Spectral and Transmittance Properties of Sm^{3+} Doped in Zinc Lithium Soda lime Potassiumniobate Molybdate Glasses

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***Abstract*: Glass of the system: (35-x)MoO_3:10ZnO:10Li_2O:10CaO:10Na_2O:10K_2O:15Nb_2O_5: xSm_2O_3. (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method (where x=1,1.5,2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption, Excitation, fluorescence and Transmittance spectra have been recorded at room temperature for all glass samples. The various interaction parameters like Slater-Condon parameters F_k (k=2,4,6), Lande parameters (ξ_{4f}), nephelauexetic ratio (β'), bonding parameters ($b^{1/2}$)and Racah parameters E^k(k=1,2 3) have been computed. Judd-Ofelt intensity parameters and laser parameters have also been calculated.**

***Keywords*: ZLSLPNM Glasses, Optical properties, Judd-Ofelt analysis, Transmittance Properties.**

I. Introduction

The glasses containing rare earth in various forms such as network formers luminescent ions are of great deal of interest for their unique optical, electrical and mechanical properties [1-5]. Glass is a continuous random network lacking both symmetry and periodicity. Glasses are super cooled liquid and amorphous in nature. It is obtained by cooling a liquid below its freezing point so quickly that the atoms do not get sufficient time to arrange themselves into an appropriate crystal structure. The classical explanation for the formation of a glass is that when a liquid is cooled, its viscosity increases and at a certain temperature below its freezing point, fluidity becomes almost zero and the liquid becomes rigid. Molybdate glasses have a low glass transition temperature, high coefficient of thermal expansion and low melting temperature [6-10]. The addition of modifiers ions such as CaO is also known to increase the stability of the glass against devitrification and corrosion. . Samarium is used in many high index glasses. A high index glass, when combined with other glass materials, improves the dispersion, which provides efficiency increase [11-15]. The optical spectra of RE ions in glasses provide important information about the effect of host–ion interaction on the electronic and vibrational energy levels of the material.

The aim of the present study is to prepare the Sm^{3+} doped zinc lithium soda lime potassiumniobate molybdate glass with different Sm_2O_3 concentrations. The Optical absorption, Excitation, fluorescence and Transmittance spectra of $Sm^{3+}$of the glasses were investigated. The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ (λ=2, 4, 6).These intensity parameter have been used to evaluate optical optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section. Large stimulated emission cross section is one of the most important parameters required for the design of high peak power solid state lasers.

II. Experimental Techniques

Preparation of glasses

The following Sm^{3+} doped zinc lithium soda lime potassiumniobate molybdate glass samples (35-x) MoO_3:10ZnO:10Li_2O:10CaO:10Na_2O:10K_2O:15Nb_2O_5:xSm_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, CaO, Na_2O, K_2O, Nb_2O_5 and Sm_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1045^0C 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 250^0C 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

Sample	Glass composition (mol %)
ZLSLPNM (UD)	$35MoO_3$:10ZnO:$10Li_2O$:10CaO:$10Na_2O$:$10K_2O$:$15Nb_2O_5$
ZLSLPNM (SM1)	$34MoO_3$:10ZnO:$10Li_2O$:10CaO:$10Na_2O$:$10K_2O$:$15Nb_2O_5$:1 Sm_2O_3
ZLSLPNM (SM 1.5)	$33.5MoO_3$:10ZnO:$10Li_2O$:10CaO:$10Na_2O$:$10K_2O$:$15Nb_2O_5$:$1.5Sm_2O_3$
ZLSLPNM (SM 2)	$33MoO_3$:10ZnO:$10Li_2O$:10CaO:$10Na_2O$:$10K_2O$:$15Nb_2O_5$: 2 Sm_2O_3

ZLSLPNM (UD) -Represents undoped Zinc Lithium Soda Lime Potassiumniobate Molybdate glass specimens.
ZLSLPNM (SM) -Represents Sm^{3+} doped Zinc Lithium Soda Lime Potassiumniobate Molybdate glass specimens.

III. Theory

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [16].

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

where, $\varepsilon(\nu)$ 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 [17], 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.

3.2. Judd-Ofelt Intensity Parameters

According to Judd [18] and Ofelt [19] 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 (S', L') 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, ν 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, Ω_λ ($\lambda = 2, 4, 6$) are known as Judd-Ofelt intensity parameters .

3.3 Radiative Properties

The Ω_λ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (τ_R), and laser parameters like fluorescence branching ratio (β_R) and stimulated emission cross section (σ_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:

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

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

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

3.4 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 [20, 21]. The Nephelauxetic Ratio is given by

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

where, ν_a and ν_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

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

IV. Result and Discussion

4.1 XRD Measurement

Figure 1 presents the XRD pattern of the sample contain - MoO_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.

