Influence of Chromium Ions on the Dielectric Properties of the PbO-Ga_2O_3-P_2O_5 Glass System

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PbO-Ga_2O_3-P_2O_5 glasses containing different amounts of Cr_2O_3, ranging from 0 to 1.0 mol%, were prepared. The dielectric properties (viz., constant ε', loss $\tan\delta$, ac conductivity σ_{ac} over a wide range of frequencies and temperatures, dielectric breakdown strength) have been studied as a function of the concentration of chromium ions. An anomaly has been observed in the dielectric properties of these glasses, when the concentration of Cr_2O_3 is about 0.4 mol%. This anomaly has been explained in the light of different oxidation states of chromium ions with the aid of data of differential thermal analysis and optical absorption spectra of these glasses.

Key words: PbO-Ga_2O_3-P_2O_5 Glass; Dielectric Properties; Cr_2O_3.

1. Introduction

The study of dielectric properties such as the dielectric constant ε', loss $\tan\delta$, ac conductivity σ_{ac} over a range of frequencies and temperatures, and dielectric breakdown strength of the glasses helps in assessing their insulating character and also throw light on structural aspects of the glasses. Work along these lines was carried out in recent years on a variety of inorganic glasses by a number of researchers yielding valuable information [1 – 3].

Phosphate glasses are well-known due to their superior physical properties such as low melting and softening temperatures and high ultra-violet and far-infrared transmission [4 – 6]. However, the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses have 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 including electrical insulating strength and the chemical durability of a variety of phosphate glass systems by adding different metal oxides.

Ga_2O_3, a heavy metal oxide, when introduced in the glass matrix, is expected to alter the physical properties like refractive index, thermal expansion coefficient, chemical resistance and glass transition temperature, infrared transmittance and the insulating strength of the glasses. Many recent studies devoted to the role of Ga_2O_3 in various glass matrices are available [7 – 9].

The modifier oxide is PbO. When added to gallium phosphate glasses, the glasses are expected to become highly stable against devitrification and chemically inert [10], since PbO, in contrast to the conventional alkali / alkaline-earth oxide / halide modifiers, has the ability to form stable glasses due to its dual role, one as modifier (with PbO_6 structural units if Pb-O is ionic) and the other as glass former (with PbO_4 structural units, if Pb-O is covalent).

Among various transition metal ions, the chromium ions have a strong influence on the electrical, optical and magnetic properties of glasses. Such ions can easily be incorporated in the glass host owing to a much looser and relaxed glass structure than that of crystalline media. Regardless of the oxidation state of chromium in the starting glass batch, these ions may exist in different valence states simultaneously in the final glass. Materials containing mixed valence chromium are of recent interest as cathode materials in rechargeable batteries owing to their very high energy density and high capacitance [11, 12]. Among various oxidation states of chromium ions, Cr^{3+}, Cr^{4+}, Cr^{5+} and Cr^{6+} are the most likely to be active and stable. Out of these, the

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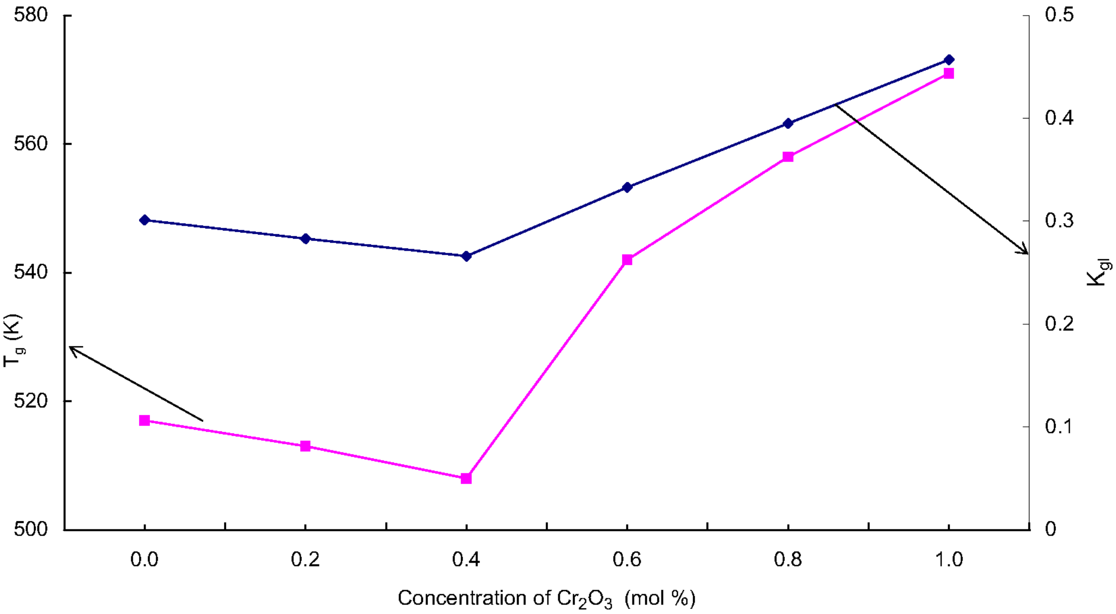

Fig. 1. Variation of the glass transition temperature (T_g) and Hruby's parameter (K_g) with the concentration of Cr_2O_3 of the PbO-Ga_2O_3-P_2O_5 glass system.

