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Structural and optical properties of lithium tetraborate glasses containing chromium and neodymium oxide

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ABSTRACT

Lithium tetraborate glass samples containing Chromium and Neodymium were prepared. The density, molar volume, Oxygen packing density and N_4 indicate the glass samples containing 0.25 and 0.75 mol% Nd_2O_3 have the opening glass structure. From the absorption spectra of glass samples the Judd-Ofelt theory has been applied to the measured oscillator strengths and determines the three phenomenological intensity parameters Ω_2, Ω_4 and Ω_6 for glass. Chromium and Neodymium addition a gradual conversion of chromium ions from Cr^{6+} ion to Cr^{3+} ion acts as modifiers breaking up local symmetry and introduces coordinated bond defects in these glasses, which effect on the environment around the Nd^{3+} ions. The large Ω_2 value suggests a lower symmetric coordination around the Nd^{3+} and they attract Nd^{3+} cations to form various B—O—Nd bonds. The deviation parameters δ_{rms}, was determined. The hypersensitive transition, found to be $^4f_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$.

1. Introduction

Glasses are mostly one of optical materials created to be transparent in the visible region. Most kinds of glass system are prepared by the mixture of formers or intermediate oxides with other modifier oxides [1].

The physical and structural properties of zinc lithium sodium borate glass containing chromium oxide have been investigated [2]. The infrared spectra of the glasses showed the presence of BO_3 and BO_4 vibration groups in the glass system. The optical absorption data such as optical band gap and Urbach energy were determined and affected with the change chromium ions from Cr^{6+} to Cr^{3+}.

Lead tellurite borate glass samples containing neodymium were prepared [3]. Judd–Ofelt (JO) analysis based on UV–visible absorption spectra was performed to calculate the JO parameters ($\Omega = 2, 4, 6$). The observed trend is $2 > 6 > 4$. The large value of Ω_2 indicates the presence of covalent bonding between the Nd^{3+} ions and the surrounding glass network.

Different content from Neodymium oxide doped Lead bismuth borate glasses have been studied [4,5] using FTIR, DTA and UV/VIS spectrometer. Therefore the glass sample containing 2 mol% of Nd_2O_3 has the higher covalence of the Nd—O bond. Judd–Ofelt theory has been applied to determine the three intensity parameters Ω_2, Ω_4 and Ω_6 for glass. It was observed that the deviation parameters, δrms, was found to be 0.56:0.58 ($\times 10^{-6}$).

Glasses containing transition metals, e.g. Cr, are active laser media, especially for solid-state lasers based on the Cr^{3+} ions, localized in the low-field sites of the glass network [6–10]. Glasses containing rare earth are a subject of attention due to their many applications as laser materials, energy concentrators and luminescent materials [11,12]. Neodymium is the most widely studied in a variety of host glasses in which laser action has been observed, many studies have been made in evaluating the effects of these glass network materials on the Nd^{3+} laser ion [13].

In the present work we studied the effect of adding different concentration of neodymium and chromium oxides in lithium borate glass on the structural groups, glass forming ability and density of glass samples using different techniques such as XRD, DTA, IR and optical absorption measurements.

2. Experimental work

A glass with the molar composition 99 $Li_2B_4O_7$ – (1-x) Cr_2O_3 –x Nd_2O_3 mol% (where x = 0, 0.25, 0.50, 0.75 and 1 mol%) was prepared by melt-quenching. This component enables the formation of a transparent glass suitable for optical applications. The mixture was melted at 1100 °C for 2 h. The molten glass is poured between two

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copper plates. The differential thermal analysis (DTA) was carried out by using (SHIMADZU DTA −50 ANALYZER) on finally powdered glass samples. This was carried out with heating rate 30 °C/min in the temperature range of 20–1000 °C, using Al_2O_3 as reference. X-Ray diffraction analysis was carried out for the prepared glass samples using Philips analytical X-Ray diffraction system to characterize the amorphous nature. X-ray unit was kept constant at 40 KV with a current of 30 mA. The FTIR absorption spectra of the prepared samples were measured at room temperature in the range 2000–400 cm^{-1} by an infrared spectrometer (type JASCO FT/IR-4100) using the KBr disc technique. The samples were pulverized into fine powder, and then mixed with potassium bromide. The IR absorption spectra were measured immediately after preparing the discs. The optical absorption spectra were measured in the range from 190 to 2500 nm using a computerized recording spectrophotometer (type JASCO, V-570).

The density of glasses was determined by the Archimedes method in which glass sample was weighed three times in the air and when immersed in toluene at 25 °C. The density was calculated from the formula

$$\rho = [Wa/(Wa-Wb)]\ 0.8635$$

where ρ is the density of the glass sample, Wa is the weight of the glass sample in air, Wb is the weight of the glass sample in toluene and 0.8635 is the density of toluene.

The morphology, purity and the homogeneity of the glass samples are analyzed by scanning electron microscopy SEM Model Quanta 250 FEG (Field Emission Gun). Chemical purity in terms of elemental traces is detected using EDX Unit (Energy Dispersive X-ray Analysis), with accelerating voltage 30 K V, magnification 14× up to 100,0000 and resolution for Gun. 1n.

