EFFECT OF CdO ON PHYSICAL AND OPTICAL PROPERTIES OF BINARY PHOSPHATE GLASSES

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Abstract

Binary cadmium phosphate glasses were synthesized by fusing CdO and P_2O_5 with composition x% CdO-(100-x) % P_2O_5, where x lies in 30-60 mole% range. In this exercise the physical and optical properties of these glasses were studied, which are reported as mass density ρ, oxygen packing density, molar volume, modulus of rigidity η, coefficient of linear expansion α, transition temperature T_g, softening temperature T_s, refractive index n and optical band gap E_{opt}. The mass density, oxygen packing density, refractive index and band tailing decrease with increasing concentration of CdO up to 40 mole% while molar volume and optical band gap increase in this range. In these glasses modulus of rigidity, transition temperature, softening temperature, refractive index and band tailing show an increasing trend with increasing concentration of cadmium oxide from 40 to 60 mole%, whereas, in this composition range molar volume, coefficient of linear expansion and optical band gap indicate a decreasing behavior with increasing concentration of cadmium oxide. It show that the results of cadmium phosphate glass system are divided into compositional regions, i.e. in first region CdO interstices in the glass network and do structural modification, where in second region it dominates its intermediate behavior and become the part of the glass structure.

Keywords: Coefficient of linear expansion, modulus of rigidity, optical band gap, phosphate glasses, physical properties.

INTRODUCTION

Melt quench technique is used to produce polycrystalline materials by controlled crystallization of glasses [Pedro *et al.* 1996]. These glasses have many applications as engineering materials and as domestic appliances. The knowledge of electrical conductivity, electromagnetic

absorption, refractive index and physical properties such as mechanical strength, chemical resistance as well as thermal expansion coefficient of these materials is very helpful in developing various devices, such as photonic switches, lasers and fibers for communications [Fujino *et al.* 1995]. Phosphate glasses have a number of applications due to their particular properties like easy preparation, electronic/ ionic conduction. These glasses can also be utilized as radiation shielding material due to which they are employed in many biological and technical applications [Kumar 1985, Pemberton 1991, Siddiqi *et al.* 1995, Murawski *et al.* 2003, Altaf *et al.* 2005]. A number of researchers studied electrical and optical properties to characterize the phosphate glasses [Gongyi and Yuli 1993, Mogus-Milankoviv *et al.* 2001, Budi *et al.* 2002, Pan and Ghosh 2002, Ralhskaran and Naido 2004, Ahmad *et al.* 2006], where as the physical properties are equally helpful to know the nature of materials. Amorphous or crystalline nature of materials under investigation can be distinguished by the observation of the thermal expansion curve. Experimental results on physical properties of some glassy materials have been reported in literature [Morey 1960, Kingery 1960, Holloway 1973], and still there is a scope for more work.

The aim of present work is to study the physical properties such as mass density, oxygen packing density, molar volume, refractive index, modulus of rigidity, transition temperature, softening temperature, coefficient of linear expansion and optical properties like refractive index and optical band gap to observe the effect of CdO on these properties of the binary cadmium phosphate glasses. No such data has been reported on the physical properties of binary cadmium phosphate glass system to the best of our knowledge.

EXPERIMENTAL

Metal oxides like CdO and P_2O_5 99.99% purity were used to prepare binary cadmium-phosphate glass system. These glass samples were prepared in a platinum crucible using 15g ingredients mixture of composition x%CdO-(100-x)%P_2O_5. The details of sample preparation have already been described else where [Chaudhry and Altaf 2000, Altaf and Chaudhry 2005].

The density of these glass samples was measured by mass and volume method. Molar volume and oxygen packing density were estimated by using following equations respectively,

$$\text{Molar volume} = M / \rho \qquad\qquad\qquad (i)$$

$$\text{Oxygen packing density} = \{1000 \times \rho \times O\}/ M \qquad (ii)$$

Where ρ is the mass density, M the molecular weight of glass, O the number of oxygen atoms in the glass and N_{avo} the Avogadro number. P is equal to 'n x', where 'x' is the mole fraction in glass composition and 'n' is

the number of atoms of element ions in a given oxide, i.e. n = 1 for oxides like CdO, ZnO etc and n = 2 for oxides like Na_2O, Li_2O, etc.

Refractive index of the glass was measured in terms of the real and apparent depths. The modulus of rigidity 'η' was measured with the dynamical method by using "an oscillating rod system" i.e. a Torsion Pendulum. The details of measurements of the density, refractive index and modulus of rigidity have already been described in an earlier communication [Altaf and Chaudhry 2005].

