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Optical absorption and fluorescence properties of Er^{3+} in sodium borate glass

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Abstract. **Spectroscopic properties of Er^{3+} ions in sodium borate glass have been studied. The indirect and direct optical band gaps (E_{opt}) and energy level parameters (Racah (E^1, E^2 and E^3), spin-orbit (x_{4f}) and configurational interaction (a)) are evaluated. Spectral intensities for various absorption bands of Er^{3+} doped sodium borate glass are calculated. Using Judd–Ofelt intensity parameters (Ω_2, Ω_4, Ω_6), radiative transition probabilities (A), branching ratios (b) and integrated absorption cross sections (Σ) are reported for certain transitions. The radiative lifetimes (t_R) for different excited states are estimated. From the fluorescence spectra, the emission cross section (s_p) for the transition, ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ is reported.**

Keywords. **Optical band gap; intensity parameter; transition probability.**

1. Introduction

In recent years, much attention has been devoted to the development of infrared and upconversion lasers and optical amplifiers. Many trivalent rare earth ions such as Er^{3+}, Tm^{3+} and Pr^{3+} were doped as luminescent ions earlier in certain hosts (Bjarklev 1993; Snoeks *et al* 1996; Higuchi *et al* 1998; Tsuda *et al* 1999). Among these RE ions, Er^{3+} is recognized as an important ion and Er^{3+} waveguide laser and upconversion laser operations have been achieved previously at room temperature (Whitley *et al* 1991; Roman *et al* 1995), because of the key role in the optical signal amplification for 1·5 μm telecommunication and the capability for emission of radiation at 1·5 μm "eye-safe" wavelength (Gopontsev *et al* 1982; Sudo 1999). Optical transitions of Er^{3+} ions in $ZnCl_2$-based glass have been reported by Shojiya *et al* (1997). Optical transitions and frequency upconversion emission of Er^{3+} doped Ga_2S_3–GeS_2–La_2S_3 glasses have been reported by Higuchi *et al* (1998). Ratnakaram *et al* (Ratnakaram and Sudharani 1997; Ratnakaram *et al* 2002) reported the optical studies of Er^{3+} doped different chlorophosphate and chloroborate glasses. In the present work, the authors have studied the optical absorption and fluorescence spectra of Er^{3+} doped sodium borate glass. Various spectroscopic parameters (Racah (E^1, E^2 and E^3), spin-orbit (x_{4f}) and configurational interaction (a)) of Er^{3+} doped sodium borate glasses are reported. Using Judd–Ofelt intensity parameters (Ω_2, Ω_4 and Ω_6), radiative properties like electric dipole line strengths (S_{ed}), radiative transition probabilities (A), radiative lifetimes (t_R), branching ratios (b) and integrated absorption cross sections (Σ) are reported. From the fluorescence spectrum, emission cross section (s_p) is obtained. The Er^{3+} doped sodium borate glasses were prepared using standard melt quenching technique. The chemicals used in the preparation of the glasses are H_3BO_3, Na_2CO_3 and Er_2CO_3 (all these chemicals are of 99·9% purity). In the glass, we have $70B_2O_3 + 29{\cdot}8Na_2O + 0{\cdot}2Er_2CO_3$. The raw materials were thoroughly mixed in an agate mortar in 5–10 g batches. The mixer was then melted in a specially made clay crucible in temperature ranging from 800–1000°C. The melt was kept at the melting temperature for 30 min. Then the melt was quickly quenched between two smoothly polished brass plates. Glass samples of 1 mm thickness and 1 cm in diameter were obtained. Optical absorption spectrum was recorded using Hitachi U-3400 spectrophotometer and the emission spectrum was obtained from Midac-FT Photoluminescence Spectrophotometer with an excitation wavelength of 512 nm. The refractive index was measured on an Abbe refractometer with a sodium vapour lamp using monobromonaptalene as adhesive coating.

2. Results

The optical band gap in oxide glasses can be determined from the position of the absorption edge. There are two types of optical transitions that can occur at the fundamental absorption edge of crystalline and non-crystalline materials. Using Davis and Mott (1970) theory and from the variation of $(a\hbar w)^{1/2}$ with $\hbar w$ and $(a\hbar w)^2$ with $\hbar w$, optical band gap values (E_{opt}) for both indirect and direct transitions of Er^{3+} doped sodium borate glasses are ob-

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tained. These values are 3·14 and 3·21 eV for indirect and direct transitions, respectively. The variation of $(a\hbar w)^{1/2}$ with $\hbar w$ and $(a\hbar w)^2$ with $\hbar w$ are shown in figures 1a and b, respectively.

