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Structural, optical absorption and luminescence properties of Nd^{3+} ions in NaO-NaF borate glasses

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ABSTRACT

Structural and spectroscopic properties of neodymium doped sodium borate and fluoroborate glasses of composition (in mol%) $(99 - X)\ B_2O_3 + X Na_2O + 1Nd_2O_3$, $X = 49.5$, 39.5 and 29.5 and $49.5B_2O_3 + X Na_2O + (49.5 - X)\ NaF + 1Nd_2O_3$, $X = 0$ and 24.75 have been investigated using XRD, FTIR, absorption and emission spectra and decay curve. The XRD of the glasses confirm their glassy nature and the FTIR spectra reveal the presence of BO_3 and BO_4 units along with the strong OH^- groups in the glasses. The UV–vis-NIR absorption spectra were used to calculate the bonding parameters ($\bar{\beta}$ and δ), to identify the ionic/covalent nature of the glasses. The spectral intensities have been calculated by using Judd–Ofelt analysis and inturn used to estimate radiative properties such as radiative transition probabilities, radiative lifetimes, branching ratios, peak stimulated emission cross-sections. Branching ratios and stimulated emission cross-sections show that the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of the glasses under investigation has the strong emission around 1060 nm. The decay from the $^4F_{3/2}$ level of Nd^{3+} ions is found to be single exponential. Multiphonon relaxation and quenching due to OH^- groups play a governing role in the luminescence quenching of $^4F_{3/2}$ level of Nd^{3+} ions in the titled glasses. The results obtained are compared with reports on similar glasses.

1. Introduction

Spectroscopic properties of rare earth (RE) elements in glasses have been widely studied for applications in laser technology and optical communications. Investigations on inorganic glasses revealed that the radiative properties of RE ions in glasses strongly depend on the host glass compositions and can be changed by changing the network forming and network modifying ions [1]. Laser action has been demonstrated for the first time in trivalent neodymium (Nd^{3+})-doped glasses by Snitzer [2], which in turn has made considerable progress in evaluating the effect of the amorphous host matrices on the Nd^{3+} ion. Most of the research has concentrated on the Nd^{3+} ions due to their efficient infrared $^4F_{3/2} \rightarrow {}^4I_{13/2,11/2,9/2}$ with emissions at wavelengths around 1350, 1064 and 946 nm which finds potential applications in the fields of laser and infrared optical communications [3–12].

Over the past several decades, lot of work has been reported on the luminescent properties of Nd^{3+} ions in a variety of glass matrices which includes phosphates [3–5], silicate [5,6], borates [7], sulphates [8], tellurites [9], chalocogenides [10], bismuth-borate [11], germanate [12] to mention a few. The luminescent properties of the Nd^{3+} ions can be considerably modified by suitably selecting the network forming and network modifying cations. Because of the influence of the modifier oxide, alkali borate glasses exhibit an abrupt change in property known as "borate anomaly" explained in terms of borons ability to exist in two distinct co-ordination states [13]. Addition of alkali oxide to boric oxide leads to the conversion of boron co-ordination from trigonal to tetragonal, and when the tetragonal reaches its maximum, the boroxyl group disappears and the formation of diborate starts. Chong et al. [14] reported that the mixed alkali borate glasses have structures that are similar to binary borate glasses. The present study reports the preparation and evaluation of structural and optical properties of Nd^{3+} ions in sodium borate and sodium fluoroborate glasses by measuring the XRD, FTIR, absorption, emission and fluorescence lifetime. Judd–Ofelt parameterization has been used to evaluate the radiative properties of the excited state of Nd^{3+} ions. Multiphonon relaxation is found to be the dominant factor for the observed discrepancy between the measured and evaluated lifetimes of the $^4F_{3/2}$ level in the studied glasses.

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2. Experimental

Table 1 presents the composition and labels of 1.0 mol% Nd^{3+}-doped sodium borate and sodium fluoroborate glasses of the present investigation. Conventional melt-quenching technique was employed to prepare transparent glasses using the reagent grade H_3BO_3, Na_2CO_3, NaF and Nd_2O_3 chemicals as starting materials. The stoichiometric compositions of these raw materials were mixed thoroughly in an agate mortar and melted in an electric furnace at 950 °C for 45 min using a porcelain crucible. The glasses were made by quenching the melts onto a brass plate. These glasses were sufficiently annealed at 350 °C temperature for 7 h and cooled slowly to release the thermal stress associated with these glasses during the quenching process.