A schematic diagram with horizontal tube heating system as shown in Fig. 1 was used up to 600 °C to measure the thermal expansion and coefficient of linear expansion of the fibers of binary cadmium phosphate glasses. These parameters were measured by using two equal bore Pyrex tubes, each of 10 cm length, were placed side by side in a single heating unit. A Chromel-Alumel thermocouple connected to a Fenwal controller was fitted in upper tube and the glass fiber 'F' of length L_o = 10.5 cm was placed in the lower tube. The temperature of the system was controlled by a temperature controller with in an accuracy of 1°C while the heating rate was controlled through a voltage regulator. To achieve the equilibrium each temperature was maintained for five minutes.
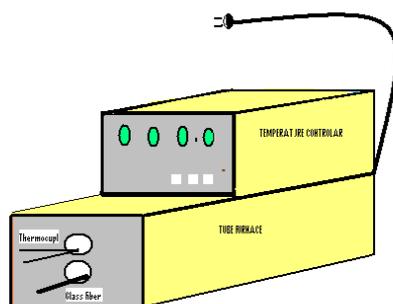

Fig. 1. Tube furnace with temperature controller for heating the fiber for measuring its linear expansion with the variation of temperature.

For every 50 °C rise in temperature (with constant rate of heating) the increase in length of the fiber was measured with a traveling microscope whose least count is 10 μm. The linear expansion versus temperature is depicted in Fig. 2. This curve was used to estimate transition temperature T_g and softening temperature T_s. The coefficient of linear expansion 'α' was then calculated using equation

$$\alpha \square = (\Delta L)/ (L_o \Delta t) \quad (°C)^{-1} \tag{iii}$$

In optical absorption measurements, absorbance versus wavelength spectra were recorded at room temperature in the UV- visible spectral range i.e. 190 nm to 700 nm using a Hitachi U-2000 spectrophotometer. The method of finding optical band gap and Urbach energy had been described in an earlier work [Altaf and Chaudhry 2000].
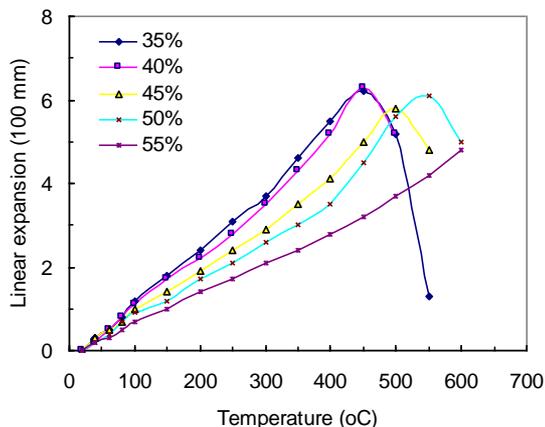
Fig. 2. Plot of linear expansion Δl versus temperature ^{o}C.

RESULTS AND DISCUSSION

Table 1 shows the measured and estimated values of mass densities. These results indicate a decreasing trend in the experimentally measured mass density of **x**% CdO-(100-x)%P_2O_5 glass system with increasing concentration of CdO from 30 to 40 mole%, but the density increases with increasing CdO concentration from 40 to 60 mole%. Theoretical values of the density were estimated by using the relation $\rho = \sum\rho_i\,x_i$, where ρ_i and x_i are the density and fraction of the free oxides respectively. The estimated and the measured values of density of these glasses are depicted in Fig. 3 as a function of CdO concentration. It can be seen that estimated values are higher than the measured values. This difference in values of density may be due to the variation of atomic arrangement in the structure of glass and molecules of the free oxides. The increase in the measured mass density with the increasing concentration of CdO agrees qualitatively with that predicted by the composition relation, and it may be due to the replacement of low density former P_2O_5 (2.39 g cm^{-3}) by a high density (8.15 g cm^{-3}) modifier/ intermediate CdO. The estimated values of CdO ion concentration, oxygen packing density and molar volume are plotted in Figs. 4, 5 and 6 respectively. These results show that oxygen packing density first decreases with increasing concentration of CdO from 30 to 40 mole% and then increases from 40 to 60 mole%, whereas molar volume shows an opposite behavior to that of the mass density and oxygen packing density. Increasing trend of molar volume at the initial stages could be due to the cleavage of the structure, but the decrease in molar volume with further addition of an intermediate/ modifier CdO in the glass compositions show that it is becoming the part of the glass network

i.e. causing more bridging oxygen than non-bridging [Othmer 1963, Mott and Davis 1979, Altaf and Chaudhry 2000, Chaudhry and Altaf 2000, Altaf and Chaudhry 2005]. The development of bridging oxygen may squeeze the glass structure and thus decreases its molar volume. The decrease in molar volume caused an increase in oxygen packing density and mass density.

Table 1: Variation of various glass properties with respect to glass composition.

