ISSN : 0974 - 7486 Volume 7 Issue 5

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(5), 2011 [321-324]

Absorption spectral studies of Er^{+3} ions in sodium-lead-barium-aluminium phosphate (SLBAP) glass

P.Kothari[1]*, R.P.Dubedi[2], U.Pathak[2]

[1]Department of Chemistry, Govt. P.G. College Gopeshwar, Chamoli - 246 401, Uttarakhand, (INDIA)

[2]Department of Chemistry, Govt. P. G. College Pithoragarh - 262 502, Uttarakhand, (INDIA)

E-mail: drpramodkothari@gmail.com

Received: 20th March, 2011 ; Accepted: 30th March, 2011

ABSTRACT

Sodium-lead-barium-aluminium phosphate (SLBAP) glass doped with tripositive erbium ion have been prepared by melt-quenching technique. The absorption spectral studies of doped SLBAP glass have been performed to compute the phenomenological Judd-Ofelt parameters ($\Omega\lambda$) and various spectroscopic parameters like Slater-Condon parameter (F_k) k=2,4,6, Lande' parameter (ζ_{4f}), Racah parameter (E^k) k=1,2,3, nephelauxetic ratio (β') and bonding parameters ($b^{1/2}$) to study the local structure of the ligands around the rare earth ion.

KEYWORDS

Phosphate glass;
Rare earth ion in glass;
Absorption spectrum;
Judd-Ofelt parameters.

INTRODUCTION

Rare earth ions are employed in optical applications due to their metastable excited states over the entire range of optical frequencies[1,2]. For many years, rare-earth doped glasses have been used to make bulk lasers and amplifier devices[3]. The past literature shows that the rare earth ions find more important application in the preparation of the laser materials[4-6]. Rare earth doped crystals like Nd:YAG are considered to be excellent laser materials[7,8], but the rare earth doped glasses have distinctive advantages[9] over doped crystals such as flexibility in size and shape and excellent optical quality. The rapid development of rare earth doped silica fiber amplifiers and lasers have considerably increased the interest in rare earth doped planar waveguide devices. Furthermore, reliable high power CW diode laser pumps provide the possibility of miniaturizing conventional solid-state lasers and amplifiers[10,11]. Such glass based rare earth doped lasers and amplifiers are highly promising for producing small, compact, efficient and reliable communication, signal processing, sensing and medicine applications.

Rare earth doped glasses are used in a large number of optical devices because of the large number of absorption and emission bands available using the various rare earth elements[12,13]. As an example, the variation in the green intensity ratio between the $^2H_{11/2}$ and $^4S_{3/2}$ energy levels to the ground state of Er^{+3} ions has been used as the measure parameter in temperature sensors[14,15].

In the present work a new kind of Phosphate Glass is prepared. Phosphate glasses on the contrary to silicate have lower melting and transition temperatures and posses no tendency to crystallization which is critical during optical fibre drawing[16]. Tellurite and fluorite glasses manifest both good optical properties and low phonon energy, however their industrial applications are limited due to their low thermal stability and relatively difficult and costly synthesis[17].

The spectroscopic properties of rare earth ions are strongly affected by the local structure at the rare earth sites[18-20] and the distribution of the doped ions in the glass matrix[21-23]. The local structure properties are the type and arrangement of the ligands around the rare earth ions. They determine the field strength and symmetry at the rare earth site and the bonding between rare earth ion and ligand. The knowledge of such relationships between the structure of the host glass and the properties of the doped laser ions is useful for designing laser glasses with definite properties.

EXPERIMENTAL

A sodium-lead-barium-aluminium phosphate glass with doping concentration of rare earth ion was prepared by melt quenching technique. The composition (by weight) was approximately $Na(PO_3)_6$ 70% -BaO 15%-PbO 10%-Al_2O_3 5%-R Ln (Where R=0.5 % and Ln= Er^{+3}). Earlier studies[24] have shown that Stimulated emission cross-section (σ) value increases with the size of the alkali metal. That is why sodium oxide has been widely used and has been chosen as primary modifier in the present study. Increase of percentage of primary modifier beyond a certain value does not further increase the value of Stimulated emission cross-section (σ). However, addition of secondary modifier further increases the σ value. The σ value also increases[24] with the increase of the size of the cation of the modifier viz MgO<CaO<BaO. Consequently, BaO was used as secondary modifier. Addition of secondary modifier shifts the IR cut of edge[25] toward longer wavelengths making the rare-earth doped glasses highly suitable for fiber amplifier to be used in telecommunication.

