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Ceramics International 30 (2004) 1655–1660

CERAMICS INTERNATIONAL

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Electrical transport studies on CdI_2 doped silver oxysalt system

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Received 18 November 2003; received in revised form 17 December 2003; accepted 23 December 2003

Available online 15 June 2004

Abstract

A new glass system $x CdI_2$-$(100 - x)[2Ag_2O–(0.7V_2O_5–0.3B_2O_3)]$, $5 \leq x \leq 20$, has been prepared by melt quenching technique. The electrical conductivity studies of the samples have been carried out at different temperatures and frequencies. The transport number of the Ag^+ determined by the emf method is 0.98. The frequency dependence of electrical conductivity has been analyzed by Jonscher's power law. Data were analyzed in terms of permittivity and modulus formalisms. The modulus spectra of the present system suggest a distribution of the relaxation time, which is found to be temperature independent. The cooperative motion due to strong coupling between the mobile Ag^+ ions are assumed to give rise to the non-Debye type of relaxation. The behavior of ac conductivity and relaxation phenomenon can be explained by the diffusion controlled relaxation (DCR) model proposed by Elliott.

Keywords: D. Glass; Silver ion conduction; Transport number; Permittivity; Modulus

1. Introduction

Considerable effort has been taken to the development of new Ag^+ ion conducting solid electrolytes, since the discovery of high ionic conductivity in $RbAg_4I_5$ in 1967 [1]. The technological interest in these glasses, characterized by a high ionic conductivity leads to their possible application as solid electrolyte in many electrochemical devices like solid state batteries, fuel cells, memory devices etc [2]. To optimize the transport properties of these systems various compositional variations of glass formers and modifiers were studied where as the dopant salt AgI remained as the host. There are only few reports in the literature having silver oxysalt system with dopant salt other than AgI like $CuI–Ag_2MoO_4$ [3], $PbI_2–Ag_2O–V_2O_5$ [4] etc. So we are studying a quaternary glass with dopant salt other than AgI to have a cost effective system having the composition $xCdI_2$-$(100 - x)[2Ag_2O–(0.7V_2O_5–0.3B_2O_3)]$, where CdI_2 is the dopant salt, Ag_2O is the glass modifier and $V_2O_5–B_2O_3$ are the glass formers. The composition of the total glass formers kept constant as $(0.7V_2O_5–0.3B_2O_3)$, glass modifier to former ratio $M/F = 2$ and x has been varied from 5 to 20 mol% in steps of five. AC electrical impedance measurements are used widely to study the ionic conduction in solids to avoid the polarization effects during the dc conductivity measurement. From the ac conductivity studies, the low frequency measurements give useful insight into mobile ion diffusion and high frequency conductivity data helps us to investigate the short time phenomena due to the local motion of mobile ions. The present paper reports the preparation, conductivity, dielectric and modulus studies of the $x CdI_2$-$(100 - x)$ $[2Ag_2O–(0.7V_2O_5–0.3B_2O_3)]$ glass system.

2. Experimental

Glasses were prepared by the melt quenching technique by mixing the calculated weights of CdI_2, Ag_2O, V_2O_5, B_2O_3 in the appropriate ratios. The mixture is placed in a quartz ampoule and heated to the temperature range 800–1000 K for 4 h. The homogeneous melt obtained was then quenched in liquid nitrogen to form the glass. The formation of the glass was verified by recording the X-ray diffractogram using the Rigaku miniflex X-ray diffractometer employing a monochromatic Cu Kα radiation. DSC spectrum were recorded using Modulated Differential Scan-

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doi:10.1016/j.ceramint.2003.12.160

ning Calorimeter 2910 model (TA Instrument) with a heating rate of 10 °C min^{-1}. Fourier transform infrared spectra were recorded using Bomem Michalsons series FTIR spectrometer, in the range 400–2500 cm^{-1} at room temperature. The electrical conductivity measurements of the glasses were carried out at different temperatures using Alpha Dielectric Analyzer in the frequency range 100 Hz–10 MHz. The solid samples were powdered and pressed into pellets at an optimum pressure of 5000 Kg cm^{-2} with silver electrodes on both sides of the pellet having the configuration Ag/electrolyte/Ag. The evaluation of the contribution of silver ions in the present CdI_2 doped system, transport number was measured by emf method. A cell of the type Ag, electrolyte/electrolyte/I_2, C, electrolyte, was made in the form of a pellet by pressing the cell components at a pelletising pressure of 5000 Kg cm^{-2}. The transport number of the silver ions, t_r can be found by the relation, $t_r = E/E_0$, where E is the emf measured and E_0 is the standard emf corresponding to the cell reaction obtained from thermo dynamical calculations.

