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Evaluation of crystallization kinetics of glasses by non-isothermal analysis

KANGGUO CHENG
Department of Materials Science and Engineering, and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, IL, 61801, USA
E-mail: kcheng2@uiuc.edu

Based on Johnson-Mehl-Avrami transition equation, this paper proposes a new non-isothermal method for evaluating the crystallization kinetics of glasses. An equation relating the kinetic parameters of the crystallization activation energy, E, and the frequency factor, v, to the inflection-point temperature, T_f, and the heating rate, β, of differential thermal analysis (DTA) experiment is established. The inflection-point temperature, T_f, can be easily determined from the derivative differential thermal analysis (DDTA) curves. The validity of the proposed method is ascertained by applying it to $Li_2O{\cdot}2SiO_2$ glass. The acquired values of the crystallization kinetic parameters by this method are excellent agreement with the isothermal analysis results. In contrast, the traditional non-isothermal methods give much higher values. © *2001 Kluwer Academic Publishers*

1. Introduction

Thermal analysis is widely used in investigating the crystallization kinetics of glasses [1–22]. It is very quick and needs very small quantities of glass samples to acquire kinetic parameters of the crystallization of glasses by thermal analysis. Two thermal analysis methods are available: one is the isothermal method [1, 4, 7, 9, 12, 13] in which glass samples are quickly heated up and held at a temperature above glass transition temperature. In this method, glasses crystallize a constant temperature. The other is so-called non-isothermal method [14–22] in which glass samples are heated up at a fixed heating rate. Generally, an isothermal experiment takes longer time than a non-isothermal experiment, but isothermal experimental data can be interpreted by the well-established Johnson-Mehl-Avrami equation [23–25]. On the contrary, non-isothermal experiments themselves are rather simple and quick, but assumptions are usually required for data interpretation because there is no uniquely accepted equation available for non-isothermal method. Several equations for interpreting non-isothermal data have been proposed and used [14–22]. However, most of these equations [15–22] assume that the variation of peak crystallization temperature, T_p, on non-isothermal analysis curves, is directly related to the heating rates, β.

Activation energy, E, is one of the most important kinetic parameters for the crystallization of glasses. Both isothermal and non-isothermal methods are equally used in determining the values of E. The values of E of some glasses determined by both isothermal and non-isothermal methods were compared in Table I. For a given glass system, the values of E given by isothermal and non-isothermal methods are roughly close. However, non-isothermal method usually gives a higher value than isothermal method does, as shown in Table I. The discrepancy between the isothermal and non-isothermal results is conventionally interpreted as the experimental error.

Starting from Johnson-Mehl-Avrami transition equation, this paper proposes a new non-isothermal analysis method for evaluating the crystallization kinetics of glasses. Activation energy, E, and frequency factor, v, can be easily determined by this equation. Its validity is ascertained by applying it to $Li_2O{\cdot}2SiO_2$ glass. Both isothermal and non-isothermal differential thermal analysis (DTA) experiments were carried out and the crystallization activation energy, E, and frequency factor, v, are determined by the method proposed in this paper as well as the traditional methods. It is found that the values of E and v determined by the proposed method are excellent agreement with the isothermal analysis results while the traditional non-isothermal methods give much higher values.

2. Theoretical analysis

An isothermal transition of glasses can be described by Johnson-Mehl-Avrami equation [23–25] as

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

where x is the crystallized fraction of glasses; n is the Avrami exponent; k is the reaction rate constant, which is related to the activation energy, E, and frequency factor v through the Arrhenius temperature dependence

$$k = v\exp(-E/RT) \tag{2}$$

where R is the gas constant.

