

Preparation and structural characterization of P₂O₅-CaO-Na₂O: CuO glasses

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Glasses of particular composition (65-x) P₂O₅-23CaO-12Na₂O: x CuO (0.5 ≤ x ≤ 2.0) mol% was synthesized. Further, the samples were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Thermal Analyses (DTA), Fourier Transform Infrared, optical Absorption and luminescence spectroscopy techniques. The XRD patterns recorded at room temperature have confirmed the non-crystalline nature to all glass samples which was also supported by SEM pictures. Shifting of glass transition temperature (T_g) towards lower temperature with the CuO addition is observed from the DTA scans. This observation is an indication of more disorder of glass network. Basic phosphate bands and possible cross linkages with CuO addition have been observed in FTIR spectra of all samples. Optical absorption spectra exhibited two bands in the regions about 335 and 795 nm. Luminescence spectra has exhibited two emission peaks corresponding to the transition of ³D₁→¹S₀ single Cu⁺ centers and Cu⁺-Cu⁺ pairs respectively. From all the results, the sample with high content of CuO found to exhibit more degree of disorder. The reasons for more disorder have been discussed in detail by means of spectroscopic properties.

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1. Introduction

Phosphate based glasses have been extensively investigated because of their superior properties [1-3]. High refractive index and low dispersion properties enable phosphate glasses to act as suitable hosts for different lasing ions than that of conventional borate and silicate glasses [4]. It also has been demonstrated that metal containing phosphate glasses can be considered as promising materials for a variety of photonic applications [4-6]. In addition, phosphate glasses may be considered as bioactive materials since they exhibit high dissolution with controlled rate in aqueous solutions [7]. Introducing transition metals into phosphate glass network would result in improving chemical durability and stability against devitrification and moisture [4-6]. Basically, phosphate network consisting of phosphate tetrahedra with different numbers of bridging oxygens, including cross-linked networks (Q³), polymer-like chains (Q²+Q¹) or small pyro(Q¹) and orthophosphate groups (Q⁰) [7].

Semiconducting copper ion, one of the interesting transition metal ions in various glasses. Usually, copper exists in two stable states viz., Cu⁺ which does not produce colouring and Cu²⁺ ions create colour centres [8]. Lot of attention has been given to the investigations on copper ions in different glass systems to provide structure-physical properties relation. It is found that copper ions have strong impact on spectral and electric features of various glass systems. The addition of CuO and Na₂O to

phosphate glass network would modify the phosphate network resulting in change of physical properties as these properties depending on metal oxide dopant concentration and coordination environments. A large number of studies on copper ions in different glass systems are available; still there is a scope to investigate the structural changes resulting from addition of CuO in phosphate glasses. Hence, a considerable interest is attached on structure-properties relation of copper doped phosphate glasses. In this scenario, to explore the structural modifications in phosphate glass network with CuO, a particular glass system P₂O₅-CaO-Na₂O: CuO has been chosen and investigated.

2. Experimental

The nominal glass composition of the present study is selected as (65-x) P₂O₅-23CaO-12Na₂O: x CuO (0.5 ≤ x ≤ 2.0) and the samples are labelled with the following:

PC₅: 64.5 P₂O₅-23CaO-12Na₂O: 0.5 CuO

PC₁₀: 64.0 P₂O₅-23CaO-12Na₂O: 1.0 CuO

PC₁₅: 63.5 P₂O₅-23CaO-12Na₂O: 1.5 CuO

PC₂₀: 63.0 P₂O₅-23CaO-12Na₂O: 2.0 CuO

P₂O₅, a strong glass former was introduced in the glass composition in a form of NH₄H₂PO₄ while CaO and Na₂O were added in their natural form of anhydrous carbonates. The hygroscopic nature of P₂O₅ is controlled by adding suitable metal oxides. It is also expected that de-

