Solid State Sciences 11 (2009) 2093–2098

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Optical absorption and near infrared emission properties of Nd^{3+} ions in alkali lead tellurofluoroborate glasses

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ARTICLE INFO

Article history:
Received 18 June 2009
Received in revised form
27 August 2009
Accepted 31 August 2009
Available online 6 September 2009

Keywords:
Glasses
J–O theory
Quality factor
Branching ratios
Fluorescence

ABSTRACT

Nd^{3+} doped H_3BO_3–PbO–TeO_2–RF (R = Li, Na and K) glasses were prepared through melt quenching technique. Optical absorption and near infrared (NIR) fluorescence spectra were recorded at room temperature. The spectral intensities were analyzed in terms of the Judd–Ofelt (J–O) parameters ($\Omega_\lambda = 2, 4, 6$). The covalency effect of Nd–O bond on the J–O parameters was estimated from the relative absorbance ratio (R) between ${}^4I_{9/2} \rightarrow {}^4F_{7/2}$ and ${}^4I_{9/2} \rightarrow {}^4S_{3/2}$ transitions. The effect of Nd–O covalency on the Ω_4 and Ω_6 intensity parameters as well as on the spontaneous emission probabilities (A_R) was discussed. Lomheim and Shazer hybrid method was applied to determine the fluorescence branching ratios (β_R) of each emission transition from the ${}^4F_{3/2}$ metastable level to its lower lying levels. The evaluated total radiative transition probabilities (A_T), stimulated emission cross-sections (σ_e) and gain bandwidth parameters ($\sigma_e \times \Delta\lambda_P$) were compared with the earlier reports.

1. Introduction

Glasses doped with rare earth (RE) ions have been used for functional photonic devices such as optical fiber amplifiers, fiber lasers, wavelength converting devices, planar waveguides and compact microchip lasers [1]. Electronic transitions between $4f^n$ levels in RE ions play important role in these applications. The spectral properties of RE ions can be monitored through the development of novel host glass materials. But the development of new glass-based optical devices requires a better understanding of inter-ionic interactions which are deeply involved in the fundamental feature of RE ions [2,3]. In general, the RE elements usually exist in the trivalent state and the characteristic sharp absorption and emission lines are due to the shielding of 4f electrons by the 5s outer shells. The absorption spectra of RE ions in glasses differ from those of crystals in the broadening of the bands. This inhomogeneous broadening is due to multiple RE ion sites in glasses.

Though different spectroscopic characterizations have been significantly studied by the alteration of compositions to improve the performance of laser hosts, still there is a great demand for novel host materials with high gain coefficient. Among the oxide glasses, tellurite and heavy metal oxide glasses catch much attention in recent years due to their low phonon energy [4,5]. Though borate glasses are suitable for optical device applications because of their high transparency, low melting point, high thermal stability and good RE ions solubility, but there is less importance in these glasses due to their high phonon energy [6]. Moreover, the addition of B_2O_3 improves the inhomogeneous broadening of absorption as well as emission bands [7]. Also, addition of alkali fluorides like LiF, NaF and KF prevents the glasses from moisture when compared to the alkali oxides and iodides [8]. In recent years, the RE doped tellurite glasses have been the subject of several spectroscopic investigations, due to their potential applications in different fields like optical sensing, telecommunications, biomedical, and biochemical studies etc. [9–11]. A lot of work has been carried out over the past several years on the spectral analysis of Nd^{3+} ions in a variety of glassy matrices including borate [12], tellurite [13], phosphate [14] and leadfluoroborate [15]. The suitability of Nd^{3+} ion in emitting strong near infrared fluorescence makes it a best possible candidate for high-power laser applications [2,16]. The photoluminescence properties of Nd^{3+} ions can be tailored over a considerable extent by the suitable selection of network formers

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doi:10.1016/j.solidstatesciences.2009.08.023

and network modifiers such as K or Ba [17]. Tanabe et al. [18] investigated the optical properties of Nd^{3+}- doped phosphate glasses with various alkali and alkaline earth ions as network modifiers.

Judd–Ofelt (J–O) theory [19,20] is only the powerful theoretical model that is available to analyze the absorption spectral intensities of forced electric dipole transitions of different RE^{3+} ions in various laser host materials. The so-called J–O intensity parameters Ω_λ ($\lambda = 2$, 4, 6) can be determined experimentally from the measurements of absorption spectra and refractive index. From these parameters several important luminescence parameters like spontaneous emission probabilities (A_R), fluorescence branching ratios (β_R), radiative lifetimes (τ_R) and stimulated emission cross-sections (σ_e) can be evaluated. The aim of the present work is to investigate the effect of chemical composition on the fluorescence intensity, spontaneous emission probabilities, stimulated emission cross-sections and band width parameters and also to know the potential lasing action of the three NIR emission transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}, {}^4I_{11/2}$, and $^4I_{13/2}$ of the Nd^{3+} ions in H_3BO_3–PbO–TeO_2–RF glasses and to compare them with those of the previously reported glass matrices.

