

# Judd–Ofelt theory: optical absorption and NIR emission spectral studies of $\text{Nd}^{3+}:\text{CdO–Bi}_2\text{O}_3\text{–B}_2\text{O}_3$ glasses for laser applications

C. Nageswara Raju · C. Adinarayana Reddy ·  
S. Sailaja · Hyo Jin Seo · B. Sudhakar Reddy

Received: 6 July 2011 / Accepted: 4 August 2011 / Published online: 17 August 2011  
© Springer Science+Business Media, LLC 2011

**Abstract** This article reports on the optical absorption and NIR emission properties of  $\text{Nd}^{3+}$  ions doped  $\text{CdO–Bi}_2\text{O}_3\text{–B}_2\text{O}_3$  (CdBiB) glasses. Judd–Ofelt theory has been applied to calculate the oscillatory strengths of the transitions in the absorption spectra and also the intensity parameters  $\Omega_\lambda$  ( $\lambda = 2, 4, \text{ and } 6$ ). These results were then used to compute the radiative properties of emission transitions of  $\text{Nd}^{3+}:\text{CdBiB}$  glasses. From the NIR emission spectra of  $\text{Nd}^{3+}:\text{CdBiB}$  glasses, three NIR emission bands are observed at 900, 1069, and 1338 nm and assigned to the transitions ( ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ ), ( ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ ), and ( ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ ), respectively. The concentration quenching phenomenon has also been explained. The stimulated emission cross-section and FWHM values were calculated for all the  $\text{Nd}^{3+}:\text{CdBiB}$  glasses.

## Introduction

Recently, research on bismuth borate glasses is of great immense because of their applications as optical fiber amplifiers, optoelectronics and magneto optical devices, laser materials, thermal and mechanical sensors, electro-optic switches, solid state laser materials, photonic switches, reflecting windows, layers for optical and electronic devices, glass ceramics and these bismuth borate glasses are also having the important properties such as high refractive index,

extensive glass formation range, high physical and chemical stability, low melting temperature, long infrared cutoff and high third order nonlinear optical susceptibility, high density and high infrared transparency [1–4]. It is a known fact that  $\text{Bi}_2\text{O}_3$  could be found as a network modifier and it is not considered as the glass network former (NWF) because of the small field strength of  $\text{Bi}^{3+}$  ions, however, in combination with  $\text{B}_2\text{O}_3$  in a relatively large composition range, there is a possibility for the glass formation [5].  $\text{B}_2\text{O}_3$  is familiar as NWF and is present in almost all important commercial glasses. Thus,  $\text{Bi}_2\text{O}_3$  and  $\text{CdO}$  are considered as network modifiers when those are added to the  $\text{B}_2\text{O}_3$  content.

The advantages such as good solubility for rare earth ions, good mechanical and thermal stability, and the low cost of the glasses make them as the potential host materials for rare earth ions. Further, rare earth ions activated glasses with emission in the NIR region are of much interest because of their use as laser host materials and optical amplifiers for use in telecommunication devices. Among different  $\text{RE}^{3+}$  ions doped glasses, Neodymium doped glasses have been proven to be one of the most efficient candidates for photonic devices such as fiber lasers, microchip lasers, and planar wave guides [6, 7]. Neodymium ( $\text{Nd}^{3+}$ ) is used as an activator in different glass and crystal hosts because of its important application to develop high peak-power solid state lasers in the near infrared (NIR) region under laser diode excitation at 1.06  $\mu\text{m}$  [8].  $\text{Nd}^{3+}$  ions in different host lattices, such as glasses and crystals, gives all the possible emissions such as UV, red, blue, green, orange, and infrared (IR) emissions and can be used as the luminescent materials for different applications [9]. Recently, research has been focused in the near infrared spectral range from 800 to 1500 nm; where  $\text{Nd}^{3+}$  ions present emission at 900, 1069, and 1338 nm originating from the electronic transitions between the  $4f^n$

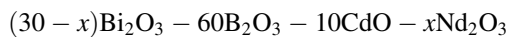
C. N. Raju · C. A. Reddy · S. Sailaja · B. S. Reddy (✉)  
Department of Physics, Sri Venkateswara Degree College,  
Kadapa 516003, India  
e-mail: drbsreddyphd@gmail.com

H. J. Seo  
Department of Physics, Pukyong National University,  
Busan 608-737, Republic of Korea

levels,  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ ,  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ ,  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ , respectively. As per our knowledge,  $Nd^{3+}$  ions doped bismuth borate glasses are less reported. In this article, we report the optical absorption and NIR emission spectral studies of  $Nd^{3+}$ :CdBiB glasses by the application of Judd–Ofelt theory to evaluate the J–O intensity parameters and radiative properties of the emission transitions.

