ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Optical Properties and Structural analysis of Pr^{3+}doped CaO-PbO-B_2O_3-SiO_2 glasses

P. Arun Kumar[1], D.V. Krishna Reddy[2], K. Neeraja[3], P. Vijaya Lakshmi[1,3], V. Uma Lakshmi[1,4], P. V. Srinivas Rao[1], M. Rami Reddy[1*]

[1]Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar- 522510, India
[2]Department of Physics, Narasaraopeta Engineering College, Narasaraopeta-522601, India
[3]Department of Physics, Gudlavalleru Engineering College, Gudlavalleru-521356, India
[4]Department of Physics, SRR&CVR Govt.Degree College, Vijayawada-520004, India

***Corresponding author: E-Mail: mramireddy2001@yahoo.co.in**

ABSTRACT

Pr^{3+} doped CaO-PbO-B_2O_3-SiO_2 (CPBS) glasses are prepared by a conventional melt quenching technique with different concentrations. All these glasses are characterized by XRD, FT-IR spectra, and Optical absorption. XRD Spectra reveals that these glasses are amorphous in nature. The FT-IR reveals the nature of bonding situation and different structural units are present in the glass network. With the introduction of Pr_2O_3, the absorption spectrum of these glass samples exhibited eight broad bands at about ~444, ~470, ~483, ~592, ~1010, ~1431, ~1521 and ~1928 nm; we have evaluated the optical band gap by drawing Tauc plot. Along with these properties some physical parameters have been calculated, they exhibit variations with increase in the concentration of Pr_2O_3 which affect all related physical parameters of the system.

KEY WORDS: XRD, FTIR, Optical absorption.

1. INTRODUCTION

In present years rare-earth doped glasses have a wide range extended applications in opto electronics, photonics, fiber amplifiers, up conversion lasers and laser sources in telecommunications systems. Among different rare-earth metals, Pr_2O_3 shows a potential yield luminescence at specific near –IR wavelength bands considering the rich multiple energy levels and it becomes an effective for several applications such as optical fibers, optical amplifiers and up-conversion laser materials. Among the oxide glass systems, borosilicate glasses have considerable interest in optical, thermal, electrical, mechanical properties. In the present glass system, the presence modifier oxide PbO is influences the physical and structural parameters of the glasses. Moreover the introduction of CaO into the lead borosilicate glasses, it improves the glass formation tendency, which extends the range of practical utility of these glasses. Martens (2000), Zhao (2000), and other researches extensively investigated on structure of glasses. They concluded that modifiers used in the network are influences the properties of the glasses. Glassy matrices (CPBS) containing Pr^{3+} ions have become an attractive area of research because of scientific and technological importance in various fields such as optical fibers, optical amplifiers, optoelectronics and photonics.

Pr^{3+} systems are also having potential applications as short wave-length up-conversion laser materials due to large number of energy levels structure and suitable life times of the excited states more over the luminescence spectra is extended form IR to UV region.

In the view of the above interesting results the present work is investigated on Optical Properties and Structural analysis of Pr^{3+}doped CaO-PbO-B_2O_3-SiO_2 glasses.

2. MATERIALS AND METHODS

Pr_2O_3 doped calcium lead borosilicate glasses were prepared by analytical reagents with 99.99% purity of $CaCO_3$, PbO, B_2O_3, SiO_2 and Pr_2O_3 powders using a melt quenching technique. The chemical compositions of the glass system are well mixed and melted in a silica crucible at 950-960º C for 15-20 minutes using a automatic temperature controlled furnace and then quenched on to an iron plate and it is subsequently annealed at 300º C to prevent the thermal stress. Finally the annealed glasses are sliced and polished to dimensions of 1 cm x 1 cm x 0.2 cm for the measurements.

