

Changes in Spectroscopic Properties of Rare Earth Doped Borate Glasses on Addition of Heavy Modifier

Abstract

Spectroscopic behavior of rare earth ion Pr^{3+} in borate glasses on addition of heavy modifier PbO has been studied. The glasses were prepared using melt quenching technique. Non crystalline character of the prepared glasses was confirmed through XRD. Spectroscopic characterization has been made using UV-Vis-NIR absorption and fluorescence of these glasses. Judd-ofelt intensity parameters $\Omega_{\lambda=2, 4, 6}$ have been calculated from absorption spectra and discussed. An enhancement in fluorescence intensity is observed on addition of lead oxide.

Keywords : Glasses, Heavy Modifier, Rare Earths, Judd-Ofelt Intensity Parameter

Introduction

Over the past few years, research on structural and optical properties of rare earth (RE) doped glasses and crystals gained lot of interest due to their technological applications in the field of photonics and optoelectronics as display devices [1-2], optical amplifiers [3-4], laser materials [5-6], sensors, high density optical memory devices [7], solid state lasers [8-10] and amplifiers for fiber -optic communication [11-12]. The spectroscopic properties of rare earth ions doped glasses mostly depend on the nature and type of local environment around the rare earth ion and on the phonon energy of host glass. Several glassy materials such as fluorides, phosphates, oxyfluoride and tellurites have been widely investigated to understand the effect of host glass on the lasing properties of rare earth ions [13-16]. The glasses containing heavy metal oxides such as lead play an important role due to their low phonon energies, high refractive indices, low transition temperature and high polarizability and hence it significantly increases the optical and electronic properties such as radiative properties, quantum efficiencies and electrical conductivity of these glasses [17]. A host glass with low phonon energies decreases non-radiative relaxation rates and gives high quantum efficiencies, which are useful to design lasers and optical fiber amplifiers. Among different rare earth ion trivalent praseodymium (Pr^{3+}) ions are attractive as they offer effective IR emission at 1.3 μm for optical communication, simultaneous blue-green-red emissions for laser action and optical imaging through upconversion emission processes [18-19]. In the present work we have chosen lead oxide as glass modifier with borate glass. The concentration of lead oxide is varied from 0 to 50 mol% by reducing the concentration of borate. Spectroscopic properties of these glasses were studied with the aim to ascertain their utility for laser material.

Experimental

The chemical composition of Pr^{3+} doped borate glasses with varying concentration of lead oxide are $(69.75-x) \text{H}_3\text{BO}_3 + x \text{PbO} + 0.25\text{Pr}_2\text{O}_3$, here $x=0, 10, 20, 30, 40, 50$. These compounds are thoroughly crushed in an agate mortar in order to mix them homogeneously. The mixture is then put in a platinum crucible and melted in an electric furnace at 1100°C for one hour. The melt is then air quenched by pouring it on a rectangular iron cast kept at 500°C . It was then slowly cooled to room temperature to get a properly annealed glass. The glasses were polished to achieve good transparency. We have tested the glasses formed in this manner to ensure their non-crystalline character through X-ray diffraction. The absence of any sharp peaks in the pattern clearly demonstrated its non-crystalline state. The absorption spectra of these glasses were recorded using Cary-2390 VARIAN double beam spectrophotometer. In all absorption measurements the glass host (without rare earth) was used in the reference beam. For fluorescence measurement we have used 476 nm line of a 10 watt Ar^+ laser (Coherent) with 200mw power and a bandwidth



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~0.01nm. The spectra were recorded using a 0.5mSpex monochromator attached with IP21 PMT.

