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Spectral properties of different concentrations of Nd^{3+} ion in barium lead borophosphate glass

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Multi-component oxide glass systems of barium lead borophosphate with 0.01-0.05 mol% of Nd^{3+} ion were prepared using meltquenching technique. The absorption spectral profile of these glasses in the UV-VIS regions was used to determine the spectroscopic characteristic parameters such as Racah (E^1, E^2, E^3), spin orbit (ξ_{4f}), configuration interaction (α, β and γ) and Judd-Ofelt (Ω_2, Ω_4 and Ω_6) intensity factors. The radiative lifetimes (τ_R) and branching ratios (β) for the fluorescent levels have been reported for all concentrations of Nd^{3+} ion in the above glass systems.

[**Keywords:** Barium lead borophosphate glasses, Absorption spectra, Judd-Ofelt parameters]
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1 Introduction

Glass matrices exhibit several advantageous properties to recognise them as more useful host materials in the development of rare earth lasing systems due to their unique properties like preparation, fabrication and less optical homogeneity[1]. Optical and luminescence properties of certain rare earth doped glasses have been reported in literature[2-4]. Binary glass systems have earlier been studied as host materials for the rare earth ions in the past[5-8]. Recently Koudelka and Mogner[9] have reported the structural and other properties of multi-component borophosphate glasses and Surana *et al.*[10] have studied the lasing properties of rare earth ions in multi component borophosphate glasses. In the present study, the authors report the spectral properties of Nd^{3+} ions in varied concentrations from 0.01 to 0.05 mol% in a multi-component barium lead borophosphate glass system.

2 Experimental Details

Nd^{3+} doped barium-lead-borophosphate glass systems (BLBP glass) under study were prepared in the following five chemical compositions.

$(80-x)B_2O_3-5BaHPO_4-15\,PbO-xNd_2O_3$
(where x = 0.01, 0.02, 0.03, 0.04, 0.05 mol%)

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These glasses were prepared using melt quenching technique as detailed in literature[11]. High grade (99.99%) pure chemicals of appropriate quantities of the B_2O_3, $BaHPO_4$, PbO, and Nd_2O_3 of 10 g batches were homogeneously mixed first and then powdered finely using agate mortar. These powder samples were kept in platinum crucibles to melt them at 950°C in an electrical furnace for 1 hr. Then each of these melts were poured onto a smooth surfaced brass plate and pressed quickly with another to obtain transparent glass discs of circular design. The optical absorption spectra of these glasses were recorded on a JASCO spectrophotometer in the wavelength regions of UV-VIS and NIR at 293 K. The densities and the refractive indices of these five glasses were determined by adopting conventional methods.

3 Results and Analysis

The optical absorption spectra of five glasses of Nd^{3+} : barium lead borophosphate have been recorded in the UV-VIS-NIR regions at 293 K. Since the spectral profiles of these glasses have shown similar features, of course with certain changes in their intensities of the energy levels, only one specimen spectrum of a glass containing 0.03 mol% Nd^{3+} is shown in the Fig. 1.

The exact coincidence of the calculated energies with that of the measured energies of the spectra reveals the perfect correlation in comparison as presented in the Table 1. The Racah parameters (E^1, E^2, E^3), spin-orbit (ξ_{4f}) and configurational interaction (α, β, γ) parameters were determined using the partial derivatives [5] and the results are reported in Table 2. The intensities of the clear bands were taken into consideration to evaluate the Judd-Ofelt[12,13] intensity parameters ($\Omega_2, \Omega_4, \Omega_6$)[12,13] and the data are presented in Table 2. The densities and the refractive indices of all the glass systems were determined using the conventional methods and reported in the Table 3. The total radiative transition probabilities (A_T) and radiative lifetimes lifetimes (τ_R) of certain fluorescent states were evaluated [14] and the results are given in Table 4. The branching ratio (β) values of some important lasing transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ are evaluated [15,16] and listed in Table 5.