The spectral measurements were carried out by spectrophotometer method. The Absorption spectra in the spectral range 200-800 nm were recorded on UV-Visible double beam spectrophotometer model Perkin Elmer spectrophotometer model lambda 35. The Absorption spectra have been recorded in terms of wavelength (nm) vs. Absorbance (a.u.). The absorption spectra of Er^{+3} doped SLBAP glass have been investigated. From these spectral data Judd-Ofelt parameters ($\Omega\lambda$), Slater-Condon parameter (F_k) k=2,4,6, Lande' parameter (ζ_{4f}), Racah parameter (E^k) k=1,2,3, nephelauxetic ratio ($\beta^{'}$) and bonding parameters ($b^{1/2}$) have been calculated to study the nature of bonding in these glasses. Intensities of the f-f transitions in the absorption spectra have been analyzed by the application of the Judd-Ofelt theory

RESULTS AND DISCUSSION

Spectral intensities

From the absorption spectra, it is observed that 8 absorption peaks are clearly observed in the wavelength range 200–800 nm and can be attributed to transitions from the ground state $^4I_{15/2}$ to the higher energy states. The oscillator strengths for electric dipole transitions from the ground state $^4I_{15/2}$ to upper energy levels can be experimentally determined using the equation

$$P_{exp} = 4.6\times10^{-9}\times\frac{1}{cl}\log\frac{I_0}{I}\times\Delta\upsilon^{1/2} \qquad (1)$$

Where c is the concentration of the absorbing ion per unit volume, l is the path length and log (I_0/I) is the absorbance and $\Delta\nu_{1/2}$ is half bandwidth. However for a solid material it is generally expressed in terms of line strength $S_{exp.}$

$$P_{exp} = \frac{8\pi^2 mc\nu}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n}\right]S_{exp} \qquad (2)$$

Where (2J + 1) is the degeneracy of the ground state of the rare-earth ions, n is the refractive index of the medium, m is the mass of the electron, ν is the mean energy of the transition, the factor $(n^2+2)^2/9$ represents the local field correction for an ion embedded in a dielectric medium. Since the bands produced by the magnetic dipole mechanism have very low spectral intensity compared to that of the electric dipole bands, S_{md} could be neglected in comparison to S_{ed}, which is given by

$$S_{ed}\left[(S,L)J:(S',L')J'\right] = \sum_{\lambda=2,4,6}\Omega_\lambda\left|\left\langle(S,L)J\left\|U^{(\lambda)}\right\|(S',L')J'\right\rangle\right|^2 \qquad (3)$$

where $\left|\left\langle(S,L)J\left\|U^{(\lambda)}\right\|(S',L')J'\right\rangle\right|^2$ are the reduced matrix elements of a unit tensor operator evaluated in the intermediate coupling approximation. The values of these matrix elements reported by Carnall et al.[26] have been used since these elements are host invariant. Substituting the oscillator strengths calculated from the absorption spectra and using the values of reduced matrix elements and other parameters, $\Omega\lambda$ (λ = 2,4,6) can be calculated by a least squares method.

The experimental oscillator strengths, experimental line strength (S_{exp}) and calculated line strength (S_{cal}) with their differences (ΔS) of all the observed bands of Er^{3+} doped glasses are presented in TABLE 1.

To find out the Judd–Ofelt intensity parameters we substitute the values of oscillator strengths from TABLE 1 in Eq. 3 and consider these relations as equations of unknowns Ω_2, Ω_4 and Ω_6. Using least squares fit method and using 8 linear equations, best set of Judd–Ofelt intensity parameters are obtained. Using these Judd–Ofelt intensity parameters, the oscillator strengths are calculated. The rms deviations between experimental and calculated oscillator strengths are very small indicating the validity of Judd–Ofelt theory.

TABLE 1 : Experimental oscillator strengths, experimental line strength (S_{exp}) and calculated line strength (S_{cal}) with their differences (ΔS) for various absorption levels in SLBAP glass

Absorption levels	$P_{exp.}$ (10^{-6})	S_{exp} (10^{-20})	S_{cal} (10^{-20})	ΔS (10^{-20})
$^4I_{15/2} \rightarrow {}^4F_{9/2}$	2.06	1.453	1.445	0.007
$^4S_{3/2}$	0.53	0.311	0.311	0.000
$^2H_{11/2}$	5.62	3.160	2.843	0.316
$^4F_{7/2}$	2.55	1.349	1.130	0.218
$^4F_{3/2}$, $^4F_{5/2}$	0.77	0.376	0.513	-0.137
$^2H_{9/2}$	0.50	0.219	0.378	-0.159
$^4G_{11/2}$	9.60	3.926	4.132	-0.206
$^2G_{9/2}$, $^2K_{15/2}$	1.89	0.747	0.741	0.005

