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Calorimetric studies on $2TeO_2$–V_2O_5 glasses

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Abstract Glasses of the composition $2TeO_2$–V_2O_5 were fabricated via the conventional melt-quenching technique. The amorphous and the glassy nature of the as-quenched samples were confirmed by X-ray powder diffraction (XRD) and differential scanning calorimetry (DSC), respectively. The glass transition and crystallization parameters were evaluated under non-isothermal conditions using DSC. X-ray diffraction studies confirmed the presence of partially oriented crystallites in the heat-treated glasses. Kauzmann temperature (lower bound for the kinetically observed glass transition) was deduced from the heating rate dependent glass transition and crystallization temperatures.

Keywords Tellurium vanadate · SAW devices · Crystallization kinetics · Surface crystallization · Glass ceramics

Introduction

Surface acoustic wave (SAW) devices are being used for an increasing number of signal processing applications especially in communications, radar and domestic video equipment [1]. $Te_2V_2O_9$ is an interesting candidate for such applications because an analysis of the crystal structure demonstrated that it possesses chains of corner-sharing trigonal bipyramids linked by Te–O bridges such that each Te^{4+} is bound to three oxygen ions. Hence, this material offered the promise of reasonable piezoelectric coupling combined with the possibility of anomalous elastic constant behavior if the VO_4^{3-} groups were sufficiently rigid to give an effect similar to that seen in α-quartz. The structure possesses mm2 symmetry and hence is both acentric and polar [2].

It would be interesting to grow these crystals in their own glass matrix as tellurites and vanadates are known to be good conditional glass formers and melt at relatively low temperatures. It is also known that glasses of tellurium vanadates are transparent to the infra red part of the electromagnetic spectrum and are of semiconducting in nature. Moreover, glass ceramics have principal advantages, over single crystals and ceramics, as these are expected to have no porosity and could have desirable properties (as one could exercise strict control over the microstructure, distribution of crystallites and their volume fraction, etc.) akin to that of their crystalline counterparts. Understanding the crystallization kinetics of such glasses would be crucial for employing them in the fabrication of SAW device. Glass crystallization kinetics has been widely discussed using DSC and DTA techniques [3–8]. We present, in this article, a detailed study on the glass transition and crystallization kinetics of $2TeO_2$–V_2O_5 glasses.

Experimental

$2TeO_2$–V_2O_5 (TVO) glasses were fabricated via the conventional melt-quenching technique. For this, stoichiometric ratio of TeO_2 (99.95%, Aldrich) and V_2O_5 (99.9%, Merck) were mixed and melted in a platinum crucible at 800 K for 30 min. Melted mixture was quenched in air ambience by pouring on a steel plate that was maintained at 423 K and pressed with another steel plate to obtain 0.5–0.7 mm thick brown colored plates. These as-quenched samples were annealed at a temperature below the

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T_g (T_g—50 K) for 12 h and cooled slowly to ease out the thermal stresses associated with them during the quenching process. X-ray diffraction studies (Phillips) were performed at room temperature on the as-quenched and the samples heat treated at crystallization temperature (T_{cr}) to confirm their amorphous and crystalline nature, respectively. The DSC runs were carried out in the 323–873 K temperature range using the power-compensated DSC (Model: Diamond DSC, Perkin-Elmer). The DSC curves were recorded with different heating rates viz. 10, 15, 20, and 25 K/min. All the experiments were conducted in dry nitrogen ambience. The as-quenched glasses weighing 10 mg were used for all the experiments. The glass sample was heat treated near the crystallization temperature (673 K/2 h) and subsequently the presence of crystallites within the glass matrix was confirmed using scanning electron microscope (SEM).

Results and discussion

XRD studies

X-ray diffraction pattern for the pulverized as-quenched and heat-treated (673 K/2 h) glass plates are shown in Fig. 1a and b, respectively. Figure 1c shows the XRD pattern for the ceramic powder of TVO prepared by solid state reaction route. The XRD patterns obtained for both the heat-treated glass plate and the ceramic powder are in good agreement with that of the standard JCPDS (card no. 71-0719) pattern for TVO. In Fig. 1b one would notice that a few selective peaks are more intense as compared to those in Fig. 1c suggesting the existence of partially oriented crystallites in the glass matrix.

