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Thermal stability and crystallization kinetics in superionic glasses using electrical conductivity–temperature cycles

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Abstract The present work demonstrates application of electrical conductivity (σ)–temperature (T) cycles to investigate thermal properties viz., crystallization and glass transition kinetics in $AgI–Ag_2O–V_2O_5–MoO_3$ superionic glasses. The σ–T cycles are carefully performed at various heating rates, viz., 0.5, 1, 3, 5, and 7 K/min. The conductivity in Ag^+ ion conducting glasses exhibit anomalous deviation from Arrhenius behavior near glass transition temperature (T_g) followed by a drastic fall at crystallization (T_c). The temperature corresponding to maximum rate of crystallization (T_p) is obtained from the derivative of σ–$1/T$ plots. With increasing heating rates, the characteristic temperatures (T_g, T_p) are found to be shifting monotonically toward higher temperatures. Thus, activation energy of structural relaxation E_s, crystallization E_c and other thermal stability parameters have been obtained from σ–T cycles using Kissinger equation and Moynihan formulation. For a comparative study, these kinetics parameters have also been calculated from differential scanning calorimetry plots. The parameters obtained from both the methods are found to be comparable within experimental error.

Keywords Superionic glasses · Thermal stability · Crystallization kinetics · Electrical conductivity

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Introduction

Superionic glasses exhibit high-ionic conductivity of $\sim 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 300 K [1–5] and thus have applications in low power ionic devices, viz., button type cells, etc. Nevertheless prior to any possible application, a critical examination of their thermal stability against the crystallization is very essential. Therefore, there have been considerable attempts to investigate the thermal stability of glassy superionic/amorphous conductors in the last few years. In a series of investigations by Dalvi et al. [6–8], Ag^+ ion conductivity of mechanochemically synthesized samples, viz. $AgI–Ag_2O–M_xO_y$ ($M_xO_y = V_2O_5$, MoO_3, CrO_3) has been thoroughly studied using crystallization kinetics by differential scanning calorimetry (DSC). Recently, $AgI–Ag_2O–P_2O_5$ glassy system [9] and Na^+ ion conducting phosphate glass [10] have also been investigated using crystallization kinetics. Investigation of thermal properties using DSC technique has been useful to understand structural properties as well. For example, amorphous AgI aggregation model has been validated by Hanaya et al. using calorimetric studies [11]. Very recently, thermal stability and crystallization kinetics parameters have been obtained in Li^+ ion conducting glasses $Li_2O–SiO_2–TiO_2$ by Moricová et al. [12].

In a broad prospective, based on DSC investigations, there are several parameters given by various researchers to scrutinize the thermal stability of glasses. For example, temperature corresponding to maximum rate of crystallization T_p, melting temperature T_m, glass forming tendency ($T_c - T_g$), T_{rg}, k_{gl}, activation energies for structural relaxation E_s and crystallization E_c, are mainly used for various glassy systems [13–17]. Recently, it is shown by Aly et al. that MoO_3 addition in $PbO–Sb_2O_3–As_2O_3$ glasses significantly affects the thermal stability parameters [18].

In the field of solid-state ionics, it is demonstrated by Adams et al. that σ–T cycles measured at a typical heating rate do infer interesting thermal events (e.g., T_g, T_c). Through these systematic σ–T cycles and high-temperature X-ray diffraction (XRD) studies, they attributed the anomalous rise in conductivity above T_g in the AgI–Ag_2O–V_2O_5 [19] system to glass–crystallite interface effect. In our recent work, we have shown by DSC and σ–T cycles obtained at a typical heating rate of 1 K/min that amount of AgI in AgI–Ag_2O–V_2O_5 glass matrix affects the E_c and E_s values significantly [20].

In the present work, we have discussed a new and extremely sensitive method, viz. electrical conductivity versus temperature cycles at various controlled heating rates, to measure the crystallization and glass transition kinetics in Ag^+ ion conducting superionic glasses. The results are compared with those of the parameters obtained from DSC.