Goodness of fit = 0.0469

TABLE 2 : Judd-Ofelt intensity parameters for various Er^{+3} doped hosts

Glass	Ω_2	Ω_4	Ω_6	Ref.
SLBAPER11	3.2127	1.5445	1.4646	Present work
$50H_3BO_3.39Li_2CO_3.10MgCO_3.1Er_2O_3$	1.33	0.39	0.62	27
Er^{+3} in $48AlO_{1.5}.36CaO.8MgO.8BaO$	5.60	1.60	0.61	28
$48(NaPO_3)_6.20BaCl_2.10ZnCl_2.20NaCl.2ErCl_3$	2.27	2.23	4.98	29

The Judd–Ofelt intensity parameters (Ω_2, Ω_4 and $_6$) depend on the host glass composition[30]. Generally Ω_2 parameter is an indicator of the covalency and crystal field asymmetry of the rare earth ion and Ω_4 and Ω_6 are related to the rigidity of host matrix. In present case the values of Ω_4 and Ω_6 are almost equal. The Judd-Ofelt theory does not permit an easy calculation of these parameters and it is very difficult to predict the behaviour of the host around the rare earth ion on the basis of their values. In SLBAP glass it seems that the rare earth ions gets surrounded by $[AlO_4]^-$. The negative charge of $[AlO_4]^-$ tetrahedra is not properly balanced by the positive charge of alkali ion thereby decreasing the covalent character between the rare earth ions and oxygen atoms provided by $[PO_4]^-$ tetrahedra. In most of the glasses the Ω_4 parameter seems to follow the trend set by Ω_2 parameter. But the Ω_4 parameter is less sensitive to the environment than the Ω_2 parameter.

Spectroscopic parameters

From the data of absorption spectra of Er^{3+} doped SLBAP glass and Using the method Of Wong[31] (and Taylor series expansion) and using the observed band energies as E_J, zero order energies E_{OJ} and partial derivatives of rare earth ion[32], the correction factors ΔE^K, $\Delta\zeta_{4f}$ are evaluated by least squares fit method. From the known free ion parameters E^K, ζ^0_{4f}, the Racah (E^1, E^2, E^3) and spin–orbit (ζ_{4f}) parameters in SLBAP glass matrices are obtained. These values are presented in TABLE 3. The hydrogenic ratios E^1/E^3 and E^2/E^3, which indicate radial properties, are also presented in TABLE 3. It is observed that the hydrogenic ratios are nearly

TABLE 3 : Calculated values of slater-condon, lande', nephelauxetic ratio, racah and bonding parameters for Er^{+3} doped SLBAP glass.

Parameters	SLBAP Glass	Parameters	SLBAP Glass
F_2 (cm^{-1})	429.82	F_4/F_2	0.157
F_4 (cm^{-1})	67.574	F_6/F_2	0.016
F_6 (cm^{-1})	7.131	E^1/E^3	10.490
ζ_{4f} (cm^{-1})	2461.67	E^2/E^3	0.048
E^1 (cm^{-1})	6663.695	β'	0.973
E^2 (cm^{-1})	30.779	$b^{1/2}$	0.116
E^3 (cm^{-1})	635.207	-	-

constant indicating that radial properties are same in the glass matrix. Using the correction factors ΔE^{K}, $\Delta\zeta_{4f}$ and using the partial derivatives, calculated energy values are obtained. The rms deviations between the experimental and calculated energies are reasonable and they are within the experimental error.

In Er^{+3} doped SLBAP glass specimen the relation among different F_k parameters are found as $F_2 > F_4 > F_6$. The ratios of $F_4/F_2 \sim 0.157$, $F_6/F_2 \sim 0.016$ and parameter $E^1/E^3 \sim 10.490$ and $E^2/E^3 \sim 0.048$ are in good approximation with the corresponding hydrogenic ratios.

CONCLUSIONS

The Absorption spectral studies of SLBAP glass doped with Er^{+3} ions have been carried out from the absorption spectra oscillator strengths of various absorption bands are evaluated. The higher value of $_2$ parameter indicates a higher asymmetry around Er^{+3} ions in this glass. The low values of goodness of fit indicate the validity of the Judd-Ofelt theory. In SLBAP glass it seems that the rare earth ions gets surrounded by $[AlO_4]^-$. The negative charge of $[AlO_4]^-$ tetrahedra is not properly balanced by the positive charge of alkali ion thereby decreasing the covalent character between the rare earth ions and oxygen atoms provided by $[PO_4]^-$ tetrahedral. The high value of spectroscopic quality factor ($\Omega_4/\Omega_6 = 1.05$) indicates that the present glass is more rigid as compared to other oxide glasses.

