



RESEARCH ARTICLE

ABSORPTION AND EMISSION CHARACTERISTICS OF Ho<sup>3+</sup>-DOPED ALKALI  
CHLOROBOROPHOSPHATE GLASSES

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ABSTRACT

Alkali chloroborophosphate glasses containing 1 mol% of HoCl<sub>3</sub> were prepared and characterized. The optical absorption spectra of three glasses have been studied in the UV-VIS-NIR region. Ho<sup>3+</sup> ion has several low lying meta stable levels, which can give rise to transitions at various wavelengths from infrared (IR) to ultraviolet (UV) regions. Racah (E<sup>1</sup>, E<sup>2</sup>, E<sup>3</sup>), spin-orbit ( $\xi_{4f}$ ), configuration interaction parameters ( $\alpha, \beta$ ) and hydrogenic ratios E<sup>1</sup>/E<sup>3</sup> and E<sup>2</sup>/E<sup>3</sup> are also obtained. Oscillator strengths (*f*) are measured from the absorption spectra and three intensity parameters  $\Omega_\lambda$  (2, 4 and 6) are calculated. Reasonable agreement between the measured and calculated *f* values has been found. For Ho<sup>3+</sup> ion, <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> is the hypersensitive transition. Using Judd-Ofelt intensity parameters, electric dipole line strengths (S<sub>ed</sub>) and magnetic dipole line strengths (S<sub>md</sub>) are calculated. From these, radiative lifetimes ( $\tau_R$ ), branching ratios ( $\beta_R$ ) and peak stimulated emission cross-sections ( $\sigma_p$ ), radiative transition rates (A) are calculated. These results were used to predict the possible potential laser transitions.

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INTRODUCTION

Glasses embedded with rare-earth (RE) ions are very good attractive materials for the development of many optoelectronic devices such as short wavelength (visible) lasers, display devices, sensors and hole burning high density memories etc. due to their laser amplification and up conversion properties (Yang et al., 2008; Liao et al., 2007). Phosphate glasses have become important materials, because of their excellent physical properties such as high thermal stability, high gain density, low optical dispersion, low refractive index and low melting point (Praveena et al., 2008). Phosphate glasses are finding ever increasing applications in many emerging technologies e.g. vitrification of radiative waste (Bergo et al., 2004), photonics, fast ion conducting (Sene et al., 2004), glass metal seals (Wei et al., 2001) and biomedical emerging etc. (Dias et al., 2005). Holmium ion is one of the most important active ion in the rare earth family due to its convenient energy-level structure

exploitable in upconversion processes. It is well known that Ho<sup>3+</sup> ions can produce laser emission in 2.0 and 2.9 μm ranges arising from the transitions, <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> and <sup>5</sup>I<sub>6</sub> → <sup>5</sup>I<sub>8</sub> respectively. Rao et al. (2012) reported the role of modifier oxide in emission spectra and kinetics of Er-Ho co-doped glasses. Optical properties of Ho<sup>3+</sup> doped novel oxyfluoride glasses were studied by Feng et al. (2007). Balaji et al. (2011) reported efficient 2.0 μm emission from Ho<sup>3+</sup> doped tellurite glass sensitized by Yb<sup>3+</sup> ions. Investigation on visible luminescence of Ho<sup>3+</sup> doped PbO-H<sub>3</sub>BO<sub>3</sub>-TiO<sub>2</sub>-AlF<sub>3</sub>-Ho<sub>2</sub>O<sub>3</sub> contents lists available at glasses was carried out by Suhasini et al. (2012). There are some reports concerning laser in the green part of the spectrum corresponding to the transitions from the excited state, <sup>5</sup>S<sub>2</sub> to the ground state (Yu et al., 1965; Podkolzina et al., 1976). Piatkowski (2008) reported the excited state absorption spectroscopy of ZBLAN: Ho<sup>3+</sup> glass. Earlier, Ratnakaram et al. (2003) studied optical properties of Ho<sup>3+</sup> ion in different mixed alkali borate glasses. In the present work, we report the optical properties of Ho<sup>3+</sup> ion doped in alkali chloroborophosphate glasses on optical absorption and emission properties in three glass matrices. Various spectroscopic parameters; Racah (E<sup>1</sup>, E<sup>2</sup> and E<sup>3</sup>), spin-orbit ( $\xi_{4f}$ ) and configuration interaction

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( $\alpha$ ) are deduced. Using Judd-Ofelt theory, radiative and non-radiative properties are studied and some of the potential lasing transitions are identified. From the emission spectra, emission cross section is evaluated to select laser transitions.

