calculated spectral intensities is small which indicates the validity of Judd-Ofelt theories.

The summary of the Judd-Ofelt intensity parameters for the four glasses doped with Sm_2O_3 is shown in Table 3.

Table 2. Experimental and calculated spectral intensities ($\times 10^{-6}$) of observed absorption bands of Sm^{3+} ions in LBWBS1-5 glasses

Transition $^6G_{5/2}$	λ (nm)	Energy (cm^{-1})	LBWBS1		LBWBS2		LBWBS3		LBWBS4		LBWBS5	
			f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^6F_{11/2}$	941	10582	0.01	0.14	1.65	0.69	1.06	0.58	1.20	0.67	0.35	0.68
$^6F_{9/2}$	1076	9277	0.67	0.89	4.70	4.42	3.64	3.62	4.33	4.21	3.74	4.24
$^6F_{7/2}$	1226	8130	1.14	1.30	6.88	7.18	5.44	5.51	6.25	6.40	6.63	6.26
$^6F_{5/2}$	1374	7246	0.58	0.72	4.53	5.44	2.93	3.47	3.25	4.03	3.11	3.53
$^6F_{3/2}$	1477	6730	0.67	0.50	6.38	4.37	3.53	2.41	4.46	2.81	2.75	2.18
$^6H_{15/2}$	1537	6566	0.22	0.00	2.69	0.03	1.22	0.02	2.29	0.03	1.24	0.03
$^6F_{1/2}$	1595	6460	0.16	0.26	1.54	2.82	0.54	0.72	0.41	1.46	0.54	0.88
Rms dev			±0.16		±1.44		±0.72		±1.18		±0.60	

Table 3. Comparison of Judd-Ofelt intensity parameters (Ω_λ, λ=2, 4 and 6) ($\times 10^{-20}$ cm^2) of sm^{3+} ions in various glass environments.

Glass	Ω_2	Ω_4	Ω_6	Order	Ω_4/Ω_6
LBWBSM1	0.50	0.79	0.39	$\Omega_4 > \Omega_2 > \Omega_6$	2.02
LBWBSM2	5.50	6.11	2.62	$\Omega_4 > \Omega_2 > \Omega_6$	2.32
LBWBSM3	2.45	4.18	2.22	$\Omega_4 > \Omega_2 > \Omega_6$	1.88
LBWBSM4	2.97	5.02	2.67	$\Omega_4 > \Omega_2 > \Omega_6$	1.88
LBWBSM5	1.76	4.68	2.66	$\Omega_4 > \Omega_2 > \Omega_6$	1.76

The values of J-O parameters are found to be in the order of $\Omega_4 > \Omega_2 > \Omega_6$ for all the four glasses. The lower value of Ω_2 indicates that the symmetry of the ligand field at rare earth site is higher [23]. The larger the size of the modifier ion causing the average Sm–O distance to increase. Such an increase in the bond lengths .produces a weaker field around Sm^{3+} ions leading to a lower value of Ω_2 for the glass. Covalency between the Sm^{3+} ion and the ligand oxygen ion also contribute to Ω_2 [24].

4. Conclusions:

The glasses of present study are fabricated using conventional melt quenching technique. The bonding parameter obtained in all the glass systems is of ionic in nature. Very low rms deviation values obtained for the experimental and calculated oscillator strengths reflect the goodness of fitting

Lead bismuth tungstonate borate glasses doped with Samarium ion

P. Sree Ram Naik[2], P. V. Ramana[1], M. Satyavani[3], *Y. N. Ch. Ravi Babu[4]

[1]A.G. & S.G.S. Degree College (A), Vuyyuru, Andhra Pradesh, India
[2]USIC, S.V.University, Tirupati- 517502, Andhra Pradesh, India
[3]D.N.R.College (A), Bhimavaram-534202, Andhra Pradesh, India
[4]The Hindu College, Machilipatnam-521002, Andhra Pradesh, India

