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Physica B 364 (2005) 248–254

PHYSICA B

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Electrical relaxation in mixed lithium and sodium iron phosphate glasses

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Received 9 May 2004; received in revised form 9 April 2005; accepted 9 April 2005

Abstract

The electrical conductivity of mixed-alkali, lithium and sodium, iron phosphate glasses has been studied in the frequency range from 0.2 to 200 kHz and over a temperature range from 323 to 493 K. The AC conductivity as a function of temperature was divided into two domains, one where the absolute magnitude of the AC conductivity was close to the DC conductivity and another where it was larger than the DC conductivity. The DC conductivity for the mixed-alkali, lithium and sodium, iron phosphate glasses is independent of the Li/Na ratio and there is no evidence of any mixed-alkali effect. The lithium and sodium ions have such a low mobility in both single- and mixed-alkali iron phosphate glasses that they make no detectable contribution to the total conductivity that is of electronic origin. Mössbauer spectral analysis indicates the presence of both Fe^{2+} and Fe^{3+} ions.

PACS: 72.80.Ng; 72.60.+g; 66.30.Ed; 61.40

Keywords: Mixed alkali effect; Electronic- Ionic conductivity; Conductivity relaxation; Activation energy

1. Introduction

Some glasses containing transition metal ions, such as iron, vanadium and tungsten, are electronically conductive [1–6]. The semiconducting behavior is due to the transition metal ions being in more than one valence state [7,8]. An example of this transition of Fe^{2+} and Fe^{3+} conduction takes place by electrons hopping from low to high valence sites. The charge transfer in such glasses is usually termed "small polaron hopping" (SPH) [9,10] and the electrical conductivity depends strongly upon the distance between the iron ions [7,8,11].

In alkali iron phosphate glasses, the electrical conductivity generally consists of both ionic and electronic conduction. The ionic conduction is

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doi:10.1016/j.physb.2005.04.016

proportional to the alkali concentration and alkali mobility while the electronic conduction follows the hopping theory [12]. Ideally, the motions of the alkali ions and electrons are independent of each other. Therefore, we expect that the electrical conductivity will increase proportionately with increasing alkali content in iron phosphate glasses. However, our recent investigation of mixed calcium and barium iron phosphate glasses has shown that the slowly moving calcium or barium ions are more lightly bound to the non-bridging oxygen ions and make no measurable contribution to the total conductivity in glasses containing up to 20 mol% calcium or barium oxide [13]. The DC conductivity in these mixed calcium and barium iron phosphate glasses is totally electronic, controlled by hopping between iron ions. Also, the electrical conductivity in mixed alkali, sodium and potassium, iron phosphate glasses is nearly independent of the different sodium and potassium contents. This independence indicates that the mobility of sodium and potassium is almost invariant in the single- and mixed-alkali iron phosphate glasses [15,16].

Mixed-alkali iron phosphate glasses have recently gained attention because of their potential use as host materials for vitrifying high-level nuclear wastes, as well as of academic interest [17]. The excellent chemical durability and high waste loading ability of these glasses are two of the several features which make them attractive for nuclear waste vitrification [17,18].

In this work, the electrical relaxation in the mixed-alkali (Li and Na) iron phosphate, $16[(1-x)Li_2O–xNa_2O]–24Fe_2O_3–60P_2O_5$, $(0\leqslant x\geqslant 1)$, glasses was examined by DC and AC conductivities. The oxidation state of iron in these glass compositions was determined by using Mössbauer spectroscopy.

2. Experimental

Glass samples were prepared using analytical reagent grade chemicals according to the formula $xLi_2O–(16-x)Na_2O–24Fe_2O_3–60P_2O_5$, where $x = 0$, 4, 8, 12 and 16 mol%. Batches that produced 50 g of glass were prepared by mixing reagent grade Fe_2O_3, P_2O_5, Na_2CO_3 and Li_2CO_3 dry crystalline powders that were melted in platinum crucibles in air at 1200 °C for 1 h with occasional stirring, poured onto a polished copper block kept at room temperature and immediately pressed by a similar copper block. The samples were then annealed at 300 °C for 3 h to remove any stress from the quenched glass. The amorphous nature of the glasses was examined using X-ray diffraction. For the conductivity measurements, disk shaped samples of 8 mm diameter were cut and polished with very fine lapping papers. Silver paste electrodes were painted on both faces of the polished sample.

