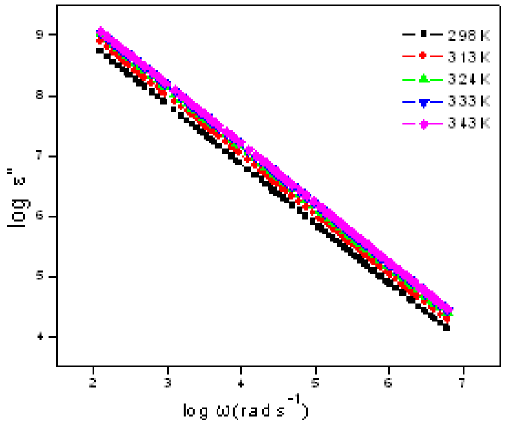

Fig. 4. Dielectric loss ε'' versus logω for $(BiI_3)_{0.3}$*–* $(Ag_2CrO_4)_{0.7}$ *at different temperatures.*

Figs. 3 and 4 illustrate the frequency – dependent logarithmic scale plots of the dielectric constant (ε') and that of dielectric loss (ε'') observed in the case of the best conducting composition $(BiI_3)_{0.3}$ – $(Ag_2CrO_4)_{0.7}$ over the varying temperature domain viz., 298, 313, 324, 333, and 343 K respectively. The observed variation in ε' and ε'' with frequency may be attributed to the formation of a space charge region at the electrode and electrolyte interface, familiarly known as the non-Debye behavior, where the space charge regions with respect to the frequency is explained in terms of diffusion of ions [17-18]. The high value of ε' observed at low frequency may be due to the contribution of thermally-activated space – charge (interfacial) polarization effect which may accumulate charge carriers near the electrode thus enhancing dipole orientation. It is also clear that the value of dielectric constant continuously decreases with frequency and finally reaches nearly a constant value i.e., frequency – independent nature in the higher frequency region. At high frequencies due to high periodic reversal of the field at the interface, the contribution of charge carriers (i.e., Ag^+ ions) decreases with increasing frequency. Also ε' exhibits, a dispersion which shifts to higher frequencies with increase in temperature. The increase in the value of dielectric constant ε' with temperature mainly as a result of the polarization may be occurring due to the increased migration of silver ions. On comparison with the dielectric constant spectra a similar trend is found to be exhibited by the dielectric loss ε'' as well with temperature in view of the fact that the dielectric loss is closely associated with the electrical conductivity. Thus, a decrease in both ε' and ε'' observed with increasing frequency may be due to the accumulation of decreased charge carriers near the electrodes.

Fig. 5 shows the variation of loss tangent (tanδ) as a function of frequency with varying temperature over the region 298 – 343 K for the composition having x=0.3 mole fraction of BiI_3. From this plot it is clear that, tanδ value increases and peaks are shifted toward higher frequency region at different temperatures and decreases thereafter, showing the relaxation behaviour of the solid electrolyte sample with temperature. The observed increase in tanδ values with temperature may be due to the increment in the number of charge carriers available for the conduction. As the temperature increases the charge carriers would have sufficient thermal energy to get activated and jump over the barrier as is evidenced from the observed shift in the peaks of relaxation towards the higher frequency region with rise in temperature.

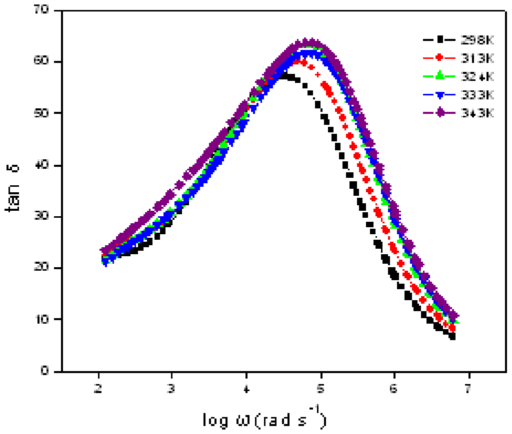

Fig. 5. tanδ versus logω for $(BiI_3)_{0.3}$*–* $(Ag_2CrO_4)_{0.7}$ *at different temperatures.*