polymerization of the phosphate network for the formation of P-OH bonds. CuO chemical powder was directly taken as per mol%. The chemical composition of the studied glass is chosen such that contents of Na_2O and CaO remain constant while the contents of P_2O_5 and CuO vary from 64.5 to 63 mol% and 0.5 to 2.0 mol% respectively. The present glasses were prepared using the melt quenching method. For preparing the glasses, powders of constituents corresponding to mol% were weighed using an electronic balance and the contents thoroughly mixed homogeneously in an agate pestle-mortar. The mixture was then poured into an aluminium crucible and placed in Termolab 1800 - Shimaden FP21 Controlled high temperature furnace set at the 1000 °C for approximately one hour. Halfway during the melting period, the mixture would be stirred to allow for proper mixing of compounds. After one hour completed, the mixture was then poured into graphite moulds and placed in an annealing furnace set at the 300 °C for approximately six hours. The glass samples were grounded and optical polished to the dimensions of 1.2 cm x 1.2 cm x 0.2 cm. The amorphous nature of the prepared glass samples was confirmed by the X-ray diffractometer (XRD, Rigaku D/Max ULTIMA III) and HITACHI S-3400N Scanning Electron Microscope. The glass transition temperature and temperatures of crystallization were determined by using the Netzsch Simultaneous DSC/TG Thermal Analyser STA409C. The densities of the samples were calculated using the Archimedes principle. Infrared absorption spectra were noted on a JASCO-FT/IR-5300 spectrophotometer up to a resolution of 0.1 cm^{-1} in the spectral range $400\text{--}4000\text{ cm}^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at $\sim 680\text{ MPa}$. Optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 250-1000 nm with a resolution of 0.1 nm using UV-3092 spectrophotometer. The

photoluminescence spectra of glass samples were carried out using F-2500 FL Spectrophotometer, Hitachi.

3. Results and discussion

At first, calculation of physical parameters was done as they provide very important information about structural changes in the glasses with rise in CuO content. The density values of all samples were measured by Archimedes principle. Addition of CuO in place of P_2O_5 results little increase in density that might be due to slightly larger molecular weight and density of copper oxide than calcium oxide, sodium oxide. Degree of structural packaging, change in coordination & position of phosphate ions were assumed as few reasons for density changes. It is also observed that the values of average molecular weight found to decrease with the content of copper oxide while ion concentration found to increase. It could be due to replacing by CuO with P_2O_5 of high molecular weight [9].

Using the measured density and average molecular weight M of glasses, other essential physical parameters viz., copper ion concentration N_i , mean copper ion separation r_i and polaron radius r_p have been evaluated and presented in Table 1. Another interesting observation is that the decreasing trend of interionic distance r_i and polaron radius r_p with CuO content which supports the loosely packed glass network resulting more structural degree of disorder.

Fig. 1 presents the X-ray diffraction patterns of P_2O_5 -CaO- Na_2O : CuO glasses recorded at room temperature. These patterns did not show any sharp peaks except wide ranging halo that confirms non-crystalline nature to the samples. The broad halo observed was the characteristic peak of glass samples. This result also supports the absence of signs of crystallization tendency that might be occurred sometimes during quenching process.

Table 1. Physical parameters of P_2O_5 -CaO- Na_2O : CuO glasses

Sample	Avg. Mol. Wt. (g/mol)	Density (g/cm ³)	Conc. of 'Cu' ions N_i ($10^{21}/\text{cm}^3$)	Interionic distance of 'Cu' ions r_i (Å)	Polaron radius r_p (Å)
PC ₅	203.8	2.616	3.85	6.38	2.57
PC ₁₀	202.7	2.635	7.80	5.04	2.03
PC ₁₅	201.8	2.658	11.84	4.38	1.77
PC ₂₀	200.5	2.679	15.98	3.97	1.59

Another interesting study is recording of scanning electron microscopic pictures which reveal the morphological details of glass samples. Fig. 2 displays the SEM images of PC₁₀ and PC₂₀ recorded at room temperature with magnification of 20 μm . These pictures clearly indicating the absence of micro-crystals those

usually might occurred due to quenching process. Thus it confirms non-crystalline nature and also supports the XRD patterns.

