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Spectral and Transmittance properties of Ho^{3+} ions doped Zinc Lithium Calcium Borosilicate Glasses

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Abstract

Glass of the system: (45-x)SiO_2:10ZnO:10Li_2O:10CaO:25B_2O_3:xHo_2O_3. (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method.(where x=1,1.5 and 2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glasssamples was confirmed by X-ray diffraction. Optical absorption, excitation and fluorescence spectra were recorded at roomtemperature for all glass samples.Judd-Ofeltintensity parameters Ω_λ (λ=2, 4 and6) are evaluated from theintensities of various absorption bands of opticalabsorption spectra. Using these intensity parameters variousradiative properties like spontaneous emission probability (A), branching ratio (β), radiative life time(τ_R) and stimulatedemission cross–section(σ_p)of various emission lines have been evaluated.

Keywords: ZLCBS Glasses,Optical Properties, Judd-Ofelt Theory, Transmittance Properties.

Introduction:

Glasses doped with rare earth ions have attracted a great deal of attention because of their applications in lasers, optical fibers, sensors, infrared detectors, marine optical communications, up-conversion lasers, optical data storage and high density memory storage devices [1–6]. Glasses are super cooled liquids, transparent and amorphous in nature.Silicate (SiO_2) based glasses possess interesting properties like lower phonon energy; high density and low melting temperature.Borosilicate glass systems exhibit high refractive indices, high gain density, high solubility and non-linear optical susceptibilities. B_2O_3 is one of the best-known glass formers and it is present in varieties of commercial glasses. The spectroscopic properties of rare-earth ions doped glass systems like borates, phosphates and silicateshave earlier been reported in the literature [8-12].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. We have studied on the absorption and emission properties of Ho^{3+}doped zinc lithium calcium borosilicateglasses. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory, The laser parameters such as radiative probabilities(A),branching ratio (β),radiative life time(τ_R) and stimulated emission cross section(σ_p) are evaluated using J.O.intensity parameters(Ω_λ, λ=2,4 and 6).

Experimental:

Preparation of glasses:

The following Ho^{3+}doped borosilicateglass samples $(45-x)SiO_2:10ZnO:10Li_2O:10CaO: 25B_2O_3:xHo_2O_3$. (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of SiO_2,ZnO, Li_2O, CaO, $B_2O_3$and Ho_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 955^0C 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 %)
ZLCBS (UD)	$45SiO_2:10ZnO:10Li_2O:10CaO:25B_2O_3$
ZLCBS (HO1)	$44SiO_2:10ZnO:10Li_2O:10CaO:25B_2O_3:1\ Ho_2O_3$
ZLCBS(HO1.5)	$43.5SiO_2:10ZnO:10Li_2O:10CaO:25B_2O_3:1.5Ho_2O_3$
ZLCBS (HO2)	$43SiO_2:10ZnO:10Li_2O:10CaO:25B_2O_3:2Ho_2O_3$

ZLCBS (UD) -Represents undopedZinc Lithium Calcium Borosilicate glass specimens
ZLCBS (HO)-Represents Ho^{3+}dopedZinc Lithium Calcium Borosilicate glass specimens

Theory:

Oscillator Strength:

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [13].

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

where, ε (*v*) is molar absorption coefficient at a given energy *v* (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 [14], 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 [15] and Ofelt [16] 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

$$S(J,J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N(S,L)J \| U^{(\lambda)} \| 4f^N(S',L')J' \rangle 2 \qquad (4)$$

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, Ω_λ (λ=2,4and 6) are known as Judd-Ofelt intensity parameters.

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 $|4f^N(S',L')J'\rangle$ to a final manifold $|4f^N(S,L)J\rangle|$ is given by:

$$A[(S',L')J';(S,L)J] = \frac{64\pi^2 v^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}\right] \times S(J,\bar{J}) \qquad (5)$$

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

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

$$\beta[(S',L')J';(S,L)J] = \sum_{SLJ} \frac{A[(S'\ L)]}{A[(S'L')J'(\bar{S}\ L)]} \qquad (6)$$

The radiative life time is given by

$$\tau_{rad} = \sum_{SLJ} A[(S',L')J';(S,L)] = A_{Total}^{-1} \qquad (7)$$

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

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

Where, λ_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 [17, 18]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \qquad (9)$$

where, ν_a and ν_g refer to the energies of the corresponding transition in the glass and free ion, respectively. The value of bonding parameter ($b^{1/2}$) is given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \tag{10}$$

Results and Discussion:

XRD Measurement:

Figure 1 presents the XRD pattern of the sample contain - SiO_2 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.