The $(Fe^{2+}/\Sigma Fe)$ ratio (C) was determined from Mössbauer spectral analysis at room temperature in a transition geometry employing $^{57}Co(Rh)$ as the radioactive source. The results obtained were analyzed using a computer program based on Lorentzian distribution.

The AC conductivity and dielectric constant were measured using a Chen Hwa 1061 LCZ meter. The DC conductivity was measured under a constant DC voltage, employing the potential probe method. Before the measurements, the ohmic behavior (I–V) was ascertained from the linearity of the voltage current characteristic.

3. Results

The electrical conductivity exhibits a low power [19] at higher frequency and terminates by constant DC conductivity at low frequencies. This leads to the empirical form of the total conductivity, $\sigma(\omega)$, for different temperatures that is expressed as $\sigma(\omega) = \sigma_{AC}(\omega) - \sigma_{DC}$, where σ_{DC} is the DC part of total conductivity $\sigma(\omega)$ and ω is the angular frequency. This equation is valid for several low-mobility amorphous and even crystalline materials [13].

The frequency dependence of $\sigma_{AC}(\omega)$ at different temperatures for the iron phosphate glass containing $8Li_2O$ and $8Na_2O$ mol% is shown in Fig. 1. The figure shows that for all glass samples at lower frequencies, the conductivity is almost independent of the frequency, approaching the DC conductivity. As the frequency is increased, the conductivity shows a dispersion, which shifts to

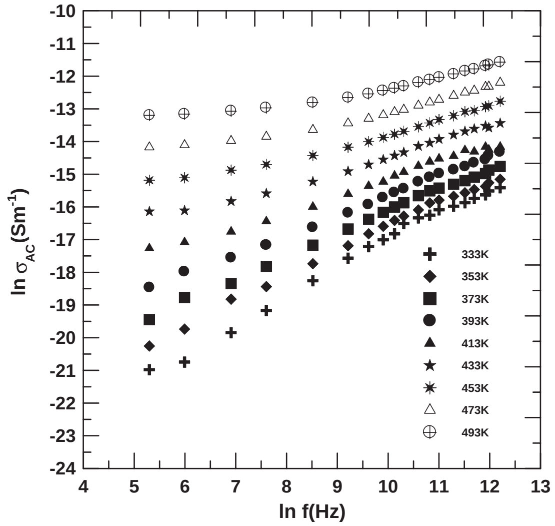

Fig. 1. Frequency dependence of AC conductivity (σ_{AC}) at various temperatures for the mixed ($8Li_2O$ and $8Na_2O$ mol%) iron phosphate glasses.

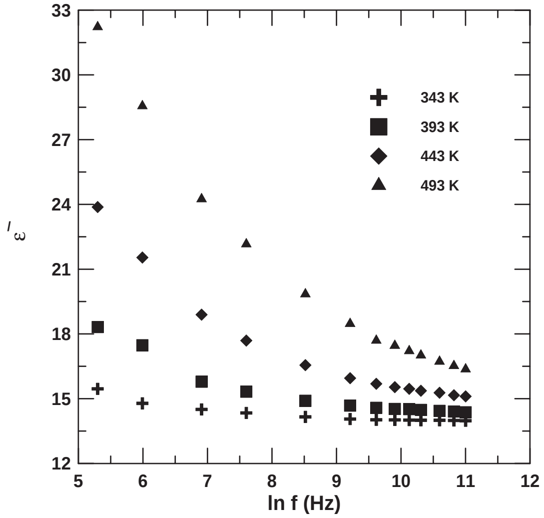

Fig. 2. Frequency and temperature dependence of dielectric constant (ε') for the mixed ($8Li_2O$ and $8Na_2O$ mol%) iron phosphate glasses.