Experimental

For the present investigation, the compositions 50AgI–33.33Ag_2O–16.67[$(V_2O_5)_{1-x}$–$(MoO_3)_x$] for $x = 0.1$, 0.2, and 0.3 have been chosen and abbreviated as 10, 20, and 30 SISOVOMO, respectively. Using the high purity raw materials AgI, Ag_2O, V_2O_5, and MoO_3, the samples were prepared by the conventional melt-quenching. All the compositions are chosen well within glass forming region. The glassy nature was confirmed by XRD (RIGAKU X-ray diffractometer) and DSC (Shimadzu, DSC-60). The DSC scans were also performed at various heating rates to study the kinetics of crystallization and glass transition. The electrical conductivity–temperature cycles (298–443 K) were carried out at various well controlled heating rates viz., 0.5, 1, 3, 5, and 7 K/min using computer controlled HIOKI LCR meter model 3532-50 at 1 kHz. A programmable PID temperature controller (Libratherm instruments PRC 309) has been used to control the heating rate.

Results and discussion

Differential scanning calorimetry

The structural and enthalpy relaxation at the glass transition temperature (T_g) is given by Moynihan et al. [16]:

$$\frac{\mathrm{d}\ln q}{\mathrm{d}\left(1/T_g\right)} = -\frac{E_s}{R}, \tag{1}$$

where q is the heating rate, R the gas constant and E_s the activation energy for structural relaxation involved in the motion of structural units at T_g.

Similarly, crystallization process in the sample can be inferred from Kissinger equation [17]:

$$\ln\left(\frac{q}{T_p^2}\right) = -\frac{E_c}{RT_p} + C, \tag{2}$$

where T_p is the peak temperature and E_c the activation energy of crystallization associated with the growth and nucleation.

In order to examine the thermal stability, two important criteria have been used in the present investigation. Considering the role of melting temperature (T_m) in the thermal stability of glasses, Kauzmann established an empirical relationship [14],

$$T_{rg} = \frac{T_g}{T_m}, \tag{3}$$

where T_{rg} is Kauzmann temperature. Second important criterion for this is given by Hruby [15],

$$k_{gl} = \frac{T_c - T_g}{T_l - T_c}, \tag{4}$$

where T_l is temperature corresponding to completion of melting. Higher the values of T_{rg} and k_{gl}, slower will be the process of crystallization.

At first, the glassy nature for all the chosen samples (10, 20, and 30 SISOVOMO) is confirmed by XRD and only pristine as-prepared glassy samples are used for the investigation. DSC patterns for samples at a heating rate of 10 K/min are shown in Fig. 1. For all these samples, there appears an endothermic smooth dip in the 333–348 K range that corresponds to glass transition temperature (T_g). On further heating, all the samples exhibit a single exothermic crystallization peak near $\sim$383 K, hence are confirmed to be glassy in nature. For the crystallization and glass transition kinetics studies, DSC scans at various heating rates, viz., 5, 10, 15, and 20 K/min were also obtained. Such scans, for one of the samples, viz. 20 SISOVOMO are shown in Fig. 2. First, at lowest rate 5 K/min, the T_g and T_c are visible but appear more prominently for higher heating rates. Second, T_p and T_g appear to shift monotonically toward higher temperatures. Using the T_g and T_p obtained at various heating rates, following Eqs. 1 and 2, the ln q vs. $1/T_g$ and ln (q/T_p^2) vs. $1/T_p$ plots are found to be linear with slope giving the E_s and E_c, respectively. The E_c, E_s, T_{rg}, and k_{gl} are thus calculated for all the samples and shown in Table 1. These parameters are further obtained from σ–T plots.

