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Crystallization Kinetics of K₂O·TiO₂·3GeO₂ Glass Studied by DTA

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Abstract:

> *Crystallization kinetics of $K_2O \cdot TiO_2 \cdot 3GeO_2$ glass was investigated by differential thermal analysis (DTA). Experiments were performed on powder samples with a particle size < 0.037 mm. The glass samples were heated at different rates in the temperature range 20-750 ^{o}C. The kinetic parameters, activation energy for the crystallization process, E_c and Avrami exponent, n were calculated. Powder X-ray diffraction analysis (XRD) of crystallized glass reveals the presence of crystalline $K_2O \cdot TiO_2 \cdot 3GeO_2$ indicating polymorphic crystallization with interface controlled crystal growth.*

Keywords: *Germanate glass, Polymorphic crystallization, Crystallization kinetics.*

1. Introduction

Germanium-containing glasses have received increased interest due to their technological applications, for example, in optical fibers and nonlinear optical devices where these materials are used as glasses or as transparent crystallized glasses. Understanding the crystallization process of these materials has an important role for their development. Many studies have been done [1-3] to obtain crystallization kinetic parameters from experimental data of thermal methods for different glass compositions.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are thermal methods applied the most to study crystallization behavior of glasses. Crystallization kinetics can be described by the activation energy for crystallization, E_c and the Avrami exponent, *n* reflecting the characteristics of nucleation and the growth process. The aim of the present work is to obtain the kinetic parameters of crystallization of $K_2O \cdot TiO_2 \cdot 3GeO_2$ glass where the temperature range of nucleation and crystal growth overlapped.

Experimental

$K_2O \cdot TiO_2 \cdot 3GeO_2$ glass was prepared using the well known melt-quench technique. The raw materials used were electronic grade GeO_2 (Acros Organics) and reagent grade K_2CO_3 and TiO_2 (Fluka Chemic). The appropriate batch composition was melted at 1300 ºC for 1h in a Pt crucible. The melt was cast on a steel plate and cooled in air. Powder X-ray

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diffraction analysis (XRD) confirmed the quenched melts to be vitreous. The glass samples were transparent, without visible residual gas bubbles.

Differential thermal analysis experiments (DTA) were performed using a Netzch STA 408 EP device and Al_2O_3 powder as the reference material with a constant weight $m = 100$ mg of powder samples having granulation < 0.037 mm. DTA curves were obtained at several heating rates (5, 8, 10, 15, 20 ºC/min) in the temperature interval 20 - 750 ºC. In this temperature interval a clear crystallization peak appeared enabling the determination of kinetic parameters of $K_2O \cdot TiO_2 \cdot 3GeO_2$ glass crystallization.

In order to identify the crystallization phase, XRD analysis of heat treated glass at T= 640 ºC for $t = 1000$ min was performed using a Philips PW -1710 automated diffractometer. The conditions of heat treatment were chosen in such a way to enable identification of the formed crystalline phase whereby the temperature of the heat treatment (T = 640 ºC) matches the temperature of the crystallization peak in the DTA curve (Fig. 2) and the time for heat treatment (t = 1000 min) was chosen to assure the formation of a high enough quantity of crystalline phase for identification.

Results and discussion

XRD analysis identified only one crystalline phase, that is $K_2TiGe_3O_9$ (JCPDS 27-0394), which according to the chemical composition corresponds to the composition of starting $K_2O \cdot TiO_2 \cdot 3GeO_2$ ($K_2TiGe_3O_9$) glass.

