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Dielectric properties and equivalent circuit analysis of molybdenum doped lead lithium borate glasses

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ABSTRACT

The dielectric properties and equivalent circuit analysis of glasses with composition xPbO•(30-x)Li_2O•$70B_2O_3$ (x = 0, 2, 5, 7, 10, 12 and 15 mol% with code PLBM1-7 respectively) containing 2 mol% of MoO_3 prepared by melt-quench technique are discussed. The dielectric properties have been studied using impedance spectroscopy. The frequency dependent conductivity investigations for prepared compositions have been carried out using impedance spectroscopy over a frequency range of 1 KHz to 5 MHz and in the temperature range of 300K-523K. The complex impedance data have been analyzed by using both the conductivity and the electric modulus formalisms. Standard dielectric behavior is observed in prepared samples. The ac conductivity obeys Jonscher's power law. The study of the equivalent circuit analysis up to a temperature of 473K shows a significant change in the equivalent circuit with change in temperature and composition.

Keywords: Dielectric Properties , Equivalent Circuit Analysis

INTRODUCTION

Lead oxide is well known heavy metal oxide that shows interesting physical and chemical properties upon glass formation with many systems such as borates, silicates and phosphates. Borate glasses containing PbO, ZnO and MgO form chemically stable glasses. Lead oxide does not form glass alone, but it can be incorporated[1] in substantial quantities into other glass forming oxide systems such as borates. B_2O_3 is a glass forming oxide and PbO is a conditional glass former. With these two chemicals in glass matrix, a low rate of crystallization, moisture resistance and transparent glasses are formed.[2,3] In addition, these glasses exhibit challenging electrical, optical and thermal properties.[4-6] The electrical conductivity of PbO-$2B_2O_3$ was measured and possible mechanism of ionic transport for Pb in the glass was proposed.[7] It is also observed that the presence of molybdenum ions in heavy metal oxide substituted borate glasses produces interesting changes in optical and electrical properties due to the existence of molybdenum ions four possible valence states viz., Mo^{3+}, Mo^{4+}, Mo^{5+} and Mo^{6+}.[8-12] Further this system is of interest because MoO_3 is conditional glass former and good oxidizing catalysts. Apart from these special optical properties, other advantages of such glasses are their good thermal and chemical stability, low tendency to crystallization and their ability to host rare earth ions. Among various transition metal ions, molybdenum ions are expected to have profound influence on the optical and electrochemical properties of lead tellurite glasses, in view of the fact that the oxide of molybdenum participate in the glass network with different structural units like $MoO_4(T_d)$ and MoO_6 (O_h) of Mo^{6+} ions and Mo^{5+} $O_{3-}(O_h)$ of Mo^{5+} ions.[13] In the present work, the focus is to examine the dielectric properties and equivalent circuit analysis of lead lithium borate glasses.

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EXPERIMENTAL

Glass samples of composition xPbO•(30-x)Li_2O•$70B_2O_3$ (x = 0(PLBM1), 2(PLBM2), 5(PLBM3), 7(PLBM4), 10(PLBM5), 12(PLBM6) and 15(PLBM7)) containing 2.0 mol% of MoO_3 were prepared by conventional melt–quench technique.[14] The appropriate proportions of starting materials Li_2CO_3, PbO, H_3BO_3, and MoO_3 were AR grade chemicals. The samples were mixed and grind with the help of pestle mortar. The mixture of powders taken in high alumina crucible was heated at 1000°C for one hour. The mixture was then melted at 1000°C for about one hour in air with intermittent stirring to ensure the homogeneity. The melt was then rapidly quenched between two stainless steel plates held at room temperature to obtain the glass samples in the form of round disc. The samples were cut in regular shapes and then polished to a thickness of 0.5-1.5 mm for various measurements by using sand paper. The samples were coated with colloidal silver paint. These samples were stored in desiccators and taken out only at the time of measurement of their properties. For impedance spectroscopy, samples were carried out on a Hioki IM 3570 in frequency range of 1KHz-5MHz and temperature range of 300-523K. The equivalent circuit analysis has been carried out as a function of temperature over the range of 300-473K with the help of an IM9000[12] firmware which is an extension plug-in to HIOKI IM3570 Impedance analyzer.

