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Optical absorption and heating rate dependent glass transition in vanadyl doped calcium oxy-chloride borate glasses

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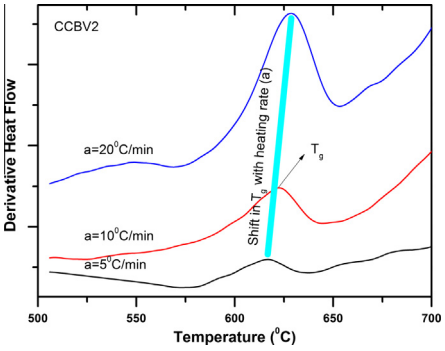
HIGHLIGHTS

- Glass transition temperature increases with increase in heating rate.
- Cl^- anions enter into the voids of borate network at low concentration.
- Cl^- anions contribute to the network formation at high concentrations.
- Prepared glasses have good thermal stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Some important results pertaining to optical and thermal properties of vanadyl doped oxy-halide glasses in the chemical composition $CaCl_2$–CaO–B_2O_3 are discussed. These glasses have been prepared by conventional melt quench technique. From X-ray diffraction (XRD) profiles the amorphous nature of the doped glasses has been confirmed. The electronic polarizability is calculated and found to increase with increase in chloride content. The optical absorption spectra have been recorded in the frequency range of 200–3200 nm. Recorded spectra are analyzed to evaluate cut-off wavelength ($\lambda_{cut\text{-}off}$), optical band gap (E_g), band tailing (B), Urbach energy (ΔE) and refractive index (n). Thermal analysis has been carried out for the prepared glasses at three different heating rates viz. 5, 10 and 20 °C/min. The glass transition temperature (T_g) along with thermal activation energy (E_a) corresponding to each heating rate are evaluated from differential scanning calorimetry (DSC) thermographs. It is found that E_a decrease and T_g increase with increase in heating rate. The variation in T_g is also observed with the substitution of calcium chloride in place of calcium oxide. The increasing and higher values of E_a suggest that prepared glasses have good thermal stability. Variation in T_g and E_g suggests that Cl^- anions enter into the voids of borate network at low concentrations (<5.0%) and contribute to the network formation at high concentration (>5.0%).

Introduction

Although the basic concepts about the structure of glasses was established by Zachariasen in 1930's [1] but the structure of borate glasses was particularly studied by Krogh-Moe [2]. Bray and O'Keefe [3] also supported the works carried out by Krogh-Moe. Borate glasses are of technological importance due to their strong Glass Forming Ability even at the lowest cooling rates [4]. Borate glasses are assumed to have the tendency to reduce the thermal expansion and provide resistance to thermal shock at high temperatures, which makes them suitable for fiberglass applications [5].

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The addition of alkali and alkaline earth oxide in borate glasses results into the network modification which gives rise to different non-linear optical properties making these glasses suitable for optoelectronic applications [6]. Many researchers studied the alkali halide borate glasses for application as fast ion conductor [7–11] but when it came to the case of alkaline earth halide borate glasses, relatively lesser attention was paid [12–15]. Farouk et al. [12] studied the $CaO–B_2O_3–Fe_2O_3–CaCl_2$ system and concluded from the Mossbauer spectroscopy results that there is a close link between Cl^- and Fe^{2+}/Fe^{3+} ions and addition of $CaCl_2$ strongly affects the Fe^{3+}/Fe^{2+} ratio. This indicated that Cl^- ions have ability to link through the glass forming network units. While studying $CaF_2–B_2O_3$ glasses, Doweidar et al. [15] found that CaF_2 forms $Ca^{2+}_{1/2}[BO_{3/2}F]^-$ units in combination with different borate units. The remaining CaF_2 forms its own unit in form of CaF_4. Also the Ca^{2+} ions contribute towards the ionic conductivity and act as main charge carriers. The spectral characterization of $B_2O_3–BaO–LiF$ system doped with rare earths (Nd^{3+}/Er^{3+}) was studied by Hemalatha Rudramadevi and Buddhudu [14] and found that these optical glasses are potential materials for progress of glass lasers and optoelectronics. Abdel-Hameed et al. [13] studied the effect of fluoride ions on preparation of transparent glass ceramic in the $BaO–B_2O_3$ glass system and found that F^- ions facilitates the glass formation.

