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Spectroscopic Properties of Tm^{3+} Doped in Zinc LithiumAluminoAntimony BorophosphateGlasses

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Abstract
Glass of the system: (35-x) P_2O_5:10ZnO:10Li_2O:10Al_2O_3:15Sb_2O_3:20B_2O_3: xTm_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 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, branching ratio, radiative life time and stimulatedemission cross–section of various emission lines have been evaluated

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

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I. Introduction

Transparent glass–ceramic as host materials for active optical ions have attracted great interest recently due to their potential application in optical devices such as frequency-conversion materials, lasers,and optical fiber amplifiers [1-5].Among different glass hosts, phosphate glasseshave unique properties. They have high thermal stability,high transparency, a low melting point, a highgain density and low dispersion rates [6-8].Phosphateglasses have excellent transparency,low melting temperatures, high thermal expansion coefficient and good mechanical and thermal stability.Phosphate glasses are very well known for their suitable mechanical, chemical properties and excellent optical properties [9-11].Wide range of special properties of phosphate glasses such as low glass transition temperature, high thermal expansion coefficient and biocompatibility guided to use these materials for photonics applications, solid-state lasers and vitrification of radio-active waste [12]. Zinc oxide is added in the glass matrix to increase glass forming ability and to ensure low rates ofcrystallization in the glass system [13].Thulium doped crystals and glasses have awaken technological interest due to their potential use as laser activemedia with emissions in the visible and near infrared spectral regions for high power, amplifying, optical reading and other applications [14,15].

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 Tm^{3+}doped zinc lithiumaluminoantimonyborophosphateglasses. 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 Tm^{3+}doped borophosphateglass samples (35-x) P_2O_5:10ZnO:10Li_2O:10 Al_2O_3:15Sb_2O_3:20B_2O_3:xTm_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 P_2O_5,ZnO,Li_2O, Al_2O_3, Sb_2O_3,$B_2O_3$and Tm_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 950^0C 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.**

Chemical composition of the glasses

Sample	Glass composition (mol %)
ZLAABP (UD)	$35P_2O_5$:10ZnO:$10Li_2O$:$10Al_2O_3$:$15Sb_2O_3$:$20B_2O_3$
ZLAABP(TM 1)	34 P_2O_5:10ZnO:$10Li_2O$:$10Al_2O_3$:$15Sb_2O_3$:$20B_2O_3$:$1Tm_2O_3$
ZLAABP (TM1.5)	33.5 P_2O_5:10ZnO:$10Li_2O$:$10Al_2O_3$:$15Sb_2O_3$:$20B_2O_3$:$1.5Tm_2O_3$
ZLAABP(TM 2)	33 P_2O_5:10ZnO:$10Li_2O$:$10Al_2O_3$:$15Sb_2O_3$:$20B_2O_3$:$2Tm_2O_3$

ZLAABP (UD) -Represents undopedzinc lithiumaluminoantimony borophosphateglass specimens.
ZLAABP (TM) -Represents Tm^{3+}dopedzinc lithiumaluminoantimony borophosphateglass 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> level and the terminal J' manifold $|4f^N$ (S', L') J'> is given by:

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

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

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

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

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:

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

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

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

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 - P_2O_5 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.

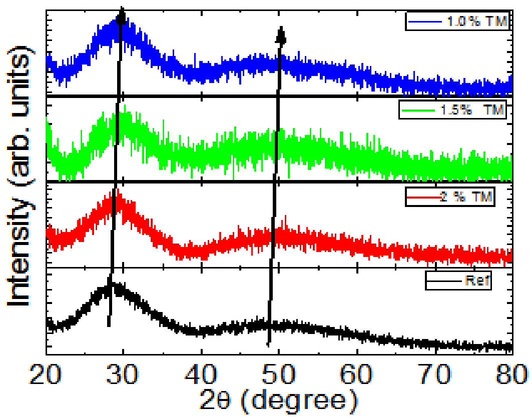

Fig. 1 X-ray diffraction pattern of P_2O_5:ZnO: Li_2O:Al_2O_3:Sb_2O_3:B_2O_3: Tm_2O_3.

