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Lead modified properties of molybdenum doped lithium borate glasses

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ABSTRACT

The current scientific investigation deals with some significant results pertaining to the effect of substituting lead oxide on properties of lithium borate glasses having composition xPbO·(30-x)Li_2O·70B_2O_3 + 2 mol% MoO_3 (x = 0, 2, 5, 7, 10, 12 and 15 mol%, PLBM1-7). These glasses have been synthesized through appropriate melt-quench route and the non-crystalline phase formation has been confirmed through peak free X-ray diffraction measurements. Theoretical optical basicity (Λ_{th}), density (ρ) and molar volume (V_m) are observed to increase with increase in PbO content. *dc* conductivity has been observed to exhibit mixed electronic-ionic behaviour. DTA has been carried out to determine glass transition (T_g), crystallization (T_x) and liquidus (T_l) temperature. FTIR spectra depicted that PbO is modifying the structure of lithium borate matrix. The optical absorption spectra reveals that optical band gap (E_{opt}) decreases with increasing contents of PbO at the cost of Li_2O.

1. Introduction

Comparing with their counterparts in silicates, the alkali borate glasses are found to exhibit some interesting properties. The density in alkali silicates generally decrease on incorporation of alkali oxide by forming non-bridging oxygen atoms (NBOs) but the alkali borates exhibit an increasing trend in density. This is because of the tendency of alkali oxides to change the coordination number of boron from 3 to 4 without any NBOs. These trends are also followed in the corresponding glass transition temperature and thermal expansion coefficients of the alkali borate glasses [1]. Such type of anomalous behaviour in the properties of alkali oxide borate glasses was termed as *borate anomaly*. Because of possessing good ionic conductivity, alkali borate glasses are considered to be potential candidates for vacuum ultra-violet (UV) optics, ion battery materials and semiconductor lithography [2–5]. Therefore, scientific studies have always been devoted towards understanding the properties of alkali borate glasses [3–8]. These studies have also resulted in exploring the existence of Mixed-Alkali Effect (MAE) in glasses with two or more alkali oxides [9–12]. The heavy metal oxides like ZnO, Bi_2O_3, PbO etc. are well known conditional glass modifiers and on incorporating in oxide matrix these oxides improve the chemical durability of glass which enables the researchers to optimize the matrix for use as non-linear optical materials [13]. Lead oxide has been used as a constituent in several borate and phosphate glasses in order to achieve useful physical properties [14–16]. The structural role of PbO in many oxide glasses is unique since lead oxide is known to play a dual role both as a network modifier (through changing the oxygen coordination and forming non bridging oxygen atoms) and a network former (through conversion of borate, B-O-B units into lead borate, Pb-O-B units) [17–18]. One important characteristic of lead oxide is its ability to record the thermal history of glass by monitoring reactivity differences of batch mixtures on reduction under H_2 [19]. Moreover, when using glass for application as a devitrifying glass material, the role of lead becomes quite important as it assist in very fast devitrification. This includes the exploitation of lead borate glasses in crystallizing solder glasses wherein high joint rigidity, lower effective thermal expansion and very low fillet stress is achieved [20]. A study of lead borate system through Density Functional Theory (DFT) by Rada et al. have shown that lead atoms forms octahedral geometries by coordinating with 6 oxygen atoms; are surrounded by octahedral oxygen environments and get involved in metal coordination process; and exhibit ionic character inside the matrix [21]. These predictions get a fine support from analysis of the corresponding infrared absorption data [21].

Molybdenum is an exceptional transition metal as it can't form glass independently but when incorporated in other oxide glass formers it can result in the formation of stable glasses [22–24]. The ability of molybdenum ions to exist in multiple valence states (+3, +4, +5 and +6) favors its network formation tendency and it can yield some novel glass compositions with interesting optical, electrochromic and

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electrical properties [23, 25]. Therefore, the glasses doped with molybdenum ions remained a subject of study amongst many researchers [22–27]. As predicted through analysis of electron paramagnetic resonance spectra of molybdenum ions in oxide matrix, the higher oxidation states of molybdenum ions could be explained after considering contributions from both crystal field theory and charge transfer mechanism. The molybdenum ions are observed to exist in form of rhombic $(MoO_6)^{7-}$ clusters which give rise to g factors and hyperfine splitting factors [27]. A study of molybdenum lead borate glasses by S. Rada et al. [23] revealed the different structural units formed by lead and molybdenum atoms with borate network. It was found that the lead ions with ionic bonding exhibit a strong affinity towards triangular borate units containing NBOs and $(MoO_4)^{2-}$ molybdate units which can assist to form crystalline phases of $PbMoO_4$. The excess oxygen atoms then form MoO_6 and Mo_2O_7 structural units. Moreover, an interpretation of optical absorption data indicated formation of color centers on account of borate-molybdate and lead-molybdate paramagnetic units. A certain possibility of reduction of molybdenum ions from +6 to +5 and +4 to +3 oxidation states was also proposed in the same report [23]. A recent study on alkali (lithium) borate classes containing different amounts of molybdenum oxide by Shaaban et al. have shown that molybdenum have a strong influence on crystallization behavior in lithium borate glasses [24]. Lithium molybdenum oxide phase, Li_4MoO_5 was found to form at lower concentrations of molybdenum whereby the higher concentrations (> 10 mol%) lead to the formation of a new phase, Li_2MoO_4. Because of the increase in ultrasonic wave velocities on introducing MoO_3, the studied matrix could prove to be a suitable media for ultrasonic wave propagation [28]. Study on lead borate glasses containing very small amount of rare earth ions (Pr^{3+}) and molybdenum oxide have shown that these glasses exhibit very interesting optical properties which could lead to their applications in photonic and optoelectronic devices [29]. The above literature survey suggests that study of molybdenum doped alkali lead borate matrix is very significant. Therefore, we have synthesized molybdenum doped lithium borate glasses substituted lead oxide in place of lithium oxide in the system $PbO{\cdot}Li_2O{\cdot}B_2O_3$ doped with MoO_3 to study the effect of lead incorporation on physical, electrical, thermal, structural and optical properties of these glasses.

