

Dielectric Investigations and Modulus Analysis of Lithium Bismuth Borate Glasses Doped with Molybdenum and Vanadium Oxides

Rajesh Rohilla, Meena Malik, Shruti and Satish Khalsa

Material Research Laboratory, Department of Physics
DCR University of Science & Technology, Murthal, Haryana, India-131039
Email: rajeshnrsrohilla@gmail.com

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Abstract: Lithium Bismuth Borate Glasses doped with Molybdenum and Vanadium oxides having composition $x(\text{MoO}_3.\text{V}_2\text{O}_5).(30-x)\text{Li}_2\text{O}.50\text{B}_2\text{O}_3.20\text{Bi}_2\text{O}_3$ where $x = 0, 2, 5, 7$ and 10 (abbreviated as MV0LBB, MV2LBB, MV5LBB, MV7LBB and MV10LBB respectively) are synthesized by standard melt quench technique. The amorphous nature of synthesized glasses has been confirmed through peak free X-ray measurements. Electrical properties of the samples i.e. different dielectric parameters are studied using Impedance Spectroscopy and their variations with frequencies (frequency range of 100 Hz to 5MHz) and different temperatures (from room temperature to 400°C) are investigated. Dielectric constant (ϵ') and dielectric loss ($\tan\delta$) are found to be increasing with the increase in temperature while these decreases with increase in the frequency which is due to energy loss by gathering of space charge near the electrode interface due to polarization and ionic conduction. Real part of modulus (M') increases with increasing frequency and a saturation in the value at higher frequency. Imaginary part of modulus shows characteristic peak with frequency variation, which confirms relaxation process in conductivity.

Keywords: Lithium Bismuth Borate, synthesized glasses, Dielectric constant, Molybdenum.

1. Introduction

For over several years, the electrical properties of glasses were investigated broadly because of their various applications in solid-state devices. The role of alkali ions into these glasses show high electrical conductivity and is used as solid electrolytes in case of high energy density batteries¹. From the literature survey, it is concluded that glasses containing

Bi_2O_3 belong to a category of “conditional glass formers”². It cannot form glass on its own, but it may be incorporated in very large quantities into other classical glass formers like SiO_2 , B_2O_3 , P_2O_5 etc. Molybdenum ($_{42}\text{Mo}$) and Vanadium ($_{23}\text{V}$) are the d-block elements or commonly known as transition metals. Molybdenum is a transition metal with some special properties and it cannot participate in formation of glass independently, but it can be consolidated with other glass formers to form substantial glasses³. The incorporation of molybdenum and vanadium ions in alkali substituted borate glasses enhance their optical and electrical properties due to the existence of molybdenum ions in four possible valence states viz., Mo^{3+} , Mo^{4+} , Mo^{5+} and Mo^{6+} and vanadium ions in V^{2+} , V^{3+} , V^{4+} and V^{5+} oxidation states. Electrical properties of these glasses are affected due to hopping of the transition metal ions in different valence states. Glasses having transition metals may show non linear changes in optical, spectroscopic and electrical properties which is also known as mixed transition effect⁴.

The above discussion concludes that the study of mixed transition metal ion doped alkali bismuth borate matrix is very prominent. The purpose of present work is to analysis the dielectric properties for lithium bismuth borate glasses doped with oxides of Mo and V.

