Transport Properties and Scaling Spectra of Lithium Gallium Titanate Phosphate Glass Ceramics Materials

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ABSTRACT

Lithium gallium phosphate glass samples were synthesized through melt quenching by varying lithium oxide, titanium oxide and gallium oxide concentrations. The de-polymarizability of glass ceramic samples was identified by Hurby's parameter (K_{gl}) with the data of DTA traces. Impedance measurements were made on all the glass ceramic samples at different temperatures. The bulk resistance (R) for all the samples relative to each experimental temperature is deduced from the intercept of imaginary Z'' impedance with real Z' impedance axes. The activation energy for conduction (E_{a}) is obtained from the temperature dependent of conductivity data, which is fitted to Arrhenius equation. The single super curve in the scaling spectra suggested the temperature independent conductivity phenomenon

Introduction

Interest on the phosphate based glasses was predominantly for high power laser applications, optical filters and also to store nuclear wastes. Pure phosphate glasses are highly hygroscopic and as a result very limited studies are conducted on them [1]. Gallium oxide (Ga_2O_3) is a wide band gap material with good chemical and thermal stability. When Ga_2O_3 is introduced in the lithium phosphate glass network, leads to enhance the range of applicability of these glasses for potential applications. Lithium titaanate phosphate glasses mixed with Ga_2O_3 content are quite stable and possess more open structure for ionic transport [2, 3]. Generally, Li^+ ions in these glasses sit in the vicinity of non-bridging oxygen sites. Non-random hopping of Li^+ ion between these sites under the influence of an external field leads to increase in the ionic conductivity. It is reported that the infrared transmission in the glasses decreases exceptionally along with crystallization and they may possibly be employed as optical memory devices, solid state batteries and electrochromic devices [4, 5]. Hence, it is worthwhile to point out crystallization of present glass samples at different temperatures above and below the crystallization temperature. Many recent devoted studies on the functionality of Ga_2O_3 in various glass matrices and its influence during crystallization at different temperatures are available in the literature [6].

Ga_2O_3 is considered to act as a network former, if Ga^{3+} ions take preferentially fourfold coordination in oxide glasses. However, in some of the glass networks, the gallium ions are also found to be in modifier positions with GaO_6 structural units [15].The excess negative charge on GaO_4 tetrahedran compensated either by localization of a modifier ion nearby or by generation of threefold oxygens. The GaO_4 tetrahedrons may enter the glass network and alternate with PO_4 tetrahedrons. In the present investigation, we report detailed studies of DTA and electrical properties as a function of frequency and temperature for the heat treated samples at different temperatures through impedance spectroscopy in view of the fact that this technique is a power full tool to probe in the glass and glass ceramics [7].

Experimental

Glass samples of compositions selected for the present investigation were synthesized by melt quenching technique, using the general formula $(30+x) Li_2O- (10-x) TiO_2-60P_2O_5$: xGa_2O_3 (x = 0,1,2, 3 and 4 mol%). Appropriate proportions of reagent grade chemicals of Li_2CO_3, Ga_2O_3, TiO_2 and P_2O_5 were thoroughly mixed in an agate mortar and melted in a platinum crucible at 800±10 °C for about 1 h until a bubble-free liquid was

formed. The resultant melt was then cast in a brass mould and subsequently annealed at 300 °C. Then resultant glasses were placed in a furnace at 500 °C for about 4 hours, the furnace was turned off and the glasses were allowed to cool in the furnace. Crystalline phases were checked by the X-ray diffraction method (XRD) at room temperature. The glass transition temperature (T_g) and crystallization temperature (T_c) were recorded simultaneously by using differential thermal analysis (DTA) at a heating rate of 20 K/min in the temperature range of 300–673 K using a-Al_2O_3 as a reference material by using DT-30 Schimadzu thermal analyzer. The accuracy in the measurement of T_g is ±2 K. The samples were then ground and optically polished. The final dimensions of the samples used for the electrical measurements were about 1 cm x 1cm x 0.2 cm. A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for electrical measurements. The real (Z') and imaginary (Z'') parts of the impedance of present glasses were obtained using a Solatron 1260 Impedance / Gain Phase analyzer controlled by personal computer in the frequency range of 10 Hz-10^6 Hz at room temperature and as well as temperatures from 303-523 K with a 10 K temperature step.

