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CRYSTALLIZATION KINETIC OF FLUOROZIRCONATE GLASSES BY NON-ISOTHERMAL ANALYSIS

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Abstract

Fluoride glasses have been extensively studied due to their high transparency in the infrared wavelength. The crystallization kinetics of these systems has been studied using DTA and DSC techniques. Most of the experimental data is frequently investigated in terms of the Johnson–Mehl–Avrami (JMA) model in order to obtain kinetic parameters.

In this work, DSC technique has been used to study the crystallization of fluorozirconate glass under non-isothermal conditions. It was found that JMA model was not fit to be applied directly to these systems, therefore, the method proposed by Málek has been applied and the Šesták–Berggren (SB) model seems to be adequate to describe the crystallization process.

Keywords: crystallization, DSC, fluoride glasses, kinetic model

Introduction

In the last 20 years fluoride glasses have been extensively investigated [1–3] due to their high transparency in the middle infrared region [4], which shows lower phonon energy than oxide glasses. This window transmission allows several applications of these materials in this spectrum range, such as fiber optics, laser hosts, chemical sensor, etc...

However these materials have a tendency to crystallize, undertaking their application, mainly in fiber optics. During fiber fabrication, the material is submitted to two thermal instability regions: first, in the preform preparation; and second, in the fiber drawing, increasing the crystallization tendency. The presence of small crystals in fiber can cause scattering of light which spreads through the fiber, which leads to an attenuation of the signal [5].

To understand the crystallization process of these materials has an important role for their technological development. Many studies have been done [6–8] to obtain crystallization kinetic parameters from experimental data of thermal methods for different vitreous compositions. Differential scanning calorimetry (DSC) and differ-

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ential thermal analysis (DTA) are the most applied thermal methods to study the behavior of glass crystallization.

The aim of this work is to calculate the kinetic parameters from DSC data, by non-isothermal method and to determine the best kinetic model that describes the crystallization process for these fluorozirconate glass compositions.

Theoretical analysis

The most practical equation to determine kinetic parameters was proposed by Johnson and Mehl [9] and Avrami [10] for isothermal process and is expressed by:

$$\alpha=1-\exp\ [-kt)^{n}] \tag{1}$$

where α is the crystallized fraction, n is the Avrami exponent and k is the rate constant, which follows an Arrhenius equation form:

$$k=A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E_a is the activation energy and R is the gas constant. Frequently the logarithmic form of Eqs (1) and (2) is used:

$$\ln[-\ln(1-\alpha)]=n\ln k+n\ln kt \tag{3}$$

$$\ln k=\ln A\left(-\frac{E_a}{RT}\right) \tag{4}$$

From isothermal DSC curve a plot of $\ln[-\ln(1-\alpha)]$ *vs.* $\ln t$ allows to determine n and k values. The activation energy is obtained from slope of $\ln k$ *vs.* $1/T$ plot Eq. (4).

From non-isothermal data, the temperature T increases in function of the time t:

$$T=\beta t+T_0 \tag{5}$$

where β is the heating rate and T_0 is the initial temperature. By inserting this equation into Eq. (1), the below equation can be obtained:

$$\ln[-\ln(1-\alpha)]=n\ln[k(T-T_0)]-n\ln\beta \tag{6}$$

If the crystallized fraction α is determined at fixed temperatures, at different heating rates, the Avrami exponent n can be obtained from slop of the $\ln[-\ln(1-\alpha)]=f(\ln\beta)$ plot.

The activation energy can be determined from slope of the $\ln[(T_p)^2/\beta]$ *vs.* $1/T_p$ plot, given by Chen's relation [11] by derivation of Eq. (1):

$$\mathrm{d}\ln\left(\frac{T_p^2}{\beta}\right)=\frac{E_a}{R}\mathrm{d}\left(\frac{1}{T_p}\right) \tag{7}$$

However Málek has proposed [8, 12, 13] a simpler method to test the applicability of JMA model. In fact, it is known that a double logarithmic function (Eqs (3) and (6)) may be linear even when JMA is not an adequate model.

