

Optical absorption and fluorescence spectral studies of Er^{3+} ions in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass system

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Several physical properties and optical absorption and photoluminescence spectra of Er^{3+} doped $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses have been studied. From the measured intensities of various absorption bands of these glasses the Judd-Ofelt parameters Ω_2 , Ω_4 and Ω_6 have been evaluated. The Judd-Ofelt theory could successfully be applied to characterise the absorption and luminescence spectra of these glasses. From this theory various radiative properties like transition probability A , branching ratio β , the radiative life time τ_R , and the emission cross-section σ^E for various emission levels of these glasses have been determined and reported. An attempt has also been made to throw some light on the environment of Er^{3+} ions in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass lattice.

1 Introduction

Optical properties like optical absorption, luminescence and infrared spectra of various Ln^{3+} ions doped alkali and alkaline earth alumino borate glasses have extensively been investigated in the recent years¹⁻³. However the alkali free alumino borate glasses like $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses are moisture resistant, possess low rates of crystallisation, high electrical resistance and mechanical strength and are low toxic when compared with the alkaline alumino borate glasses. Further in contrast to alkaline or alkaline earth oxides, PbO has the ability to form stable glasses due to its dual role, one as modifier (if Pb-O is ionic) and the other as glass former (if Pb-O is covalent). It is well established that the radiative properties of luminescence transitions of Ln^{3+} ions in glass lattice are highly sensitive even for small changes in the chemical environment. The transition probabilities of emission transitions of Ln^{3+} ions are expected to increase with increase in covalency that depends upon the network forming ions. Network modifiers also change the local environment of Ln^{3+} ions to some extent^{4,5}. It is for this reason we have chosen PbO which acts both as network former and modifier instead of conventional alkali oxide as the third component. In addition aluminium ions can also occupy both tetrahedral (network forming) sites and octahedral (modifying) sites⁶. Hence $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ is an highly interesting

environment for a lasing Ln^{3+} ion like Er^{3+} incorporated in it. Er^{3+} ion has been chosen for doping in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass network, because it is highly efficient lasing ion since it possesses strong absorption bands in the region where pumping sources are easily available⁷. Though such type of studies have been carried out on other glass systems in recent years^{8,9}, similar studies are not available on $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass system. However few studies devoted to electrical and other physical properties of this glass system are found in literature^{2,10}.

The aim of this investigation is to study the optical absorption and fluorescence spectra of Er^{3+} doped $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses and to apply the Judd-Ofelt theory for f-f transitions of Er^{3+} ion and to evaluate various radiative properties like transition probability, radiative life times of various excited states and emission cross sections of various emission levels.

2 Experimental Details

For the present study a particular¹¹ composition: $19\text{PbO-5Al}_2\text{O}_3\text{-76B}_2\text{O}_3$; $1\text{Er}_2\text{O}_3$ (all in mol%) was chosen. Appropriate amounts of Analar grade reagents of PbO , Al_2O_3 , H_3BO_3 , and Er_2O_3 powders were thoroughly mixed and melted in a platinum crucible at 1150°C for about 2 h until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 350°C . The amor-

phous state of the glasses was checked by X-ray diffraction spectrum recorded on SIEFERT Diffractometer Model SO-DEBYE FLUX – 2002 fitted with copper target and nickel filter operated at 40 kV, 30mA. The samples were then ground and optically polished. The final dimensions of the samples were about 1 cm × 1 cm × 0.2 cm. The density *d* of the glasses was determined to an accuracy of 0.001 by the standard principle of Archimedes’ using xylene (99.99% pure) as the buoyant liquid. The refractive index *n_d* of the glass was measured using sodium vapour lamp ($\lambda = 589.3$ nm) on a precession refractometer with monobromo naphthalene as the contact layer between the glass and refractometer prism.

The optical absorption spectrum of PbO-Al₂O₃-B₂O₃ glasses containing Er³⁺ ions was recorded on a JASCO MODEL 7800 UV/VIS Spectrophotometer in the wavelength range 300-850 nm using undoped glass as reference. By using xenon arc lamp, the intense line $\lambda_{exc} = 380$ nm was identified and the same was used to record the photoluminescence spectrum. The photoluminescence spectrum of the glass was recorded on Hitachi-F 3010 Fluorescence Spectrophotometer in the wavelength range 380- 800 nm up to a resolution of 0.1 nm.

