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Spectral and Up conversion Properties of Ho^{3+} Doped in Zinc Lithium Sodalime Cadmium Borosilicate Glasses

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Abstract

Glass of the system: (35-x)SiO_2:10ZnO:10Li_2O:10CaO:10Na_2O:10CdO:15B_2O_3:xHo_2O_3. (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. 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 and 6) are evaluated from theintensities of various absorption bands of opticalabsorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability (A), branching ratio (β), radiative life time(τ_R) and stimulate demission cross–section(σ_p)of various emission lines have been evaluated.

Keywords: ZLSLCBS Glasses, Optical Properties, Judd-Ofelt Theory, Up-conversion properties.

I. Introduction

Transparent glass–ceramic as host materials for active optical ions have attracted great interest recently due to their potential application such asoptical fibers, sensors, infrared detectors, marine optical communications, up-conversion lasers, optical data storage and high density memory storage devices[1-5].Among different glass hosts, silicates glasseshave unique properties. They have high thermal stability,high transparency, a low melting point and low dispersion rates.Silicate (SiO_2) based glasses possess interesting properties like lower phonon energy and high density.Borosilicate glass systems exhibit high refractive indices, high gain density, high solubility and non-linear optical susceptibilities [6-10].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 [11-15].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials.I have studied on the absorption and emission properties of Ho^{3+}doped zinc lithium sodalimecadmium borosilicate glasses. 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).

II.Experimental Techniques

Preparation of glasses

The following Ho^{3+}doped borosilicateglass samples (35-x)SiO_2:10ZnO:10Li_2O:10CaO: :10Na_2O:10CdO:15B_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,Na_2O,CdO,$B_2O_3$and Ho_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1155^0C 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 %)
ZLSLCBS(UD)	35SiO_2:10ZnO:10Li_2O:10CaO:10Na_2O:10CdO:15B_2O_3
ZLSLCBS (HO1)	34SiO_2:10ZnO:10Li_2O:10CaO:10Na_2O:10CdO:15B_2O_3:1 Ho_2O_3
ZLSLCBS(HO1.5)	33.5SiO_2:10ZnO:10Li_2O:10CaO:10Na_2O:10CdO:15B_2O_3:1.5Ho_2O_3
ZLSLCBS(HO2)	33SiO_2:10ZnO:10Li_2O:10CaO:10Na_2O:10CdO:15B_2O_3:2Ho_2O_3

ZLSLCBS (UD) -Represents undopedZinc Lithium Sodalime Cadmium Borosilicate specimen.

ZLSLCBS(HO)-Represents Ho^{3+}dopedZinc Lithium Sodalime Cadmium Borosilicateglass specimens

III.Theory

3.1Oscillator Strength

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

$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon (\nu)\, d\nu$ (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 [17], using the modified relation:

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

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 $|4f^N (S, L) J\rangle$ level and the terminal J' manifold $|4f^N (S',L') J'\rangle$ is given by:

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

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

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

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

3.3Radiative 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:

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

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

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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'> to a final manifold $|4f^N$ (S,L)J>| is expressed as

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

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

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

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

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

IV. Result and Discussion

4.1XRD 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.

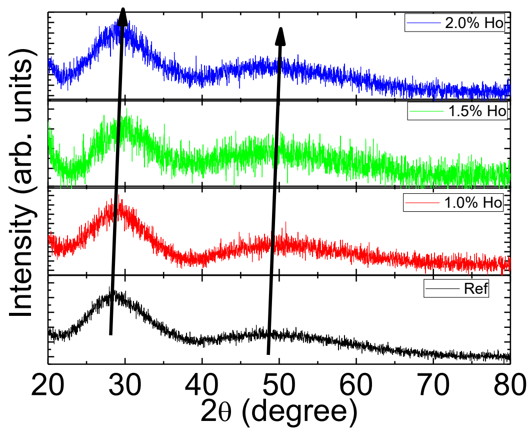

Fig. 1 X-ray diffraction pattern of SiO_2:ZnO:Li_2O:CaO:Na_2O:CdO:B_2O_3:Ho_2O_3

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4.2Up-conversion Mechanism

The up-conversion mechanism is given in Fig. (2). Two kinds of absorption took place in this mechanism; first one was ground state absorption (GSA) and then excited state absorption (ESA) occurred to populate upper levels and then emissions took place.