Results and Discussion

Absorption Spectra

The absorption spectra of different glasses are shown in fig.1. The energy corresponding to each peak and their assignments are given in table 1. The intensities of the individual peaks do not change much with increase in PbO. The oscillator strengths for the different transition have been calculated using the expression [20]

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

where $\epsilon(\nu)$ is the molar absorption (at frequency ν) and is equal to $1/CL \log(I_0/I)$ from the Beer-Lambert's law in which C is the rare-earth ion concentration (mol%) in the glass, L is the optical path length (material thickness) and $\log(I_0/I)$ is the optical density. The values of oscillator strength corresponding to each peak for different glasses are given in table-1. The transition ${}^3P_2 \leftarrow {}^3H_4$ of Pr^{3+} have been identified as hypersensitive transition. The oscillator strength of the absorption peak

corresponding to this transition shows a peculiar behavior, the oscillator strength decreases as PbO concentration increases from 0 to 40mol % (except at 20mol %) but it is larger when the concentration is 50mol%. Using the experimental values of the oscillator strengths the three Judd-Ofelt intensity parameters [21-22] have been calculated. The Judd-Ofelt theory is not very successful in the case of Pr^{3+} ion. This is explained as being due to the energy levels arising from the ground configuration $4f^2$ and those arising from the first excited configuration $4f^15d^1$ being quite close in energy. From the table-2 it is observed that the values of Ω_2 and Ω_6 show a minima when PbO concentration is near 40%. The variation of Ω_4 is however quite irregular. The parameter Ω_2 is associated with asymmetry of the ligand field near the rare earth ion and its value is expected to be higher when the symmetry of the ligand field at the rare earth site is lower. The minimum value of Ω_2 at 30% of PbO indicates that at this concentration of PbO the symmetry of the ligand field around the Pr ion is a maximum.

Table: 1

Assignment of peaks, their energies, experimental and calculated values of oscillator strength (10^{-6}) of the glasses with varying concentration of PbO

Transition from ground state 3H_4	0% PbO			10% PbO			20% PbO		
	$\nu(\text{cm}^{-1})$	f_{exp}	f_{cal}	$\nu(\text{cm}^{-1})$	f_{exp}	f_{cal}	$\nu(\text{cm}^{-1})$	f_{exp}	f_{cal}
3P_2	22462	4.58	2.05	22462	2.97	1.68	22462	4.20	1.47
3P_1	21188	0.50	0.92	21188	0.49	0.89	21188	0.49	1.39
3P_0	20694	1.25	0.91	20694	0.65	0.88	20694	1.61	1.37
1D_2	16900	0.99	0.62	16900	0.66	0.50	16900	1.05	1.49

Transition from ground state 3H_4	30% PbO			40% PbO			50% PbO		
	$\nu(\text{cm}^{-1})$	f_{exp}	f_{cal}	$\nu(\text{cm}^{-1})$	f_{exp}	f_{cal}	$\nu(\text{cm}^{-1})$	f_{exp}	f_{cal}
3P_2	22462	3.39	1.63	22462	3.22	1.25	22462	3.12	1.22
3P_1	21188	0.77	1.59	21188	0.81	0.64	21188	0.93	0.92
3P_0	20694	1.66	1.58	20694	1.29	0.77	20694	1.40	0.91
1D_2	16900	0.99	0.49	16900	0.80	0.20	16900	0.82	0.47

f_{cal} are calculated using Judd-Ofelt parameters Ω_λ , which are listed in table-2

Table:2

Variation of Judd-Ofelt parameters Ω_λ with the concentration of lead oxide

% PbO	$\Omega_2 \times 10^{-20} \text{ cm}^2$	$\Omega_4 \times 10^{-20} \text{ cm}^2$	$\Omega_6 \times 10^{-20} \text{ cm}^2$
0%	1.887	1.091	2.580
10%	0.864	1.110	1.630
20%	0.539	1.906	2.078
30%	0.373	1.345	2.054
40%	0.774	0.945	1.718
50%	0.705	1.078	1.807

Fluorescence Spectra

The fluorescence spectra in the 540-750nm range due to Pr^{3+} ions in the glasses with varying concentration of lead oxide are shown in fig-2. The assignments of the peaks to specific transitions are made on the basis of the known energy levels of Pr^{3+} as reported by earlier workers [23]. All the fluorescence spectra were recorded in the same experimental conditions. It is found that the addition of PbO has a significant effect on the fluorescence spectrum. The first and most interesting observation is that the intensity of the fluorescence peak at 614.5nm corresponding to ${}^1D_2 \rightarrow {}^3H_4$ transition increases with increasing PbO concentration and is a maximum for