Investigations on glass crystallization indicate that if the composition of the formed crystalline phase is the same as the composition of starting glass (polymorphic crystallization) long-range diffusion of certain species is not necessary but only short-range from the interface. In this case, the crystal growth is interface controlled and the morphology of the crystal is spherulitic[4]. Spherulitic crystal growth from $K_2O \cdot TiO_2 \cdot 3GeO_2$ glass was confirmed by SEM investigation of heat treated glass in our previous paper [5]. There are three mechanism of crystal interface controlled growth: normal growth, screw dislocation and surface nucleation. The criteria for determining the mechanism of interface controlled crystal growth is Jackson's criteria [4]. Accordingly, for materials with small entropies of fusion $\Delta S_m < 2R$, normal growth is expected. In contrast, for materials with large entropies of fusion $\Delta S_m > 4R$, a screw dislocation or by surface nucleation crystal growth mechanism occurs.
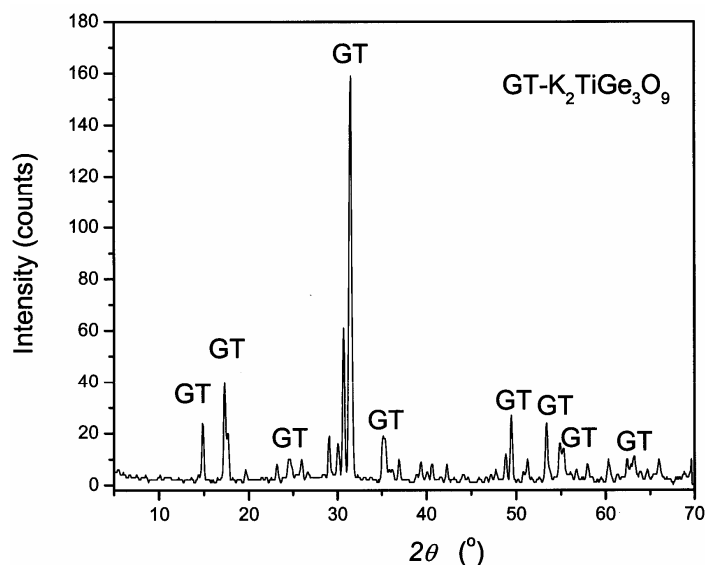
Fig. 1. The XRD pattern of heat treated $K_2O \cdot TiO_2 \cdot 3GeO_2$ glass at T= 640 ºC for $t = 1000$ min.

In our previous investigation the melting entropy was calculated, from the experimentally determined melting enthalpy of the $K_2TiGe_3O_9$ crystalline phase to be $\Delta S_m = 103$ J·mol^{-1}·K^{-1} [5], confirming that crystal growth is interface controlled and proceeds by the screw dislocation mechanism.
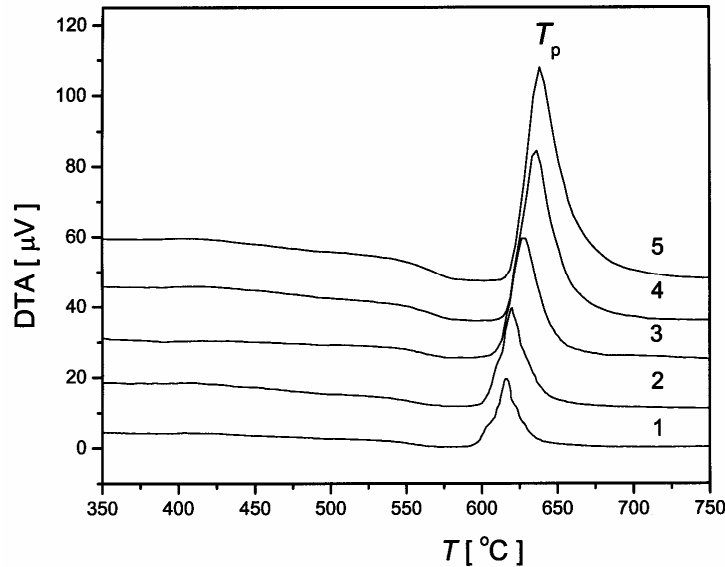
Fig. 2. DTA curves for glass sample particle size < 0.037 mm recorded at: 1) 5 ºC/min; 2) 8 ºC/min; 3) 10 ºC/min; 4) 15 ºC/min and 5) 20 ºC/min.

In the case of interface controlled crystal growth, non-isothermal methods can be used for evaluating of kinetic parameters of glass crystallization. These methods, requiring small sample masses, are relatively easy to perform. However, the majority of these methods have been criticized for assuming the Arrhenian temperature dependence of the transformation kinetics, and so do not have general validity [6]. This makes the calculated kinetic parameters reliable and unambiguous only in certain controlled cases. The Kissinger method is most often used for data analysis. The modified form of the Kissinger equations is as follows [7-9]:

$$\ln \frac{\beta^n}{T_p^2} = -\frac{m \cdot E_c}{R \cdot T_p} + const. \tag{1}$$

where β is the heating rate, n is the Avrami exponent and m is the dimensionality of the crystal growth. The values of parameters n and m depend on the rate controlling mechanism of crystallization kinetics, while the value of E_c is obtained from the ratio $\ln (\beta^n / T_p^2)$ vs. $1/T_p$ using the corresponding values for n and m. It is believed that the so obtained E_c value has little physical significance in transformations where nucleation and crystal growth proceed simultaneously. In the case when experiments were performed in such a way that the glass samples were saturated with nuclei before crystal growth, then parameter E_c may be interpreted as the activation energy of crystal growth. Recent investigation results showed that temperature ranges of nucleation and crystal growth of this glass are partially overlapped [5,10]. Accordingly, in this case the selection of conditions for non-isothermal investigation is very important. Therefore, to satisfy the condition of a constant nuclei number during crystal growth, for this experiment the glass powder with the smallest particle size of < 0.037 mm was chosen. In the range of the smallest granulation, in the total number of present nuclei, the number of surfaces with respect to internal nuclei is dominant. Therefore, the number of