The kinetic interpretation of DSC or DTA data, isothermal or non-isothermal methods, is based on the relation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\phi}{\Delta H_\mathrm{c}} \tag{8}$$

where ϕ is the heat flow normalized per mass sample and ΔH_0 corresponds to the enthalpy change associated with the crystallization process.

The rate of the kinetic process can be expressed by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha) \tag{9}$$

In this equation k is the rate constant and follows and Arrhenius form, given by Eq. (2).

The kinetic equation for a given model can be written as:

$$\phi=\Delta H_\mathrm{c} A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)f(\alpha) \tag{10}$$

where $f(\alpha)$ is an algebraic expression for a given model.

The test proposed by Málek is based on this equation and on the $y(\alpha)$ and $z(\alpha)$ functions. Under non-isothermal conditions these functions are given by:

$$y(\alpha)=\frac{\phi}{\exp\left(-\frac{E_\mathrm{a}}{RT}\right)} \tag{11}$$

$$z(\alpha)=\phi T^2 \tag{12}$$

These functions exhibit their maxima at α_M and α_p^∞, respectively, which allows to find the kinetic from the diagram formulated by Málek [7].

Experimental

The fluorozirconate glass (composition in mol%: $50.8ZrF_4$–$18.5BaF_2$–$4.0LaF_3$–$4.5AlF_3$–$20NaF$–$2YF_3$–$0.2EuF_3$) was prepared by quenching melt of the fluoride salts (BDS – Fluortran/optical grade) in a platinum tube crucible for 1 h. Melting and fining were carried out at 800°C. The melting was poured into a brass mold preheated at 260°C and annealed at a temperature close to T_g (glass transition temperature) for 2 h.

DSC curves were measured using a DSC 2910 TA Instruments and obtained at several heating rates (2, 5, 10, 15, 20 K min^{-1}) from 150 to 550°C range. Powdered samples of 30 mg were packed in a closed aluminum pan under nitrogen atmosphere.

Results and discussion

Figure 1 shows DSC curve for a powdered vitreous sample obtained at 2 K min^{-1}. In this figure the crystallization peak (T_p), which was obtained through DSC data is shown. Similar curves were obtained and procedures were carried out for different heating rates. The activation energy (E_a) was determined from these DSC data using another method, without assuming the kinetic model [14, 15]. One of the most common methods of calculation of E_a is the Ozawa–Flynn–Wall [16, 17].

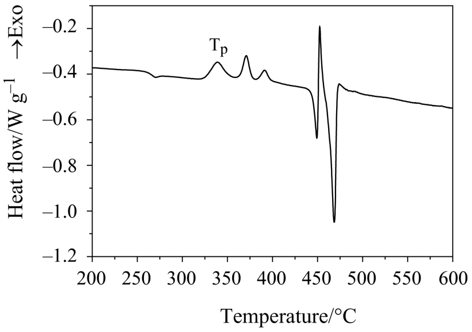

Fig. 1 DSC curve for vitreous sample at 2 K min^{-1}

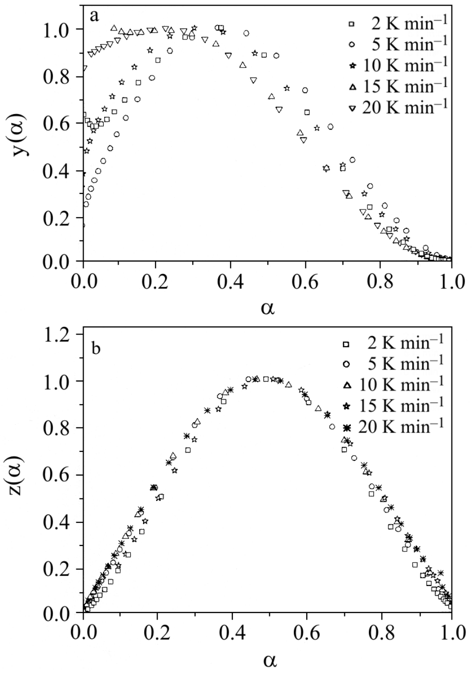

Fig. 2 Normalized $y(\alpha)$ (a) and $z(\alpha)$ (b) functions obtained from DSC data for non-isothermal method at different heating rates

