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Synthesis and characterization of lithium niobium borate glasses containing neodymium

W.H.A. Kamaruddin[1], M.S. Rohani[1,*], M.R. Sahar[1], LIU Hong[2], SANG Yuanhua[2]

(1. AOMRG Lab, Physics Department, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia; 2. State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China)

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Abstract: A series of (90–x)$Li_2B_4O_7$-10Nb_2O_5-$x$$Nd_2O_3$ glass samples (x=0, 5 mol.%, 10 mol.%, 15 mol.%, 20 mol.% and 25 mol.%) were synthesized using melt quenching technique. X-ray diffraction (XRD), differential thermal analyzer (DTA), Fourier transformed infrared (FTIR), ultraviolet-visible-near-infrared (UV-Vis-NIR) spectrometer and photoluminescence (PL) spectroscopic characterizations were made to examine the influence of Nd^{3+} concentration on the physical, structural and optical properties. Various physical properties such as glasses density, molar volume, thermal stability, ion concentration, polar on radius, inter-nuclear distance, field strength, cut-off wavelength, energy band gap and Urbach energy were calculated. The samples were amorphous in nature and confirmed from XRD pattern. The FTIR spectra revealed the presence of BO_3 and BO_4 functional groups. UV-Vis-NIR spectra exhibited nine prominent bands centered at 353, 430, 475, 524, 583, 681, 745, 803, 875 nm corresponding to the transitions from the ground state to $^4D_{3/2}$, $^2P_{1/2}$, $^2G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$ excited states, respectively. Moreover, the emission spectra at 355 nm excitation displayed three peaks centered at 903 nm ($^4F_{3/2}\rightarrow{}^4I_{9/2}$), 1059 nm ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) and 1333 nm ($^4F_{3/2}\rightarrow{}^4I_{13/2}$), respectively. Fluorescence lifetime was recorded between 53.69 to 28.43 μs. It was found that varying concentration of Nd^{3+} ions strongly affected the physical, structural and optical properties of the glass samples.

Keywords: borate glass; neodymium; optical properties; band gap; luminescence; rare earths

Glass is generally composed of different oxides playing different roles especially in science and industry. Usually, glasses are made to be transparent in the visible spectrum and essential for optical materials. The major glass forming oxides such as B_2O_3, P_2O_5, SiO_2, GeO_3 and GeO_2 are capable to form glassy network by itself. It is the most crucial component in glass and each glass has one or more component acting as primary source of structure[1].

Borate is one of the foremost glasses former. It tends to be lenient to form a binary glass system by combining with many oxides[2,3]. In comparison with other conventional glasses, borate glass is most recently analyzed due to the superior properties such as optical and mechanical, chemical durability, stable against atmospheric moisture, good solubility of rare earth (RE) ions, low melting temperature and good corrosion resistance[4]. Moreover, borate glasses are suitable host for various transition metals and rare earths.

To date, plentiful attempts have been performed to enhance the values of the borate glass. By addition of alkali oxides, it can modify coordination geometry of boron from BO_3 to BO_4[5]. As a modifier, lithium which is more electropositive will cause essential changes in binary lithium borate glass system such as enhancing the bonding strength by forming ionic bonds with oxygen (non-bridging oxygen) and decreasing the hygroscopic nature of borate[6]. Lithium borate is one of the most useful nonlinear optical materials for ultraviolet and visible laser applications. Laser systems that incorporate lithium borate as a key component in their designs are widely used in applications such as ophthalmology, materials processing, marking, optical data storage and semiconductor processing. Several transition metals such as Nb, V, Ti, Cr, etc., are used as a second modifier to alter the glass structures, to create non-bridging oxygen's (NBO), to improve bond strength and to minimize the stickiness of the glass[7]. The creation of NBO alters the chemical and physical properties of the glasses. However, the alterations are still relying on their connectivity which changed these properties.

Glasses containing RE ions have been investigated intensively for fabricating lasers and amplifiers[8]. RE ions are used to probe the local structural alterations in the glasses host due to their unique spectroscopic properties subsequently from the optical transitions in the intra 4f shell[9]. Since the demonstration of laser action in neodymium single crystal made by Krupke[10], Nd^{3+} has been

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* **Corresponding author:** M.S. Rohani (**E-mail:** mdsupar@utm.my; **Tel.:** +60-07-553-4074)