**Experimental studies**

$Nd^{3+}$ :CdBiB glasses were prepared by the melt quenching method. The starting chemicals used were reagent grade of  $H_3BO_3$ ,  $Bi_2O_3$ ,  $CdO$ , and  $Nd_2O_3$ . The chemical compositions of the prepared glasses are as follows:



where

$$x = 0.5, 1.0, 1.5, \text{ and } 2.0 \text{ mol\%}$$

The starting chemicals were taken in an appropriate stoichiometric ratio and were finely powdered and then mixed thoroughly before each of batches (10 g) was melt by using alumina crucibles in an electric furnace at 950 °C, for an hour. These melts were quenched in between two brass plates and thus obtained 2–3 cm diameter optical glasses

with a uniform thickness 0.3 cm and these glasses were annealed at 200 °C for an hour in order to remove thermal strains.

0.5, 1.0, 1.5, and 2.0 mol% of  $Nd^{3+}$ :CdBiB glasses are labeled as Glass-A, Glass-B, Glass-C, and Glass-D, respectively.

Abbe’s refractometer was employed to measure the glass refractive indices with sodium vapor lamp (589.3 nm) and the values are presented in Table 1 The optical absorption spectra (400–2500 nm) were measured on a Cary 5E spectrometer. NIR photoluminescence spectra of the  $Nd^{3+}$ : CdBiB glasses were measured on a Horiba Triax-550 grating monochromator (Jobin–Yvon Horiba) equipped with a liquid nitrogen cooled InGaAs photo detector (Electro-Optical System Inc.) in the wavelength range of 800–2400 nm and a lockin-amplifier (SR830 DSP, standard Research systems) with an  $Ar^+$  laser (514.5 nm) (Lexel Model 85 Ion Laser, 5–200 mW) as the excitation source.

**Theory**

Nephelauxetic effect: bonding parameter

The nature of the R–O bond is known by the nephelauxetic ratios ( $\beta$ ) and the bonding parameters ( $\delta$ ) which are

**Table 1** Refractive index and Judd–Ofelt parameters of  $Nd^{3+}$ :CdBiB glasses

Absorption transition ${}^4I_{9/2} \rightarrow$	Wave length ( $\lambda$ )	Oscillator strengths ( $f \times 10^{-6}$ )							
		Glass-A		Glass-B		Glass-C		Glass-D	
		$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$
${}^4F_{3/2}$	879	2.56	2.61	2.73	2.82	2.96	2.93	3.31	3.52
$({}^4F_{5/2}, {}^2H_{9/2})$	797	7.48	7.53	8.20	8.37	9.65	9.81	9.92	10.23
$({}^4F_{7/2}, {}^4S_{3/2})$	748	7.03	7.11	8.31	8.05	8.74	8.86	9.21	9.67
$({}^4G_{5/2}, {}^2G_{7/2})$	585	18.32	18.49	19.17	19.52	20.63	20.78	21.03	21.27
$({}^4G_{7/2}, {}^4K_{13/2})$	527	5.63	5.72	5.98	6.03	6.13	6.27	7.73	7.92
${}^4G_{9/2}$	513	3.91	3.89	4.03	4.11	4.27	4.38	4.69	4.87
$\delta_{rms}$ (RMS deviation)		0.1275		0.2804		0.1780		0.3991	
Refractive index ( $n_d$ )		1.6506		1.6507		1.6507		1.6508	
$\bar{\beta}$ (Nephelauxetic ratio)		0.9904		0.9927		0.9908		0.9908	
$\delta$ (Bonding parameter)		0.0096		0.0073		0.0092		0.0092	
J–O parameters									
$\Omega_2 \times 10^{-20}$		4.893		4.672		4.569		4.248	
$\Omega_4 \times 10^{-20}$		2.976		3.213		3.475		3.406	
$\Omega_6 \times 10^{-20}$		5.786		6.010		6.137		6.096	
$\Omega_4/\Omega_6$		0.514		0.534		0.566		0.558	
Other glass systems		$\Omega_2 \times 10^{-20}$		$\Omega_4 \times 10^{-20}$		$\Omega_6 \times 10^{-20}$			
Germanate [22]		3.09		5.54		4.80			
TeO <sub>2</sub> –Nb <sub>2</sub> O <sub>5</sub> –Al <sub>2</sub> O <sub>3</sub> –Nd <sub>2</sub> O <sub>3</sub> [23]		3.12		4.84		3.28			
Phosphate [24]		3.6		5.0		5.5			

computed by using the following formulae [10]. The nephelauxetic ratio is given by

$$\beta = \nu_g/\nu_a$$

where  $\nu_g$  is the wavenumber (in  $\text{cm}^{-1}$ ) of a particular transition to an ion in the glass and  $\nu_a$  is the wavenumber (in  $\text{cm}^{-1}$ ) of the same transition for the aquo ion. The bonding parameter  $\delta$  is given by

$$\delta = \frac{1 - \bar{\beta}}{\bar{\beta}}$$

where  $\bar{\beta}$  is the average value of  $\beta$ .