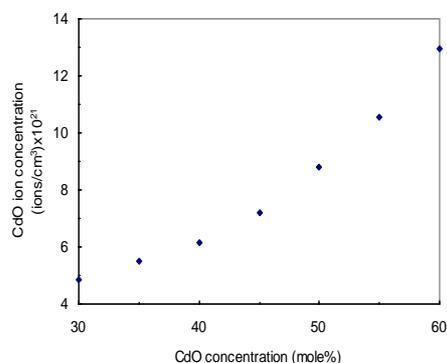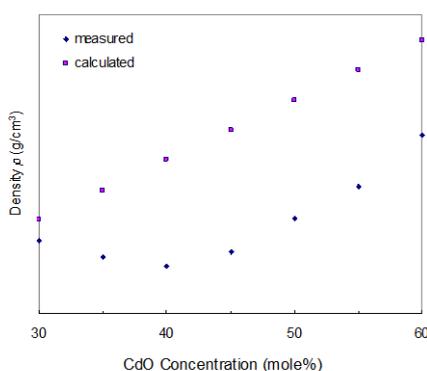| Composition Mole % CdO-P_2O_5	Density ρ (g cm^{-3})		Modulus Rigidity η (dy cm^{-2}) $\times 10^{11}$		Refractive Index n	Optical Band Gap (eV)
	Calculated	Measured	Un-annealed samples	Annealed samples		
30%-70%	3.94	3.72	-----	-----	1.54	3.44
35%-65%	4.24	3.57	2.76	2.85	1.52	3.53
40%-60%	4.54	3.47	2.85	2.89	1.50	3.62
45%-55%	4.84	3.62	3.34	3.09	1.51	3.55
50%-50%	5.14	3.95	3.29	3.42	1.55	3.50
55%-45%	5.44	4.28	3.62	3.87	1.59	3.15
60%-40%	5.74	4.79	-----	-----	1.67	2.90

Fig. 3. Variation of mass density relative to CdO concentration in mole%.
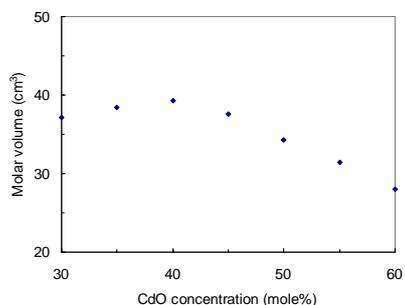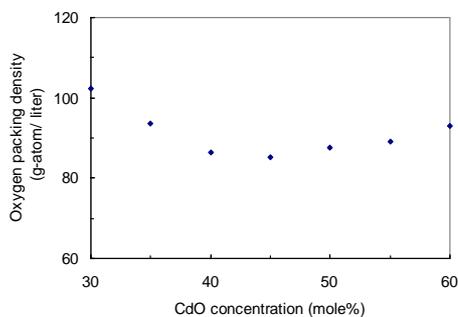**Fig. 4.** Plot of cadmium ion concentration vs. CdO concentration in mole%.

Fig. 5. Plot of oxygen packing density as a function of cadmium oxide content.
Fig. 6. Variation of molar volume with cadmium oxide concentration.

Compositional dependence of the refractive index is presented in Table 1, and the corresponding values are depicted in Fig. 7, which shows that refractive index increases with increasing amount of CdO. In many glass systems the increase in refractive index is related to an increase in their density, e.g., sodium-borate glasses [Fanderlik 1983]. The present results are in agreement with the reported one [Fanderlik 1983].
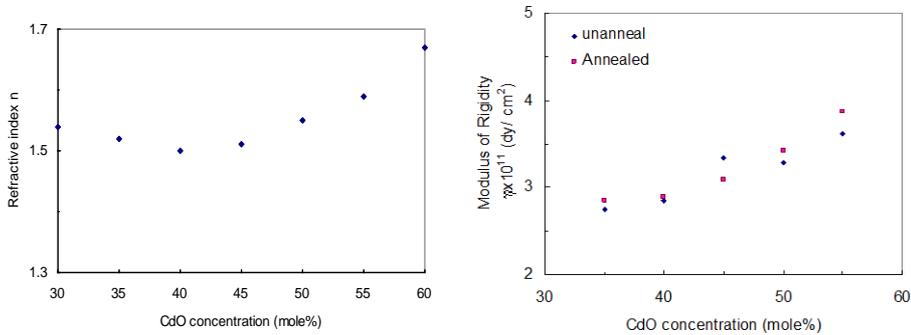

Fig. 7. Graph between refractive index and cadmium oxide content.
Fig. 8. Dependence of modulus of rigidity on cadmium oxide concentration.

