

Luminescence studies of Sm^{3+} ion in $\text{LiF-MO-B}_2\text{O}_3$ (M = Ca, Cd, Ba and Pb) glasses

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ABSTRACT: Alkali fluoroborate glasses mixed with different network modifying ions, we may expect the structural modifications and local field variations. The present study is to investigate their optical properties after incorporating a rare earth ion, Sm^{3+} in them. Samarium ion exists in Sm^{3+} and Sm^{2+} states but between these two states, Sm^{3+} is found to be more stable. The optical absorption spectrum of Sm^{3+} doped $\text{LiF-MO-B}_2\text{O}_3$ glasses have exhibited electronic transition: ${}^6\text{H}_{5/2} \rightarrow {}^4\text{I}_{11}, {}^4\text{I}_{13/2}, {}^4\text{G}_{9/2}, {}^6\text{P}_{5/2}, {}^4\text{F}_{7/2}, {}^6\text{P}_{7/2}, {}^4\text{D}_{5/2}, {}^4\text{K}_{17/2}$. The room temperature fluorescence spectra these glasses excited at 450 nm has exhibited the following transitions ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}, {}^6\text{H}_{7/2}, {}^6\text{H}_{9/2}$. The radiative properties viz., the spontaneous emission probability A , the total emission probability A_T involving all the intermediate terms, the radiative life time (τ_R) and the fluorescent branching ratio β_r and the stimulated emission cross section σ_p^E of various fluorescence levels observed for the present glasses are determined. Analysis of these results, the possibility for use of these glasses lasing emission is discussed.

KEYWORDS: Alkali fluoroborate glass, JO Parameters, Emission probability, The radiative life time, Fluorescent branching ratio.

I. INTRODUCTION

Alkali fluoroborate glasses in particular are advantageous as laser hosts in view of their optical transparency over a wide range of wavelength. In addition, these glasses possess a very lower rate of crystallization, high transparency and resistant to moisture. It is therefore felt worthwhile to investigate their optical properties after incorporating a rare earth ion, Sm^{3+} in them. Samarium ion exists in Sm^{3+} and Sm^{2+} states but between these two states, Sm^{3+} is found to be more stable. This ion has $4f^5$ electronic configuration with ${}^6\text{H}_{5/2}$ ground state. Further when these glasses are mixed with different network modifying ions, we may expect the structural modifications and local field variations around Sm^{3+} ion; such changes may have strong bearing on various luminescence transitions of Sm^{3+} ions, in $\text{LiF-MO-B}_2\text{O}_3$ glasses (where MO stands for CaO, CdO, BaO and PbO).

II. EXPERIMENTAL METHODS OF PREPARATION OF GLASSES

From the approximate glass forming region for the present ternary $\text{LiF-MO-B}_2\text{O}_3$ system seems we have chosen following composition for Sm^{3+} doping.

The details of the glasses used for the present studies are:

Glass 1: 20LiF - 4 CaO - 75 B_2O_3 - 1.0 Sm_2O_3

Glass 2: 20LiF - 4 CdO - 75 B_2O_3 - 1.0 Sm_2O_3

Glass 3: 20LiF - 4 BaO - 75 B_2O_3 - 1.0 Sm_2O_3

Glass 4: 20LiF - 4 PbO - 75 B_2O_3 - 1.0 Sm_2O_3

The glasses used for the present study are prepared by the melting and quenching techniques [1-3]. The starting materials used for the preparation of the present glasses were Analytical grade reagents of H_3BO_3 , LiF, CaO, CdO, BaO, PbO and Sm_2O_3 ; the appropriate amounts of these compounds were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a PID temperature controlled furnace. The glasses were melted in the temperature range 900°C for a $\frac{1}{2}$ hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature. The samples were subsequently annealed at 300°C in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the electrical and optical properties are 1 cm x 1 cm x 0.2 cm.

III. PHYSICAL PARAMETERS

From the measured values of the density (d), refractive index (n_d) and calculated average molecular weight (\bar{M}), physical parameters such as Sm^{3+} ion concentration (N_i), molar refractivity (R_M), molecular polarisability (α_e), Polaron radius (r_p), mean Samarium ion separation distance (r_i), and the field strength (F_i) which are useful for understanding various radiative properties of Sm^{3+} doped glasses are evaluated and presented in Table 1.

