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Physical, Microstructural (SEM), XRD, FT-IR, Raman properties of B_2O_3- SiO_2 - PbO – CaO (BSPC) glasses doped with Pr_2O_3

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Abstract

We aim to study the properties of Physical, SEM, XRD, FT-IR and Raman spectra of the prepared glass samples by traditional melt-quenching technique. The prepared glass composition 30 B_2O_3 - 20 SiO_2 - PbO (30-x) - 20CaO - x Pr_2O_3 (x = 0.1, 0.3, 0.5, 0.7, 0.9).The physical properties measured by the standard formulas. The SEM provides imaging and basic compositions of the present glass system. The X-ray diffraction confirms the prepared glass samples amorphous nature.FT-IR spectra exhibit PbO_4 structural units, bending vibrations of [SiO_4], bending vibrations of Si-O-B ,bonding vibrations of B-O-B groups and asymmetric vibrations of Si-O-Si and BO_3 units. The Raman spectra exhibits stretching vibrations of B-O bond in BO_4 units,B-O stretching modes involving with one NBO of [BO_3] triangles and molecular stretching vibration modes.

IndexTerms **- Physical properties, SEM, XRD, FT-IR, Raman, Pr^{3+} ions.**

I. INTRODUCTION

The Non crystalline materials (glasses) much more involve with rare earth (RE) ions are the aim of extensive studies because of their constructive luminescence properties that can find large applications in different fields, as telecommunication channels, sensors, laser gain media and light emitting diodes [1,2]. RE^{3+}doped multi component glasses are well known for their special features like stability, strength, and chemical durability which has increased the interest of developing the novel materials in this research field [3]The rare earth is Pr^{3+} doped glasses have good optical devices[4] Special attention has been paid to Pr^{3+} ions in silicate glass containing lead [5,6,7]. N. Wantana et al explained tungsten gadolinium borate glasses exhibt Tunable orange, yellow and white emission [8]. Sk. Mahamuda et al proved in zinc alumino bismuth borate glasses exhibt reddish-orange emission [9]. Optical display device applications in lead based phosphate glasses [10]. Optical analysis of RE^{3+} (RE = Pr^{3+}, Er^{3+} and Nd^{3+}): cadmium lead boro tellurite glasses [11]. Based upon the host glass materials, the addition of heavy metal oxides (PbO) into the glass network refines the thermal stability of the glass to a sizable extent. Chiefly, the main role of PbO is to be either a glass former or modifier, depending on its concentration present in the glass matrix. If the PbO concentration is below 50 mol%, it acts as octahedrally coordinated modifier and behaves as other conventional modifier oxides [12]. However, if the PbO concentration is above 50 mol%, it acts as a glass former and forms tetrahedral PbO_4 by sharing the corner atoms with PO4 structural units, thanks to increasing the cross linkage by formation of P–O–Pb linkages. These ions have low melting and transition temperatures, and result in high values of thermal expansion, electrical conductivity, and ultraviolet (UV) transmission [13]. This property of PbO makes it useful for fast ion conducting materials and laser host matrices, by doping with rare-earth

materials. In the studied glasses, PbO acts as a conditional glass former.In the present communication to study the Physical, Microstructural (SEM), XRD, FT-IR, Raman properties of B_2O_3- SiO_2 - PbO – CaO (BSPC) glasses doped with Pr_2O_3.

II.Experimental Procedure

2.1 Glass fabrication

The present molar compositions of Pr_2O_3, H_3BO_3, PbO, SiO2.CaCO3 Above compositions (20g) are grinded homogeneously in an agate mortar and taken in a porcelain crucible and melted in an electric furnace in the temperature range of 1200 ^{0}C for 1 h. The melt is then air quenched to get a good optical quality glasses. The details of glass composition given table.1The samples are annealed at 375C for 6h to remove thermal strains and then polished.Fabrication of glass samples shown in below fig.1.

Table.1: Details of fabricated glasses

S.no	B_2O_3 %	SiO_2 %	PbO %	CaO %	Pr_2O_3 %
1	30	20	29.9	20	0.1
2	30	20	29.7	20	0.3
3	30	20	29.5	20	0.5
4	30	20	29.3	20	0.7
5	30	20	29.1	20	0.9

Fig.1. Fabrication of glass samples – (Before & after polished)

2.2 Sample Characterization

In this connection we fabrication of glasses (amorphous nature) confirms by X-Ray diffractometer (XRD,7000 S/L,Shimadzu .Corp,Japan).Density(Archimedes method)and other physical properties can be estimated standard formulas. The Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) images of samples were recorded with an EDS OX -FORD spectrometer. The samples for SEM measurements were prepared as mentioned in the experimental details section. Using the PerkinElmer spectrometer having wave number range 400- 4000 cm^{-1} FTIR spectra of the investigated glasses are recorded. By employing back scattering technique, T64000 JobinYvon SPEX spectrometer with 532 nm/442 nm (Ar^+ laser), Raman spectrum (200–1500 cm^{-1}) was measured.