Abstract

Heavy metal multi component oxide glasses with the molar compositions of (60-x) PbO - x Bi_2O_3 -10WO_3-29B_2O_3-1Sm_2O_3 (where x = 10, 15, 20, 25, 30 mol %) were prepared using conventional melt-quenching technique. The absorption spectra of all these glasses were studied at room temperature. The spectral data from the optical absorption studies were employed to compute various spectroscopic parameters like Judd-Ofelt (Ω_λ, λ = 2, 4, 6) intensity parameters. The higher values Ω_2 of compared to other J-O parameters obtained in all the five glasses suggest the asymmetry around the rare earth ion in all the glass matrices. The magnitudes of Ω_4/Ω_6 ratio quality factor decreases with the decrease in the PbO content in the host matrices reflect the dual nature of PbO. The radiative properties obtained in our investigations suggest their lasing candidature.

Key words: *Glasses, melt-quenching technique, Judd-Ofelt parameters, lifetimes, branching ratio, absorption cross sections, emission cross sections*

1. Introduction.

Glasses with heavy metal oxides are very attractive hosts creating good environment for RE ions [1–4]. Bi_2O_3 based glasses have potential applications in optoelectronic circuits as ultra fast switches, infrared windows, optical isolators [6, 7]. The nonconventional glass forming oxide Bi_2O_3, participates in the glass structure with two possible co-ordinations [BiO_3] pyramidal and [BiO_6] octahedral units [6–8]. The property of phototropism of WO_3 mixed glasses, they are proposed as promising candidates for application in information display devices of high memory [9, 10]. WO_3 containing host materials are also widely used in smart windows to control solar input of buildings or related to large area displays [11, 12]. The dopant Sm^{3+} ($^4f_5$) ion is one of the most interesting RE ions to analyze the fluorescence properties as its emitting $^4G_{5/2}$ level exhibits relatively high quantum efficiency. The glass containing Sm^{3+} ions have the most interesting qualities due to their potential applications for high-density optical storage, under sea communication and color displays [13].

2. Experimental:

To prepare the glass system, AR grade chemicals which are used. Conventional melt quench technique is used for the preparation of glass. Chemicals were thoroughly mixed and grinded for about one hour in an agate mortar. 10gm mixture is taken in alumina crucible and is kept in a muffle furnace for about 4-5 hours. Temperature was ranged up to 900-1000°C. When this melt attain a desirable viscosity and become homogeneous, then it was poured on a metal plate. Glass was annealed at 330°C in an annealed furnace. After 2-3 hours we can take it out at room temperature. Resultant glass was characterized by characterization method. The refractive index 'n' of the samples was estimated by conventional methods [14]. Absorption spectra were characterized by taking the undoped glasses as references for all the samples on JASCO UV–vis–NIR V-670 spectrometer.

3. Results and discussion

The physical and optical parameters such as refractive index (n), density, molar volume V_m are estimated. It is interesting to note that the increase in the Bi_2O_3 content in the glass systems enhances various optical parameters such as refractive index, polaron radius, inter ionic distance, molar refractivity, electronic polarizability, optical dielectric constant and density. Concentration and field strength values show decreasing trend with the increase of bismuth content.

Table: 1. Physical properties of Sm^{3+} ions in LBWBS1-5 glasses.