Table 1: Various physical properties of Sm^{3+} doped LiF- (MO)- B_2O_3 glasses

Property	CaO	Glass 1 CdO	Glass 2 BaO	Glass 3 PbO	Glass 4
Refractive index (n_d)		1.513	1.531		1.535 1.537
		(Measured at $\lambda=589.3$ nm)			
Density d (g/cm^3)		2.589	2.828	2.706	2.82
Avg. mol. Weight (\bar{M})		61.45	65.06	66.31	69.81
Sm^{3+} ion concentration N_i		2.54 (10^{22} ions/ cm^3)	2.618	2.458	2.433
Polaron radius r_p (A°)		1.37	1.35	1.38	1.39
Inter-ionic distance r_i (A°)		3.40	3.37	3.44	3.45
Field strength F_i (10^{-16}cm^{-2})		1.596	1.629	1.562	1.551

IV. RESULTS

4.1 Optical Absorption

The optical absorption spectrum of Sm^{3+} doped LiF-MO- B_2O_3 glasses recorded at room temperature in the wavelength region 300-2500 nm has exhibited eight absorption bands, all from the ground state $^6\text{H}_{5/2}$. (Figs1 to 4) gives the absorption spectra of these glasses; these levels are assigned to the following appropriate electronic transition: $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}, ^4\text{I}_{13/2}, ^4\text{G}_{9/2}, ^6\text{P}_{5/2}, ^4\text{F}_{7/2}, ^6\text{P}_{7/2}, ^4\text{D}_{5/2}, ^4\text{K}_{17/2}$. The spectral intensities for the prominent observed bands of these glasses which can be expressed in terms of oscillator strength of forced electronic dipole transitions have been analyzed with the help of Judd-Ofelt theory.

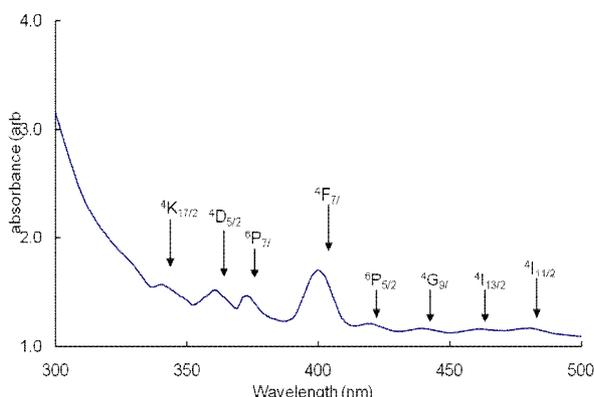


Fig. 1. Optical absorption spectrum LiF-CaO- B_2O_3 glasses doped with Sm^{3+} ions recorded at room temperature. All the transitions are from the ground state $^6\text{H}_{5/2}$

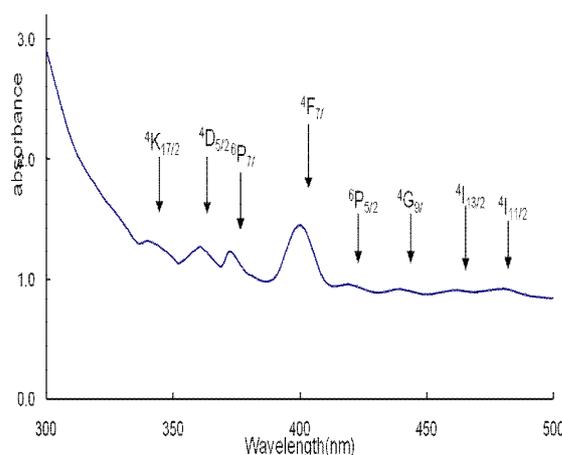


Fig. 2. Optical absorption spectrum LiF-CdO- B_2O_3 glasses doped with Sm^{3+} ions recorded at room temperature. All the transitions are from the ground state $^6\text{H}_{5/2}$