Cr^{6+} (d^0) ions have the closed shell configuration, participate in the glass network with CrO_4^{2-} structural units and are expected to strengthen the host-glass network, whereas Cr^{3+} ions act as modifiers and depolymerize the glass network. Even though a considerable number of studies on gallium phosphate glasses is available [13], most of them are concentrated on the structural aspects of theses glasses. Devoted studies on the dielectric properties of gallium phosphate glasses mixed with chromium ions as such are not available.

Thus the objective of this paper is to understand the influence of chromium ions (introduced as Cr^{3+}) on the insulating character of PbO-Ga_2O_3-P_2O_5 glasses, and to probe their role on the structural modifications of the glass network by studying the dielectric properties in detail with the aid of the data on optical absorption spectra.

2. Experimental

In the glass forming region of the PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glass system, the composition 40 PbO-$(10-x)$ Ga_2O_3-50 P_2O_5:x Cr_2O_3 (with the values of x ranging from 0 to 1.0 mol% in steps of 0.2) has been chosen for the present study. Based upon the values of x, the samples are labeled as G_0 (pure), G_2 ($x =$ 0.2%), G_4 ($x = 0.4\%$), G_6 ($x = 0.6\%$), G_8 ($x = 0.8\%$) and G_{10} ($x = 1.0\%$).

The analytical grade reagents of ammonium dihydrogen phosphate, PbO, Ga_2O_3 and Cr_2O_3 powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted, using a platinum crucible in the temperature range of 950 – 1000 °C in a PID temperature-controlled furnace for about 2 h. The resultant bubble-free melt was then poured in a brass mould and subsequently annealed at 300 °C. The X-ray diffraction pattern and scanning electron microscope photographs taken on the prepared samples confirmed the amorphous nature of the glasses.

Differential thermal analysis (DTA) was carried out using a STA 409C, Model DTA-TG instrument with a programmed heating rate of 10 °C/min, in the temperature range of 30 – 1000 °C, to determine the glass transition temperature, crystallization temperature and melting temperature of the glasses prepared.

The samples needed for dielectric and optical absorption studies were prepared by suitable grinding and optical polishing to the dimensions of 1 cm · 1 cm · 0.2 cm. A thin layer of silver paint was applied on either side of the large faces of the samples, in order to serve as electrodes for dielectric measurements. The dielectric measurements were made on an LCR Meter (Hewlett-Packard Model-4263 B) in the frequency