3 Results

From the measured values of density *d*, refractive index *n_d*, the average molecular weight *M* and various other physical parameters like Er³⁺ ion concentration *N_i*, molar refractivity *R*... molecular polarisability α ... po-

laron radius *r_p*, inter ionic distance *r_i* of Er³⁺ ions and the field strength *F_i*, which are useful in understanding various radiative properties of Er³⁺ doped glasses were evaluated using standard formulae¹² and are presented in Table 1.

The optical absorption spectrum of Er³⁺ doped PbO-Al₂O₃-B₂O₃ glasses recorded at room temperature in the wavelength region 300-850 nm exhibited seven absorption bands all from the ground state⁴I_{5/2} (Fig. 1); some of these levels are assigned to the following appropriate electronic transition¹³ as follows:

Table 1 — Various physical properties of Er ³⁺ doped PbO-Al ₂ O ₃ -B ₂ O ₃ glasses	
Refractive index, <i>n_d</i> (measured at $\lambda = 589.3$ nm)	1.509
Density <i>d</i> (gm/cm ³)	2.737
Average molecular weight <i>M</i>	103.50
Er ³⁺ ion concentration <i>N_i</i> (10 ²² ions/cm ³)	1.59
Molar refractivity <i>R_M</i> (cm ³)	11.29
Molecular electronic polarisability $\alpha_e \times 10^{24}$ (cm ³)	4.47
Polaron radius <i>r_p</i> (Å)	1.60
Inter-ionic distance <i>r_i</i> (Å)	3.97
Field strength <i>F_i</i> × 10 ⁻¹⁶ (cm ⁻²)	1.16

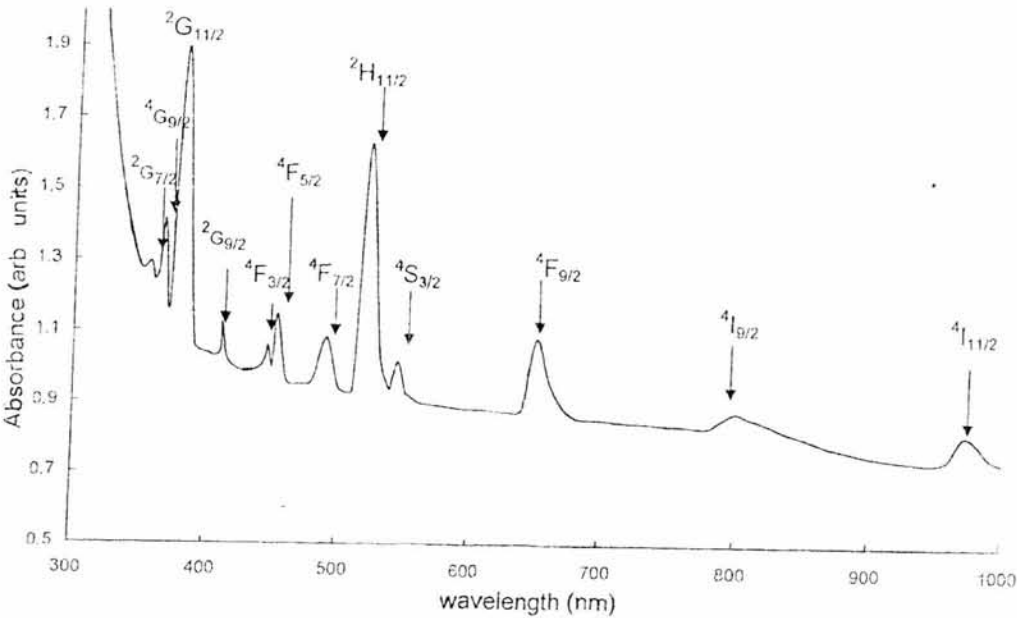


Fig. 1 — Absorption spectrum of Er³⁺ doped PbO-Al₂O₃-B₂O₃ glasses

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$^4I_{5/2} \rightarrow ^4G_{9/2}, ^2G_{7/2}, ^2G_{11/2}, ^2G_{9/2}, ^4F_{3/2}, ^4F_{5/2}, ^4F_{7/2}, ^2H_{11/2}, ^4S_{3/2}, ^4F_{9/2}, ^4I_{9/2}, ^4I_{11/2}$

The transition energies for these transitions are similar to those measured for Er³⁺ ion in other glasses^{13,14}.

The room temperature fluorescence spectrum excited at 380 nm exhibited several transitions as shown in (Fig. 2).