Results and discussion

Figure 1 shows the DTA thermograms of glass ceramic samples with various compositions. The homogeneity of the glasses is indicated by the single peak due to the glass transition temperature (T_g) in DTA pattern of all the glass samples prepared. The glass transition temperature (T_g) values are gradually decreases from the sample LGTP$_0$ (0 mol% of Ga_2O_3) to LGTP$_3$ (3 mol% of Ga_2O_3) with increase in the concentration of Li^+ ions. This can be recognized due to increasing de-polymerization of the glass ceramic network due to increase in the modifier concentration of Li^+ and Ga^{3+} ions to form a large number of non bridging oxygen sites. The decrease in the de-polymerization beyond 3 mol% of Ga_2O_3, in the present samples may be due to the effect of gallium ions that take part in the network forming positions in the glass network. The variation of glass forming ability parameter $K_{gl} = (T_c - T_g) / (T_m - T_c)$, with the concentration of Ga_2O_3 is plotted in the inset of Figure 1.
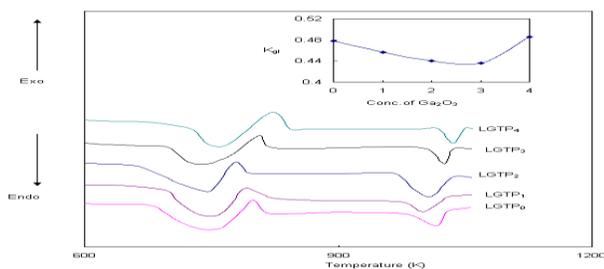

Figure 1. Shows the DTA thermograms of LGTP glass ceramic samples with various compositions

The increase in degree of disorder of the glass network can be understood with the decreasing trend in the value of K_{gl} from LGTP$_0$ to LGTP$_3$, however, from LGTP $_3$ to LGTP$_4$, K_{gl} is observed to increase. These consequences indicated that, for the lower concentrations of Ga_2O_3 (≤ 3 mol%), gallium ions may prefer to occupy network modifying positions and at the higher concentrations (≤ 4 mol%), the gallium ions mostly occupy network forming positions rather than modifying positions, enhance the mean bond strength and cross-link density. The

impedance data obtained in this analysis was fitted to nonlinear least–square method. Hence the electrical properties can be associated to a parallel resistance–capacitance (RC), equivalent circuit and therefore bulk response of the sample is detected. The complex impedance plots (Z'' vs. Z') of all the LGTP samples measured at 373 K is shown in Figure 2. The bulk resistance (R) for all the samples at each experimental temperature is deduced from the intercept of imaginary Z'' impedance with real Z' impedance axes. The resistance (R) obtained from the analyzed impedance data and pellet dimensions were used to calculate the bulk conductivity of all the samples at each experimental temperature. The bulk conductivity can be calculated at each experimental temperature by taking sample geometry into account as follows:

$$\sigma = (1/R) \times (t / A) \qquad (1)$$

where t/A is the sample geometric ratio, t is the sample thickness and A is the electrode area used to measure the properties of the sample. Using above equation, one can deduce that the highest conductivity is achieved by the LGTP$_3$ sample (inset of Figure 2, ▢▢▢▢▢▢▢▢▢x10^{-6} S/cm, at 373 K).
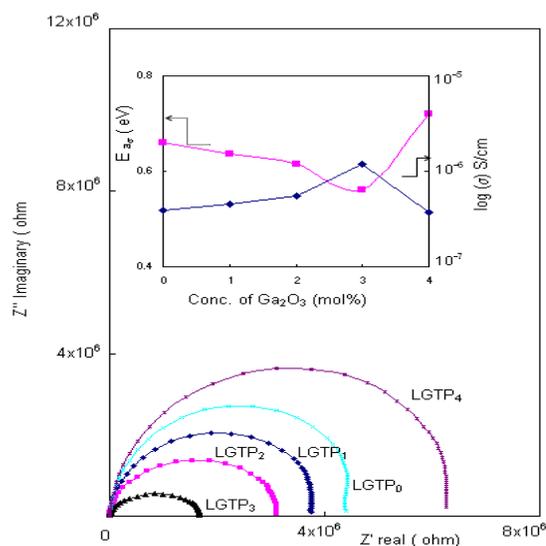

Figure 2. The complex impedance plots (Z'' vs. Z') of all the LGTP samples measured at 373 K.

