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Optical and spectroscopic properties of neodymium doped cadmium-sodium borate glasses

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ABSTRACT

Neodymium doped cadmium sodium borate glasses having composition $xCdO$-$(40-x)$ Na_2CO_3-$59.5H_3BO_3$-$0.5Nd_2O_3$; $x = 10$, 20 and 30 mol% were prepared by conventional melt-quenching technique. X-ray diffraction studies confirmed the amorphous nature of the prepared glasses. Conventional methods were used to determine the physical properties such as density, molar volume, refractive index, and rare earth ion concentration. The Judd-Ofelt theory was applied on the optical absorption spectra of the glasses to evaluate the three phenomenological intensity parameters Ω_2, Ω_4 and Ω_6. The calculated intensity parameters were further used to predict the radiative transition probability (A), radiative lifetime (τ_R) and branching ratio (β_R) for the various fluorescent levels of Nd^{3+} ion in the prepared glass series. The effect of the compositional changes on the spectroscopic characteristics of Nd^{3+} ions have been studied and reported. The value of Ω_2 is found to decrease with the decrease in the sodium content and the corresponding increase in the cadmium content. This can be ascribed to the changes in the asymmetry of the ligand field at the rare earth ion site and the change in rare earth oxygen (RE-O) covalency. Florescence spectra has been used to determine the peak wavelength (λ_p), effective line widths ($\Delta\lambda_{eff}$) and stimulated emission cross-section (σ_p) for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ transitions of the Nd^{3+} ion. The reasonably higher values of branching ratios and stimulated emission cross-section for the prepared glasses points towards the efficacy of these glasses as laser host materials. However, the glass with more sodium content is found to show better lasing properties.

1. Introduction

Rare earth doped glasses are being widely studied for their applications in the field of solid state laser, sensors, laser amplifier in optical communication, display monitors, waveguide laser, infrared-excitable phosphors, acousto-optic modulators, planar waveguides and optical data storage [1–6]. These glasses can be fabricated easily in several forms and are found to act as stable laser host materials with high gain and optical quality and minimum beam divergence. The chemical composition of the glass used for rare earth doping plays a very crucial role as the spectroscopic and optical properties of RE ions are highly sensitive to symmetry and the local structure at the rare earth sites [7–9]. Among all rare earth ions, neodymium doped glass lasers are of extreme interest because of the high-energy, short pulses emitted by them. The 1.06 μm transition of Nd^{3+} is by far the most widely used for industrial lasers because of its efficient pumping by flash-lamps and other lasers and its ease of operation at ambient temperatures. By slight variation of the chemical composition, the spectroscopic properties of Nd^{3+} can be optimized so as to increase the energy storage and energy extraction ability [10–14].

Among oxides, borate glass has a wide variety of technological applications due to its special properties which include good rare-earth ion solubility, high transparency, low melting point and high thermal stability [15,16]. However, a borate glass without any modifier will have high phonon energy ($\sim$1300 cm^{-1}) which results in the possibility of non- radiative decay and hence reduction in the intensity of rare earth ion emissions [17]. Therefore, the addition of modifiers to borate glass is vital to improve its physical and spectroscopic properties. The addition of sodium oxide to borate changes the boron coordination which modifies its structural units and improves its physical and spectroscopic properties [18].

The structural and optical investigation of cadmium sodium borate glasses without Nd^{3+} doping was carried out in our previous work [19]. It was found that cadmium oxide plays a significant role

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in modifying the glass structure. It is also found to be a favorable candidate for optoelectronics, solar cells, photo-diodes and gas sensors, etc. [20,21].

As an extension to our previous work, a systematic study of Nd^{3+} doped cadmium-sodium borate glasses has been carried out presently. The combined effect of sodium oxide and cadmium oxide on the spectroscopic properties of Nd^{3+} doped borate glasses has been undertaken. It is worth mentioning that spectroscopic properties of Nd^{3+} doped cadmium-sodium borate glasses have not been reported so far.

2. Experimental

Appropriate amounts of Analar grade reagents of high purity (99.99%) of CdO, Na_2CO_3, H_3BO_3 and Nd_2O_3 were used in the present work to prepare the glass samples by the conventional melt quenching technique. The batch composition of the Nd^{3+} doped cadmium-sodium borate glasses are as follows:

CNB1: 10CdO-30Na_2CO_3-59.5H_3BO_3-0.5Nd_2O_3
CNB2: 20CdO-20Na_2CO_3-59.5H_3BO_3-0.5Nd_2O_3
CNB3: 30CdO-10Na_2CO_3-59.5H_3BO_3-0.5Nd_2O_3

About 10 g batch of each of the above composition was thoroughly ground in an agate mortar to attain homogeneity. The mixture was then heated in a platinum crucible using an electric furnace at a temperature of 450 °C for 2 h to ensure decarbonization of carbonates used. The temperature of the mixture was further raised to 1100 °C under normal atmospheric conditions and it was frequently stirred to obtain a bubble-free homogeneous melt. The melt was then quenched onto a preheated stainless steel mould and then annealed at 400 °C to room temperature to eliminate thermal and mechanical stress and obtain structural stability. The prepared glass samples were then ground and polished to make them appropriate for spectroscopic studies.