Table.1.Glass compositions of CaO–PbO–B_2O_3–SiO_2: Pr_2O_3 glasses

Glasses	$CaCO_3$ Mol %	PbO Mol %	B_2O_3 Mol %	SiO_2 Mol %	Pr_2O_3 Mol %
Pure	20.0	30.0	25.0	25.0	-
Pr $_2$	20.0	29.8	25.0	25.0	0.2
Pr $_4$	20.0	29.6	25.0	25.0	0.4
Pr $_6$	20.0	29.4	25.0	25.0	0.6
Pr $_8$	20.0	29.2	25.0	25.0	0.8
Pr $_{10}$	20.0	29.0	25.0	25.0	1.0

To characterize the samples JASCO Model V-670 Spectrophotometer in the wavelength range 400-1200 nm is used for the optical absorption spectra. An infrared transmission spectrum is identified by Bruker IFS 66 V – IR

spectrophotometer with a resolution of 0.1 cm^{-1} in the range 400-2000 cm^{-1}. By using Archimedes's principle, the density (d) of the samples was determined with an accuracy of ±0.001.

3. RESULTS & DISCUSSION

Physical Properties: By means of conventional formulae and practically measured density, various physical parameters such as Pr^{3+} ions concentration (N_i), Mean separation (r_i) polaron radius (r_p) of the samples have been evaluated and presented in Table 2.

Table.2.Various physical parameters of CaO–PbO–B_2O_3–SiO_2: Pr_2O_3 glasses

Glass	Density (d) (g/cm^3)	Avg.Mol Weight ($\overline{M}$)	Conc.of Pr^{3+}ions Ni ($10^{22}/cm^3$)	Inter ionic distance r_i(A°)	Polaron radius r_p(A°)
Pure	4.6788	110.54	–	–	–
Pr 2	4.6727	110.75	0.5082	5.8164	2.344
Pr 4	4.6675	110.97	1.0133	4.6212	1.8623
Pr 6	4.6622	111.18	1.5154	4.0411	1.6285
Pr 8	4.6570	111.4	2.0143	3.6753	1.4811
Pr 10	4.6517	111.61	2.5103	3.4153	1.3764

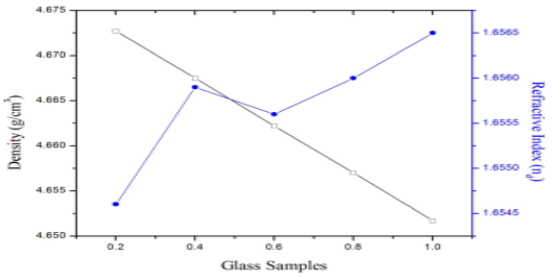

Fig.1.Variation of density and refractive index as a function ofCaO-PbO-B_2O_3-SiO_2: Pr_2O_3 glasses

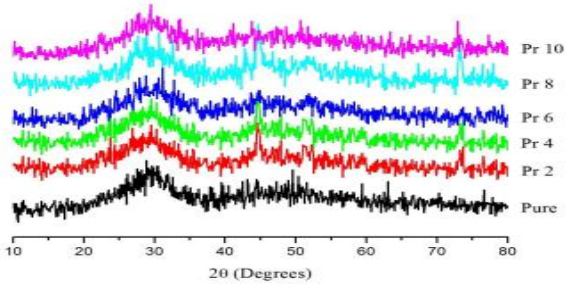

Fig.2.XRD spectra of CaO–PbO–B_2O_3–SiO_2: Pr_2O_3 glasses

The physical, elastic, thermal and other important parameters can be identified by determine the density of the samples. Pr_2O_3 is doped in to the Calcium Lead Borosilicate glasses it decreases slightly due to the changes in coordination, geometrical fluctuations. Further change in coordination and interstitial dimensions are also responsible for the changes in the density of the samples.

X-ray diffraction spectra: The XRD analysis of Pr^{3+} ions doped Calcium Lead Borosilicate glasses are shown in the Fig.2. The spectra consist a broad bump at ~30^0 (=2θ) and no intensive sharp lines are observed which reveals that the atoms in the material are distributed in the random manner and broad bump may cause the short rang order in the glass matrix.

