

Electrical Modulus and Dielectric Relaxation Studies on Solid Electrolyte System $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$

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Abstract: The a.c. impedance analysis technique has been used to investigate the dynamic and relaxation behavior of mobile Ag^+ ions in the case of the best conducting composition $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$ which exhibited the highest value of electrical conductivity (3.0×10^{-3} S/cm) at room temperature (298 K) among the various compositions, previously examined by the authors, within a silver ion conducting multiphase system $(\text{BiI}_3)_x\text{-(Ag}_3\text{PO}_4)_{(1-x)}$ (where $0.1 \leq x \leq 0.9$ mole fraction). The experimental data derived from a.c. impedance measurements carried out at various frequencies ranging from 20 Hz to 1 MHz over the temperature domain 298 to 433 K have revealed that the chosen solid electrolyte system exhibits an a.c. conductivity behavior in accordance with Jonscher's universal power law. The dielectric response and analyses of normalized impedance and modulus spectra tend to indicate the existence of more than one relaxation process occurring within the bulk material and confirm the superionic nature of the solid electrolyte sample $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$ for feasible application in an all-solid-state electrochemical cell as well.

Keywords: Dielectric, Modulus, Relaxation, Composite electrolyte, Silver phosphate, Bismuth triiodide

Introduction

A number of ionic conductors having low ionic conductivity at room temperature are found to exhibit a superionic nature at higher temperatures with their conductivity increasing drastically in magnitude along with significant decrease in the activation energy for conduction. Several superionic systems in the form of polymers, ceramics and composites have been studied over the past few decades for various device applications. Composite materials are expected to exhibit the strength of ceramic materials¹ as well as the elasticity of polymers². With the discovery of solid electrolyte systems MAg_4I_5 (where $\text{M}=\text{Rb}, \text{K}, \text{NH}_4$) and Na- β -alumina during the year 1967 which exhibited appreciably high ionic conductivity values of the order of 10^{-1} S cm^{-1} at room and moderately high temperatures, there has been a tremendous spurt in the number of composite materials which could be effectively used as superionic solids²⁻³. Silver ion conductors have gained importance as fast ionic conductors

since the discovery of AgI which behaves as a solid electrolyte exhibiting a conductivity of as high as 1 Scm^{-1} at temperatures higher than room temperature⁴. Subsequently, several attempts have been made by researchers in order to achieve ionic conductivity data close to that of α -AgI in a number of materials at room temperature itself. Heterogeneous doping technique has been adopted to arrive at a number of binary and ternary composite solid electrolyte systems with Ag^+ ions as the mobile species. Monovalent (Cu^+ , Na^+ , Li^+)⁵⁻¹¹ and divalent (Pb^{2+} , Cd^{2+} , Mg^{2+})¹²⁻¹⁶ iodide dopants have been used in various silver oxysalt and silver oxide host matrices to synthesize AgI within such composite solid electrolyte systems in order to achieve electrical conductivity at room temperature comparable to that exhibited by AgI at higher temperatures (147 °C). Such silver ion composite systems developed have proved to offer potential solid electrolyte sources for the fabrication of all-solid-state batteries.

Based on an earlier effort by Takahashi *et al.*¹⁷ successful attempts have been made by the present authors to develop new binary composite systems using trivalent metal-iodide namely BiI_3 as a dopant in two different silver oxysalt systems namely Ag_2SO_4 and Ag_3PO_4 . As a consequence, detailed investigation carried out on the BiI_3 - Ag_2SO_4 binary system has already been reported recently by the authors¹⁸. Another new solid electrolyte system $(\text{BiI}_3)_x-(\text{Ag}_3\text{PO}_4)_{1-x}$ (where $x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 mole fraction respectively) developed and investigated by the present authors has also been established to be superionic in nature based on electrical conductivity, structural and thermal studies reported previously¹⁹. A detailed analysis of a.c. conductivity, electrical modulus and dielectric properties of the typical sample $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ which yielded the highest conductivity value among the various compositions investigated is presented here.