2. Experimental Details

Glasses having composition $x(\text{MoO}_3.\text{V}_2\text{O}_5).(30-x)\text{Li}_2\text{O}.50\text{B}_2\text{O}_3.20\text{Bi}_2\text{O}_3$ where $x = 0$ (MV0LBB), 2 (MV2LBB), 5 (MV5LBB), 7 (MV7LBB) and 10 (MV10LBB) were prepared via melt-quench technique. Analar grade chemicals MoO_3 , V_2O_5 , Li_2CO_3 , H_3BO_3 and B_2O_3 were used as precursors in suitable mol%. The raw materials were weighed in appropriate amount by using “digital electronic balance (CAS CAUY 220)” and grind gently in mortar pestle and mixture was then placed in high alumina crucible⁵. Further the electrical muffle furnace was preheated in order to achieve temperature up to 1150°C and kept for 45 minutes. Samples were stirred periodically to achieve well homogeneous mixture. The molten sample was sandwiched in between preheated steel plates to obtain amorphous material with crack free flat samples. To analyze dielectric properties, prepared samples were polished and rectangularly shaped with thickness ~ 1 mm using emery paper. Opposite faces of rectangle shaped samples were coated with colloidal silver paint to make electrodes. The dielectric measurements were recorded on impedance analyzer setup (HIOKI 3532-50 LCR HiTester). The frequency range of the Impedance analyzer is 100Hz-5MHz and the temperature range

of RT to 400°C⁶. The complex dielectric permittivity, $\varepsilon^* = \varepsilon - j\varepsilon''$ (ε' and ε'' as real and imaginary part of dielectric constant), dielectric loss tangent ($\tan\delta$) and real and imaginary part of modulus of dielectric permittivity are calculated using formulas given in literature⁴.

3. Results and Discussions

X- Ray Diffraction: Figure 1 represents the XRD profiles were recorded for fine prepared powdered samples having composition $x(\text{MoO}_3.\text{V}_2\text{O}_5).(30-x)\text{Li}_2\text{O}.50\text{B}_2\text{O}_3.20\text{Bi}_2\text{O}_3$ where $x = 0, 2, 5, 7$ and 10 (abbreviated as MV0LBB, MV2LBB, MV5LBB, MV7LBB and MV10LBB respectively) at room temperature(RT) on “Rigaku Miniflex2 X-ray Diffractometer” in 2θ and the range from 20 to 80° at scan rate of 2° per minute. The amorphous nature is confirmed as an absence of sharp peaks in XRD profiles.

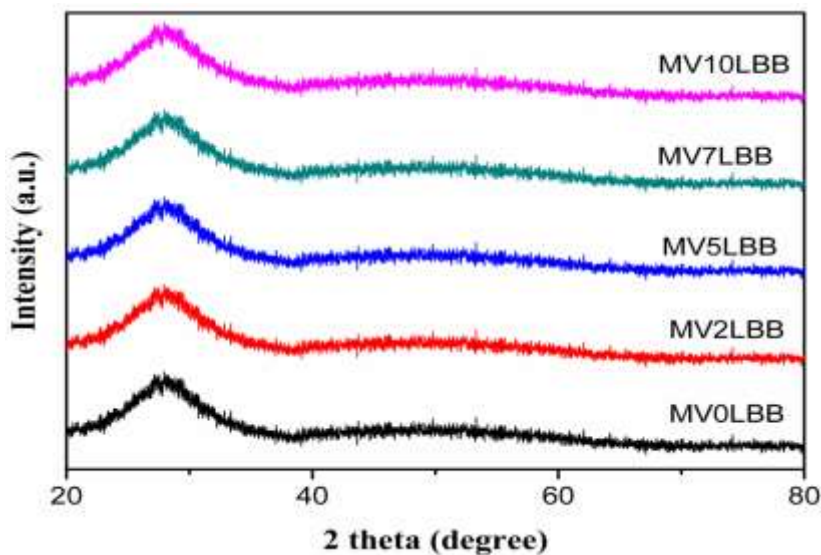


Figure 1. XRD spectra of as prepared glasses.