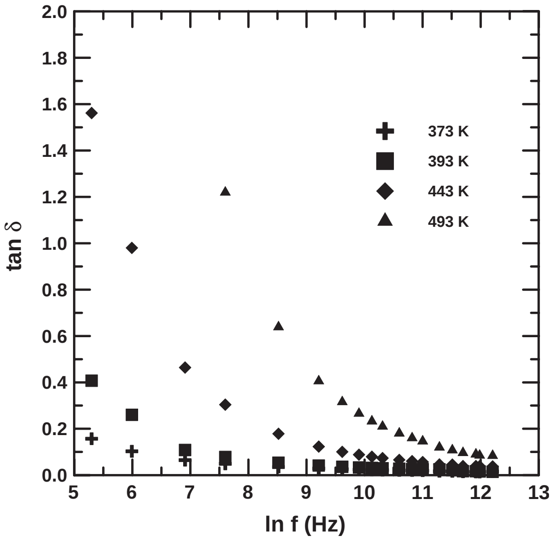

Fig. 3. Frequency and temperature dependence of dielectric loss tangent (tan δ) for the mixed ($8Li_2O$ and $8Na_2O$ mol%) iron phosphate glasses.

higher frequencies with increases in temperature [20]. On the other hand, the AC conductivity as a function of the temperature was divided into two domains, one where the absolute of AC conductivity is close to the DC conductivity and another where the absolute magnitude of AC conductivity is larger than the DC conductivity [14–16].

The complex dielectric constant (ε) of a material medium is given according to Debye [21], assuming a single relaxation time, τ, in the form $\varepsilon = \varepsilon' + j\varepsilon''$, here ε' is the real part (dielectric constant) and ε'' is the imaginary part (dielectric loss). The dielectric loss tangent, tan δ, is defined as $\tan\delta = \varepsilon''/\varepsilon'$ [22]. This measures directly the phase difference due to loss of energy within a sample at particular frequency.

Figs. 2 and 3 show ε' and tan δ as a function of frequency at different temperatures for mixed ($8Li_2O$ and $8Na_2O$ mol%) iron phosphate glass, respectively. As observed from Fig. 2, the dielectric constant increases with increasing temperature and decreases with increasing frequency. This behavior indicates a Debye-type dielectric dispersion [21]. If there is a maximum in tan δ (Fig. 3) this maximum lies at frequencies less than 50 Hz. On the other hand, the usual behavior of increasing ε' with temperature may be due to a decrease in bond energies and dissociation of more alkali cations from their sites, and the consequent increase in diffusion or oscillation process through the glass matrix [23]. These results are similar to that of $Na_2P_2O_6$–Fe_2O_3 and V_2O_5–P_2O_5 glasses [6,23].

The AC plus DC conductivity and total conductivity, $\sigma(\omega)$, for different frequencies as a function of the reciprocal temperature for the iron phosphate glass containing $8Li_2O$ and $8Na_2O$-mol% are shown in Fig. 4. At lower temperatures, σ_{AC} is greater than σ_{DC}, with smaller temperature dependence but larger frequency dependence. At higher temperatures, σ_{AC} becomes temperature dependent and approaches σ_{DC}. The temperature at which σ_{DC} equals the measured total conductivity, $\sigma(\omega)$, increases with increasing frequency.

On the other hand, Fig. 5 shows the relation between σ_{DC} for the glasses and the reciprocal temperature. These glasses have σ_{DC} values in the range 6.22×10^{-11} to $5.04\times10^{-6}\,\mathrm{Sm}^{-1}$ at temperatures from 303 to 493 K. Fig. 5 shows the linear relationship between $\ln\sigma_{DC}$ and $1/T$. The slope of the curves which gives the activation energy for conduction, however, has two different values and increases at higher temperatures. For these linear curves different slopes in two temperature regions, σ_{DC} is apparently expressed as $\sigma_{DC}=\sigma_0\exp(-W/kT)$, where σ_0 is a pre-exponential factor, k is the Boltzmann constant and W is the activation energy. The values of W in the high temperature regime are given in Table 1.

