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RESEARCH ARTICLE

MIXED AC CONDUCTIVITY STUDIES IN ALKALI AND TRANSITION METAL IONS DOPED BORATE GLASSES

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Abstract

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In the present study, B_2O_3 glasses doped with Na_2O and Fe_2O_3 was prepared via melt quenching method. The amorphous nature of the samples has been confirmed by the XRD studies. The polaronic conduction for the wide range of temperature and frequency were studied. As temperature increases the dielectric properties found to be enhanced and with increment in frequency they found to be decreased. The high temperature ac conductivity data has been analyzed by Mott's small polaron hopping model (SPH). Activation energy passed through maximum and conductivity passed through minimum at 0.20 concentrations of sodium oxide which attributes that the switch over of conduction process, taking place at 0.20 molar fraction of alkali ions from primarily polaronic to ionic in the present series of glasses.

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Introduction:-

Glasses doped with various alkali and transition metal ions [TMI] were gained much importance over the last few years due to its technological applications in solid-state devices, cathode materials for batteries, electronics and electro-optical devices. [1,2]. Among such glass systems, alkali rich containing borate glasses have been extensively studied due to their significant development on electrical properties. In this work sodium oxide seems to be the greatest beneficial alkali cation for electrochemical uses due to smaller in size, having less mass and great electro positivity [3]. Significant importance has been drawn on the conduction process in borate glasses containing various TMI and alkali ions, but majority of the experimental investigations were constrained to particular molar fractions. In order to understand the insulating behavior, conduction mechanism and the structural characteristics for the present host glasses, the study of dielectric constant (ε), dielectric loss (ε'') and ac conduction (σ_{ac}) over a wide range of frequency and temperature gives complete conduction mechanism for these glasses [4]. These glasses have several advantage over crystalline counterparts for example easy formability over extensive ranges of compositions, isotropicity, and deficiency of grain boundaries. [5, 6].

Alkali borate glasses comprising many TMI can exist in multiple valence states [7]. These glasses found to be unaffected to atmospheric moisture and are accomplished by accommodating maximum content of TMI [8, 9]. The ionic conduction in the present glass systems features to the transport of alkali ions in reply to the applied external field [10]. Conductivity studies in alkali doped borate glasses containing various TMI exposed to variation over conduction process from polaronic to ionic for a particular mole fraction [11]. The conductivity due to polaronic

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among the borate glasses having TMI can be acknowledged by the mechanism of SPH model among the ions existing in the dissimilar valence states [12]. Consequently, a mixed polaronic to ionic conduction was distinguished in such glass systems however; alkali ions live together with TMI in the glass network.With the help of impedance analyzer, an experimental study was carried out in order to investigate the behavior of mixed polaronic to ionic in transition metal oxide (TMO) containing alkali ions. When the TMO acts as a glass former, a dip in the polaronic conductivity was seen for a particular mole fraction of alkali ions. Suppose, if the host borate glass having TMO, which is glass network modifier a dual behavior, was distinguished. A mixed polaronic-ionic conduction was seen in these glasses containing copper oxide. The extensive studies were made on the mixed mobile ions effect in borate glass doped with Na- Ag [13]. The polaronic conductivity on frequency dependent studies in oxide glasses doped with Na containing TMI have been reported [14]. The purpose of our effort is to examine the occurrence of mixed conduction at particular composition in terms of dielectric constant, dielectric loss and ac conductivity.

In the present article, we report the results on ac conduction and dielectric behavior of $(Na_2O)_x-(Fe_2O_3)_{0.5-x}-(B_2O_3)_{0.5}$ (x = 0.05,0.1,0.15,0.20 and 0.25 mole fraction coded as BFN5, BFN10, BFN15, BFN20 and BFN25) glasses were measured in the temperature range 313-473 K and in the frequency range 100 Hz-5MHz.

Experimental:-

Glass series with general formula $(Na_2O)_x-(Fe_2O_3)_{0.5-x}-(B_2O_3)_{0.5}$ were prepared by adopting melt-quench method. Chemicals of analytical grade (AR) with 99.99% purity, of Na_2CO_3,Fe_2O_3 and H_3BO_3 procured from HI-media were used for synthesis of the glass samples. The chemical quantities in required weight ratios were taken in porcelain crucibles and the composition was thoroughly mixed in order to get the homogeneity. These porcelain crucibles are placed into the electrical muffle furnace and melted between the temperature ranges from 1300K to 1400K for different glass compositions. After confirming that the melt was transparent, it was rapidly quenched at room temperature by transferring the melt on to a thick steel plate and covering it with another steel plate. The samples of irregular sized were collected. The collected samples were then annealed at 473 K so as to remove thermal strains, if any, in them. As prepared samples were subjected to XRD to confirm their non-crystalline nature. For the ac conductivity measurements, the random size samples of 12 x 10 x 0.6 mm were cut and shaped with lapping papers. On the two faces of the well-shaped samples the silver paste electrodes were applied for better conductivity.