2. Experimental

H_3BO_3–PbO–TeO_2–RF (R = Li, Na, K) glasses (here after called as RLTB glasses) were prepared according to conventional melt-quenching method. High purity H_3BO_3, PbO, TeO_2, LiF, NaF, KF and Nd_2O_3 were used as the starting materials. Compositions (in mol%) chosen in the present study were 43 $H_3BO_3 + 20$ PbO + 10 $TeO_2 + 26$ RF + 1 Nd_2O_3. 10 g of mixed batch chemicals were taken into platinum crucible and then melted at 1000 °C for about 1 h in an electric furnace. The melt was poured on a pre-heated brass plate and pressed by another brass plate. The samples were annealed for 6 h at 350 °C to remove the thermal strains. The densities of these glasses were obtained by Archimedes method with xylene as the immersion liquid. The refractive indices were measured with Abbe GE-138 refractometer at sodium wavelength using 1-bromonapthalene as contact liquid.

The absorption spectra were measured using Varian Cary 5E UV-VIS–NIR Spectrophotometer in the wavelength region 400–1000 nm. The NIR fluorescence spectra were performed by exciting the samples with 514.5 nm wavelength of Argon-ion laser. The luminescence signal from the sample was collected by a TRIAX 550 monochromator system with liquid N_2 cooled InGaAs photodetector. The signal collected was sent to SR 830 lock-in amplifier and subsequently recorded by a personal computer. All the optical measurements were performed at room temperature.

3. Theory

The absorptions bands observed in the absorption spectra of lanthanides are due to intra-configurational *f-f* transitions. The majority of the transitions are induced electric dipole transitions. However, a few transitions are magnetic dipole in nature and their contribution is not significant. The intensities of the absorption bands are expressed in terms of measured oscillator strengths (f_m) and can be evaluated by the area method using the formula [21,22]

$$f_m = 4.32 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \tag{1}$$

where $\varepsilon(\nu)$ is the molar absorptivity at energy ν (cm^{-1}) and can be obtained using Beer–Lambert's law. According the J–O theory [19,20], the oscillator strength of an absorption band is given by

$$f_c(\psi J, \psi' J') = \frac{8\pi^2 m c \nu}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n} S_{ed} + n S_{md}\right] \tag{2}$$

where m is the electron mass, c is the speed of light, h is the Plank's constant, $(2J+1)$ is the degeneracy of the ground state (i.e. 10 for Nd^{3+}). The factor $(n^2+2)^2/9n$ is the Lorentz local field correction for a dielectric medium of refractive index n. S_{ed} and S_{md} are the electric and magnetic dipole linestrengths respectively. They can be calculated from the formulae [21]

$$S_{ed} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \left\langle \psi J \| U^\lambda \| \psi' J' \right\rangle \right|^2 \tag{3}$$

$$S_{md} = \frac{e^2 h^2}{16\pi^2 m^2 c^2} \left| \langle \psi J \| L + 2S \| \psi' J' \rangle \right|^2 \tag{4}$$

where Ω_λ ($\lambda = 2,4,6$) are the J–O intensity parameters that are determined by standard least-square fitting method and $\langle \psi J \| U^\lambda \| \psi' J' \rangle$are the reduced matrix elements of the unit tensor operators obtained from the Carnall et al. [23]. The J–O intensity parameters can be used to determine several radiative properties of the lanthanide ions. The spontaneous emission probability or the Einstein coefficient for spontaneous emission from ψJ excited level to $\psi' J'$ lower lying levels is given by

$$A_R(\psi J, \psi' J') = \frac{64\pi^4 \nu^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md}\right] \tag{5}$$

Since an excited state ψJ is relaxed to several lower lying states $\psi' J'$, the total radiative transition probability A_T is defined as

$$A_T(\psi J) = \sum_{\psi' J'} A_R(\psi J, \psi' J') \tag{6}$$

The radiative branching ratio is given by

$$\beta_R(\psi J, \psi' J') = \frac{A_R(\psi J, \psi' J')}{A_T(\psi J)} \tag{7}$$

These branching ratios can be used to predict the relative intensities of all emission lines originated from a given excited state. The measured branching ratios (β_m) can be found from the relative areas of the emission lines. All emission probabilities that depopulate an initial emission level $^{2S+1}L_J$ have been calculated in terms of radiative lifetimes (τ_R) by the following equation and it can be used to estimate how fast that level is depopulated. Stronger emission probabilities and more transitions from a level lead to faster decay and shorter lifetimes.

$$\tau_R(\psi J) = \frac{1}{A_T(\psi J)} \tag{8}$$

4. Results and discussion

4.1. Judd–Ofelt analysis

Room temperature optical absorption spectra of Nd^{3+} ions in RLTB glasses along with the assignments of the absorption bands are shown in Fig. 1. In the case of trivalent neodymium, the absorption takes place from the $^4I_{9/2}$ ground state to various excited states which are predominantly *4f-4f* induced electric dipole in nature. For Nd^{3+} ion, $^4I_{9/2} \rightarrow {}^4F_{9/2}$ transition is a magnetic dipole in character and its contribution is not significant [23]. Typically thirteen absorption bands are observed lying between 400–1000 nm in all three glass samples. The assignment of the