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Magnetic and spectroscopic properties of $PbO–La_2O_3–P_2O_5:Cr_2O_3$ glass system

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ABSTRACT

$PbO–La_2O_3–P_2O_5$ glasses containing different concentrations of Cr_2O_3 ranging from 0 to 0.5 mol% were prepared. A number of studies viz., differential thermal analysis, infrared, optical absorption, ESR spectra and magnetic properties of these glasses have been carried out as a function of chromium ion concentration. The analysis of the results of these studies indicated that chromium ions mostly exist in Cr^{3+} state in these glasses when the concentration of $Cr_2O_3 \leq 0.3$ mol% occupy octahedral positions and above this concentration chromium ions seem to subsist in Cr^{6+} state and occupy tetrahedral positions with $CrO^{2-}{}_4$ structural units.

1. Introduction

P_2O_5 glasses are well-known due to their high thermal expansion coefficients (~20 to 27 × 10^{-6}/°C) [1], low melting and softening temperatures and high ultra-violet and far infra red transmission [2,3]. Interest on these glasses was simulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing [4]. They are also the materials of choice particularly for high power laser applications [5]. However, many phosphate glasses are volatile in nature, have poor chemical durability, and highly hygroscopic in nature. These disadvantages have prevented the phosphate glasses 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 glasses by introducing a number of glass formers and modifiers such as Al_2O_3, MoO_3, Ga_2O_3, Cr_2O_3, Ta_2O_3, Sb_2O_3, As_2O_3, etc., into P_2O_5 glass network [6,7]. The addition of heavy metal oxides like PbO to the phosphate glasses is expected to improve the thermal stability of the glasses to a large extent. A considerable amount of work has been reported on PbO based glasses in the recent years [8,9]. Earlier extensive investigations like Raman, FTIR, NMR, X-ray diffraction and various other studies [10,11] on $PbO–P_2O_5$ glasses have revealed that, PbO takes the role of both glass former and glass modifier. As glass former, PbO enters the network with PbO_4 structural units by sharing the corners of phosphate network which in turn form P–O–Pb linkages. When PbO acts as network modifier, Pb is octahedrally coordinated and behaves like any other conventional alkali oxide modifier. The addition of Lanthanum(III) oxide (La_2O_3) improves the alkali resistance of glass, and is used in making special optical glasses, such as infrared-absorbing glass, as well as camera and telescope lenses, because of the high refractive index and low dispersion of rare-earth glasses.

Transition metal ions are being greatly used in the present days to probe the glass structure since their outer d-electron orbital function has a broad radial distribution and due to their high sensitive response to the changes in the surrounding actions. Among various transition metal ions, the chromium ion, a paramagnetic metal ion, when dissolved in glass matrices in very small quantities makes the glasses colored and has a strong influence over the optical properties of the glasses. It is due to the simple reason that it exists in different oxidation states viz., Cr^{3+} (acting as modifier with CrO_6 structural units) and Cr^{6+} (acting as network former with CrO^{2-}_4 structural units). The content of chromium in different states with different structural units in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strengths, mobility of the modifier cation, etc. Further, the most common optical absorption transition, ${}^4A_2 \rightarrow {}^4T_2$ (which has a strong bearing on the luminescence efficiency) of Cr^{3+} ion is found to be very sensitive to its chemical environment. Extensive investigations on the optical absorption, luminescence and ESR spectroscopy of Cr^{3+} ion in a variety of inorganic glasses have been made in recent years in view of their importance in

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the development of tunable solid state lasers and new luminescence materials [12–16]. However, so far no systematic study has been made on the rare earth and transition metal ions doped lead phosphate glasses in the literature.

The present investigation is intended to have a comprehensive understanding over the influence of chromium ions on the structure of $PbO–La_2O_3–P_2O_5$ glasses from a systematic study of the spectroscopic properties, viz., optical absorption, IR, ESR spectra and magnetic susceptibility along with differential thermal analysis.

2. Experimental

For the present study a particular composition viz., $40PbO–(10-x) La_2O_3–50P_2O_5$: x Cr_2O_3 with x = 0 (C_0), 0.1 (C_1), 0.2 (C_2), 0.3 (C_3), 0.4 (C_4) and 0.5 (C_5) all by mol%, has been chosen.

The materials were $(NH_4)_2HPO_4$, PbO, La_2O_3, and Cr_2O_3 of reagent grade purity. The samples were prepared by weighing suitable proportions of the components; the powder was mixed thoroughly in an agate mortar and melted in a thick-walled platinum crucible between 1000 °C–1200 °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 300 °C with a cooling rate of 1 °C/min. Differential thermal analysis was carried out using STA 409C, Model DTA TG instrument (to an accuracy of ±1 °C) with a programmed heating rate of 10 °C/min, in the temperature range 30–1000 °C to determine the glass transition temperature and crystalline temperature. The samples were then ground and optically polished. The final dimensions of the samples used optical studies were about 1 cm × 1cm × 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 samples were recorded at room temperature in the wavelength range 300–800 nm up to a resolution of 0.1 nm using CARY 5E UV–VISNIR Spectrometer. Infrared transmission spectra were recorded on a Bruker IFS 66V-IR spectrometer with a resolution of 0.1 cm^{-1} in the range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing powder form of the glass (1.5 mg). The ESR spectra of the fine powders of the samples were recorded at room temperature on E11Z Varian X-band ($\gamma = 9.5GHz$) ESR spectrometer Magnetic susceptibility of $PbO–La_2O_3–P_2O_5$ glasses containing different concentrations of Cr_2O_3 is measured at room temperature by Guoy's method.