The measurements of capacitance, C, and dissipation factor, tan δ, were obtained using a computer controlled LCR meter (ZM2376, NF Corporation, Japan) for different frequencies in the range 1mHz to 5.5 MHz and temperature from 313K to 473K. The dielectric constant (ε′), dielectric loss factor (ε″) and ac conduction (σ_{ac}) were calculated using the expressions [15],

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \quad (1)$$

$$\varepsilon'' = \varepsilon' \tan\delta \quad (2)$$

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon'' \quad (3)$$

where, ε_o is the permittivity of free space, d is thickness of the glass sample and A is cross-sectional area of the sample.

Results and Discussion:-

XRD

The X-Ray Diffraction pattern obtained for two samples i.e. BFN10 and BFN15 were depicted in Figure. 1.The nonappearance of sharp peak in intensity versus 2θ curves represents the amorphous behavior of the glass sample.The profile of the recorded spectra does not have any sharp peaks confirmed the glass samples studied are perfectly non-crystalline in nature. The remaining samples has been observed to be similar profiles.

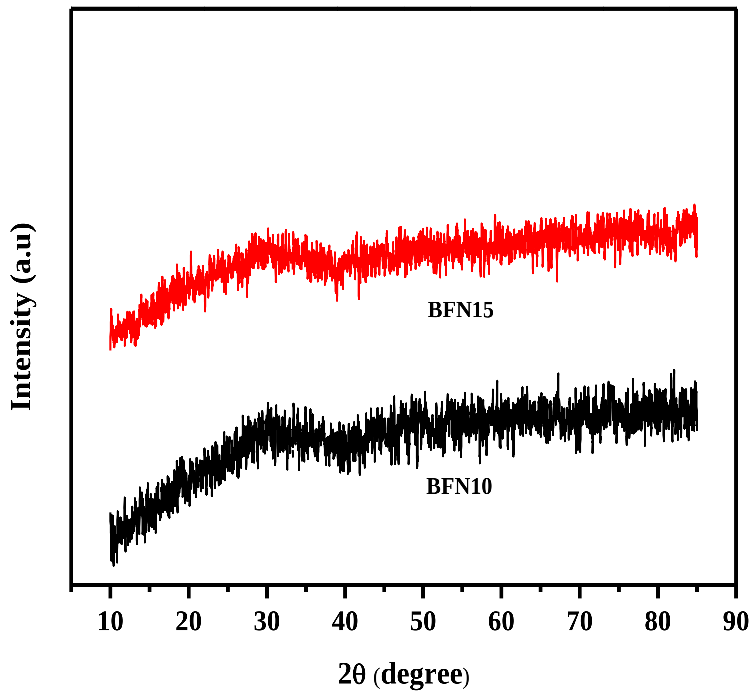

Figure 1:- X-ray diffraction pattern of BFN10 and BFN15 samples.

Dielectric constant and loss

The graph of ε′ against frequency for all glass samples for different composition at 453K is displayed in Figures. 2 and 3, separately. The measured ε′ and ε″ were found to in the range of 1 $x10^1$ to 2.2 $x10^2$ and 10^1 to 10^4 correspondingly. It can be observed from Figures. 2 and 3 that both ε′ and ε″ declined with rise in frequencies and rises with rise in temperature. Analogous outcomes were noticed in the occasion of different TMI doped borate glasses [16.17]. This is owing to the fact that at higher frequency, the alkali ions cannot follow the field variation and because of interfacial effects for example, space charge polarization may occur [18]. The typical plot of dielectric constant, ε′ versus frequency for BFN20 glasses at various temperature is depicted in Figure.4. It can be noted that ε′ reduced with increment in frequency.

The compositional dependence of dielectric constant, ε′, for the BFN glasses at 453K and for different frequencies is illustrated in Figure.5. From Figure 5, it can be noted that dielectric constant, ε′, at 453K decreases and passes through lowest value at 0.20 molar fraction of Na_2O content and rises for further doping of Na_2O concentrations. An interesting observation was noted from the Figure 5, that for higher frequencies i.e., 100 kHz and 1 MHz, variation of dielectric constant, ε′, with Na_2O is found to be less deep at 0.20 mole fraction. Similar observations have been observed for ε″.

