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Structural, thermal, and optical analysis of zinc boro-aluminosilicate glasses containing different alkali and alkaline modifier ions

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ABSTRACT

In this article, structural, thermal, and optical properties of zinc boro-aluminosilicate glasses with addition of different alkali (Li, Na, and K) and alkaline oxides (Mg, Ca, Sr, and Ba) have been reported. 10 mol% of alkali and alkaline oxides were incorporated into Zinc boro-aluminosilicate glasses and all these glasses possess high optical quality. Samples were characterized using X-ray diffraction (XRD), scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDAX), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, Raman spectroscopy, thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), and optical absorption spectroscopy. The XRD and SEM measurements demonstrated the amorphous origin for all the prepared glasses and EDAX confirms that all the elements are presented in the prepared glasses. The presence of various functional groups such as triangular and tetrahedral-borate (BO_3 and BO_4) was confirmed by ATR-FTIR and Raman spectra, and both of the ATR-FTIR and Raman spectra show lower phonon energy for H3 (K_2O) in alkali series, and H7 (BaO) for alkaline. From TGA analysis we found a lower weight loss <0.1% in K_2O, MgO, and BaO; and from the DSC profiles the glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization temperature (T_c), and melting temperature (T_m) were identified and related different thermal parameters are evaluated. Alkali and alkaline influenced Zinc boro-aluminosilicate glasses demonstrate excellent glass stability. From the optical absorption spectra, we calculated cut-off wavelength and it shows spectral shifting to longer wavelength with alkali (Li → Na → K), and alkaline (Mg → Ca → Sr → Ba) modifiers. We investigated optical band gap energy also for allowed transitions in UV–visible region using three methods; direct, indirect, and absorption spectrum fitting (ASF).

1. Introduction

Recently, glasses doped with different rare earth (RE) ions are considered as promising materials for lasers and optical amplifiers applications. Generally the structural, thermal and optical properties of these RE ions doped glasses are mainly dependent on the host matrix [1–3]. B_2O_3 as a network former has attractive optical features among silicate, phosphate, tellurite and germinate due to promising properties like high transparency, low melting point, high thermal stability, different coordination numbers, and good solubility of rare-earth ions [4,5]. Such features justify B_2O_3 as a good candidate for optical applications. Borate glasses possess phonon energy (~1400 cm^{-1}) [6] higher than tellurite (~700 cm^{-1}) [7], germanate (~900 cm^{-1}) [8], silicate (~1100 cm^{-1}) [9] and phosphate glasses (~1300 cm^{-1}) [10]. However, the addition of glass former or modifier reduce the non-radiative transition probability substantially, in addition the combination of B_2O_3 with other lower phonon energy glass former gives more probability to bridge the energy difference in rare earth dopant such as the Er^{3+}:$^4I_{11/2}$ → $^4I1_{3/2}$ transition and the Ce^{3+}:$^2F_{5/2}$ → $^2F_{7/2}$ [11]. Borate glasses have unique feature of producing super structure of B_xO_y [12], in the fact, the BO_3 and BO_4 can form different structural units such as boroxol ring, pentaborate, tetraborate and diborate. Besides that, the glassy structure of B_2O_3 is a laminar matrix having of 3 atoms coordination with oxygen which can form six membered boroxol rings B_3O_6 [13]. SiO_2 and B_2O_3 behave as network formers, borosilicate glasses containing boron oxide have been widely used because of high refractive index and low dispersion characteristics [14]. Zinc borosilicate system which contain high amount of zinc oxide shows ability to break the bonds between oxygen and glass former ions [15], besides that ZnO plays an important role in RE doped glasses due to its unique electronic and optical properties, and used in combination with B_2O_3 as glass stabilizer to break the bonds and forming BO_4 [13,14]. Aluminum oxide and zinc oxide can be employed to increase mechanical strength and enhance

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the chemical durability of glass. In the same way Al_2O_3 as a traditional intermediate [16] improves the geometric distribution of RE depend to avoid clustering of the rare earth ions [15,17,18]. Boro-aluminosilicate glasses gained interest due to easy obtainability and also because of the wide variety of structural units [19]. It's also decrease the glass viscosity, delayed crystallization giving better wettability of glasses [20]. Our present study focused on the effect of introducing alkali (Li_2O, Na_2O, K_2O) and alkaline (MgO, CaO, SrO, BaO) modifiers on the structural, thermal, and optical features of the B_2O_3-SiO_2-Al_2O_3-ZnO glass. The structural and thermal properties of the synthesized glasses is analyzed using X-ray diffraction (XRD), scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDAX), Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, Raman spectroscopy, Thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC) and optical absorption show existence of low phonon energy and high thermal stability host glass for optical amplifier applications.