3. Results and discussion

The X-ray diffractogram showed that all the present glass samples are X-ray amorphous. DSC spectrum shows the glass transition temperature (T_g) decreases with the CdI_2 content. The IR transmittance spectra recorded for all the glasses to understand the type of the vanadoborate structural unit. The spectra contain absorption bands near 500, 714, 856, 894, 923, 966, 1008, 1333–1408 cm^{-1}. The bands observed at 1008 cm^{-1} results from the vibration of the independent V=O vanadyl group in VO_5 groups. The absorption bands at 894, 923,966 cm^{-1} are assigned to the VO_3 terminal stretching of the pyrovanadate ions whereas the bands at 500 cm^{-1} (ν_{sym}) and at 714 cm^{-1} (ν_{asym}) are assigned to V–O–V bridge stretching. The absorption bands at 1333–1408 cm^{-1} are assigned to the ν_3 mode in BO_3 groups and the band at 856 cm^{-1} corresponding to BO_4 groups. Further it is found that the IR band positions are not changing much with the dopant salt CdI_2 content.

The dc conductivity of the glass composition obtained from the impedance measurements are shown in Fig. 1 as a function of inverse of temperature. The variation of conductivity with temperature can be represented by the Arrhenius Eq.

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where σ_0 is the pre-exponential factor, k the Boltzmann constant, T the absolute temperature and E_a is the activation energy for conduction. Table 1 shows the room temperature conductivity values, activation energy and glass transition temperature obtained for the composition studied. It can be seen that the room temperature conductivity reaches a maximum value for the composition of 20 mol% of CdI_2 and hence it is the best conducting system among the various compositions investigated during the present study. This observation is found to be similar to the PbI_2–Ag_2O–V_2O_5 system studied [4].

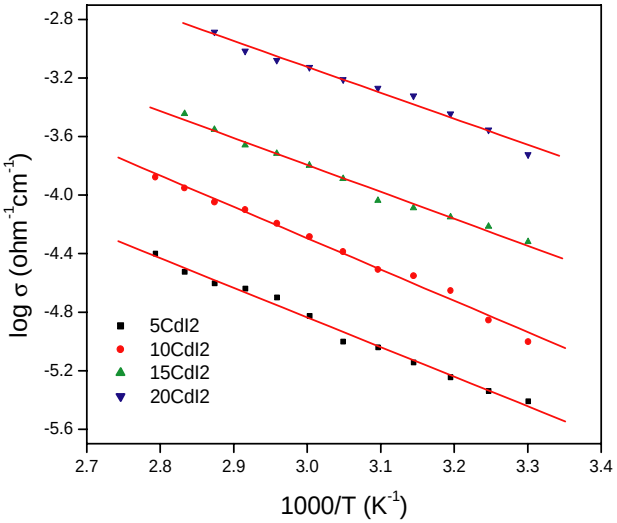


Fig. 1. Arrhenius plots for various compositions in the system xCdI$_2$-(100 − x) [2Ag$_2$O–(0.7V$_2$O$_5$–0.3B$_2$O$_3$)].