3. Results

Using the values of measured density (d) and calculated average molecular weight $(\overline{M})$ various physical parameters that are useful for understanding the physical properties of these glasses have been evaluated and presented in Table 1. Fig. 1 shows typical traces of differential thermal analysis (DTA) of all the glasses under study. From these traces the values of T_g (glass transition temperature) and T_c (crystalline temperature) have been evaluated and presented in Table 2. With the increase of chromium content in the glass matrix up to 0.3 mol%, the quantity (T_c–T_g), which is proportional to glass forming ability, is found to decrease; for further increase of Cr_2O_3, a reversal trend is observed.

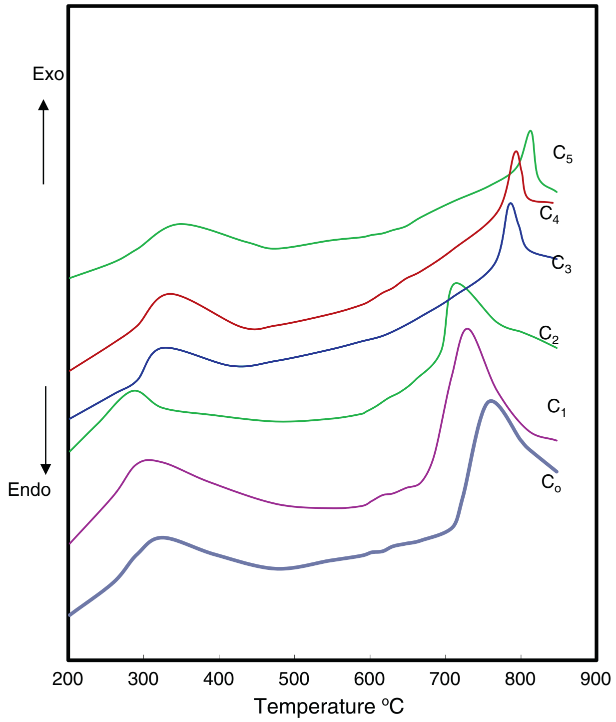

Fig. 1. DTA traces of $PbO–La_2O_3–P_2O_5:Cr_2O_3$ glasses.

Fig. 2(a) shows the optical absorption spectra of $PbO–La_2O_3–P_2O_5$ glasses containing different concentrations of Cr_2O_3. From the spectra we observe that the cutoff wavelength shifted towards higher wavelength with increase in the concentration of Cr_2O_3 up to 0.3 mol% and there after the edge is shifted gradually towards lower wavelength. The spectrum of glass C_1, has exhibited two prominent absorption bands with the peaks at 433 nm (peak 1) and 662 nm (peak 2); with increasing concentration of Cr_2O_3 up to 0.3 mol%, no considerable changes in the positions of these bands have been observed. However, beyond this concentration (0.3 mol%), the peak positions of these two bands observed to shift towards slightly lower wavelength with decreasing intensity. Further, an additional kink (the intensity of which is found to increase gradually at the expense of other two prominent peaks) at about 370 nm has also been observed in the spectra of glasses C_4 and C_5. Two additional shoulders at 670 and 700 nm have also been observed on peak-2 of all the glasses.

From the observed absorption edges, we have evaluated the optical band gaps (E_0) of these glasses by drawing a plot between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ as per the equation

$$\alpha(\omega)\,\hbar\omega = C(\hbar\omega - E_0)^2. \tag{1}$$

Table 1
Physical parameters of $PbO–La_2O_3–P_2O_5:Cr_2O_3$ glasses.

Glass	Density d (g/cm^3) (±0.001)	Average molecular weight, $\overline{M}$ (±0.001)	Conc. of Chromium ions, N_i ($10^{22}/cm^3$) (±0.001)	Interionic distance R_i (A°) (±0.00001)	Polaron radius R_p (A°) (±0.0001)	Field strength F_i (10^{16}, cm^{-2}) (±0.00001)
C_o	5.658	192.831	–	–	–	–
C_1	5.663	192.982	1.767	8.27081	3.3326	0.54025
C_2	5.668	193.134	3.535	6.56425	2.6449	0.85767
C_3	5.673	193.286	5.303	5.73414	2.3105	1.12397
C_4	5.678	193.438	7.072	5.20958	2.0991	1.36172
C_5	5.684	193.591	8.842	4.83593	1.9485	1.58027