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extensively used as a laser active ion in amorphous and crystalline state[11]. The result shows that by adding Nd_2O_3 into the glass system, it is predictable to produce efficient upconversion, fluorescence or luminescence, with potential use for solid-state lasers[12–17]. It can cause significant differences in lasing characteristics through changes in physical processes such as radiative transition strength, radiation less decay probabilities, excited-state absorption, and cross relaxation quenching[9]. It can operate as either a pulsed or continuous-wave laser with a sharp emission line. When doped in glass, usually it lases at wavelengths ranging from 1.054 to 1.056 μm, but it depends on the type of glass used. Nd can be doped to very high concentration in glass and leads to increased collision decay, resulting in a reduced upper laser level lifetime. The optical quality can be excellent, and beam angles approaching the diffraction limit can be achieved. As compared to crystal, Nd:glass laser gain media can be produced in very large size that is capable for high-energy applications. It can be cut into slabs, fibers as well as rods. In advanced laser technology of high power laser system, Nd:glass amplifier chains are capable to deliver up to 2.6 kJ of laser energy in long pulses (nanosecond duration) and up to 1 PW (10^{15} W) peak power in a short pulse (500 fs duration) at 1053 nm[9]. The great prospect of lithium niobium borate containing neodymium in laser field, motivated us to investigate the role of Nd^{3+} in the physical, structural and optical properties of the glasses with different concentrations of neodymium oxide.

1 Experimental

1.1 Sample preparation

Glasses with chemical compositions in mol.% $(90–x)Li_2B_4O_7$-$10Nb_2O_5$-xNd_2O_3, where x=0, 5, 10, 15, 20 and 25, defined as LNB (pure glass), 5NdLNB, 10NdLNB, 15NdLNB, 20NdLNB, and 25NdLNB respectively were prepared by melt-quenching technique. Batches of 20 g were prepared from certified reagent grades of $Li_2B_4O_7$ (98% purity), Nb_2O_5 (97%), and Nd_2O_3 (99.9%). The chemicals were mixed thoroughly in a ball mill for 3 h before being heated in a platinum crucible at 1150 ºC for 1 h. After the batch was completely melted, the melts was cast onto the preheated stainless steel plate followed by annealing at 330 ºC for 5 h before allowed to cool down to room temperature. The prepared samples were then ground and polished until the appropriate thickness was achieved. The thickness of glass samples used for optical studies was around 1.1–1.5 mm.

1.2 Characterization

The density (ρ) and molar volume (V_M) of glasses are important parameters to study since slight change in glass structure immediately change the density. Based on the Archimedes principle, the densities of the prepared samples were measured with distilled water as the immersion liquid. All weight measurements were made using a digital balance with a Precisa Model XT 220A. Density measurements were repeated three times per glass samples to get an accurate value. The concentration of the lanthanide ions is a very essential parameter because it influences the laser gain of the host material. The number density N of the laser active ions, i.e., the number of ions per cubic centimeter can be evaluated using the relation as given by[18]:

$$N\left(\frac{\text{ions}}{\text{cm}^3}\right)=\frac{x\rho N_A}{M} \tag{1}$$

where ρ is the density of the glass, N_A is the Avogadro's number, x is the mole fraction of rare earth oxide and M is the average molecular weight of the glass. Some other physical properties such as molar volume (V_m), polar on radius (r_p), inter-nuclear distance (r_i) and the field strength (F) of the rare-earth ions are identified by using following equations:

$$V_m=\Sigma M/\rho \tag{2}$$

$$r_p=\left(\frac{1}{2}\right)\left[\frac{\pi}{6N}\right]^{\frac{1}{3}} \tag{3}$$

$$r_i=\left(\frac{1}{N}\right)^{\frac{1}{3}} \tag{4}$$

$$F=\left(\frac{Z}{r_p^2}\right) \tag{5}$$

where Z is molecular mass of dopant.

The amorphous nature of samples were confirmed using Bruker D8 advance diffractometer attached with diffraction software analysis using Cu Kα radiation (λ=0.154 nm) at 40 kV and 30 mA, with 2θ varying from 20º to 70º, in steps of 0.0216º and 0.2 s counting time per step.

The glassy nature of the as-quenched samples were established by using PerkinElmer, Pyris Diamond diffractometer fitted with copper target and nickel filter, operated at 40 kV and 30 mA. A uniform heating rate of 15 ºC/min was implemented in the temperature range of 300–1000 ºC. All samples were subjected to DTA and the average value of the glass transition (T_g) and crystallization temperatures (T_c) were determined.

IR analysis was carried out to confirm the presence of functional groups and their vibration modes in the glasses samples. FTIR was recorded in 400–4000 cm^{-1} using Perk in Elmer Spectrum GX spectrometer. The FTIR samples were prepared in the form of thin pellets by grinding each sample with potassium bromide (KBr). The mixture was then pressed with a pressure of ~120 MPa to obtain a pellet with approximate thickness and diameter of 2.0 and 10.0 mm, respectively.