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Photoacoustic study of Pr and Ho ions doped in Ca–Li–B–O glass

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Abstract : The photoacoustic (PA) spectra of Pr and Ho ions doped in Ca–Li–B–O glass have been recorded in the visible region using an indegenous single beam photoacoustic spectrometer The main spectral features in the photoacoustic spectra are found to be due to triply ionized rare earth atoms and the assignment reveals a red shift in their spectral features as compared to their positions in the free ions The PA branching ratio have also been determined and compared with PA branching ratio of pentaphosphate crystal which may be useful in understanding the mechanism of laser action

Keywords : Photoacoustic spectroscopy, PA branching ratio, doped glasses, nephelauxetic effect, relative intensity

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1. Introduction

Glasses doped with rare earth ions have been extensively used as materials for high power laser [1–4]. The lasing characteristics are determined essentially by the electronic energy levels of rare earth ions and presence of other ions on their vicinity may have considerable influence on them. It has therefore, become increasingly of interest to study the absorption and luminescence characteristics of various glasses doped with rare-earth ions.

Previously, we have reported certain important results from our studies carried out on Nd and Er ions doped in calibo glass [3]. In the present paper, we report another

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rare-earth ions Pr and Ho as a dopant in order to have an insight into different optical behaviour through measurement of photoacoustic spectra of Ca–Li–B–O glass.

2. Experimental

Rare earth ions doped Ca–Li–B–O glasses for our study, were prepared by melting a mixture of calcium oxide, lithium oxide, boric acid and rare earth ion in its elemental powder form in platinum crucible at 1100°C for about five hours and pouring the melts into a suitable cast. The compound CaO, Li_2O_3 and B_2O_3 were obtained from BDH with a stated purity of 99% and rare earth powders were obtained from Aldrich company with a stated purity of 99%.

The weight percentages were 20% CaO, 10% Li_2O_3, 70% B_2O_3 and 4% of required rare earth ion. The glass were cast in stainless steel disc of about 10 mm diameter and 5.1 mm thickness and disc were annealed at 350°C for one hour to reduce the strain in the glass.

The photoacoustic spectra of glasses have been recorded by using a single beam photoacoustic spectrometer in 400–700 nm region [5]. The excitation source is a 600 Watt halogen lamp and we use a 0.25 m grating Jarrel ash monochromator, with an excitation bandwidth of 7 nm. The light beam is chopped at 22.5 Hz using a mechanical chopper (EG & G model PAR 125A) and the acoustic signal is detected in an indigenous photoacoustic cell, filled with an electret condenser microphone. The output of the microphone is amplified by a preamplifier and then fed to a Lock-in amplifier (EG & G model 186A). The PA spectra of sample were normalized using the PA signal from carbon black recorded under identical experimental condition.

3. Result and discussion

The PA spectra of Pr and Ho ions doped in calibo glass have been recorded in the visible region and are shown in Figures 1 and 2. The assignments of the peaks in the spectrum have been made on the basis of earlier absorption and fluorescence spectra of the respective ions either in the free state or in compound [6–9]. The assignments of peaks are shown in Tables 1 and 2. We have also recorded the PA spectra of Pr and Ho ions in the form of oxides.

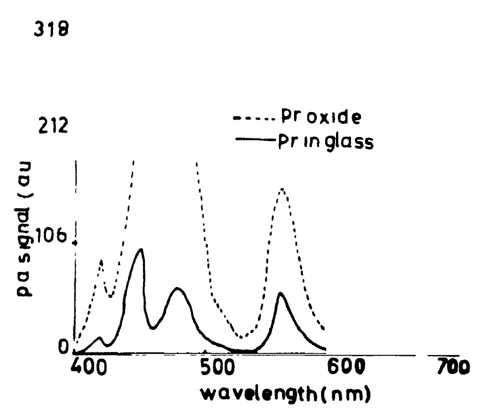

Figure 1. p.a. spectra of Pr in glass.

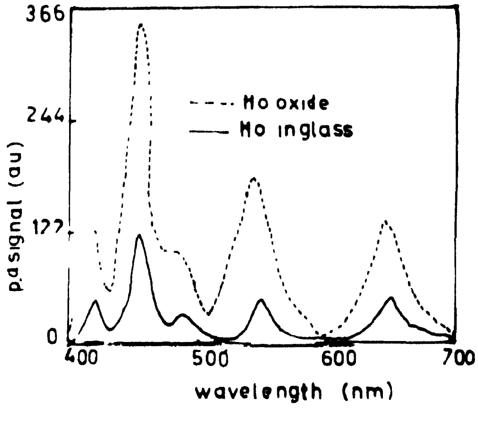

Figure 2. p.a. spectra of Ho in glass.