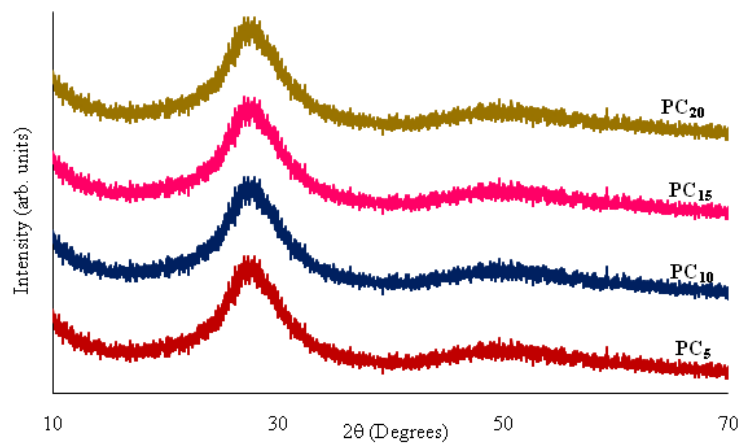


Fig. 1. XRD patterns of P_2O_5 -CaO- Na_2O : CuO glasses.

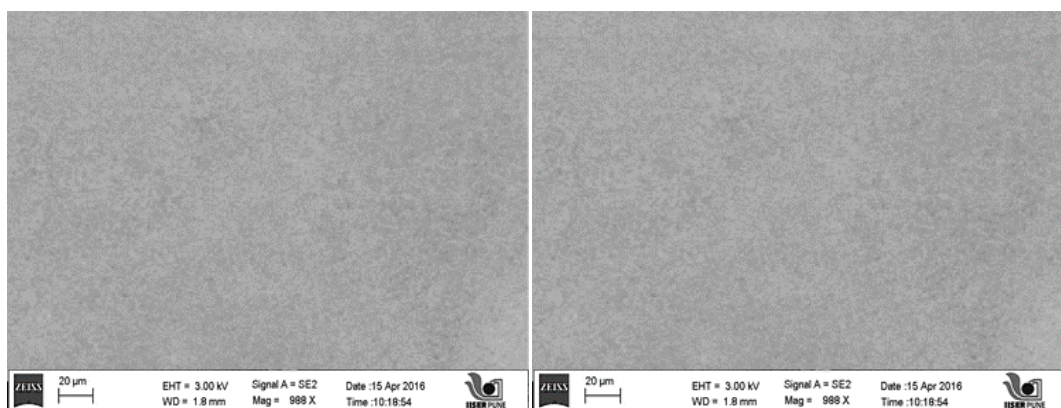


Fig. 2. Scanning Electron Microscopic pictures of P_2O_5 -CaO- Na_2O : CuO glasses.

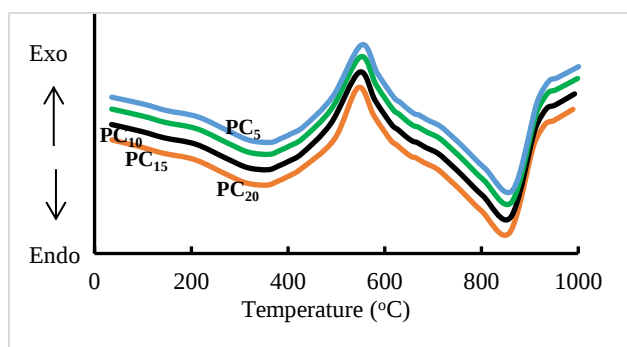


Fig. 3. DTA traces of P_2O_5 -CaO- Na_2O : CuO glasses

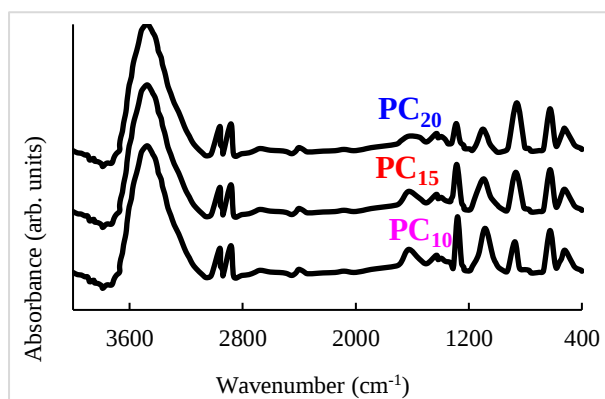


Fig. 4. FT-IR absorption spectra of P_2O_5 -CaO- Na_2O : CuO glasses.