Experimental

One of the most common and powerful techniques of electrical characterization tools namely impedance spectroscopy has been employed for understanding the complex nature of the freshly-synthesized superionic material BiI_3 - Ag_3PO_4 . The electrical conductivity data obtained from complex impedance analysis has been used to take a closer look at the dynamic behavior and dielectric response of the sample. A.c. conductivity measurements were carried out on pellets prepared with the sample $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ as electrolyte and silver as non-blocking electrodes using a computer-controlled Hewlett-Packard model HP4284A Precision LCR meter at various temperatures of the sample ranging from room temperature (298 K) to 433 K.

Results and Discussion

A.C. conductivity spectra

Figure 1 shows the frequency dependence of electrical conductivity obtained at selected temperatures of 298, 313, 323, 333, 343, 353 and 363 K. There are apparently three distinct regions namely a low frequency dispersion region which may be attributed to the effects of polarization taking place at the electrode and electrolyte interface and secondly a plateau corresponding to the frequency-independent conductivity or dc conductivity σ_0 , followed by the high-frequency dispersion region²⁰⁻²¹. At all temperatures, a drop in conductivity is clearly seen as the frequency decreases which may be attributed to an increased accumulation of charges at the electrode-electrolyte interface. At high frequencies, the periodic reversal of the applied alternating field does not favor the accumulation of charges at the interface and hence conductivity increases rapidly with increasing frequency resulting in the observed dispersion which is characteristic of a multiphase system. A careful examination of the conductivity spectra obtained at various temperatures in the case of the sample $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ reveals a behavior similar to the one proposed by Jonscher's power law for a superionic solid.

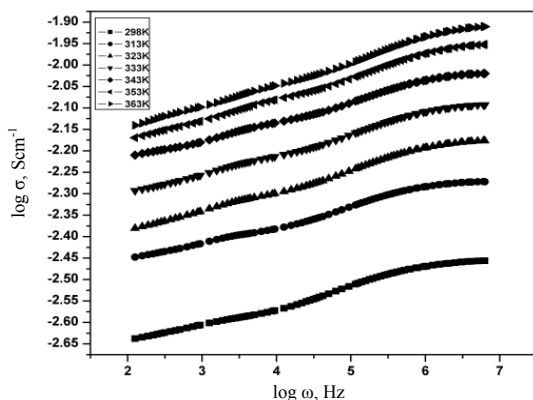


Figure 1. Conductivity spectra obtained for the solid electrolyte material $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$

$$\sigma_{ac}(\omega) = \sigma_o + A\omega^n \quad (1)$$

Where A is a pre-exponential constant, $\omega=2\pi f$ is the angular frequency, σ_o , dc conductivity and n is the power law exponent with the limitation $0 < n < 1$. The fitting parameters A and n have been evaluated and tabulated in Table 1. Both A and n are found to be temperature-dependent and their values contribute significantly in understanding the conduction mechanism within the sample under study. The decrease in the value of n with increasing temperature indicates a gradual opening up of channels which may provide a more flexible structure within the sample for faster ionic movement thus resulting in an increased ionic conductivity²². The dc conductivity value σ_o has been evaluated by the extrapolation of the frequency-independent plateau region towards the Y-axis in the above conductivity plots. The σ_o value obtained at room temperature (298 K) is found to lie close to that estimated from impedance analysis and reported earlier by the authors¹⁹.

Table 1. The dc conductivity and fitting parameters of Jonscher's power law obtained from the conductivity spectra and conductivity values obtained from the complex impedance plots for the composition $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$

T(K)	$\sigma_o \times 10^{-3}$ S/cm	A S cm ⁻¹ rad ⁻ⁿ s ⁿ	n	$\omega_p = [\sigma_o / A]^{1/n}$ rad ⁿ s ⁻ⁿ	Relaxation time sec	σ_{dc} from impedance plots $\times 10^{-3}$ S/cm
298	2.6	8×10^{-7}	0.51	7.69×10^6	1.3×10^{-7}	3
313	4.1	4×10^{-6}	0.41	2.2×10^7	4.5×10^{-8}	4.5
323	5.1	1×10^{-5}	0.35	5.44×10^7	1.8×10^{-8}	5.5
333	6.1	3×10^{-5}	0.29	9.11×10^7	1.1×10^{-8}	6.7
343	7.4	7×10^{-5}	0.23	6.32×10^8	1.58×10^{-9}	7.9
353	8.5	16×10^{-3}	0.19	1.2×10^9	8.3×10^{-10}	9
363	9.1	41.4×10^{-3}	0.13	2.11×10^{10}	4.74×10^{-11}	9.7

The values of dc conductivity as determined from the conductivity plots at selected higher temperatures are also found to be in good agreement with those obtained from corresponding impedance plots analyzed using Boukamp equivalent circuit software. The characteristic frequency ω_p at which dispersion begins at high frequencies and the corresponding relaxation time have also been evaluated from the conductivity spectra at different temperatures²³. It is found that the hopping frequency increases with increase in temperature thus confirming that ω_p is thermally-activated.