Results of the modulus of rigidity 'η' of the binary cadmium phosphate glasses are listed in Table 1 and are depicted graphically in Fig. 8 as a function of cadmium oxide concentration. These results show that 'η' increases with increasing amount of CdO. The increase in modulus of rigidity may be due to increase in oxygen packing density [Farley and Saunders 1975, Rao and Karat 1994], which is a consequence of increasing number of bridging oxygen due to which the glass structure has further contracted and cause an increase in rigidity.
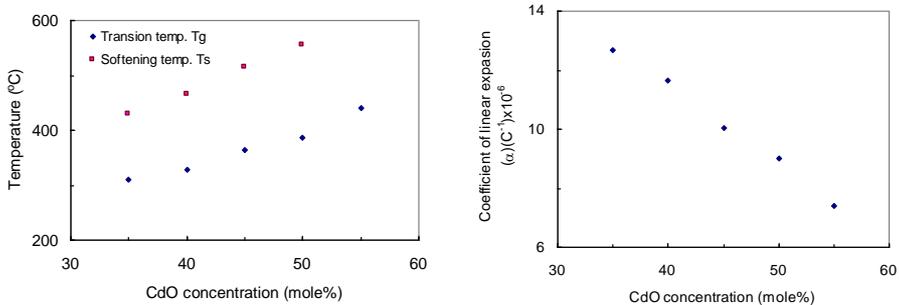

Fig. 9. Variations of transition and softening temperatures with CdO content.
Fig. 10. Variation of coefficient of linear expansion with respect to CdO content.

The linear thermal expansion of these glasses is shown in Fig. 2. The estimated values of transition temperature T_g, softening temperature T_s and calculated values of coefficient of linear thermal expansion are depicted in Figs. 9 and 10 respectively. T_g and T_s show an increasing

trend while coefficient of linear expansion decreases with increasing concentration of CdO. Being an intermediate, the CdO becomes part of the P_2O_5 glass network [Othmer 1963, Siddiqi *et al.* 1995]. This increases the number of bridging oxygen and thus develops a more condensed structure. Consequently, contraction of the structure decreases the molar volume which causes an increase in the oxygen packing density and hence an increase in the density of the glass sample. The increase in oxygen packing density along with the increase of mass density and decrease of molar volume of these glasses make them more resistive mechanically [Morey 1960]. This explains a decrease in the coefficient of linear expansion and rise in the transition and the softening temperatures. Fig. 11 shows E_{opt} versus CdO concentration. It can be observed that the optical band gap increases as the CdO concentration increases from 30 to 40 (mole%) and a further increase in CdO concentration beyond 40 (mole%) causes a decrease in the value of the optical band gap. There is an increase in the optical band gap, E_{opt}, at smaller values of CdO which may be due to the cleavage of P-O-P bonds with the substitution of CdO [Othmer 1963]. At high concentrations of CdO the decrease in E_{opt} is attributed to the intermediate nature of CdO. The variation in the optical band gap is parallel to the molar volume of these glasses. Both results are depending upon bridging and non-bridging oxygen atoms that appeared in the glass structure.
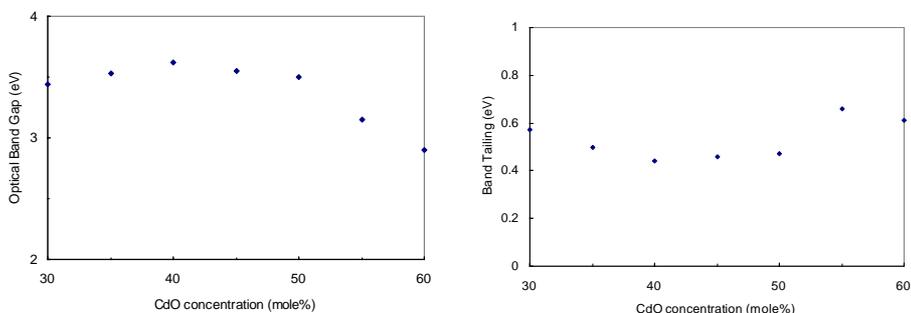

Fig. 11. A plot of optical band gap energy with respect to CdO concentration.
Fig. 12. Variation of Urbach energy with respect to CdO concentration.

The contents used as modifier support to develop the band tailing in the energy gap which causes the decrease in the E_{opt} [Urbach 1953, Mott and Davis 1979, Hogarth and Ghauri 1979]. Present experimental results are in good agreement with the published data of Hogarth *et al.* [1979] and Ghauri *et al.* [1981].

As a whole variation in the physical properties are attributed to structural changes occurring with a change in composition [Rao and Karat 1994]. Results reported in the present study are similar to those reported by other research workers [Morey 1960, Kingery 1960, Fanderlik 1983].

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