4 Discussion

It is well known that there is a shielding of the 4f electrons of the rare-earth ions and this shielding allow these ions to serve as active centres in solid state laser hosts. These ions exhibit sharp absorption and luminescence transitions as they are weakly perturbed by surrounding ligand atoms. The spectral intensities for the observed bands of these glasses which are often expressed in terms of oscillator strength of forced electronic dipole transitions have been analysed with the help of Judd-Ofelt theory^{15,16} using:

$$f = \frac{8 \pi^2 m c (n_d^2 + 2)^2 v}{3 h (2J + 1) 9 n_d} \sum_{\lambda=2}^6 \Omega_{\lambda} (\psi_j || U^{\lambda} || \psi_j)^2$$

... (1)

where (2J + 1) is the multiplicity of the lower states, m is the mass of the electron and v is the peak absorption in cm⁻¹. The Judd-Ofelt parameters Ω_2 , Ω_4 and Ω_6 were computed by the least square fitting analysis of the experimental oscillator strengths using matrix elements¹⁵ and are presented in Table 2. Experimental values of oscillator strengths were evaluated from the expression:

Table 2 — Absorption band energies, the oscillator strength f for some of the transitions and Judd-Ofelt intensity parameters and spectroscopic quality factor (Ω_4/Ω_6) of Er³⁺ doped PbO-Al₂O₃-B₂O₃ glasses

Absorption	Energy (cm ⁻¹)	$f_{exp} \times 10^6$	$f_{cal} \times 10^6$	J-O parameters $\Omega \times 10^{20}$ (cm ²)
$^4I_{15/2} \rightarrow ^2G_{11/2}$	26440	12.50	13.14	$\Omega_2 = 11.85$
$\rightarrow ^4F_{5/2}$	22084	0.77	0.76	$\Omega_4 = 24.37$
$\rightarrow ^4F_{7/2}$	20408	0.87	0.88	$\Omega_6 = 2.23$
$\rightarrow ^2H_{11/2}$	19230	7.44	7.59	$\Omega_4/\Omega_6 = 10.88$
$\rightarrow ^4S_{3/2}$	18375	0.52	0.43	
$\rightarrow ^4F_{9/2}$	15384	0.67	0.87	
$\rightarrow ^4I_{9/2}$	12500	0.15	0.20	
$\rightarrow ^4I_{11/2}$	10309	0.80	0.53	

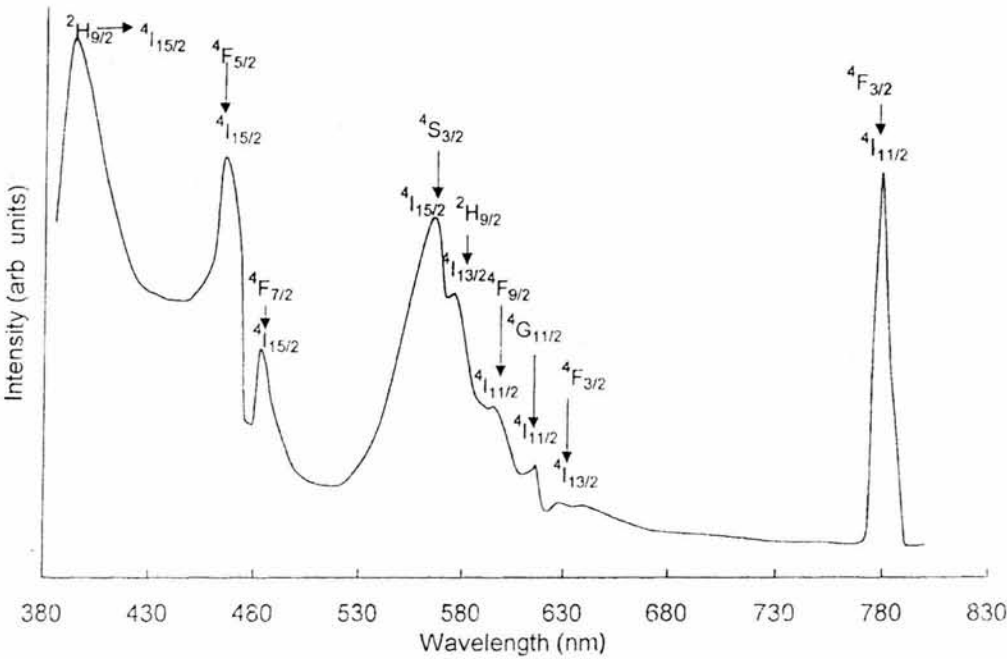


Fig. 2 — Fluorescence spectrum of Er³⁺ doped PbO-Al₂O₃-B₂O₃ glasses

$$f_{\text{exp}} = 2.302 \left(\frac{m c^2}{N_A \pi e^2} \right) \int \epsilon(v) dv \quad \dots(2)$$

where N_A is the Avagadro's number and $\epsilon(v)$ is the molar absorption coefficient determined from Beer's law. The comparison of experimental and theoretical strengths show a reasonable agreement (Table 2). The larger differences observed between the calculated and the experimental values of oscillator strengths for some of the transitions are because of $4f-5d$ mixing¹⁷ which may contribute to intensities with odd values of λ in $\parallel U^\lambda \parallel$ matrix elements which are neglected in Judd- Ofelt model. Using $J-O$ parameters