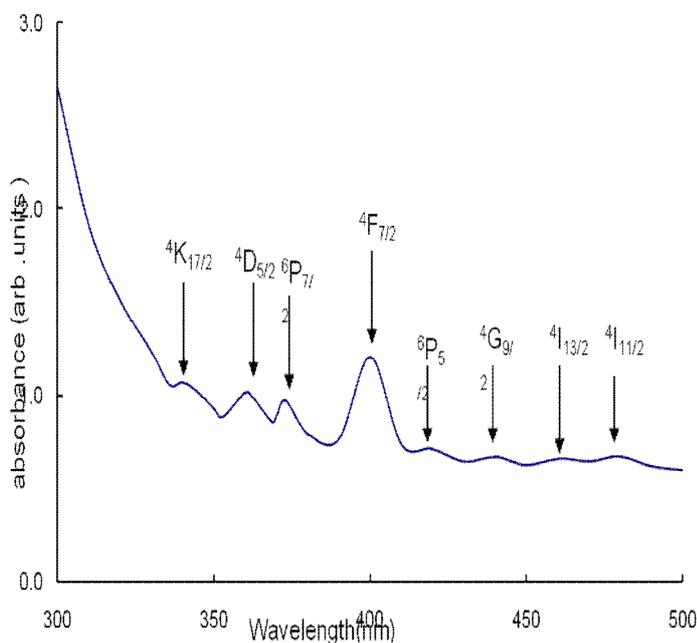


Fig. 3 Optical absorption spectrum LiF-BaO-B₂O₃ glasses doped with Sm³⁺ ions recorded at room temperature. All the transitions are from the ground state ⁶H_{5/2}

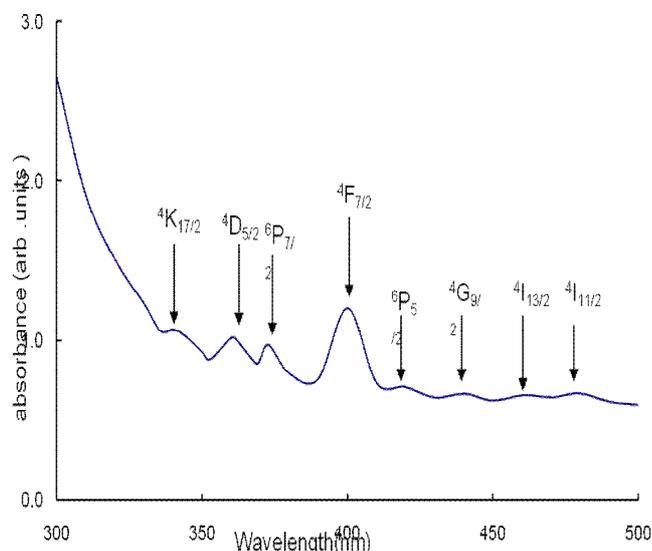


Fig. 4 Optical absorption spectrum LiF-PbO-B₂O₃ glasses doped with Sm³⁺ ions recorded at room temperature. All the transitions are from the ground state ⁶H_{5/2}

By performing least square fit analysis, the electric dipole line strength S_{ed} , the oscillator strength f_{exp} for some transitions and Judd – Ofelt intensity parameters Ω_{λ} for these glasses were evaluated and these parameters are presented in Tables 2 and 3.

Table 2: The absorption band energies and the oscillator strength (f) for some transitions of Sm³⁺: LiF- (MO)-B₂O₃ glasses

Transition	Glass-1 (CaO)			Glass-2 (CdO)			Glass-3 (BaO)			Glass-4 (PbO)		
	Energy (cm) ⁻¹	$f_{exp} \times 10^{-6}$	$f_{theri} \times 10^{-6}$	Energy (cm) ⁻¹	$f_{exp} \times 10^{-6}$	$f_{theri} \times 10^{-6}$	Energy (cm) ⁻¹	$f_{exp} \times 10^{-6}$	$f_{theri} \times 10^{-6}$	Energy (cm) ⁻¹	$f_{exp} \times 10^{-6}$	$f_{theri} \times 10^{-6}$
⁶ H _{5/2} → ⁴ I _{11/2}	20833	1.36	1.09	20838	1.07	0.86	20843	0.89	0.72	20853	0.7	0.6
⁶ H _{5/2} → ⁴ I _{13/2}	21739	1.06	1.9	21744	0.83	1.59	21749	0.69	1.3	21759	0.6	1.1
⁶ H _{5/2} → ⁴ G _{9/2}	22727	2.35	5.9	22732	1.85	4.63	22737	1.53	3.8	22747	1.35	3.3
⁶ H _{5/2} → ⁶ P _{5/2}	23810	2.84	4.75	23815	2.25	3.78	23820	1.89	3.21	23830	1.68	2.8
⁶ H _{5/2} → ⁴ F _{7/2}	25000	1.81	1.19	25005	1.53	0.99	25010	1.38	0.87	25020	1.27	0.8
⁶ H _{5/2} → ⁶ P _{7/2}	26824	0.98	0.69	26829	0.81	0.57	26834	0.72	0.50	26844	0.65	0.45
⁶ H _{5/2} → ⁴ D _{5/2}	27670	10.1	9.7	27675	8.4	8.9	27680	7.4	8.5	27690	6.7	8.1
⁶ H _{5/2} → ⁴ K _{17/2}	29411	2.8	6.56	29416	2.34	5.03	29421	2.07	4.11	29431	1.88	3.53

