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RESEARCH ARTICLE

Spectroscopic Parameters of Nd^{3+} Ions in Sodium-Lead-Barium-Aluminium Phosphate Glass

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Abstract: Tripositive neodymium ion doped sodium-lead-barium-aluminium phosphate (SLBAP) glass has been prepared by melt-quenching technique. The final composition (by weight) was approximately $Na(PO_3)_6$70%-BaO15%-PbO 10%-Al_2O_3 5%-R Ln (Where R=0.5% and Ln= Nd^{+3}). The absorption and Fluorescence spectra in the range of 200 to 800 nm at room temperature of doped SLBAP glass have been recorded to compute various spectroscopic parameters like Slater-Condon parameter (F_k) k=2,4,6, Lande. Parameter (ζ_{4f}), Racah parameter (E^k) k=1,2,3, Nephelauxetic ratio (β') and bonding parameters ($b^{1/2}$) to study the local structure of the ligands around the rare earth ion.

Keywords: Phosphate glass, Fluorescence spectrum, Absorption spectrum, Spectroscopic Parameters

Introduction

Phosphorus pentoxide (P_2O_5) acts as one of the most important glass former and flux material. Phosphate glasses exhibit very important physical properties such as low melting temperature, high thermal expansion coefficient, low glass transition temperature, low softening temperature and high ultraviolet (UV) transmission[1,2]. Despite their solubility, the low processing temperature has led these glasses to be used in applications such as glass to metal seals, low temperature enamels for metals and for optical elements[3]. On phosphate-based glasses, several works have been carried out in the last decade, especially concerning an optimization of glass preparation, investigation of their properties and information about the glass structure. Phosphates glasses with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties[4-6]. Combining sodium carbonate (Na_2CO_3), lead Carbonate ($PbCO_3$) with phosphorus pentaoxide allows one to tune the optical properties in a wide range depending on the glass composition. Stimulated emission cross-section (σ) value increases with the size of the alkali metal. That is why sodium carbonate has been widely used and has been chosen as primary modifier in the present study.

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$70%-BaO15%-PbO 10%-Al_2O_3 5%-R Ln (Where R=0.5% and Ln= Nd^{+3}). The absorption spectrum was recorded at room temperature in the visible region using a double beam spectrophotometer with a resolution of 0.5 nm. The length and width of the rectangular glass specimen was measured with the help of Vernier calipers, while the path length was measured with a screw gauge. The refractive index of glass specimen was measured on an Abbé refractometer (ATAGO 3T). An ordinary lamp was used as the light source. From these data Slater-Condon parameter (F_k) k=2,4,6, Lande parameter (ζ_{4f}), Racah parameter (E^k) k=1,2,3, Nephelauxetic ratio (β’) and bonding parameters ($b^{1/2}$) have been calculated to study the nature of bonding in this glass specimen.

Results and Discussion

On the basis of separation of energy levels of Nd^{+3} free ion and the observed intensity of the band, the Absorption spectrum of Nd^{+3} doped phosphate glass specimen has been assigned to transitions from ground state $^4I_{9/2}$ to the various excited states are observed in the above named glass specimen. These transitions were assigned by comparing the band positions in the absorption spectra with a standard wavelength chart for the Nd^{3+} ion[8]. Eighth absorption bands have been observed from the ground state $^4I_{9/2}$ to the various excited states (Table 1). The experimental and calculated energy band positions are given in Tables 2.

The values of various energy interaction parameters such as Slater-Condon (F_2, F_4 and F_6), Racah (E^1, E^2 and E^3), Lande’ (ζ_{4f}), Nephelauxetic ratio ($\beta^{'}$) and bonding parameters ($b^{1/2}$) have been computed by using the observed energies of the bands, the values of zero order energies (E_{0j}) and partial derivatives (Table 3) with the help of partial regression and least square fitting method[9]. The values of F_k, E^k and ζ_{4f} parameters have been given in Table 4.