RESULT AND DISCUSSION

It can be observed that ε' decreases with an increases in frequency and approaches a constant value which probably results from rapid polarization processes occuring in the glass. In low frequency region, ε' increases due to electrode polarization arising usually from space charge accumulation at glass-electrode interface. Therefore, at high frequency region dielectric constant follows a non–debye behaviour.[16,17] Figure 1(a) and (b) show the frequency dependence of ε' *and* ε'' for different glass samples PLBM1, PLBM3, PLBM5, PLBM7 at 623K temperatures. Similar types of variations were observed in other samples also. It can be observed that ε' increases with increase in temperature. This may be due to the increase in polarization due to thermal activation acquired by the charge carriers.[18]

Figure 2 shows the variation of dielectric loss tangent with frequency for different glass sample at 623K temperature. Similar types of variations are observed in other samples. The dielectric loss factor is the phase difference due to the loss of energy within the sample at a particular frequency and is expressed as $\tan\delta(\varepsilon'' / \varepsilon')$. The contribution to the dielectric loss is mainly attributed to thermally activated relaxation of freely rotated dipoles where thermal energy is the only type of relaxation and at higher temperatures it is due to the electrical conduction with hopping motion of the ions. It can be clearly observed from the Figure 2 that pattern in loss tangent are very much similar to that of dielectric constant as there is no peaks. The dielectric losses at high frequency are much lower than those occurring at low frequencies. This kind of dependence of $\tan\delta$ on frequency is typically associated with losses by conduction. Dielectric losses decrease with increase in the PbO content.[19]

The real (*M')* and imaginary (*M'')* parts of the electric modulus as a function of frequency for PLBM1 glass sample at various temperatures are shown in figures 3(a) and (b) respectively. The variations of electric modulus are qualitatively similar for all other glass samples under study. Figure 3(a) reveals that the low-frequency value of (*M)'* is zero (representing a lack of restoring force for the electric field induced mobile alkali ions), which increases with increasing frequency and reaches a maximum asymptotic value M'_{∞} at high frequency.

Thus the study of frequency dependent electric modulus spectra provides the information about the relaxation mechanism in the absence of a well-defined dielectric loss peak. It can be assumed that at high frequency region the

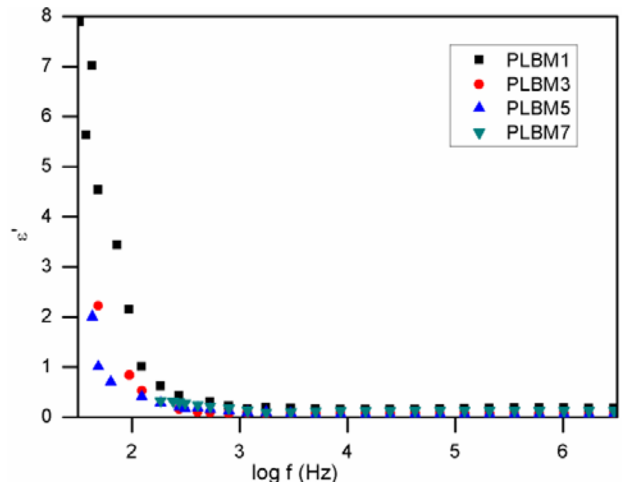

Figure 1(a): Variation of (ε') with frequency at 623K for PLBM1, PLBM3, PLBM5 and PLBM7 glass samples.