2. Experimental

2.1. Synthesis

Using melt quenching technique, we have synthesized the Zinc-boro-aluminosilicate glasses introduced by 10 mol% alkali (Li_2O, Na_2O, K_2O) and alkaline (MgO, CaO, SrO, BaO) modifiers. All the raw materials were purchased in high purity powders from Sigma-Aldrich, B_2O_3 (339,075–99.98%), Al_2O_3 (11,028–98%), ZnO (96,479–99%), Li_2CO_3 (431,559–99.99%), Na_2CO_3 (791,768–99.5%), K_2CO_3 (791,776–99%), MgO (342,793–99%), CaO (208,159–99.9%), SrO (472,018–99.9%), BaO (554,847–99.99%) and Fisher Scientific SiO_2 (437,151,000–99.99%). In the present work we indicate samples as "H1", "H2", "H3", "H4", "H5", "H6", and "H7", respectively (Table 1). All the required chemicals were measured using stoichiometric ratio and weighed using high accurate micro balance in 20 g batch. Then all the compositions were mixed carefully and placed in high purity alumina crucibles, then heated in electric furnace up to 1400 °C. Based on our preliminary study we choose one hour as a suitable time to fully melt the glass. The homogeneous melts were subsequently poured onto a stainless steel plate and then quickly pressed with another steel plate. The obtained glass disks were clear, bubble free with average diameters varying within 3–4 cm. They possessed thickness of ~0.6 cm and good optical transparency. All of our glasses were weighed again to find out the evaporation of the low melting point chemicals like B_2O_3, the total loss was 2–3% of the original powders considering the amount which is stick to the crucibles. All (H1–H7) obtained glasses were totally colorless. The internal stress induced in the glasses during the melt quenching was released by annealing the samples below glass transition temperature (T_g) at 450 °C for 5 h in air. Afterwards they were cooled slowly to ambient temperature. Furthermore, to achieve smoothness all the glasses were cut and polished using low speed saw machine and mechanically to a mirror surface, and finally SiC/water was used. These glass samples were prepared in two forms: powders were characterized by employing different structural and thermal techniques; solid form with 3.0 mm thickness as shown in Fig. 1 for optical analysis.

Table 1
Nominal composition of (H1–H7) synthesized glasses (mol%).

Sample code	B_2O_3	SiO_2	Al_2O_3	ZnO	Li_2O	Na_2O	K_2O	MgO	CaO	SrO	BaO
H1	40	10	10	30	10	–	–	–	–	–	–
H2	40	10	10	30	–	10	–	–	–	–	–
H3	40	10	10	30	–	–	10	–	–	–	–
H4	40	10	10	30	–	–	–	10	–	–	–
H5	40	10	10	30	–	–	–	–	10	–	–
H6	40	10	10	30	–	–	–	–	–	10	–
H7	40	10	10	30	–	–	–	–	–	–	10

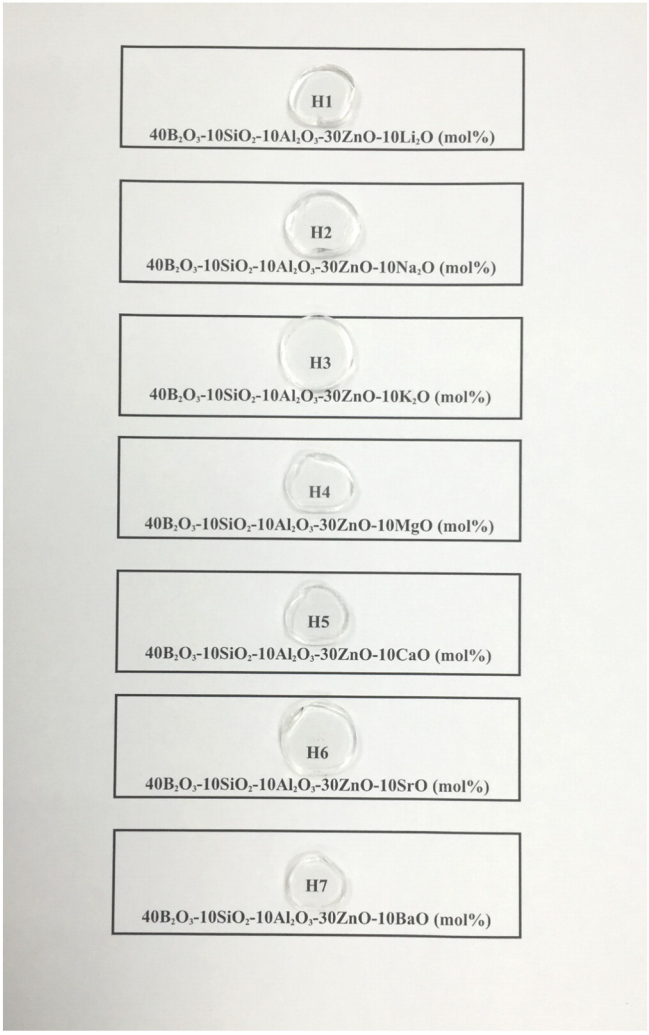

Fig. 1. Photograph of all the synthesized glasses (thickness = 0.3 cm).

2.2. Characterization

Using sliding caliper gauge, we measured the thickness for the all glass samples. The density of the glasses was measured using the buoyancy method based on the Archimedes principle with toluene as an immersion liquid to a precision of 0.001 g. An Abbe refractometer was used to measure the refractive indices of the glasses at n_d (589.3 nm) wavelength using sodium lamp with an error ± 0.001. X-ray diffraction (XRD) profiles were obtained using Ital Structure APD 2000 diffractometer with CuKα (λ = 1.542 Å) radiation with an applied voltage of 40 kV and 20 mA anode current. The scan rate was 2°/min., and the scan range was varied between 10° and 80°. The surface morphology was monitored using FE-SEM equipment FEI-NOVA NanoSEM 230 with an acceleration voltage 5 kV, equipped with an EDX detector from EDAX-Ametek that allowed semi-quantitative analysis of elements. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the glass powders were measured over the 400–4000 cm^{-1} range by a Perkin Elmer Spectrum 100 FTIR spectrometer with a spectral resolution of ~4 cm^{-1}. The finely ground glass powder was pressed directly onto the ATR diamond crystal for the FTIR measurement. The Raman spectra of the glasses were obtained with a WITec alpha 300R Confocal Raman system equipped with an Nd: YAG laser (532 nm) as the excitation source. An incident power of 10 mW was typically used. The Raman spectra were recorded within the spectral range of 0–3800 cm^{-1} for the Raman shift, with an integration time of 5 s for each single Raman

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