4.2 Absorption Spectrum

The absorption spectra of Tm^{3+}doped ZLAABP glass specimens have been presented in Figure 2 in terms of optical density versus wavelength.Five absorption bands have been observed from the ground state $^3H_6$to excited states $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3$ and$^1G_4$for Tm^{3+} doped ZLAABPglasses.

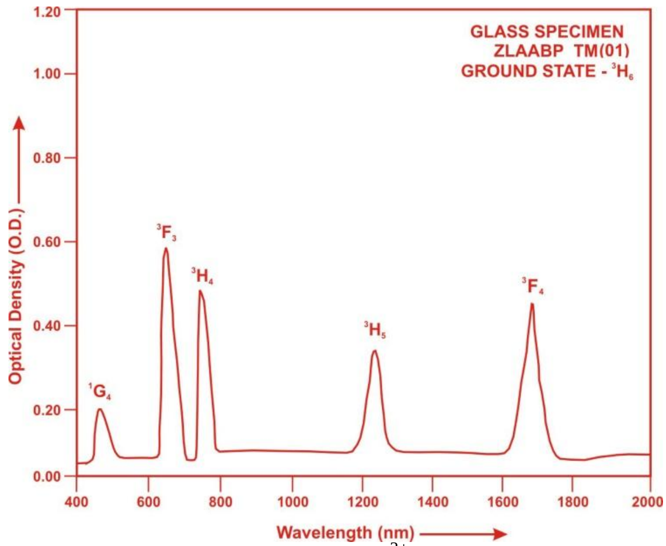

Fig. (2) Absorption spectrum of Tm^{3+}doped ZLAABP glasses

The experimental and calculated oscillator strength for Tm^{3+}ions in ZLAABP glasses are given in **Table 2.**
Table 2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Tm^{3+}ions in ZLAABP glasses.

Energy level from $^3H_6$	**Glass ZLAABP(TM01)**		**Glass ZLAABP(TM1.5)**		**Glass ZLAABP(TM02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^3F_4$	1.82	1.86	1.80	1.84	1.77	1.81
$^3H_5$	1.36	1.44	1.33	1.43	1.31	1.42
$^3H_4$	1.97	2.03	1.95	2.02	1.93	2.01
$^3F_3$	2.95	3.02	2.92	2.99	2.89	2.97
$^1G_4$	0.76	0.88	0.74	0.87	0.72	0.86
r.m.s. deviation	±0.07851		±0.08703		±0.09761	

*Low r.m.s.deviationvalues clearly indicate the accuracy of fitting.

In theZincLithiumAluminoAntimonyBorophosphateglasses (ZLAABP)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 $\Omega_4>\Omega_2>\Omega_6$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 1.468 and 1.500 in the present glasses.
The values of Judd-Ofelt intensity parameters are given in **Table 3.**

Table3:Judd-Ofelt intensity parameters for Tm^{3+} doped ZLAABPglass specimens.

Glass Specimen	**$\Omega_2(pm^2)$**	**$\Omega_4(pm^2)$**	**$\Omega_6(pm^2)$**	**Ω_4/Ω_6**	**Ref.**
ZLAABP (TM 01)	6.729	8.516	5.677	1.500	P.W.
ZLAABP (TM 1.5)	6.691	8.417	5.623	1.497	P.W.
ZLAABP (TM 02)	6.621	8.248	5.619	1.468	P.W.
BiB_3O_6 Glasses	3.254	4.830	1.316	3.670	[22]

4.3. Fluorescence Spectrum

The fluorescence spectrum of Tm^{3+}doped in zinc lithiumaluminoantimony borophosphateglass is shown in Figure 3. There are two broad bands observed in the Fluorescence spectrum ofTm^{3+}dopedzinc lithiumaluminoantimony borophosphate glass. The wavelengths of these bands along with their assignments are given in Table 4. The peak with maximum emission intensity appears at 1810nm and corresponds to the ($^3F_4 \rightarrow {}^3H_6$) transition.