III. Results and Discussions

3.1. XRD analysis

In this connection fabrication of glasses (amorphous nature) confirms bump peak obsorved in fig.2.Due to this reason fabricated samples are confirms amorphous nature.

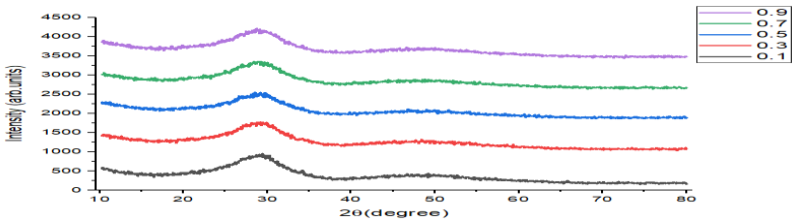


Fig.2 XRD pattern of fabricated glasses

3.2. Physical Properties

The density is the main important property and related other physical properties. The chemical formulas of different physical properties mentioned below Table 2. The density of fabricated glasses increased from 5.458 to 5.643 with different Pr_2O_3 ion concentration. Pr_2O_3 molecular weight (329.813 g/mol) is more comparing to other mixtures (B_2O_3 69.62 g/mol),(SiO_2 60.08

g/mol),(CaO 56.0774 g/mol) & (PbO 223.2 g/mol) molecular weight of fabricated glass samples.The Molar Volume decreased 20.370 to 19.853 with increasing doping concentration 0.1 to 0.9.Fig.3 represents dopant concentration versus Density&Molar Volume. Fig.4 represents dopant concentration versus Polaron radius & Field strength, Polaron radius decreases from 2.807 to 1.338 and Field strength increased from 3.807 to 16.751 with increasing dopant concentration. . Fig.5 represents dopant concentration versus Refractive index & Metallization constant, Refractive index increases 2.126 to 2.197, Metallization constant decreases from 0.462 to 0.441 due to this reason all fabricated glasses are amorphous nature. Fig.6 represents Oxygen Packing Density (OPD) is increased from 88.462 to 91.573 with increasing doping concentration.

(i). Density (D) =($W_1 / W_1 - W_2$) 0.86 g / cm^3 ------- (1)

(ii) Molar Volume (V_m) = M / D

(iii).The Pr^{3+} ion concentration (N_i) = $\frac{N_A M(mol\%) D}{\overline{M}}$ ------- (3)

(iv). Inter – ionic distance r_i (Å) = $\left[\frac{1}{N_i}\right]^{1/3}$ ------- (4)

(v). Polaron radius r_p (Å) = $\frac{1}{2}\left[\frac{(\pi)}{(6N_i)}\right]^{1/3}$ ------- (5)

(vi). Field strength F_i (cm^{-2}) = $\frac{Z}{r_p^2}$ ------- (6)

(vii) Oxygen packing density (OPD) =1000×C×D/M

(viii). Fresnel's formula for reflection loss R= $\frac{\mu 2-1}{\mu 2+2}$ ------- (8)

(ix).The molar refractivity R_m (cm^{-3}) = $\frac{M(\mu^2-1)}{D(\mu^2+2)}$ ------- (9)