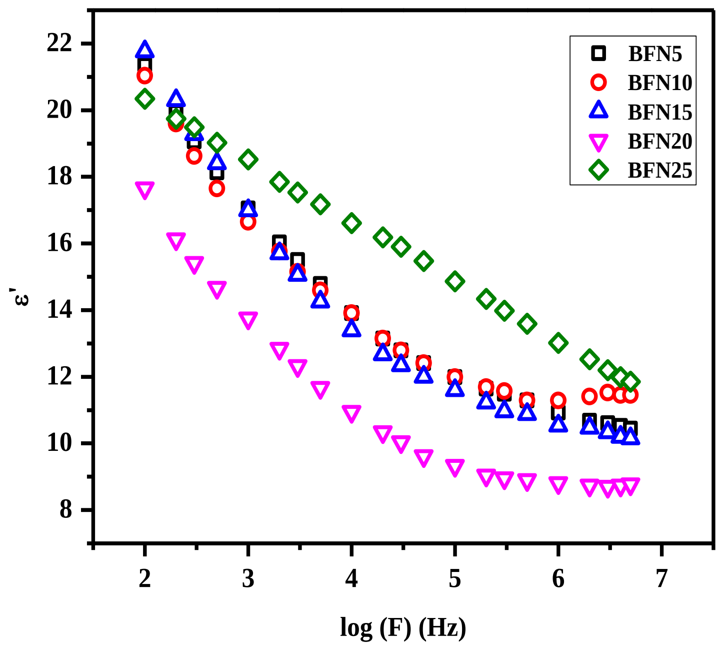

Figure 2:- Plot of log (F) versus (ε′) at T=453K temperature for all glasses.

AC Conductivity:-

In the present glass systems, the ac conductivity variation was noticed to be due to thermally stimulated mechanism and is due to the hopping of polarons among the different states of Fe ions in the glass network [19]. Mott's SPH model was considered to be appropriate for analyzing the high temperature dependent ac conductivity The patterns of ln (σ_{ac}T) versus (1/T) at 100 kHz for BFN glasses are shown in Figure.6. Within the studies temperature, the ac conductivity varied from 10^{-5} $\Omega^{-1}m^{-1}$ to 10^{-6} $\Omega^{-1}m^{-1}$ and these values are found to be similar with the reported literature values on related and other glass systems [11, 14, 20]. The electronic conductivity for the studied composition of glasses dropped with rise in the alkali ion concertation upto 0.20 molar fraction and in addition to this increase in alkali concentration, conductivity found to increased.

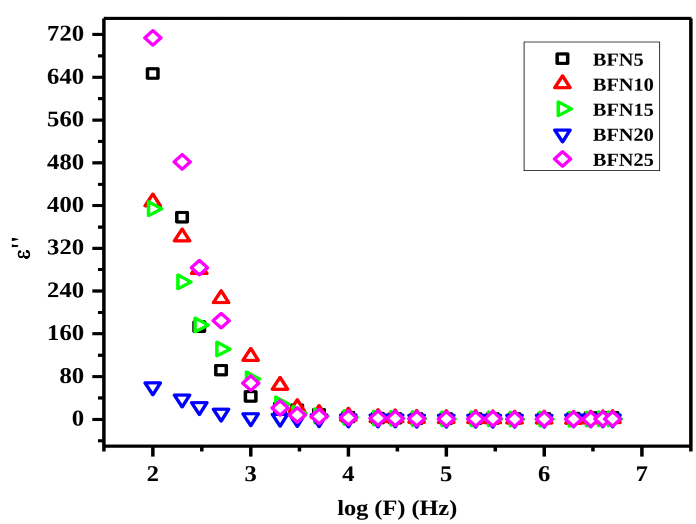

Figure. 3:- Plot of log(F) versus (ε″) at T=453K temperature for all glasses.