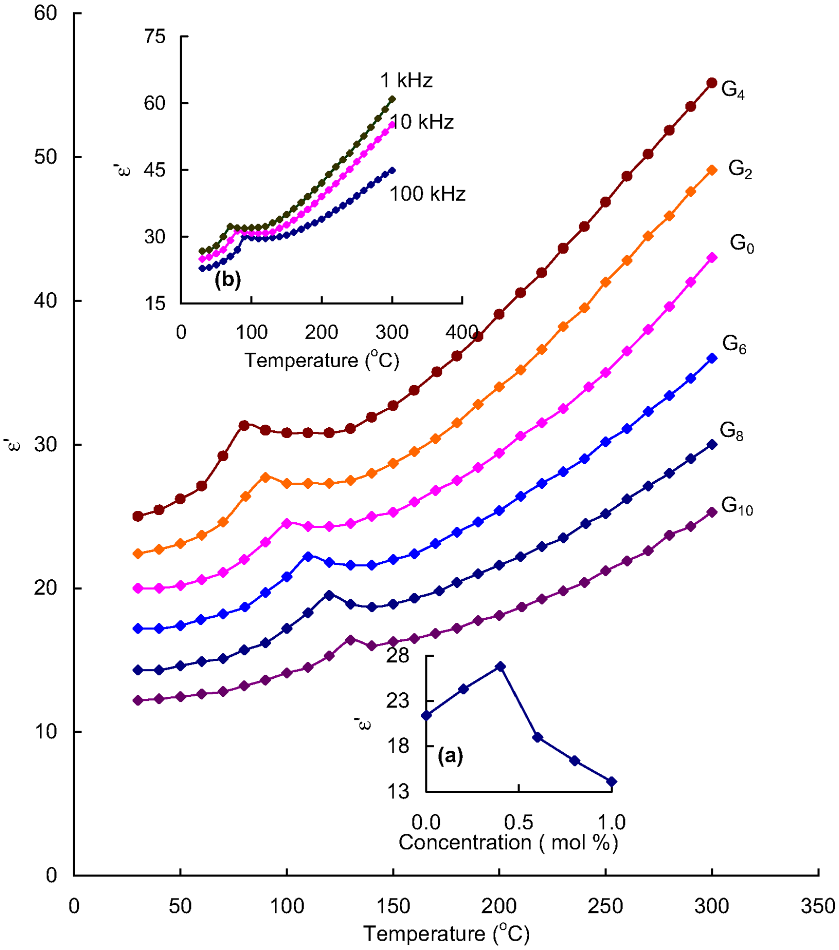

Fig. 2. Comparision plot of the variation of the dielectric constant at 10 kHz, with the temperature of $PbO-Ga_2O_3-P_2O_5:Cr_2O_3$ glasses. Insets: (a) Variation of ε' with the concentration of Cr_2O_3 measured at 10 kHz at room temperature. (b) Variation of the dielectric constant with the temperature at different frequencies for $PbO-Ga_2O_3-P_2O_5$ glass containing 0.4 mol% of Cr_2O_3.

range $10^2 - 10^5$ Hz. The accuracy in the measurement of the dielectric constant is ~ 0.001 and that of loss is $\sim 10^{-4}$. The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300 – 800 nm up to a resolution of 0.1 nm, using a CARY 5E UV-VIS-NIR spectrophotometer. Other details of the preparation of the samples and the experimental techniques adopted are similar to those reported in our earlier papers [14].

3. Results

The differential thermal analysis curves recorded at the rate of 10 °C/min have exhibited an endothermic effect due to the glass transition temperature T_g; the values of T_g are evaluated from the point of inflection of this change. At still higher temperatures an exothermic peak T_c due to the crystallization followed by an endothermic effect due to the melting effect, symbolized by T_m, are also observed. From the measured values of T_g, T_c and T_m, the glass forming ability parameter, known as Hruby's parameter, $K_{gl} = (T_c - T_g)/(T_m - T_c)$, is evaluated; the variations of the parameters T_g and K_{gl} with the concentration of Cr_2O_3 exhibited a downward kink at $x = 0.4$ (Fig. 1), indicating the increasing glass forming ability of the glasses containing Cr_2O_3 beyond 0.4 mol%.

The dielectric constant ε' and loss $\tan\delta$ at room temperature (≈ 30 °C) of the sample G_0 (Cr_2O_3-free $PbO-Ga_2O_3-P_2O_5$ glass) at 100 kHz are measured to be 17.4 and 0.0053, respectively; the values of these parameters are found to increase considerably with decrease in frequency. The dielectric constant ε' measured at room temperature is found to increase gradually with increase in the concentration of Cr_2O_3 in