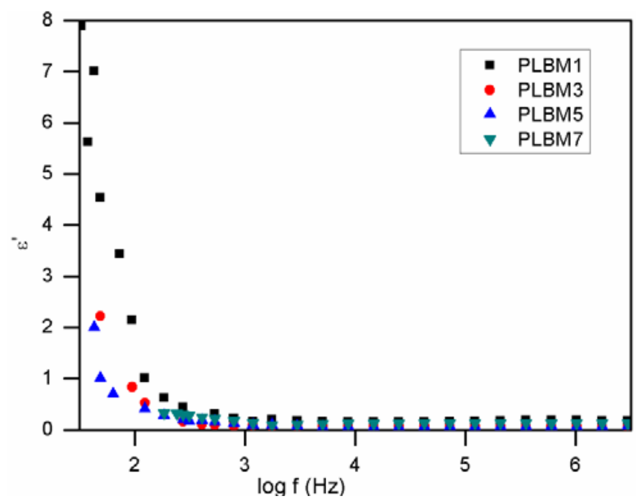

Figure 1(b): Variation of (ε'') with frequency at 623K for PLBM1, PLBM3, PLBM5 and PLBM7 glass samples.

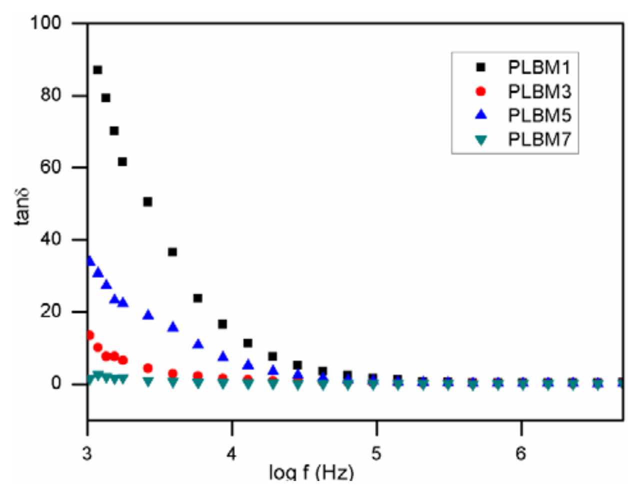

Figure 2: Variation of dielectric loss ($\tan\delta$) with frequency at 623K

electric field changes so rapidly as the ions can move only within their potential wells.[20] As a result, mobile ions have been frozen into the glass structure that makes the glass

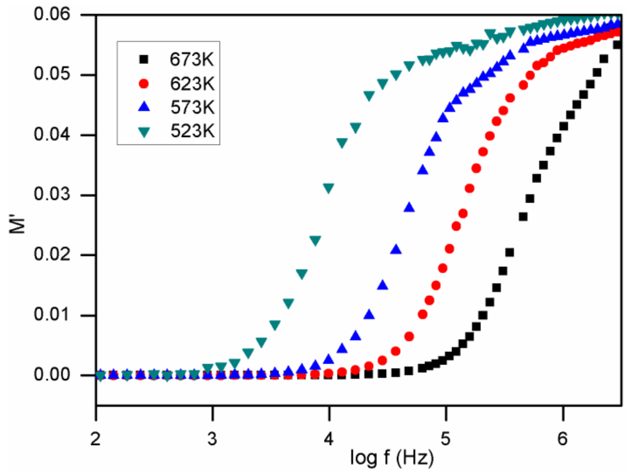

Figure 3(a): Variation of real part of electrical modulus(*M'*) with frequency for PLBM1 glass sample at different temperatures.

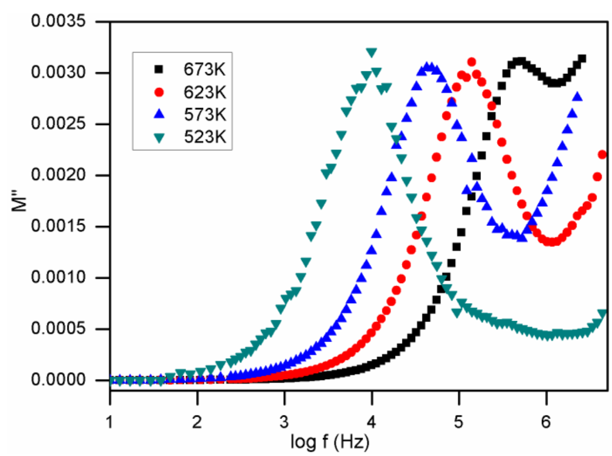

Figure 3(b): Variation of imaginary part of electrical modulus (*M''*) with freq uency for PLBM1 glass sample at different temperature.