Table 1. Experimental line strength (S_{exp}) and Calculated line strength (S_{cal}) with their differences (ΔS) for various Absorption levels in Nd^{+3} doped SLBAP Glass

Absorption levels	S_{exp} (10^{-20})	S_{cal}(10^{-20})	ΔS (10^{-20})
$^4I_{9/2}\rightarrow$ $^4F_{5/2,}$ $^2H_{9/2}$	4.179	4.054	0.124
$^4F_{7/2,}$ $^4S_{3/2}$	3.394	3.561	-0.167
$^4F_{9/2}$	0.431	0.265	0.165
$^4G_{5/2,}$ $^2G_{7/2}$	6.908	6.890	0.017
$^4G_{7/2}$	1.996	1.386	0.609
$^4G_{9/2}$	0.886	0.580	0.305
$^2P_{1/2,}$ $^2D_{5/2}$	0.195	0.231	-0.036
$^4D_{3/2,}$ $^4D_{1/2}$	2.107	0.186	1.920

Goodness of fit = 0.8452

Table 2. Experimental energy (E_{exp}) and Calculated energy (E_{cal}) with their difference (ΔE) for various Absorption levels in Nd^{+3} doped SLBAP Glass

Absorption levels	E_{exp}, cm^{-1}	E_{cal}, cm^{-1}	ΔE
$^4F_{5/2}$	12531	12521.52	-9.47
$^2H_{9/2}$	12612	12631.28	19.27
$^4F_{7/2}$	13368	13361.45	-6.54
$^4S_{3/2}$	13611	13518.55	-92.45

Contd…

$^4F_{9/2}$	14705	14820.12	115.11
$^4G_{5/2}$	17152	16946.05	-205.94
$^2G_{7/2}$	17353	17300.7	-52.30
$^4G_{7/2}$	19011	19192.41	181.40
$^4G_{9/2}$	19569	19276.35	-292.64
$^2P_{1/2}$	23148	23124.77	-23.23
$^2D_{5/2}$	23878	23833.69	-44.31
$^4D_{3/2}$	28571	28471.08	-99.91

r.m.s. deviation (σ) = 128.61

Table 3. Zero order energies (cm^{-1}) and partial derivatives of the energy levels with respect to F_k and ξ_{4f} parameters for Nd^{+3} dopent ion

Bands	E_{0i}	$\partial E_i/\partial F_2$	$\partial E_i/\partial F_4$	$\partial E_i/\partial F_6$	$\partial E_i/\partial \xi_{4f}$
$^4I_{9/2}$	0000.0	00.00	00.00	00.0	0.00
$^4I_{11/2}$	1928.2	-0.16	-2.54	-11.8	2.39
$^4I_{13/2}$	3976.3	-0.11	-3.24	-16.3	4.70
$^4I_{15/2}$	6099.0	0.11	-1.90	-13.7	6.87
$^4F_{3/2}$	11523.3	35.27	39.50	-588.9	1.02
$^4F_{5/2}$	12606.7	34.93	39.86	-631.4	2.06
$^2H_{9/2}$	12612.0	12.59	121.28	238.2	1.30
$^4F_{7/2}$	13453.7	35.02	41.04	-602.5	3.24
$^4S_{3/2}$	13611.0	33.53	48.07	-598.6	3.54
$^4F_{9/2}$	14902.4	28.58	58.06	-382.8	5.06
$^2H_{11/2}$	15980.0	9.26	123.31	406.0	5.22
$^2G_{7/2}$	17353.6	30.09	133.23	-368.3	2.82
$^4G_{5/2}$	17357.5	540.98	63.01	-991.2	1.29
$^2K_{13/2}$	18977.7	24.99	137.34	236.8	3.01
$^4G_{7/2}$	19288.9	41.95	101.66	-620.8	4.13
$^4G_{9/2}$	19718.0	43.14	88.67	-723.4	45.12
$^2K_{15/2}$	21270.2	26.31	132.96	235.2	5.04
$^2G_{9/2}$	21254.0	28.18	132.02	-215.4	70.44
$^2D_{3/2}$	21248.2	40.74	85.49	239.8	2.47
$^4G_{11/2}$	21825.0	52.28	70.75	-940.8	6.52
$^2P_{1/2}$	23147.0	42.63	93.71	226.5	3.56
$^2D_{5/2}$	23878.2	35.38	165.56	-93.8	4.80
$^2P_{3/2}$	26349.9	41.46	78.98	329.1	7.56
$^4D_{3/2}$	28640.1	85.69	112.82	-1382.8	2.13

Zero order parameters F_2 = 331.567 cm^{-1}, F_4 = 49.056 cm^{-1}, F_6 = 5.170 cm^{-1}, ξ_{4f} = 906.00 cm^{-1}