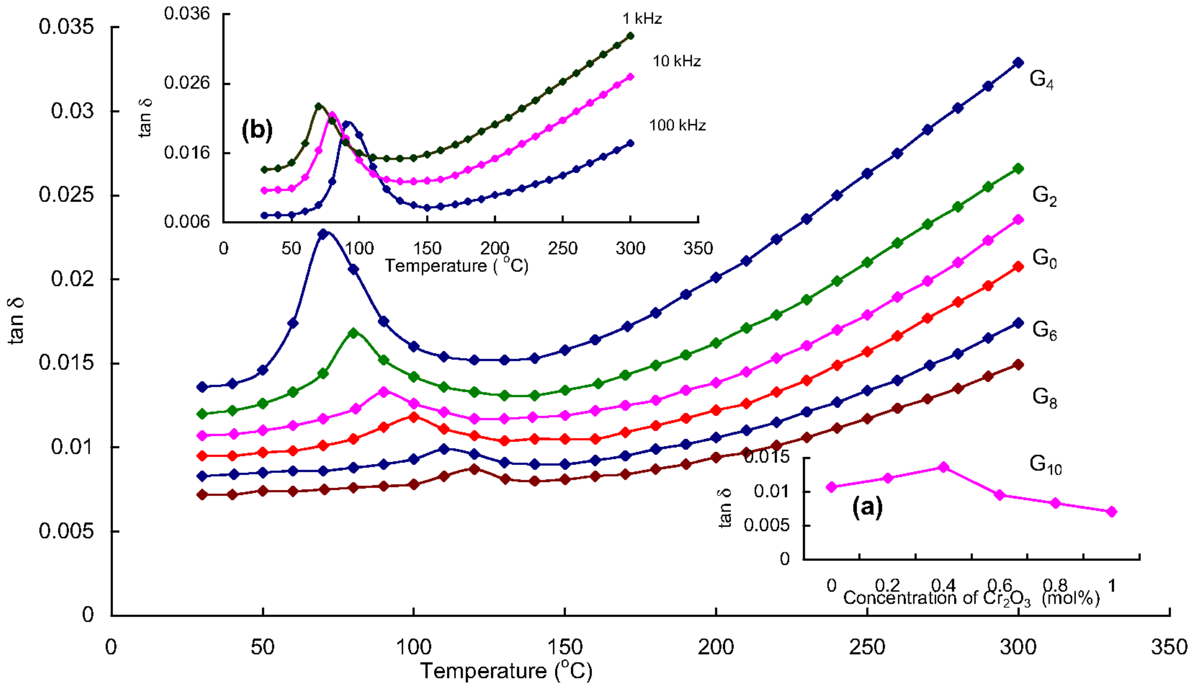

Fig. 3. Comparision plot of the variation of the dielectric loss at 1 kHz, with the temperature of PbO-Ga$_2$O$_3$-P$_2$O$_5$:Cr$_2$O$_3$ glasses. Insets: (a) Variation of $\tan\delta$ with the concentration of Cr$_2$O$_3$ measured at 10 kHz at room temperature. (b) Variation of the dielectric loss with the temperature at different frequencies for PbO-Ga$_2$O$_3$-P$_2$O$_5$ glass containing 0.4 mol% of Cr$_2$O$_3$.

the glass matrix up to 0.4 mol%; for further increase of Cr$_2$O$_3$, ε' is found to decrease [inset (a) of Fig. 2]. The temperature dependence of ε' for different concentrations of Cr$_2$O$_3$, measured at 10 kHz, is shown in Fig. 2 and for the particular glass G$_4$ (containing 0.4 mol% of Cr$_2$O$_3$) at different frequencies it is shown as inset (b) of Figure 2. The value of ε' is found to exhibit a considerable increase at higher temperatures, especially at lower frequencies.

The variation of dielectric loss with the concentration of Cr$_2$O$_3$ measured at room temperature has exhibited a similar behaviour as that of ε' [inset (a) of Fig. 3]. The temperature dependence of $\tan\delta$ of all the glasses measured at a frequency of 1 kHz is presented in Figure 3. Inset (b) of the same figure represents the variation of $\tan\delta$ for one of the glasses (glass G$_4$) at different frequencies. The curves of both the pure and Cr$_2$O$_3$-doped PbO-Ga$_2$O$_3$-P$_2$O$_5$ 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 the dielectric losses of these samples. The observations on dielectric loss variation with the temperature for different concentrations of Cr$_2$O$_3$ further indicates a gradual increase in the broadness and $(\tan\delta)_{\max}$ of relaxation curves with increase in the concentration of Cr$_2$O$_3$ up to 0.4 mol% with a shift of the relaxation region towards lower temperature. The summary of the data on the relaxation effects of PbO-Ga$_2$O$_3$-P$_2$O$_5$ glasses is presented in Table 1 along with other pertinent data, using the relation

$$f = f_0 \exp(-W_d/KT), \tag{1}$$

where the effective activation energy, W_d, for the dipoles is calculated for samples doped with different concentrations of Cr$_2$O$_3$. The activation energy is found to be lowest for the sample G$_4$.

The ac conductivity σ_{ac} is calculated at different temperatures using the equation

$$\sigma_{ac} = \omega\varepsilon'\varepsilon_0 \tan\delta, \tag{2}$$

where ε_0 is the vacuum dielectric constant, for different frequencies for all the glasses. The variation of the conductivity at 100 kHz with $1/T$ is shown in Fig. 4; the conductivity is observed to pass through a maximum at

Table 1. Data on the dielectric loss of PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glasses.

Glass	$(\tan\delta_{max})_{avg}$	Temperature region of relaxation (°C)	Activation energy for dipoles (eV)	$N(E_F)$ (10^{20} eV^{-1} cm^{-3})	Activation energy for conduction (eV)	Spreading factor β	Dielectric breakdown strength (kV/cm)
G_0	0.011	90 – 110	2.80	–	0.253	0.53	16.1
G_2	0.015	78 – 100	2.65	7.86	0.237	0.56	15.4
G_4	0.021	70 – 95	2.27	10.1	0.224	0.58	14.2
G_6	0.009	98 – 120	2.44	6.59	0.245	0.55	16.9
G_8	0.0074	110 – 130	2.57	4.52	0.270	0.54	17.8
G_{10}	0.0063	123 – 140	2.96	2.97	0.301	0.52	18.6