Electrical conductivity

Figure 3 shows electrical conductivity versus temperature plot at a typical heating rate of 1 K/min for 10, 20, and 30 SISOVOMO glassy samples. For all these samples, apparently the conductivity increases Arrheniusly till

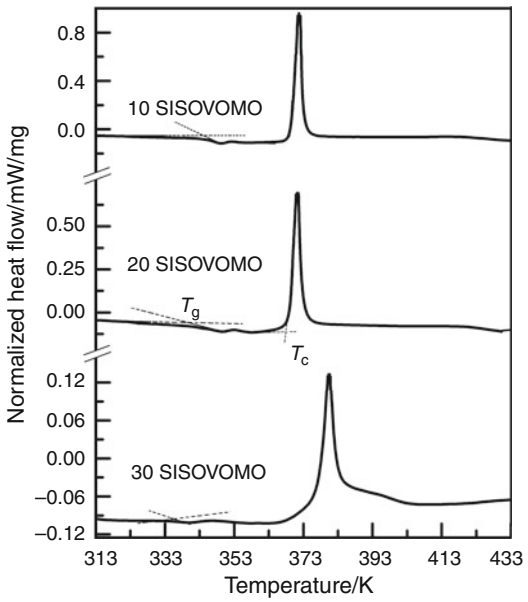

Fig. 1 DSC scans at a heating rate of 10 K/min for the glassy system 50AgI–33.33Ag_2O–16.67 $[(V_2O_5)_{1-x}$–$(MoO_3)_x]$ ($x = 0.1$–0.3)

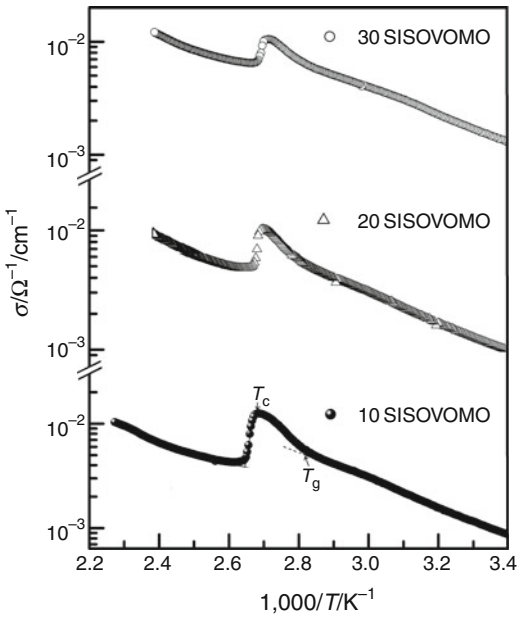

Fig. 3 Electrical conductivity versus inverse of temperature for various compositions at a heating rate of 1 K/min

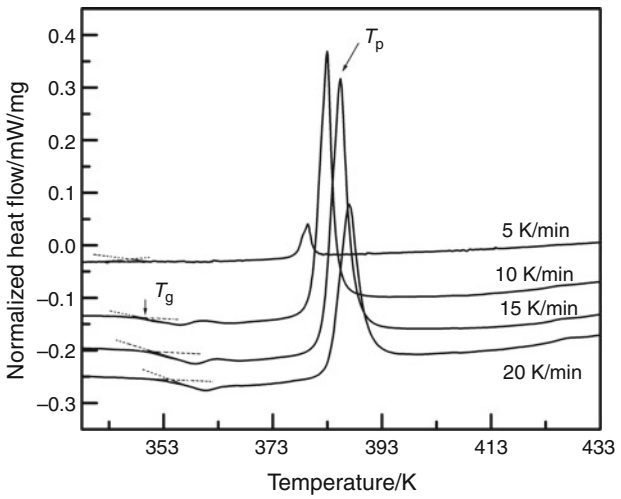

Fig. 2 DSC scans at various heating rates for 20 SISOVOMO sample

~343 K. Above this, the conductivity shows anomalous rise deviating from Arrhenius behavior. The σ–T cycles for all the samples are reproducible within this temperature range ($T \leq T_g$). Interestingly, as evident, such a notable deviation in the conductivity at T_g is seen for each of the sample. The conductivity rise at T_g may be expressed by free volume approach proposed by Souquet [21]. The glassy state exists below the glass transition temperatures and the system remains in a "frozen" state. Thus, at $T \leq T_g$, the system is highly viscous. For $T_g \leq T \leq T_c$, the viscosity decreases due to which the increase in the free volume, providing pathways for ions, eventually increases the ionic conductivity. Thus, a sudden and significant deviation in conductivity from Arrhenius behavior may be attributed to the presence of T_g. On further heating, the conductivity approaches a maximum and falls drastically. Such a notable fall in the conductivity is due to crystallization occurring in the samples, as also seen in various investigations [19, 20, 22].