The Judd–Ofelt theory

The optical absorption spectra of rare earth ions helped for understanding their radiative properties. The sharp absorption lines arising from the  $4f-4f$  electronic transitions can be electric dipole or magnetic dipole in character. The qualitative calculations of the intensities of these transitions have been developed independently by Judd [11] and Ofelt [12]. A brief outline of the Judd–Ofelt theory is given below.

The oscillatory strengths

The spectral intensities are expressed in terms of oscillator strengths. Experimentally, the oscillator strength could be calculated from the area of the absorption band under the Gaussian curve [13].

$$f_{\text{exp}} = (2303 \text{ mc}^2/N_A \pi e^2) \int \epsilon(\nu) \text{ d}\nu$$

where  $N_A$  is the Avogadro number and  $\epsilon(\nu)$  is the molar absorption coefficient. This equation reduces to

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int \epsilon(\nu) \text{ d}\nu$$

The molar absorption coefficient  $\epsilon(\nu)$  at a given energy is evaluated from the Beer–Lambert Law [13].

$$\epsilon(\nu) = \frac{1}{cl} \log \frac{I_0}{I}$$

where ‘ $c$ ’ is the concentration of lanthanide ion (mol%), ‘ $l$ ’ is the thickness of the glass (cm) and  $\log(I_0/I)$  is the absorptivity (A) or the optical density (OD). According to the J–O theory, an expression for the theoretical evaluation of the electric dipole oscillator strength is given by

$$f = \sum_{\lambda=2}^6 T_{\lambda} \nu \left( \psi_j \| U^{\lambda} \| \psi_j^1 \right)^2$$

in which the  $\|U^{\lambda}\|^2$  are unit tensor operators of the rank  $\lambda = 2, 4, \text{ and } 6$  and  $T_{\lambda}$  are the three J–O parameters which

can be evaluated from the experimental absorption spectra. A relationship has been established between the  $T_{\lambda}$ ,  $\Omega_{\lambda}$ , and  $n_d$  as shown below [14].

$$\Omega_{\lambda} = \frac{3h}{8\pi^2 mc} \left[ \frac{9n_d}{(n_d^2 + 2)^2} \right] (2J + 1) T_{\lambda}$$

For trivalent lanthanides ions, the oscillator strength ‘ $f$ ’ or allowed magnetic dipole (MD) and forbidden (induced) electric dipole (ED) transition is of the order of  $10^{-6}$ .

According to the J–O theory, the calculated oscillator strength of a transition of average frequency ( $\nu$ ) from a level ( $\psi_J$ ) to a level ( $\psi'_{J'}$ ) is

$$f_{\text{cal}}(\psi_J, \psi'_{J'}) = \frac{8\pi^2 m \nu}{3h(2J + 1)e^2} \left[ \frac{(n_d^2 + 2)^2}{9n_d} \right] S_{\text{ed}} + n_d^3 S_{\text{md}}$$

where  $n_d$  is the refractive index of the medium at the sodium D line,  $S_{\text{ed}}$  is the electric dipole line strength [15].

$$S_{\text{ed}} = e^2 \sum_2^6 \Omega_{\lambda} \left( \psi_J \| U^{\lambda} \| \psi'_{J'} \right)^2$$

$S_{\text{md}}$  is the line strength for the magnetic dipole transitions that could be obtained by the expression

$$S_{\text{md}}(\psi_J, \psi'_{J'}) = \frac{e^2 h^2}{16\pi^2 m^2 c^2} \left( \psi_J \| L + 2S \| \psi'_{J'} \right)^2$$

The magnetic dipole line strengths have not been considered, since the sharp lines arising due to  $f-f$  transitions are essentially electric dipole in nature.

Over the years, the Judd–Ofelt theory has been proved to be quite successful for the intensity analysis of the trivalent lanthanide ions. Earlier a lot of pioneering work on the intensities of the  $f-f$  transitions of the lanthanide series and the systematic intensity parametrization has been done by Carnall and his co-workers [16–18].