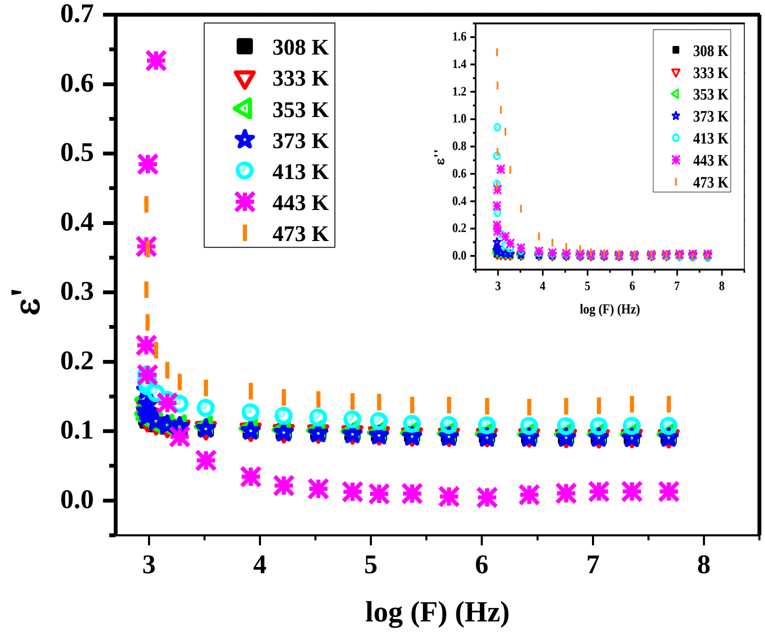

Figure 4:- Plotof log(F) versus (ε″) for the glass BFN20 at different temperatures. Inset shows the frequency dependency of ε″ for the glass sample BFN20.

Figure. 7 represents the temperature dependence of ac conductivity at different frequencies for BFN20 glass systems. From this figure, it is observed that conductivity was found to decrease with increase in frequencies and further increase in frequencies, the conductivity was found to increased.

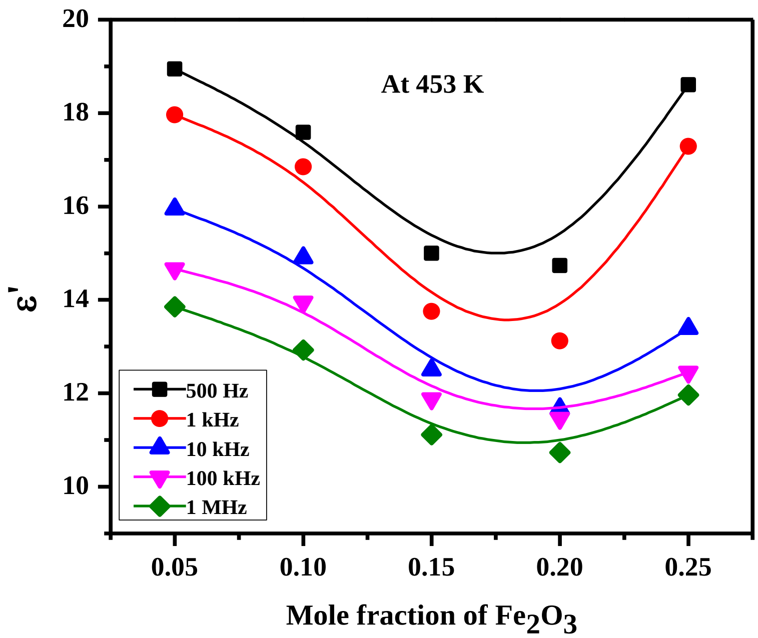

Figure 5:- Compositional dependence of dielectric constant, ε′, for the BFN glasses at453K and for different frequencies. Solids lines drawn are guides to the eye.

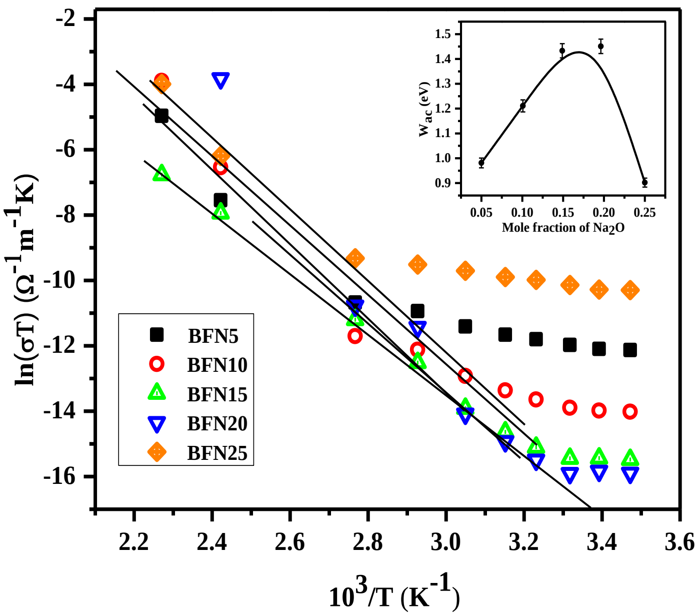

Figure 6:- Temperature dependence of ac conductivity at 100 kHz for BFN glasses. Solids lines are the least square linear fits to the high temperature data. Inset shows the variation of ac activation energy with composition.