nuclei does not significantly change with heating, while the crystal growth rates become considerable. Confirmation of such a possibility can be obtained comparing the value of Avrami exponent n which is determined experimentally with its theoretical value for the case of surface nucleation and interface – controlled crystal growth.

The DTA curves of a powder sample with granulations < 0.037 mm were recorded at different heating rates ranging from 5 to 20 ^{o}C /min, and are shown in Fig. 2. The values of crystallization peak temperatures, T_p, increased as the heating rate, β increased.

The value of the parameter n can be determined from the same DTA curves by the Ozawa method [11]. This method avoids the assumption about the temperature dependence of the rate coefficient. For this reason, this analysis can provide a more reasonable assessment of the Avrami exponent [6]. The following relationship is used:

$$\frac{d\left\{\log[-\ln(1-\alpha)]\right\}}{d\log\beta} = -n \qquad (2)$$

The volume fraction of crystals, α was calculated using partial area analysis. At a selected temperature α is given by:

$$\alpha = \frac{A}{A_o} \qquad (3)$$

where A_o is the total area of the crystallization peak between the temperature T_1 where the crystallization just starts and temperature T_2 where the crystallization is completed and A is the area between T_1 and selected T, (Fig. 3).
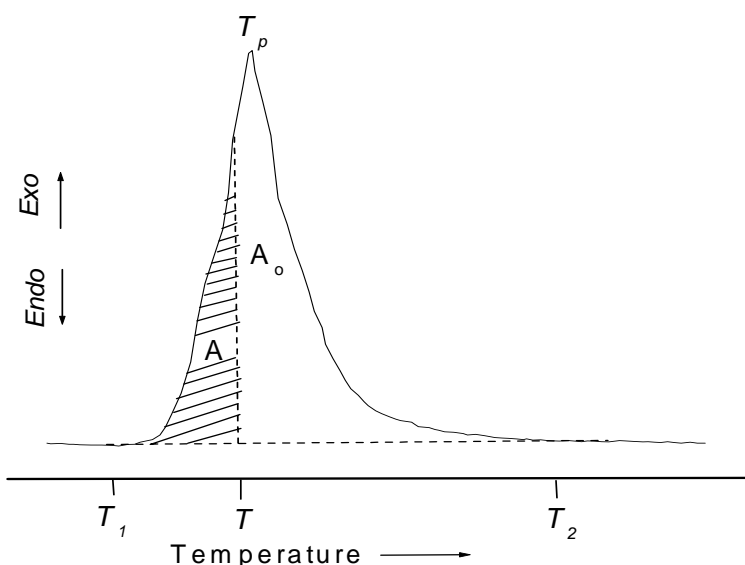

Fig. 3. Method of calculating volume fraction of crystals, α by partial area analysis at the temperature T.

The positions of the crystallization peaks at various heating rates on the DTA curves of this sample enable determination of three values of α at the selected temperature $T = 640$ ^{o}C. DTA curves recorded at heating rates of $\beta = 5$; 15 and 20 ^{o}C/min were used for these calculations. Fig. 4 shows a plot of $\log[-\ln(1-\alpha)]$ versus $\log \beta$. From the slope the value of $n = 1.29 \pm 0.09$ was calculated.