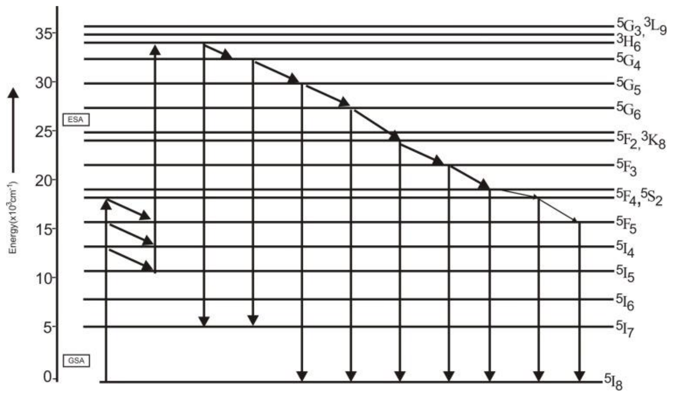

Fig. (2). Energy level diagram of Ho^{3+} ion and up conversion mechanism of Ho^{3+}doped ZLSLCBS glasses.

4.3 Absorption Spectrum

The absorption spectra of Ho^{3+}doped ZLSLCBS HO (01) glass specimen 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 ZLSLCBS HO(01)glass.

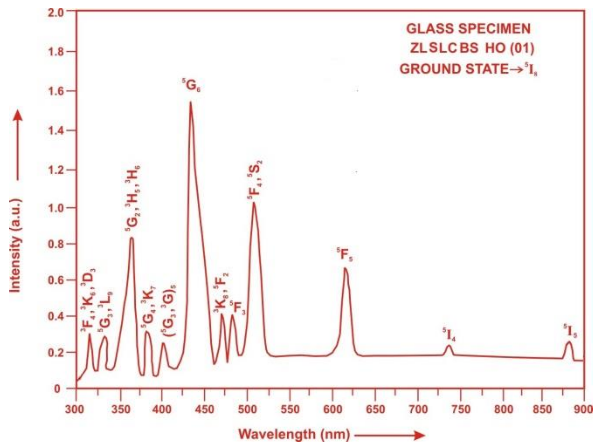

Fig. (3) Absorption spectra of ZLSLCBS HO (01) glass.

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

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

Energy level from $^5I_8$	Glass ZLSLCBS(HO01)		Glass ZLSLCBS(HO1.5)		Glass ZLSLCBS(HO02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5I_5$	0.38	0.24	0.35	0.24	0.31	0.24
$^5I_4$	0.07	0.02	0.04	0.02	0.03	0.02
$^5F_5$	3.62	2.80	3.58	2.77	3.49	2.74
$^5F_4$	4.66	4.33	4.62	4.30	4.57	4.26
$^5F_3$	1.56	2.40	1.52	2.39	1.48	2.37
$^3K_8$	1.41	1.97	1.38	1.94	1.32	1.92
$^5G_6$	24.81	24.81	23.46	23.49	22.87	22.94
$(^5G,^3G)_5$	3.84	1.71	3.78	1.69	3.67	1.64
$^5G_4$	0.09	0.61	0.07	0.60	0.05	0.59
$^5G_2$	5.65	5.30	5.61	5.06	5.57	4.96
$^5G_3$	1.49	1.38	1.43	1.35	1.38	1.34
$^3F_4$	1.37	4.19	1.34	4.14	1.27	4.04
r.m.s. deviation	±1.1075		±1.1036		±1.0921	

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

Table 3: F_2,ξ_{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 Sodalime Cadmium Borosilicateglasses (ZLSLCBS)Ω_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 spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 0.600 and 0.618 in the present glasses.

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

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

Glass Specimens	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4 / Ω_6	Ref.
ZLSLCBS (HO01)	6.012	1.358	2.197	0.618	P.W.
ZLSLCBS(HO1.5)	5.631	1.337	2.182	0.613	P.W.
ZLSLCBS(HO02)	5.497	1.300	2.165	0.600	P.W.
TEOS(HO)	8.139	4.513	5.996	0.762	[22]
ZLCBS(HO)	5.674	1.205	2.005	0.601	[23]
ABCMF(HO)	5.507	1.165	1.963	0.593	[24]

4.4Excitation Spectrum

The Excitation spectra of Ho^{3+}doped ZLSLCBSHO (01) glass specimen has 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 at349,419, 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 450nm.So this is to be chosen for excitation wavelength.