(x) Dielectric constant (ε) = μ^2

(xi) Electronic polarizability (α_e) = 3 R_m / 4πN_A

Table.2. Different Physical Properties of fabricated glasses

Glass sample	0.1	0.3	0.5	0.7	0.9
Density (D)	5.458	5.512	5.563	5.612	5.643
Thickness (cm)	0.15	0.16	0.14	0.14	0.13
Average Molecular Weight	111.183	111.396	111.61	111.823	112.036
Molar Volume (V_m)	20.370	20.209	20.062	19.925	19.853
The Pr^{3+} ion concentration (N_i) $\times 10^{21}$	2.956	8.940	15.01	21.159	27.302
Inter – ionic distance r_i (Å)	6.956	4.818	4.053	3.615	3.32
Polaron radius r_p (Å)	2.807	1.941	1.633	1.456	1.338
Field strength F_i (cm^{-2}) $\times 10^{15}$	3.807	7.959	11.251	14.137	16.751
Oxygen packing density (OPD)	88.462	89.367	90.216	91.041	91.573
Refractive index	2.126	2.142	2.171	2.183	2.197
Reflection loss (R_L)	0.5398	0.5446	0.5531	0.5565	0.5605
Molar refractivity(R_m) (cm^{-3})	10.979	10.988	11.075	11.098	11.116
Metallization constant (M)	0.462	0.457	0.448	0.445	0.441
Dielectric constant (ε)	4.519	4.588	4.713	4.765	4.826
Electronic polarizability (α_e) $\times 10^{-24}$	4.353	4.357	4.382	4.397	4.408

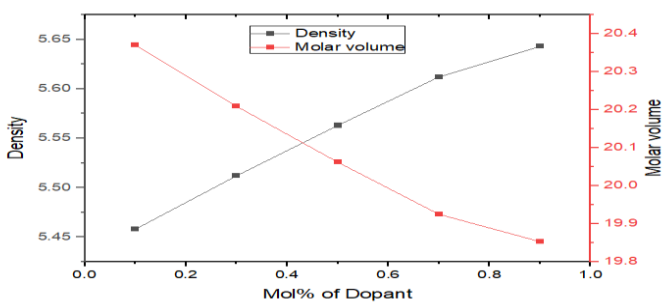


Fig.3.Dopant Vs Density & Molar Volume

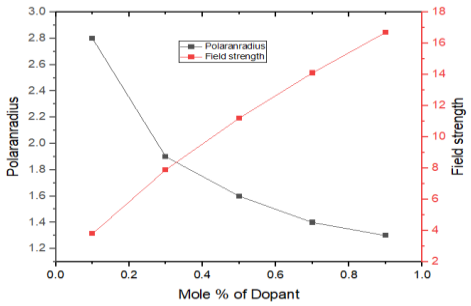
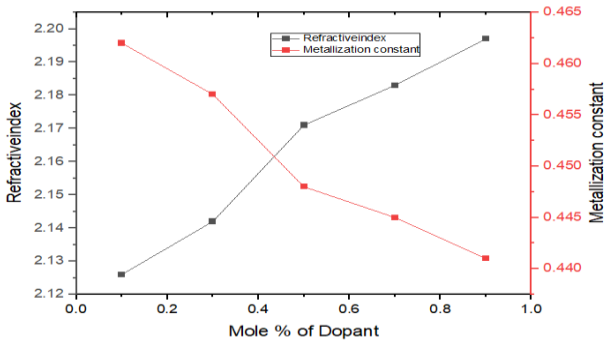


Fig.4.Dopant Vs Poloron Radius &Field Strength



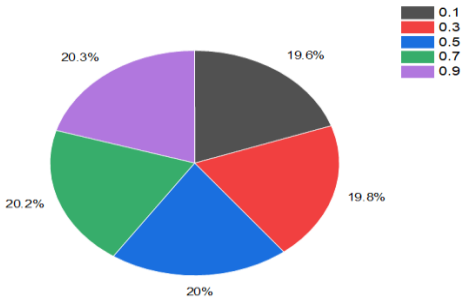
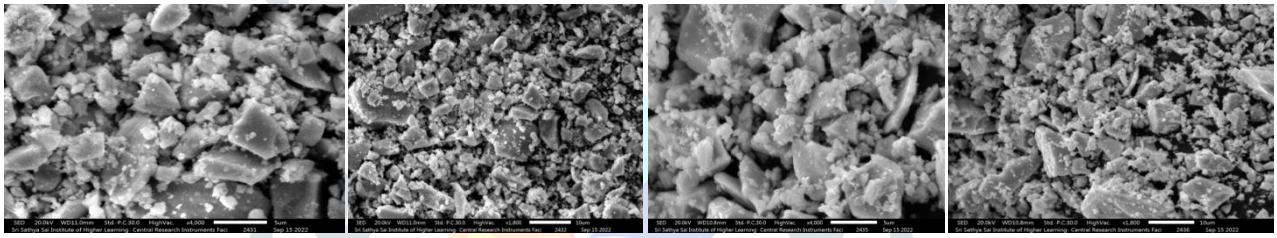