3.3 Modulus spectra

In the case of ac conductivity and dielectric studies, low frequency measurements give useful insight into ion mobile diffusion and high frequency conductivity data enable to investigate the short time phenomena due to local motion of mobile ions. The modulus spectrum is therefore necessary to be examined since it has a major advantage that it suppresses those low-frequency peaks corresponding to the grain-boundary (intergranular) and information about electrode effects [19]. Complex modulus formalism $M^* = M' + jM'' = \frac{1}{\varepsilon^*}$ has been adopted in order to analyze the present ac conductivity data for understanding the distribution of relaxation time, commonly found in superion conducting glasses. In the present investigation, the frequency response data in terms of normalized modulus spectra pertaining to the composition with x = 0.3 mole fraction of BiI_3 in the mixed system $(BiI_3)_x-(Ag_2CrO_4)_{1-x}$, have been obtained at various temperatures for understanding the heterogeneous electrical nature of the solid electrolyte. Fig. 6 represent the normalized modulus spectra (M''/M''_{max} versus logω) obtained for the sample having x = 0.3 mole fraction of BiI_3 at five different temperatures viz., 298, 324, 353, 393 and 412 K respectively.

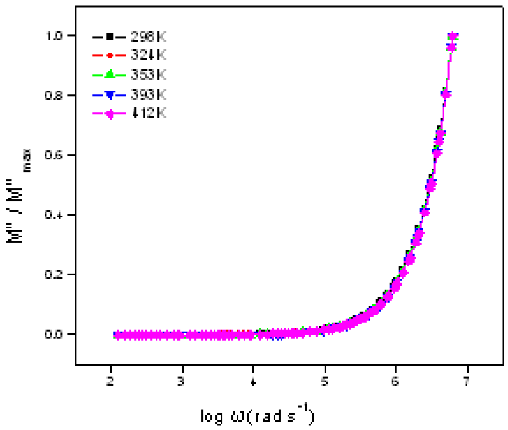

Fig. 6. The normalized modulus spectra (M''/M''_{max} versus logω) for $(BiI_3)_{0.3}-(Ag_2CrO_4)_{0.7}$ at different temperatures.

It is seen from Fig. 6 that the observed modulus spectra show a long tail and that curves observed at different temperature are also superimposable. The observed long tail in the low frequency region may be attributed to the large capacitance associated with the electrodes. The peaking curve noticed on the high frequency side may be attributed to the bulk effect occurring at different temperatures. Thus, it is clear from Fig. 6 that the relaxation associated with bulk property alone is highlighted and interfacial effects tend to be eliminated. The superimposability of the modulus curves obtained at different temperatures suggests the temperature-independence of the distribution of relaxation times [20]. In other words, the distribution of conductivities in the sample arising due to various layers within the solid is temperature-independent. As is seen from Fig. 6 the position of maximum, the loss peak in the modulus spectra is not accessible within the frequency range of investigation as it may occur at still higher frequencies. The fact that the shape of the curve is not changed due to the temperature clearly shows a temperature-independent distribution of relaxation times (DRT).

4. Conclusion

Silver ion conducting fast ionic glassy system $(BiI_3)_{0.3}-(Ag_2CrO_4)_{0.7}$ prepared by melt quenching technique exhibits the frequency - dependent conductivity behavior which obeys the Jonscher's universal expression. The observed variation of dielectric constant with frequency is attributed to silver ion diffusion and polarization occurring within the mixed system. The conductivity and dielectric constant of the present system are frequency - dependent and exhibit dispersion effects due to the distribution of relaxation times as in the case of other practical solid electrolytes. The modulus spectra also suggest a distribution of relaxation time which is independent of temperature.

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