TABLE I Comparison of the crystallization activation energy, E, of some glasses determined by isothermal and non-isothermal methods

	$E/\mathrm{kJ \cdot mol^{-1}}$	
Glass	Isothermal method	Non-isothermal method
$Fe_{40}Ni_{40}P_{14}B_6$	350 [1]	396 [2]
$36InF_3 \cdot 20BaF_2 \cdot 20ZnF_2 \cdot 20SrF_2 \cdot 4GaF_2$	240 [3]	259 [3]
$Li_2O \cdot 2SiO_2$	271 [4]	305 [5]
$40Li_2O \cdot 60SiO_2$	307 [6]	328 [6]
$30GeS_2 \cdot 70Sb_2S$	150 [7]	159 [8]
$Se_{0.7}Te_{0.3}$	157 [9]	174 [10]
Aluminosilicate gel	735 [11]	865 [11]

Taking logarithms and rearranging Equation 1 gives

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

The above equation indicates that a plot of $\ln[-\ln(1-x)]$ versus $\ln t$ is expected to be linear and gives the values of n and k. By taking logarithms Equation 2 can be rewritten as

$$\ln k = \ln v - E/RT \tag{4}$$

A Plot of $\ln k$ against $1/T$ for different isothermal temperatures is also expected to be linear. From these plots, the values of E and v can thus be obtained by isothermal method.

However, applying Johnson-Mehl-Avrami equation to the non-isothermal transition of glasses needs to take into account the dependence of k on time, t. Thus

$$x = 1 - \exp\left[-\left(\int_0^t k(t)\,\mathrm{d}t\right)^n\right] \tag{5}$$

At a certain temperature, T_f, the crystallization rate of a glass, $\mathrm{d}x/\mathrm{d}t$ reaches its maximum, i.e.,

$$\left.\frac{\mathrm{d}^2x}{\mathrm{d}t^2}\right|_{T=T_\mathrm{f}} = 0 \tag{6}$$

By taking the second derivative of Equation 5 and combining with Equation 6, one can finally derive an equation relating the crystallization kinetics parameters of glasses to temperature, T_f, and heating rate, β

$$\ln T_\mathrm{f}^2/\beta = E/RT_\mathrm{f} + \ln E/R - \ln v \tag{7}$$

Obviously a plot of $\ln(T_\mathrm{f}^2/\beta)$ versus $1/T_\mathrm{f}$ would be linear and activation energy, E, and frequency factor, v, can be easily determined from the slope and the interception of the plot. It should be note that, however, so far we have not explicate how to determine the temperature, T_f, from non-isothermal experiments.

During a DTA run with the a constant heating rate, β, temperature, T, is related to time, t, by

$$\mathrm{d}T = \beta\,\mathrm{d}t \tag{8}$$

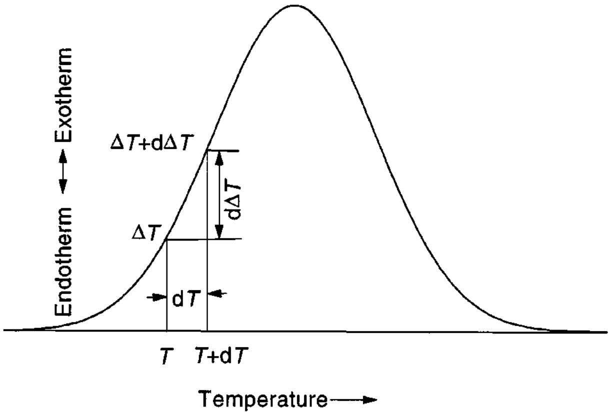

Figure 1 A typical crystallization peak on a DTA curve.

In duration of $t \sim t + \mathrm{d}t$, the temperature of the reference material increases from T to $T + \mathrm{d}T$. Correspondingly, the temperature of glass samples increases from $T + \Delta T$ to $T + \Delta T + \mathrm{d}\Delta T$, as shown in Fig. 1. Assume the crystallized fractions of a glass at t and $t + \mathrm{d}t$ are x and $x + \mathrm{d}x$, respectively. Consideration of energy conservation yields

$$C_\mathrm{g}[1-(x+\mathrm{d}x)]\,\mathrm{d}\Delta T + C_\mathrm{c}(x+\mathrm{d}x)\,\mathrm{d}\Delta T = h\,\mathrm{d}x \tag{9}$$

where C_g is the molar heat capacity of the base glass; C_c is the heat capacity of the crystallized glass; h is the molar enthalpy change of glass-crystal transition. The term of $h\,\mathrm{d}x$ on the right hand of Equation 9 represents the heat generation due to the crystallization of the glass with amount of $\mathrm{d}x$. The sum on the left hand of Equation 9 is the total heat required to cause a temperture increase of $\mathrm{d}\Delta T$ for the crystalline fraction, $(x + \mathrm{d}x)$, and the remaining glass, $[1-(x+\mathrm{d}x)]$.