Differential thermal analysis (DTA) traces of P_2O_5 -CaO- Na_2O : CuO glasses are presented in Fig. 3. The traces indicating broad range endothermic and exothermic peaks that confirms homogeneity of glass samples. It is observed that the addition of copper oxide resulted decrease in glass transition and melting temperatures. DTA trace of PC₂₀ glass exhibits glass transition at about 375°C which was small among other samples. From the traces, it was very clear that the glass transition T_g and melting temperature shift towards lower temperature region with copper oxide addition. Divalent copper ions act as modifiers and make the phosphate glass network weak by inducing many non-bridging oxygens leading to

more structural network disorder. This could be the reason for above thermal changes [9].

The prepared glass samples are mixtures of glass network former (P_2O_5), intermediate oxides and modifiers (CaO & Na_2O). Phosphorous pentoxide is one of the strong glass network formers and possesses PO_4 tetrahedron network structure. With bridging oxygens, PO_4 tetrahedrons forming chains through covalent bonding. Modifier calcium oxide enters the phosphate glass network by breaking P–O–P bonds that causing bonding defects leading to network disorder. Na_2O is considered to be incipient glass network formers which can form glass with the help of modifier oxides like CaO [10, 11].

Table 2. Summary of data on optical absorption spectra of P_2O_5 -CaO- Na_2O : CuO glasses

Sample	Cut-off wavelength (nm)	$^2B_{1g} \rightarrow ^2B_{2g}$ (nm)	Optical band gap E_o (eV)
PC ₅	325	752	2.88
PC ₁₀	329	757	2.82
PC ₁₅	336	759	2.76
PC ₂₀	339	764	2.70

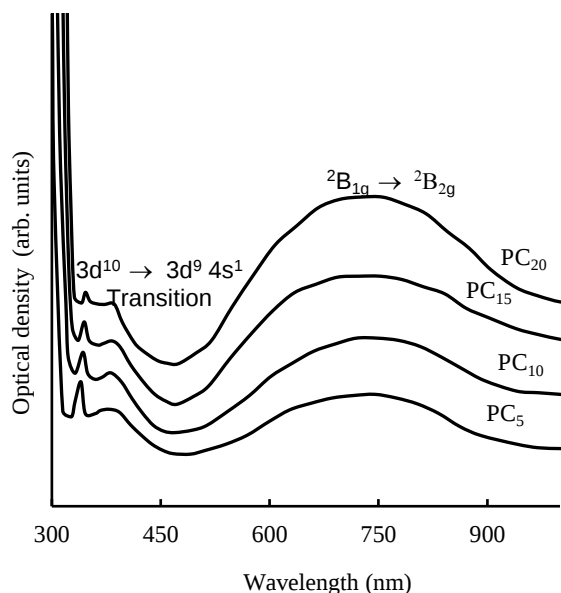


Fig. 5. Optical absorption spectra of P_2O_5 -CaO- Na_2O : CuO glasses.

To investigate the structural changes in P_2O_5 -CaO- Na_2O : CuO glasses, FTIR absorbance spectra is recorded and shown in Fig. 4. The positions of spectral bands for samples PC₅ and PC₁₀ almost ensemble the same due to low concentration of CuO. Hence, the Fig. 4 has shown only three IR traces corresponding to samples PC₁₀, PC₁₅ and PC₂₀. Various characteristic absorption bands corresponding to P–O–P stretching, PO_4^{3-} group, P–O–P asymmetric bending and pyrophosphate groups ($P_2O_7^{4-}$) in the wavenumber regions 1265–1286, 1057–1085 and 887–893 cm^{-1} have been observed in the spectra of all samples [2, 12–15]. Another interesting observation is that the small band located in the region 1600–1640 cm^{-1} could be due to the deformation mode of water molecule. Stretching mode vibrations of hydroxyl groups were also observed in the region 3140 to 3740 cm^{-1} . One more interesting vibrational band located in the region 440–610 cm^{-1} was identified and assigned to Na^+ and Ca^{2+} modifier cations [16]. With rise in the content of CuO, PO_2^- vibrational bands observed to grow and bending mode of PO_4^{3-} tetrahedron groups found to decrease. Reduction in wavenumber of vibrational bands corresponding to O–P–O vibrations and PO_4^{3-} tetrahedral groups clearly supports the more structural degree of disorder around phosphate groups. From these observations, the glass sample with high amount of CuO found to exhibit high degree of disorder due to more loosely cross-linked phosphate glass network with cations and it also supports DTA results.