4. Dielectric Properties

Figure 2(a) represents the variation of real part of dielectric constant (ε') as the function of frequency (at temperature $T = 300^\circ\text{C}$) for all the compositions. ε' shows decreasing behavior with an increment in frequency and becoming constant at the higher frequency that may influence from the

rapid polarization process that occurs in the glass. At lower frequency range, there is an increase in ϵ' due to polarization in electrode that usually arises from space charge compilation at the interface of glass-electrode which further does not let the transfer of ions in the electrical circuit. Therefore, dielectric constant obeys some non-Debye behavior at region of high frequency. Alike variations are shown in case of other samples also. Figure 2(b) represents the variation of dielectric loss (ϵ'') with frequency for the MV0LBB, MV2LBB, MV5LBB, MV7LBB and MV10LBB at temperature 270°C. At lower frequencies, due to the presence of blocking electrodes, large bulk polarization takes place. As a result of this, the whole charge gathers near the electrode-sample interface giving a bulk polarization. Further, due to this compilation and polarization in space charge, there is raise in ϵ'' value which increases with the higher rates at the lower frequency range. There is contribution in polarization from ionic and other sources which decrease with increase in frequency.

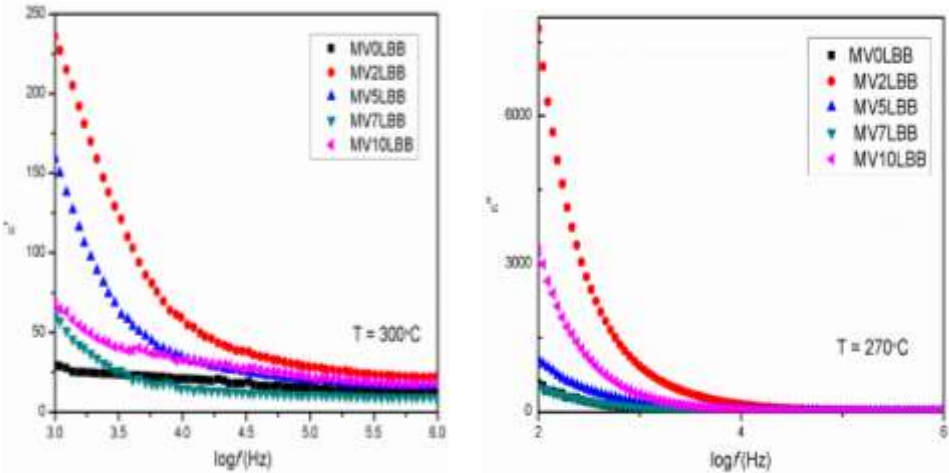


Figure 2. (a) Variation of ϵ' with $\log f$ at $T=300^{\circ}\text{C}$; **(b)** Variation of ϵ'' with $\log f$ at $T=270^{\circ}\text{C}$ for all prepared compositions

Figure 3 represents the frequency dependence of “dielectric loss tangent ($\tan\delta$)” at constant temperature for all prepared compositions. It is observed that $\tan\delta$ exhibits similar kind of trends as that of dielectric loss ϵ'' . A reason for such behavior might be that when frequency increases, the polarizability arising from ionic and the orientation sources decreases and then vanishes because of their respective inertia. Due to low dielectric loss and low

tangent loss at higher frequencies, these glasses are suitable candidate for non-linear optical materials.

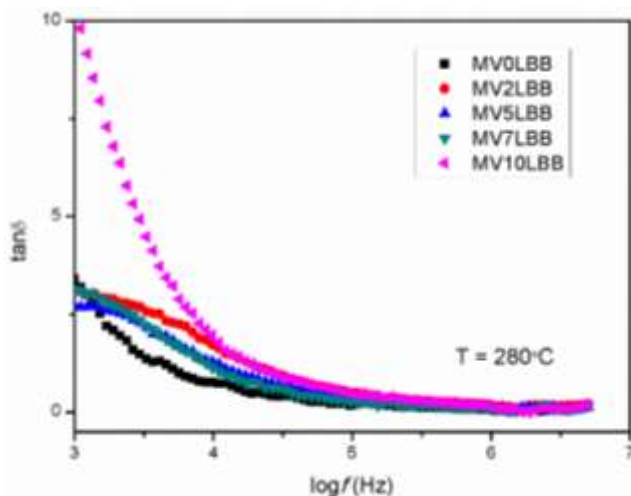


Figure 3. Variation in tangent loss with $\log f$ at $T = 280^\circ\text{C}$ for all synthesized composition