The bonding parameter, (δ'), defined as [4,5]

$$\delta' = [(1 - \bar{\beta}) / \bar{\beta}] \times 100, \tag{1}$$

has also been computed for all the glasses. In the above equation, $\bar{\beta} = \sum_{i=1}^N \beta_i / N$ and β (the nephelauxetic ratio) = v_c / v_a . v_c and v_a are the energies in cm⁻¹ of the corresponding transitions in the complex and aquo-ion respectively and N refers to the number of levels used to compute $\bar{\beta}$ values. The computation shows the highest δ' value for CaO followed by PbO modifier glass (Table 3).

Table 3: J-O parameters of Sm³⁺ doped LiF- (MO)-B₂O₃ glasses

Glass	Ω_2 (x10 ⁻²⁰) (cm ²)	Ω_4 (x10 ⁻²⁰) (cm ²)	Ω_6 (x10 ⁻²⁰) (cm ²)	(Ω_4 / Ω_6)	Bonding parameter, δ^1
Glass 1(Cao)	27.8	4.6	1.5	3.066	- 0.02
Glass 2 (Cdo)	24.0	3.56	1.26	2.825	- 0.04
Glass 3 (Bao)	23.5	2.91	1.1	2.645	- 0.06
Glass 4 (Pbo)	22.4	2.5	0.99	2.525	- 0.10

The larger the value of δ , the larger is the covalent environment of Sm³⁺ ions in the glass matrix. Among the three alkaline earth oxide (CaO, CdO, BaO) modifier glasses doped with Sm³⁺ ions, the highest values of δ obtained for CaO mixed glass (Glass 1) glasses indicate the highest covalent environment of Sm³⁺ in this glass. The J-O parameters have been observed to be in the following order for all the glasses $\Omega_2 > \Omega_4 > \Omega_6$. The collection of the data on Ω_λ parameters of Sm³⁺ ion in various glass matrices is shown in Table 4 along with the comparison of the parameters for each glass host.

4.2 Fluorescence Properties

The room temperature fluorescence spectra of Sm³⁺: LiF- (MO)-B₂O₃ glasses excited at 450 nm has exhibited the following transitions (Fig 5 to 8). $^4G_{5/2} \rightarrow ^6H_{5/2}, ^6H_{7/2}, ^6H_{9/2}$. The radiative properties viz., the spontaneous emission probability A, the total emission probability A_T involving all the intermediate terms, the radiative life time (τ_R) and the fluorescent branching ratio β_r and the stimulated emission cross section σ_p^E of various fluorescence levels observed for the present glasses are determined. (Figs 5 to 8). Similar transitions have been observed with slight deviations in the peak positions in the spectra of other two glasses also. Using the J-O parameters the radiative properties such as radiative transition probability A, total radiative transition probability A_T, the branching ratio β_r for these glasses have been calculated and presented in Table 5. The measured wavelength λ of the peak, half width $\Delta\lambda$ and the computed value of the stimulated emission cross section σ_p^E for two prominent emission transitions viz., $^4G_{5/2} \rightarrow ^6H_{5/2}, ^6H_{7/2}, ^6H_{9/2}$ are also presented in Table 5 for all the four Sm³⁺ doped glasses.

V. DISCUSSION

The transition energies for optical absorption can be analyzed by diagonalising the full matrices corresponding to the Hamiltonian $H = H_c + H_{so} + H^1$ -----2
In equation 2 H_c interaction between pairs of electron, which can be expressed in terms of the Racah parameters ($E^K, K = 0, 1, 2, 3$). H_{SO} and H^1 stand for spin orbital coupling and configuration interaction respectively. The matrix elements of the electrostatic interaction are reported by Nielson and Koster [6]. The matrix elements due to spin orbit coupling are also reported in the literature [7, 8]. The configuration interaction terms were well evaluated by Wybourne [9].