In the present series of glasses, at different frequencies and temperature the glass samples showed decrease in electrical conduction with rise in Na_2O ion concentration up to 0.20 molar fraction and enhanced for additional content of sodium ions. This type of variation indicates the changeover of conduction process from primarily polaronic to ionic taking place at 0.20 molar fraction of sodium content.

Due to the semiconductor nature in all the present glass systems, the high temperature dependence of ac conductivity follows Arrhenius law. As per the Arrhenius law, the electrical conductivity in non-adiabatic system is expressed as [21],

$$\sigma = \frac{\sigma_o}{T}\exp\left(-\frac{W_{ac}}{k_B T}\right) \quad (4)$$

where, W_{ac} is the activation energy and σ_o is the pre-exponential factor.

The profiles of $\ln(\sigma_{ac}T)$ against (1/T) at a frequency of 100 kHz for BFN glass systems are plotted as per Eq. (4) and they are illustrated in Figure. 6. At high temperature, the plotted curves were found to be linear and at low temperature, the curves were observed to be non-linear. The data at high temperature were fit with the linear lines and slopes were measured. With the help of slope form linear line fit, the $W_{ac,}$ were determined. The determined W_{ac} values are in the range0.902-1.450 eV.

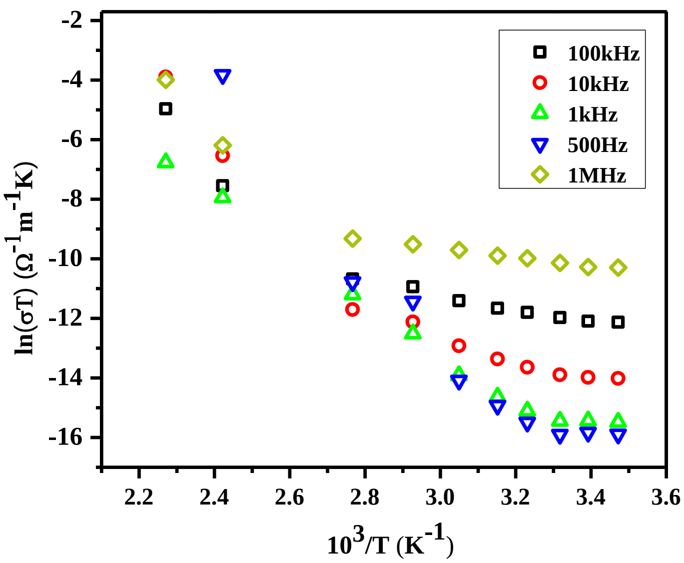

Figure 7:- Temperature dependence of ac conductivity at different frequencies for the glass BFN20.

Figure. 8 shows the nature of W_{ac} and the ac conduction with the molar fraction of Na_2O content. From this figure, it is noted that, the W_{ac} were observed to rise with rise in Na_2O concentrations upto 0.20 molar fraction and reduced for additional increment in Na_2O ion concentrations. Moreover, this supports a variation of ac conduction process is from major polaronic to ionic, which is noticed in terms of ac conductivity. On the basis of these remarks, one may conclude that, mixed electronic-ionic behavior is occurring in the present glass series.