3.1. Coductivity spectra

Frequency dependent conductivity spectra obtained for x = 5 mol% of CdI_2 in the xCdI$_2$-(100 − x)[2Ag$_2$O–(0.7V$_2$O$_5$–0.3B$_2$O$_3$)] system at various temperatures are shown in Fig. 2. Fig. 3 shows the log σ versus log f plot for x = 5, 10, 15, 20 mol% of CdI_2 at room temperature. As the mole percentage of CdI_2 increases conductivity shows a gradual increase. As seen in Fig. 2, the frequency dependent conductivity plots show two distinct regions; an almost frequency independent plateau region at low frequencies and a dispersion at high frequencies. The high frequency dispersion is predominant at lower temperatures and with increase in temperature it shifts towards the high frequency region. Finally the high frequency dispersion region almost disappears at higher temperatures, since the jump frequency of the charge carriers increases with temperature [5]. The dc plateau and the extended conductivity dispersion at higher frequencies usually follow Jonschers power law [6].

$$\sigma_{(\omega)} = \sigma_0 + A\omega^n \quad (2)$$

Table 1
Composition of the glass studied, conductivity at room temperature, activation energy E_a and glass transition temperature T_g for the CdI_2 doped quaternary system

CdI_2	Ag_2O	V_2O_5	B_2O_3	σ_{RT} (Ω^{-1} cm^{-1})	E_a (eV)	T_g (K)
5	63.4	21.12	9.48	3.9×10^{-6}	0.4218	380.3
10	60.0	21.00	9.00	9.9×10^{-6}	0.4207	376.0
15	56.7	19.81	8.49	4.8×10^{-5}	0.3939	369.1
20	53.4	18.62	7.98	1.7×10^{-4}	0.3518	352.5

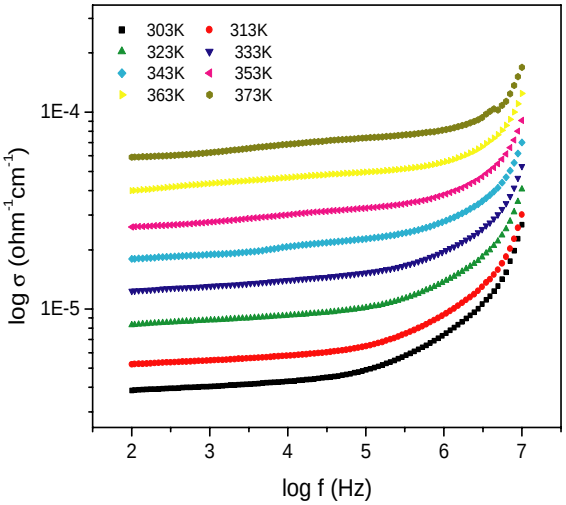


Fig. 2. Conductivity spectra at different temperatures for the $5CdI_2$–$63.4Ag_2O$–$21.12\ V_2O_5$–$9.48B_2O_3$ glass.

where, $\sigma_{(\omega)}$ is the conductivity at a particular frequency, σ_0 the dc conductivity of the sample at zero frequency, A and n are weakly temperature dependent parameters and n is the power law exponent varies from zero to one ($0 < n < 1$). The power law of ac behavior is observed in a wide range of systems, Jonscher called it the Universal behavior, since Eq. (2) is accepted universally for finding the sample conductivity, hopping rate, frequency dependence of conductivity etc. The power law variation has been widely investigated and the strong dispersion at low temperature in the high frequency region is attributed to many body effects.

3.2. Dielectric studies

Complex permittivity is related to the impedance data as, $\varepsilon^* = 1/j\omega C_0 Z^* = \varepsilon' + j\varepsilon''$, where Z^* is the complex impedance, $\omega = 2\pi f$ is the angular frequency and C_0 is

