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Copper ion as a structural probe in $PbO–CaF_2–P_2O_5$ glass system by means of spectroscopic and dielectric studies

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ABSTRACT

$PbO–CaF_2–P_2O_5$ glasses containing small concentrations of CuO from 0 to 0.6 mol% were prepared. A number of studies viz., dielectric studies (constant ε', loss tan δ, ac conductivity σ_{ac} over a range of frequency and temperature), infrared, optical absorption ESR and photoluminescence spectra of these glasses, have been carried out. The variations observed in all these properties with the concentration of copper ions have been analyzed in the light of different oxidation states and environment of copper ions in the glass network.

1. Introduction

P_2O_5 glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultra-violet and far infrared transmission [1,2] and are also the materials of choice particularly for high power laser applications. During the last two decades, phosphate glasses have been investigated extensively, yet there is still a great interest in developing new glasses suited to the demands of both industry and technology. Many phosphate glasses are prone to crystallization or devitrification either during processing or while put into applications where they may be held at high temperatures for longer periods. Further, the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in a wide range of technological applications. In recent years, there has been an enormous amount of research on improving the physical properties and the chemical durability of phosphate by introducing a number of glass formers and modifiers such as TiO_2, V_2O_5, Cr_2O_3, Al_2O_3, Ga_2O_3, Sb_2O_3, etc., into P_2O_5 glass network [3–6].

Among various phosphate glass systems, the alkali free $PbO–P_2O_5$ glass systems are known to be more stable against devitrification and moisture resistant. In contrast to the conventional alkali/alkaline earth oxide modifiers, PbO has the ability to form stable glasses due to its dual role; one as the modifier if Pb—O is ionic and the other as the glass former if Pb—O is covalent. When Pb^{2+} ions are present in the glass as network formers, they impart a three-dimensional character to the glass. This fact accounts for the ability of PbO to form glasses up to 90 mol%. Clearly this peculiar behavior, which distinguishes lead from alkali and alkaline earth metals, depends on the electronic structure of the Pb^{2+} ion. In fact the easily polarizable valence shell of the Pb^{2+} ion strongly interacts with highly polarizable O^{2-} ion, giving rise to a rather covalent Pb—O bond [7]. Wasylak et al. have carried out extensive investigations of a variety of PbO mixed glass systems along these lines [8,9]. Addition of CaF_2 to lead phosphate glass matrices is anticipated to lower the viscosity and to decrease the liquidus temperature to a substantial extent and further it also acts as an effective mineralizer [10]. Calcium phosphate glasses are also well known for their bioactive properties. Further, the lead phosphate glasses with fluorine content find variety of applications in low temperature moulding operations for optical elements and glass to metal seals; the fluoro phosphate glasses have interesting optical characteristics including non-linear refractive indices that make them useful in high power lasers [11].

Copper is being extensively used in several commercial glasses, such as red glass hematite, aventurine and rubies. CuO containing glasses are also important in technological point of view, because of their semiconducting properties and other potential applications [12,13]. In various glasses, copper exists in two stable ionic states viz., monovalent Cu^{+}, divalent Cu^{2+} ions and may also exists as metallic copper. The electronic structure of the copper atom is [Ar] $3d^{10}$ $4s^{1}$; the cuprous ion, having its five d orbitals occupied,

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does not produce coloring [14], while Cu^{2+} ions create color centers with an absorption band in the visible region [15,16] and produce blue and green glasses. The color of the glass depends on the Cu^{2+} content, its specific coordination, composition and basicity of the glass. Colors produced by Cu^{2+} ions in various glasses have been interpreted [17–20] in terms of ligand field theory. Though, a considerable number of recent studies are available on the glasses containing copper ions most of them are focused on structural investigations by means of Raman and IR spectroscopic studies. Virtually, no studies are available on dielectric properties of lead calcium fluoro phosphate glasses containing copper ions. The study of dielectric properties such as dielectric constant ε', loss $\tan\delta$ and ac conductivity σ_{ac}, over a wide range of frequency and temperature of the glass materials not only help in accessing the insulating character and understanding the conduction phenomenon but also throw information on the structural aspects of these materials to a large extent. Work along these lines has been carried out in the recent years on a variety of inorganic glass materials giving valuable structural information [21–24]. The objective of this paper is to have a comprehensive understanding over the topology and valence states of copper ions in $PbO–CaF_2–P_2O_5$ glass system, by a systematic study of dielectric properties coupled with spectroscopic investigations (optical absorption, luminescence emission, ESR and IR spectra).

2. Experimental methods

With in the glass-forming region of $PbO–CaF_2–P_2O_5$ glass system, a particular composition 30 PbO–10 CaF_2–(60 − *x*) P_2O_5:*x* CuO (with *x* ranging from 0 to 0.6) is chosen for the present study. The details of the composition are

- C_0: 30 PbO–10 CaF_2–60 P_2O_5;
- C_1: 30 PbO–10 CaF_2–59.9 P_2O_5:0.1 CuO;
- C_2: 30 PbO–10 CaF_2–59.8 P_2O_5:0.2 CuO;
- C_3: 30 PbO–10 CaF_2–59.7 P_2O_5:0.3 CuO;
- C_4: 30 PbO–10 CaF_2–59.6 P_2O_5:0.4 CuO;
- C_5: 30 PbO–10 CaF_2–59.5 P_2O_5:0.5 CuO;
- C_6: 30 PbO–10 CaF_2–59.4 P_2O_5:0.6 CuO.