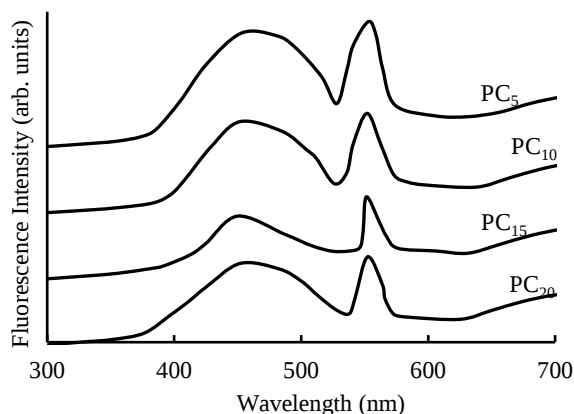


Fig. 6. Luminescence spectra of P_2O_5 -CaO- Na_2O : CuO

Room temperature UV-visible absorption spectra of CuO doped P_2O_5 -CaO- Na_2O glasses is presented as Fig.5. One strong absorption band and another small kink located at about 335 and 375nm assigned to $3d^{10} \rightarrow 3d^9 4s^1$ transitions observed in the spectrum of every glass sample [17, 18]. The CuO content rise in sample has shown that intensity and half-width of these bands found to decrease which caused by the larger existence of monovalent copper ions. One more broad absorption band centered at 794nm assigned to the transition $^2B_{1g} \rightarrow ^2B_{2g}$ of divalent copper ions in octahedral coordination. [17, 19, 20]. Increase in CuO content has resulted in changing of absorption edge from higher wavenumber to lower wavenumber side. Interesting observation is that increase of intensity and half-width of broad absorption band with CuO rise at the expense of primary two bands. It is strongly felt that there exists conversion of Cu^+ ions to Cu^{2+} ions into octahedral environment. There was decrease in optical band gap with rise of CuO content.

Divalent octahedrally coordinated copper ions act as modifiers leading to growth of non-bridging oxygens (NBOs) that resulting prominent rise in donor centres by localized electrons. This rise moves the absorption edge to higher wavelength side by causing decrease in optical band gap (Table 2).

Fig. 6 shows the luminescence spectra of P_2O_5 -CaO- Na_2O : CuO glasses excited with their corresponding absorption edges recorded in the wavelength region 300 to 900 nm at room temperature.

The spectra exhibited two emission peaks; one broad band at about 484 nm and another sharp peak at 595 nm. Both the bands are assigned to $^3D_1 \rightarrow ^1S_0$ single Cu^+ centres and Cu^+-Cu^+ pairs transitions respectively [20]. Interesting detail is that the intensity and half width of these emission peaks found to diminish with CuO. This could be due to the fact that the conversion of Cu^+ ions into octahedrally coordinated Cu^{2+} ions. From the fluorescence results, it is clear that the sample PC₅ exhibit high emission intensity due to the presence of more Cu^+ ions [8]. With increase in the content of CuO, there is a change in the glass structure and was observed by FTIR, which also supports the conversion of Cu^+ to Cu^{2+} .

4. Conclusion

Glasses of particular composition P_2O_5 -CaO- Na_2O : CuO were synthesized by melt quenching. Later, characterization of samples by XRD, SEM, DTA, optical absorption, FTIR and photoluminescence spectra. Absence of sharp peaks in XRD confirming amorphous nature, but characteristic glassy broad halo was observed. SEM pictures indicating signs of absence of micro-crystals which also supports XRD results. DTA traces have clearly indicated that glass transition and melting temperatures move close to lower temperature with CuO reveals decrease in rigidity of glass network that supports FTIR result. Infrared spectra have shown various distinctive phosphate vibrational bands and possible cross linkages. The sample PC₂₀ found to exhibit more structural degree of disorder. Optical absorption spectra indicated the characteristic copper absorption transitions and decrease in band gap due to the larger concentrations of donor centres. Luminescence spectra has exhibited two emission peaks; one broad band at about 484 nm and another sharp peak at 595 nm corresponding to the transition of $^3D_1 \rightarrow ^1S_0$ single Cu^+ centres and Cu^+-Cu^+ pairs respectively.

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