To check the amorphous nature of the prepared glass samples XRD patterns of the powdered glass samples were recorded using XRD-7000 Shimadzu X-ray diffractometer (Cu K_α, $\lambda = 1.504$ Å) at the scanning rate of 2°/min and 2θ was varied from 10° to 80°. By employing the Archimedes' principle, densities of the prepared samples were determined with benzene as the immersion liquid (buoyant), using the relation

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \quad (1)$$

where W_a is the weight of sample in air, W_b is the weight of sample in buoyant and ρ_b the density of buoyant. The refractive indices of the prepared glasses were measured ~ at 30 °C using an Abbe refractometer with mono-bromonaphthalene as an adhesive coating. Optical absorption spectra of the polished glasses were recorded using a UV–Vis Perkin Elmer Lambda 35 Spectrometer with an optical resolution of 0.5 nm, in the wavelength range 200–1100 nm at normal incidence. The fluorescence spectra of the prepared glasses were recorded using Perkin-Elmer Fluorescence LS-spectrometer, with a spectral resolution of 1 nm, at an excitation wavelength of 402 nm.

3. Results and discussion

3.1. Physical properties

The XRD pattern is found to exhibit a few broad diffused peaks rather than any sharp peaks which indicates the absence of any crystalline phase and hence points towards the long range structural disorder inside the prepared samples. This reflects the amorphous nature of the prepared glasses. As a representative case, the X-ray diffraction pattern of the CNB1 glass is shown in Fig. 1.

From the measured values of density (ρ) and refractive index (n), various other physical properties such as molar volume (V_m), rare earth ion concentration (N), polaron radius r_p (Å), inter nuclear distance r_i (Å) and dielectric constant (ε) were determined using standard formulae [22] and are presented in Table 1.

The density is considered to be a very important tool to detect the structural changes taking place inside the glass network with the change in composition of the glass. The variation in modifier ions can result in a corresponding change in geometrical configuration, coordination number, cross-link density and dimensions of the interstitial space of glass. The density for the present glass series is found to increase with the increase in concentration of CdO and a corresponding decrease in the concentration of Na_2O. The network formed by borate contains a large number of interstices and when the modifiers are added, they fill up these spaces, which results in an increase in density of the glass network. In the prepared glasses, there are two modifiers: sodium and cadmium, which can fill up these interstitial spaces. The density of cadmium element (8.65 gm cm^{-3}) is more than sodium element (0.97 gm cm^{-3}), therefore the replacement of Na_2O with CdO would result in an increase in density of the glass [23].

The pure boron oxide consists of trigonal boron atoms (BO_3). With the addition of modifiers to pure borate, the additional oxygen obtained by the oxide dissociation results in conversion of trigonal BO_3 units to tetrahedral BO_4 units [24]. These four coordinated BO_4 groups are more strongly bonded and are responsible for increase in connectivity of the glass network and hence an increase in density of glass. The increase in density with replacement of CdO by Na_2O in the present work, points towards the conversion of three coordinated boron (B_3) to four coordinated boron (B_4) with the increase in cadmium content. The non-bridging oxygens (NBO's) also decrease with increase in content of CdO, which results in a more compact structure and an increase in density of the glass. The molar volume, which indicates the spatial distribution of the oxygen in the glass network follows an opposite trend and is found to be maximum for glass with highest content of Na_2O *i.e.* CNB1 glass. The increase in content of CdO leads to compactness of the structure and hence a decrease in molar volume, due to the smaller cation size of cadmium in comparison to sodium.

3.2. Oscillator strengths and Judd-Ofelt parameters

Judd-Ofelt theory [25,26] is a semi-empirical method used for the systematic investigation and selection of rare earth doped crystals and glasses for specific purposes. With the help of this theory, the absorption spectrum of trivalent rare earth ions doped in dif-

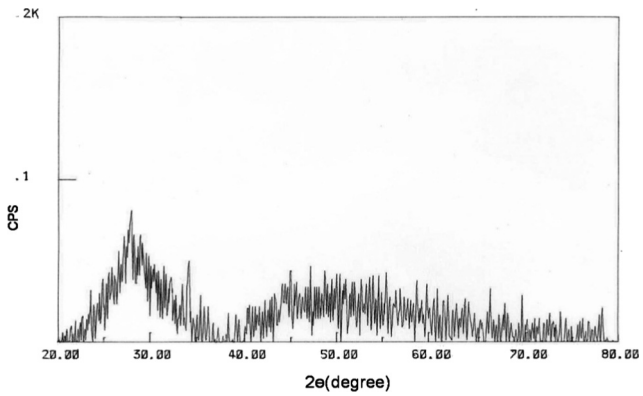

Fig. 1. X-ray diffraction spectra of CNB1 glass.