Appropriate amounts (all in mol%) of reagent grades of PbO, CaF_2, P_2O_5 and CuO powders were thoroughly mixed in an agate mortar and melted in a thick-walled platinum crucible in the temperature range 600–700 °C in an automatic temperature controlled furnace for about 1 h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed from 250 °C with a cooling rate of 1 °C/min. The amorphous state of the glasses was checked by X-ray diffraction and scanning electron microscopy.

The samples were then ground and optically polished. The final dimensions of the samples used for dielectric, optical absorption and luminescence studies were about 1 cm × 1 cm × 0.2 cm. The density *d* of the glasses was determined to an accuracy of 0.001 by standard principle of Archimedes' using *o*-xylene (99.99% pure) as the buoyant liquid. The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300–1200 nm up to a resolution of 0.1 nm using CARY 100 (Varian) Spectrophotometer. The luminescence spectra of these glasses were recorded in the wavelength region 300–900 nm on FluroMax-3 (Jobin-Yvon, Horiba) using Xenon lamp of power 150 W as excitation source. The ESR spectra of the fine powders of the samples were recorded at room temperature on E11Z Varian X-band (ν = 9.5 GHz) ESR spectrometer. Infrared transmission spectra were recorded on a Bruker IFS 66V-IR spectrophotometer with a resolution of 0.1 cm^{-1} in the range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized glass (1.5 mg). A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for dielectric measurements. The painted samples were then dried with a hot blower for about 10 min on either side. The dielectric measurements were taken at various temperatures and frequencies using HP 4263B LCR meter. The accuracy in measuring the dielectric constant is $\sim 10^{-3}$ and that in loss is $\sim 10^{-4}$.

3. Results

From the measured values of density d and calculated average molecular weight $\overline{M}$, various physical parameters such as copper ion concentration N_i and mean copper ion separation r_i of these

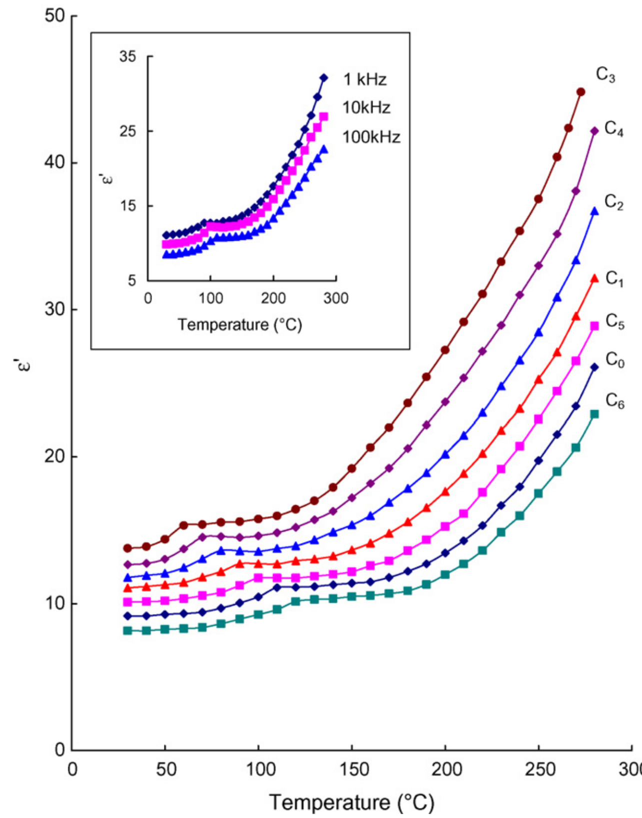

Fig. 1. A comparison plot of variation of dielectric constant with temperature at 1 kHz for $PbO–CaF_2–P_2O_5$:CuO glasses. Inset gives the variation of dielectric constant with temperature at different frequencies of glass C_1.

glasses are evaluated using the conventional formulae and are presented in Table 1.

The dielectric constant ε' and loss $\tan\delta$ at room temperature (≈30 °C) of pure $PbO–CaF_2–P_2O_5$ glasses at 100 kHz are measured to be 6.85 and 0.0055, respectively; the values of ε' and $\tan\delta$ of the glasses are found to increase considerably with decrease in frequency.

The temperature dependence of ε' of the glasses containing different concentrations of CuO at 1 kHz is shown in Fig. 1 and at different frequencies of glass C_1 is shown as the inset. The value of ε' is found to exhibit a considerable increase at higher temperatures especially at lower frequencies; however, the rate of increase of ε' with temperature is found to be the highest for the glass containing 0.3 mol% of CuO.

A comparison plot of variation of $\tan\delta$ with temperature, measured at a frequency of 10 kHz is presented in Fig. 2. The inset (a) of Fig. 2 represents the temperature dependence of $\tan\delta$ of glass C_2 at different frequencies. Inset (b) of Fig. 2 represents the variations of dielectric constant and loss of $PbO–CaF_2–P_2O_5$ glasses with the concentrations of CuO at 10 kHz, measured at room temperature; the variations exhibit maxima at 0.3 mol% of CuO.

The curves of both the pure and CuO doped glasses have exhibited distinct maxima; with increasing frequency the temperature maximum shifts towards higher temperature and with increasing temperature the frequency maximum shifts towards higher frequency, indicating the dielectric relaxation character of dielectric losses of these glasses. Further, the observations on dielectric loss variation with temperature for different concentrations of CuO indicate an increase in the broadness and $(\tan\delta)_{max}$ of relaxation curves with the shifting of maxima towards lower temperature