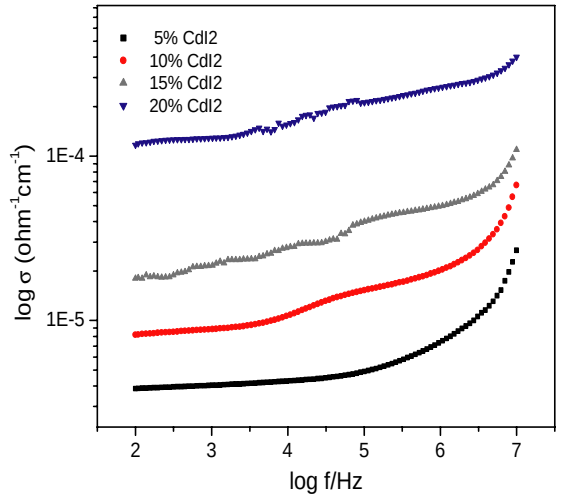
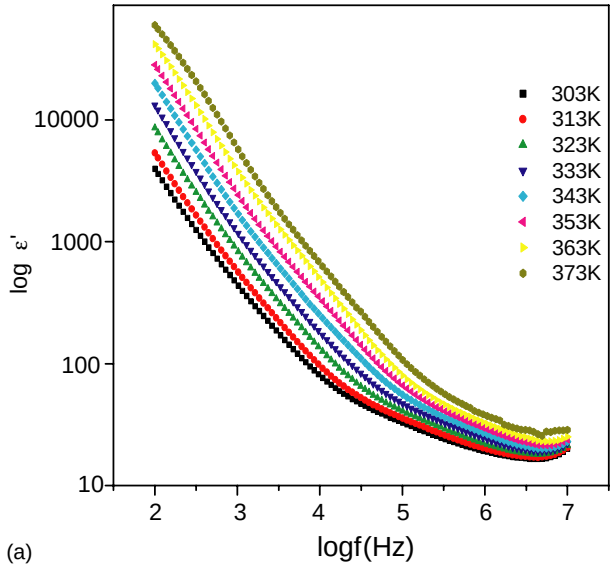


Fig. 3. Conductivity plot for different composition at room temperature for the system xCdI$_2$-$(100 - x)$[$2Ag_2O$–$(0.7V_2O_5$–$0.3B_2O_3)$] glass.



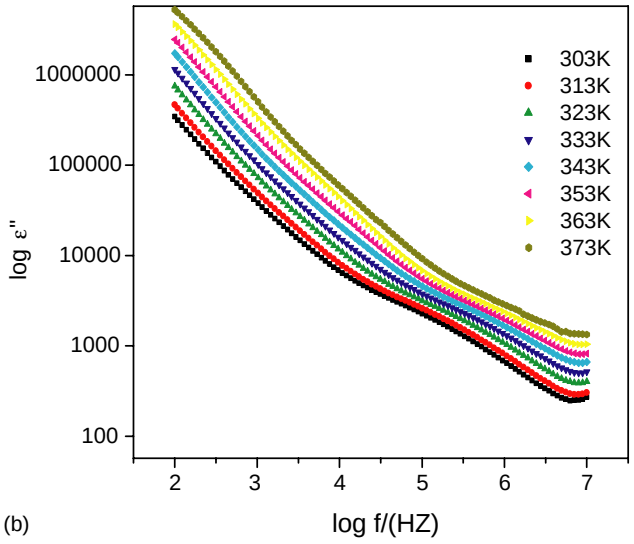


Fig. 4. (a) Dielectric constant and (b) dielectric loss versus frequency for 5 mol% of CdI_2 system at different temperatures.

the vacuum capacitance of the cell. Dielectric constant, ε' and the dielectric loss, ε'' as a function of log frequency for 5 mol% of CdI_2 is plotted in Fig. 4(a) and (b) at various temperatures. The observed high value of ε' at low frequency is due to the presence of large capacitance at the electrode electrolyte interface. The value of ε' is found to decrease with increase in frequency and saturates at higher frequencies. At high frequencies due to high periodic reversal of the field at the interface, the contribution of charge carriers decreases with increasing frequency. ε' exhibit a dispersion which shift to higher frequencies with increase in temperature. This is because at high temperature the jump frequency of mobile ion is large and it resonate with the frequency of the applied electric field. ε'' is found to vary linearly with frequency for all the studied glasses. The dielectric will not show a peak unless the dc conductance is subtracted. Complete under-

