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# Spectral and Thermal Properties of $Sm^{3+}$ Doped Zinc Lithium Alumina Boromolybdate Glasses

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## Abstract

*Zinc lithium alumina boromolybdate glasses containing $Sm^{3+}$ in (45- x): $MoO_3$:10ZnO:10$Li_2O$:10$Al_2O_3$:25$B_2O_3$:x$Sm_2O_3$ (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by x-ray diffraction studies. Optical absorption spectra were recorded at room temperature for all glass samples. The experimental oscillator strengths were calculated from the area under the absorption bands. Slater-Condon parameter $F_2$, Lande's parameter $\xi_{4f}$, Nephlauxetic ratio ($\beta'$) and Bonding parameter ($b^{1/2}$) have been computed. Using these parameters energies and intensities of these bands has been calculated. Judd-Ofelt intensity parameters $\Omega_\lambda$ ($\lambda$=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross–section of various emission lines have been evaluated.*

***Keywords:*** *ZLABM Glasses, Optical Properties, Judd-Ofelt Theory, Rare earth ions.*

## INTRODUCTION

Glasses containing rare-earth (RE) ions such as $Sm^{3+}$ and $Dy^{3+}$ ions have received much attention, because such materials have high potential for practical applications. Glasses pertaining rare earth metal oxides have significant applications for solid state, luminescent applications, Laser hosts, lamp phosphors, broad band amplifiers, sensors, optical data storage devices and optical fiber communication systems [1-6].The optical and spectroscopic properties of rare earth ions are strongly dependent on host materials. Boromolybdate glasses are more suitable due to its high refractive index and low phonon energy. Glasses have some unique properties such as high hardness and transparency at room temperature, along with sufficient strength and excellent corrosion resistance. Due to potential applications in various engineering and technological fields, the study of the properties of glasses is of great significance [7-10].

The aim of the present study is to prepare the $Sm^{3+}$ doped zinc lithium alumina boromolybdate glass with different $Sm_2O_3$ concentrations. The absorption spectra, fluorescence spectra of $Sm^{3+}$of the glasses were investigated. The Judd-Ofelt theory has been applied to compute the intensity parameters $\Omega_\lambda$ ($\lambda$=2, 4, 6).These intensity parameter have been used to evaluate optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section.

## EXPERIMENTAL TECHNIQUES

### Preparation of glasses

The following $Sm^{3+}$ doped Boromolybdate glass samples (45-x): $MoO_3$:10ZnO:10$Li_2O$:10$Al_2O_3$:25$B_2O_3$:x$Sm_2O_3$ (where x=1, 1.5, 2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of $MoO_3$, ZnO, $Li_2O$, $Al_2O_3$, $B_2O_3$ and $Sm_2O_3$. They were thoroughly mixed by using an agate pestle mortar. then melted at $1190^0$C by an electrical muffle furnace for 2h., After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of $390^0$C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

**Table 1** Chemical composition of the glasses

| Sr. | Sample | Glass composition (mol %) |
|---|---|---|
| 1 | ZLABM (UD) | 45 $MoO_3$:10ZnO:10$Li_2O$:10$Al_2O_3$:25$B_2O_3$ |
| 2 | ZLABM (SM1) | 44 $MoO_3$:10ZnO:10$Li_2O$:10$Al_2O_3$:25$B_2O_3$: 1 $Sm_2O_3$ |
| 3 | ZLABM (SM 1.5) | 43.5 $MoO_3$:10ZnO:10$Li_2O$:10$Al_2O_3$:25$B_2O_3$: 1.5 $Sm_2O_3$ |
| 4 | ZLABM (SM 2) | 43 $MoO_3$:10ZnO:10$Li_2O$:10$Al_2O_3$:25$B_2O_3$: 2 $Sm_2O_3$ |
| 5 | ZLABM (UD) | Represents undoped Zinc lithium alumina boromolybdate glass specimens. |
| 6 | ZLABM (SM) | Represents $Sm^{3+}$ doped Zinc lithium alumina boromolybdate glass specimens. |

### Oscillator Strength

The intensity of spectral lines is expressed in terms of oscillator strengths using the relation [11].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \qquad (1)$$

where, ε (*ν)* is molar absorption coefficient at a given energy *ν* ($cm^{-1}$), to be evaluated from Beer–Lambert law.

Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated [12], using the modified relation:

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \qquad (2)$$

where c is the molar concentration of the absorbing ion per unit volume, I is the optical path length, $\log I_0/I$ is optical density and $\Delta\upsilon_{1/2}$ is half band width.

### Judd-Ofelt Intensity Parameters

According to Judd [13] and Ofelt [14] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N (S, L) J>$ level and the terminal J' manifold $|4f^N (S'L') J'>$ is given by:

$$\frac{8\Pi^2 mc\bar{\upsilon}}{3h(2J+1)} \frac{1}{n} \left[ \frac{(n^2+2)^2}{9} \right] \times S(J, J') \qquad (3)$$

Where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum \Omega_\lambda \langle 4f^N (S, L)\, J \| U^{(\lambda)} \| 4f^N (S', L')\, J' \rangle^2$$

$$\lambda = 2, 4, 6$$

In the above equation m is the mass of an electron, c is the velocity of light, *v* is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, $\Omega_\lambda$ ($\lambda = 2, 4, 6$) are known as Judd-Ofelt intensity parameters.

**Radiative Properties**

The $\Omega_\lambda$ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time ($\tau_R$), and laser parameters like fluorescence branching ratio ($\beta_R$) and stimulated emission cross section ($\sigma_p$).

The spontaneous emission probability from initial manifold $|4f^N (S', L') J'>$ to a final manifold $|4f^N (S, L) J>|$ is given by:

$$A[(S', L') J'; (S, L) J] = \frac{64\pi^2\nu^3}{3h(2J'+1)}\left[\frac{n(n^2+2)^2}{9}\right] \times S(J', \bar{J}) \qquad (4)$$

Where, $S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$

The fluorescence branching ratio for the transitions originating from a specific initial manifold $|4f^N (S', L') J'>$ to a final many fold $|4f^N (S, L) J>$ is given by

$$\beta[(S', L') J'; (S, L) J] = \sum_{SLJ} \frac{A[(S' L)]}{A[(S' L') J' (\bar{S} L)]} \qquad (5)$$

where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{SLJ} A[(S', L') J'; (S, L)] = A_{Total}^{-1} \qquad (6)$$

where, the sum is over all possible terminal manifolds. The stimulated emission cross - section for a transition from an initial manifold $|4f^N (S', L') J'>$ to a final manifold $|4f^N (S, L) J>|$ is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S', L') J'; (\bar{S}, \bar{L})\bar{J}] \qquad (7)$$

where, $\lambda_p$ the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

**Nephelauxetic Ratio (β) and Bonding Parameter ($b^{1/2}$)**

The nature of the R-O bond is known by the Nephelauxetic Ratio (β') and Bonding Parameters ($b^{1/2}$), which are computed by using following formulae [15, 16]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \qquad (8)$$

where, $\nu_a$ and $\nu_g$ refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter ($b^{1/2}$) are given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \qquad (9)$$

## RESULT AND DISCUSSION

### XRD Measurement

Figure 1 presents the XRD pattern of the sample contain - $B_2O_3$ which is show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

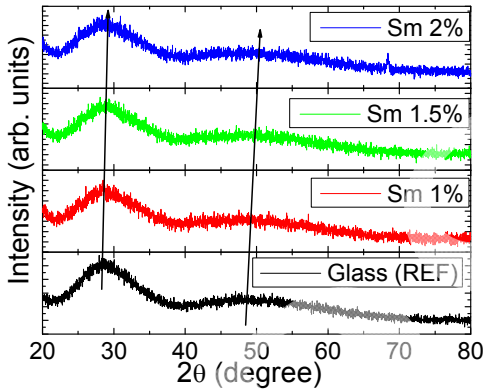


Figure 1: X-ray diffraction pattern of $MoO_3$: ZnO: $Li_2O$:$Al_2O_3$:$B_2O_3$

### Thermal Properties

Figure 2 shows the thermal properties of ZLABM glass from $300^0$C to $1000^0$C. From the DSC curve of present glasses system, we can find out that no crystallization peak is apparent and the glass transition temperature $T_g$ are $352^0$C, $456^0$C and $586^0$C respectively. The $T_g$ increase with the contents of $Sm_2O_3$ increase. We could conclude that thermal properties of the ZLABM glass are good for fiber drawing from the analysis of DSC curve.