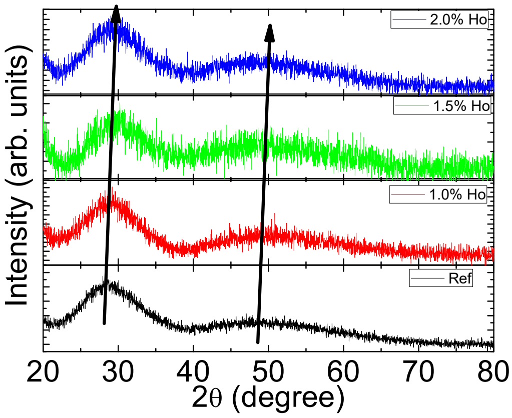

Fig.1: X-ray diffraction pattern of of SiO_2: ZnO: Li2O: CaO: B2O3:Ho2O3glasses.

Transmittance Spectrum:

The Transmittance spectrum of Ho^{3+}doped in zinc lithium calcium borosilicate glass is shown in Figure 2.

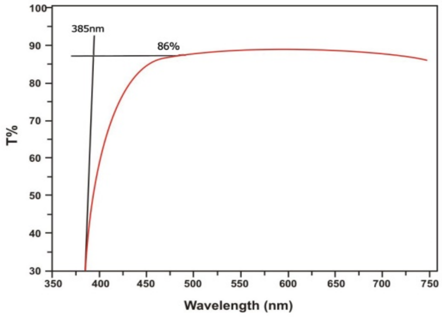

Fig.2: Transmittance spectrum of Ho^{3+}doped ZLCBSglasses.

Absorption spectra:

The absorption spectra of Ho^{3+}doped ZLCBS glass specimens have been presented in Figure 3 in terms of optical density versus wavelength.Twelve absorption bands have been observed from the ground state $^5I_8$to excited states $^5I_5$, $^5I_4$, $^5F_5$, $^5F_4$, $^5F_3$, $^3K_8$, $^5G_6$, $(^5G,^3G)_5$, $^5G_4$, $^5G_2$, $^5G_3$, and$^3F_4$for Ho^{3+} doped ZLCBS glasses.

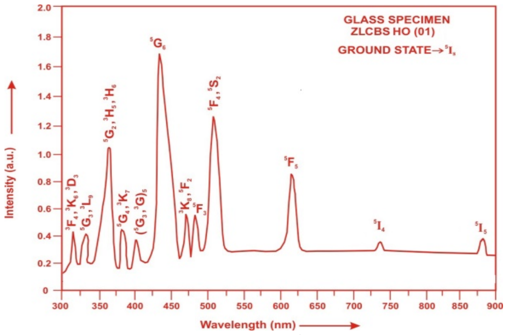

Fig.3: Absorption spectra of Ho^{3+}doped ZLCBSglasses.

The experimental and calculated oscillator strength for Ho^{3+}ions in ZLCBS glasses are given in **Table 2.**

Table 2: Table 2: Measured and calculated oscillator strength (P_m×10^{+6}) of Ho^{3+}ions in ZLCBS glasses.

Energy level from $^5I_8$	**Glass ZLCBS (HO01)**		**Glass ZLCBS(HO1.5)**		**Glass ZLCBS(HO02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5I_5$	0.46	0.24	0.42	0.24	0.38	0.23
$^5I_4$	0.07	0.02	0.06	0.02	0.03	0.02
$^5F_5$	3.45	2.73	3.42	2.71	3.38	2.68
$^5F_4$	4.60	4.25	4.56	4.22	4.52	4.19
$^5F_3$	1.55	2.36	1.52	2.35	1.48	2.33
$^3K_8$	1.38	1.95	1.35	1.93	1.31	1.91
$^5G_6$	25.63	25.62	24.78	24.79	23.98	24.02
$(^5G,^3G)_5$	3.65	1.65	3.62	1.63	3.58	1.60
$^5G_4$	0.09	0.60	0.07	0.59	0.06	0.59
$^5G_2$	5.45	5.43	5.41	5.28	5.38	5.13
$^5G_3$	1.42	1.38	1.38	1.36	1.35	1.34
$^3F_4$	1.38	4.07	1.32	4.02	1.26	3.96
r.m.s. deviation	±1.04694		±1.04964		±1.05097	

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

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

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

In theZinc Lithium Calcium Borosilicate glasses (ZLCBS)$\Omega_{2,}$ Ω_4 and $\Omega_6$parameters decrease with the increase of x from 1 to 2 mol%. The order ofmagnitude of Judd-Ofelt intensity parameters is $\Omega_2>\Omega_6>\Omega_4$for all the glass specimens. The high valuesobtained for $\Omega_2$in all glasses indicate that the Ho^{3+} ion is subjected to higher covalency with low symmetry. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 0.596 and 0.605 in the present glasses. The values of Judd-Ofelt intensity parameters are given in **Table 4.**

Table 4: Judd-Ofelt intensity parameters for Ho^{3+} doped ZLCBS glass specimens.