## MATERIALS AND METHODS

Ho<sup>3+</sup> doped alkali chloroborophosphate glasses with chemical composition 39 Na(PO<sub>3</sub>)<sub>6</sub> - 30B<sub>2</sub>O<sub>3</sub> -10BaCl<sub>2</sub> -20RCl- 1HoCl<sub>3</sub> were prepared using the melt quenching technique and designated as glasses A, B and C according to the content of alkali R= Li, Na and K respectively. The appropriate mixtures of these compounds were thoroughly crushed in an agate mortar in order to have proper mixing and homogeneity. Then the homogeneous mixtures are melted at a temperature range of 950-1050 °C for 30 min. depending on the composition. The melts are then poured on a preheated (200 °C) brass mould and annealed at 300 °C for about 1 h to remove thermal strains. Then the glass samples are allowed to cool to room temperature and are polished for optical measurements. The glass densities and refractive indices are measured. Using the measured glass densities and refractive indices, lanthanide ion concentrations, are obtained. The non-crystalline behavior of these glasses is tested through XRD profiles which are recorded using Seifert X-ray diffractometer.

The optical absorption spectrum is measured using JASCO V-570 spectrometer. The luminescence spectra are obtained using SPEX Fluorolog-2 fluorometer (Model-II).

## RESULTS AND DISCUSSION

### X-ray diffraction

The XRD spectra of Ho<sup>3+</sup> doped alkali chloroborophosphate glass matrices were recorded and they exhibit a broad diffuse scattering at small angles instead of crystalline peaks, confirming a long range structural disorder characteristic of amorphous network and thus glassy state was confirmed.

### Spectroscopic Parameters

The room temperature optical absorption spectra of Ho<sup>3+</sup> ion in alkali chloroborophosphate glasses are shown in Fig. 1. A total of eleven absorption bands have been observed in all the three glasses, which are rather intense, but do not overlap too much. This allows an accurate location of the energy positions and their corresponding assignments from the <sup>5</sup>I<sub>8</sub> ground state. The spectral intensity of an absorption band can be expressed in terms of the oscillator strength ( $f_{\text{exp}}$ ) of the absorption transition using (Carnall *et al.*, 1978) as

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

Table 1. Experimental and calculated oscillator strengths ( $\times 10^6$ ) and Judd-Ofelt intensity parameters ( $\Omega_\lambda \times 10^{-20}$ ) (cm<sup>2</sup>) ( $\lambda=2, 4, 6$ ) of Ho<sup>3+</sup> ions in alkali chloroborophosphate glasses

Transition	Glass A		Glass B		Glass C	
	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$
<sup>5</sup> I <sub>7</sub>	7.502	7.043	8.695	7.801	7.098	6.327
<sup>5</sup> I <sub>6</sub>	5.470	5.285	5.632	5.828	4.548	4.629
<sup>5</sup> F <sub>5</sub>	8.535	10.656	5.999	9.424	6.425	8.444
<sup>5</sup> S <sub>2</sub> , <sup>5</sup> F <sub>4</sub>	12.390	13.024	11.318	13.109	8.466	11.109
<sup>5</sup> F <sub>3</sub>	3.623	5.948	3.990	6.766	3.081	5.458
<sup>5</sup> F <sub>2</sub> , <sup>3</sup> K <sub>8</sub>	3.378	3.390	3.392	3.351	2.279	3.115
<sup>5</sup> G <sub>6</sub>	65.751	65.775	46.301	46.360	47.628	47.681
<sup>5</sup> G <sub>5</sub>	8.736	6.270	6.229	1.901	6.355	3.170
rms deviation	±1.441		±2.29		±1.876	
$\Omega_2$	17.636		13.385		13.266	
$\Omega_4$	5.466		1.656		2.761	
$\Omega_6$	9.266		10.567		8.525	