Rearrangement of Equation 9 yields

$$[C_\mathrm{g} + (C_\mathrm{c} - C_\mathrm{g})x]\,\mathrm{d}\Delta T = h\,\mathrm{d}x \tag{10}$$

For most glass systems, the difference between C_c and C_g is very small. Since x is always less than 1, so $(C_\mathrm{c} - C_\mathrm{g})x$ is much less than C_g and therefore it can be neglected in Equation 10. Thus

$$C_\mathrm{g}\,\mathrm{d}\Delta T = h\,\mathrm{d}x \tag{11}$$

Derivatives of Equation 11 yields

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{C_\mathrm{g}}{h}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} = \frac{\beta C_\mathrm{g}}{h}\frac{\mathrm{d}\Delta T}{\mathrm{d}T} \tag{12}$$

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = \frac{C_\mathrm{g}}{h}\frac{\mathrm{d}^2\Delta T}{\mathrm{d}t^2} = \frac{\beta^2 C_\mathrm{g}}{h}\frac{\mathrm{d}^2\Delta T}{\mathrm{d}T^2} \tag{13}$$

Equation 12 indicates that the crystallization rate, $\mathrm{d}x/\mathrm{d}t$, is proportional to the slopes of DTA curves, $\mathrm{d}\Delta T/\mathrm{d}T$. Correspondingly, Equation 13 indicates that the crystallization rate, $\mathrm{d}x/\mathrm{d}t$, reaches its maximum at the first inflection-point temperature, T_f on the DTA curves. Now it is clear that the temperature T_f in Equation 7 is just the first inflection-point temperature on DTA curves.

3. Experimental procedures

The composition of the glass used in present investigation is $Li_2O{\cdot}2SiO_2$. Analytical grade reagents of Li_2CO_3 and SiO_2 were well mixed by ball-milling, and then melted in a platinum crucible at 1400°C for 4 h. The liquid was quenched by pouring it into cold water. Since the nucleation rate of $Li_2O{\cdot}2SiO_2$ glass reaches its maximum at about 460°C [26, 27], some glass was heated at 460°C for 24 h in order to form a large number of nuclei in these samples. The amorphous nature of both the as-quenched and the well-nucleated glasses was confirmed by X-ray diffraction.

Glass powders of 200 ± 5 mg with an average size of 90 μm were employed for each DTA run. The glass samples were contained in a platinum crucible. The reference material of DTA experiment was alumina. It was contained in another platinum crucible. Temperature calibrations of the instrument were performed using the well-determined melting temperature of high-purity indium.

The isothermal experiments were carried out by heating the samples to 50°C below the required temperature, holding at this temperature for about 30 s and heating at a rate of 100°C/min to the required temperture. The temperature range for isothermal experiments was selected between 530–550°C because the glass shows reasonable peak shapes in this range for data analysis. The crystallized fraction, x, at any time, t, is given as $x = (A_t/A)$, where A is the total area of the exotherm between the time t_i at which crystallization just begins and the time t_f at which the crystallization is completed. A_t is the area between t_i and t [28]. The area was determined by employing a computer program.

The non-isothermal experiments were performed in air with the heating rate of 0.5, 1, 2, 4°C/min. Peak crystallization temperature, T_p, was directly determined from DTA curves. To determine the inflection-point temperature, T_f, DTA curves were differentiated, generating derivative differential thermal analysis (DDTA) curves. The inflection-point temperature T_f, then can be easily determined as the peak temperature on DDTA curves. A minimum of five samples was employed for each isothermal and non-isothermal determination.

4. Result and discussion

4.1. Isothermal method

The isothermal measurements were performed on both the as-quenched and well-nucleated glasses between 530–550°C with an interval of 5°C. The crystallized fraction, x, as a function of time for both glasses are shown in Figs 2 and 3, respectively. As expected, it takes longer time for both glasses to complete crystallization at lower temperature.