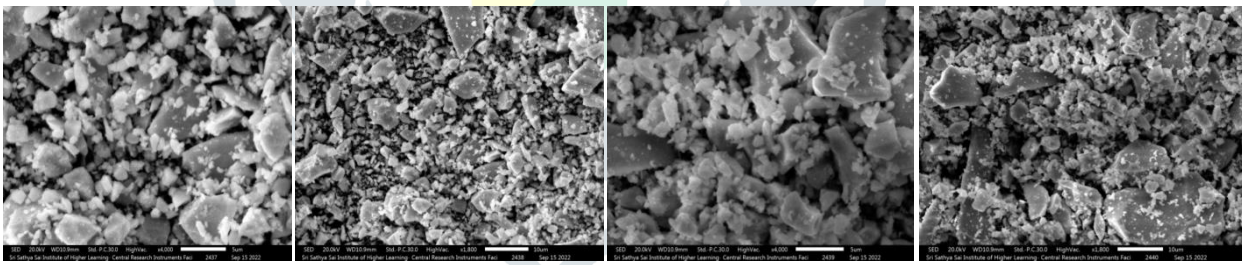
Fig.5.Dopant Vs Refractive Index & Metallization Constant **Fig.6.Dopant Vs Oxygen Packing Density (OPD)**

3.3. SEM and EDS analysis

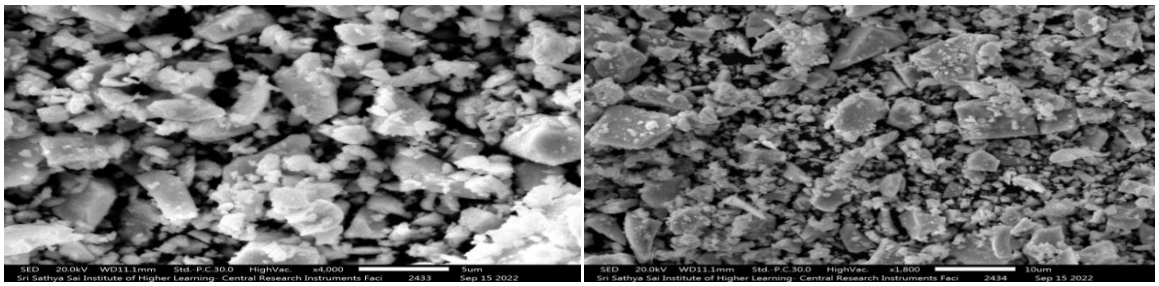
SEM morphology of samples is shown in Fig. 7. SEM images explore the smooth surface of the samples with high uniformity and without any crystals. This smooth surface indicates the amorphous behavior of the glass system. Any grain boundaries were not observed in the surface morphological image of the fabricated glasses. Different magnifications of glass images can observed in below figures.The compositional analysis of the glasses was also studied by using the EDS technique. The EDS spectra of the BSPC glass system was shown in Fig. 8. Compositional elements of Borate (B), Lead(Pb), silica (Si), Calcium Oxide(CaO), Praseodymium (Pr) are found in the EDS spectra. Those results show that corresponding elements present in the respective glass matrices that were used at the time of preparing glass samples.



GLASS-1 **GLASS-3**



GLASS-5 **GLASS-7**



GLASS-9

Fig.7. SEM images of BSPC glass system (glass 1 to glass9) with different magnifications

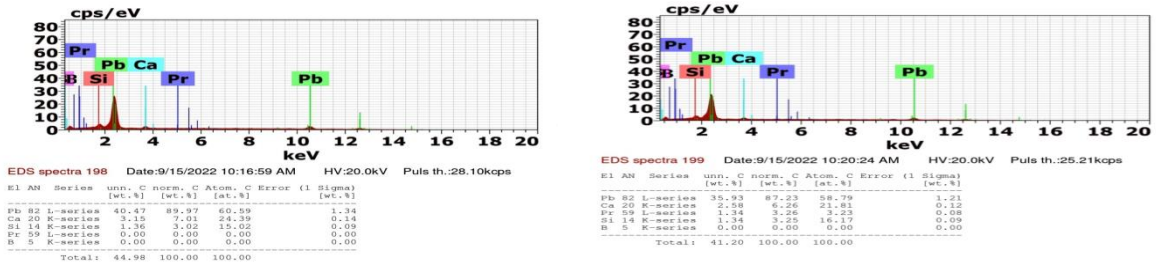


Fig.7. EDS spectra of BSPC glass system(0.1& 0.9 concentration).