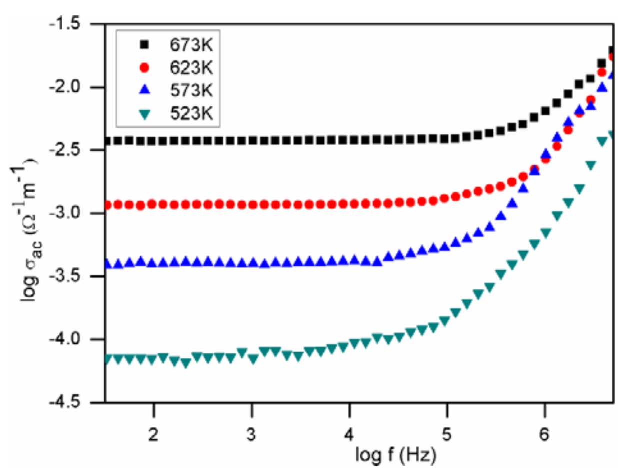

Figure 4: Variation of ac conductivity with frequency for (PLBM1) glass samples at different temperatures.

stiffer in this frequency region and *M'* Goes to M'_∞ while *M''* exhibits a relaxation peak centered at the dispersion region of *M'* from the physical point of view, the electrical modulus corresponds to the relaxation of the electric field in the materials when the electric displacement remains constant, the relaxation peak for *M'* 'move toward lower frequencies during cooling of the sample. Consequently, it means that the relaxation rate for this process decreases with decrease temperature. The frequency region below peak maximum (M_{max}'') determines the range in which charge carries are mobile on the long distances at frequency above peak maximum the carriers are confined to potential wells, being mobile on short distances.[21]

The study of frequency dependent conductivity spectra is well established method for characterizing the hopping dynamics of ions. Figure 4 shows the frequency dependence of ac conductivity for PLBM1 glass sample for different temperature. Similar types of variations are observed in other samples. It is evident from this figure that at low frequencies and high temperatures, conductivity shows frequency independent nature of the glasses, which gives rise to dc–conductivity arising from the random diffusion of the ionic charge carriers via activated hopping process. However, at the higher frequencies, σ_{ac} exhibits frequency dispersion. At low frequency the conductivity is dc in nature (σ_{dc}) and at high frequency the conductivity obeys a power law described by the Jonscher.[22] This leads to the empirical form of the total conductivity $\sigma(\omega)$ for different temperatures expressed as: σ, where *s* is a material and temperature dependent parameter.

Circuit Analysis

The equivalent circuit analysis has been studied over the temperature range of 300-473K using an IM 9000[12] firmware which is an extension plug-in to HIOKI IM 3570 Impedance Analyzer. Five different models: A to D (with three elements) and E (with four elements) that are best suited to the circuit element (rectangular glass samples here) are available in this Firmware.[12] Model A corresponds to an inductor with high core loss and low ESR (equivalent series resistance). Model B represents a low resistance with significant inductance and high ESR. Model C shows a high resistance value with significant capacitance effect. Model D shows a typical capacitor and model E represent a piezoelectric element.[15] As we were uncertain about the behaviour of prepared samples, therefore measurements were executed in automatic mode. In automatic mode, IM9000 automatically selects the equivalent circuit model out of different models available with it. The acceptance/rejection of a circuit model is made on the basis of detailed analysis of values of inductance, capacitance and resistance comprising the circuit element and the resonance sharpness (mechanical quality Co-efficient i.e Q_m).