Table 1. Assignment of the peak of Pr in oxide and calibo glass (ground state $^3H_4$)

Level assignment	Observed peak in oxide nm	Observed peak in glass nm	Relative intensity oxide/glass nm	Energy peak in free oxide cm^{-1}	Energy peak in glass cm^{-1}	(β)	Spectral range and PA branching ratio in calibo glass nm	Spectral range and PA branching ratio of strek *et al* [2] nm
$^3P_2$	420	420	88/27 = 3.3	23160	23809	1.02	400 – 460 = 0.39	400 – 460 = 0.32
$^3P_1$	460	465	300/100 = 3	22007	21505	0.98	460 – 525 = 0.35	460 – 500 = 0.28
$^3P_0$	480	480	256/56 = 4.5	21390	20833	0.97	525 – 600 = 0.26	500 – 636 = 0.40
$^1D_2$	610	615	160/55 = 2.9	17334	16260	0.94		

Table 2. Assignment of the peak of Ho in oxide and calibo glass ground state ($^5I_8$).

Level assignment	Observed peak in oxide nm	Observed peaks in glass nm	Relative intensity nm	Energy of peak in free oxide cm^{-1}	Energy of peak in glass cm^{-1}	(β)	Spectral range and branching ratio in calibo glass nm	Spectral range and PA branching ratio of Strek *et al* [2] nm
$^5G_5$	422	422	130/43 = 3	23950	23696	0.99	400 – 475 = 0.47	400 – 480 = 0.49
$^5F_1$	455	460	350/116 = 3	21000	17857	0.85	475 – 525 = 0.13	480 – 500 = 0.09
$^5F_3$	488	490	100/32 = 3.1	20600	20408	0.99	500 – 600 = 0.19	500 – 620 = 0.27
							600 – 700 = 0.21	620 – 700 = 0.14
$^5S_2$	542	550	180/41 = 4	18500	18181	0.98		
$^5F_5$	642	650	120/45 = 2.6	15500	15503	1.00		

These spectra are also shown in figures and wavelength of the peaks are tabulated in Tables 1 and 2. By comparing the peak intensities in oxide and calibo glass, we see that the peak intensities of the PA spectra of rare earth ions doped in calibo glass are small compared to the corresponding peak intensities in the pure oxide. The relative peak intensity in the PA spectra are defined by PA branching vector Y^{PA} which correspond to the ratio of the integrated intensity of one of the peak in the spectrum to the total intensity of all the peak *i.e.*

$$Y_n^{PA} = I_K^{PA} / \sum_{K=1}^{n} I_K^{PA}$$

The branching ratios thus obtained for the various peaks in the PA spectrum in glass, have been given in Tables 1 and 2 and they are compared with those observed in penta-phosphate crystal [2]. It is interesting to note that the PA signal at 480 nm in Pr originating from $^3P_0 - {}^3H_4$ transition is very intense in oxide form of the sample, but the corresponding PA signal in calibo glass is low. As may be inferred from Table 1, the relative intensity corresponding to oxide and calibo glass is highest for the level $^3P_0$. Similarly, the PA signal at 550 nm originating from $^5S_2 - {}^5I_8$ transition is intense in the oxide form, but very low in Ho doped in calibo glass. From the theory of photoacoustics, the signal intensity depends linearly on the quantum efficiency of non-radiative relaxation. $I^{PA} \sim I_o \beta \eta_{nr}$, where η_{nr} is the efficiency at which the absorbed light at wavelength λ is converted into heat, I_0 is the intensity of incident light flux, β is the absorption coefficient of the sample. Usually, it is assumed that in a system which does not exhibit luminescence at room temperature, the non-radiative efficiency may be taken to be 100%. So one can expect that for the term which exhibit luminescence, the photoacoustic bands should be of diminished intensity. This means that the fraction of luminescence energy which does not contribute to the PA signal play a minor role in glass.

The peaks due to the rare earth in the glasses exhibit a red-shift as compared to the corresponding rare earth oxides. This red-shift has been termed as the nephelauxetic effect by Schaffer [10] and has been discussed in details by Jorgensen [11]. The nephelauxetic effect is defined quantitatively by a parameter β which is equal to the ratio of inter-electron repulsion parameters in the glass and the free ions. In general, it is defined as the ratio of Slater's integrals F_K or Racoh parameter E_K such that

$$\beta = \frac{(F_K)g}{(F_K)f} \quad \text{or } \beta = \frac{(E^K)g}{(E^K)f}.$$

In the case of lanthanide glasses, generally the value of β is very nearly unity for *f–f* transitions and one can take β as the ratio of frequency of transition of the particular band in the glass to its frequency in the free ion.

In our measurements, the free ion data has been taken from reference [7] and hence the β value can be calculated as given in Tables 1 and 2.

4. Conclusion

In this paper, we have reported the PA spectrum of Pr and Ho in calibo glass as a quantitative measure of the PA intensity of *f–f* transition bands. The intensity branching vector is proposed. The relative intensity at 480 nm in Pr and 550 nm in Ho doped calibo glass is very large. This suggests that Pr and Ho doped in calibo glass may be used as lasing material at these wavelengths.

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