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Role of non-bridging oxygen defect in the ionic conductivity and associated oxygen trap centers in lead-borate oxide glass: Effect of structural substitution of PbO for Ag_2O and Li_2O modifiers

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ABSTRACT

Two series of Lead Borate glass with compositions $25B_2O_3$-(73.8-x)PbO-$x$$M_2O$-$0.6Cr_2O_3$–$0.6SeO_2$ (M = Ag and Li) with $x = 3$, 4.5 and 6 mol% in case Ag_2O and 3, 6 and 9 mol% for Li_2O are prepared using conventional melt quenching technique. The anomalous behavior observed in the measured hydrostatic density and the calculated molar volume at $x = 3.0$ mol% are explained on the base of the bridging and non-bridging Oxygen bonds formed as a result of introduction of Ag_2O as well as Li_2O modifiers in the PbO-B_2O_3 host network. The irregular trend distinguished in the calculated values of the activation energy of ionic conduction are argued to the work done by modifier ions during its motion through the pathways between two non-bridging Oxygen defects.

The relaxation frequency peaks observed in the temperature dependent capacitance-frequency measurements indicated that the incorporation of Ag_2O and Li_2O in lead-borate network produces a non-bridging Oxygen hole centers (NBOHC) trap defect. This relaxation takes place due to an emission from shallow acceptor NBOHC like defect level with an activation energy ≤ 52 meV for the investigated compositions.

1. Introduction

Borate oxide (B_2O_3) is known as one of the best glass formers. Its structure is mainly composed of planar trigonal (BO_3) as a major structural unit and a BO_4 as a minor. BO_3 units can be connected together through Oxygen atom (bridging oxygen) to form Boroxol rings. On the other hand, introduction of a given modifier in the network of Borate oxide B_2O_3 can transform trigonal BO_3 to tetragonal BO_4 and produce bridging oxygen (BO). On the contrary BO_4 could be also transform into BO_3 and produce an oxygen dangling bond or non-bridging oxygen (NBO) defect. The ratio between the two structural units (BO_3/BO_4), which controls the physical properties of Borate oxide, depends mainly on the annealing temperature and/or concentration of modifier oxide [1–4] in the networks.

PbO is a unique in its influence on the structure of the host glasses network because it is non-conventional glass oxide. It can act as a glass modifier or former [5, 6] depending on its content in the host structural network and bonding type of Lead and Oxygen. In case of low PbO concentration it plays the role of network modifier. On the other hand at high content of PbO it acts as former with both PbO_3 and PbO_4 as structural units [5, 7–9]. This structure provides an opportunity to tailor the physical properties of PbO containing glasses to match technological needs such as x and γ ray absorbers [10].

Many techniques such as NMR, XRD [11] and FTIR [12] are used to investigate the role played by PbO in Borate glass network. It showed that PbO increase the ratio of BO_3/BO_4 with PbO content up to 50 mol% followed by a decreases against the increase of PbO content. This means that at low PbO content (< 50 mol%) it plays the role of modifier. The PbO modifier brakes up the symmetry of the structural network and produces NBO which makes the network are more open and ready to accept other modifier ions such as Li^+ or Ag^+. Also, increasing PbO content in PbO-B_2O_3 glass (> 50 mol%) increases not only the role of PbO as glass former but also polarization of Pb^{2+} which in turn increase the polarizibility of the network and affect the dielectric and other properties of the glass. This makes the glass are applied in many applications such as optical telecommunication [10].

Non-bridging Oxygen atom or Oxygen dangling bond is a localized defect in the glass network, consisting of one half of the permanent broken Oxygen bond [13, 14]. Such defects are formed by introduction of monovalent network modifier such Li_2O, Na_2O, Ag_2O, etc. in the structural network of the host glass. The modifier ions break the Oxygen bonds which connects the structural building blocks and creates

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non-bridging Oxygen defect (NBO). The negative charge on the broken Oxygen bond can trap a moving hole in its range of the trapping capture cross section of NBO and in this case it is called non bridging Oxygen hole center (NBOHC) trap [15–17]. The capturing and emission rates of NBOHC trap depends mainly on its concentration in the structural network of the studied glass and the applied temperature range.

The main goal of the present study is to correlate the behavior of the measured hydrostatic density and associated molar volume with the number of bonds per unit volume formed as a result of bridging Oxygen and non-bridging Oxygen defect which is produced due to introduction of Ag_2O and Li_2O on the expense of PbO in Lead-Borate glass network. Also, the study aims to gain a better investigation for the role of Ag^+ and Li^+ modifier ions in the ionic conductivity of Lead-Borate oxide glass and its dependence on the temperature in the studied range. On the other hand the temperature dependent capacitance-frequency measurements are employed to explore the correlation between relaxation frequency peaks and temperature of non- bridging Oxygen hole centers (NBOHC) traps formed by Oxygen dangling bonds defects in the host network. Indeed, the emission rate values of these traps calculated from frequency peaks are applied to locate the NBOHC defect state in the energy gap with respect to the conduction band edge.

