

Optical Absorption Studies of Sm³⁺ Ions in Lead Containing Sodium Fluoroborate Glasses

C. MADHUKAR REDDY, G.R. DILLIP, K. MALLIKARJUNA,
SD. ZULFIQAR ALI AHAMED, V. RAMESH KUMAR¹
AND B. DEVA PRASAD RAJU²

Department of Physics, Sri Venkateswara University, Tirupati

¹*Department of Physics, Gout. Degree College, Rajampet*

²*Dept. of Future Studies, Sri Venkateswara University, Tirupati*

E-mail: drdevaprasadraju@gmail.com

ABSTRACT

Lead containing sodium fluoroborate glasses (PbSFB) with molar composition of $20\text{PbO} + 5\text{CaO} + 5\text{ZnO} + 10\text{NaF} + (60 - x)\text{B}_2\text{O}_3 + x\text{Sm}_2\text{O}_3$, ($x = 0.1, 0.25, 0.5, 1.0$ and 2.0 mol%) were prepared and investigated by the XRD, FTIR, optical absorption studies. The XRD pattern of the glasses shows the amorphous nature of the present glass. The FTIR profile has revealed that the glass has both BO_3 and BO_4 units. The various physical properties were measured for the 1.0 mol % Sm^{3+} doped PbSFB glasses. Band gap has been calculated based on the glasses UV absorption spectra. The absorption transitions in the UV-VIS-NIR regions were assigned to different transitions from the ${}^6\text{H}_{5/2}$ ground state to various excited states. The observed and calculated oscillator strengths are found to be in reasonable agreement with one another. The small δ_{osc} deviation of 0.7610^{-6} between the experimental and calculated oscillator strengths of the absorption bands indicates a good fit. Judd-Ofelt theory was applied to the experimental oscillator strengths to evaluate the phenomenological J-O intensity parameters Ω_λ ($\lambda = 2, 4$ and 6). The derived J-O intensity parameters are $\Omega_2 = 3.2910^{-20}\text{cm}^2$, $\Omega_4 = 9.1 \times 610^{-20}\text{cm}^2$, $\Omega_6 = 5.2 \times 810^{-20}\text{cm}^2$. The tendency of the J-O parameters in the present glass is found to be in the order $\Omega_4 > \Omega_6 > \Omega_2$. Thus the higher

magnitude of Ω_2 in the present work indicates the increase of covalent bonding and suggests that the Sm^{3+} ion possess higher site symmetry in PbSFB glass host. The reasonably high value of spectroscopic quality factor = 1.75, predicts efficient stimulated emission in the present host.

Keywords: Glasses; Rare earths, Judd Ofelt theory, Fluorescence, Lifetimes, Energy transfer

INTRODUCTION

Over the past several years, trivalent lanthanide ions doped heavy metal oxide based glasses have been prepared and investigations on the optical absorption and fluorescence studies of these glasses are found wide commercial applications in the fields of lasers and telecommunications. Efficient laser hosts can be realize using heavy metal oxide glasses in view of their low phonon energy [1]. Host glasses with low phonon energies allow large radiative transition rates that are useful for the design and development of optical devices such as up converters, light emitting diodes (LEDs), fiber amplifiers, memory devices etc. In this direction a great amount of research has been carried out to develop new glass matrices containing rare earth (RE) ions

Among RE ions, the Sm^{3+} ion is one of the most interesting ions for analyzing the fluorescence properties because of its use in high density optical storage, under sea communication, color displays and visible solid state lasers. Especially, glasses doped with Sm^{3+} ions were extensively investigated by optical spectroscopy to characterize these materials for optical devices applications [2, 3].

In the present work, we have studied the XRD, FTIR and absorption studies of Sm^{3+} ions with different concentrations in PbSFB glasses. From the absorption analysis, the oscillator strengths, the radiative lifetimes and branching ratios for different excited levels have been obtained by applying Judd-Ofelt theory [4, 5] and are compared with the experimental results. An attempt was made to assess the potential of Sm^{3+} doped PbSFB glasses as laser active materials.

EXPERIMENTAL METHOD

The chemical composition of different concentrations of Sm^{3+} -doped PbSFB : $20\text{PbO} + 5\text{CaO} + 5\text{ZnO} + 10\text{NaF} + (60 - x)\text{B}_2\text{O}_3 + \text{Sm}_2\text{O}_3$, where $x = 0.1, 0.25, 0.5, 1.0$ and 2.0 mol% glasses were prepared by melt quenching method. Approximately 10 gm batches of chemicals were mixed and grinded in required proportions in an agate mortar. The mixture was taken into a porcelain crucible

and kept for melting at a temperature 950°C in high temperature furnace at ambient atmosphere. After 1 h, the melt was quenched on a pre heated brass plate at 360°C and are kept for annealing for 8h at the same temperature. The glasses were shaped and polished to measure their physical and optical properties.