Physical property	LBWBS1	LBWBS2	LBWBS3	LBWBS4	LBWBS5
Average molecular weight	203.4	215.5	227.6	239.8	251.9
Density (g/m^3)	7.421	7.457	7.510	7.552	7.596
Refractive index 'n'	2.17	2.13	2.101	2.066	2.031
Concentration 'N' (10^{20}ions/cm^3)	4.356	4.121	3.943	3.756	3.594
Polaron radius 'r_p' (A^0)	6.671	6.797	6.906	7.014	7.131
Interionic distance 'r_i' (A^0)	1.689	1.599	1.677	1.757	1.846
Field strength F (10^{16}cm^{-2})	6.74	6.49	6.28	8.29	7.98
Molar volume 'V_m'	27.47	28.90	30.31	31.75	33.17
Optical dielectric constant	3.708	3.536	3.414	3.268	3.127

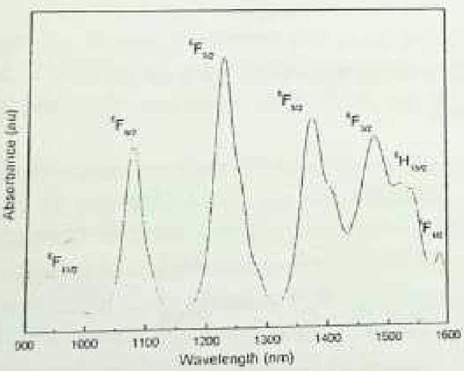

Fig 1. NIR absorption spectra of Sm^{3+} ions in LBWBS

The absorption spectra of Sm^{3+}: lead bismuth tungstonate borate glasses are presented in Fig.1 with seven distinctive and sharp absorption bands at 940nm, 1077nm, 1227nm, 1374nm, 1477nm, 1523nm and 1586nm. These bands are assigned to corresponding electronic transitions $^6H_{5/2} \rightarrow {}^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6F_{1/2}$ respectively [15-18]. J-O theory is applied for the computation of these sharp absorption bands [19]. Masking of many characteristic absorption bands of Sm^{3+} ions in UV-Visible region takes place with gradual increase of bismuth content in the glass series [20].

The squared reduced matrix elements $\|U^\lambda\|^2$ of the unit tensor operators available in the literature [21] is employed for the evaluation of certain spectroscopic parameters. The oscillator strengths f_{exp} are evaluated from the following expression (1). Experimental oscillator strengths are obtained using Beer-Lambert's law.

$$f_{exp} = 4.32 \times 10^{-9} \int \varepsilon(\upsilon)\, d\upsilon \qquad \ldots\ldots (1)$$

Where ε is the molar extinction coefficient at energy υ cm^{-1}. $\int \varepsilon(\upsilon)\, d\upsilon$ was evaluated by measuring the area under the curve shown in Fig 1. Theoretical the intensities of spectral lines were evaluated using the literature [19]. The experimental and calculated oscillator strengths f_{exp} and f_{cal} are shown in Table 2. Computed J-O intensity parameters Ω_2, Ω_4, Ω_6 [13, 22] obtained by least square fit method are reported in Table 3. The rms deviation [13] between observed and procedure and the validity of the Judd-Ofelt theory. It is also worth to note that the magnitude of the spectroscopic quality factor is less than unity in all the glass matrices.

References

[1] I.V. Kityk, J.Wasylak, J.Kucharski, D.Dorosz, J. Non-Cryst. Solids 297 (5) (2002) 285- 289

[2] P. Srivastava, S.B. Rai, D.K. Rai, Spectrochim. Acta, Part A 59 (14) (2003) 3303-11.

[3] Y.S. Han, J.H. Song, J.J. Heo, J. Appl. Phys. 94 (5) (2003) 2817-2820.

[4] A.G.S. Filho, J.M. Filho, F.E.A. Melo, M.C.C. Custodio, R. Lebullenger, A.C.Hernandes, J. Phys. Chem. Solids 61 (2000) 1535-42.

[5] K. Nassau and D. L. Chadwick, J. Am. Ceram. Soc., 65 (1982) 486-491.

[6] R. Luciana, P. Kassab, H. Sonia Tatumi, C. M. S. Mendes, C. Lilia. Courrol, Niklaus and U. Wetter, Optics Express, 6 (2000) 104-108.

[7] L.Baia, R.Stefan, W. Kiefer, J.Pop and S. Simon, J. Non-Cryst. Solids 303 (2002) 379-386.