It is worth noting, however, that the values of $\ln[-\ln(1-x)]$ function for $(0 < x < 0.1)$ are strongly affected by slight differences in x values, so a high precision for determining the values of x is required [28, 29]. In this part of the isothermal peak, the exact measurements of the small areas under the peak for determining the values of x are very difficult and this may lead to incorrect values for the slopes of $\ln[-\ln(1-x)]$ versus $\ln t$ plot. At the final stage of crystallization $(x > 0.9)$, the saturation of nucleation sites and the mutual contacts of crystals also lead to the deviation of the plot of $\ln[-\ln(1-x)]$ versus $\ln t$ from linearity [15, 16]. In order to minimize such influence, only values corresponding to a limited range of x were employed, $(x = 0.1\text{–}0.9)$ for determining the values of n and k. Plots of $\ln[-\ln(1-x)]$ against $\ln t$, as shown in Figs 4 and 5. Values of Avrami exponent, n, and the reaction rate constant, k, were determined by least-squares fits of the experimental data and summarized in Table II.

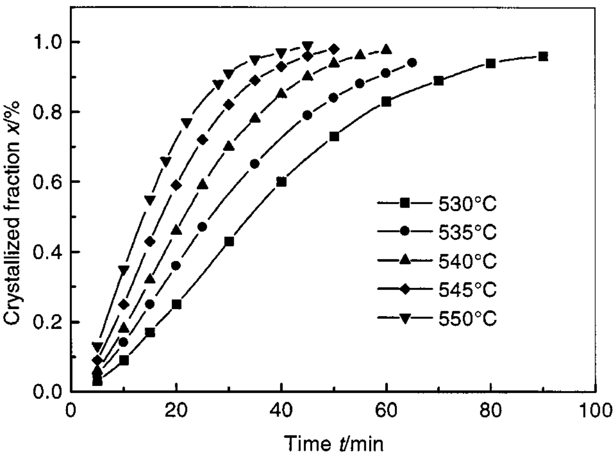

Figure 2 The crystallized fraction, x, of the as-quenched $Li_2O{\cdot}2SiO_2$ glass as a function of isothermal time.

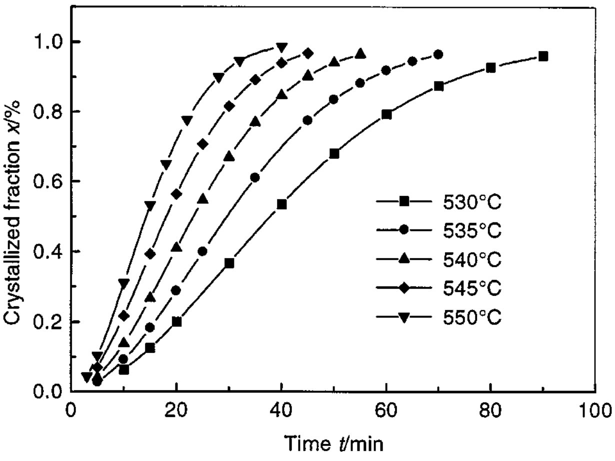

Figure 3 The crystallized fraction, x, of the well-nucleated $Li_2O{\cdot}2SiO_2$ glass as a function of isothermal time.

A plot of $\ln k$ as a function of $1/T$, as shown in Fig. 6, yields the values of activation energy, E and the frequency factor, v, for the crystallization of as-quenched and well-nucleated glasses, respectively. These values are shown in Table III.

4.2. Non-isothermal methods

The DTA curves of the as-quenched glass with various heating rates are shown in Fig. 7. Apparently, the maximum peak temperature, T_p, on DTA curves increases with the increase of heating rate. The DDTA curves are shown in Fig. 8. The inflection-point temperature, T_f, is determined as the maximum peak temperature on DDTA curve, corresponding to the maximum slope

TABLE II Data employed in the determination of activation energy, E, and frequency factor, v, of the as-quenched and the well-nucleated $Li_2O{\cdot}2SiO_2$ glasses by isothermal method