The absorption spectrum of Er^{3+} doped sodium borate glass is shown in figure 2. The calculated and observed band positions and their assignments are shown in table 1. The rms deviation between experimental and calculated energies is very small which indicates validity of full matrix diagonalization. Racah (E^1, E^2 and E^3), spin-orbit (x_{4f}) and configurational interaction (a) parameters are evaluated by a least squares fit method using the pro-

Table 1. Experimental and calculated energies (E) (cm^{-1}) and spectral intensities (f) of Er^{3+} doped sodium borate glass.

Energy level	E_{exp}	E_{cal}	f_{exp} (10^{-6})	f_{cal} (10^{-6})
$^4G_{11/2}$	26659	26642	19·14	16·33
$^2G_{9/2}$	24684	24677	0·56	0·54
$^4F_{5/2}$	22216	22190	0·27	0·65
$^4F_{7/2}$	20486	20522	1·56	1·57
$^2H_{11/2}$	19262	19287	6·63	9·23
$^4S_{3/2}$	18310	18302	0·37	0·34
$^4F_{9/2}$	15309	15315	1·96	1·95
rms deviation	± 40		± 1·76	

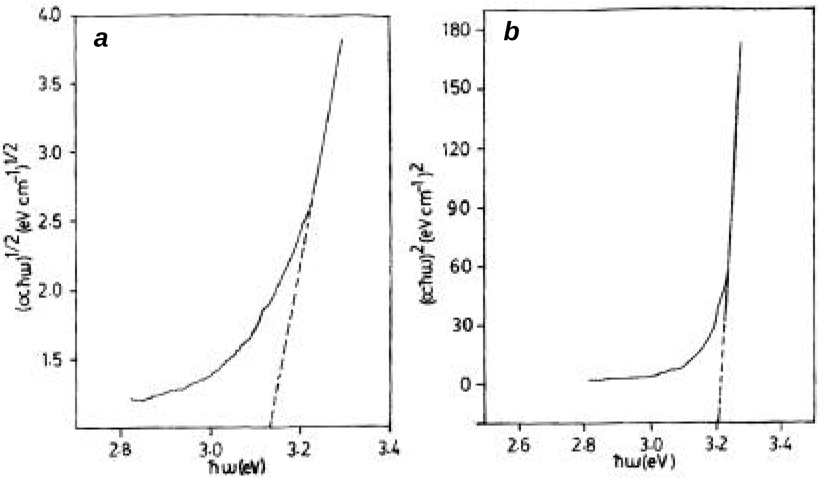

Figure 1. Variation of **a**. $(a\hbar w)^{1/2}$ with $\hbar w$ and **b**. $(a\hbar w)^2$ with $\hbar w$ in Er^{3+} doped sodium borate glasses.

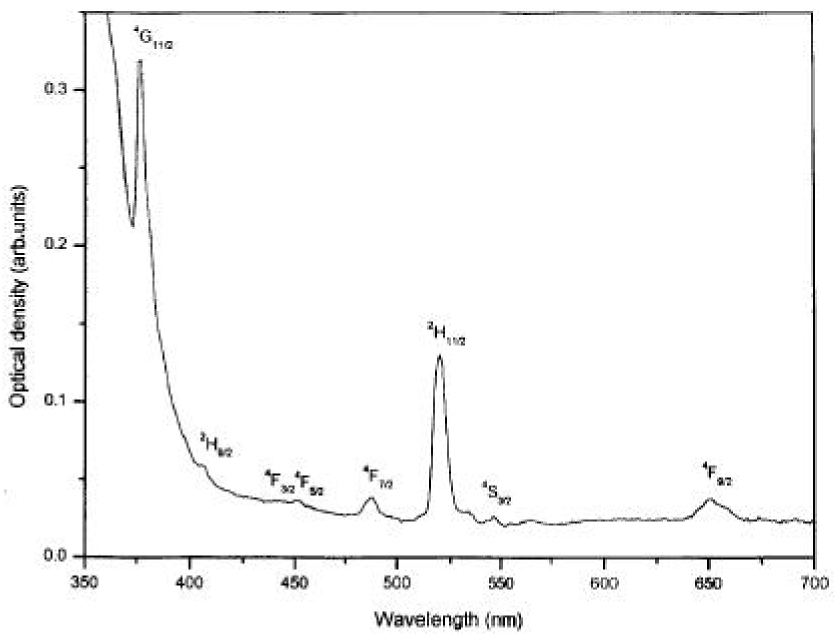

Figure 2. Optical absorption spectrum of Er^{3+} doped sodium borate glass.