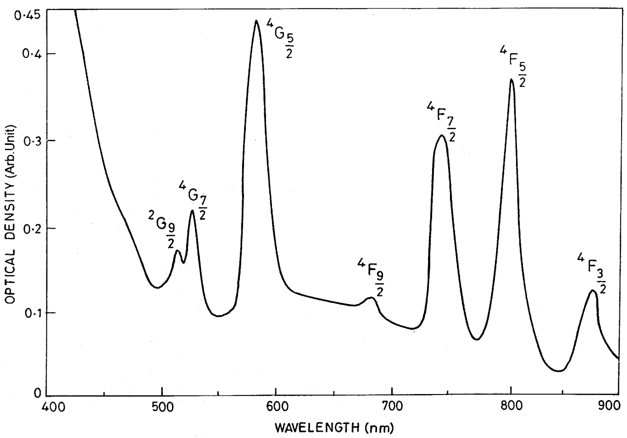

Fig. 1—Optional absorption spectrum of Nd^{3+} doped barium lead borophosphate glass with 0.03 mole % concentration

4 Discussion

4.1 Racah parameters

It is observed from Table 2 that the hydrogenic ratios E^1/E^2 and E^2/E^3 of five Nd^{3+} ion doped BLBP glasses do not vary much from the hydrogenic[17] ratios 9.89 and 0.05[17]. This indicates that Nd^{3+} ion exhibit similar radial properties[14] even though their concentrations are varied from 0.01 to 0.05 mol% in BLBP glass systems. The Slater Condon parameters (F_2) obtained from Racah parameters[15-16] of Nd^{3+} ion in all the five glasses do not vary much from the values obtained from the atomic number[12-15] of the neodymium 322.4 .

Table 1—Experimental/calculated energies of five concentrations of Nd^{3+} ion in BLBP glass

Energy level	0.01 mol%	0.02 mol%	0.03 mol%	0.04 mol%	0.05 mol%
$^4F_{3/2}$	11392	11410	11392	11392	11357
$^4F_{5/2}$	12411	12419	12411	12411	12397
$^4F_{7/2}$	13407	13419	13405	13405	13335
$^4F_{9/2}$	-	-	14624	14678	14631
$^4G_{5/2}$	17119	17089	17154	17116	17098
$^4G_{7/2}$	18974	18952	18977	18888	19021
$^4G_{9/2}$	19435	19412	19480	19387	19476

Table 2—Spectroscopic parameters of five concentrations of Nd^{3+} ion in BLBP glass

Parameter	0.01 mol%	0.02 mol%	0.03 mol%	0.04 mol%	0.05 mol%
E^1 (cm^{-1})	4795.61	4705.98	4125.89	4861.70	3759.93
E^2 (cm^{-1})	25.46	25.67	22.69	25.95	23.76
E^3 (cm^{-1})	489.74	489.17	493.26	489.50	490.28
ξ_{4f} (cm^{-1})	884.61	884.60	866.43	887.99	861.48
α (cm^{-1})	2.73	2.92	2.84	3.27	–1.17
β (cm^{-1})	–67.16	–116.84	–49.21	–92.42	119.20
γ (cm^{-1})	1378.99	1920.53	3735.30	862.04	6213.63
$\Omega_2 \times 10^{20}$ cm ^{2}	2.09	1.47	4.93	2.08	2.21
$\Omega_4 \times 10^{20}$ cm ^{2}	0.12	0.18	0.80	0.36	0.15
$\Omega_6 \times 10^{20}$ cm ^{2}	3.2.7	2.03	2.52	4.84	4.11
F_2	329.10	327.57	304.66	332.31	302.66
E^1 / E^3	9.79	9.62	8.36	9.83	8.36
E^2 / E^3	0.05	0.05	0.05	0.05	0.05
D (gm/cc)	2.582	2.586	2.589	2.593	2.597
μ	1.866	1.8759	1.8752	1.8745	1.8738

4. 2 Intensity parameters

The environmentally sensitive covalency indicative Ω_2 parameter is found to be maximum for 0.03 mol% and is minimum for 0.02 mol % of Nd^{3+} doped glass systems. The vibration sensitive parameter $\Omega_{6,}$ is maximum for 0.4 mol% and minimum at 0.02 mol% of Nd^{3+} doped glasses. The magnitude of higher intensity of the hypersensitive transition $^4G_{5/2}$ in the case of 0.03mol% Nd^{3+} glass is reflected quite clearly in the magnitude of Ω_2 intensity parameter.