Radiative properties

J–O intensity parameters are used to calculate the radiative properties of the emission transitions. The electric and magnetic dipole line strengths of a transition  $\Psi_J \rightarrow \Psi_{J'}$  are given by

$$S_{\text{ed}} = e^2 \sum_2^6 \Omega_{\lambda} \left( \psi_J \| U^{\lambda} \| \psi'_{J'} \right)^2$$

and

$$S_{\text{md}}(\psi_J, \psi'_{J'}) = \frac{e^2 h^2}{16\pi^2 m^2 c^2} \left( \psi_J \| L + 2S \| \psi'_{J'} \right)^2,$$

respectively. For emission (or luminescence) spectra, the spontaneous emission coefficient (also called transition probability for spontaneous emission or the Einstein

coefficient for spontaneous emission)  $A(\psi_J, \psi'_{J'})$  can be written as

$$A(\psi_J, \psi'_{J'}) = \frac{64\pi^4 \nu^3}{3h(2J+1)} \left[ \frac{n_d(n_d^2+2)^2}{9} S_{ed} + n_d^3 S_{md} \right]$$

Like in the case of absorption spectra, for the measured emission spectra also, the electric dipole line strength ( $S_{ed}$ ) has been calculated for all excited state manifolds of the rare earth glassy materials concerned. Because an excited state  $\psi_J$  is relaxed to several lower-lying states  $\psi'_{J'}$ , the radiative branching ratio  $\beta_R$  is defined as

$$\beta_R(\psi_J, \psi'_{J'}) = \frac{A(\psi_J, \psi'_{J'})}{\sum_{\psi'_{J'}} A(\psi_J, \psi'_{J'})}$$

where the factor in the denominator is the total radiative transition probability.

The branching ratios can be used to predict the relative intensities of all emission lines originating from a given excited state. The experimental branching ratio can be found from the relative areas of the emission lines. Once all emission probabilities that depopulate an initial level  $^{2S+1}L_J$  have been calculated, they can be used to determine how fast that level is depopulated. This rate is given by the radiative lifetime  $\tau_R(\psi_J)$

$$\tau_R(\psi_J) = \frac{1}{\sum_{\psi'_{J'}} A(\psi_J, \psi'_{J'})}$$

stronger emission probabilities and more transitions from a level lead to faster decay and shorter lifetimes. The stimulated emission cross-section ( $\sigma_p^E \text{cm}^2$ ) for all emission transitions have been computed from the formula.

$$\sigma_p^E = \frac{\lambda_p^4}{8 \prod cn_d^2 \Delta\lambda_p \tau_m}$$

where  $\lambda_p$  is the emission peak wavelength and  $\Delta\lambda_p$  is the full width at half maximum of the emission transition.

## Results and discussion

### Absorption spectra and Judd–Ofelt theory

Figure 1 presents the Vis–NIR absorption spectra of  $\text{Nd}^{3+}:\text{CdBiB}$  glasses. From the absorption spectra, six absorption bands are observed and are assigned to the transitions  $^4I_{9/2} \rightarrow ^4G_{9/2}$ ,  $(^4G_{7/2}, ^4K_{13/2})$ ,  $(^4G_{7/2}, ^2G_{7/2})$ ,  $(^4F_{7/2}, ^4S_{3/2})$ ,  $(^4F_{5/2}, ^2H_{9/2})$  and  $^4F_{3/2}$  at 513, 527, 585, 748, 797, and 879 nm, respectively. Assignments have been made by our previously published article [19]. From the absorption spectra, experimental oscillator strengths have