Table 2. Predicted branching ratios ( $\beta_R$ ) and the integrated cross sections ( $\Sigma \times 10^{18}$  cm) for certain selected potential laser transitions of Ho<sup>3+</sup> in alkali chloroborophosphate glasses

SLJ	S <sup>1</sup> L <sup>1</sup> J <sup>1</sup>	Glass A		Glass B		Glass C	
		$\beta_R$	$\Sigma$	$\beta_R$	$\Sigma$	$\beta_R$	$\Sigma$
<sup>5</sup> G <sub>5</sub>	<sup>5</sup> I <sub>6</sub>	0.104	7.647	0.117	5.488	0.114	5.614
	<sup>5</sup> I <sub>7</sub>	0.555	26.934	0.674	21.007	0.612	20.494
	<sup>5</sup> I <sub>8</sub>	0.282	8.467	0.134	2.562	0.207	4.273
<sup>5</sup> F <sub>3</sub>	<sup>5</sup> I <sub>7</sub>	0.266	10.378	0.210	8.358	0.232	7.827
	<sup>5</sup> I <sub>8</sub>	0.583	12.837	0.657	14.570	0.620	11.759
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> I <sub>8</sub>	0.852	22.150	0.887	22.129	0.867	18.792
	<sup>5</sup> S <sub>2</sub>	0.398	14.083	0.396	16.028	0.396	12.882
<sup>5</sup> F <sub>5</sub>	<sup>5</sup> I <sub>8</sub>	0.526	19.691	0.531	11.080	0.526	8.882
	<sup>5</sup> I <sub>7</sub>	0.187	7.981	0.180	6.898	0.183	6.265
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>8</sub>	0.761	14.616	0.759	12.906	0.754	11.565
	<sup>5</sup> I <sub>6</sub>	0.372	4.456	0.375	4.921	0.396	4.087
	<sup>5</sup> I <sub>7</sub>	0.472	1.819	0.468	2.012	0.451	1.615
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>8</sub>	0.099	0.145	0.104	0.164	0.099	0.131
	<sup>5</sup> I <sub>7</sub>	0.570	6.345	0.567	6.973	0.559	5.559
	<sup>5</sup> I <sub>8</sub>	0.388	1.281	0.395	1.390	0.393	1.128
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>7</sub>	0.103	4.206	0.091	4.268	0.089	3.463
	<sup>5</sup> I <sub>8</sub>	0.897	6.136	0.909	6.749	0.911	5.366
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>8</sub>	1.000	7.549	1.000	8.301	1.000	6.818