4. 3 Radiative lifetimes

The total radiative transition probabilities (A_T) and radiative lifetimes (τ_R) of the fluorescent levels of $^4F_{3/2,}$ $^4F_{5/2}$, $^4F_{9/2}$, $^4G_{5/2}$, $^4G_{7/2}$ and $^4G_{9/2}$ of all five concentrations of Nd $^{3+}$ ion in BLBP glass are presented in the Table 4. It is interesting to note that the trend of the highest and the lowest values of transition probabilities (A_T) (i.e lowest and highest values of radiative lifetimes, τ_R) are observed for the fluorescent states $^4G_{5/2}$ and $^4F_{3/2}$ respectively, in all the five glass systems under study. The variational trend of radiative transition probabilities (A_T) of the fluorescent levels under study in all the glass systems are detailed below:

0.01, 0.02 and 0.05 mol% of Nd^{3+} glasses: $^4G_{5/2} > {}^4G_{7/2} > {}^4G_{9/2} > {}^4F_{9/2} > {}^4F_{5/2} > {}^4F_{3/2}$

0.03 and 0.05 mol% of Nd^{3+} glass systems: $^4G_{5/2} > {}^4G_{7/2} > {}^4G_{9/2} > {}^4F_{5/2} > {}^4F_{9/2} > {}^4F_{3/2}$

4.4 Branching ratios

The branching ratio (β) of a particular transition characterises its lasing efficiency and therefore, the stimulated emission cross section is higher. The evaluated branching ratios of $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ transitions are presented in Table 5. The branching ratio $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{15/2}$ lasing transitions exhibit higher and lower magnitudes of branching ratios in all the five glass systems under study. The highest lasing behaviour could be obtained

Table 3—Experimental and calculated spectral intensities ($f \times 10^{6}$) of five concentrations of Nd^{3+} ion in BLBP glass

Energy level	0.01 mol%		0.02 mol%		0.03 mol%		0.04 mol%		0.05 mol%	
	f_{expt}	f_{calc}	f_{expt}	f_{calc}	f_{expt}	f_{calc}	f_{expt}	f_{calc}	f_{expt}	f_{calc}
$^4F_{3/2}$	0.81	0.46	1.74	1.19	1.22	1.01	1.09	0.78	0.84	0.58
$^4F_{5/2}$	2.65	3.23	2.27	3.07	0.44	0.52	4.55	4.87	2.89	4.06
$^4F_{7/2}$	2.97	2.02	0.25	1.30	4.21	3.04	3.55	2.98	4.43	2.54
$^4F_{9/2}$	—	—	—	—	0.32	0.62	0.24	0.60	0.26	0.50
G 5/2	6.83	6.87	7.13	7.16	9.22	9.30	7.34	7.33	7.76	7.36
$^4G_{7/2}$ 1.91	1.17	2.35	1.79	3.44	1.99	1.61	1.62	2.14	1.38	
$^4G_{92}$	1.15	0.58	—	—	1.17	1.01	0.87	0.88	1.00	0.72
rms deviation	± 0.59		± 0.68		± 0.72		± 0.91		± 0.84	

Table 4 —Total radiation transition probabilities (A_T) (in sec^{-1}) and radiative lifetimes (τ_R) (in μ s) of certain excited states of five concentrations of Nd^{3+} ion in BLBP glass