The T_g and T_c, as indicated in Fig. 3a for 10 SISOVOMO sample, could be likewise obtained for all the samples under present investigation (Fig. 3b, c) and given in Table 1. The T_g and T_c obtained by DSC as well as σ–T cycles appear to exhibit similar trends and decrease with MoO_3 content. Moreover, the two parameters T_{rg} and k_{gl}

Table 1 Different thermal parameters obtained from differential scanning calorimetry and conductivity–temperature cycles with MoO_3 content

x	T_g/K		T_c/K		E_s/kJ/mol		E_c/kJ/mol		T_{rg}		k_{gl}	
	σ–T cycles	DSC	σ–T cycles	DSC	σ–T cycles	DSC	σ–T cycles	DSC	σ–T cycles	DSC	σ–T cycles	DSC
0.1	355	351	391	380	160 ± 15	140 ± 15	235 ± 25	210 ± 20	0.37	0.35	0.27	0.28
0.2	353	359	381	378	130 ± 13	118 ± 12	280 ± 30	250 ± 25	0.36	0.34	0.26	0.27
0.3	350	335	378	373	200 ± 20	170 ± 17	135 ± 15	110 ± 10	0.36	0.33	0.25	0.25

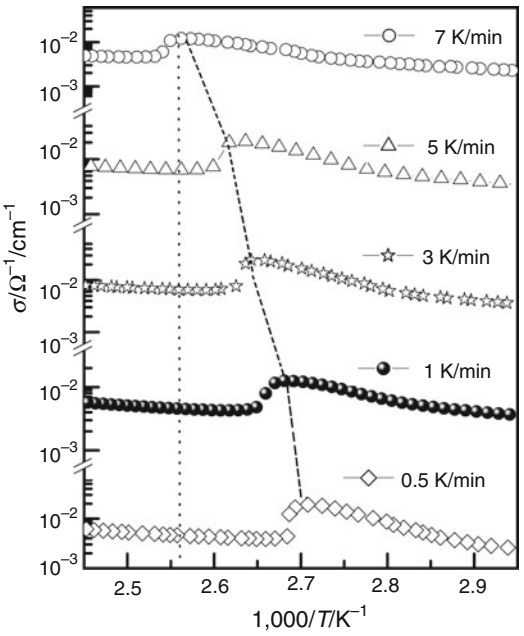

Fig. 4 Electrical conductivity versus inverse of temperature at various heating rates 0.5, 1, 3, 5, and 7 K/min for 20 SISOVOMO. The *dotted line* joins conductivity peak positions that shift toward higher temperatures

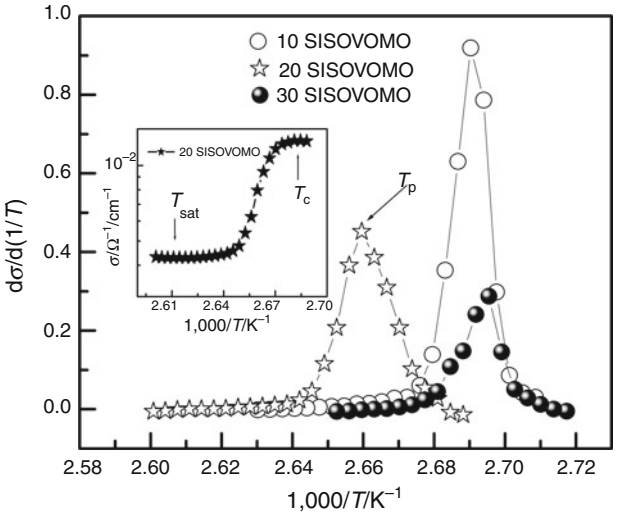

Fig. 5 Derivative of σ–$1/T$ cycles for the determination of the peak temperature (T_p). *Inset*: electrical conductivity vs. inverse temperature on an extended scale in the range $T_{sat} \geq T \geq T_c$

obtained from both the methods are (i) comparable and (ii) do not show any appreciable change with MoO_3 addition into the glass matrix.