Thermal analysis

The DSC traces that were obtained for the as-quenched samples of $2TeO_2–V_2O_5$ for various heating rates (viz. 10, 15, 20, and 25 K/min) are shown in Fig. 2. An endotherm followed by an exotherm (sluggish) and again an intense endotherm, corresponding to the glass transition (T_g), crystallization (T_{cr}), and melting temperatures (T_m) of the glass sample, respectively, are observed for all the DSC traces. The glass transition (T_g) and the crystallization (T_{cr}) temperatures shift towards higher temperatures with increasing heating rate (as illustrated in Fig. 2), indicating the kinetic nature of the glass transition and the crystallization. Therefore, the investigation into the heating rate dependent glass transition and crystallization could be helpful for understanding the thermal behavior of $2TeO_2–V_2O_5$ glasses.

The effect of heating rate (α) on T_g and T_{cr} has been rationalized using the Lasocka's relation [9]. The relation between the T_g, T_{cr}, and α could be represented empirically (Lasocka's relation) as follows:

$$T_g = A_g + B_g \log \alpha \tag{1}$$

and

$$T_{cr} = A_{cr} + B_{cr} \log \alpha \tag{2}$$

where A_g and A_{cr} are the glass transition and crystallization temperatures for the heating rate of 1 K/min. B_g and B_{cr} are the constants. The plots of T_g and T_{cr} versus log α for $2TeO_2–V_2O_5$ pulverized glasses along with the theoretical fits (solid lines) are shown in Figs. 3 and 4, respectively. The above relations (Eqs. 1 and 2) can be written as;

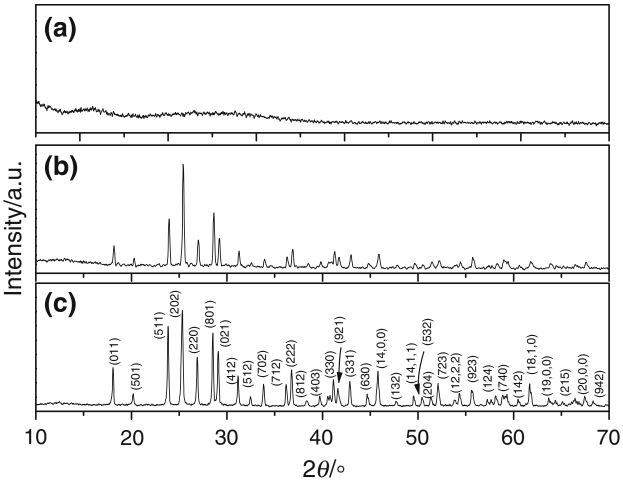

Fig. 1 X-ray diffraction patterns for the (*a*) pulverized as-quenched, (*b*) heat-treated (673 K/2 h) glass plates, and (*c*) crystallized powdered samples ($Te_2V_2O_9$)

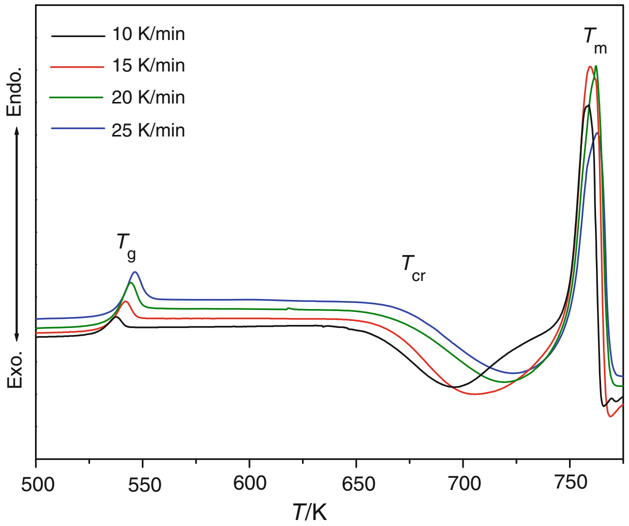

Fig. 2 DSC traces for as-quenched pulverized TVO glasses at various heating rates