Impedance and modulus spectra

The normalized complex impedance spectra obtained for the best conducting composition $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$ at selected temperatures are shown in Figure 2. It is observed that as the temperature increases, the position of peak in the high frequency region is found to shift towards higher frequencies suggesting the existence of a distribution of relaxation times within the solid electrolyte system. The low frequency peaking may be attributed to the electrode polarization and grain-boundary effects.

Figure 3 shows the normalized modulus spectra observed as a function of temperature. A long tail in the low frequency region is observed which may be due to the large capacitance associated with the electrodes²⁴. Further, the peaking on the high frequency side may be ascribed to the effect of the bulk material with the maxima occurring beyond the frequency range of investigation. It is also seen that the modulus curves obtained at different temperatures overlap suggesting that the distribution of relaxation times is independent of temperature²⁵.

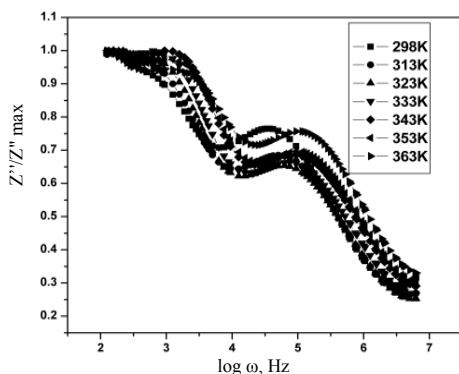


Figure 2 Normalised impedance spectra obtained for the solid electrolyte $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$ at different temperatures

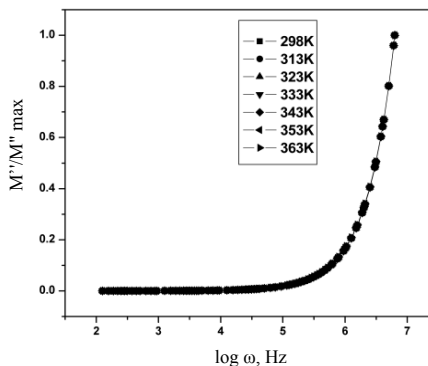


Figure 3 Normalised modulus spectra obtained for the solid electrolyte $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$ at different temperatures

Dielectric studies

The dielectric property of the best conducting composition $(\text{BiI}_3)_{0.4}\text{-(Ag}_3\text{PO}_4)_{0.6}$ of the already established polycrystalline superionic system, $\text{BiI}_3\text{-Ag}_3\text{PO}_4$, has been analyzed at selected temperatures with reference to variation of the real component, ϵ' and imaginary component, ϵ'' , of the complex dielectric permittivity and dielectric loss over the whole experimental frequency range of 20 Hz^{-1} MHz.

It may be clearly seen from Figure 4 that the dielectric constant decreases exponentially with frequency and becomes almost constant at very high frequencies. At a high temperature and low frequency the large value of dielectric constant may be due to ionic migration²⁶. As the temperature increases the value of the dielectric constant is found to increase at low frequencies thus indicating the contribution of different polarizations towards the conductivity in the highly-disordered solid system. As the frequency increases the value of dielectric constant decreases and is found to become almost independent of temperature at higher frequencies which may be attributed to ionic polarization²⁷. A similar response has been observed with dielectric loss as shown in Figure 5.