40% PbO. The fluorescence measurement was made using the 476 nm line of Ar^+ laser as the exciting line. The energy for this radiation is 20986 cm^{-1} and is considerably higher (~ by more than 500 cm^{-1}) than the energy required for excitation of the 3P_0 level (20474 cm^{-1}) of Pr^{3+} but is less than the excitation energy for the 3P_1 level (21066 cm^{-1}). The most intense fluorescence peak at 614.5 nm (16268 cm^{-1}) in all the spectra is ascribed to the ${}^1D_2 \rightarrow {}^3H_4$ transition. The peak observed at 655.9nm is ascribed to ${}^3P_0 \rightarrow {}^3F_2$ transition. It can be seen from the fluorescence spectrum that the intensity of the line due to ${}^1D_2 \rightarrow {}^3H_4$ transition increases with PbO concentration. The enhancement of the fluorescence intensity is probably

to be attributed to the structural change in the glasses following the addition of lead oxide. It has already been noted that conversion of BO_3 to BO_4 is maximum at 40% of PbO [24]. The phonon energy for BO_4 is less than the corresponding value for BO_3 and this might be the reason for the enhanced fluorescence as the reduced phonon frequency decreases the rate of non-radiative relaxation. An enhancement in intensity of fluorescence suggests that quantum efficiency increases.

Conclusion

Spectroscopic properties of Pr^{3+} ions in borate glasses with heavy modifier lead oxide were analyzed. Judd-ofelt intensity parameters were determined for all concentration of lead oxide and their variations are correlated with some of structural changes in glasses. It is observed from fluorescence spectra that there is enhancement in intensity of fluorescence on addition of lead oxide.

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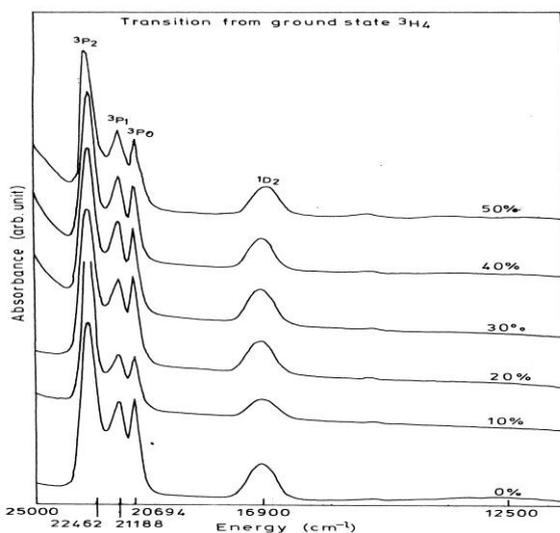


Fig.1 Absorption spectra of Pr^{3+} doped glasses with varying concentration of lead oxide

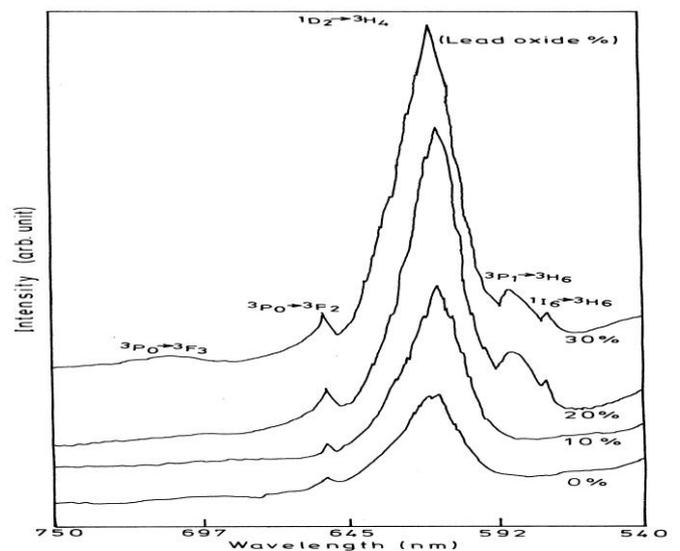


Fig.2. Fluorescence spectra of Pr^{3+} doped glasses for varying concentration of lead oxide