The E_a value obtained, 270.2 kJ mol^{-1}, allows to find the kinetic model which best describes the crystallization process. Figures 2a and b shows the $y(\alpha)$ and $z(\alpha)$ functions for ZBLAN glass at different heating rates. From the analysis of these curves was possible to find the maximum of $y(\alpha)$ and $z(\alpha)$ functions, as previously discussed. Therefore, analyzing the diagram proposed by Málek, these values correspond to the Šesták–Berggren (SB) model. The results are summarized in Table 1.

Table 1 Maximum of the $y(\alpha)$ and $z(\alpha)$ functions at different heating rates and kinetic exponents

β/K min^{-1}	α_M	α_p^∞	n	m
2	0.37	0.50	2.5	1.4
5	0.37	0.50	1.6	0.93
10	0.30	0.50	1.6	0.70
15	0.31	0.51	2.1	0.94
20	0.22	0.49	1.9	0.54

In previous pieces of work [18], a direct application of JMA model gives a kinetic exponent n around 1.0. However a range of 2.5–3.5 JMA kinetic exponent values to describe crystallization kinetic of the fluoride glasses has been shown [19, 20]. As demonstrated from this study, the method to verify the applicability of the kinetic model proposed by Málek was applied and the results do not match previous studies. Málek has pointed out that the JMA model has limited validity in both isothermal and non-isothermal conditions and it is recommended to test its applicability for a given crystallization process, as previously described.

The SB model was tested by simulating the theoretical curve of crystallization process, given by the kinetic equation:

$$\phi = \Delta H_c A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{13}$$

where the function $f(\alpha)$ is the algebraic expression of the kinetic model [21]. In this case:

$$f(\alpha) = \alpha^m (1-\alpha)^n \tag{14}$$

To calculate the theoretical heat flow (ϕ), first the kinetic exponent value, n, had to be found from the $\ln[y(\alpha)]\cdot\ln[\alpha^p(1-\alpha)]$ plot, where the slope gives this value. The second kinetic exponent, m, was calculated by the relation:

$$m = np, \text{ where } p = \frac{\alpha_M}{(1-\alpha_M)} \tag{15}$$

The exponents n and m found are shown in the Table 1 at different heating rates. As observed before that the kinetic exponents show considerable variation, mainly the m exponent. It can be inferred that the value of the m exponent increases as the heating rate decreases, indicating that the crystallized phase may be controlling the kinetic. For $n>1$ indicates an increasing complexity of the process.

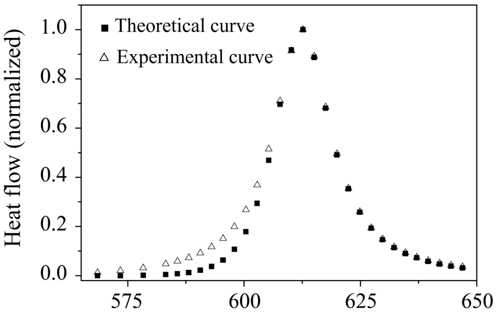

Fig. 3 Theoretical and experimental curves for SB model

The theoretical and experimental curves are shown in Fig. 3 and, as observed, it is very close to the experimental DSC curve, showing that the SB model obtained from $y(\alpha)$ and $z(\alpha)$ functions is the best model to describe the crystallization process to this fluorozirconate glass.

Conclusions

From non-isothermal DSC data the maxima of $y(\alpha)$ and $z(\alpha)$ functions were calculated, which allows to obtain the n and m kinetic parameters and to find an adequate model. From the results presented, the SB kinetic model showed to be the best model to describe the crystallization process for the fluorozirconate glasses studied.

Despite the fact the SB kinetic model has been adequate to this system, the kinetic exponents are changeable depending on the heating rate.

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