2. Experimental details

Two series of Lead Borate glasses are prepared with compositions $25B_2O_3$-$(73.8\text{-}x)PbO$-xM_2O-$0.6Cr_2O_3$–$0.6SeO_2$ with M = Ag and Li and x = 3, 4.5 and 6 mol% for Ag_2O and 3, 6 and 9 mol% for Li_2O as listed in Table 1. The used row materials were in the form of H_3BO_3, Cr_2O_3, SeO_2 and Pb_3O_4, Li_2CO_3 and $AgNO_3$. The glass is prepared by melt quenching technique using porcelain crucibles in an electric furnace. The temperature of melting was 900–1100 °C, the duration of melting was 1 h after the last traces of batches were disappeared. The amount of the glass batch was 50 g. To avoid the presence of bubbles the glasses were continues stirred during the glass melt preparation. Then the melt was poured onto stainless steel mold and annealed at around 350 °C to remove the thermal strains. The thickness of the glass slabs used for electrical measurements ~3 mm.

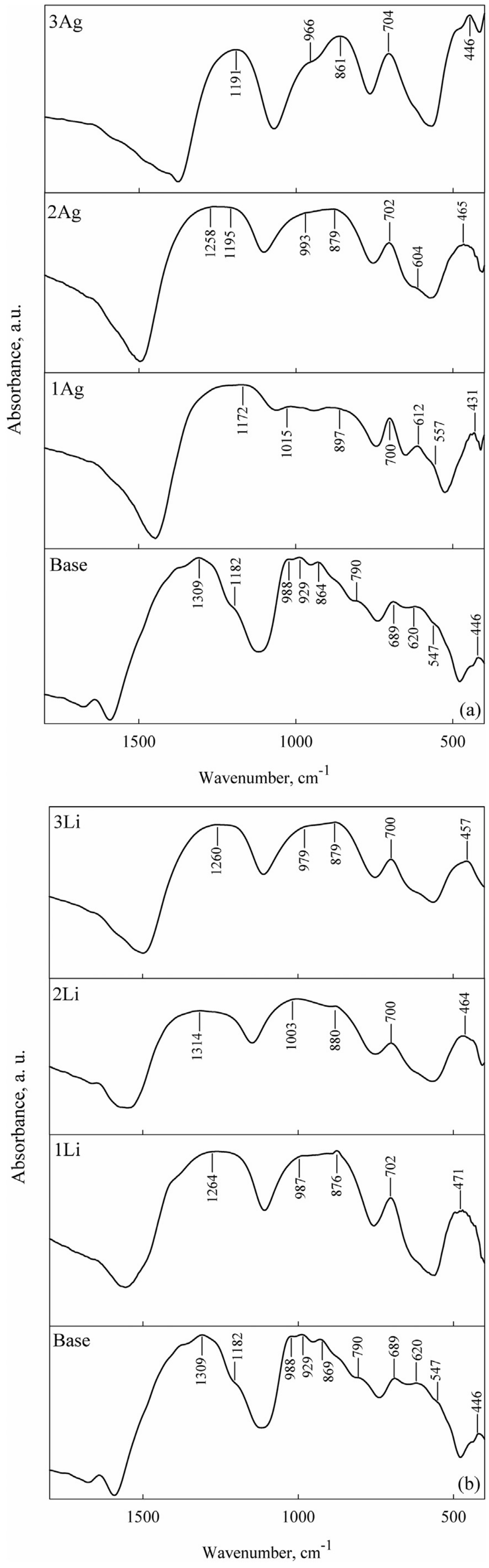
For IR measurements, dried Potassium Bromide is mixed with each studied sample and the mixture is sufficiently ground and then mechanically pressed at 70 MPa in the form of discs. These disks are used to measure the IR absorbance at room temperature using Jasco FT/IR − 300 E infrared spectrophotometer in the wavenumber range 2000–400 cm^{-1}.

The structural phase of as-prepared samples has been identified using an X-ray diffraction pattern (XRD) computerized system (model: Philips EXPERT-MPDUG PW-3040 diffractometer with Cu Kα radiation source). The obtained pattern showed absence of any diffraction peaks which ensure the amorphous nature of the investigated glass samples.

The ionic conductivity is evaluated by measuring the electrical a.c. admittance over a temperature and frequency ranges 303–373 K and 0.1 kHz–100 kHz in sequence using an impedance analyzer model Schlumberger Solartron 1260. The error in these measurements is ± 2%. The reproducibility of the measurements is tested by re-measuring the admittance after performing the experiment once again.

Table 1
Electronegativity of cations χ_C, anions χ_A and ionicity of different used oxides in the investigated samples.

Chemical composition	χ_C	χ_A	$\Delta\chi = \lvert\chi_A - \chi_C\rvert$	I_c
B_2O_3	4.08	10.5	6.42	99.99
PbO	2.33	3.5	1.17	93.46
Cr_2O_3	3.27	10.5	6.78	99.99
SeO_2	2.55	7.0	4.45	99.99
Ag_2O	3.86	3.5	0.36	78.03
Li_2O	1.69	3.5	1.54	97.67



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