The refractive index of the samples was determined with an Abbe refractometer using mono bromonaphthalene as the contact liquid. The density measurements were made employing Archimedes principle with xylene as the contact liquid. The physical properties of the prepared Nd^{3+}-doped glasses were presented in Table 1. The XRD spectra were recorded using JEOL 8530 X-ray diffractometer employing Cuk_{α} radiation and information about local structural units were explored using Perkin–Elmer Paragon 500 FTIR spectrometer at a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}. Optical absorption spectra of the polished samples were recorded at room temperature using Perkin–Elmer Lambda 35 UV–vis spectrometer in the range of 400–1100 nm with a spectral resolution of ±0.1 nm. Luminescence spectra were recorded using EG&G Princeton Applied Research model 5210 with a spectral resolution of ±.5 nm in the wavelength range of 900–1500 nm. The luminescence decay curves were carried out by exciting the samples with a 10 ns pulsed OPO pumped by a Q-switched Nd-YAG laser (EKSPLA NT342/3/UVE) and the signal from the extended PMT was acquired by a digital oscilloscope (LeCroy wavesurfer 424). All measurements were made at room temperature and were corrected by the spectral response of the equipments.

3. Results and discussion

3.1. XRD and FTIR spectra

The X-ray diffraction pattern (not shown) of the prepared glasses exhibits a broad scattering which represents a typical long range structural disorder and confirms the amorphous nature of the glasses. FTIR spectra of Nd^{3+}-doped sodium borate and sodium fluoroborate glasses were recorded, employing KBr pellet technique and are shown in Fig. 1 along with the band assignments (Table 2). As seen from the Fig. 1, the FTIR spectra of the Nd^{3+}-doped sodium borate and fluoroborate glasses consists of several peaks which are broad or moderate in bandwidth. The broad bands results from the highly degenerate vibrational states and thermal broadening of the lattice dispersion of the glass samples. The broad and strong band around 3500 cm^{-1} is attributed to the presence of O–H stretching vibration. The peaks around 2800 and 2900 cm^{-1} are due to the presence of hydrogen bonding [15,16]. The peak

Table 1
Glass composition and physical properties of Nd^{3+}-doped sodium borate and sodium fluoroborate glasses.

Glass composition	Label	Refractive index	Density, d (gm/ml)	Concentration, C (10^{20} ions/cc)	Optical path length (cm)
$49.5B_2O_3 - 49.5Na_2O - 1Nd_2O_3$	BNa5	1.625	2.62	2.605	0.522
$59.5B_2O_3 - 39.5Na_2O - 1Nd_2O_3$	BNa4	1.636	2.79	2.662	0.504
$69.5B_2O_3 - 29.5Na_2O - 1Nd_2O_3$	BNa3	1.645	2.87	2.896	0.492
$49.5B_2O_3 - 24.75Na_2O - 24.75NaF - 1Nd_2O_3$	BNa*Nf*	1.629	2.58	2.421	0.482
$49.5B_2O_3 - 49.5NaF - 1Nd_2O_3$	BN*f*5	1.618	2.63	2.893	0.518

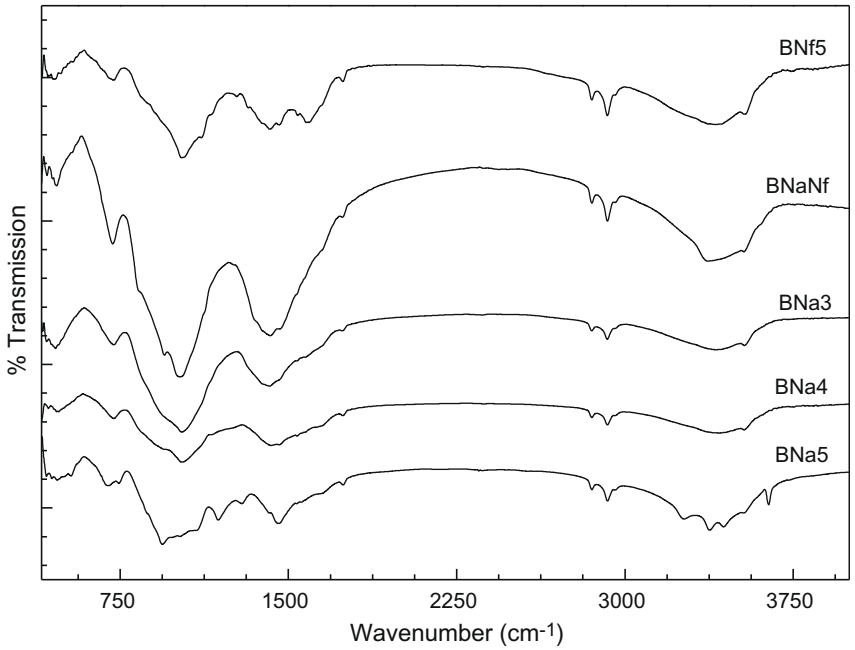

Fig. 1. FTIR spectra of Nd^{3+}-doped sodium borate and sodium fluoroborate glasses.