Glass	T/°C	$\ln k$/min^{-1}	n
As-quenched glass	530	−3.75	1.62 ± 0.07
	535	−3.51	1.55 ± 0.08
	540	−3.29	1.63 ± 0.08
	545	−3.06	1.60 ± 0.07
	550	−2.85	1.58 ± 0.09
Well-nucleated glass	530	−3.85	1.80 ± 0.08
	535	−3.60	1.78 ± 0.07
	540	−3.35	1.80 ± 0.09
	545	−3.11	1.78 ± 0.08
	550	−2.88	1.77 ± 0.07

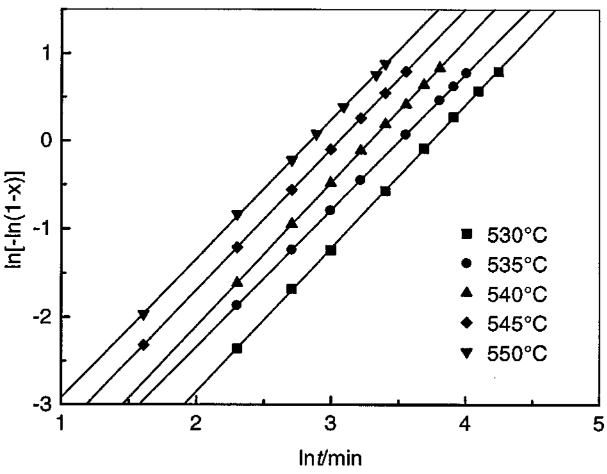

Figure 4 Plot of $\ln[-\ln(1-x)]$ versus $\ln t$ for determining the values of n and k of the as-quenched $Li_2O{\cdot}2SiO_2$ glass.

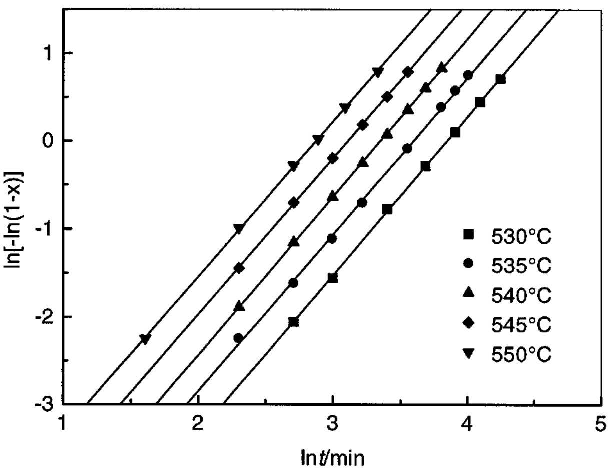

Figure 5 Plot of $\ln[-\ln(1-x)]$ versus $\ln t$ for determining the values of n and k of the well-nucleated $Li_2O{\cdot}2SiO_2$ glass.

of the DTA curve. It also increases with the increase of heating rate. The DTA and the DDTA curves of the well-nucleated glass are similar to those of the as-quenched glass.

The plot of $\ln(T_f^2/\beta)$ versus $1/T_f$ of $Li_2O{\cdot}2SiO_2$ glass based on Equation 7 is given in Fig. 9, from which, the determined values of E are 248 kJ/mol and 268 kJ/mol corresponding to as-quenched and well-nucleated samples, respectively. Both values are excellent agreement with these values determined by isothermal method. The determined values of v are 5.3×10^{12} s^{-1} and 1.0×10^{14} s^{-1} corresponding to as-quenched and well-nucleated glasses, respectively, which are also good agreement with these values determined by isothermal method within the errors of 10% and 20% respectively.

TABLE III Crystallization kinetic parameters of $Li_2O{\cdot}2SiO_2$ glass determined by different methods

Measuring technique	As-quenched glass		Well-nucleated glass	
	E/kJ·mol^{-1}	v/s^{-1}	E/kJ·mol^{-1}	v/s^{-1}
Isothermal equation	247	4.8×10^{12}	267	8.4×10^{13}
Our equation	248	5.3×10^{12}	268	1.0×10^{14}
Kissinger equation	269	3.4×10^{13}	289	6.0×10^{14}
Owaza equation	283	—	303	—