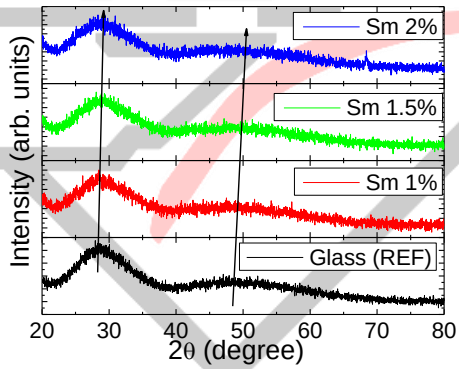

Fig. 1: X-ray diffraction pattern of MoO_3:ZnO:Li_2O:CaO:Na_2O:K_2O:Nb_2O_5:Sm_2O_3

4.2 Transmittance Spectrum

The Transmittance spectrum of Sm^{3+}doped in zinc lithium soda lime potassiumniobate molybdate glass is shown in Figure 2.

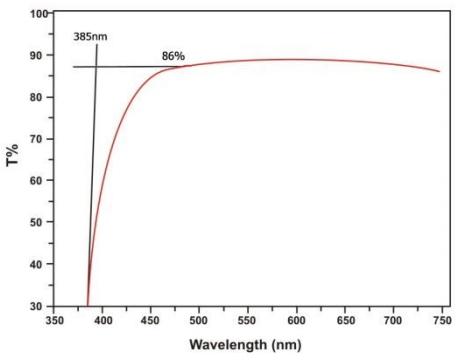

Fig. (2) Transmittance spectrum of ZLSLPNM SM (01) glass.

4.3 Absorption Spectrum

The absorption spectra of Sm^{3+} doped ZLSLPNM (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 ZLSLPNM glasses.

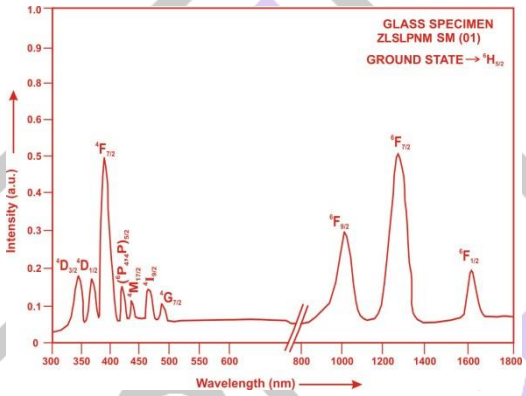

Fig.3: Absorption spectrum of ZLSLPNM SM (01) glass.

The experimental and calculated oscillator strengths for Sm^{3+} ions in zinc lithium soda lime potassiumniobate molybdate glasses are given in Table2

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

Energy level from $^6H_{5/2}$	**Glass ZLSLPNM (SM01)**		**Glass ZLSLPNM (SM1.5)**		**Glass ZLSLPNM (SM02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^6F_{1/2}$	1.60	1.65	1.55	1.61	1.52	1.59
$^6F_{7/2}$	5.47	5.53	5.45	5.51	5.42	5.51
$^6F_{9/2}$	3.79	3.83	3.75	3.82	3.72	3.80
$^4G_{7/2}$	0.19	0.12	0.17	0.12	0.16	0.12
$^4I_{9/2}$,$^4M_{15/2}$,$^4I_{11/2}$	1.17	1.88	1.14	1.87	1.11	1.86
$^4M_{17/2}$,$^4G_{9/2}$,$^4I_{15/2}$	0.28	0.25	0.25	0.24	0.22	0.24
$(^6P,^4P)_{5/2}$,$^4L_{13/2}$	1.27	1.32	1.24	1.33	1.20	1.33
$^4F_{7/2}$,$^6P_{3/2}$,$^4K_{11/2}$	5.65	5.72	5.62	5.73	5.58	5.78
$^4D_{1/2}$,$^6P_{7/2}$,$^4L_{17/2}$	2.40	2.43	2.36	2.42	2.32	2.67
$^4D_{3/2}$, $(^4D,^6P)_{5/2}$	2.65	3.50	2.60	3.50	2.58	3.51
r.m.s. deviation	0.3536		0.3715		0.4039	

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

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

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

Judd-Ofelt intensity parameters Ω_λ (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 Ω_λ parameters follow the trend $\Omega_2 > \Omega_4 > \Omega_6$. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 1.1185 and 1.1423 in the present glasses.