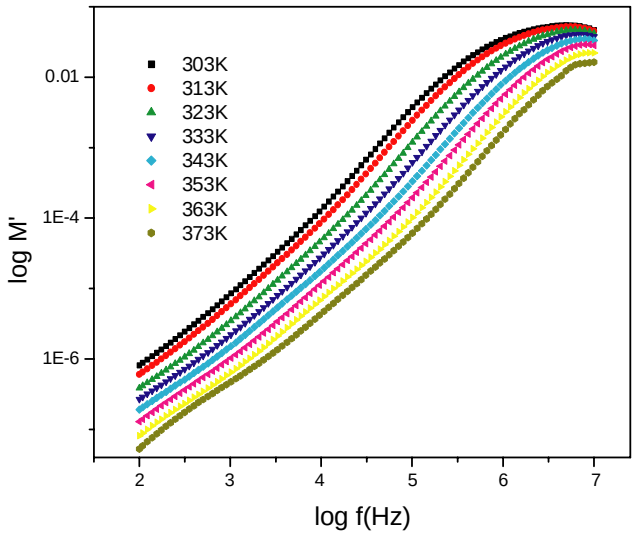


Fig. 5. Real part of modulus spectra with frequency at different temperatures for 5 mol% of CdI_2 glass.

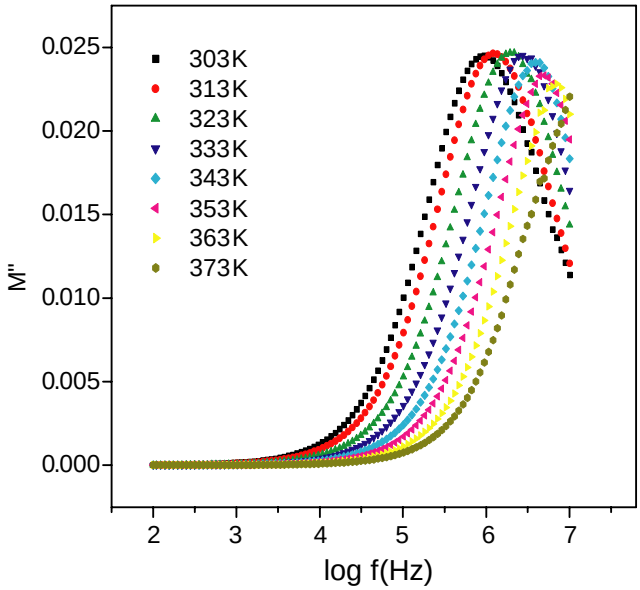


Fig. 6. Variation of the imaginary part of complex modulus M'' for $5CdI_2$–$63.4Ag_2O$–$21.12V_2O_5$–$9.48B_2O_3$ glass.

standing of the transport mechanism of mobile ions from the dielectric studies is possible only when the loss factor peaks at a frequency or at a temperature. Hence the modulus formalism is necessary to study and has its advantage that it suppress the information about electrode effects [7] and transforms the monotonically increasing conductivity with frequency into one exhibiting a peak, scaling behavior of the data is rather more evident in modulus representation.

3.3. Modulus analysis

Complex modulus formalism ($M^* = M' + jM'' = 1/\varepsilon^*$) has been adopted to analyze the ac conductivity data for understanding the distribution of relaxation time, commonly found in super ion conducting glasses. The frequency dependence of M' for the glass composition with 5 mol% of CdI_2 is shown in Fig. 5 at several temperatures. M' reaches a maximum saturation value, $M_\infty = 1/\varepsilon_\infty$, as frequency increases and at low frequencies M' approaches to zero which indicate the electrode polarization makes a negligible contribution [8]. The variation of M' at low and high frequency can be predicted by the model proposed by Macedo et al. [9].

$$\lim_{\omega\tau \ll 1} M' = 0 \quad \text{and} \quad \lim_{\omega\tau_\sigma \ll 1} M' = M_\infty = \frac{1}{\varepsilon_\infty} \tag{3}$$