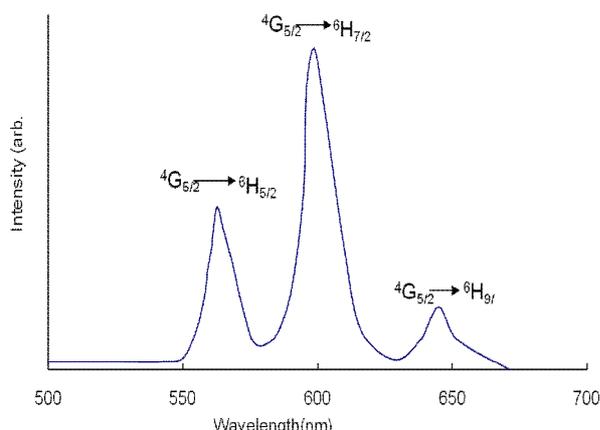


Fig. 5 Photoluminescence spectrum of Sm³⁺ doped LiF-CaO-B₂O₃ glasses ($\lambda_{exc} = 400\text{nm}$)

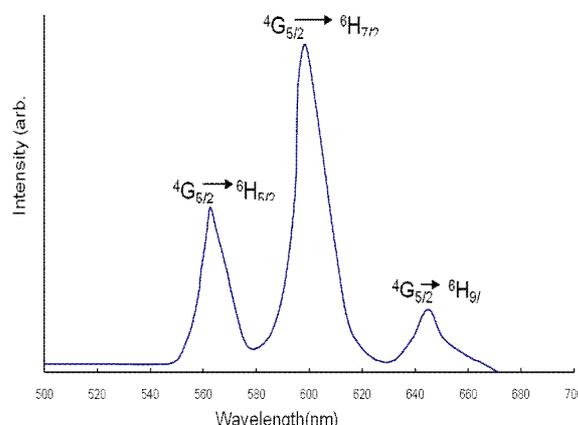


Fig. 6 Photoluminescence spectrum of Sm³⁺ doped LiF-CdO-B₂O₃ glasses ($\lambda_{exc} = 400\text{nm}$)

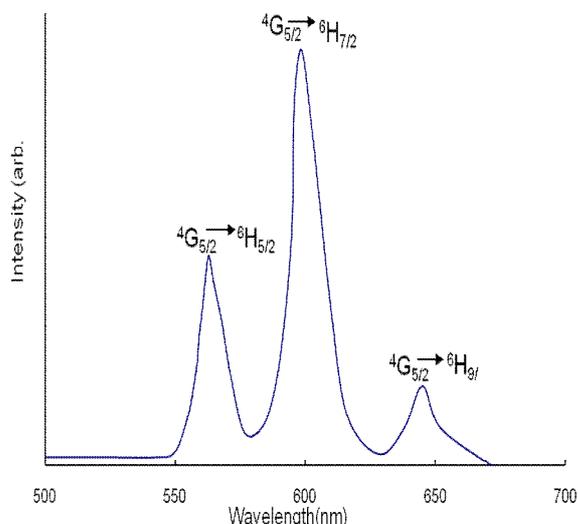


Fig. 7 Photoluminescence spectrum of Sm³⁺ doped LiF-BaO-B₂O₃ glasses (λ exc = 400nm) recorded at room temperature. All the transitions

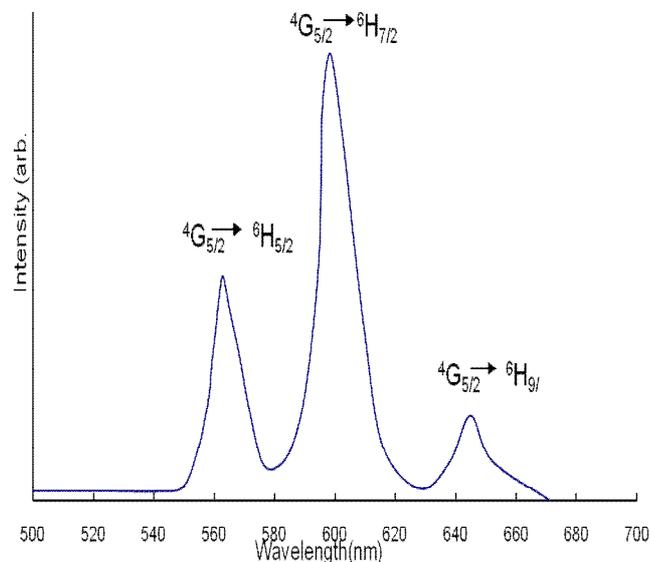


Fig. 8 Photoluminescence spectrum of Sm³⁺ doped LiF-PbO-B₂O₃

Table 5 : Data on radiative properties of Sm³⁺: LiF- (MO)-B₂O₃ glasses
Glass1: (CaO)