Table 2. Electric dipole line strengths (S_{ed}), radiative transition probabilities (A), branching ratios (b) and integrated absorption cross sections (Σ) of Er^{3+} doped sodium borate glass.

Transition	Energy (n) (cm^{-1})	$(S_{ed}/e^2) \times 10^{22}$ (cm^2)	A (s^{-1})	b	$\Sigma \times 10^{18}$ (cm)
${}^4G_{11/2} \rightarrow {}^2H_{9/2}$	1965	237·2	3·4	0	0·51
${}^4F_{3/2}$	4152	12·3	1·7	0	0·06
${}^4F_{5/2}$	4452	13·9	2·3	0	0·07
${}^4F_{7/2}$	6120	76·6	33·4	0·002	0·51
${}^2H_{11/2}$	7355	31·0	23·4	0·001	0·25
${}^4S_{3/2}$	8340	22·6	24·9	0·001	0·20
${}^4F_{9/2}$	11327	270·3	746·7	0·044	3·33
${}^4I_{9/2}$	14250	42·9	236·6	0·014	0·67
${}^4I_{11/2}$	16183	9·8	78·6	0·005	0·17
${}^4I_{13/2}$	19811	131·1	1937·7	0·114	2·82
${}^4I_{15/2}$	26642	388·0	13946·0	0·819	11·24
${}^4F_{5/2} \rightarrow {}^4F_{7/2}$	1668	64·7	1·1	0·001	0·23
${}^2H_{11/2}$	2903	27·0	2·5	0·001	0·17
${}^4S_{3/2}$	3888	4·9	1·1	0·001	0·04
${}^4F_{9/2}$	6875	73·0	90·1	0·045	1·09
${}^4I_{9/2}$	9798	27·5	98·2	0·049	0·59
${}^4I_{11/2}$	11731	17·3	106·1	0·053	0·44
${}^4I_{13/2}$	15359	62·5	860·2	0·429	2·09
${}^4I_{15/2}$	22190	20·4	847·8	0·422	0·99
${}^4F_{7/2} \rightarrow {}^2H_{11/2}$	1235	116·6	0·6	0	0·23
${}^4S_{3/2}$	2220	0·95	0·0	0	0·00
${}^4F_{9/2}$	5207	14·7	5·9	0·002	0·12
${}^4I_{9/2}$	8130	65·5	100·4	0·036	0·87
${}^4I_{1/2}$	10063	62·1	180·3	0·065	1·02
${}^4I_{13/2}$	13691	45·8	429·6	0·156	1·32
${}^4I_{15/2}$	20522	82·9	2045·0	0·740	2·78
${}^4S_{3/2} \rightarrow {}^4F_{9/2}$	2987	2·1	0·3	0	0·02
${}^4I_{9/2}$	5910	36·8	43·4	0·041	0·71
${}^4I_{11/2}$	7843	7·9	21·7	0·021	0·20
${}^4I_{13/2}$	11471	31·4	270·5	0·257	1·18
${}^4I_{15/2}$	18302	20·4	715·1	0·68	1·22
${}^4F_{9/2} \rightarrow {}^4I_{9/2}$	2923	7·8	4·4	0·004	0·29
${}^4I_{11/2}$	4856	162·1	42·3	0·034	1·03
${}^4I_{13/2}$	8484	40·8	56·9	0·046	0·45
${}^4I_{15/2}$	15315	137·8	1129·1	0·916	2·75
${}^4I_{9/2} \rightarrow {}^4I_{11/2}$	1933	27·2	0·4	0·003	0·06
${}^4I_{13/2}$	5561	66·9	26·3	0·177	0·49
${}^4I_{15/2}$	12392	28·1	122·1	0·821	0·45
${}^4I_{11/2} \rightarrow {}^4I_{13/2}$	3628	150·2	13·6	0·105	0·59
${}^4I_{15/2}$	10459	53·2	115·7	0·895	0·61
${}^4I_{13/2} \rightarrow {}^4I_{15/2}$	6831	163·9	85·1	1·000	1·04

Table 3. Total radiative transition probabilities (A_T) (s^{-1}) and radiative lifetimes (t_R) (μs) of certain excited states and branching ratios (b) and integrated absorption cross-sections ($\Sigma \times 10^{18}$ cm^{-1}) of certain transitions of Er^{3+} doped sodium borate glass.

