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Optical and thermal investigations on vanadyl doped zinc lithium borate glasses

Seema Dalal [a,c], S. Khasa [a,*], M.S. Dahiya [a], Arti Yadav [a], A. Agarwal [b], S. Dahiya [c]

[a] Department of Physics, Deenbandhu Chhotu Ram University of Science and Technology, Murthal 131039, India
[b] Department of Applied Physics, Guru Jambheshwara University of Science and Technology, Hisar 125001, India
[c] Department of Physics, Baba Mast Nath University, Asthal Bohr, Rohtak 124001, India

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ABSTRACT

Using standard melt-quench technique, transition metal oxide (2 mol% of V_2O_5) doped glasses having composition $xZnO{\cdot}(30-x)Li_2O{\cdot}70B_2O_3$ ($x = 0$, 2, 5, 7 and 10) are prepared. The density (D) is measured using buoyancy and found to be lying between 2.21 and 2.45 g/cm^3 with an increasing trend on substituting ZnO contents in place of Li_2O. The theoretical optical basicity (Λ_{th}) is calculated and found to increase with increasing inclusion of ZnO indicating an increase in the ionic character. The molar refraction (R_m), refractive index (n_r) and molar polarizability (α_m) are calculated and explained on the basis of structural changes. The optical absorption spectra have been used to evaluate the values of optical band gap (E_{opt}) and band tailing parameter (B). It is observed that E_{opt} decreases with the increasing contents of ZnO in base glass matrix. The decrease in E_{opt} is an evidence of enhancement in the number of non-bridging oxygen atoms (NBOs) thereby increasing the four-coordinated boron atoms. The as-quenched samples in bulk form are subjected to differential thermal analysis (DTA) to assess the glass transition temperature (T_g), which is 476 °C for pure lithium borate glass. The variations suggest that the structure is being modified by the substitution of ZnO.

1. Introduction

Initially, various applications of glasses were within the domain of silicate glasses (a class of oxide glasses). But with the passage of time the other oxide glasses including phosphate, borate, bismuthate, germanate, etc. were also studied with a great deal of academic, scientific, and technological interest. The non-silicate glasses proved their justifiable existence to nurture a large portion of scientific community. Out of such glasses, the borate glasses have the advantage of having highest glass forming ability among all types of glasses and they do not reach crystalline state even at the lowest cooling rates [1]. B_2O_3 can be found in many commercially important glasses. Besides owing to the property of boron anomaly, it is mostly used as a dielectric material [2]. The higher bond strength, lower cationic size and smaller heat of fusion also make B_2O_3 as a strong glass former [3]. The borate glasses are presumed to be an arrangement of irregular network of BO_3 triangles with each oxygen atom being shared by two boron atoms [4].

The borate glasses containing alkali metal ions (particularly Li^+) have been studied with great interest for applications in solid state batteries, fast ion conductors, etc. [5–9]. The addition of alkali metals at low concentrations to pure borate glasses is presumed to convert the triangular borate units into the tetrahedral coordinated borate units without the creation of NBOs unlike their silicate counterparts. But this is not the case for borate glasses containing high alkali concentrations where the trends in physical properties (such as T_g) just reverse, suggesting the creation of non-bridging oxygen atoms (NBOs) which is termed as the "boron anomaly" [10]. The thermal stability of the oxide glasses is also enhanced by the addition of Li_2O due to the increase in NBO bonding. Substituting ZnO makes these glasses promising materials for photonic and optoelectronic applications [11]. Depending upon the nature of bonding between metal and oxygen atom, ZnO can play the role of a modifier or a glass former [12]. The study of adding ZnO to oxide glasses is also important due to their non-toxicity, non-hygroscopic nature, lower cost of production, higher polarizability and lower

* Corresponding author at: Department of Physics, DCR University of Science and Technology, Murthal 131039, Sonepat, Haryana, India. Tel.: +91 98128 18900/130 2484114; fax: +91 130 2484003.
E-mail addresses: skhasa@yahoo.com, ms.dahiya12@gmail.com (S. Khasa).
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melting point [13–15]. Due to these aspects, the lithium borate glasses containing zinc ions have been studied for their structure and properties by many authors [16–20].

Incorporation of vanadium oxide doping assists to analyze different structural and physical properties of the base glass matrix. In recent past, vanadyl doped glasses have remained a subject of interest for many researchers [5–7,21]. Mixing vanadium ions in small quantities in the glass matrices makes them suitable for use in memory and switching devices [6]. As V^{4+}, vanadium is usually coordinated to six ligands which forms an octahedral complex. With oxygen as ligand, one V—O bond of this complex becomes very distinct and termed as vanadyl ion (VO^{2+}) [22]. In a previous work, one of the authors studied electron paramagnetic resonance (EPR) of the vanadyl ion in $CoO{\cdot}ZnO{\cdot}B_2O_3$ glasses [21] and an improvement in the octahedral symmetry of the V^{4+} site is observed. Gahlot et al. [20] studied ZnO doped alkali bismuthate glasses and found that optical band gap and dc conductivity has a decreasing trend. After considering above mentioned properties and literature survey, authors have prepared a series of lithium borate glasses doped with V_2O_5 containing different amounts of ZnO and studied the physical, thermal and optical properties of glasses.