REFERENCES

[1] J.Simpson; Opt.Comm., **2**, 234-240 **(1992)**.

[2] W.J.Wang; Passive and Active Ion-Exchanged Glass Waveguides and Devices, Ph.D. Thesis, Ecole Polytechnique de Montreal Canada, **(1992)**.

[3] O.Lumholt, H.Berns, A.Chabli; SPIE Proceedings, **1**, 127, 130 **(1992)**.

[4] R.Reisfield, C.K.Jorgensen; Lasers and Excited States of Rare Earths, Springer-verlag, Berlin, **(1977)**.

[5] A.A.Kaminskii; Laser Crystals: Their Physics and Properties, Translation, H.F.Ivey (Ed), Springer-Verlag, Berlin, **(1981)**.

[6] E.Sintzer, C.G.Young; Lasers, A.K.Levine, (Ed); Marcel Dekker, New York, **2**, 191 **(1968)**.

[7] G.T.Forrest; Laser Focus World, **26**, 30 **(1990)**.

[8] K.Wallmeroth; Opt.Lett., **15**, 903 **(1990)**.

[9] M.J.Weber; Handbook of the Physics and Chemistry of Rare Earths, K.A.Gschneidner Jr., L.Eyring (Eds); North-Holland Publishing Co., Amsterdam, **4**, 275 **(1979)**.

[10] C.F.Kane; SPIE Proceedings, **1**, 1538 **(1991)**.

[11] T.Kitagawa, Y.Ohmori; SPIE Proceedings, **2**, 434-440 **(1991)**.

[12] B.G.Potter, M.B.Sinclair; J.Electroceramics, **2-4**, 295-308 **(1998)**.

[13] A.J.Kenyon; Prog.Quantum Electron., **26**, 225-284 **(2002)**.

[14] E.Maurice, G.Monnom, B.Dussardier, A.Saissy, D.B.Ostrowsky, G.W.Baxter; Appl.Opt., **34**, 8019-8025 **(1995)**.

[15] P.V.Dos Santos, M.T.De Araujo, A.S.Giuvela-Neto, J.A.Medeiros Neto, A.S.B.Sombra; Appl.Phys. Lett., **73**, 578-580 **(1998)**.

[16] M.J.Dejneka; J.Non-Crystalline Solids, **239**, 149-155 **(1998)**.

[17] M.J.F.Digonnet; Rare-Earth-Doped Fiber Lasers and Amplifiers, Marcel Dekker, New York, **(2002)**.

[18] R.D.Peacock; Structure Bonding, **22**, 83 **(1975)**.

[19] R.Reisfeld; Structure Bonding, **22**, 123 **(1975)**.

[20] M.J.Weber, R.A.Saroyan, R.C.Ropp; J.Non-Cryst. Solids, **44**, 137 **(1981)**.

[21] S.Tanabe, K.Hirao, N.Soga; J.Non-Cryst.Solids, **142**, 148 **(1992)**.

[22] V.P.AIekseev, V.P.Gapontsev, M.E.Zhabotinskii, V.P.Kravchenko, Yu.P.Rudnitskii; Laser Phosphate Glass, Nauka, Moscow, **(1980)**.

[23] K.G.Karapetyan, A.P.Kuznezkov, S.I.Nikitina; Fiz.Khim.Stekla, **16**, 774 **(1990)**.

[24] S.P.Tandon, Y.K.Sharma, N.B.Bishnoi, K.Tandon; Def.Sci.J., **47**, 225 **(1997)**.

[25] F.Gervais, A.Blin, D.Massiot, J.P.Coutures, H.M.Chopinet, F.Naudin; J.Non-Cryst.Solids, **89**, 384 **(1987)**.

[26] W.T.Carnall, P.R.Fields, K.Rajnak; J.Chem.Phys., **49**, 4424-4442 **(1968)**.

[27] A.R.Devi, C.K.Jayasankar; J.Non-Cryst.Solids, **197**, 111 **(1996)**.

[28] X.Zou, T.Izumitani; J.Non-Cryst.Solids, **162**, 68 **(1993)**.

[29] K.Subramanyam Naidu, S.Buddhudu; Mater.Lett., **14**, 355 **(1992)**.

[30] M.B.Saisudha, J.Ramakrishna; Phys.Rev.B, **53(10)**, 6186 **(1996)**.

[31] E.Y.Wong; J.Chem.Phys., **35**, 544 **(1961)**.

[32] Y.C.Ratnakaram; Ph.D. Thesis, SV University, Tirupati, **(1987)**.