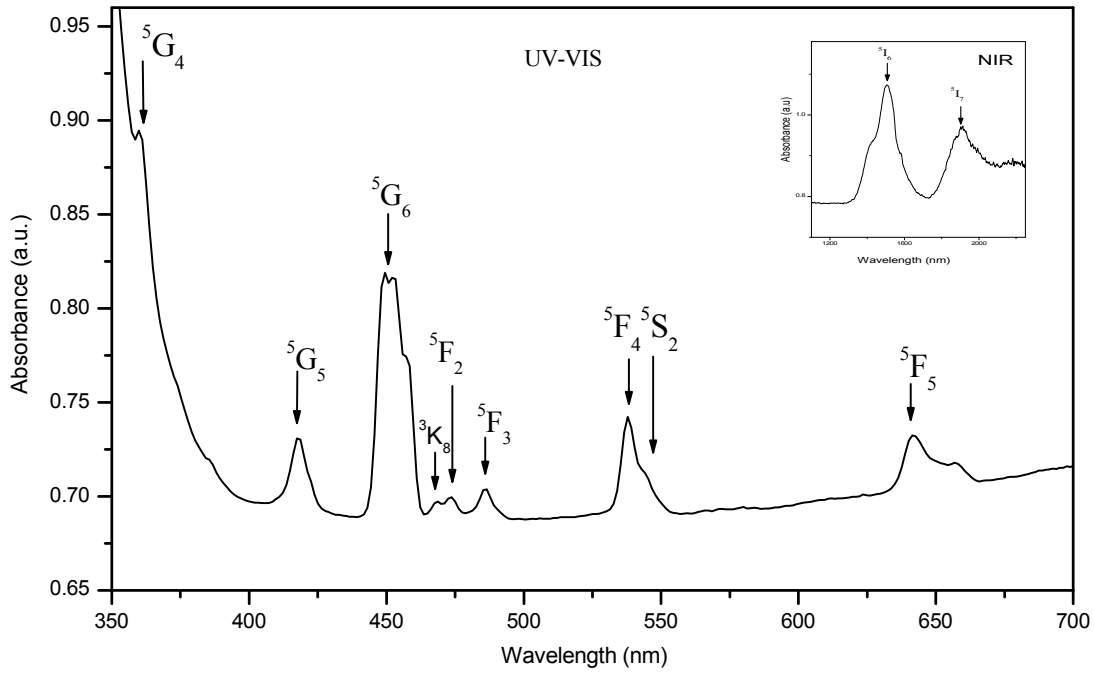


Fig. 1. Optical absorption spectrum of Ho<sup>3+</sup> doped alkali chloroborophosphate glass-A

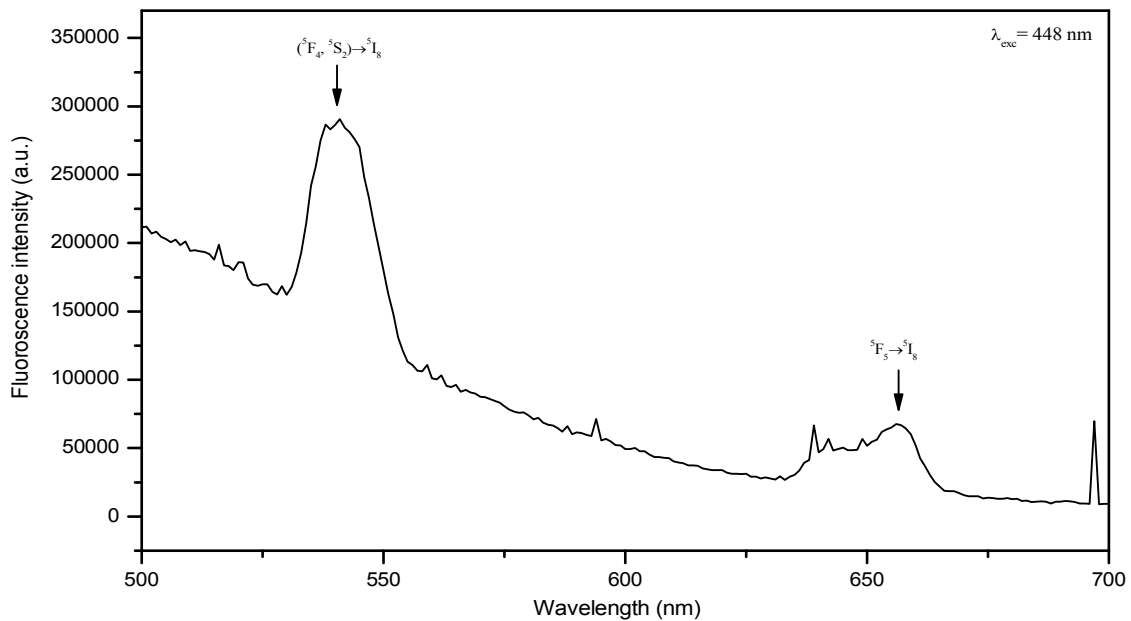


Fig.2. Emission spectrum of Ho<sup>3+</sup> doped alkali chloroborophosphate glass-A