Energy level	0.01 mol%		0.02 mol%		0.03 mol%		0.04 mol%		0.05 mol%	
	(A_T)	(τ_R)	(A_T)	(τ_R)	(A_T)	(τ_R)	(A_T)	(τ_R)	(A_T)	(τ_R)
$^4F_{3/2}$	2681	373	3254	307	2037	491	2274	440	2139	468
$^4F_{5/2}$	3720	269	4487	223	2720	368	2889	346	2967	337
$^4F_{9/2}$	3763	266	4486	223	2552	392	2431	411	3002	333
$^4G_{5/2}$	11981	90	11462	87	21946	46	11234	89	10043	100
$^4G_{7/2}$	9256	108	9702	103	18048	55	9253	108	8428	119
$^4G_{9/2}$	5176	193	5686	176	8542	117	5250	19	4555	22

Table 5—Branching ratios (β) of certain laser transitions of five concentrations of Nd^{3+} ion in BLBP glass

Transition	0.01 mol%	0.02 mol%	0.03 mol%	0.04 mol%	0.05 mol%
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	0.164	0.399	0.272	0.181	0.164
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	0.660	0.497	0.585	0.648	0.660
$^4F_{3/2} \rightarrow {}^4I_{15/2}$	0.166	0.097	0.134	0.161	0.166
$^4F_{3/2} \rightarrow {}^4I_{15/2}$	0.010	0.006	0.008	0.010	0.010

for an important lasing transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ in all the glasses.

5 Conclusions

It is summarised that good optical glasses with 01 to 0.05 mol% of Nd^{3+} were prepared .Any further increase in the concentration of Nd^{3+} ion in the above glass matrix does not provide good transparency with these glasses. The calculated energies of the transitions using least square fit method are exactly coinciding with the experimentally obtained energies of the transitions, reflecting the good accuracy of the experimentation. The hypersensitive transition $^4G_{5/2}$ exhibits high intensity as a function of Judd-Ofelt intensity (Ω_2) parameter in the case of 0.03 mol% Nd^{3+} glass system. The important potential lasing transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ exhibits maximum values in all the five glass systems investigated.

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References

1 Reisfeld R & Jorgensen C K, in the *Handbook on the physics and chemistry of rare earths,* edited by Gschneidner, Jr K A & Eyring L (Elsevier, 1987) p. 1.

2 Battisha J K, *Indian J Pure & Appl Phys*, 40 (2002) 122.

3 Kistaiah P, Sagar O K D, Venkata Reddy P & Veeraiah N, *Indian J Pure & Appl Phys*, 41 (2003) 780.

4 Kathuria R, Chandra B, Ramakhiani M & Bisen D P, *Indian J Pure & Appl Phys,* 40 (2002) 122.

5 Lakshman S V J & Suresh Kumar A, *Phys and Chem of Glasses,* 30 (1985) 35.

6 Binnemans K, Van Deum R, Gorler-Walrand C & Adam J L, *J Alloys Compd*, 275, (1998) 455.

7 Li H, Li L, Vienna J D, Qian M, Wang Z, Darab J G & Peeler D K, *J Non-Cryst. Solids*, 278 (2000) 35.

8 Lu K & Dutta N K, *J Appl Phys*, 89.5 (2001) 3079.

9 Koudelka L & Mogner P, *J Non-Cryst Solids*, 293 (2001) 635.

10 Surana S S L, Sharma Y K & Tandon S P, *Mat. Sci Engg*, 83 (2001) 204.

11 Lakshman S V J & Suresh Kumar A, *J Non-Cryst Solids*, 85 (1986) 162.

12 Lakshman S V J & Jayasankar C K, *Proc Indian Natl Acad A*, 642 (1982) 48.

13 Carnall W T, Fields P R & Wybourne W G, *J Chem Phys*, 42 (1965) 3797.

14 Carnall W T, Crosswhite H & Crosswhite H M, *Energy level structure and transition probabilities of Trivalent lanthanides in* LaF_3*, Argonne National Laboratory Report ANL – 78 – XX – 95*, Argonne, IL, 1978.

15 Reisfeld R & Jorgensen C K, *Lasers and Excited States of Rare Earths* (Springer, Berlin), 1977.

16 Kaminskii A A, *Laser Crystals* (Springer. Berlin), 1981.

17 Dieke G H, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, (Academic Press, New York), 1965.