In Figure 3, we show the characteristic complex impedance plots at different temperatures for the highest conducting sample LGTP$_3$, where it can be seen that increase in temperature caused the impedance semicircles to be shifted to lower and lower Z' values. Once again, one can use the intersection points of the imaginary impedance onto the real axis of semicircles to use equation (1) to calculate the bulk conductivity of LGTP$_3$ sample as a function of temperature. The bulk conductivities calculated from the analyzed impedance data obtained at different temperatures for all the glass samples are plotted in inset of Figure 3 (shown as log ▢T versus 1000/T).
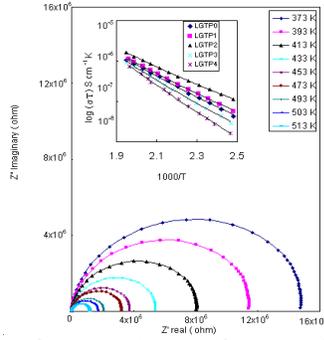
Figure 3. Characteristic complex impedance plots at different temperatures for the highest conducting sample LGTP₃. Inset shows log σT versus 1000/T for all the LGTP glass ceramic samples.

The conductivity data is fitted to the Arrhenius equation

$$\sigma_{dc} = \sigma_0 \exp(-E_{a\sigma}/kT) \qquad (2)$$

σ_0 is the pre exponential factor and $E_{a\sigma}$, k and T are the activation energy for the conduction, Boltzman's constant and absolute temperature respectively. The activation energy for conduction ($E_{a\sigma}$) was calculated from the slope of the straight lines obtained in the inset of Figure 3. The compositional dependence of activation energy ($E_{a\sigma}$) at 373 K is shown in the inset of Figure 2, where, it is observed that highest conducting sample (LGTP₃) exhibits the lowest the activation energy. Since the inset of Figure 2 (activation energy ($E_{a\sigma}$), vs conc. of Ga_2O_3) does not show the non linear behavior of conductivity; the non linearity between the conductivity and the activation energy suggests that the conductivity enhancement is directly related to the increasing mobility of Li^+ ions and Ga^{3+} ions, which act as network modifiers [9]. The gallium ions can be considered as immobile within the time window of hopping processes of the alkali (Li^+) ions, the contribution to the conduction for the glasses investigated in this paper can be attributed mainly due to motion of Li^+ ions [10]. This is further affected by the presence of the gallium ions as will be described next. As the Raman spectra of our glass samples revealed the presence of Li_2O in the glass network results in the formation of large number of non bridging sites, where the Li^+ ions are weakly bonded to non bridging sites. As it appears, due to the increasing modifying action of the Li^+ ions and Ga^{3+} ions (from LGTP₀ to LGTP₃), easy paths for the movement of the charge carriers are created and hence increase in the conductivity is observed. However, from LGTP₃ to LGTP₄, the conductivity is found to decreases with increase in activation energy as a result of large repulsion between the same Li^+ ions and replacement of network forming Ti^{4+} ions by network modifying Ga^{3+} ions [9]. Hence, the variation of conductivity with concentration of lithium and gallium ions depends heavily on the structural modifications of the glass system [9].

In order to evaluate conductivity non-linearities, it is useful to present the ac conductivity for all the glass ceramic samples. The dependence of the electrical conductivity with the frequency can be analyzed by the power law equation:

$$\sigma(0)=K\ f_o, \qquad (4)$$

where $\sigma(0)$ is the conductivity at zero frequency, which is normally termed the dc conductivity, A is a constant and s is a characteristic parameter ($0 < s < 1$). The low frequency part of the conductivity is normally frequency independent and the frequency independent conductivity$\sigma\ (\sigma(0))$ is obtained by extrapolation of the conductivity to $\omega = 0$. The high frequency part of the conductivity exhibits the dispersion and increases in a power-law fashion [11]. Typical plots of ac conductivity as a function of frequency at 373 K for all the samples are presented in Figure 4. Similarly the ac conductivities for the highest conducting glass sample LGTP₃ at different temperatures are shown in Figure 5. The values of $\sigma(0)$ or σ_{dc} obtained for all the samples at 373 K (from Figure 2) are listed in Table 1. From Figure 4, it can be seen that the critical frequency ($\omega_p = f_o$), at which the conductivity deviates from the frequency independent part and change with the concentration of Ga_2O_3. The change in the critical frequency is a more obvious for the ac conductivity of LGTP₃ at different temperatures presented in Figure 5. Nevertheless, the relation between frequency independent conductivity $\sigma(0)$ and the critical frequency (f_o) can be represented by the following equation:

$$\sigma_{(ac)} = \sigma(0) + A\ \omega^s \qquad (3)$$

Where $K = (Ne^2a^2/kT)\sigma c(1-c)$, is the empirical constant, where σ is the geometrical factor which include correlated factor, c is the concentration of mobile ions on N equivalent lattices per unit volume, a is the hopping distance, e is the electronic charge, T is absolute temperature and k is Boltzman's constant, which depends on the concentration of mobile ions, temperature and the conduction mechanism [12].