Optical absorption spectra: Absorption spectra of Pr_2O_3 doped CPBS glasses were measured at room temperature within the region 200-2200 nm are as shown in Fig.3. The sample of un-doped glasses does not exhibit any bands. While Pr_2O_3 is introduced in to the glass network, it exhibit eight broad absorption bands at about ~444, ~470, ~483, ~592, ~1010, ~1431, ~1521 and ~1928nm are assigned to the transition from ground state $^3H_4$ to specified excited states $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^1G_4$, $^3F_4$, $^3F_3$ and $^3F_2$ respectively. It is observed that the intensity of the bands increases up to 0.8 mol % of Pr^{3+} ions and then reversal trend is observed. To evaluated the optical band gap (E_o) drawing the tauc plot from the observed absorption edge between $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$ as a function of hν as per the given equation.

$$\alpha(\nu)\, h\nu = C\,(h\nu - Eo)^{n}$$

Here C is a constant and the exponent (n) can take values 1/2 and 2 for indirect, direct transitions in glasses respectively. Tauc plots to evaluate indirect (a) and direct (b) band gap. Fig.4 (a) & 4(b) Tauc plots to evaluate direct and indirect band gap of the glasses. By extrapolating the linear portion of these plots as $(\alpha h\nu)^{1/2} = 0$, $(\alpha h\nu)^2 = 0$ gives optical band gap, along with the theoretical optical band gap energy also calculated using equation $E=hc/\lambda$. Here h is the plank's constant, c is the velocity of light and λ is cutoff wavelength respectively. The value of Urbach energy (ΔE) is calculated by taking the reciprocal of the slope of the linear portion in the lower photon energy region of ln (α) verses hν plot are shown in Fig.4(c). Urbach energy which corresponds to the width of localized states, and used to characterizes the degree of disorder in the glass systems. The related to optical absorption spectra of the Pr_2O_3 doped CPBS glasses are presents in Table.3. The concentration of dopants Pr_2O_3 is increases in the glass system, the optical band gap of direct and indirect transitions is decreases due to increase of non-bridging oxygen ions.

Table.3.Optical data of $CaO–PbO–B_2O_3–SiO_2$: Pr_2O_3 glasses

Glass samples	Cut-off wavelength	Theoretical band gap	Direct band gap(eV)	Indirect band gap(eV)	Urbach energy (ΔE)(eV)
Pure	317	3.92	3.65	3.64	0.2767
Pr_2	327	3.79	3.62	3.61	0.2790
Pr_4	332	3.74	3.61	3.60	0.2800
Pr_6	340	3.65	3.59	3.58	0.2812
Pr_8	346	3.59	3.58	3.57	0.2829
Pr_{10}	352	3.52	3.56	3.55	0.2800

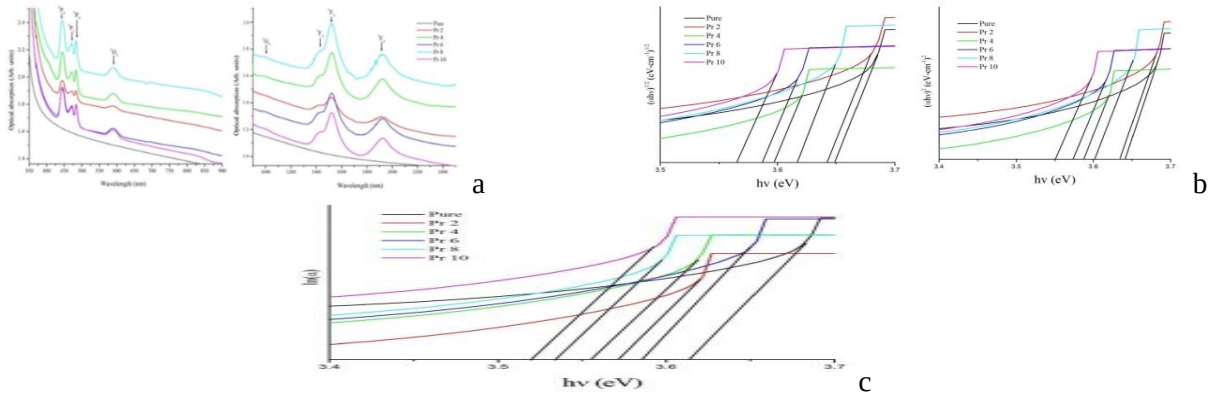

Fig.4(a),(b),(c): Tauc plots to evaluate direct, indirect and Urbach energy band gap of $CaO–PbO–B_2O_3–SiO_2$: Pr_2O_3 glasses

Infrared transmission spectra: In the host glass network, B_2O_3 and SiO_2 are to be acts as a strong glass formers and the borate is participated in the glass network with $BO_3$and BO_4 structural units, whereas SiO_2 is participated in the glass network with tetrahedral $[SiO_{4/2}]^o$ units and all the four oxygen in SiO_4 tetrahedron are shared.