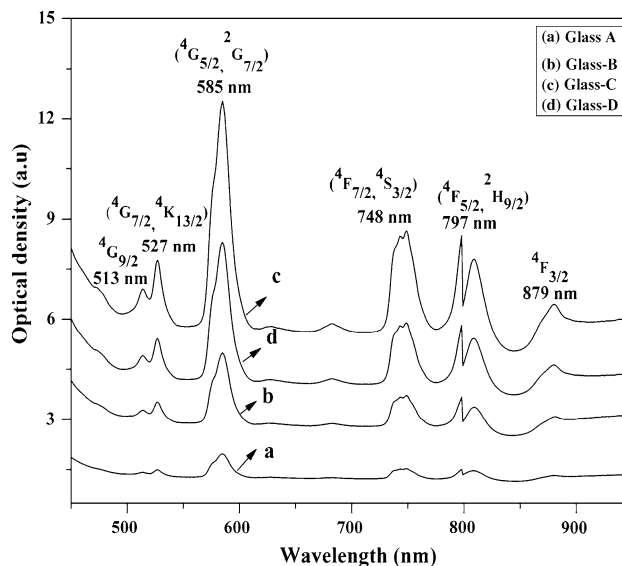


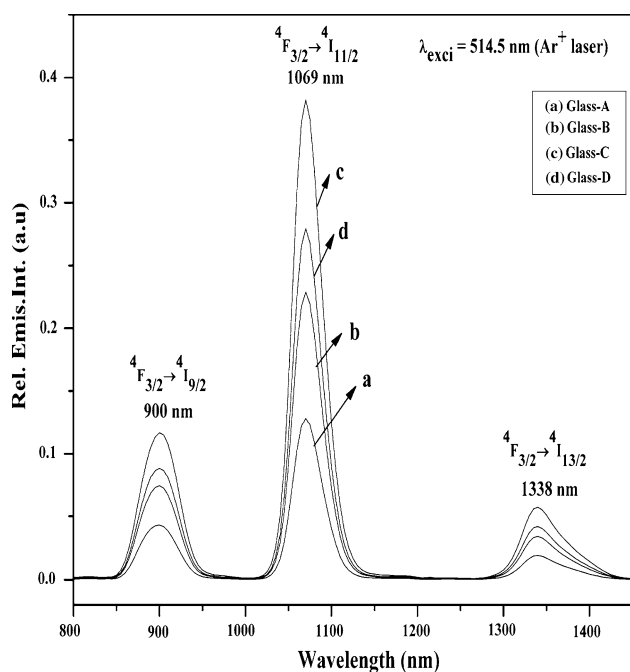
Fig. 1 Vis–NIR absorption spectra of  $\text{Nd}^{3+}:\text{CdBiB}$  glasses

been calculated for all the absorption bands. Further, Judd–Ofelt intensity parameters  $\Omega_\lambda$  ( $\lambda = 2, 4,$  and  $6$ ) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. The fairness of the fitting approximation is examined by the root mean square deviations ( $\delta_{rms}$ ). Low  $\delta_{rms}$  values clearly indicate the accuracy of fitting. The experimental, calculated oscillatory strengths and J–O intensity parameters of all  $\text{Nd}^{3+}:\text{CdBiB}$  glasses are presented and compared with the other glass systems which are listed out in Table 1. From Table 1, it is observed that, for the transition  $^4I_{9/2} \rightarrow (^4G_{5/2}, ^2G_{7/2})$  at 585 nm, the oscillator strength is very high compared with the other absorption transitions in all glasses. Thus, the transition  $^4I_{9/2} \rightarrow (^4G_{5/2}, ^2G_{7/2})$  is known as the hypersensitive transition (HST) and follows the selection rules  $\Delta S = 0$ ,  $\Delta L = 2$ , and  $\Delta J \leq 2$ . Because of its hypersensitivity this transition shows the maximum intensity in the absorption spectra compared with the other transitions [19]. The nephelauxetic ratio ( $\beta$ ) and bonding parameters ( $\delta$ ) have been computed and the values are presented in Table 1.

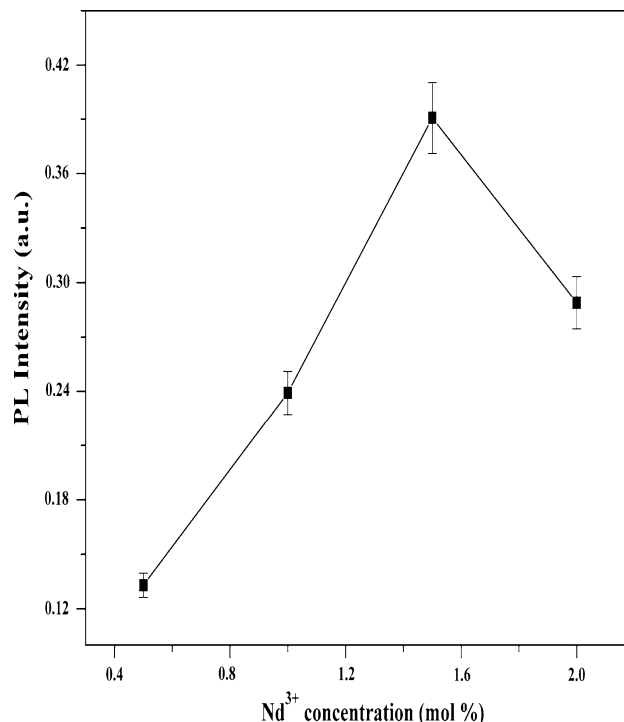
The nature of the R–O bond is known from the bonding parameter ( $\delta$ ). The bond is ionic if  $\delta$  takes the negative sign and it is covalent if  $\delta$  gets the positive sign. For the present glasses the value of  $\delta$  is having positive sign that indicates the covalent nature of the R–O bond. From Table 1, it is also observed that, J–O intensity parameters for all the  $\text{Nd}^{3+}:\text{CdBiB}$  glasses follow the trend of  $\Omega_4 < \Omega_2 < \Omega_6$ . Among the three intensity parameters,  $\Omega_2$  is known as the sensitive parameter because it is easily affected by the local structure changes of the host. From Table 1, it is also clear that all the J–O parameters are varying with the variation in

**Table 2** Computed values of spontaneous emission transition probabilities ( $A$   $s^{-1}$ ), radiative rate ( $A_T$   $s^{-1}$ ), radiative lifetime ( $\tau_R$   $\mu s$ ), and branching ratios ( $\beta\%$ ) of emission transitions of  $Nd^{3+}$ :CdBiB glasses

Emission from excited state ${}^4F_{3/2} \rightarrow$	Glass-A		Glass-B		Glass-C		Glass-D	
	$A$ ( $s^{-1}$ )	$\beta\%$	$A$ ( $s^{-1}$ )	$\beta\%$	$A$ ( $s^{-1}$ )	$\beta\%$	$A$ ( $s^{-1}$ )	$\beta\%$
${}^4I_{15/2}$	46	0.83	49	0.76	61	0.71	68	0.68
${}^4I_{13/2}$	693	12.6	887	13.79	1003	11.76	1163	11.70
${}^4I_{11/2}$	2875	52.4	3186	49.56	4708	55.21	5298	53.29
${}^4I_{9/2}$	1871	34.1	2306	35.87	2754	32.3	3411	34.31
$A_T$ ( $s^{-1}$ )	5485		6428		8526		9940	
$\tau_R$ (ms)	0.182		0.155		0.117		0.100	

**Fig. 2** NIR emission spectra of  $Nd^{3+}$ :CdBiB glasses

the  $Nd_2O_3$  content, this implies that  $Nd^{3+}$  ions occupy different sites in different glasses. It is well known that, J-O intensity parameter  $\Omega_2$  depends on the asymmetry nature of the local environments around  $Nd^{3+}$  sites, which implies that it also depends on the covalency between  $Nd^{3+}$  ions and ligand anions [20]. The smaller value of intensity parameter ( $\Omega_2$ ) indicates the lower asymmetric nature of the ion sites and the ionic nature of the chemical bond between  $Nd^{3+}$  ions and the ligands. In the present investigation,  $\Omega_2$  is having the larger value for Glass-A when compared with the other glasses (Glass-B–D), which indicates that the sites occupied by  $Nd^{3+}$  ions are the most asymmetric in nature and the chemical bond between  $Nd^{3+}$  ions and ligands is covalent in nature [21]. For the present  $Nd^{3+}$ :CdBiB glasses, the value of  $\delta$  (bonding parameter) is

**Fig. 3** The concentration of  $Nd^{3+}$  ions as a function of its emission intensity in  $Nd^{3+}$ :CdBiB glasses

also having positive sign that confirms the covalent nature of the Nd–O bond.

Moreover, it is interesting to note that the values of  $\Omega_2$  for all  $Nd^{3+}$ :CdBiB glasses are in the range from 4.893 to 4.248, which are very large when compared with other glass hosts [22–24]. This indicates more nonsymmetrical nature of  $Nd^{3+}$  sites and the stronger covalency of the Nd–O bond in the present glasses. The spectroscopic quality factor ( $X$ ) is determined by taking the ratio between the intensity parameters  $\Omega_4$  and  $\Omega_6$ . This value indicates the stronger emission performance of the transition from the  ${}^4F_{3/2}$  level of  $Nd^{3+}$  ions. If  $X$  value is smaller than unity, then the emission intensity is stronger for the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition than that of the  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  transition. In the

**Table 3** Emission transition peak position ( $\lambda_p$  nm), band width ( $\Delta\lambda_p$  nm) transition probability ( $A$  s<sup>-1</sup>), and emission cross-section ( $\sigma_p^E \times 10^{-20}$  cm<sup>2</sup>) of measured emission transitions of Nd<sup>3+</sup>:CdBiB glasses

Emission from excited state <sup>4</sup> F <sub>3/2</sub> →	Glass-A			Glass-B			Glass-C			Glass-D			
	$\lambda_p$ (nm)	$\Delta\lambda_p$ (nm)	$\sigma_p^E$ (cm <sup>2</sup> )	$\lambda_p$ (nm)	$\Delta\lambda_p$ (nm)	$\sigma_p^E$ (cm <sup>2</sup> )	$\lambda_p$ (nm)	$\Delta\lambda_p$ (nm)	$\sigma_p^E$ (cm <sup>2</sup> )	$\lambda_p$ (nm)	$\Delta\lambda_p$ (nm)	$\sigma_p^E$ (cm <sup>2</sup> )	
<sup>4</sup> I <sub>13/2</sub>	1338	55	13.47	1338	55	18.30	1338	48	27.79	1338	52	30.01	
<sup>4</sup> I <sub>11/2</sub>	1069	41	8.245	1069	38	10.79	1069	41	13.25	1069	41	15.50	
<sup>4</sup> I <sub>9/2</sub>	900	55	0.316	900	55	0.316	900	55	0.316	900	55	0.316	
Other glass systems							FWHM (nm)						$\sigma_p^E$ (cm <sup>2</sup> )
Commercial phosphate glasses [27]							22–35						2–4.8
Barium fluorophosphates glasses [28]							25.7						4.08
LHG-80 [29]							24						4.2
LG-770 [29]							25						3.9
Q-88 [29]							22						4.0
LHG-8 [29]							26.5						3.7
LG-750 [29]							25.3						3.6
Phosphate [30]							25.5						3.9
Borate [30]							36.8						2.2
Germanate [30]							34.7						1.9
Silicate [30]							34.0						2.9
Tellurite [29]							28.9						2.9
Fluorophosphate [29]							27.2						3.5
Fluorozirconate [29]							26.7						2.9

present investigation, the value of spectroscopic quality factor ( $X$ ) for all the glasses is smaller than unity indicating that the transition <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> at 1069 nm is having the greater intensity [8]. From Table 1, it is clear that  $\Omega_2$  decreases from  $4.893 \times 10^{-20}$  to  $4.248 \times 10^{-20}$  cm<sup>2</sup> as the concentration of Nd<sup>3+</sup> increases from 0.5 to 2.0 mol% where as  $\Omega_4$  and  $\Omega_6$  values are first increasing with increase in the Nd<sup>3+</sup> concentration up to 1.5 mol% and then decreased for 2.0 mol% of Nd<sup>3+</sup> concentration.

In addition to that the spectroscopic quality factor ( $\Omega_4/\Omega_6$ ) has also been reported to characterize the glasses concerned. Glass-C is having larger value of  $\Omega_4/\Omega_6$  than other four glasses and it shows that glass-C is a kind of better optical glass. By using the Judd–Ofelt intensity ( $\Omega_\lambda$ ) parameters, radiative properties of emission transitions of Nd<sup>3+</sup>:CdBiB glasses have been computed and the results relating to spontaneous emission transition probability ( $A$ ), radiative transition rate ( $A_T$ ), radiative life time ( $\tau_R$ ), and branching ratios ( $\beta$ ) of the various emission transitions are calculated and are presented in Table 2. From Table 2, it was found that the total radiative transition probability  $A_T$  (s<sup>-1</sup>) values of all Nd<sup>3+</sup>:CdBiB glasses are in the range from 5485 to 9940 (s<sup>-1</sup>) and the radiative lifetime  $\tau_R$ (ms) values are in the range from 0.100 to 0.182 ms.

### Luminescence properties

Figure 2 presents the NIR emission spectra of Nd<sup>3+</sup>:CdBiB glasses excited by 514.5 nm (Ar<sup>+</sup> laser) as the excitation wavelength. From this spectra, three NIR emission bands are observed at 900, 1069, and 1338 nm and are assigned to the transitions (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub>), (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub>), and (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>13/2</sub>), respectively. Assignments have been made by our previously published article [25].

Among these, the transition <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> at 1069 nm is a lasing transition having prominent intensity. From the NIR emission spectra, it is also observed that the emission intensity of Nd<sup>3+</sup>:CdBiB glasses increases with the increase of Nd<sup>3+</sup> concentration from 0.5 to 1.5 mol% and reached the maximum value at  $x = 1.5$  mol% and then decreases indicating the concentration quenching phenomena. For Nd<sup>3+</sup> concentrations more than 1.5 mol%, the emission intensity was quenched because at higher concentrations the interactions between Nd<sup>3+</sup> ions increases and causes the energy transfer processes [26].

Thus, 1.5 mol% is the optimized concentration for Nd<sup>3+</sup>:CdBiB glasses. Figure 3 shows the emission intensity of Nd<sup>3+</sup> as a function of its doping concentration (mol%). The FWHM and stimulated emission cross-section values for all the emission bands of all Nd<sup>3+</sup>:CdBiB

glasses are calculated and are presented in Table 3. The FWHM, stimulated emission cross-section values of the lasing transition at 1.06  $\mu\text{m}$ , is compared with the other glass systems which are listed out in Table 3. From the Table, it was found that the FWHM values for all the emission bands of Glass-C are having the larger values when compared with the other glasses. Further, the stimulated emission cross-section ( $\sigma_c^p$ ) value describes the laser performance of a material and also estimates the rate of energy extracted from the lasing material. From Table 3, it is clear that the stimulated emission cross-section values of the transition at 1.06  $\mu\text{m}$  of all  $\text{Nd}^{3+}:\text{CdBiB}$  glasses are comparable with the other commercial laser glasses [27–30] as listed out in Table 3. Moreover, CW laser action can be obtained from the glasses having large stimulated emission cross-section values and also these glasses are used for low-threshold, high gain applications. In bismuth borate glasses, there is a possibility for doping larger amounts of rare earth ions and can be used for high concentration mini-lasers [1]. From this we can conclude that the bismuth borate glasses are suitable as laser hosts. Further, 1.5 mol% of  $\text{Nd}^{3+}:\text{CdBiB}$  glass is a good candidate for laser materials.

## Conclusions

$\text{Nd}^{3+}:\text{CdBiB}$  glasses with various compositions were prepared via a melt quenching method. Spectral properties were studied by applying the Judd–Ofelt theory. The intensity parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  and radiative properties of the emission levels of  $\text{Nd}^{3+}:\text{CdBiB}$  glasses were evaluated.  $\Omega_2$  is having the larger values for the present glasses that indicates the covalent nature of Nd–O bonds and more asymmetric nature of  $\text{Nd}^{3+}$  sites. The spectroscopic quality factor is having the smaller values than unity that indicates the laser transitions ( ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ ) are more intense. The stimulated emission cross-section values are calculated for the present glasses, which are very large when compared with the other commercial laser glasses. The concentration of  $\text{Nd}_2\text{O}_3$  is also optimized for the better results. Thus, we could suggest that 1.5 mol% of  $\text{Nd}^{3+}:\text{CdBiB}$  glasses are the potential candidates for laser applications.

**Acknowledgements** This study was supported by the CSIR, New Delhi in the form of Major Research Project No. 03 (1172)/10/

EMR-II sanctioned to the author (BSR), and also provided the financial assistance to one of the author (SS) in the form of SRF, who would like to thank the Head, CSIR, New Delhi, India.

## References

- Saisudha MB, Ramakrishna J (2002) *Opt Mater* 18:403
- Xu Z, Chen Y, Lin Y, Gong X (2009) *J Alloys Comp* 481:411
- Culea E, Pop L, Simon S (2004) *Mater Sci Eng B* 112:59
- Rajyasree Ch, Krishna Rao D (2011) *J Non-Cryst Solids* 357:836
- Mahmoud KM, Abdel-Rahim FM, Atef K, Saddeek YB (2011) *Curr Appl Phys* 11:55
- Lim K-S, Lee C-W (2000) *J Lumin* 87:1008
- Azevedo J, Coelho J, Hungerford G, Sooraj Hussain N (2010) *J Phys Condens Matter* 405:4696
- Surendra Babu S, Rajeswari R, Jang K, Jin CE, Jang KH, Seo HyoJin, Jayasankar CK (2010) *J Lumin* 130:1021
- Wan J, Cheng L, Sun J, Zhong H, Li X, Lu W, Tian Yue, Bo W, Chen B (2010) *Physica B* 405:1958
- Sinha SP (1966) In: *Complexes of the rare earths*. Pergamon Press, Oxford
- Judd BR (1962) *Phys Rev* 127:750
- Ofelt GS (1962) *J Chem Phys* 37:511
- Bunzil JCG, Choppin GR (1989) *Lanthanide probes in life. Chemical and earth sciences*. Elsevier, Amsterdam
- Hufner S (1978) *Optical spectra of transparent rare earth compounds*. Academic Press, New York
- Yen WM (1986) In: *Zschokke IZ, Reidel D (eds) Optical spectroscopy of glasses*. Publishing Company, Dordrecht
- Carnall WT, Fields PR, Wybourne BG (1965) *J Chem Phys* 42:3797
- Carnall WT, Fields PR, Rajnak K (1968) *J Chem Phys* 49:4412
- Carnall WT (1979) *Hand book on the physics and chemistry of rare earths*, Chap 3, vol 24. North Holland, Amsterdam, p 171
- Sudhakar Reddy B, Buddhudu S (2008) *Indian J Phys* 82(7):871
- Ratnakaram YC, Viswanatha Reddy A (2000) *J Non-Cryst Solids* 277:142
- Sunil Kumar S, Khatei J, Kasthuriangan S, Koteswara Rao KSR, Ramesh KP (2011) *J Non-Cryst Solids* 357:842
- Klimesz B, Dominiak-Dzik G, Solarz P, Zelechower M, Ryba-Romanowski W (2005) *J Alloys Compd* 403:76
- Zambelli M, Speghini A, Ingletto G, Locatelli C, Bettinelli M, Vetrone F, Christopher Boyer J, Capobianco JA (2004) *Opt Mater* 25:215
- Ehrmann PR, Carlson C, Campbell JH, Click CA, Brow RK (2004) *J Non-Cryst Solids* 349:105
- Sudhakar Reddy B, Buddhudu S, Rao SRK, Naresh Babu P (2008) *J Optoelectron Adv Mater* 10:2777
- Nie Q, Li X, Dai S, Xu T, Jin Z, Zhang X (2008) *Spectrochim Acta A* 70:537
- Weber MJ (1990) *J Non-Cryst Solids* 123:208
- Kumar GA, De la Rosa-Curz E, Ueda K, Martinez O, Barbosa-Garcia (2003) *Opt Mater* 22:201
- Campbell JH, Suratwala TI (2000) *J Non-Cryst Solids* 263:318
- Reisfeld R (1985) *J Less Common Met* 112:9