[8] D. K. Durga and N. Veeraiah, J. Mater. Sci., 36 (2001) 5625-5632.

[9] Lee, E. K. P. S.; Ma, J. Euro. Electrophoretic deposition (EPD) of WO_3 nanorods for electrochromic application. Journal of Ceramic Society 2010, 30, 1139–1144.

[10] Baetens, R.; Jelle, B. P.; Gustavsen, A. Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: a state-of-the-art review. Solar Energy Materials and Solar Cells 2010, 94, 87–105.

[11] Xu, N.; Sun, M.; Cao, Y. W.; Yao, J. N.; Wang, E. G. Influence of pH on structure and photochromic behavior of nanocrystalline WO_3 films. Applied Surface Science 2000, 157, 81–84.

[12] Avellaneda, C. O.; Bueno, P. R.; Bulhoes, L. O. S. Synthesis and electrochromic behavior of lithium-doped WO_3 films. Journal of Non-Crystalline Solids 2001, 290, 115–121.

[13] Vekatramu V, Babu P, Jaya Sankar CK, Th. Troester, Sievers W, Wortmann G. Optical spectroscopy of Sm^{3+} ions in phosphate and fluorophosphate glasses. Opt Mater 2007;29: 1429–39.

[14] Korotkov AS, Atuchin VV. Accurate rediction of refractive index of inorganic oxides by chemical formula. J Phys Chem Solids 2010;71: 958–64.

[15] Reddy RR, Nazeer Ahmmed Y, Abdul Azeem P, Ramgopal K, Rao TVR, Buddhudu S, Sooraj Hussain N. Absorption and emission spectral studies of Sm^{3+} and Dy^{3+} doped alkali fluoroborate glasses. J.Quantum spectrosc.Radiat.Transfer. (2003);77: 149-63

[16] Lakshminarayana G, Qiu J. Photoluminescence of Pr^{3+},$Sm^{3+}$and Dy^{3+}:SiO_2–Al_2O_3–LiF–GdF_3 glass ceramics and Sm^{3+},Dy^{3+} : GeO_2 –B_2O_3–ZnO–LaF_3 Glasses. Physica B (2009); 404: 1169-80.

[17] Aruna V, Sooraj Hussain N, Buddhudu S. Spectra of Sm^3 and Dy^3: B_2O_3–P_2O_5–R_2SO_4 Glasses. Mater. Res. Bull. (1998); 33 : 149-59

[18] Sooraj Hussain N, Aruna V, Buddhudu S. Absorption and photoluminescence spectra of Sm^{3+} :TeO_2 – B_2O_3–P_2O_5–Li_2O glass' of Mater. Res. Bull. (2000); 35:703-9

[19]Judd BR. Optical absorption intensities of rare-earths. Phys. Rev (1962); 127:750-61.

[20] Atul D Sontakke, Kaushik Biswas, Anal Tarafder, Sen R, Annapurna K. Broadband Er^{3+} emission in highly nonlinear Bismuth modified Zinc-Borate Glasses. Opt. Mater. Express (2011); 1: No. 3, 344-56

[21] Ofelt GS. Intensities of crystal spectrum of rare-earth ions. J.Chem.Phys. (1962); 37: 511-20.

[22] Carnall WT, Goodman GL, Rajnak K, Rana RS. A systematic analysis of the spectra of the lanthanides doped into single crystal LaF^3. J.Chem.Phys. (1989); 90: 3443– 57

[23] Ratnakaram YC, Thirupathi Naidu D, Vijay Kumar A, Gopal NO.Influence of mixed alkalies on absorption and emission properties properties of Sm^{3+} ions in borate glasses. Phys B 2005;358: 296–307.

[24] Rukmini E, Jayasankar CK. Optical properties of Sm^{3+} ions in zinc borosulphate glasses and alkali zinc borosulphate glasses. Opt Mater 1997;29:193–205.