At higher temperatures M' levels off at higher frequencies shows the relaxation processes are spread over a range of frequencies. The plot of M'' versus $\log f$ at various temperatures are shown in Fig. 6. The obtained plot is asymmetric with respect to peak maxima and the peaks are considerably broader on both side of the maxima than would be predicted by the ideal Debye behavior. The peak maxima shift to higher frequencies with increase in temperature. The peak heights at different temperatures are nearly the same. The region to the left of the peak is where the charge carriers are mobile over long distances while the region to the right is where they are spatially confined to the potential wells. The frequency ω_m where the maximum in M'' occurs is indicative of the transition from a long range to a short-range mobility and is defined by the condition $\omega\tau_\sigma = 1$, where τ_σ is the conductivity relaxation time. Full width half height (FWHH) for the systems is nearly constant at various temperatures, which indicate that the distribution of relaxation time is independent of temperature. From the figure it is seen that the frequency corresponding to M''_{max} shifts towards to higher frequencies with increase in temperature. The plot of ω_m (where ω_m is the frequency corresponding to M''_{max}) versus inverse of temperature obeys the Arrhenius relation. The activation energies calculated from both impedance and modulus spectrum are comparable which suggests that the dispersions were not caused by dielectric loss or by electrode polarization and the transport of silver ions in the present system by the hopping mechanism [8]. The reduced plot for the modulus data at different temperature is shown in Fig. 7. The perfect overlap of the curves for all temperature in to a single master curve indicates that the dynamical process occurring at different frequencies are independent of temperature. The plots are characterized by a broad peak, which can be assigned to the summation of relaxations occurring in the bulk material [8]. The full width half height obtained is greater (∼1.8) than the Debye type of relaxation with single time constant is attributed to the presence of strong ion-ion interaction [10]. The β parameter obtained is ∼0.6, comparing with the FWHH value, Moynihan et al. [11], is the exponent in the stretched exponential or KWW (Kohlrausch–William–Watts) Eq.

$$\phi = \exp\left[\left(-\frac{t}{\tau}\right)^\beta\right] \quad 0 < \beta < 1, \tag{4}$$

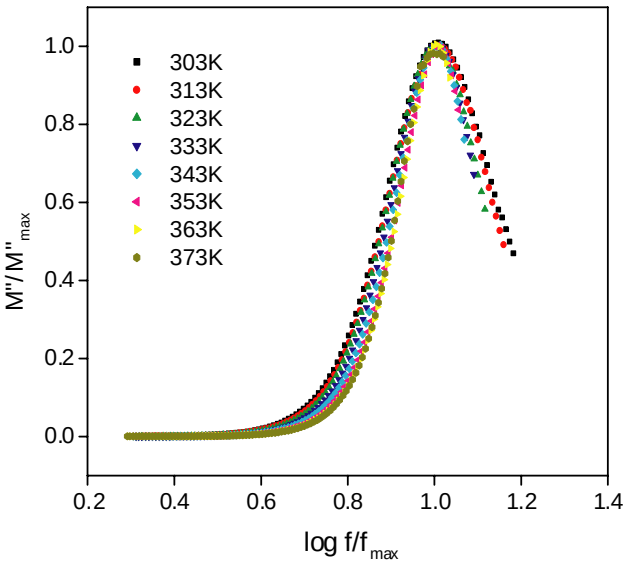


Fig. 7. Reduced plot of modulus at different temperatures for 5 mol% of CdI_2 glass system.

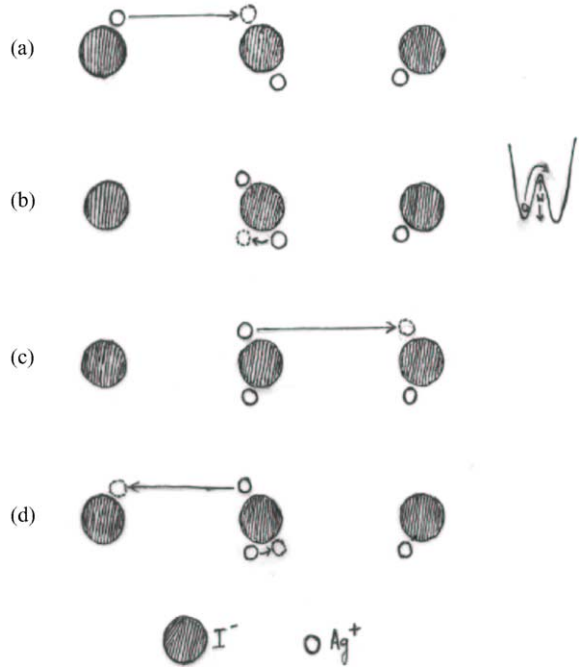


Fig. 8. Schematic representation of DCR model to explain the relaxation process in the CdI_2–Ag_2O–V_2O_5–B_2O_3 glass.