where  $\epsilon(\nu)$  is the molar absorption coefficient in  $(\text{mol cm})^{-1}$ ,  $\nu$  is the transition energy in  $\text{cm}^{-1}$  and  $\Delta\nu$  is the half bandwidth of the transition. The oscillator strengths measured for all the observed transitions and Judd-Ofelt intensity parameters for the three glass matrices are given in Table 1. These oscillator strengths are larger in magnitude suggesting that the non-symmetric terms in the crystal field expansion are higher in glass A, B and C or in other words Ho<sup>3+</sup> ion is situated in a lower symmetry. The small rms deviations indicate good agreement between the experimental and calculated spectral intensities which shows the validity of Judd-Ofelt theory (Judd, 1962; Ofelt, 1962). It is well known that the parameter,

$\Omega_2$  exhibits the dependency on the covalency between rare earth ions and ligand anions, since  $\Omega_2$  reflect the asymmetry of the local environment at the Ho<sup>3+</sup> ion site (Jorgensen and Reisfeld, 1983).  $^5I_8 \rightarrow ^5G_6$  is the hypersensitive transition (HST) for Ho<sup>3+</sup> ion in all the three glasses. These transitions will obey the selection rules  $L \leq 0$ ,  $J \leq 0$  and  $S=0$  and they are sensitive to the environment.

#### Branching Ratios

The branching ratios ( $\beta_R$ ) and cross-sections for the stimulated emission ( $\Sigma$ ) calculated for certain selected excited

luminescent levels are shown in Table 2. It should be noted that the branching ratios do not depend strongly on the type of the glass host in which Ho<sup>3+</sup> is incorporated. It is well established that the majority of potential laser lines possess large branching ratios ( $\beta_R$ ) as well as cross-sections for the stimulated emission ( $\Sigma$ ). Examination of Table 2 shows that the laser transitions  $^5I_7 \rightarrow ^5I_8$  and  $(^5S_2, ^5F_4) \rightarrow ^5I_8$  have greater branching ratios ( $\beta_R$ ) and cross-sections which are consistent with most other Ho<sup>3+</sup> doped rare earth lasers (Caird, 1974). It is interesting to note that the  $^5F_4 \rightarrow ^5I_8$  transition may be more important than  $^5S_2 \rightarrow ^5I_8$  transition for green laser emission and therefore the relative positions of the  $^5S_2$  and  $^5F_4$  energy levels may have the large effect on laser performance.

### Emission spectra

The photoluminescence spectra of Ho<sup>3+</sup> doped alkali chloroborophosphate glasses recorded under excitation wavelength 448 nm are shown in Fig.2. The emission spectra contains two transitions  $(^5F_4, ^5S_2) \rightarrow ^5I_8$  and  $^5F_5 \rightarrow ^5I_8$ . Peak stimulated emission cross-section ( $\sigma_p$ ) for the above two transitions are calculated to know the lasing transition.

### Conclusion

In the present work, optical absorption spectra of Ho<sup>3+</sup> doped alkali chloroborophosphate glasses were recorded in the UV-VIS and NIR region. The energy levels of the absorption spectrum have been analysed through the FI Hamiltonian model. A reasonable agreement was obtained between the experimental and calculated energy levels. The Judd–Ofelt intensity parameters have been calculated. The calculated oscillator strengths obtained using these parameters are in good agreement with the experiment. Significant optical emission properties, such as radiative transition probabilities, radiative lifetimes, integrated cross-sections for the stimulated emission, branching ratios, ground state and excited state absorptions have been theoretically predicted for certain selected potential laser transitions. Judd–Ofelt theory thus provides a satisfactory basis for the interpretation of absorption band intensities of induced electric dipole transitions and also appears to be a power tool in the identification and prediction of various laser transitions. The results presented herein may open the way for the development of efficient frequency up conversion devices based on Ho<sup>3+</sup> doped alkali chloroborophosphate glasses.

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