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Thermal analysis of $\text{Li}_2\text{O}-\text{TeO}_2$ glass

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Abstract

The thermal properties of $0.30\text{Li}_2\text{O}-0.70\text{TeO}_2$ glass are studied. Specific heat, C_p , is measured in the $170^\circ\text{C} < T < 270^\circ\text{C}$ interval. The Einstein temperature, $\theta_A = 840$ K, is determined from the temperature course of C_p . In the glass transition interval, the heat capacity undergoes an S-shaped transition from the value, C_{gl} , of the glass to that of undercooled melt, C_p . It is found that $C_{gl}/C_p \approx 0.62$. The activation energy, $E(T_f)$, for structural relaxation depends on a fictive temperature, T_f . For the glass under study, it is demonstrated that: $E(T_f) = 655 + 300(\frac{520}{T_f} - 1)$ kJ/mol. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

According to Vogel [1], the coordination of the Te^{4+} ion in the crystalline forms of TeO_2 is usually 4 (in a trigonal bipyramid). Together with network modifying oxides, the $[\text{TeO}_4]$ polyhedra form chain structures that have a strong tendency for glass formation. The structure of tellurite glasses derives from the para-tellurite structure in which Te^{4+} ion is four-coordinated and the $[\text{TeO}_4]$ polyhedra are exclusively connected at the corners [1]. Within the framework of the rigidity concept, tellurite glasses are analogous to silicates, but have two additional, somewhat weaker non-covalent bonds. That is one of the reasons why the thermal properties, relaxation and crystallization behavior of TeO_2 based glasses are relevant and why it is important to compare them to those of silicates.

The glass transition and associated anomaly of relaxation behavior are the subject of many theoretical and experimental investigations. The thermodynamic indication of the transition is the drop, upon cooling, of the measured specific heat from that of the liquid C_l to the heat capacity, C_{gl} , of the glass. The transition also has a strong dynamic signature. The measuring time, thus, plays an important role. It can be observed that the transition region shifts to higher temperatures if the measuring time is reduced (or, conversely, if the applied temperature rate is increased). When a melt is cooled through the glass transition region, there is a sharp increase in the relaxation time. For a given cooling rate, $q^- = -dT/dt$, a given structure is fixed. To define a parameter that would account quantitatively for structural changes, Tool and Eichlin [2] introduced the so-called 'fictive' temperature, T_f – this is the temperature at which the system with the present fixed structure will be in equilibrium. The system tends to relax when T_f deviates from the actual temperature, T . The well-known equation of Ritland–Bartenev

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[3–5] relates the frozen fictive temperature to the cooling rate as

$$\ln q^- = \text{Const}_1 \frac{E}{RT_f(q^-)}, \quad (1)$$

where R is the ideal gas constant and E is the activation energy of the relaxation process. It can be seen that $T_f(q^-)$ is the limit temperature at which the system is still in equilibrium. On the other hand, if a glass with a given $T_f(q^-)$ is reheated at a $q^+ = dT/dt$ rate, then the structure begins to change measurably towards equilibrium at a T_0 onset. The equation of Bartenev et al. [3,4,6] gives

$$\ln q = \text{Const}_2 \frac{E}{RT_0}. \quad (2)$$

2. Experimental

2.1. Glass preparation

The $0.30\text{Li}_2\text{O} \cdot 0.70\text{TeO}_2$ glass was prepared using LiCO_3 and TeO_2 (Merck) as starting reagents. To avoid loss of TeO_2 through volatilization, the melting temperature did not exceed 800°C . At this temperature, the liquid already presents a very low viscosity that requires only 11–15 min for homogenization. The liquid is then poured onto a polished metal plate and immediately squeezed with an upper metal plate to avoid rapid crystallization of the glass. One to two mm thick glass samples were obtained in this way.

2.2. Differential scanning calorimetry

Thermal analysis and, particularly, differential scanning calorimetry, DSC, are two of the most useful tools to investigate relaxation and crystallization phenomena in glasses. The DSC instrument used in this study was calibrated by melting pure In, Sn and Pb. The experiments were performed in an open atmosphere, and the instrument was sapphire calibrated for heat capacity measurements.