Table 4. Calculated values of Slater-Condon, Lande', Nephelauxetic ratio, Racah and bonding parameters for Nd^{+3} doped SLBAP Glass specimen

Parameters	Free ion	SLBAPND06	Parameters	Free ion	SLBAPND06
F_2 (cm^{-1})	331.16	330.963	E^3 (cm^{-1})	497.00	490.633
F_4 (cm^{-1})	50.72	49.200	F_4/F_2	0.15	0.148
F_6 (cm^{-1})	5.15	5.254	F_6/F_2	0.02	0.015
ζ_{4f} (cm^{-1})	884.00	897.853	E^1/E^3	10.11	10.202
E^1 (cm^{-1})	5024.00	5005.680	E^2/E^3	0.05	0.049
E^2 (cm^{-1})	23.90	24.460	β'	-	0.999
-	-	-	$b^{1/2}$	-	0.022

The spectroscopic parameters presented in Table 4 have been used to evaluate the theoretical energy (E_{cal}) for various bands observed in the absorption spectra. The evaluated values along with the experimentally observed energies (E_{exp}) and the rms deviation between the two are also presented in Table 2. The rms deviations observed are within the experimental limits thus confirming that the Taylor series expansion method is suitable for evaluating the energy levels without diagonalizing the $4f^n$ energy matrix. Using Slater-Condon parameters, Nephelauxetic ratio and bonding parameter have been computed. The calculated values of β' and $b^{1/2}$ are 0.998-0.999 and 0.022-0.031 respectively.

Conclusion

In the SLBAP glass specimens, the relation among different F_k parameters are found as $F_2 > F_4 > F_6$. The calculated values of $F_4/F_2 \sim 0.148$ and $F_6/F_2 \sim 0.015$ are nearly same as observed considering radial Eigen function to be hydrogenic ratio ($F_4/F_2 \sim 0.14$ and $F_6/F_2 \sim 0.015$)[10]. The ratio of Racah parameter $E^1/E^3 \sim 10.130\text{-}10.203$ and $E^2/E^3 \sim 0.049$ are found to remain constant and are in good approximation with the corresponding hydrogenic ratios[11]. The above values indicate that the Nd^{+3} ions are subjected to almost similar force fields. The values of spectroscopic parameters indicates that Nd^{3+} doped SLBAP glass may be used in applications such as fabrication of electroluminescent devices for use in display technology.

References

1. Franks K, Abrahams I, Georgiou G and Knowles J C, *Biomaterials*, 2001, **22(5),** 497-501; DOI:10.1016/S0142-9612(00)00207-6
2. Talib Z A, Loh Y N, Sidek H A A, Yusoff M D W, Yunus W M M and Shaari A H, *Ceramic International*, 2004, **30(7)**, 1715-1717; DOI:10.1016/j.ceramint.2003.12.146
3. Shih P Y, Yung S W and Chin T S, *J Non-Cryst Solids*, 1998, **224(2)**, 143-152; DOI:10.1016/S0022-3093(97)00460-2x
4. Al-Ani S K J and Higazy A A, *J Mater Sci*., 1991, **26(13),** 3670-3674; DOI:10.1007/BF00557161
5. Al-Ani S K J, Al-Hassany I H O and Al-Dahan Z T, *J Mater Sci*., 1995, **30(14),** 3720-3729; DOI:10.1007/BF00351890
6. Dayanand C, Sarma R V G K, Bhikshamaiah G and Salagram M, *J Non-Cryst Solids*, 1994, **167(1-2)**, 122-126; DOI:10.1016/0022-3093(94)90376-X
7. Tandon S P, Sharma Y K, Bishnoi N B and Tandon K, *Def Sci J*., 1997, **47**, 225.
8. Gorller-Walrand C and Binnemans K, Handbook on the Physics and Chemistry of Rare Earths, Ed., By Gschneidner K A, Jr. and Eyring L, *Elsevier Science B V*, 1988, **25**, Chap. 167, 101.
9. Goublen C H, Method of Statistical Analysis, Asia Publishing House Bombay, 1964, Chap. **8**, 134.
10. Judd B R, Proc Roy Soc London, 1955, **A228,** 120.
11. Dieke G H, Spectra and Energy Levels of Rare Earth Ions in Crystals, Ed., Crosswhite H M and Crosswhite H, Interscience Publishers, New York, 1968.