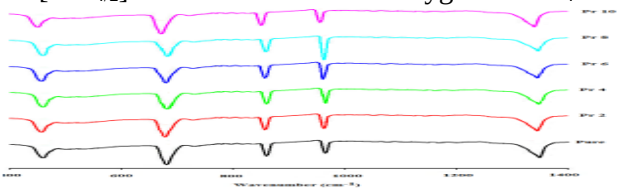

Fig.5.FT-IR spectra of $CaO–PbO–B_2O_3–SiO_2$: Pr_2O_3 glasses

Table.4.The FT-IR band positions of $CaO–PbO–B_2O_3$-SiO_2: Pr_2O_3 glasses

FTIR bands (cm^{-1})	Band assignments
~490	Asymmetrical bending vibrations (υ4) of Si–O–Si
~692	Symmetrical bending vibrations (υ2) of Si–O–Si
~841	Stretching vibrations B–O bond of the BO_4 tetrahedral units
~980	Asymmetric vibration of B–O–Si units
~1380	Symmetric stretching relaxation of the B–O band of trigonal BO_3 units

Fig.5 shows the FTIR spectra of Pr_2O_3 doped CPBS glasses recorded at room temperature with a range 400-1400 cm^{-1}. These glasses exhibit five conventional bands of different intensive bands and data related to IR spectra are presented in Table.4. it is observed that the band at around ~490 cm^{-1} is identified by the Asymmetrical bending vibrations (υ_4) of Si–O–Si units, another band is observed at ~692 cm^{-1} by the combination of BO_4 and PbO_4 groups and the deformation of the Si-O-B linkage, the third band is observed at around ~841 cm^{-1} are identified as the stretching modes of BO_4 units and the band at ~980 cm^{-1} as a asymmetric vibrations of B-O-Si units and the fifth band is located at ~1380 cm^{-1} due to the stretching relaxation of B-O band of trigonal BO_3 units.

4. CONCLUSIONS

Pr_2O_3 doped CPBS glasses are prepared by the process of melt quenching technique, The observed parameters density and refractive index varying nonlinearly with increasing Praseodymium concentration in x mol% as well as molar volume and refractivity of the Pr_2O_3 doped CPBS glasses also varying nonlinearly with increasing Praseodymium concentration, the increase in the density of the glass material makes suitable for reduction shielding materials. From the x-ray diffraction spectra reveals that the samples have amorphous nature. The analysis of the absorption spectra of Pr_2O_3 doped CPBS glasses the band intensities are gradually increased up to the 08 mol% of

the dopants and then decreases, it indicates the conversion of a part of Pr^{3+} ions higher and stable valence state and the decreasing the optical band gap indicate the glass materials have higher covalency when the increasing the dopants Pr_2O_3 in the CPBS glass network. Infrared spectra have also been analyzed for the Pr_2O_3 doped CPBS glasses, which reveals different structural and vibrational units are present in the glass network.

REFERENCES

Baney D.M, Yang L, Ratcliff J, Chang K.W, Red and orange Pr^{3+}/Yb^{3+} doped ZBLAN fibre up conversion lasers, Electron. Lett., 31, 1995, 1842–1843.

Elliot S. R, Physics of amorphous materials, Longman, London, 1990.

Gatch D.B, Holmstrom S.A, and Yen W.M, Photon avalanche in Pr^{3+}:LaCl3, J. Lumin., 83, 1999, 55–59.

Gurr G. E, Montgomery P.W, Knutson C.D, Gorres B.T, The Crystal Structure of Trigonal Diboron Trioxide, Acta Crystallogr.Sec. B, 26 (7), 1970, 906–915.