Sl. no.	Excited state	A_T	t_R	Transition	b	Σ
1	$^4G_{11/2}$	17034	58	$^4G_{11/2} \rightarrow {}^4I_{15/2}$	0·82	11·24
2	$^4F_{5/2}$	2007	498	$^4F_{5/2} \rightarrow {}^4I_{13/2}$	0·43	2·09
3	$^4F_{7/2}$	2762	362	$^4F_{7/2} \rightarrow {}^4I_{15/2}$	0·74	2·78
4	$^4S_{3/2}$	1051	951	$^4S_{3/2} \rightarrow {}^4I_{15/2}$	0·68	1·22
5	$^4F_{9/2}$	1233	811	$^4F_{9/2} \rightarrow {}^4I_{15/2}$	0·92	2·75
6	$^4I_{9/2}$	149	2000	$^4I_{9/2} \rightarrow {}^4I_{15/2}$	0·82	0·45
7	$^4I_{11/2}$	129	7734	$^4I_{11/2} \rightarrow {}^4I_{15/2}$	0·89	0·61
8	$^4I_{13/2}$	85	11751	$^4I_{13/2} \rightarrow {}^4I_{15/2}$	1	1·04

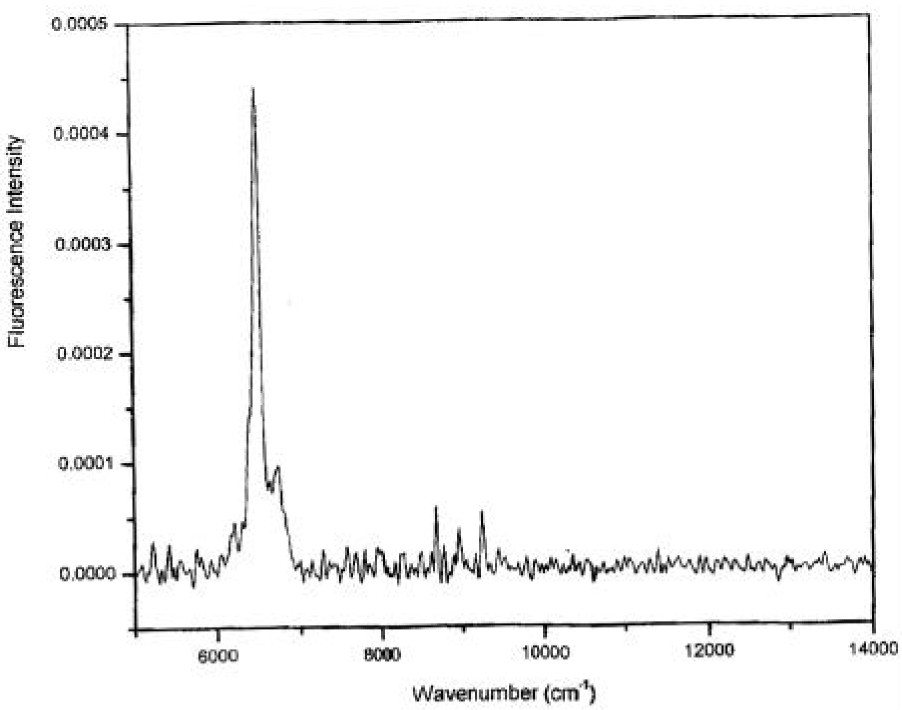

Figure 3. Photoluminescence spectrum of Er^{3+} doped sodium borate glass.

cedure explained by Ratnakaram *et al* (2002) and these parameters are $E^1 = 6769{\cdot}8$ cm^{-1}, $E^2 = 32{\cdot}4$ cm^{-1}, $E^3 = 646{\cdot}6$ cm^{-1}, $x_{4f} = 2380{\cdot}7$ cm^{-1} and $a = 18{\cdot}4$ cm^{-1} for the glass studied. The experimental (f_{exp}) and calculated (f_{cal}) spectral intensities of all the observed bands are obtained using the method described earlier (Ratnakaram *et al* 2002) and are presented in table 1. The rms deviation between the experimental and calculated spectral intensities is small which indicates the validity of the Judd (1962) and Ofelt (1962) theories. As there is some uncertainty in the measurement of the intensities of the bands, $^4F_{5/2} + {}^4F_{3/2}$ and $^4S_{3/2}$, these intensities are not included in the least square fit in calculating the intensity parameters.