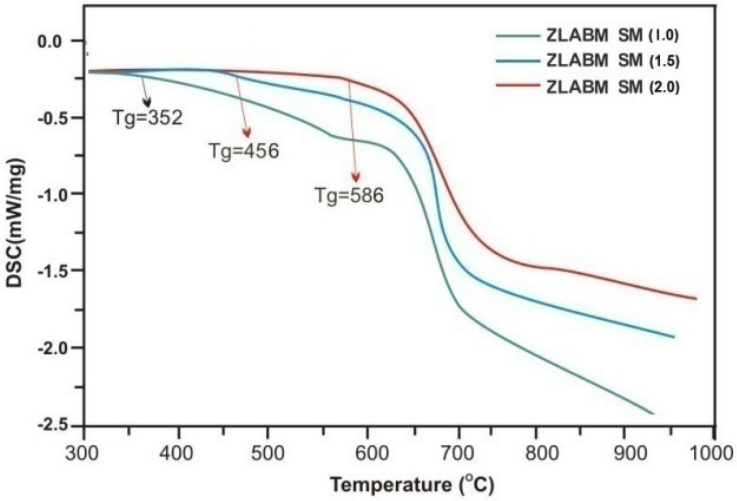


**Figure 2:** DSC curve of ZLABM (SM) glasses.

### Absorption Spectrum

The absorption spectra of $Sm^{3+}$ doped ZLABM (SM 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm). Ten absorption bands have been observed from the ground state $^6H_{5/2}$ to excited states $^6F_{1/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^4G_{7/2}$, $^4I_{9/2}$, $^4M_{7/2}$, $(^6P,^4P)_{5/2}$, $^4F_{7/2}$, $^4D_{1/2}$, and $(^4D,^6P)_{5/2}$ for $Sm^{3+}$ doped ZLABM glasses.

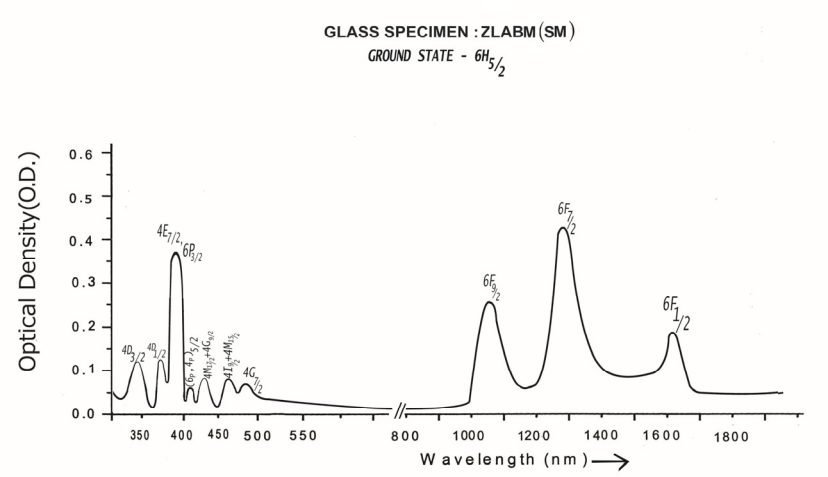


Fig.3: Absorption spectrum of $Sm^{3+}$doped ZLABM (01) glass

The experimental and calculated oscillator strengths for $Sm^{3+}$ ions in zinc lithium alumina boromolybdate glasses are given in Table 2

