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Effect of substituting iron on structural, thermal and dielectric properties of lithium borate glasses

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ABSTRACT

Glasses with composition $xFe_2O_3\cdot(30-x)Li_2O\cdot70B_2O_3$ ($x = 0, 2, 5, 7$ and 10 mol%) were prepared via melt-quenching technique and their physical, thermal and dielectric properties are discussed. XRD was carried out to confirm the amorphous nature of prepared glasses. Density (ρ) and molar volume (V_m) were found to increase with increase in Fe_2O_3 content. Infrared absorption spectra depicted that Fe_2O_3 is acting as a network modifier. DTA has been carried out to determine glass transition temperature (T_g) and crystallization temperature (T_x). Electrical properties have been studied using impedance spectroscopy and dc conductivity. The dc conductivity decreases and activation energy increases on replacing Li^+ ions with Fe^{3+}. The impedance measurements reveal that the total conductivity obeys Jonscher's power law. Study of the equivalent circuit analysis up to a temperature of 523 K shows a significant change in the equivalent circuitry with change in temperature and composition.

1. Introduction

The amorphous materials such as glasses have their own significance over the corresponding crystalline counterparts [1–3]. Addition of alkali and alkaline earth oxides can result into the network modification giving rise to non-linear optical properties [4]. Incorporation of transition metal ions in alkali borate glasses results in many technological applications such as solar energy convertors, lasers, phosphors etc. [5–7]. The borate matrix having iron oxide becomes important as it can exist in two valance states and the electrical conduction occurs by hopping of polaron (electron) from Fe^{2+} to Fe^{3+} valence state. In mixed electronic-ionic conductors, a remarkable change in the conductivity with composition leads to understanding of the interdependence between the electronic and ionic components of the total conductivity [8]. Fe^{2+} ions can only be six-fold coordinated in glasses leading to its modifying role [9], on the other hand Fe^{3+} ions exist in both tetra and octahedral environments. Thermal, structural and electrical properties of glasses containing iron oxide have been studied by several groups [8–13]. An increase in glass transition temperature with Fe_2O_3 content in iron lead borate glasses along with the existence of conduction through non-adiabatic hopping was observed [11]. Li^+ ion dynamics in the presence of Fe_2O_3 in bismuth–borate glasses has been studied and it was shown that the iron oxide shows "the blocking effect" on Li^+ ion conduction [12]. A recent study on sodium–lead borate glasses containing up to 15 mol% of iron oxide was done by Ibrahim et al. [13] and it was observed that the incorporation of iron oxide lead to the conversion of BO_3 borate units into BO_4 ones and the conductivity decreased and dielectric constant increased on increasing the amount of iron oxide due to structure compactness. The above studies are not sufficient to explain the role of iron oxide in lithium borate matrix and there is need to carry out impedance spectroscopy. In the presence of ac electric fields, the study of equivalent circuitry of glassy materials (i.e., whether these act as pure capacitor/inductor/resister or a combination of these) is not reported. Therefore authors have prepared glasses with composition $xFe_2O_3\cdot(30-x)\cdot Li_2O\cdot70B_2O_3$ ($x = 0, 2, 5, 7$ and 10mol %) and tried to study the structural, electrical and thermal properties of prepared glasses using density, molar volume, basicity, IR, thermal, dc conductivity, impedance spectroscopy and equivalent circuit analysis.

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Table 1
Density (D), molar volume (V_m), theoretical optical basicity (Λ_{th}), glass transition temperature (T_g) and crystallization temperature (T_x) glass stability (S) and stability ratio (S/T_g) for $x Fe_2O_3 \cdot (30-x) \cdot Li_2O \cdot 70B_2O_3$ (x = 0, 2, 5, 7 and 10 mol%) glasses.

Sample ID	x	D (gm/cc)	V_m (cc/mol)	Λ_{th}	T_g (K)	T_x (K)	S (K)	S/T_g
LFB1	0	2.22	25.93	0.4806	787	951	164	0.2084
LFB2	2	2.26	26.74	0.4907	767	944	177	0.2308
LFB3	5	2.35	27.32	0.5052	776	848	72	0.0928
LFB4	7	2.34	28.61	0.5145	787	845	58	0.0737
LFB5	10	2.41	29.24	0.5279	783	840	57	0.0728

2. Experimental

2.1. Glass preparation

The starting materials used for synthesis were AR grade reagent of Li_2CO_3, Na_2CO_3, Fe_2O_3 and H_3BO_3 procured from Loba Chemie. Synthesis was carried out by normal melt-quenching method at 1050 °C [14]. The composition is provided in Table 1. The prepared samples were powdered for XRD and FTIR measurements and were cut into regular shapes for impedance spectroscopy including equivalent circuit analysis and dc conductivity measurements.

