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Mixed alkali effect and samarium ions effectiveness on the structural, optical and non-linear optical properties of borate glass

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ABSTRACT

Borate glasses containing lithium, sodium, and samarium ions were prepared by conventional melt annealing technique. The structural units show the presence of BO_3, and BO_4 units while samarium ions favored to link with −OH group. Density and molar volume show the impact of the replacement sodium ions by lithium. The density values increase with increasing lithium content up to 20 mol% and decrease for free sodium borate glass (30 Li_2O or 0 Na_2O). Optical and photoluminescence investigations were carried to determine the optical parameters such as optical band gap, refractive index, etc. The optical band gap and refractive index values show the nonlinearity trend due to the change occurred at 10% Li_2O content. The non-linear optical parameters were determined and studied in terms of the refractive index and the impact of the mixed alkali effect.

1. Introduction

Borate network glass former comprising of BO_3, BO_4 and boroxol groups is an excellent active host medium for rare earth element (RE) ions. Generally, RE ions are strongly affected by the local structure as well as the symmetry of the glass matrix and the glass composition [1,2]. Such glasses containing RE ions have interesting technological applications in fields of glass and solid state lasers, optical fiber amplifiers, acousto-optic modulators, optical communications, infrared quantum counters and infrared-visible converters [1–6].

If Samarium ions embedded to the host glass network, the optical and fluorescence properties were improved. Their high quantum efficiency originates from the emission in $^4G_{5/2}$ level leading to use it in high- density optical storage [7–9]. Moreover, the presence of samarium ions as network modifier (4 and 4.5 mol%) in borate glasses leads to increase BO_4 structural units [10,11] and the increment of Sm^{3+} ions enhances the dipole-quadrupole interaction between samarium ions and hence a concentration quenching in Sm^{3+} ions happen.

On the other hand, it is known that vitreous borate glass is mostly comprised of boroxol rings and BO_3 units to form 2D randomly network [12–14]. If alkali oxide/mixed alkali oxides intercalated through vitreous borate network, the formation of BO_4 groups is mostly happened below 25% of alkali(s) content [15,16]. Moreover, the resistivity of such materials goes to be the maximum when mixed alkali oxides are presented in equal ratios (alkali oxide effect). Hence, the mixed alkali effect (MAE) in glasses describes the nonlinear changes such as conductivity, glass transition temperature, viscosity, etc. [17,18].

Since borate glass containing alkali ions earns the nonlinear behavior in the physical properties of such glasses. Moreover, the presence of rare earth ions in borate glasses as a dopant and modifier enhances the physical, optical and the photoluminescence properties. From these points of view, the article concerns on studying the optical and structural properties of mixed alkali (Li and Na) ions in borate network former when samarium ions are embedded in the network as modifier. How the ratio of the alkali content effects on the physical parameters like density, molar volume, optical band gap, refractive index, etc. and knowing the role of samarium ions in such glasses is investigated.

2. Experimental details

2.1. Glass synthesis

The mixed alkali oxide borate glasses containing samarium oxide were prepared by conventional melt annealing technique. Table 1 shows the chemical nomial/composition in mol% of such glasses; $x Li_2O-(30-x)Na_2O-65B_2O_3-5Sm_2O_3$ where $x = 0$, 10, 20 and 30 mol%. The starting materials are lithium carbonate (Li_2CO_3), sodium

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Table 1
Denisty ρ and molar volume V_m data of lithium sodium borate glasses containing Sm_2O_3.

Glass symbol	xLi$_2$O [mol%]	Density ρ ± 0.002 [g/cm^3]	Molar volume V_m cm^3/mol
0 Li	0	2.876	28.262 ± 0.017
10 Li	10	3.883	20.106 ± 0.009
20 Li	20	4.315	17.349 ± 0.007
30 Li	30	3.45	20.757 ± 0.010

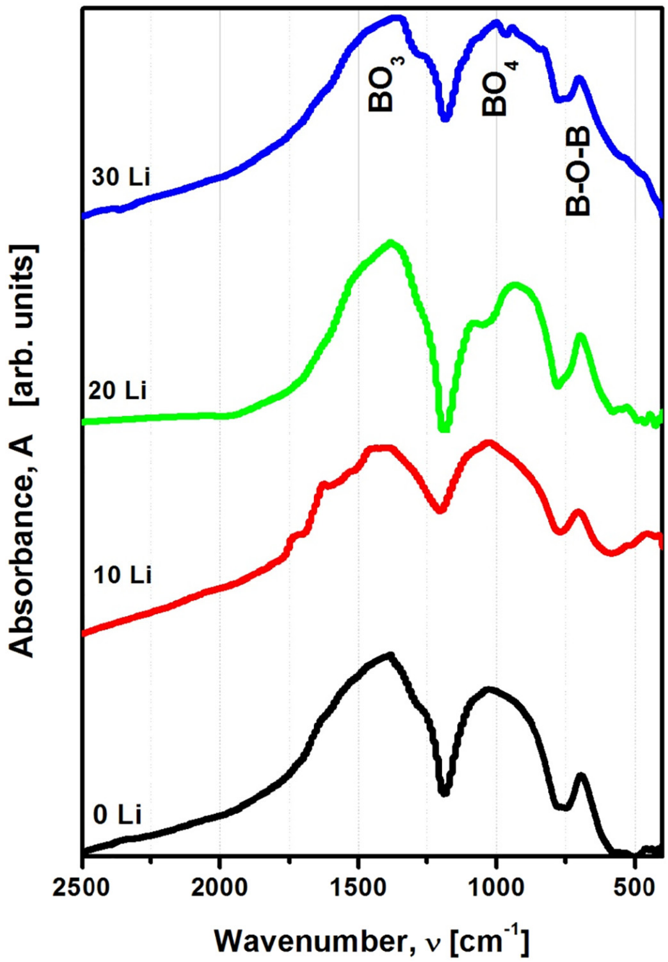

Fig. 1. Structural groups of lithium sodium borate glass containing samarium.