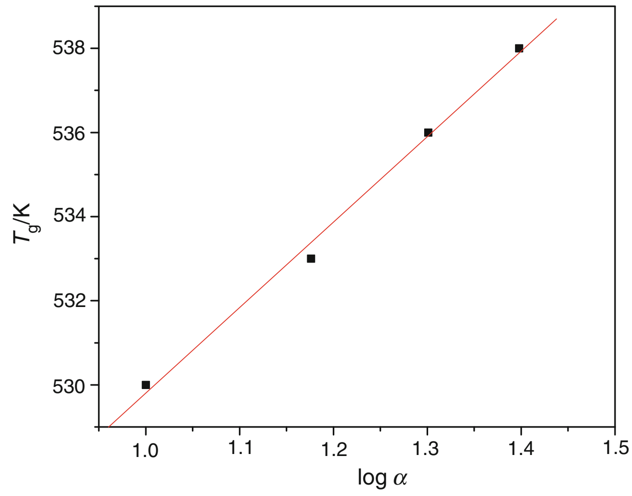

Fig. 3 T_g versus log α for TVO glasses

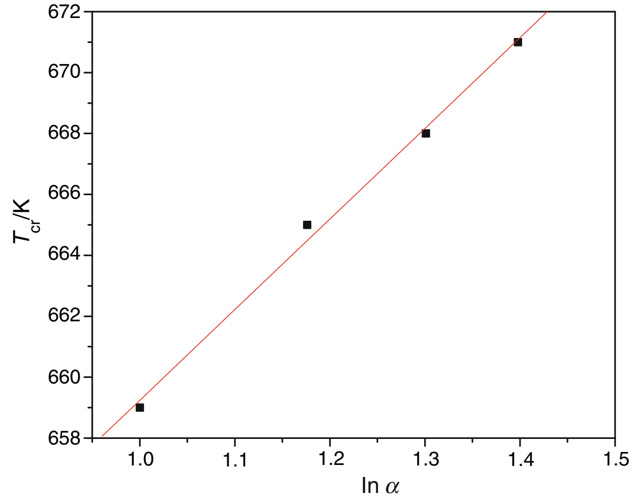

Fig. 4 T_{cr} versus log α for TVO glasses

$$T_g(\mathrm{K}) = 509 + 20\log\alpha\,(\mathrm{K/min}) \tag{3}$$

and

$$T_{cr}(\mathrm{K}) = 629 + 30\log\alpha\,(\mathrm{K/min}) \tag{4}$$

The Lasocka equations for the glass transition and the crystallization temperatures could be used to evaluate Kauzmann temperature [10]. The Kauzmann temperature (T_k) is an important parameter to characterize glassy materials from thermodynamic view point. T_k is the temperature at which the entropy of liquid becomes equal to that of crystal. Thus, the Kauzmann temperature is the lowest theoretical boundary for the glass transformation. It is clear from Eqs. 1 and 2 that at some heating rate, one can assume that $T_g = T_{cr} = T_k$.

After solving Eqs 1 and 2 for T_k (which is equal to T_g or T_{cr}), one would arrive at [10]

$$T_k = \frac{B_{cr}A_g - A_{cr}B_g}{B_{cr} - B_g} \tag{5}$$

The value obtained for Kauzmann temperature is 261 K for $2TeO_2$–V_2O_5 glasses.

It is of interest to investigate the activation energy of the glass transition for the $2TeO_2$–V_2O_5 glass samples. The activation energy (E_g) associated with the glass transition is involved in the molecular motion and rearrangement of atoms. The activation energy for the glass transition for the present glasses could be evaluated using Kissinger's method [11] and is given by the following relation:

$$\ln\left(\alpha/T_g^{\,2}\right) = -E_g/RT_g + \mathrm{constant} \tag{6}$$

where R is the universal gas constant. The above equation (Eq. 6) was formerly derived for the process of crystallization. However, it is known in the literature [12] that the Kissinger equation could also be used to evaluate the activation energy associated with the glass transition. A plot of $\ln(\alpha/T_g^{\,2})$ versus $(1000/T_g)$ yields a linear relation which is depicted in Fig. 5. The experimental points of the present work along with a linear fit (solid line) to the above relation suggest its validity. From the slope of the straight line, the value of E_g is found to be 258 kJ/mol. Kissinger equation, which could be used commonly for analyzing the crystallization data in non-isothermal DSC or DTA experiments. According to which

$$\ln\left(\frac{\alpha}{T_{cr}^{\,2}}\right) = -\frac{E_c}{RT_{cr}} + \mathrm{const.} \tag{7}$$

The plots of $\ln(\alpha/T_{cr}^{\,2})$ versus $1000/T_{cr}$ for the samples are shown in Fig. 6. The value obtained for E_c is 272 kJ/mol.