Ω_λ , the radiative properties of various fluorescence levels observed for the present glasses are determined. The spontaneous emission probability A , for electric dipole transition was calculated using the expression:

$$A(\psi_J, \psi_{J'}) = \frac{64 \pi^2 e^2 v^3}{3 h (2J' + 1)} \frac{n_d (n_d + 2)^2}{9} \sum_{\lambda=2}^6 \Omega_\lambda \parallel U^\lambda \parallel^2 \quad \dots(3)$$

where $(2J' + 1)$ is the multiplicity of the upper state and v is the wavenumber of the fluorescence peak.

Then the total emission probability A_T involving all the intermediate terms is calculated using [Ref. 18].

$$A_T(\psi_J) = \sum_{\psi_{J'}} A(\psi_J, \psi_{J'}) \quad \dots(4)$$

The radiative life time (τ_R) of a state is calculated using the relationship:

$$\tau_R = \frac{1}{A_T(\psi_J)} \quad \dots(5)$$

The fluorescent branching ratio is obtained from the equation:

$$\beta_r(\psi_J, \psi_{J'}) = \frac{A(\psi_J, \psi_{J'})}{A_T(\psi_J)} \quad \dots(6)$$

Finally the stimulated emission cross-sections of the measured fluorescent levels are evaluated using:

$$\sigma^E = \frac{A(\psi_J, \psi_{J'}) \lambda^4}{8 \pi c n_d^2 \Delta \lambda} \quad \dots(7)$$

where λ is the peak position of the emission line and $\Delta \lambda$ is the effective band width of the emission transitions.

The values of the transitions probability $A(\psi_J, \psi_{J'})$, the total transition probability $A_T(\psi_J)$ and the fluorescence branching ratio β_r obtained for some of the luminescence transition are presented in Table 3.

Earlier ESR and optical absorption experiments and simulation studies indicated that the rare earth ions when present in the glass matrices, impose virtually no specific or narrowly defined site preference in the network though there is a possibility for these ions to occupy sites with non-centro symmetric potential¹⁹ which is known to contribute significantly to Ω_2 . However the energy and certain spectral profiles of some transitions in the absorption of Er^{3+} ions throw some light on their coordination. The energy value 19230 cm^{-1} for $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ for Er^{3+} ions in the present system suggest predominantly 8-9 coordination²⁰. Eight coordination for Er^{3+} ions in these glasses may be assumed due to four pair of oxide ions coming from four tetrahedra constituted by AlO_4 or BO_4 units. The presence of BO_4 units in these glasses is confirmed by studying IR spectra of these glasses (Fig. 3). The IR spectrum of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:Er}^{3+}$ glasses recorded in KBr matrices at room temperature shows absorption bands (in addition to the standard bands due to stretching vibrations of B-O bonds of BO_3 units between $1200\text{-}1600 \text{ cm}^{-1}$) at 1083.6 cm^{-1} and 833.6 cm^{-1} which are due to the stretching vibrations of BO_4 units. The presence of even PbO_4 units cannot be

Table 3 — Various radiative properties of Er^{3+} doped $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses

Emission Transition	λ (nm)	$\Delta \lambda$ (nm)	A (s^{-1})	A_T (s^{-1})	τ_R (ms)	β_r %	Emission cross-section $\sigma^E \times 10^{20} (\text{cm}^2)$
$^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$	392.5	39.0	2333	6591	0.15	35.30	0.08
$^4\text{F}_{5/2} \rightarrow ^4\text{I}_{15/2}$	465.0	16.0	1825	6236	0.16	29.52	0.31
$^4\text{S}_{5/2} \rightarrow ^4\text{I}_{15/2}$	564.0	37.0	1526	2834	0.35	53.80	0.24

ruled out in these glasses as there is a presence of some weaker bands in IR spectrum² of these glasses (Fig. 3) around 550 cm^{-1} .