It has been observed that, the relaxation effects begin to appear at the critical frequency (f_o) and moves towards the higher frequency within the wider experimental frequency range. Further, it is observed that the critical frequency (f_o) is thermally activated with same activation energy as σ_0T [13]. The characteristic parameter(s) has been observed to be material dependent and calculated from the equation (3). The composition dependence of characteristic parameter (s) is shown in the inset of Figure 4 and it is observed that the 's' is found to be lowest for highest conducting LGTP₃ glass sample. The minimum value of 's' is found to be related to the high degree of modification and is found to be dependent on the concentrations of Li^+ ions and network modifying Ga^{3+} ions. When the concentration of Ga_2O_3 is beyond 3 mol%, gallium ions occupy the network forming sites in the sample network, as a result the 's' value increases from LGTP₃ to LGTP₄. The frequency independent part of the conductivity may be attributed due to the long-range transport of Li^+ ions and network modifying Ga^{3+} ions. The frequency dependent part of the conductivity could be explained through diffusion controlled relaxation model [14]. The summary of a.c conductivity, activation energy, and characteristic parameter at 373 K for all the glass ceramic samples is listed in the Table 1.
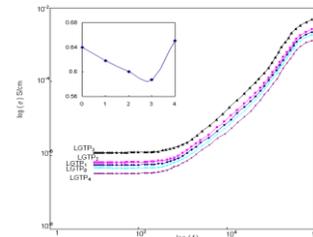

Figure 4. Typical plots of ac conductivity as a function of frequency at 373 K for all the LGTP samples.

Scaling analysis is a characteristic element for any data evolution program. Inset of Figure 5 is presented to demonstrate that the mechanism of ion transport in the glass ceramic system is unaffected by composition and temperature. In this Figure, the ac conductivity data obtained at various temperatures for $LGTP_3$ is scaled with the frequency independent conductivity σ_{dc} along y axis (log σ/σ_{dc}) and on x axis, frequency scaled with characteristic frequency (f_0) log (f/f_0) [13, 14]. From inset of Figure 5, it is observed that all the curves observed at different temperatures collapse in to single super curve; this single super curve suggests that the present glass samples show confirmation of the temperature independent conduction transport mechanism.
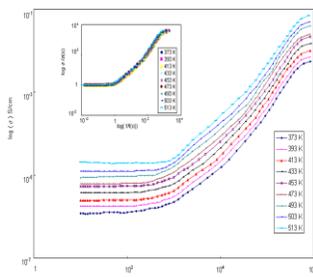

Figure 5. Ac conductivities for the highest conducting glass sample $LGTP_3$

Glass	σ (373 K)S/cm	E_a (eV)	s (403 K)	$E_{a\sigma}$ (e V)	τ_0 (sec)	$E_{a\tau}$ (K)
$LGTP_0$	3.91E-07	0.663	0.643	0.678	0.581	0.456
$LGTP_1$	4.56E-07	0.637	0.618	0.645	0.553	0.689
$LGTP_2$	5.51E-07	0.646	0.602	0.652	0.517	0.965
$LGTP_3$	1.20E-08	0.588	0.587	0.694	0.508	1.239
$LGTP_4$	3.72E-02	0.670	0.651	0.683	0.596	0.449

at different temperatures

Conclusion

The lowest values of Hurby's parameter (K_{gl}) and the glass transition temperature (T_g) for the highest conducting sample $LGTP_3$ in the differential thermal analysis indicates highest de-polymerizability.The conductivity enhancement from $LGTP_0$ to $LGTP_3$ is directly related to mobile Li^+ ions and network modifying Ga^{3+} ions. The decrease in the conductivity from $LGTP_3$ to $LGTP_4$ is directly related to the replacement of network modifying Ga^{3+} ions by network forming Ti^{4+} ions.The bulk conductivity of highest conducting sample $LGTP_3$ was determined as 1.202x 10^{-06} S/cm at 373 K.AC Conductivity data is fitted to a power law equation.The activation energy for conduction (E_a = 0.558 eV) and power exponent (s = 0.587) are low for the highly conducting glass sample $LGTP_3$. The single super curve in scaling spectra of both ac conductivity in the scaling analysis suggests that the present glass samples follow temperature independent conductivity distribution relaxation mechanism.

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