The X-ray diffraction (XRD) profile using Seifert X-ray diffractometer and FTIR spectrum in the range $450\text{--}4000\text{ cm}^{-1}$ using Perkin – Elmer Spectrum One FTIR spectrophotometer was recorded. Room temperature visible and near infrared absorption spectra for 1.0 mol% Sm^{3+} -doped *PbSFB* glass were recorded using Varian Cary 5E UV-VIS-NIR spectrophotometer in the wavelength region $450\text{--}1800\text{ nm}$.

RESULTS AND DISCUSSION

XRD and FTIR Spectral Studies

The absence of diffraction peaks in XRD pattern indicates the amorphous nature of Sm^{3+} -doped *PbSFB* glass shown in Fig. 1.

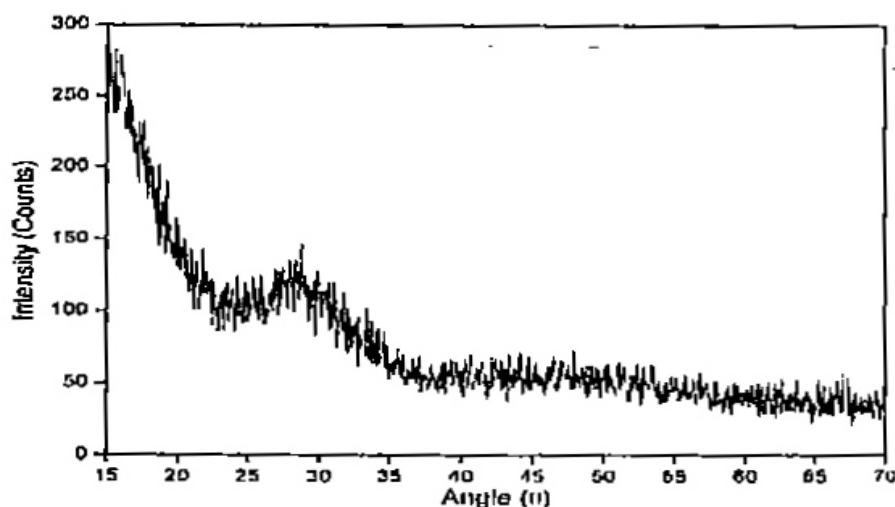


Fig. 1: XRD Pattern of 1.0 mol% Sm^{3+} - Doped *PbSFB* Glasses

The transmission spectrum of 1.0 mol% Sm^{3+} -doped *PbSFB* glass in the IR region $450\text{--}4000\text{ cm}^{-1}$ is shown in Fig. 2. The peak at 497 cm^{-1} could be due to lose BO_4 units [6]. The bands at 708 and 975 cm^{-1} could be due to the bending and stretching vibrations of BO_4 , while the peak around 1296 cm^{-1} is due to B-O stretching vibrations of BO_3 units [7]. The peak around 1636 cm^{-1} may be due to asymmetric stretching relaxation of the B-O bond of trigonal

BO_3 units [8]. Similarly the well known peaks in the region $2700\text{-}3400\text{ cm}^{-1}$ are due to OH bond vibrations [9].

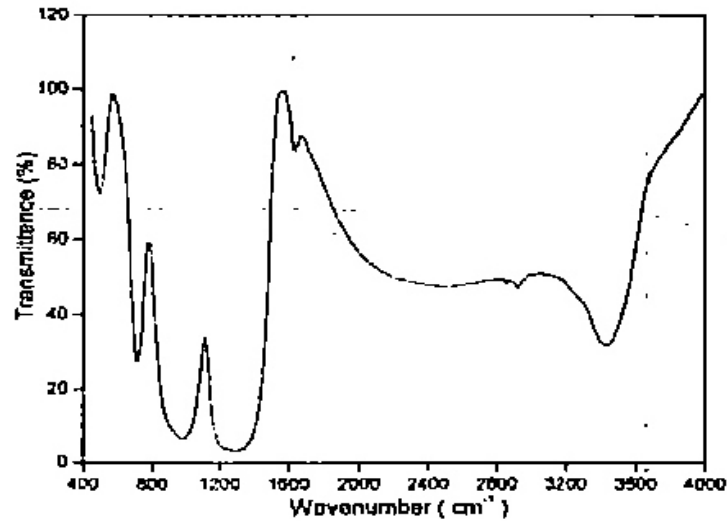


Fig. 2: FTIR spectrum of 1.0 mol% Sm^{3+} -doped *PbSFB* glasses.