3.4. FTIR Studies

Fig. 8.shows the FTIR absorption spectra of different concentrations of Pr^{3+} doped 30 B_2O_3 - 20 SiO_2 - PbO (30-x) - 20CaO - x Pr_2O_3 (x = 0.1, 0.3, 0.5, 0.7, 0.9).glass matrix. FTIR spectra of samples were measured in the wave number range 1600–400 cm^{-1} at room temperature. Previously expalind FTIR spectra band positions [14], [15]. FTIR band positions of the BSPC glass samples, their band positions and assigned vibrational bands are listed in Table3.

Table 3. FTIR band assignments of Pr^{3+} doped BSPC glass system.

Wave number (cm^{-1})	Assignments
464-453	(PbO_4 ,SiO_4 bending vibrations)
615-613	Bending vibrations of Si-O-B
702-709	Bending vibrations of B-O-B/ BO_3
862-867	Symmetric stretching of Si-O- Si Units
1166-1172	Si-O- Si asymmetric vibrations / Trigonal BO_4 Units

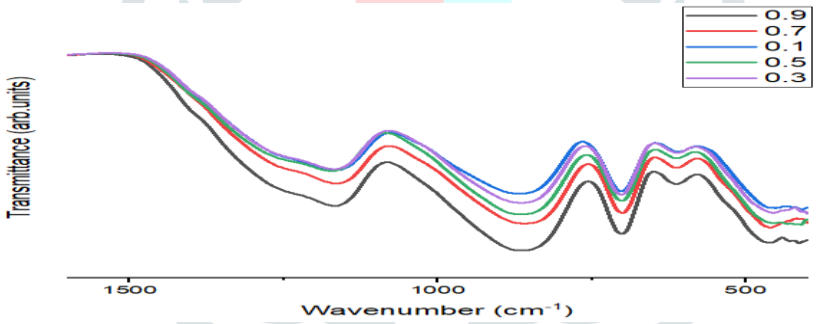


Fig.8. FTIR spectra of BSPC glass system.

3.5. Raman spectroscopy

Raman spectra of Pr^{3+} doped 30 B_2O_3 - 20 SiO_2 - PbO (30-x) - 20CaO - x Pr_2O_3 (x = 0.1, 0.3, 0.5, 0.7, 0.9) were shown in Fig. 8. The deconvoluted spectra of BSPC glass system in the wavenumber range of 500–2500 cm^{-1} is shown in Fig. 8. Raman spectroscopy is used to study the presence of different structural units and the additional modifier ions of the glass matrix. The Raman spectra of the glass system are complementary to the FTIR spectrum. [14]. The peak positions and assignments of the Raman bands are tabulated in Table 4.

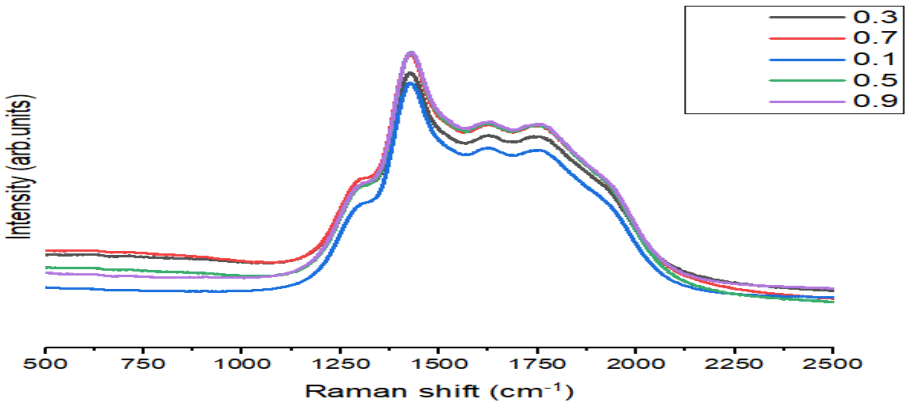


Fig.9. Raman spectra of BSPC glass system

Table. 4. Raman spectra of Pr^{3+} doped BSPC glass system.

Wave number (cm^{-1})	Assignments
1310	Stretching vibrations of B-O bond in BO_3 units from different borate groups
1430	B-O stretching vibrations
1625	Molecular oxygen stretching vibration modes
1755	H-O-H groups

IV. Conclusions

We prepared glass samples with different compositions of Pr_2O_3 , XRD Spectra confirms the amorphous nature. Densities and other physical properties are measured prepared glass samples.SEM and EDX spectra confirm elementals in prepared glass samples. FTIR spectra of samples were measured in the wave number range 1600–400 cm^{-1} at room temperature. The Raman spectra of the glass system are complementary to the FTIR spectrum.

II. Acknowledgment

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