3. Results

Fig. 1 shows a thermogram of a glass heated at 10 K/min and then cooled at the same rate. The glass transition region, crystallization region and first melting peak are indicated in the figure. Crystallization, as one can see, consists of three stages. The crystallization enthalpy of the first peak is $\Delta H_1 = 330 \pm 10$ J/g, while that of the second one is $\Delta H_2 = 110 \pm 10$ J/g. The melting enthalpy is $\Delta H_m = 400$ J/g. The melting point of the second crystalline phase is too high to be reached without causing decomposition of the sample. Cooling leads to a sharp crystallization peak. A remarkable result is that crystallization begins exactly at the melting point, with no undercooling, and the crystallization enthalpy is equal to the melting enthalpy (see Fig. 1). The reason for this phenomenon is that the remaining crystalline phase serves as solid nucleus. It is important to note that the melting peak is much broader than the crystallization one (onset point (435°C) of crystallization appears at the maximum of the melting peak, much higher than the onset point (423°C) of melting). This means that a large number of minute defective crystals with lower T_m were formed during the first crystallization.

4. Discussion

The samples were cycled repeatedly between 443 and 543 K to investigate the influence of the cooling rate, q^- , on the ‘fictive’ $T_f(q^-)$ and that of the heating rate, q^+ , on the onset temperature, T_g . The absolute value of the heat capacity is obtained by the ‘three runs’ method, according to which a run with empty pans is compared to similar runs, one with pans with sapphires and one with the sample. Fig. 2 shows the heat capacity measured after different cooling rates. Because the fictive temperature depends on the previous cooling rate, different ‘noses’ are obtained in the glass transition region. One advantage of the cycling method is that the sample is never heated to the crystallization temperature so that even very low cooling rates can be applied without provoking crystallization. The heat capacity in the glassy region can

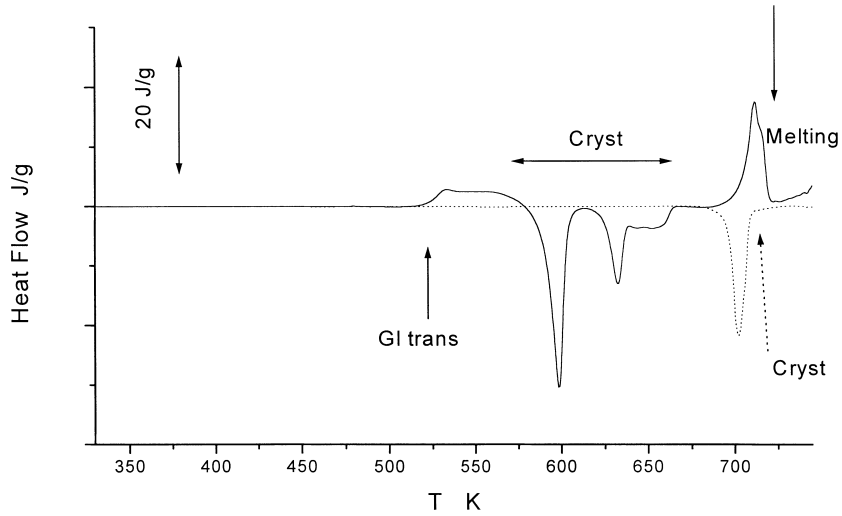


Fig. 1. Heat flow at heating with 10 K/min (solid line) and subsequent cooling with 10 K/min (broken line). The lines are shifted so that the heat flow under the glass transition region is zeroed.

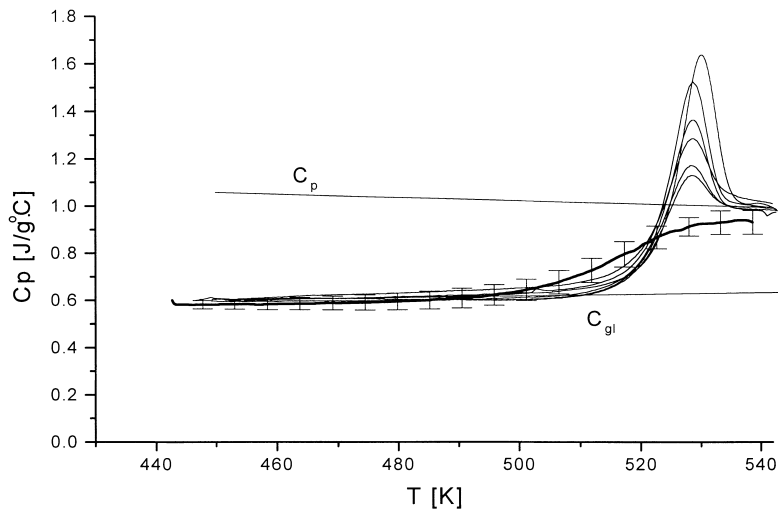


Fig. 2. Heat capacity data. Samples were cooled from 543 K at rates varying from 0.5 to 20 K/min; data were obtained during the subsequent heating at the same rate. Error bars include the average heat capacity measured upon cooling at 10 K/min. It can be seen that the instrument measures more accurately at heating.

be described by the Einstein function $\Psi(\theta_A/T)$ and the relation

$$C_p = 3Rn \Psi\left(\frac{\theta_A}{T}\right) \quad (3)$$

with the following parametrical values: $\theta_A = 840 \pm 30$ K, and $n = 6$ is the number of

independently vibrating atoms in $\text{Li}_2\text{O TeO}_2$. The solid line in Fig. 2 marked C_{gl} is drawn according to Eq. (3). It should be noted that the temperature interval is insufficient for a high accuracy measurement of Einstein temperature.