Optical Absorption Spectra

The optical absorption spectra of 1.0 mol% Sm^{3+} -doped *PbSFB* glass measured at room temperature in near infrared region is shown in Fig. 3. The assignment of absorption transitions has been done based on the earlier literature[10].

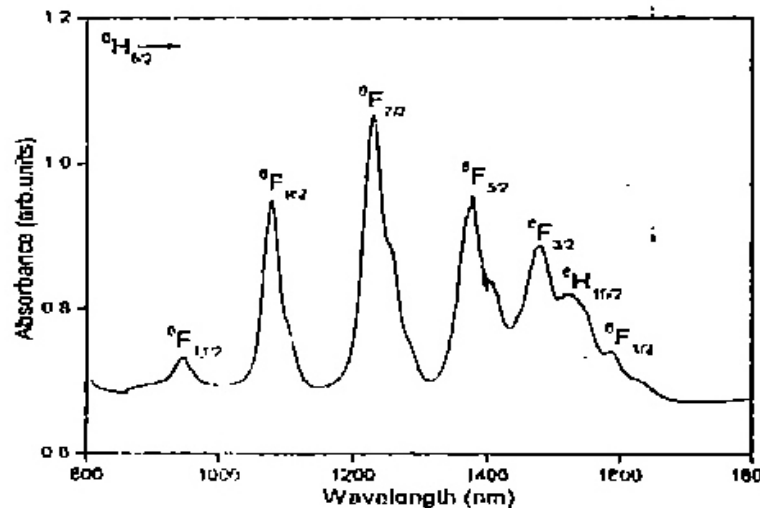


Fig. 3: NIR Absorption Spectra of 1.0 mol% Sm^{3+} -Doped *PbSFB* Glasses.

Optical Band Gap

The optical band gap is an important parameter for describing solid-state materials. The optical band gap is calculated from the absorption spectrum using the Tauc equation [11], $\alpha(\nu) = A[(h\nu - E_g)/h\nu]^2$

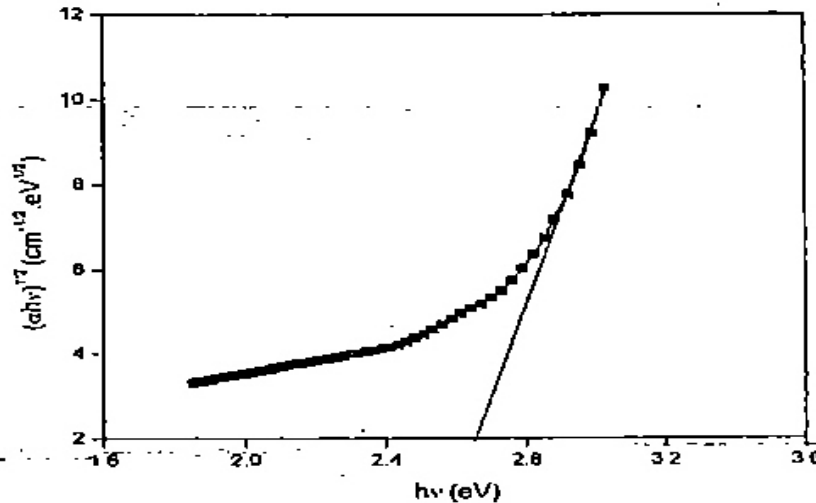


Fig. 4: Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for 1.0 mol% Sm^{3+} -doped *PbSFB* glasses.

Where $\alpha(\nu)$ is the absorption coefficient, A is a constant and (E_g) is the optical band gap determined by extrapolating from the linear region of plots of $(\alpha h\nu)^{1/2}$ against $h\nu$. The value of the optical band gap (E_g) is found to be 2.64 eV for 1.0 mol% Sm^{3+} -doped *PbSFB* glass, which was determined by plotting the graph between $(\alpha h\nu)^{1/2}$ and $h\nu$ from the absorption spectrum as shown in Fig. 4.