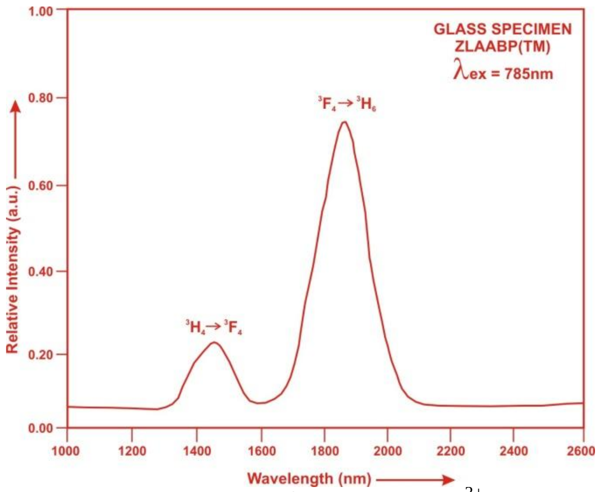

Fig. (3). Fluorescence spectrum of doped with Tm^{3+}ZLAABPglasses.

Table4: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 Tm^{3+} doped ZLAABP glasses

Transition		ZLAABP(TM01)				ZLAABP(TM1.5)				ZLAABP(TM 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)
$^3H_4 \rightarrow {}^3F_4$	1450	354.85	0.4412	4.963	1243.43	352.22	0.4413	4.794	1252.85	349.32	0.4423	4.599	1266.25
$^3F_4 \rightarrow {}^3H_6$	1810	449.38	0.5588	6.540		445.96	0.5587	6.392		440.41	0.5577	6.251	

V. Conclusion

In the present study, the glass samples of composition (35-x) P_2O_5:10ZnO:10Li_2O:10Al_2O_3:15Sb_2O_3:20B_2O_3: xTm_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 ($^3F_4 \rightarrow {}^3H_6$) for glass ZLAABP(TM 01), suggesting that glass ZLAABP(TM 01) is better compared to the other two glass systems ZLAABP (TM1.5) and ZLAABP(TM02).

References:

[1]. Hatefi,Y.,Shahtahmasebi, N.,Moghimi,A.,Attaran,E.(2011). Ultraviolet to visiblefrequency-conversion properties of rare earths doped glass–ceramics, J. RareEarths 29, 484–488.

[2]. Swapna, K., Mahamuda,S.K., Srinivasa,Rao A., Jayasimhadri, M., Sasikala, T., Rama, M. L. (2013). Visible fluorescence characteristics of Dy3+doped zinc alumino bismuth borate glasses for optoelectronic devices. Ceramics International, 39: 8459.

[3]. Silversmith, A.J., Nguyen, N.T.T., Campbell, D.L., Boye,D.M., Ortiz, C.P., Hoffman, K.R. (2009).Fluorescence yield in rare-earth-doped sol – gel silicate glasses, J. Lumin. 129, 1501–1504.

[4]. Rao,TVR. Reddy, R.R., NazeerAhammed, Y., Parandamaiah, M. (2000). Luminescence properties of Nd3+, TeO2-B2O3–P2O5–Li2O glass. Infrared Physics & Technology, 41: 247.

[5]. Kawamoto, Y.,Kanno, R.,Qiu, J. (1998).Up conversion luminescence of Er3+ in transparent SiO2—PbF2—ErF3 glass–ceramics, J. Mater. Sci. 33, 63–67.

[6]. Reddy, A. ,Sekhar,M. C. ,Pradeesh, K. , Babu, S. S. ,Prakash,G. V. (2011).Optical properties of Dy3+-doped sodium-aluminumphosphateglasses, J Mater Sci., 46 ,2018-2023.