The alkaline earth borate systems exhibit glass formation at high borate contents. In $MO–B_2O_3$ (M = Ba, Ca and Mg) systems the glass melting temperature increases gradually as we increase the alkaline earth content. It depicts the decrease in Glass Forming Ability (GFA) of these systems [16]. The glass formation region in alkaline earth borate glasses shrinks gradually as the size of alkaline earth cation decreases due to which the glass formation region is narrowest in case of $MgO–B_2O_3$ systems [17]. The alkaline earth carbonates due to their high optical transparency and thermal stability can act as promising hosts to investigate effect of chemical environment on optical properties [18–20]. Rojas et al. [21] reported that calcium borate glasses are useful for application as thermo luminescent dosimeter. Non-linear optical (NLO) properties of the alkaline earth materials were studied by Zou et al. [22] and found that these materials are suitable for non linear optical and ultraviolet applications. The above literature survey suggests that the alkaline earth oxy-halide borate glasses are of technological importance. Therefore we have prepared vanadyl doped calcium oxy-chloride borate glasses having composition $x CaCl_2·(30 - x)CaO·70B_2O_3$ + 2 mol% of V_2O_5 (x = 0, 2, 5, 7, 10, 12, 15, 20, 25 and 30). The optical absorption and thermal properties of these glasses are studied and reported.

Experimental

Glass preparation

The AR/GR grade reagents of $CaCl_2$, $CaCO_3$, H_3BO_3 and V_2O_5 were used as the starting chemicals. The powdered chemicals were weighed in batches of 20 gm as per the composition in mol% by using a digital electronic balance (CAS CAUY 220). The weighed chemicals were crushed and mixed homogenously in an agate pestle and mortar for four hours. The mixture so obtained was melt at 1373 K in an electrical muffle furnace for 45 minutes. The melt was shaken at regular intervals so as to obtain fine homogeneity. Thereafter quenching was carried out by sandwiching the melt between two stainless steel plates to obtain glass samples in form of round discs.

XRD measurements

The XRD profiles of fine powdered samples were recorded at room temperature (RT) on a Rigaku Miniflex-II X-ray diffractometer in the 2θ range of 20–80° at a scan rate of 2° per minute. Cu k_α radiations at 40 kV and 15 mA with a high speed Si strip detector were used as source and detectors respectively.

Optical absorption measurements

Samples having thickness between 0.5 and 1.2 mm were polished to optical quality for recording of optical absorption and transmission spectra. The spectra were recorded in the frequency range of 200–3200 nm at RT using a UV–Vis–NIR spectrophotometer (CARY 5000).

DSC analysis

The differential scanning calorimetry (DSC) of samples in bulk form was carried out in the temperature range of 200–1000 °C on a Perkin Elmer simultaneous thermal analyzer (Model STA 6000). Three different heating rates (5, 10 and 20 °C/min) were used to record the thermographs. Nitrogen was used as purge gas with a gas flow rate of 20 ml/min. The instrument was calibrated with Indium, Silver and Calcium Oxalate as the reference materials before recording thermographs. Complete data analysis along with data smoothening was carried out using Pyris thermal analysis software provided with STA 6000.

Results and discussion

Electronic polarizability (α_0^{2-}) and XRD

The oxide ion polarizability (α_0^{2-}) is related to theoretical optical basicity (Λ_{th}) as

$$\Lambda_{th} = 1.67\left(1 - \frac{1}{\alpha_0^{2-}}\right) \tag{1}$$

where Λ_{th} is calculated by using the relation [23]

$$\Lambda_{th} = \frac{Z_i r_i}{Z_o \gamma_i} \tag{2}$$

where Z_i is the oxidation number of the cation i, r_i is the ratio of cation of a particular oxide to the total number of oxides in whole glass matrix and Z_o is the oxidation number of the anion (Z_o = 2.0 for oxides) [24], γ_i is the basicity moderating parameter. It is given as:

$$\gamma_i = \sum_i 1.36(x_i - 0.26) \tag{3}$$

where x_i is Pauling electro-negativity [25]. The values of theoretical optical basicity so calculated are available in literature [26].The calculated values of polarizability are reported in Table 1. The polarizability is strongly related to many microscopic and macroscopic physical and chemical properties such as UV absorption, ionic refraction, optical non-linearity and chemical stability. Fig. 1 shows the variation of polarizability with corresponding $CaCl_2$ content. The increasing trend in polarizability suggests that there is an increase in ionic nature of the glasses. This can be explained on the basis of the fact that optical basicity expresses the basicity of glass in terms of the electron density carried out by oxygen. The trends in polarizability are in good agreement with the literature [27].

The XRD spectra for all compositions recorded at RT are shown in Fig. 2 along with the inset. It is generally considered that the non-crystalline materials do not exhibit sharp peaks in XRD spectra. This is due to the non-periodic arrangement of atoms in these solids which does not satisfy the diffraction condition. The spectra from Fig. 2 exhibit absence of peaks in the prepared samples and shows broad hump which reveals the amorphous nature of these