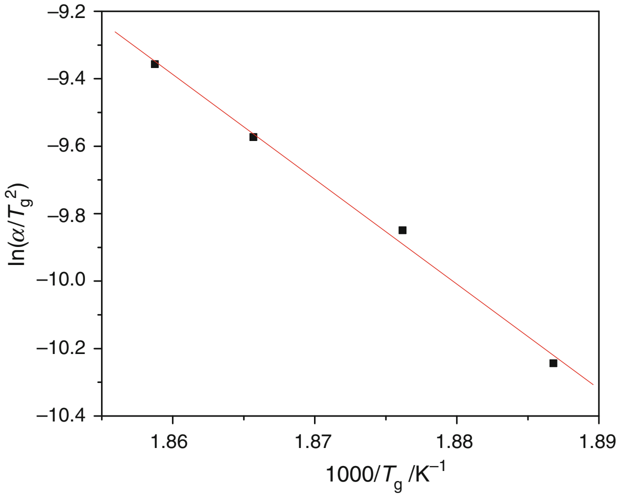

Fig. 5 $\ln(\alpha/T_g^{\,2})$ vs. $1000/T_g$ for TVO glasses

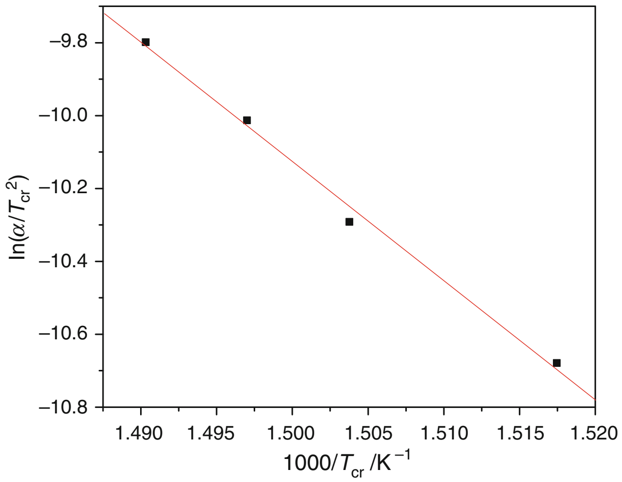

Fig. 6 ln(α/T_{cr}^2) vs. 1000/T_{cr} for TVO glasses

In order to estimate Avrami exponent, the fraction of crystallization (x) was calculated at different temperatures and heating rates (using the partial area technique). Fraction of crystallization versus temperature plots at different heating rates for $2TeO_2$–V_2O_5 glasses are illustrated in Fig. 7. Matusita–Sakka equation [13] could be used for analyzing the crystallization data in non-isothermal DSC/DTA experiments, according to which

$$\ln[-\ln(1-x)] = -n\ln\alpha - 1.052\frac{nE_c}{RT} + \text{const.} \tag{8}$$

It allows estimation of n as;

$$\left.\frac{\mathrm{d}(\ln\alpha)}{\mathrm{d}(1/T)}\right|_x = 1.052\frac{m}{n}\frac{E_c}{R} \tag{9}$$