Taking into account experimental errors, this value is close to $n = 1$ which is

characteristic for one-dimensional or surface crystallization growth controlled by the interface for a constant number of nuclei. Thus, the assumption made previously, that appropriate selection of glass particle size enables determination of a reliable value of E_c for the case where nucleation and crystal growth proceed simultaneously was confirmed.
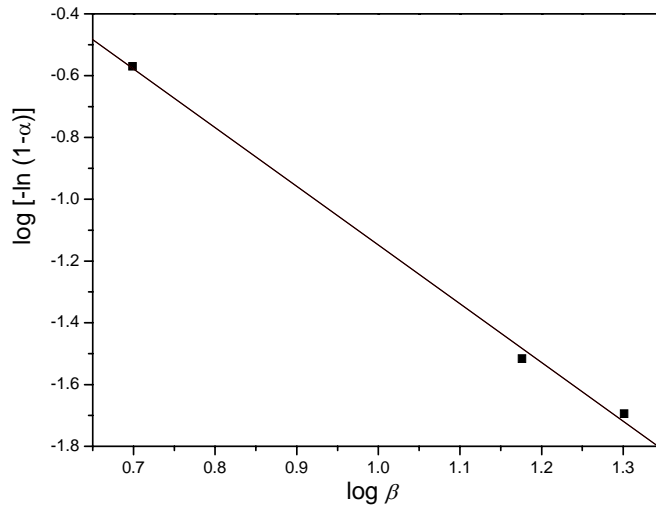
Fig. 4. Plot of log [-ln(1-α)] versus log β at T = 640 ºC.

On the basis of the recorded T_p 's at various heating rates and experimental and theoretical values of parameter n, the values of the activation energy of crystal growth were calculated according to Equation 1.
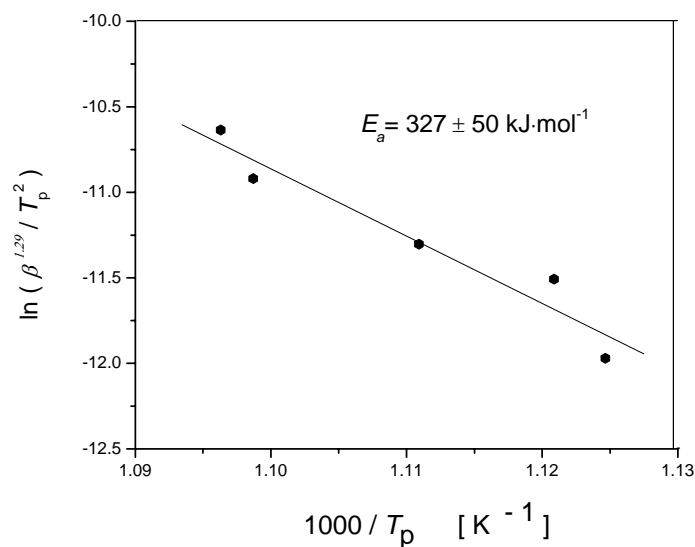
Fig. 5. The plot of ln ($\beta^{1.29} / T_p^2$) versus 1/ T_p for powder sample particle size <0.037 mm, n = 1.29.

Fig. 5 shows the plot of ln ($\beta^{1.29} / T_p^2$) versus 1/ T_p for the case of experimentally determined parameter n. The E_c = 327± 50 kJ·mol^{-1} for both values of parameter n were

calculated. In literature, there is no data on the activation energy for $K_2TiGe_3O_9$ crystalline phase growth from glass. The obtained value E_c is in accordance with the activation energy for growth of the $Li_2TiGe_6O_{15}$ crystalline phase, $E_c = 357$ kJ·mol^{-1} [12] and activation energy for growth of the $Li_2TiGe_3O_9$ crystalline phase, $E_c = 353$ kJ·mol^{-1} [13], calculated using Eq. 1.

Conclusion

XRD analysis of heat treated $K_2O·TiO_2·3GeO_2$ glass showed the existence of a $K_2O·TiO_2·3GeO_2$ crystalline phase indicating polymorphic crystallization (compositions of crystalline phase and glass are same). For the case of polymorphic crystallization, crystal growth is interface-controlled.

The study showed that DTA analyses of glass powder with a particle size < 0.037 mm enabled the determination of reliable values of crystallization kinetic parameters for the glass where nucleation and crystal growth simultaneously occurred. The Avrami exponent determined by Ozawa method was $n = 1.29 \pm 0.09$. The E_c value obtained using this method was $E_c = 327 \pm 50$ kJ·mol^{-1}.

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Садржај: Кинетика кристализације $K_2O·TiO_2·3GeO_2$ стакла је проучавана применом диференцијално термијске анализе (DTA). Експерименти су изведени на узорцима стакла гранулације <0,037mm који су загревани различитим брзинама у температурском интервалу 20-750 °C. На основу резултата испитивања одређени су кинетички параметри: енергија активације кристализације, E_c и Аврамијев параметар, n. XRD анализом искристалисалог узорка стакла је утврђено присуство $K_2O·TiO_2·3GeO_2$ $K_2O·TiO_2·3GeO_2$ кристалне фазе, што указује на полиморфну кристализацију са растом кристала контролисаним реакцијама на граници фаза.
***Кључне речи**: Германитно стакло, полиморфна кристализација, кинетика кристализације.*