2. Experimental

2.1. Sample preparation

Glass samples of composition xPbO·(30–x)$Li_2O{\cdot}70B_2O_3$ + 2 mol% of MoO_3 (x = 0, 2, 5, 7, 10, 12 and 15 mol%, PLBM1-7 respectively) were prepared by conventional melt-quench technique. The starting materials Li_2CO_3, PbO, H_3BO_3 and MoO_3 were AnalaR grade chemicals procured from Himedia, India. The fine powdered chemicals were weighed using a digital electronic balance (CAS CAUY 220) in amounts sufficient to yield 20 g of the desired glass composition. The weighed chemicals were pulverized to mix homogenously in an agate pestle and mortar. Obtained mixture powders were collected in high alumina crucibles for melting at 1273 K in an electrical muffle furnace for 45 min. Better homogeneity of the melt was achieved by periodic shaking during the complete melting process. Finally quenching was carried out by pouring the melt on a stainless steel (SS) plate and subsequently pressing with another SS plate (both plates were pre-heated at ~150 °C to minimize the thermal stress) to obtain glass samples in disc form [30]. Samples were further fine powdered to use for FTIR and thermal analysis.

2.2. XRD and physical properties

The XRD profiles of fine powdered samples were recorded on a X-ray diffractometer (Rigaku Ultima-IV) in the 2θ range of 20–80° (2°/min). The Density (D) of the prepared samples was measured using buoyancy with xylene as immersion liquid and molar volume (V_m), of the samples was calculated using the relation $V_m = M_T/D$, where M_T is the total molecular weight. Λ_{th} was also calculated using the relation [31]

$$\Lambda_{th} = X_{PbO}\Lambda_{PbO} + X_{Li_2O}\Lambda_{Li_2O} + X_{B_2O_3}\Lambda_{B_2O_3} + X_{MoO_3}\Lambda_{MoO_3} \quad (1)$$

where Λ is the optical basicity assigned to different oxides [32] and X is the mole fraction of oxides.

2.3. DTA, FTIR, UV–Vis spectroscopy and dc conductivity

The differential thermal analysis (DTA) thermographs of the samples in pulverized form were recorded on a simultaneous thermal analyzer (Perkin Elmer STA6000) at 20 °C/min. FTIR measurements were carried out on a Perkin Elmer Frontier FTIR in mid-IR range (400–4000 cm^{-1}) using KBr pellet technique [33]. Baseline and noise correction was achieved using Spectrum10 software (provided with FTIR spectrophotometer). For peak identification of the processed spectrum, multiple peaks fitting of each spectrum was carried out using Origin 16 Pro by adding peaks till the fit parameter became ≥0.999. The samples obtained in the form of slices were polished to optical quality for UV–Vis spectroscopic measurements. The optical absorption measurements were then carried out in the wavelength range of 200–800 nm at ambient temperature on a UV–Vis spectrophotometer (Shimadzu UV2401). The dc electrical conductivity of rectangular shaped samples (0.7–1.5 mm thickness and 100–230 mm^2 area) was carried out by two probe method on a Keithley low voltage source meter (Model 2401) in the temperature range of 353–623 K with a heating rate of 1 K/minute [33]. Colloidal silver paint (Structure Probe, Inc., USA) was used on both sides of surfaces for electrode formation.

3. Results and discussion

3.1. XRD, density (D), molar volume (V_m) and theoretical optical basicity (Λ_{th})

The peak free XRD profiles of as-prepared fine powdered samples as shown in Fig. 1 confirms the non-crystalline form (within instrument resolution) of all synthesized glasses [34]. The measured values of density (D) and calculated values of molar volume (V_m) are presented in Table 1. Density is an important physical parameter that can be considered as an intrinsic property of glass which is capable of predicting

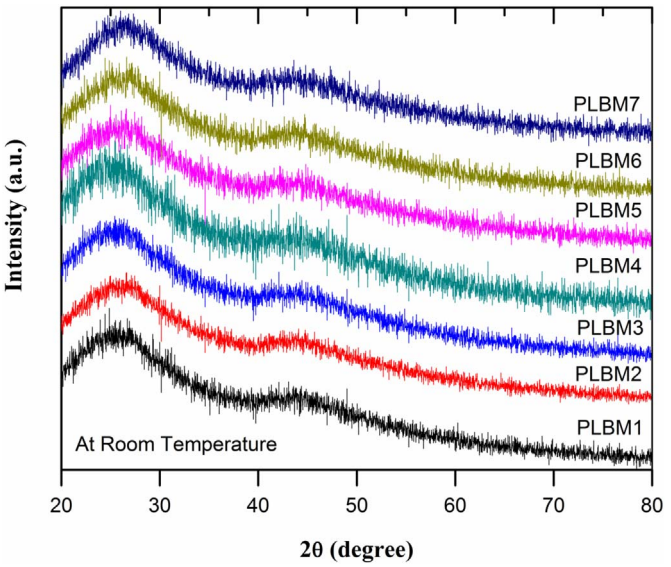

Fig. 1. XRD profiles of xPbO·(30-x)$Li_2O{\cdot}70B_2O_3$ + 2 mol% MoO_3 (x = 0, 2, 5, 7, 10, 12 and 15 mol%, PLBM1-7) glasses recorded at room temperature.