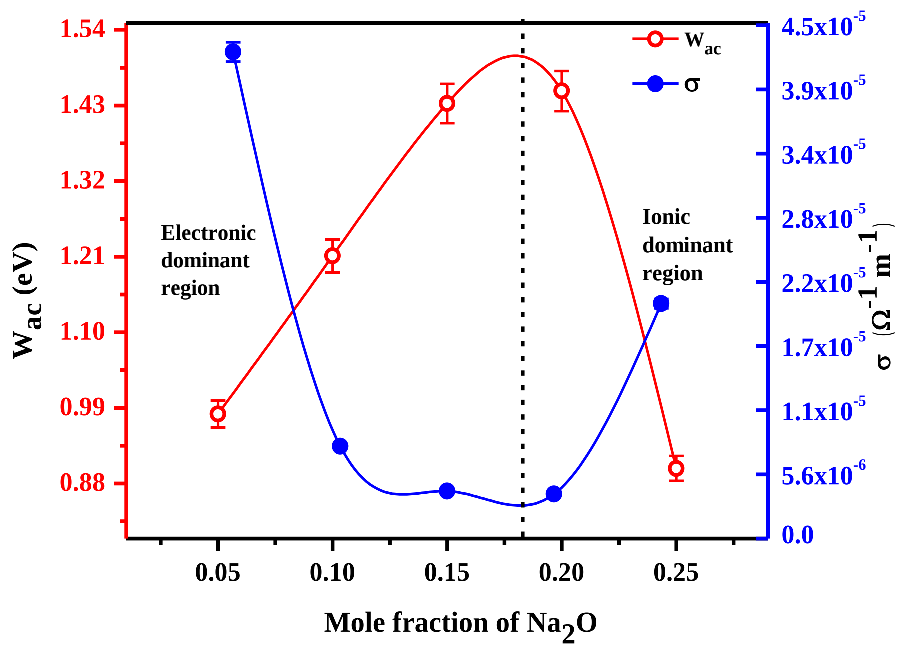

Figure 8:- Compositional variation of activation energy, W_{ac}, and conductivity at 453K and at 100 kHz for the BFN glasses. The lines are drawn as guide to eye.

Conclusions:-

A borate glass system containing Na_2O and Fe_2O_3 were prepared by melt quenching method. The amorphous nature of the samples has been confirmed by the XRD studies. The ac electrical conductivity and dielectric properties as a function of temperature and frequency over a wide range have been examined. The ε′ and ε″ reduced with increase in frequency. This is attributed to the reduction in polaronic conductivity.

The ac conduction at high temperature was explained using Mott's SPH model. The ac conductivity reduced and activation energies enhanced with rise of sodium concentrations at with respect to all frequencies upto 0.20 molar fraction of sodium oxide concentration and then the ac conduction raised and ac activation energy reduced for more addition of Na ion. These outcomes are established that a changeover of conduction process primarily from polaronic to ionic taking place at 0.20 mole fraction of sodium oxide content.

Reference:-

1. J. Livage, J.P. Jolivet, E. Tronc, J. Non-Cryst. Solids 121 (1990) 35.
2. D. L. Sidebottom, M. A. Hruschka, B. G. Potter, R.K. Brow, Appl. Phys. Lett. 71 (14) (1997) 1963.
3. A. Sheoran, S. Sanghai, S. Rani, A. Agarwal, V.P. Seth, J. Alloys Compd., 475 (2009) 804.
4. T. Suzuki, M. Hirano, H. Hosono, J. Appl. Phys. 91 (2002) 41.
5. S. Sanghi, A.Sheoran, A. Agarwal, S. Khasa, Physica B 405 (2010) 4919.
6. M. D. Ingram, Phys. Chem. Glasses 28 (1987) 215.
7. R. Chakradhar, P. Sreekanth, A. Murali, J.L. Rao, Physica B 293 (2000) 108.
8. B. Roling, J. Non-Cryst. Solids 244 (1999) 34.
9. B.S. Rawal, R.K. Maccrone, J. Non-Cryst. Solids 22 (1978) 347.
10. R.J. Barczynski, P. Krol, L. Murawski, J. Non-Cryst. Solids 356 (2010) 1965.
11. R.C. Agarwal, R. Kumar, J. Phys. D: Appl. Phys. 27 (1994) 2431.
12. L. Murawaski, C.H. Chung, J.D. Mackenzie, J. Non-Cryst. Solids 32 (1979) 91.
13. G. El-Damrawi, Phys. Chem. Glasses 42 (2001) 56.
14. G.D.L.K. Jayasinghe, M.A.K.L. Dissanayake, M.A. Careem, J.L. Souquet, Solid State Ionics 93 (1999) 291.
15. D. Dutta, A. Ghosh, Phys. Rev. B 72 (1993) 24201.
16. R. El-Mallawany, A. El- Sayed, M. El- Gawad, Mater. Chem. Phys. 41 (1995) 87.
17. M.M. Elkholy, Phys. Chem. Glasses 42 (2001) 49.
18. M. Prashant Kumar, T. Sankarappa, S. Kumar, J. Alloys Compd. 464 (2008) 393.
19. M. Sayer, A. Mansingh, Phys. Rev. B 6 (1972) 4629.
20. J. Zhong, P.J. Bray, J. Non-Cryst. Solids 111 (1989) 67.
21. N.F. Mott, J. Non-Cryst Solids 01 (1968) 01.