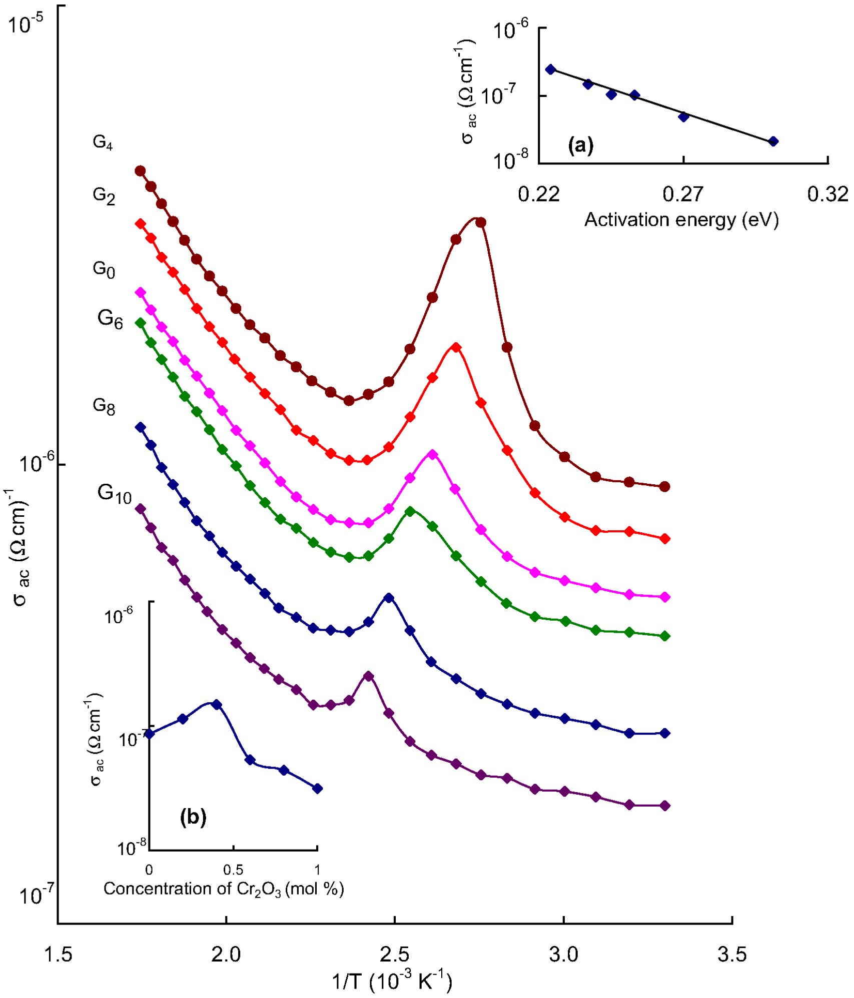

Fig. 4. Comparison plot of ac conductivity at 100 kHz with $1/T$ for PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glasses. Insets: (a) Variation of the conductivity with the activation energy. (b) Variation of the conductivity with the concentration of Cr_2O_3 of PbO-Ga_2O_3-P_2O_5 glasses.

$x = 0.4$ mol% [inset (b) of Fig. 4]. From these plots, the activation energy for the conduction in the high temperature region, over which a near linear dependence of $\log\sigma_{ac}$ with $1/T$ could be observed, is evaluated and presented in Table 1; the activation energy is found to be minimum for the glass G_4. The values of the dielectric breakdown strength at room temperature in air of PbO-Ga_2O_3-P_2O_5 glasses is presented in Table 1. The value of the breakdown strength is observed to be maximum for glass G_{10}.

The optical absorption spectra of all these glasses have exhibited two intense absorption bands due to conventional transitions, viz. $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_2$ of Cr^{3+} (d^3) ions at 430 and 641 nm, respectively; additionally two significant kinks at 671 and 712 nm (due to $^4A_2 \rightarrow {}^2T_1$ and $^4A_2 \rightarrow {}^2E$, spin- and parity-