The fictive temperature was obtained at each run, as shown in Fig. 3. This figure shows the

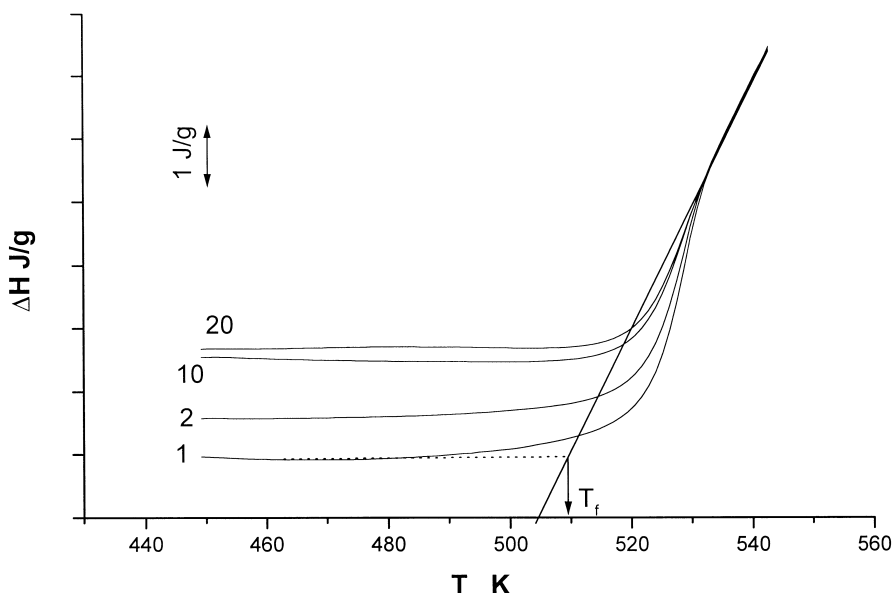


Fig. 3. The excess enthalpy ΔH . Determination of fictive temperature is readily seen. The previous cooling rate is given as a parameter at each curve.

excess enthalpy change of samples that were previously cooled at rates given as the parameter for each curve. It can be seen that, depending on the cooling rate, different enthalpies are frozen. Thus, the enthalpy frozen at a 20 K/min cooling rate is about 3.6 J/g higher than the one fixed at a 1 K/min cooling rate. The dependence of fictive temperatures is plotted in Fig. 4, in Arrhenius coordinates.

Another set of sample runs was cooled at a $q^- = 10$ K/min rate and then reheated at different heating rates. The onset temperature, T_g (i.e., the temperature at which the frozen system starts to relax at a rate comparable to the observation time), is also plotted in Fig. 4.

Earlier [7–9] we demonstrated that, in Arrhenius coordinates, the relations between $\ln q^-$ and the reciprocal of the ‘fictive’ temperature, as well as between $\ln q^+$ and the reciprocal of the onset temperature, T_g , look very much like straight lines. However, the difference in the two slopes is a strong indication that the activation energy depends on a fictive temperature. Indeed, the slope, L_f , of the $\ln q^-$ against the $1/T_f$ line (see Eq. (1)) is

$$-L_f = \frac{E(T_f)}{R} + \frac{1}{RT_f} \frac{\partial}{\partial (1/T_f)} E(T_f). \quad (4)$$

On the other hand, when a glass is reheated below the onset temperature, the system is frozen; therefore, T_f is fixed and the activation energy is constant. For this reason, the slope, L_0 , is given by

$$-L_0 = \frac{E(T_f)}{R}. \quad (5)$$

The relaxation of glass is generally investigated in a relatively narrow region so that experimental curves look very much like straight lines. That is why so many authors (see [10,11]) assume that the activation energy is constant. However, there are very strong indications that this is not so. It is often found that the activation energy for relaxation is almost equal to the activation energy for shear viscosity; the latter, however, is studied in a wide temperature interval and it is well known that it is quite sensitive to temperature. The two-slope method discussed here is an additional argument supporting the assertion that activation energy is sensitive to T_f . If one expresses $E(T_f)$ in a Taylor’s series in the vicinity of a given temperature T_g ,