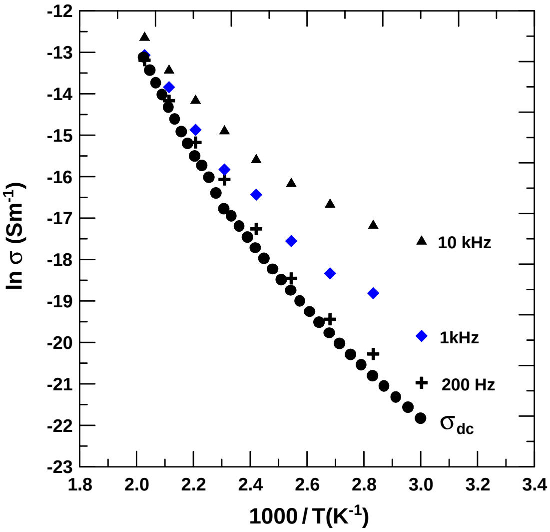

Fig. 4. Temperature dependence of total (AC plus DC) conductivity for the mixed ($8Li_2O$ and $8Na_2O$ mol%) iron phosphate glasses.

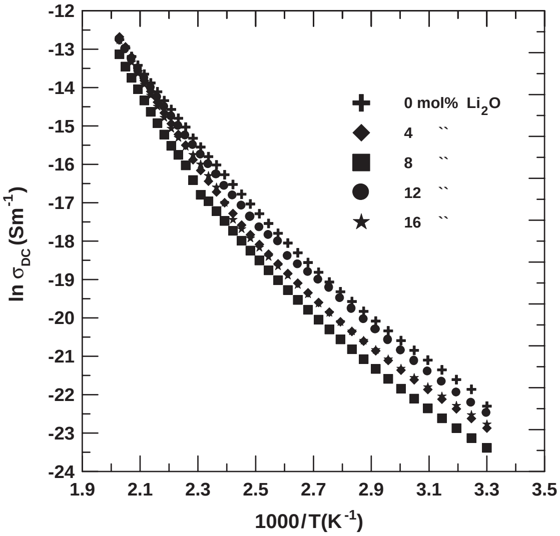

Fig. 5. Temperature dependence of DC conductivity (σ_{DC}) for the mixed (Li_2O and Na_2O) iron phosphate glasses.

On the basis of a simple diffusion model, Mott [9,10] proposed the following equation for the electronic conductivity of semiconducting glasses:

$$\sigma = \nu_0 \mathrm{Ne}^2 R^2 C(1-C)\exp(-2\alpha R)/kT \times \exp(-W/kT), \tag{1}$$

where ν_0 is the longitudinal optical phonon frequency, R is the average site separation, α is the inverse localization length of the S-like wave function assumed to describe the localized state at each site, C ($=\mathrm{Fe}^{2+}/\Sigma\mathrm{Fe}$) is the fraction sites occupied by an electron (or polaron) and therefore is the ratio of the transition metal (TM) ion concentration in the low-valence state to the total TM ion concentration and W is the activation energy for the hopping conduction. Eq. (1) describes a non-adiabatic regime of small polaron hopping and is usually used to analyze the σ_{DC} of glasses containing transition metal oxides such as iron oxide.