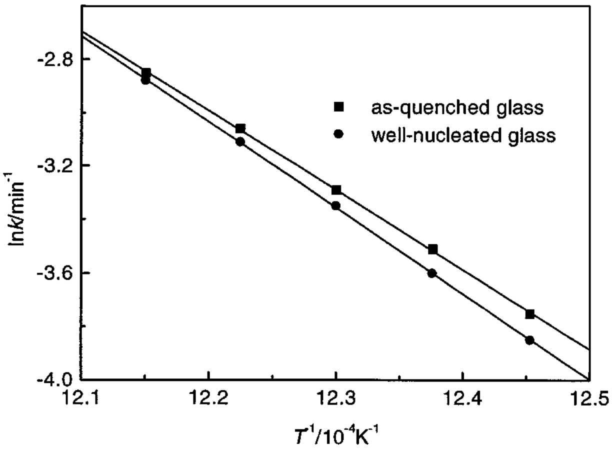

Figure 6 Plot of $\ln k$ against $1/T$ for determining the values of activation energy E, and frequency factor, v, of $Li_2O{\cdot}2SiO_2$ glass.

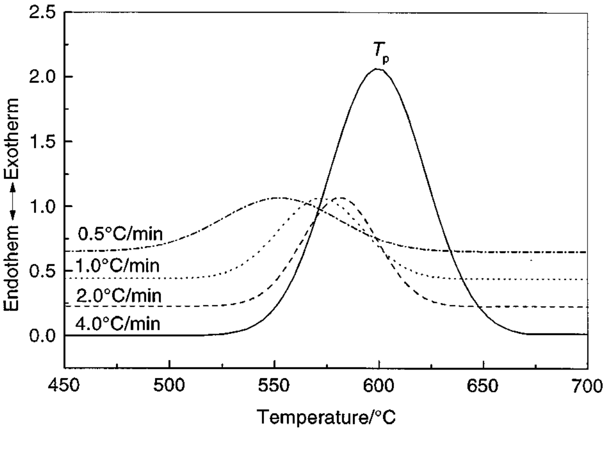

Figure 7 DTA curves of $Li_2O{\cdot}2SiO_2$ glass at different heating rate.

A widely used non-isothermal method is so-called Kissinger plot based on the following Equation 14

$$\ln T_p^2/\beta = E/RT_p + \ln E/R - \ln v \tag{14}$$

A plot of $\ln(T_p^2/\beta)$ versus $1/T_p$ is expected to be linear. Fig. 10 gives plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ for

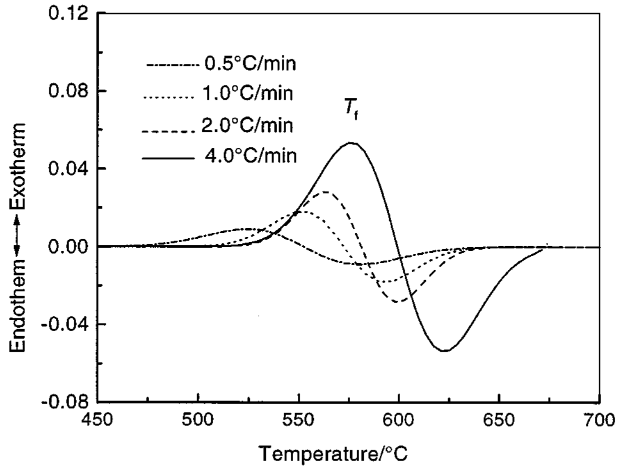

Figure 8 DDTA curves of $Li_2O{\cdot}2SiO_2$ glass at different heating rate.

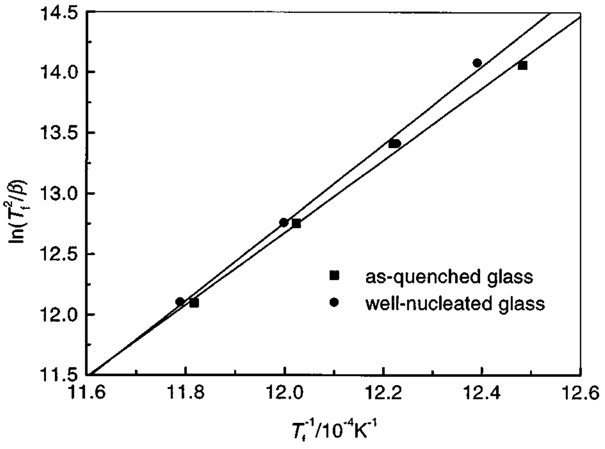

Figure 9 Plots of $\ln(T_f^2/\beta)$ versus $1/T_f$ of $Li_2O{\cdot}2SiO_2$ glass.