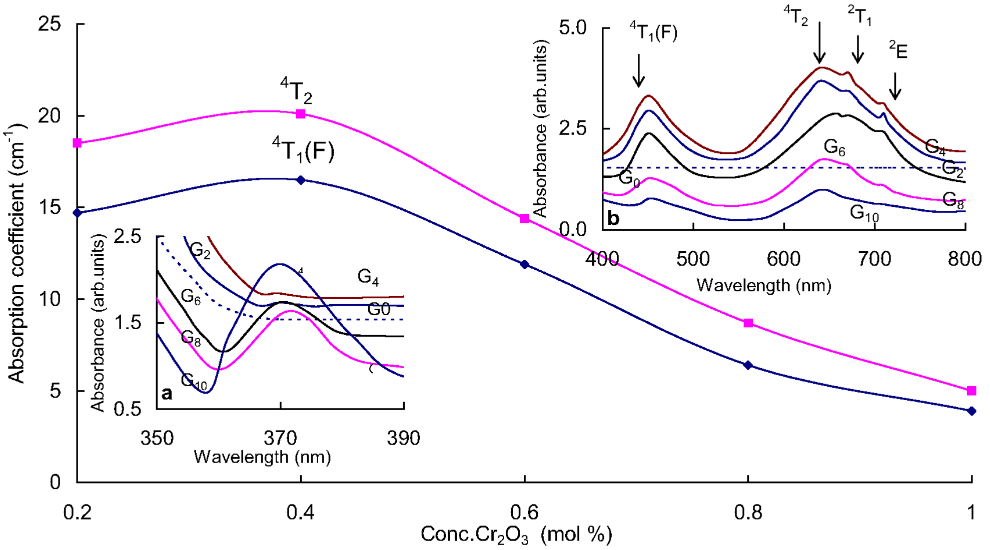

Fig. 5. Variation of the absorption coefficient cf the two primary transitions of Cr^{3+} ions with the concentration of Cr$_2$O$_3$. Insets (a) and (b) represent the optical absorption spectra of PbO-Ga$_2$O$_3$-P$_2$O$_5$:Cr$_2$O$_3$ glasses in the wavelength region 350 to 390 nm and 400 to 800 nm, respectively.

forbidden transitions) have appeared on the $^4A_2 \rightarrow {}^4T_2$ band in the spectra of the glasses G$_2$ and G$_4$. As the concentration of Cr$_2$O$_3$ is increased gradually beyond 0.4 mol%, the intensity of these two bands is observed to decrease (Fig. 5). Additionally, a kink at about 370 nm, identified due to charge transfer or the transformation of chromium ions from the Cr^{6+} (3d^{0}2p^6) state into the Cr^{5+} (3d^{1}2p^5) state, is also observed. As the concentration of the dopant is raised from 0.4 to 1.0 mol%, the intensity of this new band is observed to grow [inset (a) of Fig. 5] at the expense of the bands due to Cr^{3+} ions.

4. Discussion

P$_2$O$_5$, a well-known strong glass-forming oxide, participates in the glass network with PO$_4$ structural units. One of the four oxygen atoms in the PO$_4$ tetrahedron is doubly bound to the phosphorus atom with a substantial π-bond character to account for the pentavalency of phosphorus. The PO$_4$ tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygen atoms. Neighbouring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each PO$_4$ tetrahedron; in general, the P-O-P bond between PO$_4$ tetrahedra is much stronger than the cross bond between chains via the metal cations [16]. PbO, in addition to participating in the glass network with PbO$_4$ structural units, may also enter as modifier by transforming two Q^3 tetrahedra (viz., PO$_4$ tetrahedra with three bridging oxygen atoms and one terminal de-bound oxygen atoms) into two Q^2-tetrahedra (viz., PO$_4$ tetrahedra with two bridging oxygen atoms and two terminal de-bound oxygen atoms). And thus a PbO polyhedron is formed when it is surrounded by such two Q^2 and several Q^3 tetrahedrons. Ga$_2$O$_3$ is considered to act as a network former if Ga^{3+} ions take preferentially four-fold coordination in oxide glasses. The excess negative charge on GaO$_4$ tetrahedra is compensated either by localization of a modifier ion nearby or by generation of three-fold oxygen atoms. The GaO$_4$ tetrahedrons may enter the glass network and alternate with PO$_4$ tetrahedrons. In some of the glass networks, the gallium ions are also found to be in modifier position with GaO$_6$ structural units [16].

Chromium ions are normally expected to exist in Cr^{3+} state in the present glasses. However, conversion of these ions into Cr^{5+} and Cr^{6+} states appear to be viable during melting and annealing processes. The presence of chromium ions in these two states in the present glasses could be established from optical absorption spectra of these glasses. These ions [viz., Cr(VI) ions] exist in the form of Cr^{6+}O^{2-} centres in the frame of CrO$_4^{2-}$ groups [17]. Cr(VI) ions may enter the glass network with CrO$_4^{2-}$ structural units, al-

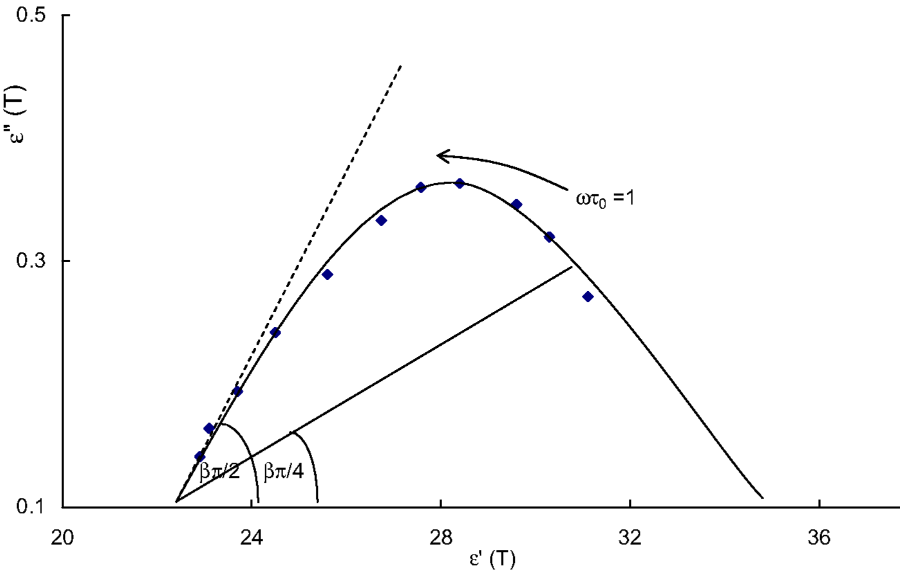

Fig. 6. Pseudo-Cole-Cole plot drawn at 100 kHz for the glass G_4.