5. Modulus Formalism

Formalism in electrical modulus ($M = M' + jM''$) is broadly used for the analysis of electrical relaxation behavior in case of conducting materials as it intone the bulk properties of polarization in interface and average relaxation times. Figure 4(a) illustrates the dependence on real part (M') of complex electric modulus with the frequency for the samples MV0LBB, MV2LBB, MV5LBB, MV7LBB and MV10LBB at 275°C . From this figure, it is observed that the M' is almost zero for lower frequency values which represents that there is a lack in restoring force for which electric field with alkali ions. It rises with rise in frequency and approaches an asymptotic value M_∞ at maximum as we go to higher frequencies.

Figure 4 (b) shows the presence of a characteristic peak and it is observed that variation of imaginary part (M'') of dielectric modulus for MV5LBB composition at different temperatures. Due to relaxation processes, the plot (M'' vs $\log f$) exposed a non-Lorantzian type asymmetric peak at the frequency ($f_{\max}$) which is remarked to shift towards high frequency side with rise in temperature. The peaks in M'' values give an indication of the time relaxation process in composition labeled as MV5LBB. The time relaxation process indicated in the composition labeled

as MV5LBB by the peaks in M'' values. . The frequency range where ion movement take place as hopping of carriers for long range while the falling off M'' values above $f_{\max}$ (high frequency region) indicates the mobile ions confinement in regular manner in their potential wells. Shift towards high frequency ($f_{\max}$) with rise in temperature is because of weakness in bonds and that will responsible for decrease in relaxation time. The characteristic peak indicates the carriers' movement with increase in frequency ranging from long to short mobility region⁷.

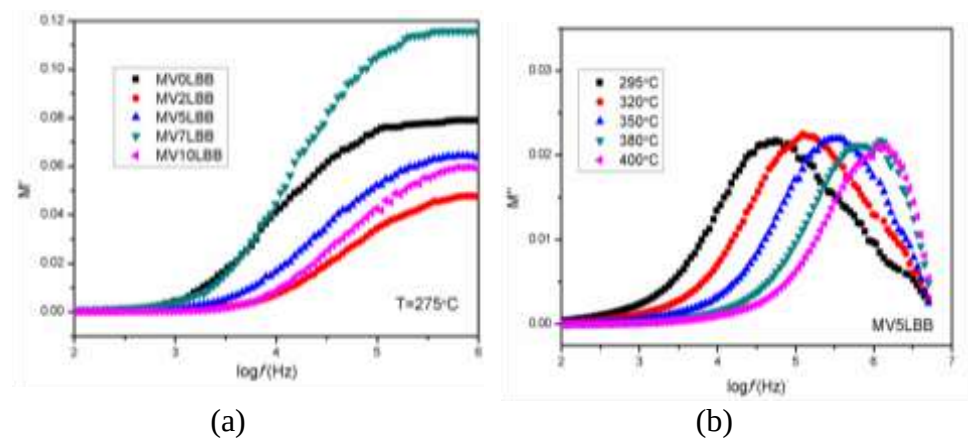


Figure 4. (a) Variation of the real part of modulus of dielectric constant with frequency $T = 270^{\circ}\text{C}$ (b) Variation of the imaginary part of modulus of dielectric constant with the frequency for sample MV5LBB at various temperatures.

6. Conclusion

Glasses made with composition $x(\text{MoO}_3.\text{V}_2\text{O}_5).(30-x)\text{Li}_2\text{O}.50\text{B}_2\text{O}_3.20\text{Bi}_2\text{O}_3$ where $x = 0, 2, 5, 7$ and 10 were successfully synthesized by standard melt-quench technique. Variation in dielectric parameters, dielectric constant, dielectric loss and tangent loss confirms presence of a single relaxation process which shows that the prepared compositions follow non-Debye behavior. Imaginary part, M'' spectra found to exhibits a non-Lorentzian type peak which is antisymmetric, also confirmed the real time relaxation.

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