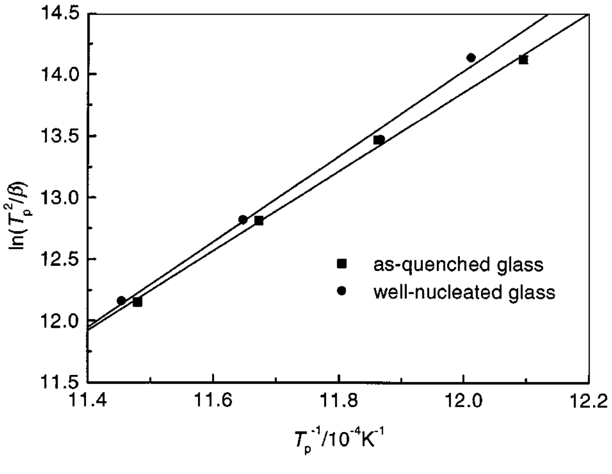

Figure 10 Plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ of $Li_2O{\cdot}2SiO_2$ glass.

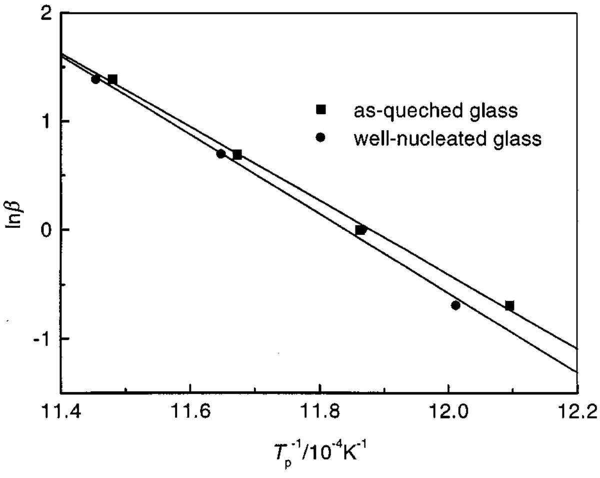

Figure 11 Plots of $\ln\beta$ versus $1/T_p$ of $Li_2O{\cdot}2SiO_2$ glass.

the as-quenched and the well-nucleated $Li_2O{\cdot}2SiO_2$ glasses. The determined values of activation energy, E, are 269 kJ/mol and 289 kJ/mol corresponding to as-quenched and well-nucleated glasses, respectively. Both values are ~8% higher than these values determined by Equation 7 and the isothermal method. Also, the determined values of v are 3.4×10^{13} s^{-1} and 6.0×10^{14} s^{-1} corresponding to as-quenched and well-nucleated $Li_2O{\cdot}2SiO_2$ glasses, respectively, which are one-order magnitude higher than these values determined by Equation 7 and the isothermal method.

Another widely used non-isothermal method is so-called Ozawa plot, based on the following Equation 21

$$\ln\beta = -E/RT_p + C \qquad (15)$$

where C is a constant. Only activation energy can be determined by this method. A plot of $\ln\beta$ versus $1/T_p$ is shown in Fig. 11. The activation energy values are determined as 283 kJ/mol and 303 kJ/mol corresponding to the as-quenched and the well-nucleated glasses, respectively. Again, these values are much higher than determined by Equation 7 and the isothermal method, as shown in Table III.

5. Conclusion

A new non-isothermal method is proposed to evaluate the crystallization kinetics of glasses. An equation, which relates the crystallization activation energy, E, and the frequency factor, v, to the inflection-point temperature, T_f, and the heating rate, β, of DTA experiments, is established. The activation energy, E, and the frequency factor, v, can be easily determined by this method. Its validity is verified by applying it to $Li_2O{\cdot}2SiO_2$ glass. The acquired values by this method are excellent agreement with the isothermal results while the traditional non-isothermal methods give much higher values than the values determined by the proposed method as well as the isothermal method.

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