**Table2:** Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of $Sm^{3+}$ions in ZLABM glasses.

| **Energy level from $^6H_{5/2}$** | **Glass ZLABM (SM01)** | | **Glass ZLABM (SM1.5)** | | **Glass ZLABM (SM02)** | |
|---|---|---|---|---|---|---|
| | $P_{exp.}$ | $P_{cal.}$ | $P_{exp.}$ | $P_{cal.}$ | $P_{exp.}$ | $P_{cal.}$ |
| $^6F_{1/2}$ | 1.58 | 1.63 | 1.52 | 1.58 | 1.46 | 1.53 |
| $^6F_{7/2}$ | 5.46 | 5.52 | 5.38 | 5.42 | 5.30 | 5.36 |
| $^6F_{9/2}$ | 3.78 | 3.83 | 3.62 | 3.73 | 3.56 | 3.69 |
| $^4G_{7/2}$ | 0.18 | 0.118 | 0.16 | 0.116 | 0.12 | 0.114 |
| $^4I_{9/2}, ^4M_{15/2}, ^4I_{11/2}$ | 1.15 | 1.88 | 1.13 | 1.83 | 1.09 | 1.80 |
| $^4M_{17/2}, ^4G_{9/2}, ^4I_{15/2}$ | 0.28 | 0.25 | 0.24 | 0.24 | 0.18 | 0.236 |
| $(^6P, ^4P)_{5/2}, ^4L_{13/2}$ | 1.25 | 1.321 | 1.21 | 1.323 | 1.16 | 1.309 |
| $^4F_{7/2}, ^6P_{3/2}, ^4K_{11/2}$ | 5.62 | 5.71 | 5.57 | 5.75 | 5.48 | 5.69 |
| $^4D_{1/2}, ^6P_{7/2}, ^4L_{17/2}$ | 2.38 | 2.43 | 2.34 | 2.36 | 2.29 | 2.33 |
| $^4D_{3/2}, (^4D, ^6P)_{5/2}$ | 2.62 | 3.49 | 2.56 | 3.48 | 2.48 | 3.44 |
| r.m.s. deviation | ±0.3636 | | ±0.3731 | | ±0.3898 | |

Computed values of $F_2$, Lande's parameter ($\xi_{4f}$), Nephlauxetic ratio( β') and bonding parameter($b^{1/2}$) for $Sm^{3+}$ doped ZLABM glass specimen are given in Table 3.

**Table 3.** $F_2$, $\xi_{4f}$, β' and $b^{1/2}$ parameters for Samarium doped glass specimen.

| Glass Specimen | $F_2$ | $\xi_{4f}$ | β' | $b^{1/2}$ |
|---|---|---|---|---|
| $Sm^{3+}$ | 358.82 | 1258.16 | 0.9337 | 0.1821 |

Judd-Ofelt intensity parameters $\Omega_\lambda$ (λ=2,4,6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. In the present case the three $\Omega_\lambda$ parameters follow the trend $\Omega_2 > \Omega_4 > \Omega_6$. The spectroscopic quality factor ($\Omega_4 / \Omega_6$) related with the rigidity of the glass system has been found to lie

between 1.1162 and 1.1616 in the present glasses. The value of Judd-Ofelt intensity parameters are given in **Table4.**

**Table4:** Judd-Ofelt intensity parameters for $Sm^{3+}$ doped ZLABM glass specimens.

| Glass Specimen | $\Omega_2(pm^2)$ | $\Omega_4(pm^2)$ | $\Omega_6(pm^2)$ | $\Omega_4/\Omega_6$ | Ref. |
|---|---|---|---|---|---|
| ZLABM (SM01) | 5.109 | 4.765 | 4.269 | 1.1162 | P.W. |
| ZLABM(SM1.5) | 4.943 | 4.803 | 4.147 | 1.1582 | P.W. |
| ZLABM (SM02) | 4.780 | 4.751 | 4.090 | 1.1616 | P.W. |
| LBGS(SM) | 9.930 | 9.840 | 7.510 | 1.310 | [17] |
| TWB | 6.060 | 1.570 | 0.950 | 1.653 | [18] |
| TNN | 6.860 | 1.530 | 1.120 | 1.366 | [19] |
| TRZL(YB/ER) | 6.380 | 1.820 | 1.640 | 1.110 | [20] |