J-O Parameters and Radiative Properties

The intensity of an absorption band is expressed in terms of its oscillator strength [12]. From the absorption spectra the experimental oscillator strengths (f_{exp}) are determined. Calculated oscillator strengths (f_{cal}) and J-O intensity parameters are determined by using least squares fit method. The experimental and calculated oscillator strengths of observed absorption bands along with δ_{ms} deviation are tabulated in Table 1. The small deviation of 0.76×10^{-6} between the experimental and calculated oscillator strengths of the absorption bands indicates a good fit. The derived J-O parameters are $\Omega_2 = 3.2 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 9.16 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 5.28 \times 10^{-20} \text{ cm}^2$. The tendency of the J-O parameters in the present glass is found to be in the order

$\Omega_4 > \Omega_6 > \Omega_2$. These J-O parameters are host dependent and are important for the investigation of glass structure, transition rates of rare-earth ion energy levels and bonding in the vicinity of RE ions. Table 2 presents the comparison of J-O intensity parameters, their trend and spectroscopic quality factors of Sm^{3+} ions in *PbSFB* glass with different hosts.

Table 1: Experimental and Calculated Oscillator Strengths ($\times 10^{-6}$) for 1.0 mol% Sm^{3+} -doped *PbSFB* Glass

Transition	Energy (cm^{-1})	f_{exp}	f_{cal}
${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{1/2}$	6293	0.57	1.03
${}^6\text{H}_{15/2}$	6540	1.74	0.04
${}^6\text{F}_{3/2}$	6757	3.74	3.01
${}^6\text{F}_{5/2}$	7252	4.77	6.08
${}^6\text{F}_{7/2}$	8130	7.32	7.53
${}^6\text{F}_{9/2}$	9268	4.97	4.78
${}^6\text{F}_{11/2}$	10582	1.26	0.76
	$\delta_{Tm2} = 0.76 \times 10^{-6}$		

Table 2: Comparison of J-O Intensity Parameters ($\times 10^{-20} \text{ cm}^2$), their Trends and Spectroscopic Quality Factors ($X = \Omega_4/\Omega_6$) for Sm^{3+} Ion in Different Glass Hosts

Glass system	Ω_2	Ω_4	Ω_6	X
LCZSFB[Present glass]	3.29	9.16	5.28	1.75
ZBLAN [16]	2.15	3.05	1.56	1.96
BPS30 [13]	2.96	5.73	3.25	1.76
Fluorozirconate [17]	2.37	4.24	2.99	1.41

In general, the intensity parameter Ω_2 is related to the covalency, structural change and symmetry of ligand field around the Sm^{3+} site [13]. On the other hand, Ω_4 and Ω_6 values depend on the bulk properties such as viscosity and dielectric of the media and are also affected by the vibronic transitions of the RE ions bound to the ligand atoms [14]. Among the three Ω_i parameters the value of Ω_2 is relatively large for oxide glasses, smaller for fluoride glasses while intermediate values are noticed for oxyfluoride glasses. This implies that Ln-O covalency decreases when pure oxide glasses are modified with fluorine content [15]. Thus the higher magnitude of Ω_2 in the present work indicates the increase of covalent bonding and suggests that the Sm^{3+} ion

possess higher site symmetry in *PbSFB* glass host. Jacob and Weber [15] reported that the magnitude of spectroscopic quality factor $X = \Omega_4/\Omega_6$ is used to characterize the stimulated emission in any host glass matrix. The reasonably high value of spectroscopic quality factor $X = 1.75$, predicts efficient stimulated emission in the present host, and is comparable to other Sm³⁺-doped glass systems as presented in Table 2. Once the values of Ω_i are obtained, the other radiative parameters such as electric dipole line strength (S_{ed}), magnetic dipole line strength (S_{md}), spontaneous transition probabilities (A_R), total transition probability (A_T), radiative lifetime (ρ_R) and branching ratios (β_R) corresponding to different emission channels from ⁴G_{5/2} level have also been calculated and are presented in Table 3.