2. Experimental

The starting materials used were analar grade chemicals Li_2CO_3, ZnO, H_3BO_3 and V_2O_5 obtained from Loba Chemie. The detailed preparation technique is available in literature [23]. The prepared samples in the compositional range of $xZnO{\cdot}(30-x)Li_2O{\cdot}70B_2O_3$ (x = 0, 2, 5, 7 and 10) containing 2 mol% of V_2O_5 were abbreviated as ZLBV1–5 respectively. The density (D) of the prepared samples in the bulk form was measured using buoyancy with xylene as immersion liquid. Data obtained for density were used to calculate the molar volume (V_m) [24]. The theoretical optical basicity (Λ_{th}) was calculated by the method explained in literature [25]. 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 an ambient temperature on a UV–vis spectrophotometer (Shimadzu UV2401). The optical absorption data were used to calculate optical band gap and band tailing [26]. The differential scanning calorimetric (DSC) studies of the samples in the bulk form amounting to 30–40 mg were carried out on a simultaneous thermal analyzer (Perkin Elmer STA6000) [27,28].

3. Results and discussion

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

Density is an important intrinsic property for providing information on short range structure of oxide glasses. Although it is not possible to conclude exactly about the atomic arrangements from experimental data of densities, yet density remains to be a fundamental test for a short range order model [29]. The measured values of D and calculated values of V_m for all prepared compositions are reported in Table 1. It can be noticed from Table 1 that D is increasing with increasing content of ZnO which is an expected result as the relative molecular weight of ZnO is higher than that of Li_2O. Obtained values of density have same order as reported by El-Alaily et al. for lithium borate glasses (containing ~10 mol% of Li_2O) [30]. The obtained values of V_m (as observed from Table 1) are in between 26.57 and 27.36 cm^3/mol which are in good agreement with those reported for lithium borate glasses [10]. The alkali/alkaline oxides are known to be acting as glass modifiers in oxide glasses [31]. It is observed from Table 1 that the variations in molar volume are not consistent. This may be because of two reasons: first due to the fact that V_m depends on both D and molecular weight and the second because of the role of ZnO which is not clearly defined for oxide glasses (as it can act as both glass former and modifier) [14].

The optical basicity has been studied by Duffy and Ingram [32,33] by relating it with the spectroscopic probe ion data or the Pauling electro-negativity [34] and the values have been predicted for the optical basicity of many oxide systems. Another way to calculate the theoretical optical basicity (Λ_{th}) for multi-component glass systems was proposed by Duffy and Ingram [35,36], in which Λ_{th} is calculated by the algebraic sum of basicity values of each component in glass stoichiometry. However the values calculated using this method reflect only the trends in the optical basicity rather than true basicity as determined experimentally, reason being why in some cases the theoretical and experimental values of the optical basicity deviates from each-other. So the concept proposed by Duffy and Ingram [35,36] represents the bulk density and does not assist in obtaining information about the cation (B^{3+} here) coordination number. To understand the role of basicity in obtaining information about the changes governed in the glass matrix by the addition of ZnO, Λ_{th} was calculated whose values are reported in Table 1. These values are in good agreement with the values of Λ_{th} obtained for alkali borate glasses [37,38] and the increasing trends in optical basicity suggest an enhancement in the ionic character of prepared glasses on substituting ZnO in place of Li_2O. To understand the role of trends in basicity it is important to relate it with the oxide ion polarizability (α_o^{2-}, also termed as oxide ion activity [39]) through an intrinsic relationship proposed by Duffy [40] as: $\Lambda_{th} = 1.67(1-(1/\alpha_o^{2-}))$. This relationship suggests that the trends in basicity are similar to polarizability. The values of polarizability calculated by this relation are also reported in Table 1. Extensive studies have been done by researchers [41–43] to study the variation in polarizability with substance in crystalline and amorphous materials and it was concluded that the polarizing power of cation increases with increase in its positive charge. Hence the trends in optical basicity in present study are in accordance with the expectations. Moreover, Λ_{th} assists us in understanding the structure modification in the vanadyl ion doped in the host glass. An increase in Λ_{th} leads to a decrease in oxygen covalency resulting in an enhancement in sigma bonding which decreases the positive charge on V^{4+}. This leads to an increase in bond length of

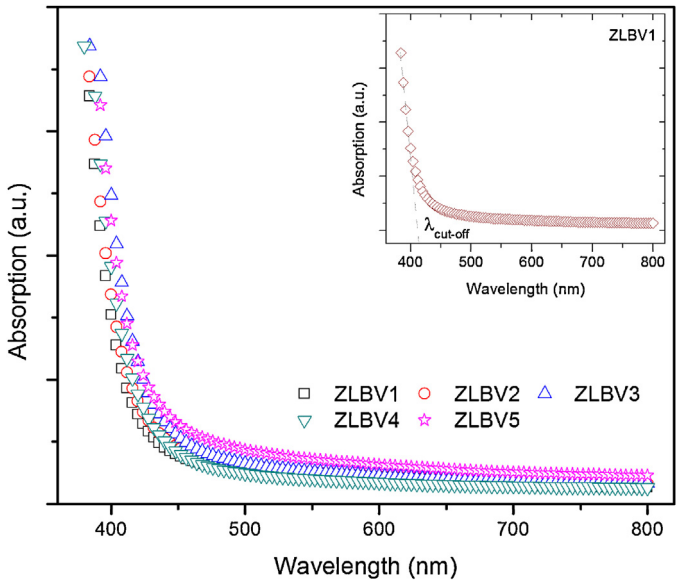

Fig. 1. Optical absorption curves for samples ZLBV1–5 (inset: cut-off intercept for sample ZLBV1).