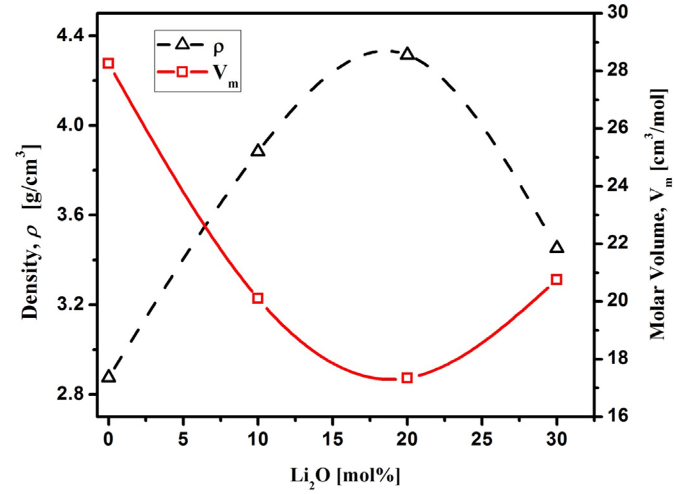

Fig. 2. Density and molar volume as function of lithium content ratio.

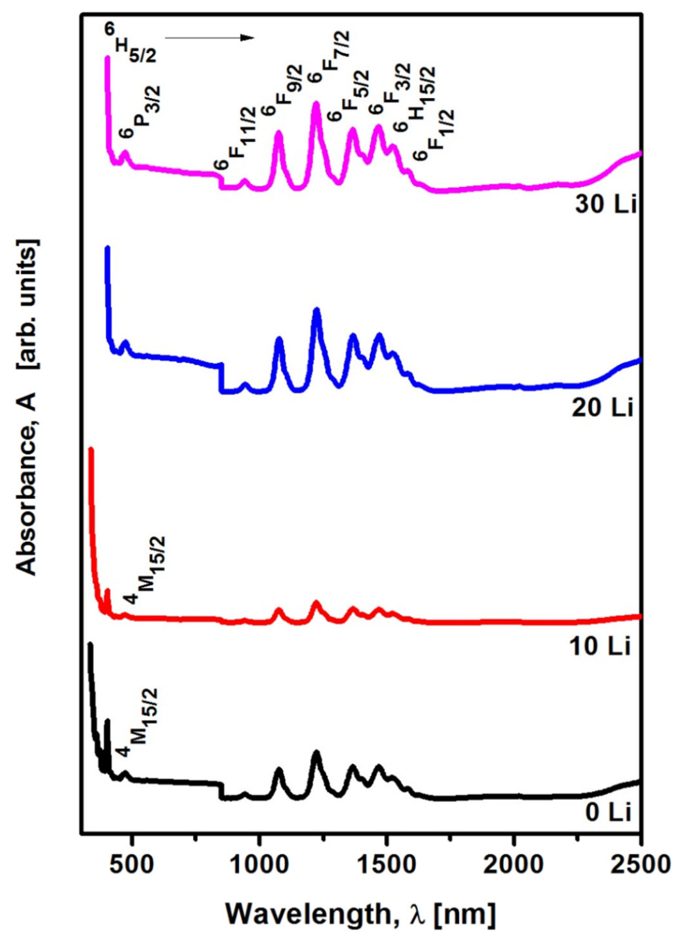

Fig. 3. Optical absorption spectra of Li_2O-Na_2O-B_2O_3-Sm_2O_3 glasses.

carbonate (Na_2CO_3), samarium oxide (Sm_2O_3) and orthoboric acid (H_3BO_3). Accurately weighed batches of 50 g were melted in an electrically heated furnace in porcelain crucibles for 2 h in the temperature range 1100–1250 °C depending on the glass composition. Samples were rotated and shacked thoroughly at fixed time intervals (every 30 min) to ensure homogeneity and to remove air bubbles. The molten glasses were poured on preheated stainless steel mold of required dimensions transferred immediately to annealing muffle at 350 °C for 1 h which was turned off and kept to cool gradually to room temperature with rate of 30 °C/h.

2.2. Fourier transform infrared absorption measurements

The infrared absorption spectra of the prepared glasses were measured in the wavenumber range 4000–400 cm^{-1} by a Fourier transform infrared (FTIR) spectrometer type Nicolet i10. The prepared glasses were examined as pulverized powders mixed with KBr with ratio 1:100 mg, respectively. The weighted mixtures were then subjected to a pressure 5 tons/cm^2 to produce clear homogeneous discs.

2.3. Density measurements

The density of the glass was measured using the Archimedes technique. The measurements were done by a digital balance and the known stable liquid density such as toluene (0.87 g/cm^3). The density is calculated from the expression: