

Optical band gap and physical properties of Nd³⁺ doped cadmium borate glasses

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Abstract: Nd³⁺-doped cadmium borate glasses were prepared and characterized optically. The oscillator strengths and Judd-Ofelt parameters for the glass containing 0.1, 0.3 and 0.5 wt% of Nd₂O₃ were computed. Density, refractive index and optical absorption spectra were measured. The values of Judd-Ofelt parameters suggested an increase in the degree of asymmetry the local ligand field at Nd³⁺ sites. The optical band gap energy and physical parameters was calculated for all glass samples. It was found that with increasing the concentration of Nd₂O₃ contents, the values of the optical band gap energy decrease.

Keywords: Cadmium Borate Glasses, Optical Energy Band Gap, Judd-Ofelt Parameters, Absorption Spectra

1. Introduction

In recent years an increasing interest in rare earth doped glasses is due to their spectroscopic properties and technological applications in various fields are observed [1-8]. Ever since the first solid state laser was demonstrated in 1961 by Snitzer in Nd³⁺ doped glasses, a lot of efforts are being done for the development of laser glasses [5]. Neodymium doped glasses have attracted attention as they act as key element for optical amplifier around 1.3μm and for higher power laser applications around 1.05μm. Since the 4f shell is efficiently shielded by the closed 5s and 5p shells, the ligand environment has only a weak influence on the electronic cloud of the rare earth ion. Although weak, this perturbation is responsible for the spectral fine structure. The absorption spectra of rare earth ions doped into single crystal show groups of many fine lines, resembling an atomic spectrum. In solutions and glasses, the line transitions within one group have been broadened to one band. However the line width of this band is still much smaller than in absorption spectra of transition metal ions. The peak position of the spectral lines reveals the electronic structure (of a part) of the 4fⁿ configuration. The crystal field splitting gives information about the symmetry of the rare earth site and about the shape of the coordination polyhedron. The intensities of spectral transition reflect also the interaction between the rare earth ion and its environment [10].

In general, the optical and spectroscopic properties of rare

earth ions are strongly dependent on host materials. The host glass materials should have high refractive index with good chemical and thermal stability along with low melting temperature of heavy metals in order to become more practically useful industries. Many potential host materials for rare earth ions have been developed. One of the preferred host materials is oxide glasses which are chemically durable, thermally stable, and optically transparent at the excitation and lasing wavelength [11].

In this paper we have taken cadmium borate glass with different concentrations of neodymium ion have wide applications as laser materials and luminescent solar concentrators [12]. We have calculated Judd-Ofelt parameters, optical band gap and various physical properties of Nd³⁺ doped cadmium borate glasses.

2. Experimental Details

Cadmium borate glasses of the composition (in wt%) (Table 1) were prepared by melt quenching technique from reagents of analytical grade in 10 gm batches [13]. Nd₂O₃ added to the host glass was 99.99% pure. The glass materials were mixed in an agate pestle mortar for two hours and were thermally treated for 4 hours in a platinum crucible at 900 ± 25°C in electric furnace. Homogeneity of the melt was ensured by stirring the melt with a platinum rod from time to time. The melt was quenched by pouring it into rectangular shaped steel moulds placed on a preheated (300°C) heavy steel plate. The glass specimens so prepared were taken away

after 24 hours and annealed for three hours at 250°C so as to remove stresses and to give them thermal stability and strength. Samples of the size 20x15x1.5 mm³ were cut and polished on all sides to make the faces flat and parallel for optical measurements.

Table 1. Compositions of various undoped and Nd³⁺(4f³) doped cadmium borate glass specimens.

S. No.	Composition of Glass Specimens (wt%)	Dopant ions (wt%)
1.	69B ₂ O ₃ -27.2Li ₂ O-1.5Al ₂ O ₃ -2.2CdCl ₂	Undoped
2.	69B ₂ O ₃ -27.2Li ₂ O-1.5Al ₂ O ₃ -2.2CdCl ₂	Nd ₂ O ₃ (0.1)
3.	69B ₂ O ₃ -27.2Li ₂ O-1.5Al ₂ O ₃ -2.2CdCl ₂	Nd ₂ O ₃ (0.3)
4.	69B ₂ O ₃ -27.2Li ₂ O-1.5Al ₂ O ₃ -2.2CdCl ₂	Nd ₂ O ₃ (0.5)

Optical absorption spectra were recorded at room temperature using a Hitachi double beam UV-VIS/NIR spectrophotometer model F-3010 with a resolution of 0.5 nm. The refractive index of the glass specimens were measured on an Abbé refractometer (ATAGO3T). The densities of the materials were calculated using Archimede's principle with distilled water as immersion liquid. Optical path lengths of the glass materials were measured using digital venire calipers.

3. Results and Discussion

Various physical properties of cadmium borate glass for different concentration were determined as follows from the experimental data [14] and are listed in table 2.

1) Dielectric constant

$$\epsilon = n_d^2$$

where n_d=refractive index

2) Optical dielectric constant

$$p(dt/dp) = (\epsilon - 1) = (n_d^2 - 1)$$

3) Reflection losses

$$R = [(n_d - 1)/(n_d + 1)]^2$$

4) Molar refractivity

$$R_m = [(n_d^2 - 1)/(n_d^2 + 2)] M/D$$

Where, M=average molecular weight

Table 2. Various physical properties of Nd³⁺ doped cadmium borate glasses.

Physical Properties	0.1 wt%	0.3 wt%	0.5 wt%
Refractive Index n _d	1.552	1.562	1.568
Density d (g/cm ³)	5.103	6.245	7.387
Thickness t (cm)	0.288	0.385	0.258
Average molecular weight (g)	62.084	62.749	63.414
Dielectric constant (ε)	2.408	2.439	2.458
Optical dielectric constant (pdt/dp)	1.408	1.439	1.458
Molar Volume V _m (g/cm ³)	12.613	10.047	8.584
Reflection losses (R)	4.679	4.812	4.892
Molar Refractivity (R _m)	3.887	3.493	2.807

It is clearly observed in table 2 that refractive index, density, average molecular weight, dielectric constant, optical dielectric constant and reflection losses increases by increasing Nd³⁺ concentration. But molar volume and molar refractivity decreases by increasing Nd³⁺ concentration. As we can see thickness first increases then decreases.

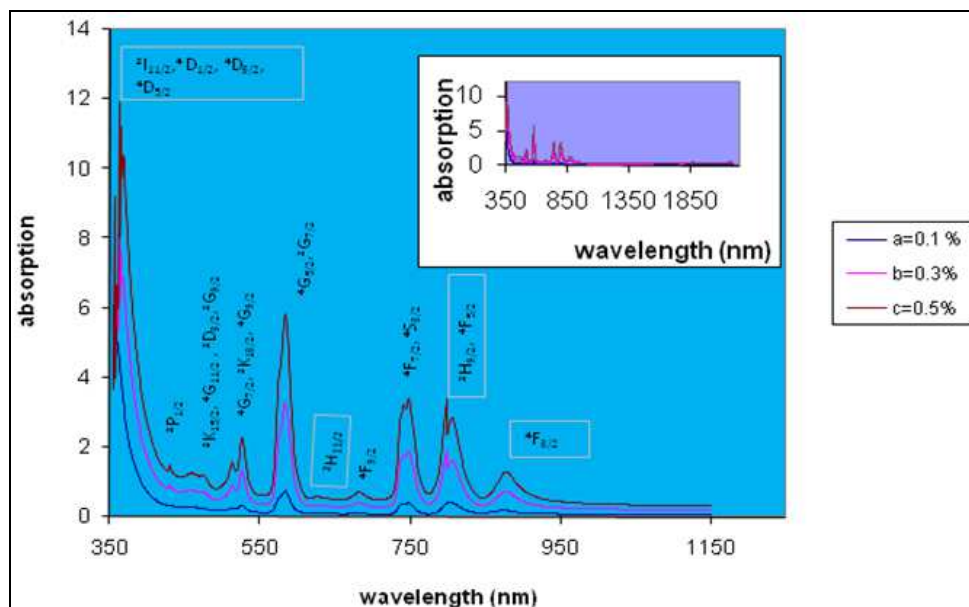


Fig. 1. Absorption spectra of Cadmium borate glass materials with different concentration of Nd³⁺ ion.

The absorption spectra of cadmium borate glasses were measured in the range of 350-1850 nm at room temperature and shown in fig. 1. These absorption spectra show sharp peaks at 354, 428, 472, 525, 583, 623, 681, 747, 798 and 868 nm. The intensities of absorption transitions are measured in

terms of P_{exp} which represents the number of classical oscillators present in one ion, more commonly referred to as the probability for absorption of radiant energy or oscillator strength. In the case of absorption band, it is given [15] by

$$P_{\text{exp}} = 2303 \text{ mc}^2 / N \pi e^2 \int \epsilon \, d\nu$$

band

$$P_{\text{exp}} = 4.318 \times 10^{-9} \times \int \epsilon \, d\nu$$

band

$$P_{\text{exp}} = 4.6 \times 10^{-9} \times \epsilon \times \Delta \nu_{1/2}$$

where ϵ is the molar absorptivity of a band at the energy. The molar absorptivity at a given energy is computed from the Beer-Lambert law $\{\epsilon = 1/cl (\log I_0/I)\}$

$$P_{\text{exp}} = 4.6 \times 10^{-9} \times (1/cl) \log (I_0/I) \times \Delta \nu_{1/2} \quad (1)$$

Where, c is the molar concentration of the absorbing ion per unit volume, l is the path length and $\log (I_0/I)$ is the absorptivity or optical density and $\Delta \nu_{1/2}$ is half band width. However, for a solid material it is generally expressed in terms of line strength S_{exp} which is related to oscillator strength P_{exp} by

$$P_{\text{exp}} = \{8\pi^2 m c \bar{\nu} / 3h (2J+1)\} (1/n) [(n^2 + 2)^2 / 9] S_{\text{exp}} \quad (2)$$

where $\bar{\nu}$ is the average energy of the transition in cm^{-1} , J is the total angular momentum of the initial level, the factor $(n^2 + 2)^2 / 9$ represents the local field correction for an ion embedded in a dielectric medium of refractive index, n , under the tight binding approximation and the other symbols have their usual meaning.

Table 3. Measured values of wavelength, oscillator strength, and experimental and calculated line strengths of Nd³⁺ doped cadmium borate glass materials along with their matrix elements.

Absorption levels	Wave-length (nm)	U Matrix			Experimental O.S. (P_{exp}) 10^{-6}			Line Strengths					
		$\ U^2\ ^2$	$\ U^4\ ^2$	$\ U^6\ ^2$	0.1 %	0.3%	0.5%	0.1%		0.3%		0.5%	
								$S_{\text{exp}} 10^{-20}$	$S_{\text{cal}} 10^{-20}$	$S_{\text{exp}} 10^{-20}$	$S_{\text{cal}} 10^{-20}$	$S_{\text{exp}} 10^{-20}$	$S_{\text{cal}} 10^{-20}$
⁴ F _{3/2}	868	0.0000	0.2239	0.0549	0.245	0.285	0.65	0.14	0.042	0.162	0.044	0.342	0.118
² H _{9/2} , ⁴ F _{5/2}	798	0.0102	0.2439	0.5124	0.599	0.621	1.24	0.314	0.215	0.324	0.218	0.599	0.518
⁴ F _{7/2} , ⁴ S _{3/2}	747	0.0010	0.0449	0.6597	0.644	0.661	1.75	0.316	0.311	0.323	0.315	0.781	0.748
⁴ F _{9/2}	681	0.0009	0.0092	0.0417	0.0758	0.076	0.142	0.033	0.013	0.034	0.013	0.058	0.314
⁸ H _{11/2}	623	0.0001	0.0027	0.0104	0.049	0.051	0.059	0.020	0.003	0.021	0.003	0.022	0.008
⁴ G _{5/2} , ² G _{7/2}	583	0.9736	0.5941	0.0673	2.05	2.1	3.4	0.785	0.748	0.801	0.759	1.194	1.141
⁴ G _{7/2} , ² K _{13/2} , ⁴ G _{9/2}	525	0.0664	0.2180	0.1271	0.437	0.439	1.21	0.150	0.136	0.151	0.139	0.384	0.298
² K _{15/2} , ⁴ G _{11/2} , ² D _{3/2} , ² G _{9/2}	472	0.0010	0.0441	0.0364	0.237	0.260	0.251	0.073	0.009	0.080	0.009	0.071	0.024
² P _{1/2}	428	0.0000	0.0367	0.0000	0.093	0.097	0.213	0.026	0.009	0.027	0.01	0.055	0.027
² I _{11/2} , ⁴ D _{1/2} , ⁴ D _{3/2} , ⁴ D _{5/2}	354	0.0050	0.5257	0.0479	0.344	0.35	0.860	0.080	0.008	0.081	0.081	0.188	0.222

The measured values of wavelength, oscillator strength, and experimental and calculated line strengths along with their matrix elements were given in table 3. The band intensities, defined in terms of line strength (S), in the absorption spectra of different specimens vary due to the use of different glass formers, modifiers, and intermediates. This variation of the line strength is reflected in the values of Judd-Ofelt parameters, which are a function of crystal field parameters, inter configurational radial integrals and energy separation between the 4fⁿ configurations of opposite parity. The angular part of 4f wave function is sensitive to covalence changes. However, these effects are small. The largest effect

The oscillator strength, P_{exp} , of these transitions may be due to electric dipole, magnetic dipole or electric quadrupole or contribution from more than one of these modes. Thus the oscillator strength of the observed absorption band is given by

$$P_{\text{exp}} = P_{\text{ed}} + P_{\text{md}} + P_{\text{eq}}$$

Where P_{ed} , P_{md} and P_{eq} refer to oscillator strengths due to electric dipole, magnetic dipole and electric quadrupole transitions respectively. The values of P_{eq} ($\sim 10^{-11}$) and P_{md} ($\sim 10^{-9}$) are very small in comparison with P_{ed} ($\sim 10^{-6}$).

It is interesting to note that f-f transitions if considered as magnetic dipole transitions, are parity allowed and in R-S coupling scheme they follow the selection rules [16]:

$$\Delta l = 0, \Delta S = 0, \Delta L = 0, \Delta J \leq 1, (J' = 0 \rightarrow J'' = 0)$$

Similar selection rules are followed by electric quadrupole transitions. Since both these modes have very small values of oscillator strength, it is clear that the contribution is mainly from electric dipole mode. However, for true electric dipole transitions the initial and final levels should have different parity, whereas no parity change is involved in f-f transitions. Hence for f-f transitions, though electric dipole transitions are forbidden, both magnetic dipole and electric quadrupole transitions are allowed ones. Considering the observed intensities of these bands it is proposed that the induced electric dipole transitions may be operative.

of composition on Ω_λ values arises through their dependence on the odd order terms in the expansion of local field at the rare earth site. Small highly charged ions polarize the neighbouring oxygen ions more strongly, which in turn, increase the field at the rare earth ions. These Judd-Ofelt parameters are computed [17,18] for each specimen by using partial regression and least square method [19] taking into consideration all the absorption peaks observed.

Judd-Ofelt intensity parameters (Ω_2 , Ω_4 and Ω_6) and optical band gap of Nd³⁺ doped cadmium borate glass materials have been given in table 4. These parameters show the general tendency $\Omega_4 < \Omega_6 < \Omega_2$.

Table 4. Judd-Ofelt intensity parameters and optical band gap for Nd³⁺ doped cadmium borate glass specimens.

Dopent % of Nd	$\Omega_2(10^{-20})$	$\Omega_4(10^{-20})$	$\Omega_6(10^{-20})$	Ω_4/Ω_6	E_{opt} (eV)
0.1%	0.5860692	0.1190949	0.2765977	0.43057	0.99
0.3%	0.5932213	0.1231657	0.279902	0.44003	0.98
0.5%	0.7366358	0.3555333	0.6598081	0.53884	0.97

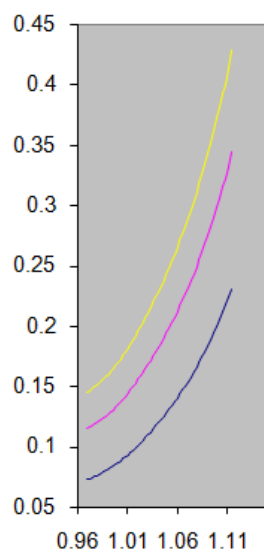
The absorption coefficient $\alpha(\omega)$, for amorphous semiconductors, glassy materials and thin films is believed to obey the following power law:

$$\alpha(\omega) = (B/\hbar\omega)(\hbar\omega - E_o)^n$$

where B is assumed to be a constant in the optical frequency range. $\hbar\omega$ is photon energy and n signifies the nature of electronic transitions associated with optical processes and normally takes a value in range $1 < n < 3$. E_o , which is defined as the optical energy gap, will normally takes a values greater than the energy band gap of the same material in crystalline form, and this difference is direct consequence of disorder in solids [12].

The absorption coefficients, α , were determined near the edge for the whole range of glass compositions and the results are displayed by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ (fig 2) [12].

The values of E_o determined from fig. 2 by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$ lie within close limits between 0.97 to 0.99 eV. From table it is clear that on increasing rare earth ion concentration value of optical band gap decreases. Similar trend has been found in neodymium doped borophosphate glasses. [12]

**Fig. 2.** Optical band gap of Cadmium borate glass materials with different concentration of Nd³⁺ ion.

4. Conclusion

In this paper we have calculated various physical properties of cadmium borate glass with different concentrations. The absorption spectra of Nd³⁺ ions doped

glasses have been analyzed on the basis of Judd-Ofelt theory. Ten absorption bands have been observed in the visible region. Judd-Ofelt parameter increases on increasing concentration of Nd³⁺ ion. JO parameters show the general tendency $\Omega_4 < \Omega_6 < \Omega_2$. In the Physical properties, Optical dielectric constant, density and reflection losses are increasing on increasing Nd³⁺ concentration whereas molar refractivity decreases. Optical band gap was calculated for different concentration of neodymium doped cadmium borate glasses. Increasing Nd³⁺ ions concentration the value of E_o decreases.

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