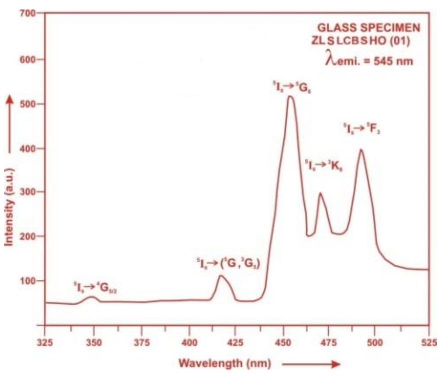

Fig. (4) Excitation spectrum of ZLSLCBS HO(01) glass.

4.5 Fluorescence Spectrum

The fluorescence spectrum of Ho^{3+}doped zinc lithium sodalimecadmium borosilicateglass(ZLSLCBS HO 01) is shown in Figure 5. There are nine broad bands observed in the Fluorescence spectrum ofHo^{3+}dopedzinc lithium sodalimecadmium borosilicateglass. The wavelengths of these bands along with their assignments are given in Table 5. The peak with maximum emission intensity appears at 501nm and corresponds to the ($^5F_4 \rightarrow {}^5I_8$) transition.

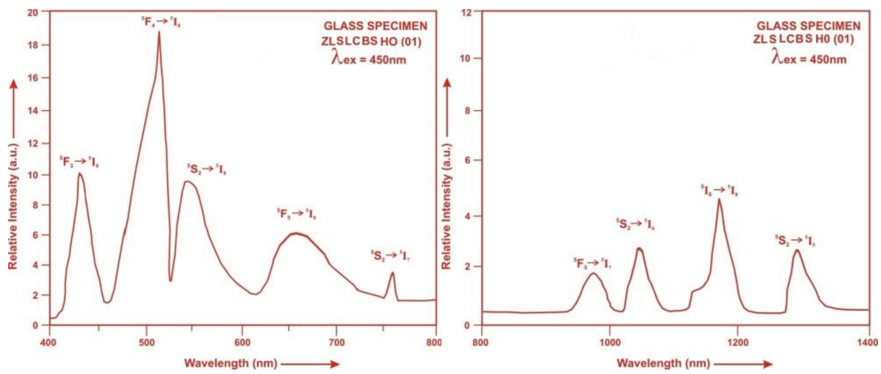

Fig. (5). Fluorescence spectrum of ZLSLCBS HO(01)glass.

Table5: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 ZLSLCBS glasses.

Transition		ZLSLCBS(HO 01)				ZLSLCBS(HO 1.5)				ZLSLCBS (HO 02)			
	λ_{max} (nm)	A_{rad}(s^{-1})	β	σ_p (10^{-20} cm^2)	τ_R(μs)	A_{rad}(s^{-1})	β	σ_p (10^{-20} cm^2)	τ_R (μs)	A_{rad}(s^{-1})	β	σ_p(10^{-20} cm^2)	τ_R(10^{-20} cm^2)
$^5F_3 \rightarrow {}^5I_8$	435	4163.48	0.2499	0.598		4140.42	0.2501	0.585		4119.18	0.2506	0.566	
$^5F_4 \rightarrow {}^5I_8$	501	6615.40	0.3971	1.239		6575.49	0.3971	1.215		6523.37	0.3969	1.188	
$^5S_2 \rightarrow {}^5I_8$	55	1737.8	0.10	0.432		1729.4	0.104	0.425		1719.	0.10	0.415	

	5	9	43			6	5			40	46		
$^5F_5 \rightarrow ^5I_8$	652	1888.50	0.1134	0.738		1874.18	0.1132	0.725		1851.55	0.1127	0.706	
$^5S_2 \rightarrow ^5I_7$	761	1318.41	0.0792	1.116	6003.15	1312.02	0.0792	1.092	6039.52	1304.39	0.0794	1.073	6084.63
$^5F_5 \rightarrow ^5I_7$	995	439.35	0.0264	1.211		434.16	0.0262	1.174		428.55	0.0261	1.137	
$^5I_6 \rightarrow ^5I_8$	1032	202.31	0.0121	0.700		201.23	0.0122	0.686		199.75	0.0122	0.672	
$^5S_2 \rightarrow ^5I_5$	1195	230.96	0.0139	1.208		229.36	0.0139	1.186		227.76	0.0139	1.163	
$^5S_2 \rightarrow ^5I_6$	1310	61.62	0.0037	0.617		61.30	0.0037	0.605		60.91	0.0037	0.588	

V. Conclusion

In the present study, the glass samples of composition (35-x) SiO_2:10ZnO:10Li_2O:10CaO:10Na_2O:10CdO:15B_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 ZLSLCBS (HO 01), suggesting that glass ZLSLCBS (HO 01) is better compared to the other two glass systems ZLSLCBS (HO1.5) and ZLSLCBS(HO02).

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