The calculated Judd–Ofelt intensity parameters of Er^{3+} doped sodium borate glass are $\Omega_2 \times 10^{20}$ cm$^2 = 6{\cdot}13$, $\Omega_4 \times 10^{20}$ cm$^2 = 1{\cdot}73$ and $\Omega_6 \times 10^{20}$ cm$^2 = 0{\cdot}92$. It is observed that Ω_2 parameter increases with the addition of lithium or potassium to the sodium borate glass matrix (Ratnakaram *et al* 2004) which indicates increase in covalency. Using Judd–Ofelt intensity parameters (Ω_2, Ω_4 and Ω_6) and employing the expressions given in our earlier paper (Ratnakaram *et al* 2002), electric dipole line strengths (S_{ed}), radiative transition probabilities (A), branching ratios (b) and integrated absorption cross sections (Σ) have been calculated and presented in table 2. It is observed that the radiative transition probabilities increased with the addition of lithium or potassium to the sodium borate glass matrix. The radiative lifetimes for the excited states $^4G_{11/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ of Er^{3+} are estimated and presented in table 3. Branching ratios (b) and integrated absorption cross sections (Σ) of certain important transitions of Er^{3+} doped sodium borate glass are also presented in table 3. From the data, it is observed that the magnitude of the transitions, $^4G_{11/2} \rightarrow {}^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^4I_{15/2}$, $^4I_{9/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$, are high in sodium borate glass. The emission spectrum with excitation at 512 nm is shown in figure 3. From the emission spectrum, the stimulated emission cross section (s_p) of the transition, $^4I_{13/2} \rightarrow {}^4I_{15/2}$, has been calculated and it is $1{\cdot}907 \times 10^{-22}$ cm^2.

3. Conclusions

Study of optical absorption and fluorescence spectra of Er^{3+} doped sodium borate glass has been made. Using Judd–Ofelt intensity parameters, radiative properties are estimated. It is observed that covalency of metal ligand bond and radiative transition probabilities are increasing with the addition of lithium or potassium to the sodium borate glass matrix. From the emission spectra, peak stimulated emission cross section is evaluated for the transition, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ and of the erbium glass investigated.

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References

Bjarklev A 1993 in *Optical fibre amplifiers: Design and system applications* (London: Artech House)

Davis E A and Mott N F 1970 *Philos. Mag.* **22** 903

Gopontsev V P, Matitsim S M, Isiner A A and Kravchenko V B 1982 *Opt. Laser Technol.* **14** 189

Higuchi H, Takahashi M, Kawamoto Y, Kadono K, Ohtsuki T, Peyghambarian N and Kitamura N 1998 *J. Appl. Phys.* **83(1)**

Judd B R 1962 *Phys. Rev.* **127** 750

Ofelt G S 1962 *J. Chem. Phys.* **37** 511

Ratnakaram Y C and Sudharani N 1997 *J. Non-Cryst. Solids* **217** 291

Ratnakaram Y C, Viswanadha Reddy A and Chakradhar R P S 2002 *Spectrochemica Acta* **A58** 1809

Ratnakaram Y C, Vijaya Kumar A, Tirupathi Naidu D and Rao J L 2004 *Spectrochemica Acta A* **61** 2169

Roman J E, Camy P, Hempstead M, Brocklesby W S, Nouth S, Beguin A and Lerminiaux Wilkinson J S 1995 *Electron. Lett.* **31** 1345

Shojiya M, Takahashi M, Kanno R, Kawamoto Y and Kadono K 1997 *J. Appl. Phys.* **82** 6259

Snoeks E, van den Hoven G N and Polman A 1996 *IEEE J. Quantum Electron.* **32** 1680

Sudo S 1999 *Erbium doped fibre amplifiers* (Tokyo: Optronics)

Tsuda M, Soga K, Inoue H, Inoue S and Makishima A 1999 *J. Appl. Phys.* **85** 29

Whitley T J, Miller C A, Wyatt R, Brierley M C and Szebesta D 1991 *Electron. Lett.* **27** 1785