In general, plots of the $\ln\sigma_{DC}$ as a function of $1/T$ in electronically conductive oxide glasses deviated from linearity at low temperature [9,10] and the relation for this type of glass has been proposed on the basis of hopping mechanism [9,10]. However, σ_{DC} is thermally activated and the

Table 1
Physical properties of mixed Li_2O and Na_2O iron phosphate glasses

Code	Composition (mol%)				C ($Fe^{2+}/\Sigma Fe$)	$\ln \sigma_{303\,K}$ (Sm^{-1})	$\ln \sigma_{450\,K}$ (Sm^{-1})	W (330–493 K) (eV)
	Li_2O	Na_2O	Fe_2O_3	P_2O_5				
F40[a]	none	none	40	60	—	−17.12	−14.30	0.40
I	0	16	24	60	0.11	−22.3	−14.80	0.44
II	4	12	24	60	0.043	−22.87	−15.3	0.52
III	8	8	24	60	0.035	−23.38	−15.75	0.54
IV	12	4	24	60	0.064	−22.48	−15.03	0.46
V	16	0	24	60	0.060	−22.77	−15.30	0.50

[a] $40Fe_2O_3$–$60P_2O_5$ mol%.

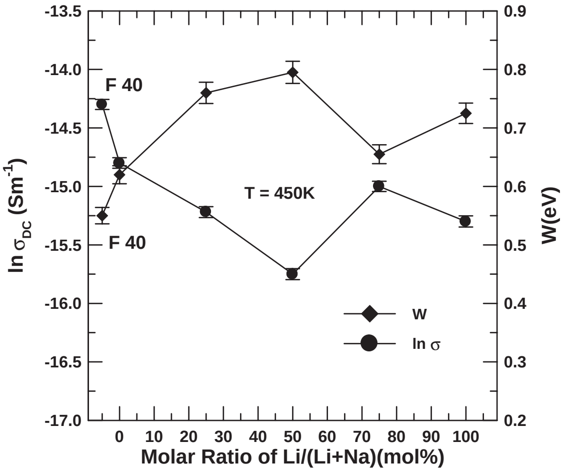

Fig. 6. DC conductivity (σ_{DC}) at 450 K and activation energy (W) as a function of the $Li_2O/(Li_2O+Na_2O)$ molar ratio (lines drawn as a guide for the eye).

activation energy, W, for σ_{DC} can be determined at temperatures $T > 330$ K from the slope of the function $\ln \sigma_{DC} = A + B/T$ fitted to the data.

Fig. 6 shows the electrical conductivity, σ_{DC}, and the activation energy, W, as a function of molar ratio of $Li_2O/(Li_2O+Na_2O)$ in the glass. From the figure it can be seen that the activation energy, W, for conductivity decreases with increasing conductivity for all the mixed Li_2O and Na_2O iron phosphate glasses. This indicates no mixed alkali effect in the present glasses.

The alkali-free iron phosphate glass [$40Fe_2O_3$–$60P_2O_5$ mol%] [13] has the largest σ_{DC} over temperature used (Table 1). We expect that the total σ_{DC} would increase with the addition of either lithium or sodium ions due to the motion of the alkali ions. On the other hand, when the second alkali, sodium, was added to the glass, the σ_{DC} was expected to decrease as observed for the mixed-alkali iron phosphate glasses [24].

4. Discussion

The logarithm of the conductivity (Fig. 5) shows linear temperature dependence up to a critical temperature $\theta_D/2$ (where, θ_D is the Debye temperature) and then the slope changes with deviation from linearity, and then the activation energy is temperature dependent. This indicates that the conduction of the glasses is mainly electronic [3–5]. In the low temperature region ($T < 330$ K) the conductivity is believed to be of electronic nature. This is assured by the results obtained from the Mössbauer analysis (Table 1), while in the high- temperature ($T > 330$ K) Li_2O and Na_2O ions may become mobile and contribute to the conduction process, similar to that for some alkali phosphate glasses containing iron [6].

The smallest activation energy $W = 0.4$ eV and largest DC conductivity $\sigma_{DC} = 6.16 \times 10^{-7}\ Sm^{-1}$, for the alkali-free iron phosphate glass (Fig. 6) indicate that the reduction in iron content from 40 to 24 mol% decreases the σ_{DC}. Since the charge carriers concentrations are related to iron ion content (see Mössbauer results in Table 1), the decrease in σ_{DC} is attributed to the decrease in the number of carriers with decreasing Fe_2O_3 content.