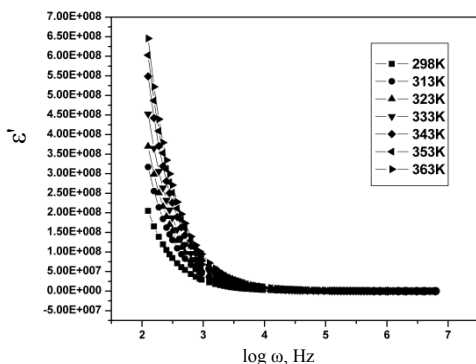


Figure 4. ϵ' vs. $\log\omega$ plots for the solid electrolyte $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ at different temperatures

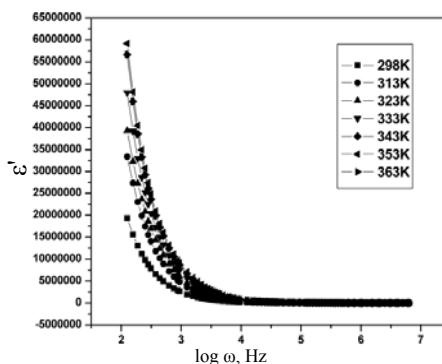


Figure 5. ϵ'' vs. $\log\omega$ plots for the solid electrolyte $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ at different temperatures

Loss tangent

The dependence of the dielectric loss tangent ($\tan \delta$) on frequency for three different compositions (*i.e.* $x=0.6, 0.5, 0.4$ and 0.3 mole fraction) of the dopant BiI_3 in the host material Ag_3PO_4 is shown in Figure 6. As the concentration of Ag_3PO_4 is increased in the composite system $\text{BiI}_3\text{-Ag}_3\text{PO}_4$, it is observed that in the high frequency region, the dielectric loss tangent decreases and shows the least value for the composition with 0.6 mole percent of Ag_3PO_4 content at higher frequencies which lies within the measured frequency limit thereby ascertaining the high electrical conductivity recorded by the best conducting composition analyzed. Figure 7 shows $\tan \delta$ vs. $\log\omega$ curves for the best conducting composition at different selected temperatures wherein two distinct relaxation peaks are seen, one in the low frequency region and another in the high frequency region. The low frequency peak may be attributed to the grain boundary and electrode effect whereas the high frequency peak may be associated with the bulk relaxation²⁸. The maxima of $\tan \delta$ in the bulk material appear to shift towards higher frequency indicating a decrease in the value of relaxation time and hence the height of the peak increases with increasing temperature. The dielectric relaxation phenomenon occurring within the bulk material is therefore found to be of the non-Debye type and may be due to the many-body interactions involved within the ionic conductor²⁹.

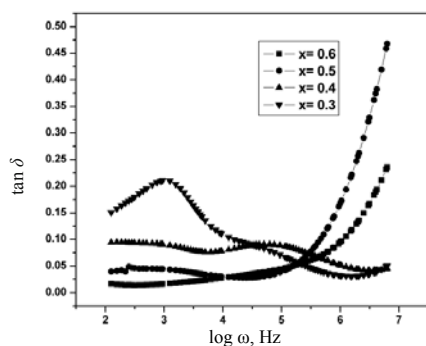


Figure 6. $\tan \delta$ vs. $\log\omega$ plots for the solid electrolyte system $(\text{BiI}_3)_x-(\text{Ag}_3\text{PO}_4)_{1-x}$ ($x=0.6, 0.5, 0.4$ and 0.3 mole fraction)

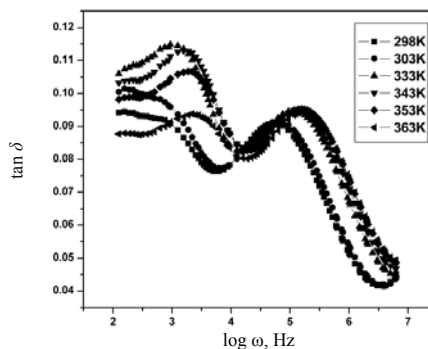


Figure 7. $\tan \delta$ vs. $\log\omega$ plots for the solid electrolyte $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ at different temperatures

Conclusion

The dielectric response of the typical solid electrolyte system $(\text{BiI}_3)_{0.4}-(\text{Ag}_3\text{PO}_4)_{0.6}$ suggests a non Debye-type of relaxation mechanism resulting from a distribution of relaxation times. Inferences from impedance and modulus spectra suggest that the prepared sample may be considered as a potential solid electrolyte material for the fabrication of an all-solid-state electrochemical device.

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