For the kinetics of crystallization and glass transition, electrical conductivity versus temperature cycles obtained at various heating rates are shown in Fig. 4. Interestingly, observed T_g and T_c in the σ–T plots do shift monotonically toward higher temperatures with increasing ramps. It is important to note that generally it is not possible to see the glass transition very apparently for lower rates in the DSC scans (Fig. 1). Whereas, the thermal events are very much apparent in σ–T cycles even for rates as low as 0.5 K/min.

Examining the behavior of σ–T cycles between two important temperatures T_c and T_{sat}, the T_p values are obtained for crystallization kinetics studies. Here, T_{sat} is defined as temperature where the conductivity saturates instantly after a drastic fall at T_c. The σ vs. $1/T$ plot between these two temperatures is shown for one of the sample 20 SISOVOMO in the inset of Fig. 5. Further, derivative of conductivity shows a maximum and its corresponding temperature is taken as T_p. Figure 5 shows the differential conductivity as a function of inverse of temperature for all the three samples for a typical rate of 1 K/min. Similarly, T_p values for each sample at various other rates are also calculated. Using T_p and T_g values obtained from σ–T plots, the ln q vs. $1/T_g$ and ln (q/T_p^2) vs. inverse of T_p are plotted in Fig. 6. Interestingly, both the plots are apparently linear. From the slope, using the Eqs. 1 and 2, the E_s and E_c are calculated. All these values thus obtained from σ–T cycles and DSC scans are presented in Table 1. Interestingly, these values obtained from σ–T cycles are in good agreement with those of determined from DSC.

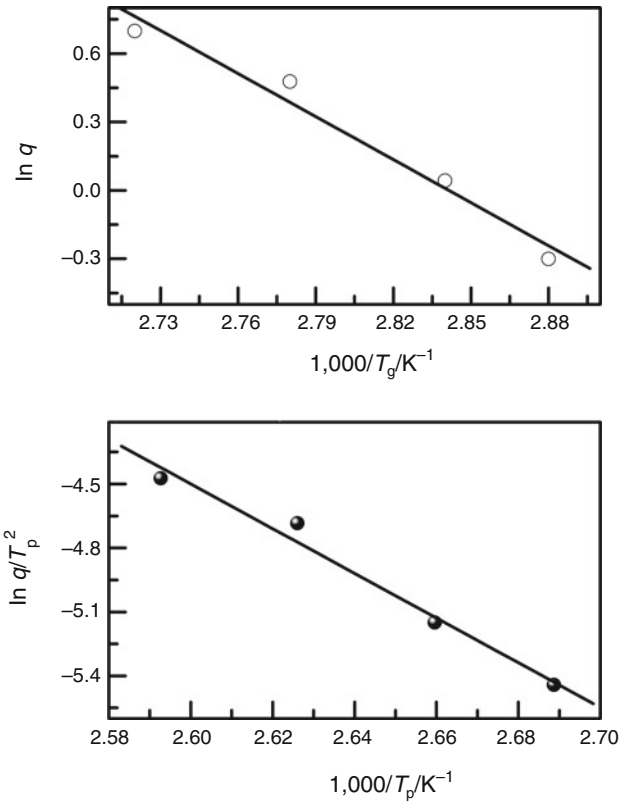

Fig. 6 Moynihan (**a**) and Kissinger (**b**) plots for 20 SISOVOMO obtained from σ–T cycles

Conclusions

The thermal stability parameters obtained for these superionic glasses from σ–T cycles are in good agreement with those of determined from DSC scans. The E_s and E_c values obtained from both methods are comparable within experimental error.

Thus, our results strongly suggest that electrical conductivity versus temperature cycles at various controlled heating rates can be successfully used to examine the thermal behavior and stability of the superionic glasses. In addition, for these Ag^+ ion conducting superionic glasses, σ–T cycles at controlled heating rates are found to be more sensitive than DSC scans and especially useful for samples (i) which show single crystallization and (ii) for which $T_c - T_g$ is high. Finally, as a future prospective, such σ–T cycles may be extremely useful in thermal characterization of ion conducting glassy/amorphous thin films and multilayers.

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