2.2. XRD, density, molar volume and basicity measurements

XRD patterns of the powdered samples were recorded at ambient temperature (RT) on a Rigaku Mini-Flex II X-Ray Diffractometer in the 2θ range of 20–80° at a scan rate of 2°/min. The density (ρ) was measured at RT using Archimedes method with xylene as the buoyant liquid. The molar volume (V_m) was calculated from the density by using the relation $V_m = M/\rho$, with M as the molecular weight of glass samples. The theoretical optical basicity (Λ_{th}) is a tool to know about the ionic nature of glass. Hence Λ_{th} was also calculated using the relation [15]

$$\Lambda_{th} = X_{Fe_2O_3}\Lambda_{Fe_2O_3} + X_{Li_2O}\Lambda_{Li_2O} + X_{B_2O_3}\Lambda_{B_2O_3} \quad (1)$$

where Λ is the optical basicity assigned to different oxides [16] and X is the mole fraction of constituent oxides.

2.3. FTIR and DTA

FTIR measurements were carried out on a Perkin Elmer Frontier FTIR in mid-IR range (400–4000 cm^{-1}) using KBr pellet technique as described in literature [14]. The differential thermal analysis (DTA) of as prepared samples was carried out in the temperature range of 573–1073 K using a Perkin Elmer STA 6000 thermal

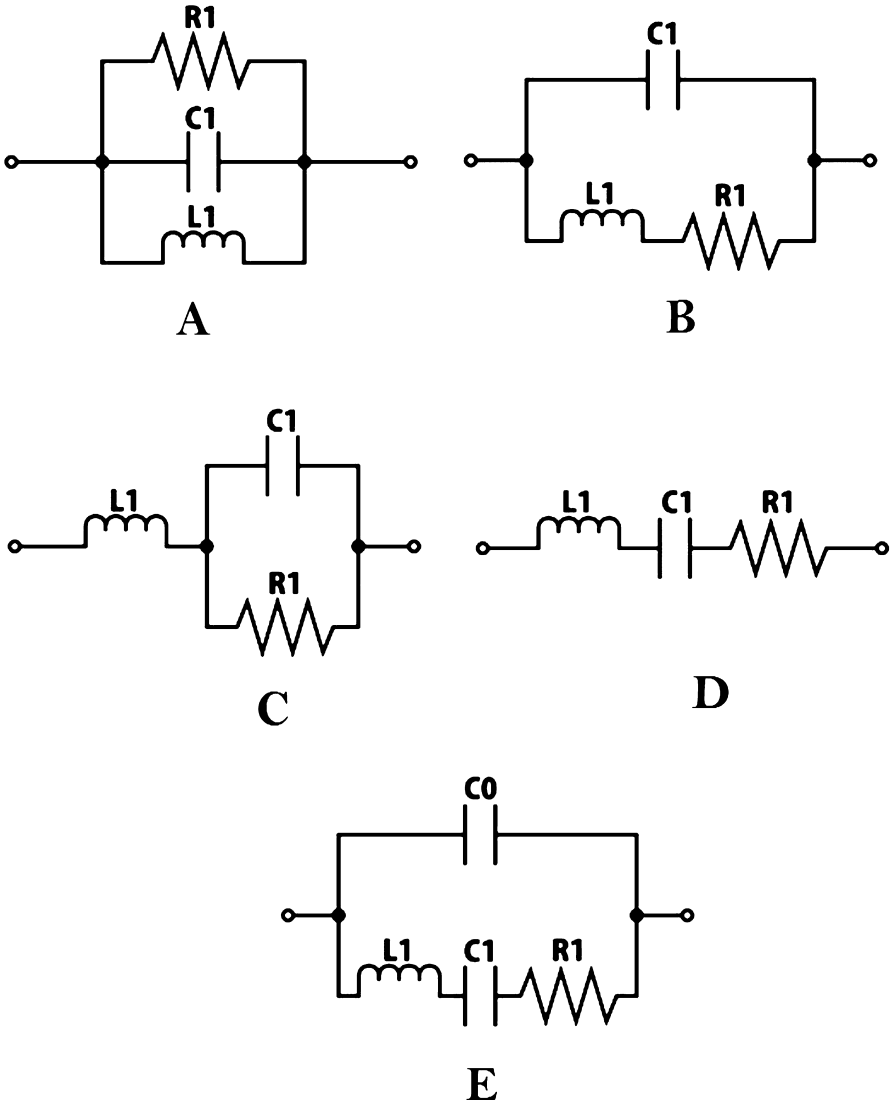

Fig. 1. Circuit combinations for different models (A–E) in IM9000.