Glass Specimen	**$\Omega_2(pm^2)$**	**$\Omega_4(pm^2)$**	**$\Omega_6(pm^2)$**	**Ω_4/Ω_6**	**Ref.**
ZLCBS (HO01)	5.890	1.222	2.019	0.605	P.W.
ZLCBS (HO1.5)	5.669	1.206	2.006	0.601	P.W.
ZLCBS (HO02)	5.465	1.186	1.989	0.596	P.W.
TEOS(HO)	8.139	4.513	5.996	0.762	[19]
Fluoride(HO)	2.40	1.70	1.80	0.944	[20]

Excitation Spectrum:

The Excitation spectra of Ho^{3+}doped ZLCBS glass specimens have been presented in Figure 4 in terms of Excitation Intensity versus wavelength.The excitation spectrum was recorded in the spectral region 325–525 nm fluorescence at 545nm having different excitation band centered at 349,419, 450, 473and 486 nmare attributed to the $^5G_3$,(^5G, $^3G)_5$,$^5G_6$,$^3K_8$and$^5F_3$ transitions, respectively. The highest absorption level is $^5G_6$ and is at 450 nm. So this is to be chosen for excitation wavelength.

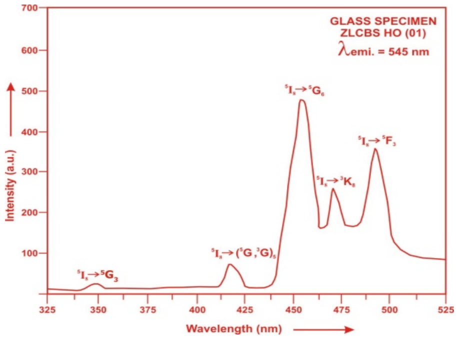

Fig.4: Excitation spectrum of doped with Ho^{3+}ZLCBS glasses.

Fluorescence Spectrum:

The fluorescence spectrum of Ho^{3+}doped in zinc lithium calcium borosilicate glass is shown in Figure 5. There are four broad bands observed in the Fluorescence spectrum ofHo^{3+}dopedzinc lithium calcium borosilicateglass. The wavelengths of these bands along with their assignments are given in Table 5. The peak with maximum emission intensity appears at 555nm and corresponds to the ($^5F_4 \rightarrow {}^5I_8$) transition.

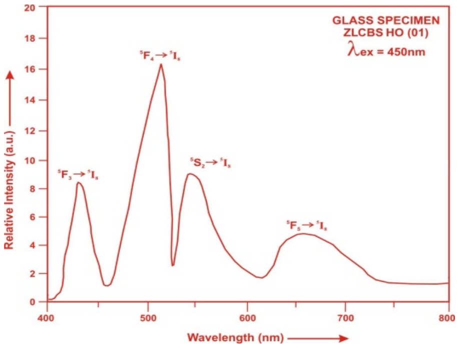

Fig.5: Fluorescence spectrum of doped with Ho^{3+}ZLCBSglasses

Conclusion:

In the present study, the glass samples of composition (45-x)SiO_2:10ZnO:10Li_2O:10CaO:25B_2O_3:xHo_2O_3. (where x =1, 1.5and 2mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^5F_4 \rightarrow {}^5I_8$) for glass ZLCBS (HO 01), suggesting that glass ZLCBS (HO 01) is better compared to the other two glass systems ZLCBS (HO1.5) and ZLCBS(HO02).On the basis of spectrophotometric, transmittance reaches about 86% for all silicate glasses doped with Ho^{3+} ions.

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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 Ho^{3+} doped ZLCBS glasses.

Transition		**ZLCBS (HO 01)**				**ZLCBS (HO 1.5)**				**ZLCBS (HO 02)**			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R (μs)	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20}$ $cm^2)$	$\tau_R(10^{-20}$ $cm^2)$
$^5F_3 \rightarrow {}^5I_8$	435	4510.63	0.2895	0.588	6417.86	4493.42	0.2898	0.580	6449.21	4464.02	0.2900	0.561	6497.09
$^5F_4 \rightarrow {}^5I_8$	501	7155.84	0.4593	1.263		7117.21	0.4590	1.239		7062.92	0.4589	1.212	
$^5S_2 \rightarrow {}^5I_8$	555	1882.06	0.1208	0.443		1874.60	0.1209	0.435		1862.33	0.1209	0.434	
$^5F_5 \rightarrow {}^5I_8$	652	2032.98	0.1305	0.759		2020.54	0.1303	0.747		2002.23	0.1301	0.725	