where ϕ is an external stress such as electric field, t the time and τ is the relaxation time for the overall process. The β parameter has been interpreted either as representative of the distribution of relaxation times or as characteristic of co-operative motions between charge carriers [12]. The co-operative motion due to strong coupling between the mobile silver ions are assumed to give rise to the non-Debye type of relaxation [13].

3.4. Ag^+ ion transport number

The emf of the galvanic cell constructed using 20 mol% of CdI_2 composition as solid electrolyte phase and silver powder as anode and I_2 as cathode has been measured to be 0.671 mV at room temperature, where as the corresponding theoretical value of the open circuit voltage for Ag/I_2 couple is 0.687 mV. Accordingly, the transport number of silver ion in this composition is evaluated as 0.98 at room temperature. Thus it is evident that Ag^+ ions would be the majority charge carriers in the CdI_2 doped silver oxysalt system.

The high silver ion conductivity observed in the present system has been achieved as a result of the reciprocal role of Cd^{2+} ions in the Ag_2O–V_2O_5–B_2O_3 matrix. Similar results have been reported for CuI doped [10] and PbI_2 doped systems [11] etc. There seems to be an exchange reaction taking place in the glassy matrix as per the following Eq.

$$Cd_{[I]}{}^{2+} + 2Ag_{[O]}{}^{+} = 2Ag_{[I]}{}^{+} + Cd_{[O]}{}^{2+}$$

where the subscript [I] indicates the iodine environment and [O] indicates the oxygen environment. This is in accordance with the Pearsons theory, [14] of hard and soft acids and bases [HSAB]. The HSAB theory indicates that a hard acid would prefer to bind with a hard base and a soft acid would prefer to bind with a soft base. So the soft acid Ag^+ and soft base I^- prefer to form AgI clusters resulting in high silver ion conductivity.

The observed behavior of ac conductivity and relaxation phenomena in the presently investigated systems can be explained on the basis of diffusion controlled relaxation (DCR) model proposed by Elliott [15]. The AgI molecule formed after the exchange mechanism are assumed to be separated by a distance λ. First the Ag^+ ion near I^- ion diffuses to another I^- ion Fig. 8(a), forms an interstitial (defect) pair. Then the position occupied by the original silver ion can no longer be in the lowest energy configuration as a result both the silver ions rearrange itself to achieve the new lowest energy configuration Fig. 8(b). Following that one of the two Ag^+ ion at the defect site can diffuse to a third site and thereby repeating the relaxation process and contributing to dc conductivity, Fig. 8(c). Alternatively one of the Ag^+ ion at the defect site can hop back to the original site and this consequent back and forth motion between the neighboring sites will contribute to ac conductivity, Fig. 8(d). Hence through this model two contributions to ac conductivity can be observed as inter site hopping motion of ions and the intra site motion of ions.

4. Conclusion

The present study deals with the preparation, characterization and electrical conductivity study of the different amount of CdI_2 doped silver oxysalt system. The composition with 20 mol% of CdI_2 is found to exhibit the highest electrical conductivity. The high silver conductivity

observed in the present system has been explained on the basis of Pearsons theory of hard and soft acid and bases. Ag^+ ion transport number found by emf technique is almost unity. Frequency dependent conductivity of the system studied obeys the Jonschers power law. The variation of dielectric constant with frequency is attributed to ion diffusion and polarization occurring in the glass system. The FWHH of the asymmetric spectrum obtained in the modulus analysis is nearly constant at various temperatures, which indicates the distribution of relaxation time is independent of temperature.

Acknowledgements

The authors acknowledge with thanks the financial help rendered as minor research project by the M.S. University of Baroda and Dr. A.M. Awasthi, IUC-DAEF, Indore, for the DSC facility.

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