ternate with PO_4 and GaO_4 units and strengthen the glass network. Cr(V) ions, if any, either enter the network with CrO_4^{3-} structural units [19] or act as modifier and may also exhibit dielectric relaxation effects similar to any other d^1 modifier ions (like W^{5+}, Mo^{5+}, V^{4+}, Ti^{3+}) [19]. Cr(III) ions, however, seem to act as modifiers like the conventional alkali oxide modifiers. As modifier, chromium ions may enter the glass network by breaking up local symmetry, and introduce coordinated defects known as dangling bonds along with the non-bridging oxygen atoms in these glasses [21].

The dielectric constant of a material is due to electronic, ionic, dipolar and space charge polarizations. Out of these, the space charge contribution depends on the purity and the perfection of the glasses. Its influence is in general negligible at very low temperatures and noticeable in the low frequency region. The dipolar effects can some times be seen in the glasses even up to 10^6 Hz. Recollecting the data, the slight increase in the dielectric constant and loss at low frequencies at room temperature for PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glasses may be ascribed to the defects produced in the glass network which contribute to the space charge polarization.

The temperature has a complicated influence on the dielectric constant of the glasses. Normally, increasing the temperature of the glasses decreases the electronic part of the dielectric constant by about 3% for a temperature change of about 200 K. Similarly, it appears that the changes in the ionic polarization are not large. Even assuming the presence of a small number of dipoles and their contribution to the dielectric constant, we know from Debye's theory, ε^1 is inversely proportional to the temperature. The considerable increase of ε' and $\tan\delta$ (beyond the relaxation region) with the temperature of the present glasses can only be attributed to space charge polarization [21] due to the bonding defects of the type mentioned earlier in these glasses.

With the successive increase of Cr_2O_3 from 0 to 0.4%, the values ε', $\tan\delta$ and σ_{ac} are found to increase at any frequency and temperature, and the activation energy for ac conduction is observed to decrease with respect to the one of the pure sample indicating an increase in the space charge polarization. It is quite clear from opical absorption spectra, that the chromium ions mostly exist in the trivalent state when $x \leq 0.4$ mol%, act as modifiers similar to Pb^{2+} ions and generate bonding defects by breaking the P-O-Ga, P-O-P, Ga-O-Ga bonds. The defects thus produced create easy pathways for the migration of charges that would build up space charge polarization leading to an increase in the dielectric parameters, as observed [20, 21].

With the gradual increase of Cr_2O_3 from 0.4 to 1.0%, the values ε', $\tan\delta$ (beyond the relaxation region) and σ_{ac} are found to decrease at any frequency and temperature, and the activation energy for ac conduction is observed to increase indicating a decrease in the space charge polarization; such a decrease may be due to the presence of a part of chromium ions that exist in the Cr^{6+} state, which act as network former with CrO_4 structural units. Further, there is a possibility for the cross linking of these CrO_4 units with PO_4 and GaO_4 groups to form P-O-Cr and Ga-O-Cr bonds in the glass network, as mentioned earlier. Such cross linkages obviously reduce the degree of disorder in the glass network and decreases the space charge polarization. Such an augmented cross link density may also be responsible for the observed increase in the glass transition temperature (T_g) and the glass forming ability parameter (K_{gl}) in this concentration range of Cr_2O_3.