It is observed that when no lead oxide content is present in the sample PLBM1, it initially follows model D and at temperature355K it jumps in to model A as shown in Figure 5(a). On adding PbO, sample PLBM2 remain in the same model D for all temperature as no change in model take place. Further, PLBM3 found to follow D model and at 370K it jumps toA model. Sample PLBM4 follows model D and jumps in to the model E at 375K and again, it switches to model D at 440K as shown in Figure 5(b). Moreover, sample PLBM5, PLBM6, PLBM7 initially follows the model D but they jump in to model A at temperature 375K, 385K, 375K respectively.

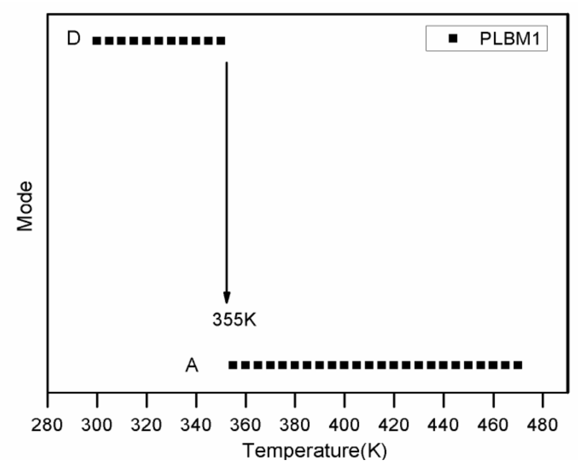

Figure 5(a): Variation of circuit models with temperature for PLBM1 glass sample.

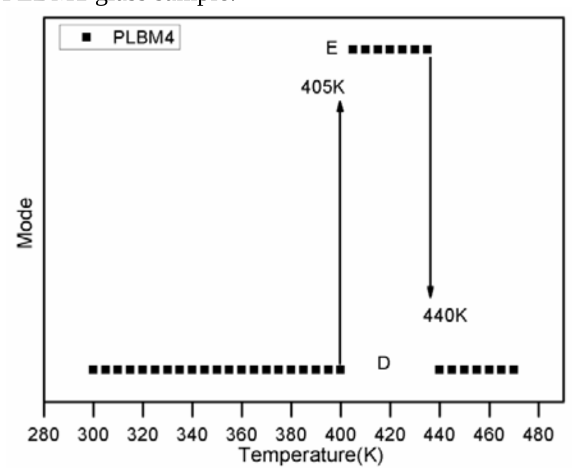

Figure 5(b): Variation of circuit models with temperature for PLBM4 glass sample.

Conclusion

Dielectric constant ε' increases with increase in temperature and at high frequency region dielectric constant follows a non–debye behaviour. Dielectric losses decrease with increase in the PbO content. Standard dielectric behavior is observed in prepared samples. The Variation of ac conductivity with frequency obeys Jonscher's power law. The study of the equivalent circuit analysis up to a temperature of 473K shows a significant change in the equivalent circuit with change in temperature and composition.