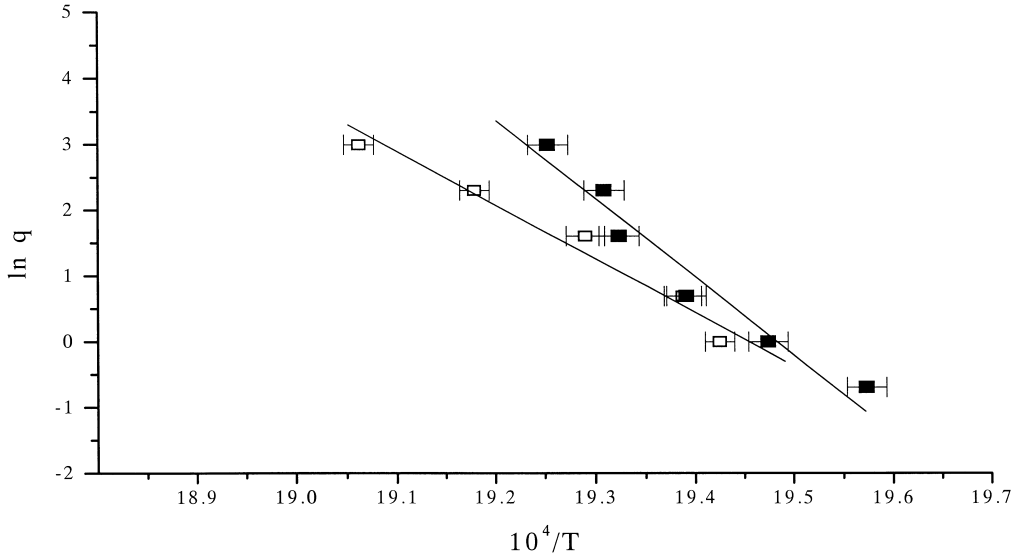


Fig. 4. Scanning rate as a function of reciprocal temperature. ■ – $\ln q^-$ against $10^4/T_f$; □ – $\ln q^+$ against $10^4/T_g$.

(here it is convenient to do it around the glass transition temperature) in linear approximation, the result is:

$$E(T_f) = E(T_g) + R\Delta \left(\frac{T_g}{T} - 1 \right), \quad (6)$$

where $\Delta L = -(L_f - L_0)$. For the parameters in Eq. (6), the following values were found: $E(T_g) = 655 \pm 55$ kJ/mol; and at $T_g \approx 520$, $E(T_f = 520) = 985 \pm 120$ kJ/mol so that $R\Delta L = 300 \pm 175$ kJ/mol. Thus, the temperature dependence of the activation energy becomes

$$E(T_f) = 655 + 300 \left(\frac{520}{T_f} - 1 \right) \text{ kJ/mol.}$$

It should be noted that the present method cannot give accuracy better than 10% for each slope. The configurational contribution to the activation energy $R\Delta L$ is the difference of the two slopes and the error increases. So far, this is the only method to determine $R\Delta L$, so it has to be used. The other possibility is to broaden the interval of cooling rates. This cannot be done in one instrument for thermal analysis. Moreover, a number of uncertainties appears when extreme cooling rates are used. In addition, each instrument has a particular

absolute error that again will reduce the accuracy of the combined master curve. Improvement of the accuracy of determination of $R\Delta L$ is a tempting problem for the future.

Earlier [7,8,12] we demonstrated that the ratio $x = (L_0/L_f)$ is about C_{gl}/C_p . In the present case, $x = 0.69$ is in good agreement with $C_{gl}/C_p \approx 0.62$. It would be interesting to investigate the ratio $x = L_g/L_f$ at $T_g = T_f$ for different substances, since that would give one an idea of how large the activation energy is for structural relaxation compared to the rate at which it changes [9,12,13]. The result presented herein is in agreement with experimental evidence: $x = 0.6$ for NaPO_3 and for LiPO_3 [7,8]; $x = 0.41$ for poly(vinyl acetate) [14]. We have also recently found $x = 0.27$ for PMMA.

5. Conclusions

The specific heat of $0.30\text{Li}_2\text{O} \cdot 0.70\text{TeO}_2$ glass can be described by the Einstein formula $C_p = 3Rn\Psi(\theta_A/T)$ with $n = 6$ and $\theta_A = 840$ K. It is demonstrated that the activation energy for structural relaxation depends on temperature. We find that it can be expressed according to the formulae: $E(T_f) = 655 + 300((520/T_f) - 1)$ kJ/mol.

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