The value of Judd-Ofelt intensity parameters are given in **Table 4**

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

Glass Specimen	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4/Ω_6**	**Ref.**
ZLSLPNM (SM01)	5.120	4.740	4.238	1.1185	P.W.
ZLSLPNM (SM1.5)	4.987	4.750	4.214	1.1272	P.W.
ZLSLPNM (SM02)	4.940	4.784	4.188	1.1423	P.W.
LFB (SM)	3.41	2.92	2.17	1.346	[22]

4.4 Excitation Spectrum

Excitation spectra of ZLSLPNM SM (01) glass recorded at the emission wavelength 602 nm is depicted as figure 4. The excitation spectra consists of seven peaks corresponding to the transitions from the ground state $^6H_{5/2}$ to the various excited states $^4H_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^4M_{19/2}$, $^4G_{9/2}$ and $^4I_{11/2}$+$^4I_{13/2}$ at the wavelengths of 337, 362, 375,401, 413, 436 and 478 nm respectively. Among these, a prominent excitation band at 401 nm has been selected for the measurement of emission spectrum of Sm^{3+} glass.

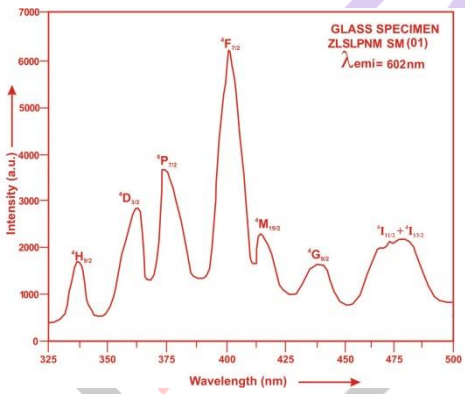

Fig. 4: Excitation spectrum of ZLSLPNM SM (01) glass.

4.5 Fluorescence Spectrum

The fluorescence spectrum of Sm^{3+}doped in zinc lithium soda lime potassiumniobate molybdate glass is shown in Figure 5. There are four broad bands observed in the Fluorescence spectrum of Sm^{3+}doped zinc lithium soda lime potassiumniobate molybdate glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig.(5).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.

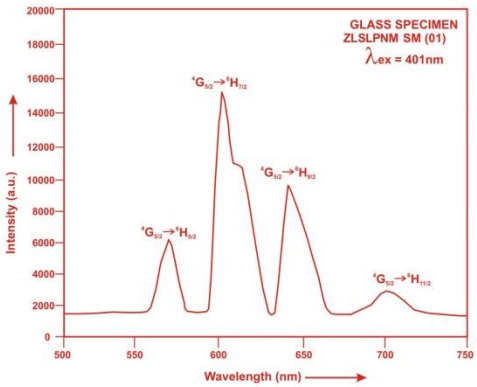

Fig.5: fluorescence spectrum of ZLSLPNM SM (01) glass.

Table 5. Emission peak wave lengths (λ_p),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R) for various transitions in Sm^{3+} doped ZLSLPNM glasses.

Transition		ZLSLPNM SM 01				ZLSLPNM SM 1.5				ZLSLPNM SM 02			
	λ_{max} (nm)	A_{rad}(s^{-1})	β	σ_p (10^{-20} cm^2)	τ_R(μs)	A_{rad}(s^{-1})	β	σ (10^{-20} cm^2)	τ_R(μs)	A_{rad}(s^{-1})	β	σ_p (10^{-20} cm^2)	τ_R(μs)
$^4G_{5/2}\rightarrow{}^6H_{5/2}$	562	10.59	0.0416	0.0042	3928.46	10.55	0.0042	0.0045	3949.13	10.61	0.0042	0.0049	3945.76
$^4G_{5/2}\rightarrow{}^6H_{7/2}$	602	110.41	0.4337	0.0465		110.42	0.4361	0.0494		110.61	0.4365	0.0535	
$^4G_{5/2}\rightarrow{}^6H_{9/2}$	645	106.34	0.4178	0.0446		104.99	0.4147	0.0462		104.82	0.4136	0.0484	
$^4G_{5/2}\rightarrow{}^6H_{11/2}$	705	27.21	0.1069	0.0135		27.26	0.1076	0.0141		27.40	0.1081	0.0148	

V. Conclusion

In the present study, the glass samples of composition (35-x) MoO_3:10ZnO: 10Li_2O:10CaO:10Na_2O:20K_2O:15Nb_2O_3:xSm_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 Ω_λ (λ=2, 4, 6). The radiative transition probability, branching ratio are highest for ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_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 most probable transition. On the basis of spectrophotometric, transmittance reaches about 86% for all silicate glasses doped with Sm^{3+} ions.

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