Jenn-Ming Wu, & Hong-Lin Huang, Microwave properties of zinc, barium and lead borosilicate glasses, J. Non-Cryst. Solids, 260 (1), 1999, 116-124.

Jose G, Thomas V, Paulose P.I, Application of a modified Juddofelt theory to Pr^{3+} doped phosphate glasses and the evaluation of radiative properties, N. J. Non-Cryst. Solids, 319, 2003, 89-94.

Kaminskii A.A, Laser Crystals, 2nd Edition, Springer, Berlin, 1990.

Khanna A, Bhati S.S, Singh K.J, & Thind K.S, Nucl. Instrum. Methods, Phys.Res.B, 114, 1996, 217.

Martens R, Muller-Warmuth, Structural groups and their mixing in borosilicate glasses of various compositions – an NMR study, J. Non-Cryst, Solids, 265 (1-3), 2000, 167-175.

Mendez-Blas A, Rico M, Volkov V, Cascales C, Zaldo, Coya, Kling A, and Alves L.C, Optical spectroscopy of Pr^{3+} in $M+Bi(XO_4)_2$, M+=Li or Na and X=W or Mo, locally disordered single crystals, J. Phys: Condens. Matter, 16, 2004, 2139–2160.

Moorty R, Jagasin M, Lasing properties of Pr^{3+}-doped tellurofluorophosphate glasses, Mater. Chem. Phys., 93 (2), 2005, 455-460.

Nagesh V.K, Tomsia A.P, & Pask, Wetting and reactions in the lead borosilicate glass-precious metal systems, J.A.J. Mater. Sci., 18 (7), 1983, 2173 -2180.

Ohishi Y, Mitachi S, Kanamori T, and Manabe T, Optical Absorption of 3d Glasses, Physics and Chemistry of Glasses, 24, 1983, 135-140.

Paul A, Chemistry of glasses, Chapman & Hall, London, 1982.

Ratnakaram Y.C, Vijaya Kumar A, and Chakradhar R.P.S, Optical absorption and emission properties of Pr3+ and Er^{3+} in lithium cesium mixed alkali borate glasses, J. Lumin., 118 (2), 2006, 227-237.

Sardar D.K, Castano F, Characterization of spectroscopic properties pr $^{3+}$ in sr 5(po 4) 3f crystal, J. Appl. Phys., 91 (3), 2002, 911-915.

Scherzer J, Dealuminated faujasite-type structures with SiO_2/Al_2O_3 ratios over 100, Journal of Catalysis, 54, 1978, 285.

Shackl Ford J.F, Introduction to Materials Science for Engineers, Macmillan, New York, 1985.

Sharma Y.K, Tandon S.P, Surana S.S, Laser action in praseodymium doped zinc chloride borophosphate glasses, Mater. Sci. Eng., B, 77 (2), 2000, 167-171.

Skinner B.J, Appleman D.E, Melanophlogite, a cubic polymorph of silica, American Mineralogist 48, 1963, 854.

Strong S.L, Wells A.F, Kaplow R, On the crystal structure of B_2O_3, Acta Crystallogr.Sec.B, 27 (8), 1971, 1662.

Wei K, Machewirth D.P, Wenzel J, Snitzer E, Sigel Jr. G.H, Pr^{3+}-doped Ge-Ga-S glasses for 1.3 μm optical fiber amplifiers, J. Non-Cryst. Solids, 182 (3), 1995, 257-261.

With W.B, Brawer S.A, Furukawa T, Mc-Carty G.J, Gastric emptying of a nutritionally balanced, in: L.D. Pye, V.D. Frechette (Eds.), Borate Glasses:Structure, Properties, Applications, Plenum, New York, 1978. pplications, Plenum, New York, 1978.

Zhao P, Scott Kroeker, Jonathan F Stebbins, Non-bridging oxygen sites in barium borosilicate glasses: results from 11B and 17O NMR, J. Non-Cryst. Solids, 276 (1-3), 2000, 122-131.

Zhao Y, Fleming S, Theory of Pr^{3+}-doped fluoride fiber up conversion lasers, IEEE J. Quant. Electron., 33 (5), 1997, 905-915.