and

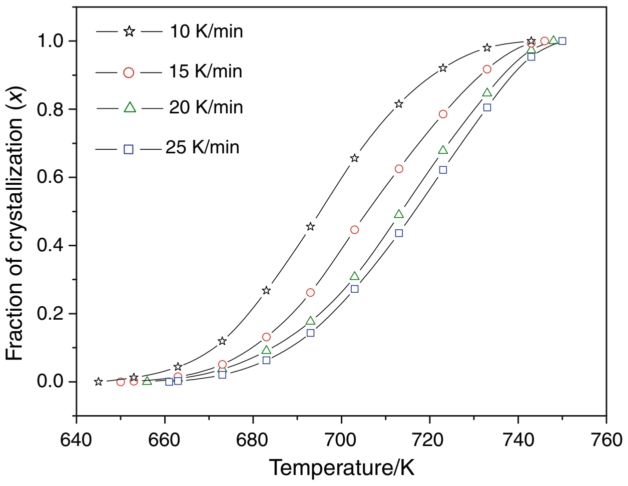

Fig. 7 Fraction of crystallization vs. temperature at various heating rates

$$\left.\frac{\mathrm{d}\ln[-\ln(1-x)]}{\mathrm{d}(1/T)}\right|_\alpha = -1.052\frac{mE_c}{R} \tag{10}$$

One obtains the value of n from the slope of Eqs. 9 and 10 as;

$$n = \text{ slope of Eq. 10/slope of Eq. 9} \tag{11}$$

Figures 8 and 9 represent experimental data along with the linear fits for Eqs. 9 and 10, respectively. The value that is obtained for n is 1.65. The value of n indicates the mode of crystallization [14]. This value suggests that there is one-dimensional surface and bulk crystallization behavior of this glass system. The surface crystallization process could be exploited for the fabrication of SAW devices as there is going to be subtle refractive index difference between the top crystalline layer and the bulk glass below.

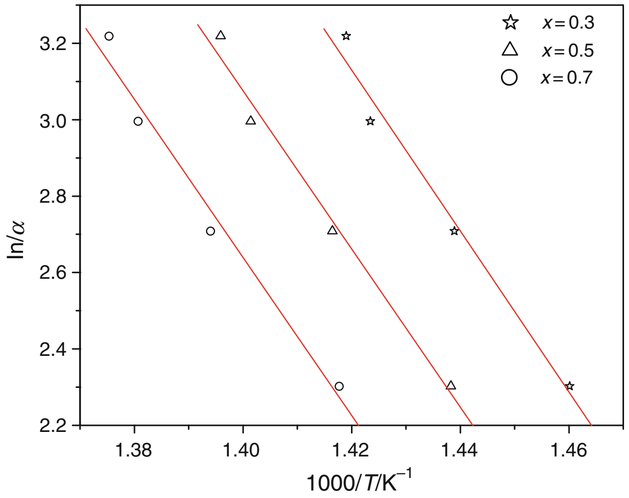

Fig. 8 ln α vs. 1000/T plots for TVO glasses

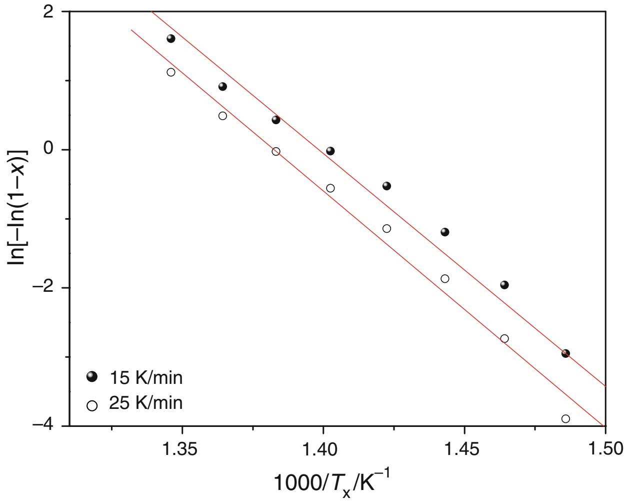

Fig. 9 Plots of ln[−ln(1 − x)] against 1000/T_x at two heating rates

Conclusions

The glass transition and crystallization kinetics of $2TeO_2$–V_2O_5 glasses, which are of scientific relevance, have been studied. Kauzmann temperature was found to be 261 K based on heating rate dependent glass transition and crystallization temperatures. The value of the Avrami exponent, *n*, was found to be 1.65, suggesting a mixed crystallization mechanism (one-dimensional surface and bulk crystallization). The thermal parameters that are obtained in the present studies are crucial for controlling the crystallization in bulk samples.

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