Table 3: Radiative Properties such as Peak Emission Wavelength (λ_p) Electric (s_{ed} , $\times 10^{-22}$ cm²) and Magnetic (s_{md} , $\times 10^{-22}$ cm²) dipole line Strengths, Radiative Transition Probabilities (A_R , s⁻¹), Total Radiative Transition Probability (A_T , s⁻¹), Radiative Lifetimes (τ_R , ms) and Branching Ratios (β_R) for 1.0 mol% Sm³⁺-Doped *PbSFB* Glass

Transition	S_{ed}	S_{md}	A_R	β_R
⁶ F _{11/2}	0.35	0	0.64	0.001
⁶ F _{9/2}	0.97	0	2.93	0.005
⁶ F _{7/2}	1.66	0.27	8.60	0.014
⁶ F _{5/2}	3.92	0.66	26.20	0.043
⁶ F _{3/2}	0.45	0.85	9.00	0.015
⁶ H _{15/2}	0.11	0	0.70	0.001
⁶ F _{1/2}	0.33	0	2.26	0.004
⁶ H _{13/2}	1.13	0	10.70	0.018
⁶ H _{11/2}	5.96	0	72.59	0.120
⁶ H _{9/2}	10.87	0	173.50	0.288
⁶ H _{7/2}	12.61	0.58	264.88	0.440
⁶ H _{5/2}	0.65	0.57	31.02	0.051
	$A_T = 603$	$\tau_R = 1.66$		

The radiative transition rates (A_R) and branching ratios (β_R) have been determined for the ⁴G_{5/2} level of 1.0 mol% Sm³⁺-doped *PbSFB* glass, and are presented in Table 3. From the values of radiative transition probabilities of Table 3, it is noted that ⁴G_{5/2} → ⁶H_{7/2} transition has highest radiative transition rate compared to other transitions. Hence this transition is very useful for laser emission. The

predicted branching ratios are found to be high for those transitions having A_R values. The levels having the relatively large values of A_R , β_R and energy gap to the next lower level may exhibit laser action. The contribution of these transitions to the total branching ratio is nearly 99%, thereby suggesting that these transitions have the most potential for visible laser action for 1.0 mol% Sm^{3+} ions in *PbSFB* glass.

CONCLUSION

The absorption and fluorescence studies of Sm^{3+} ions doped in *PbSFB* glasses have been studied. From the analysis of optical absorption the oscillator strengths, the J-O intensity parameters, radiative transition rates, branching ratios and radiative lifetimes are calculated and are found to be comparable with other reported values. Usually, a good material for a laser emission should have high radiative transition rates and high branching ratios. Based on the physical and optical properties such as strong visible emissions and high branching ratios, it is concluded that 1.0 mol% Sm^{3+} ions doped *PbSFB* glass may be used as luminescent novel optical materials for the development of lasers and photonic devices operating in the visible region.

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REFERENCES

1. P. Srivastava, S.B. Rai, D.K. Rai, *Spectrochim. Acta. Part A.* 60 (2004) 637-642.
2. M. Dejneka, E. Snitzer, R.E. Riman, *J. Lumin.* 65 (1995) 227-245.
3. R. Van Deun, K. Binnemans, C. Gorller-Walrand, J.L. Adam, *J. Alloy. Compd.* 283 (1999) 59-65.
4. B.R. Judd, *Phys. Rev.* 127 (1962) 750-761.
5. G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511-519.
6. N. Syam Prasad, K.B.R. Varma, *Mater. Sci. Eng. B90* (2002) 246-253.
7. S.G. Motke, S.P. Yawale, S.S. Yawale, *Bull. Mater. Sci.* 25 (2002) 75-78.
8. G. Lakshminarayana, S. Buddhudu, *Spectrochim. Acta Part A.* 62 (2005) 364-371.
9. J. Suresh Kumar, K. Pavani, A. Mohan Babu, Neeraj Kumar Giri, S.B. Rai, L. Rama Moorthy, *J. Lumin.* 130 (2010) 1916-1923.

10. B.C. Jamaliah, J. Suresh Kumar, A. Mohan Babu, T. Suhasini, L. Rama Moorthy, *J. Lumin.* 129 (2009) 363-369.
11. R. Jose, T. Suzuki, Y. Ohishi *J. Non. Cryst. Solids.* 352 (2006) 5564-5571.
12. M.B. Saisudha, J. Ramakrishna, *Phys. Rev. B* 53 (1996) 6186-6196.
13. S. Tanabe, T. Ohayagi, N. Soga, T. Hanada, *Phys. Rev. B* 46 (1992) 3305-3310.
14. W.F. Krupke, *Phys. Rev.* 145 (1966) 325-337.
15. R.R. Jacobs, M.J. Weber, *IEEE J. Quantum Electron.* 12 (1976) 102-111.
16. L.J.F. Broer, C.J. Gorter, J. Hoogschagen, *Physica* 11. (1945) 231-250.
17. M. Canalejo, R. Cases, R. Alcalá, *Phys. Chem. Glass.* 29 (1988) 187-191.