Emission	λ (nm)	δλ (nm)	A (S ⁻¹)	A _T (S ⁻¹)	B _r %	Emission cross section (σ _P ^E) X 10 ⁻²¹ (cm ⁻²)	Transition
⁴ G _{5/2} → ⁶ H _{9/2}	645	12.1	30877	46380.8		66.57	0.023
⁴ G _{5/2} → ⁶ H _{7/2}	598	13.4	4206.2	46380.8		9.06	0.221
⁴ G _{5/2} → ⁶ H _{5/2}	562	16.2	1097.6	46380.8		2.36	3.66
Life time (τ _R) = 21.56μs							

Glass 2 : (CdO)

Emission Transition	λ (nm)	δλ (nm)	A (S ⁻¹)	A _T (S ⁻¹)	B _r %	Emission cross section (σ _P ^E) X 10 ⁻²¹ (cm ⁻²)
⁴ G _{5/2} → ⁶ H _{9/2}	640	11.9	31583	47196		66.91
⁴ G _{5/2} → ⁶ H _{7/2}	593	13.3	4313	47196		9.13
⁴ G _{5/2} → ⁶ H _{5/2}	557	16.0	1100	47196		2.33
Life time (τ _R) = 21.18 μs						

Glass 3 : (BaO)

Emission Transition	λ (nm)	δλ (nm)	A (S ⁻¹)	A _T (S ⁻¹)	B _r %	Emission cross section (σ _P ^E) X 10 ⁻²¹ (cm ⁻²)
⁴ G _{5/2} → ⁶ H _{9/2}	635	11.8	32311.8	48037.7		67.26
⁴ G _{5/2} → ⁶ H _{7/2}	588	13.1	4423	48037.7		9.20
⁴ G _{5/2} → ⁶ H _{5/2}	552	15.8	1102.9	48037.7		2.29
Life time (τ _R) = 20.81μs						

Glass 4 : (PbO)

Emission Transition	λ (nm)	$\delta\lambda$ (nm)	A (S ⁻¹)	A _T (S ⁻¹)	B _r %	Emission cross section (σ_p^E)
			X 10 ⁻²¹ (cm ⁻²)			
⁴ G _{5/2} → ⁶ H _{9/2}	630	11.6	33063.28	48905.04	67.60	0.023
⁴ G _{5/2} → ⁶ H _{7/2}	583	13.0	4538.5	48905.04	9.28	0.215
⁴ G _{5/2} → ⁶ H _{5/2}	547	15.6	1103.26	48905.04	2.25	3.410

Life time (τ_R) = 20 μ s

By incorporating these terms in to the matrices and the energy parameters, the energy levels for various rare earth ions in LiF- (MO)-B₂O₃ glass host lattice can be obtained. The experimental oscillator strengths are compared with those of calculated values a reasonable match is obtained between experimental and calculated oscillator strengths.

The Judd-Ofelt parameters obtained from the least square analysis of experimental oscillator strengths of are given in Table 3 for CaO, CdO, BaO and PbO modifier glasses. The experimental oscillator strengths are compared with those of calculated; a reasonable match is obtained between experimental and calculated oscillator strengths except for Sm³⁺.

The energies and spectral profiles of certain transitions in the absorption spectra of Ln³⁺ ions throw some light on their coordination [10-12]. Ω_λ alues for Ln³⁺ ions in the glasses systems in general give information about the environment of the rare earth ions in the glass lattice. The rare earth ions in the glass systems are randomly distributed over non equivalent sites with distribution in the crystal fields; this was proved by simulation studies and a number of optical and ESR studies [13-14].