We have also evaluated Ω_λ values for various lanthanide ions (starting from Pr^{3+} to Er^{3+}) doped $\text{PbO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glasses. The Ω_2 values for Pr^{3+} glasses $4.88 \times 10^{-20}\text{ cm}^2$, Ho^{3+} glasses $5.829 \times 10^{-20}\text{ cm}^2$, and Er^{3+} glasses $11.85 \times 10^{-20}\text{ cm}^2$ show an increasing trend with increasing atomic number of Ln^{3+} ions. But according to Krupke's theoretical calculations²¹, the values of Ω_2 for free Ln^{3+} ions should decrease with increasing atomic number. The present discrepancy may be accounted for as being due to the effects of covalency, nephelauxetic and dielectric of the medium²². The Ω_2 value is in general strongly dependent on covalent bonding and on structural changes in the vicinity of Ln^{3+} ions. Ln^{3+} ions may have coordination number 4 to 12 with decreasing trend (or increasing covalency effects) with increasing atomic²³ number z of Ln^{3+} ions. Hence the present Er^{3+} ions may have high coordination number in the present glasses when compared with other Ln^{3+} ions; this may be assumed due to the decreasing bond lengths of metal ligand ions. While Ω_2 is related to short range effects, the parameters Ω_4 and Ω_6 are related to the long range effects. The values of these two parameters viz., Ω_4 and Ω_6 , are in fact strongly dependent on the vibrational frequencies of Ln^{3+} ion linked to the ligand atoms. Earlier detailed studies on rare earth spectroscopy²⁴ revealed that the vibrational transitions are more intense for lower atomic number ions (like Pr^{3+}) and the higher

atomic number ions (like Ho^{3+} , Er^{3+}) of rare earth series and hence higher values of Ω_4 and Ω_6 at the beginning and the end of the series; we have in fact obtained the values of Ω_4 for Pr^{3+} , Ho^{3+} and Er^{3+} glasses as 22.22×10^{-20} , 17.15×10^{-20} and 24.37×10^{-20} respectively. The hypersensitive nature of transitions ${}^2\text{G}_{11/2}$ and ${}^2\text{H}_{11/2}$ may be understood due to strong $4f-5d$ mixing and / or due to the contribution of odd terms of $\|U^\lambda\|$.

The radiative properties of Er^{3+} ions (or any of Ln^{3+} ions) depend on a number of factors such as network former and modifier of the glass. The value of β_r (i.e.) the branching ratio (Table 3) of the luminescence transitions characterise the lasing power of the potential laser transitions. The β_r values obtained for the important lasing transitions ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{F}_{5/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ are found to be comparable to that of alkali aluminoborate glasses¹⁴.

From this study it may be concluded that $J-O$ parameters combined with the photoluminescence spectra of alkali free aluminoborate glasses doped with Er^{3+} have allowed calculations of induced emission transitions and yielded useful information on the radiative properties.

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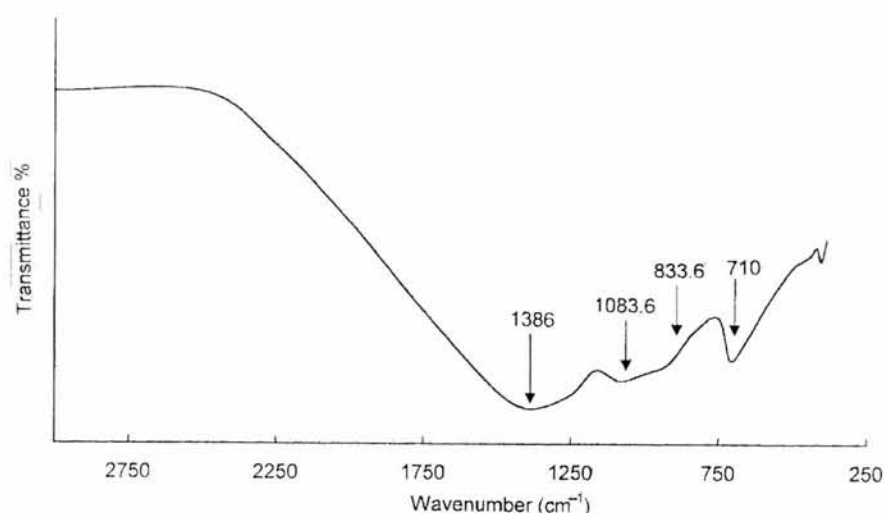


Fig. 3 — Infrared transmission spectra of Er^{3+} doped $\text{PbO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glasses

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