These results agree with the results reported elsewhere [14–16], where the σ_{DC} in alkali-free iron phosphate glasses is attributed to the migration of polarons and the charge transport could be visualized as carriers hopping a distance between the phosphate chains. The hopping conductivity depends upon the distance between iron ions and the conductivity is less than that in ionic conductive glass [14–16]. The DC conductivity is expected to increase with the addition of 16 mol% of alkali ions due to their mobility. However, the results show that the σ_{DC} for the single alkali iron phosphate glasses, $16Li_2O$ or $16Na_2O$ mol% is less than that for alkali-free iron phosphate glasses. These results agree with those previously reported [14–16] where polaron hopping was found to be the dominant conduction in the iron phosphate glasses containing less than 20 mol% sodium ions. Tsuchiya and Yoshimura [25] have reported a minimum conductivity for iron phosphate glasses containing $15Na_2O$ mol% due to decrease of the number of carriers by interaction of Na^+ and Fe^{3+} ions. They suggested that $[FeO_{4/2}]^-$ Na^+ are formed in iron phosphate glasses and Na^+ ions are trapped which decreases the DC conductivity. The lack of any experimentally significant increase in σ_{DC} with Li_2O or Na_2O content indicate that the Li^+ or Na^+ are immobile and the σ_{DC} in these glasses is mainly controlled by polaron hopping [14,25].

Fig. 7 shows the variation of electrical conductivity σ_{DC} and the fraction of reduced transition metal (TM) ion C as a function of molar ratio of $Li_2O/(Li_2O+Na_2O)$ in the glass. The σ values are within an order of magnitude of that of iron phosphate glasses [14–16,26]. Since the electrical conduction is dominated by hopping from Fe^{2+} to Fe^{3+} sites, it is reasonable to assume that the value of conductivity at $x = 75\%$ is higher than that at $x = 25\%$, similar behavior is shown for the transition metal ion ratio (C) results. This indicates the mechanism of σ_{DC} of alkali ionic conductivity and electronic conductivity. We suggest that the present results are also consistent with the hypothesis that in the alkali-containing iron phosphate glasses the fraction of ionic conductivity is small compared to the electronic conductivity [15–16,26].

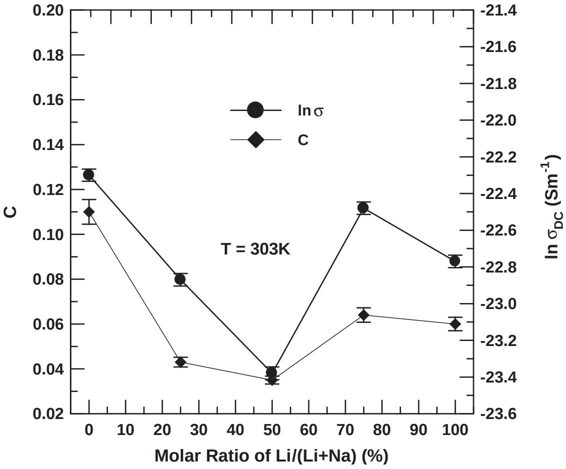

Fig. 7. DC conductivity (σ_{DC}) at 303 K and the fraction of reduced transition metal ion (C) as a function of $Li_2O/(Li_2O+Na_2O)$ molar ratio (lines drawn as a guide for the eye).

Finally, the σ_{DC} conductivity for the mixed-alkali Li and Na iron phosphate glasses is independent of Li/Na ratio and there is no evidence of any mixed-alkali effect as show in Fig. 6. Apparently, the lithium and sodium ions have such a low mobility in both, single- and mixed-alkali iron phosphate glasses that they make no detectable conduction to the total conductivity that is electronic in origin [14–16].