## Fluorescence Spectrum

The fluorescence spectrum of $Sm^{3+}$doped in zinc lithium alumina boromolybdate glass is shown in Figure 4. There are four bands observed in the Fluorescence spectrum of $Sm^{3+}$doped zinc lithium alumina boromolybdate glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (4).Shows the fluorescence spectrum with four peaks ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), ($^4G_{5/2}\rightarrow{}^6H_{7/2}$), ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) and ($^4G_{5/2}\rightarrow{}^6H_{11/2}$), respectively for glass specimens.

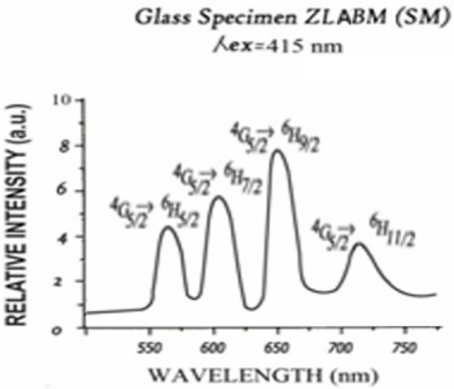


Figure 4: fluorescence spectrum of $Sm^{3+}$doped ZLABM (01) glass

**Table 5.** Emission peak wave lengths ($\lambda_p$),radiative transition probability ($A_{rad}$),branching ratio ($\beta$),stimulated emission cross-section( $\sigma_p$) and radiative life time( $\tau_R$ ) for various transitions in $Sm^{3+}$ doped ZLABM glasses

| Transition | | ZLABM SM 01 | | | | ZLABM SM 1.5 | | | | ZLABM SM 02 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ (nm) | $A_{rad}(s^{-1})$ | $\beta$ | $\sigma_p$ ($10^{-20}$ $cm^2$) | $\tau_R(\mu s)$ | $A_{rad}(s^{-1})$ | $\beta$ | $\sigma$ ($10^{-20}$ $cm^2$) | $\tau_R(\mu s)$ | $A_{rad}(s^{-1})$ | $\beta$ | $\sigma_p$ ($10^{-20}$ $cm^2$) | $\tau_R(\mu s)$ |
| $^4G_{5/2}\rightarrow{}^6H_{5/2}$ | **562** | **10.413** | **0.0415** | **0.0045** | | **10.395** | **0.0419** | **0.0048** | | **10.26** | **0.0415** | **0.0523** | |
| $^4G_{5/2}\rightarrow{}^6H_{7/2}$ | **600** | **109.88** | **0.4466** | **0.0497** | **3982.91** | **108.94** | **0.4387** | **0.0515** | **4027.14** | **107.76** | **0.4354** | **0.0548** | 4040.40 |
| $^4G_{5/2}\rightarrow{}^6H_{9/2}$ | **645** | **103.94** | **0.4225** | **0.0475** | | **102.20** | **0.4116** | **0.0494** | | **101.28** | **0.4092** | **0.0512** | |
| $^4G_{5/2}\rightarrow{}^6H_{11/2}$ | **706** | **26.84** | **0.1091** | **0.0140** | | **26.78** | **0.1078** | **0.0145** | | **28.20** | **0.1139** | **0.0160** | |

## CONCLUSION

In the present study, the glass samples of composition (45- x): $MoO_3$: 10ZnO: 10$Li_2O$: 10$Al_2O_3$: 25$B_2O_3$: x$Sm_2O_3$ (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. The Judd-Ofelt theory has been applied to calculate the oscillator strength and intensity parameters $\Omega_\lambda$ ($\lambda$=2, 4, 6).The $\Omega_2$ parameter shows the covalent nature of the prepared glass. The stimulated emission cross section ($\sigma_p$) has highest value for the transition ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) in all the glass specimens doped with $Sm^{3+}$ ion. This shows that ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) transition is useful for laser action.

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