$\tan\delta$ vs. temperature curves for $PbO-Ga_2O_3-P_2O_5:Cr_2O_3$ glasses show dipolar relaxation effects; the relaxation intensity however, seems to be decreasing with decreasing relaxation character and increasing concentration of Cr_2O_3 beyond 0.4 mol%. To know whether there is a single relaxation time or spreading of relaxation times in $PbO-Ga_2O_3-P_2O_5:Cr_2O_3$ glasses, we have adopted a pseudo-Cole-Cole plot method [instead of conventional Cole-Cole plot between $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ at a fixed temperature] suggested by Sixou [21], in which $\varepsilon'(T)$ vs. $\varepsilon''(T)$ can be plotted at a fixed frequency. The plot cuts the ε' axis (as per Sixou) at the low temperature side at an angle of $(\pi/2)\beta$, where β is the spreading factor for relaxation times. For $PbO-Ga_2O_3-P_2O_5:Cr_2O_3$ glass containing 0.4% of Cr_2O_3 (glass G_4), the pseudo-Cole-Cole plot at 100 kHz is shown in Figure 6. The spreading factor β estimated from this plot is 0.58. Such plots have also been drawn for the other glasses, and the value of β is estimated and presented in Table 1. The value of β is found to increase with increase in the concentration of Cr_2O_3 from 0 to 0.4 mol%. The observed dielectric relaxation effects may be attributed to the association of octahedrally positioned Pb^{2+} ions with a pair of PO^{2-} groups (which exhibit the vibrational bands on the high frequency side of the P=O vibrational region) in analogy with the mechanism association of a divalent positive ion with a pair of cationic vacancies – in conventional glasses, glass ceramics and crystals [22, 23]. It was also reported that even d^1 ions, like W^{5+}, Mo^{5+}, V^{4+}, Ti^{3+}, exhibit dipolar relaxation effects [18, 24]. In view of this, it is quite likely that even Cr^{5+} (d^1) ions, if any, participate in the relaxation effects. The decreasing value of $(\tan\delta)_{max}$ and the increasing value of the activation energy for dipoles in the network with increase in the concentration of Cr_2O_3 beyond 0.4 mol% (Table 1) suggests a decreasing degree of freedom for dipoles to orient in the field direction. The spreading of relaxation times in these glasses may be understood due to the experience of an approximately random potential energy by the dipoles on diffusing through the distorted structure of the glass [25]. The highest value of activation energy for dipoles obtained for glass G_{10} suggests the highest rigidity of this glass network.

When a plot is made between $\log\sigma(\omega)$ vs. activation energy for conduction (in the high temperature region) a near linear relationship is observed [inset (a) of Fig. 4]; this observation suggests that the conductivity enhancement is directly related to the increasing mobility of the charge carriers in the high temperature region [26].

The conductivity curve (at any frequency and temperature) as a function of the Cr_2O_3 concentration passes through a maximum at $x = 0.4$ mol% [inset (b) of Fig. 4]. Thus Fig. 4 and its insets suggest a kind of transition from predominantly ionic (zone-I, for $x <$ 0.4 mol%) to electronic (zone-II for $x >$ 0.4 mol%) conductivity [27]. The mobile electrons or polarons in the process of transfer between different valence states of chromium ions are attracted by the oppositely charged cations. This cation polaron pair moves together as a neutral entity. The migration of this pair is not associated with any net displacement of the charge. Hence, this process does not contribute to the electrical conductivity. As a result there will be a decrease in the conductivity, as observed in zone-II [28].

The ac conductivity in the region where it is nearly temperature-independent (low temperature region nearly up to 340 K) and varies linearly with the frequency can be explained on the basis of a quantum mechanical tunneling model (QMT) [29]. According to this model, conduction can be described by the equation

$$\sigma(\omega) = \pi/3e^2kT[N(E_F)]^2\alpha^{-5}\omega[\ln(\nu_{ph}/\omega)]^4. \quad (3)$$

From (3) the value of $N(E_F)$, i. e. the density of the energy states near the Fermi level, is evaluated, taking the value of α (electronic wave function decay constant) as 0.46 $Å^{-1}$ (obtained by plotting log σ_{ac} against R_i) and ν_{ph} the phonon frequency $\sim 5 \cdot 10^{12}$ Hz, is computed for a frequency of 10 kHz and presented in Table 1.

Among various mechanisms of conduction in the amorphous materials (such as band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in localized states near the Fermi level), the conduction in the localized states near the Fermi level occurs when the ac conductivity is nearly temperature-independent and varies linearly with the frequency. The conduction in PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glasses in the low temperature region (up to 340 K) can safely be supposed to take place by the mechanism. The value of $N(E_F)$ is found to increase up to 0.4 mol% and there after to decrease. Furthermore, the range of $N(E_F)$ values obtained is $\sim 10^{20}$ eV^{-1} cm^3; such values of $N(E_F)$ suggest the localized states near the Fermi level [29].

Our observations on the dielectric parameters of PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glasses, as mentioned earlier, indicate that the rate of increase of $\varepsilon' \tan\delta$ with the temperature decreases gradually with the increase in the concentration of Cr_2O_3 beyond 0.4 mol%. Though the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown raises the temperature of the glasses and hence raises the value of $\varepsilon' \tan\delta$. Since the rate of increase of $\varepsilon' \tan\delta$ with temperature is the lowest for the glasses G_{10}, the breakdown strength (which is inversely proportional to $\varepsilon' \tan\delta$) is the highest when compared with the other glasses.

5. Conclusions

The analysis of the results of dielectric properties and dielectric breakdown strength coupled with optical absorption spectral studies of PbO-Ga_2O_3-P_2O_5:Cr_2O_3 glasses revealed that the glass G_{10} possesses the highest electrical insulating strength among all the other samples investigated, owing to the presence of chromium ions largely in Cr^{6+} state that take part of network-forming positions with Cr_2O_3 structural units.

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