3. Results and discussion

Fig. 1 shows the DTA curves of the $99Li_2B_4O_7$ – (1-x) Cr_2O_3-xNd_2O_3 glass samples. From Fig. 1, the values of Tg, Tc and Tm determined and tabulated in Table 1.

From Fig. 1, it can be shown the glass samples exhibit an endothermic peak due to the glass transition temperature T_g. At still higher temperatures an exothermic peak due to the crystallization temperature, Tc, and followed by an endothermic peak due to their melting of the glass T_m. the values T_g, T_c and T_m which used to calculate the glass forming ability (Hruby's) parameters $K_{gl} = (T_c-T_g)/(T_m-T_c)$, which give the information about the stability of the glasses against nucleation and crystallization [14–16]. Hruby's parameters were evaluated and presented in Table 1.

Table 1
The values of Tg, T_c and T_o^m DTA of the ($Li_2B_4O_7$ −Nd_2O_3-Cr_2O_3) glass samples.

(mol%)		Tg (°C)	Tc (°C)	Tm (°C)	Kg1
Nd	Cr				
0.00	1.00	518	648	878	0.57
0.25	0.75	514	673	871	0.8
0.50	0.5	516	669	864	0.78
0.75	0.25	519	660	864	0.69
1.00	0.00	521	674	850	0.87

Glass transition temperature is very important indication of the change of glass structure. Many factors such as the density of covalent cross linking, the oxygen density of the network and the number and strength of the crosslink between oxygen and the cation changed the glass structure; hence the change of Glass transition temperature.

In the present work, the glass composition containing a constant number of oxygen atoms, then the glass transition temperature Tg depends on and related to the density of covalent cross-linking, strength of the cross-links between oxygen and the cation and not depends on the oxygen density of the network. Also the value of Tg affected by the concentration of BO_4 and BO_3 [5] and from Table 1 it can be observed that the value of Tg increase with the increase the Nd concentration that may be due to the glass structure have more NBOs. From Table 1 can be shown that the glass with 1 mol% Nd have high glass stability. The large values of T_g of the samples are advantageous because it involves a high resistance to crystallization and high thermal stability, which is a principal for applications in optical communication systems and optoelectronic applications.

Fig. 2 shows the XRD for the prepared glass samples. From Fig. 2, it can be observed that no diffraction peaks exposed the absence of atomic lattice in the glass network. From it can be observed that the all samples in glassy amorphous nature.

Fig. 3 illustrates the scanning electron microscope (SEM) images of Cr^{3+} and Nd^{3+} doped lithium tetraborate glass samples and the percentages of the elements present in the studied glass samples obtained using the Energy Dispersive X-ray spectra (EDS). The morphologies of these glass samples do not show any grains, confirming the amorphous nature of the glass sample. This

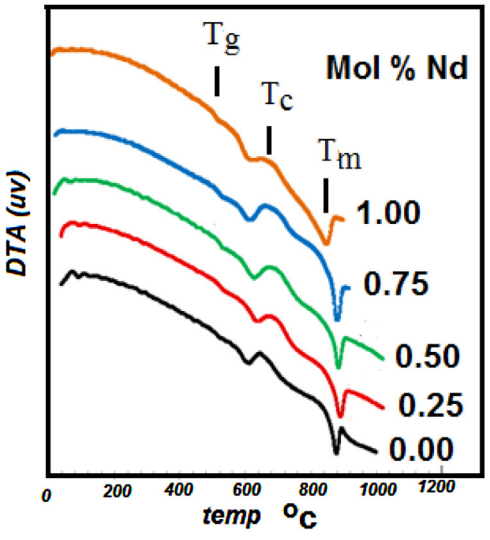

Fig. 1. The DTA curves of the $90Li_2B_4O_7$ - (1-x) Cr_2O_3-xNd_2O_3 glass as prepared samples.

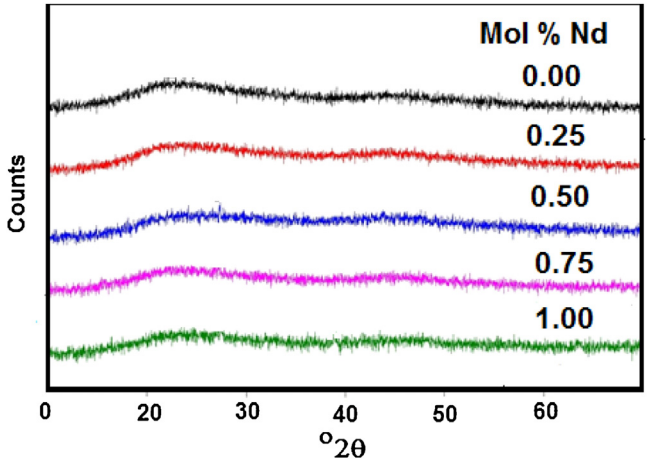

Fig. 2. The XRD for the prepared glass samples.