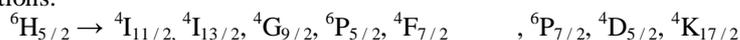
These ions which occupy sites with non-centro symmetric potential contribute significantly to Ω_2 [15]. For the crystalline systems it is generally expected the higher values for Ω_2 than those of free ions. Such discrepancies may arise due to the influences of the dielectric of media, the covalence and nephelauxetic effect [16,17]. However in glass matrices differences are quite different from those of crystalline systems. The higher value of Ω_2 with different trends in the present glass systems may be explained due to the following reasons; The Sm³⁺ ions may occupy different coordination. Even with similar coordination the differences in the distortion at these ion sites may lead to a distribution in the crystal field. The sites with non-centro symmetric potential lead to enhancement of Ω_2 value. Normally, the parameter Ω_2 is related to the covalency and / or structural changes in the vicinity of the Sm³⁺ ion (short-range effect) and Ω_4 are related to the long-range effects. The larger modifier ion (Ba²⁺ ionic radius, 1.34 Å) in Glass 3 give rise to a large average distance between the B-O-B chains which results in the average Sm-O distance to increase, therefore producing a weaker field around the Sm³⁺ ion leading to a low value of Ω_2 when compared with that of other glasses (Ca²⁺ ionic radius, 0.99 Å, Cd²⁺ ionic radius, 0.97 Å). Further support for this argument can also be cited from the value of the bonding parameter δ ; the value of δ for these glasses follows the order Glass 1(CaO) > Glass 2(CdO) > Glass 3 (BaO) indicating the high covalent environment for Sm³⁺ ions in Glass 1 and high ionic environment in Glass 3. However in the case of Glass 4(PbO) the decrease can not be accounted for in terms of the ionic radii (Pb²⁺ ionic radius, 1.2 Å) but rather that the Pb²⁺ ion is more strongly bounded to the oxygen which reduces the covalency of the Sm-O bond [18].

The values of Ω_4 and Ω_6 are strongly influenced by the vibrational levels associated with the central rare earth ions bound to the ligand atoms. Spectral studies of vibronic transitions for rare earth systems show that they are most intense at the beginning and the end of the series [19]. Contributions due to vibrational interactions by terms common to Ω_4 and Ω_6 can qualitatively account for the observed trends in the present cases.

The radiative properties of Sm³⁺ ions (or any of Ln³⁺ ions) depend on the number of factors such as network former and modifier of the glass. The value of β_r (i.e. the branching ratio) of the luminescence transitions characterizes the lasing power of the potential laser transitions. The β_r values obtained for the luminescent transitions originated from ⁴G_{5/2} level for all the four glasses have been furnished in Table 3.5. It is well established that an emission level with β_r value greater than 50% becomes a potential laser emission [20]. Referring to the data on emission transitions, the transition ⁴G_{5/2}→⁶H_{9/2}, has the highest value of β_r for all the four glasses; this transition may therefore be considered as a possible laser transition. However, the comparison of β_r values of this transition for the four glasses show the largest value for glass 4 (PbO) indicating these glasses to exhibit better lasing action among the four glasses (Table 5).

VI. CONCLUSIONS

1) The recorded optical absorption spectral profiles of Sm³⁺ ions doped LiF-MO-B₂O₃ glasses have revealed the following transitions:



- 2) By performing least square fitting analysis the J-O parameters for these glasses are computed and are found to show the following trend for all four glasses. $\Omega_2 > \Omega_4 > \Omega_6$
- 3) The value of δ (bonding parameter), gives information on the covalent environment of Sm^{3+} ions in the glass matrix. The larger the value of δ , the larger is the covalent environment of Sm^{3+} ions in the glass matrix. Among the three alkaline earth oxide (CaO, CdO, BaO) modifier glasses doped with Sm^{3+} ions, the highest values of δ obtained for CaO mixed glass (Glass 1) glasses indicate the highest covalent environment of Sm^{3+} .
- 4) The photoluminescence spectra recorded at room temperature for these glasses have exhibited the bands corresponding to the following transitions: Sm^{3+} glasses: ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}, {}^6\text{H}_{7/2}, {}^6\text{H}_{9/2}$.
- 5) The comparison of the values the branching ratio, β_r for the transition ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$, for the four glasses show the largest value for glass 4 (PbO) indicating these glasses to exhibit better lasing action among the four glasses.

Summing up the entire work, it is felt that the study on various spectroscopic properties of Samarium doped LiF-MO-B₂O₃ glasses has yielded some valuable information which may be helpful for using these glasses for practical applications.

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