5. Conclusion

Over the temperature and frequency range used in the present study, the electrical conductivity of the mixed-alkali iron phosphate glasses varied only slightly with alkali content. These results lead to the conclusion that the electrical conductivity is dominated by electron hopping between Fe^{2+} to Fe^{3+} sites in the glass and the mobility of the lithium and sodium ions is so low that they make no detectable contribution to the overall electrical conductivity.

Unlike other types of mixed-alkali glasses where the electrical conductivity decreases by several orders of magnitude with the addition of a second alkali, no mixed-alkali effect of any significance was seen in mixed-alkali lithium and sodium iron phosphate glasses, even at a total alkali content of

16 mol%. The near absence of the mixed-alkali effect is further evidence of the low mobility of lithium and sodium ions in these iron phosphate glasses.

References

[1] M. Sayer, A. Mansingh, Phys. Rev. B 6 (1972) 4629.
[2] L. Murawski, C.H. Chung, J.D. Mackenzie, J. Non-Cryst. Solids 32 (1979) 91.
[3] M.M. El-Desoky, J. Mater. Sci.: Mater. Electronics 14 (2003) 215.
[4] A. Al-Shahrani, A. Al-Hajry, M.M. El-Desoky, Phys. Stat. Sol. A 200 (2003) 378.
[5] M.M. El-Desoky, Phys. Stat. Sol. A 195 (2003) 422.
[6] M.M. El-Desoky, K. Tahoon, M.Y. Hassaan, Mater. Chem. Physics 69 (2001) 180.
[7] A. MoguŠ-Milanković, D.E. Day, A. Šantić, Phys. Chem. Glasses 40 (1999) 69.
[8] A. MoguŠ-Milanković, D.E. Day, J. Non-Cryst. Solids 162 (1993) 275.
[9] N.F. Mott, Philos. Mag. 19 (1969) 835.
[10] I.G. Austin, N.F. Mott, Adv. Phys. 18 (1969) 41.
[11] H. Nasuand, N. Soga, J. Non-Cryst. Solids 53 (1982) 123.
[12] T. Tsuchiya, N. Yoshimua, J. Mater. Sci. 24 (1989) 493.
[13] M.M. El-desoky, I. Kashif, Phys. Stat. Sol. A 194 (1) (2002) 89.
[14] A. MoguŠ-Milanković, B. Šantić, C.S. Ray, D.E. Day, J. Non-Cryst. Solids 119 (2001) 283.
[15] A. MoguŠ-Milanković, B. Šantić, S.C. Ray, D.E. Day, J. Non-Cryst. Solids 263–264 (2000) 299.
[16] X. Fang, C.S. Ray, G.K. Marasinghe, D.E. Day, J. Non-Cryst. Solids 263–264 (2000) 293.
[17] C.S. Ray, X. Fang, M. Karabulut, G.K. Maarasinghe, D.E. Day, J. Non-Cryst. Solids 249 (1999) 1.
[18] G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, D.K. Shuh, P.G. Allen, M.L. Saboungi, M. Grimsditch, D. Haeffiner, J. Non-Cryst. Solids 263–264 (2000) 146.
[19] A.K. Jonsher, Nature 267 (1977) 673.
[20] I. Shaltout, J. Phys. Chem. Solids 60 (1999) 1705.
[21] K.S. Cole, R.H. Cole, J. Chem. Phys. 9 (1941) 341.
[22] H. Fröhlich, Theory of Dielectrics, Oxford University Press, London, 1958.
[23] L. Murawski, R.J. Barczynski, J. Non-Cryst. Solids 185 (1995) 84.
[24] P.F. Green, D. Sidebottom, R.K. Brow, J. Non-Cryst. Solids 172–174 (1994) 1353.
[25] T. Tsuchiya, N. Yoshimura, J. Mater. Sci. 24 (1989) 493.
[26] M. Karabulut, G.K. Marasinghe, C.S. Ray, D.E. Day, G.D. Waddill, C.H. Booth, P.G. Allen, J.J. Bucher, D.L. Caulder, D.K. Shuh, J. Non-Cryst. Solids 306 (2002) 182.