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References

1. H. Rawson, Inorganic Glass Forming Systems (Academic Press, London, **1967**).
2. Y. He, D.E. Day. Development of a low temperature phosphate sealing glass. *Glass Technol*. 1992, 33, 201-214.
3. R Bala, A Agarwal, S Sanghi, S Khasa, Influence of SiO2 on the structural and dielectric properties of ZnO· Bi2O3· SiO2 glasses, *J. Integr. Sci. Techn.*, **2015**, 3(1), 6-13.
4. D. Ehrt. The effect of ZnO, La_2O_3, PbO and Bi_2O_3 on the Properties of Binary Borate Glasses and Melts. *Phys. Chem. Glasses* **2006**, 47, 669-674.
5. M. Ganguli, M.H. Bhat, K.J. Rao. Structural Role of PbO in Li_2O-PbO-B_2O_3 Glasses. *Mater Res Bull*. **1999**, 34(10-11),1757-1772.
6. S Khasa, M.S. Dahiya, A Agarwal , Structural Investigations of Lithium Vanadoxide Bismo-Borate Glasses, *J. Integr. Sci. Techn.*, **2013**, 1(1), 44-47.
7. J.P. Deluca, C.G. Bergeron, Crystal Growth in the System PbO-B_2O_3. *J. Am. Ceram. Soc*. **1970**,53, 214-219.
8. C. Ivascu, A. Timar Gabor, O. Cozar, L. Daraban, I. Ardelean. FT-IR,Raman and thermoluminescence investigation of P_2O_5-BaO-Li_2O glass system. *J. Mol. Struct*. **2010**, 993, 249-253.
9. S. Rada, E. Culea, FTIR spectroscopic and DFT theoretical study on structure of europium-phosphate-tellurate glasses and glass ceramics, *J. Mol. Struct*. **2009**, 929, 141-148.
10. F.H. ElBatal, M.A. Marzouk, A.M. Abdelghany, Gamma rays interaction with bismuth borate glasses doped by transition metal ions, *J. Mater. Sci.* **2011**, 46, 5140-5152.
11. O. Cozar, D.A. Magdas, I. Ardelean, EPR study of molybdenum-lead-phosphate glasses, *J. Non-Cryst. Solids* **2008**, 354, 1032-1035.
12. M. Lather, P. Aghamkar, S. Sanghi. Optical absorption and fluorescence spectral analysis of Ho3+ ions doped zinc bismuth borate glasses, *J. Integr. Sci. Techn*. **2015**, 3(2), 28-33.
13. L.S. Rao, M.S. Reddy, D.K. Rao, N. Veeraiah. Influence of redox behavior of copper ions on dielectric and spectroscopic properties of Li_2O-MoO_3-B_2O_3: CuO glass system,.*J. Solid State Sci*. **2009**, 11**,** 578-587.
14. S. Khasa, V.P. Seth, P.S. Gahlot, A. Agarwal, S.K. Gupta. Effect of cobalt ions on the EPR and d.c. conductivity in vanadyl doped CoO-M_2O-B_2O_3(M=Li, K) glasses. *Phys Chem Glasses* **2006**, 47(4), 371-376.
15. S. Dalal, S. Khasa, M.S. Dahiya, A. Agarwal, A. Yadav, V.P. Seth, S. Dahiya. Effect of substituting iron on structural, thermal and dielectric properties of lithium borate glasses. *Mater. Res. Bull.* **2015**, 70, 559-566.
16. M.D. Ingram. Ionic conductivity in glasses. *Phys. Chem. Glasses* **1987**, 28**,** 215-234.
17. S. Ramesh, A.K. Arof. Ionic conductivity studies of plasticized poly(vinylchloride) polymer electrolytes, *Mater. Sci. Eng. B* **2001**, 85, 11-15.
18. A. Hooda, S. Sanghi ,A. Agarwal, R.Dahiya. Structural, dielectric and magnetic properties of Cd/Pb doped W-type hexaferrites. *J.Magn. Magn.Mater*. **2014**, 349, 121-127.
19. A. Hooda, S. Sanghi, A. Agarwal, R. Dahiya. Crystal structure refinement, dielectric and magnetic properties of Ca/Pb Substituted $SrFe_{12}O_{19}$ hexaferrites. *J. Magn. Magn. Mater*. **2015**, 387, 46-52.
20. J. Maier, S. Prill, B. Reichert. Space charge effects in polycrystalline, micropolystalline and thin film samples: Application to AgCl and AgBr. *Solid State Ionics* **1988**, 28, 1465-1469.
21. S.W. Martine, A. angell. Dc and ac conductivity in the wide composition range Li_2O P_2O_5Glasses, *J. Non-Cryst. Solids* **1986**, 83,185-207.
22. A.K. Jonscher, The universal dielectric response, *Nature*, **1977**, 267, 673-679.