[7]. Liu, Y.,Ren, J., Tong, Y.,Wang, T.,Xu, W. and Chen,G. (2012).Observation of Intra-and Inter-Configurational Luminescence of Pr3+-Doped Strontium Phosphate Glasses, Journal of the American Ceramic Society 95, 41.

[8]. Rasool,N., Rama Moorthy, L. and Jayasankar,C. (2013).Spectroscopic Investigation of Sm3+ doped phosphate based glasses for reddish-orange emission, Optics Communications,311, 156.

[9]. Gapontsev, V.P.,Matitsin, S.M.,Isineev, A.A.,Kravchenko, V.B.(1982). Erbium glass lasers and their applications.Opt. Laser Technol., 14, 189–196.

[10]. Jiang, S.,Myers, M.J.,Rhonehouse, D.L., Hamlin, S.J., Myers, J.D.,Griebner, U., Koch, R., Schonnagel, H. (1997).Ytterbium-doped phosphate laser glasses.SPIE International Conference onPhotonics West, San Jose, CA, USA.

[11]. Campbell, J.H.,Suratwala, T.I. (2000). Nd3+-doped phosphate glasses for high-energy/high-peak-power lasers. J. Non-Cryst. Solids, 263, 318–341.

[12]. Krishnaiah, K. V. ,Rajeswari, R. ,Kumar,K. U. ,Babu,S. S. ,Martín, I. andJayasankar, C. (2014).Spectroscopy and radiation trapping of Yb3+ ions in lead phosphate glasses, Journal of Quantitative Spectroscopy and Radiative Transfer 140, 37.

[13]. Pavani,P. G.,Sadhana, K. and Mouli,V. C. (2011).“Optical, physical and structural studies of boro-zinc tellurite glasses,” Physica B: Condensed Matter, 406, 7, 1247.

[14]. Miazato, K., de Sousa, D.F., Delben, A., Delben, J.R., de Oliveira, S.L. Nunes, L.A.O. (2000). “Upconversionmechanisms in Tm3+ doped lead fluoroindogallate glasses”. J. of Non-Crystalline Solids, 273, 246.

[15]. Gaël, P., Cassanjes,F.C.,deAraújo, Cid B., Jerez, Vladimir A. ,Ribeiro, Sidney J. L.,Messaddeq,Y.

andPoulain,M.(2003). Optical properties and frequency upconversion fluorescence in a Tm3+ -doped alkaliniobiumtelluriteglass.AIP Journal of Applied Physics 93, 3259 .
[16]. Gorller-Walrand, C. and Binnemans, K. (1988). Spectral Intensities of f-f Transition. In: Gshneidner Jr., K.A. and Eyring,L., Eds.,Handbook on the Physics and Chemistry of Rare Earths, Vol. 25, Chap. 167, North-Holland, Amsterdam, 101-264.
[17]. Sharma, Y.K., Surana, S.S.L. and Singh, R.K. (2009). Spectroscopic Investigations and Luminescence Spectra of Sm3+ Doped SodaLime Silicate Glasses. Journal of Rare Earths, 27, 773.
[18]. Judd, B.R. (1962). Optical Absorption Intensities of Rare Earth Ions. Physical Review, 127, 750.
[19]. Ofelt, G.S. (1962). Intensities of Crystal Spectra of Rare Earth Ions. The Journal of Chemical Physics, 37, 511.
[20]. Sinha, S.P. (1983).Systematics and properties of lanthanides, Reidel, Dordrecht.
[21]. Krupke, W.F. (1974).IEEE J.Quantum Electron QE, 10,450.
[22]. Majchrowski,A.,Jaroszewicz, L.,Kuznik, W. Brik, M.G. ,Klosowicz, S., I.V. Kityk(2012).Specific features of Tm3+ doped BiB3O6 glasses fluorescence spectra and theirkinetics.SpectrochimicaActa PartA87, 154.

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