A Criterion for Evaluating the Thermal Stability of Glasses

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To evaluate the stability of glasses, a new criterion $k_f(T) = \nu \exp[-E/RT \cdot (T_p - T_f)/T_f]$ is proposed, where T_f is the inflection point temperature and T_p is the maximum peak temperature on the differential thermal analysis curves. Not only the kinetic parameters of the crystallization of glasses, namely, activation energy, E, and frequency factor, ν, but also a thermodynamic factor $(T_p - T_f)/T_f$ have been taken into account in the $k_f(T)$ criterion. A higher value of $k_f(T)$ means a poor stability of glasses. Two glasses with the compositions of $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 1.5SiO_2$ were prepared by the conventional melting process and the validity of the proposed criterion is ascertained by applying it on these glasses. The stability of these two glasses was also evaluated by the existing criteria. The results indicate that all existing criteria are either affected by the heating rate or they are not suitable for evaluating the stability of these glasses. On the contrary, the new criterion is independent of the heating rate and gives consistent results on the evaluation of the stability of $Li_2O–SiO_2$ glasses within a large temperature range. The $Li_2O \cdot 1.5SiO_2$ glass is less stable than the $Li_2O \cdot 2SiO_2$ glass.

1. Introduction

In the past decades, glass and glass–ceramics have attracted much attention because of their unique properties, such as excellent chemical durability, amazing optical transparency, and excellent electrical properties. Besides the traditional silicate glass, numerous new glass systems have been developed under the demand of modern industrial applications.[1–4] These glasses include phosphate glass,[5,6] amorphous metal alloy[7–9] and fluoride glass,[10,11] etc. The critical issue for the existing or potential applications of these glasses is their thermal stability against crystallization. They should be stable against thermal aging during their application. On the other hand, those glasses that serve as the intermediate products for fabricating glass–ceramics are expected to possess an appropriate thermal stability. They should be sufficiently stable against devitrification when the liquid glasses are quenched, but they should not be too stable to form nuclei and subsequently grow to crystals when they are annealed to form glass–ceramics.

Therefore, it is very important to evaluate the thermal stability of glasses against crystallization when they are subjected thermal aging during their application, or subjected to reheating on purpose during the fabrication of glass–ceramics. Dietzel[12] introduced the first simple criterion, $\Delta T = T_x - T_g$, where T_x is the crystallization starting temperature and T_g is the glass transition temperature. Besides T_x and T_g, other characteristic temperatures, such as the maximum peak temperature, T_p, and the melting temperature, T_m, are also used to evaluate the stability of glasses.[13–16] For example, Hruby[15] proposed the H_r criterion, $H_r = (T_x - T_g)/(T_m - T_p)$. Two other criteria developed from the H_r criterion are H' and S criteria, where $H' = (T_x - T_g)/T_g$ and $S = (T_p - T_x)(T_x - T_g)/T_g$, respectively.[16] Some authors[17–19] suggested that the crystallization activation energy, E, could also be used to evaluate the glass stability, but criteria based on the activation energy do not always fit with the actual experimental observation in some glass systems.[20] The crystallization rate constant, $k(T) = \nu \exp(-E/RT)$, takes into account both activation energy, E, and frequency factor, ν, so it was

believed to be a good criterion for the evaluation of the glass stability.[20,21] Unfortunately, it was found later that the $k(T)$ criterion is susceptible to the heating rate and temperature.[22,23] It goes the opposite way when heating rates are changed. More recently, two modified k criteria were proposed. One is $k_y(T) = \nu \exp[-E/RT \cdot (T_x - T_g)/T_m]$[22] and the other is $k_b(T) = \nu \exp(-E/RT \cdot H_r)$.[23]

In this paper, a new criterion for evaluating the thermal stability of glasses is proposed and its validity is ascertained by applying it to $Li_2O–SiO_2$ glass systems. Comparisons are also made between the new criterion and the existing criteria.

2. Theoretical Analysis

An isothermal transition of glasses can be described by the Johnson–Mehl–Avrami equation[24–26] 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 ν through the Arrhenius temperature dependence

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

where R is the gas constant.

Applying the Johnson–Mehl–Avrami equation to the nonisothermal transition of glasses, however, requires to take into account the dependence of k on time, t. Thus

$$x = 1 - \exp[-(\int_0^t k(t)dt)^n] \tag{3}$$

At a certain temperature, T_f, the crystallization rate of a glass, dx/dt reaches its maximum, i.e.,

$$\frac{d^2x}{dt^2}\Big|_{T=T_f} = 0 \tag{4}$$

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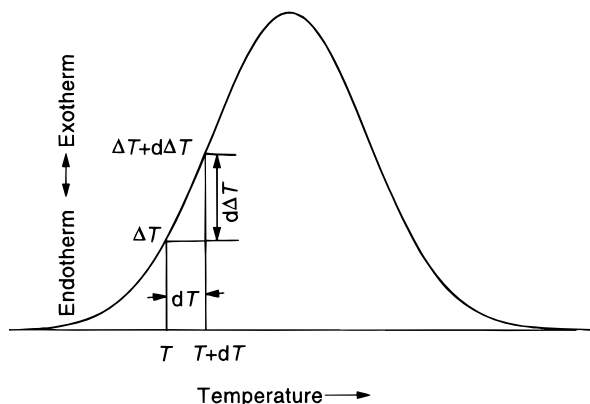*J. Phys. Chem. B, Vol. 103, No. 39, 1999* **8273**

Figure 1. Typical crystallization peak on a DTA curve.

By taking the second derivative of eq 3, combining it with eq 4, and following the procedure in ref 20, one can finally derive an equation relating the crystallization kinetics parameters of glasses to temperature, T_f, and heating rate, β

$$\ln T_f^2/\beta = E/RT_f + \ln E/R - \ln \nu \qquad (5)$$

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

$$dT = \beta dt \qquad (6)$$

Obviously a plot of $\ln(T_f^2/\beta)$ versus $1/T_f$ would be linear and activation energy, E, and frequency factor, ν, can be easily determined from the slope and the interception of the plot. It should be noted that, however, so far we have not explained how to determine the temperature, T_f, from nonisothermal experiments.

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

$$C_g[1 - (x + dx)]d\Delta T + C_c(x + dx)d\Delta T = hdx \qquad (7)$$

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 hdx on the right-hand side of eq 7 represents the heat generation due to the crystallization of the glass with amount of dx. The sum on the left-hand side of eq 7 is the total heat required to cause a temperature increase of $d\Delta T$ for the crystalline fraction, $(x + dx)$, and the remaining glass, $[1 - (x + dx)]$.

Rearrangement of eq 7 yields

$$[C_g + (C_c - C_g)x]d\Delta T = hdx \qquad (8)$$

For most glass systems, the difference between C_c and C_g is very small. Since x is always less than 1, $(C_c - C_g)x$ is much less than C_g and therefore it can be neglected in eq 8. Thus,

$$C_g d\Delta T = hdx \qquad (9)$$

Derivatives of eq 9 yield

$$\frac{dx}{dt} = \frac{C_g}{h}\frac{d\Delta T}{dt} = \frac{\beta C_g}{h}\frac{d\Delta T}{dT} \qquad (10)$$

$$\frac{d^2x}{dt^2} = \frac{C_g}{h}\frac{d^2\Delta T}{dt^2} = \frac{\beta^2 C_g}{h}\frac{d^2\Delta T}{dT^2} \qquad (11)$$

Equation 10 indicates that the crystallization rate, dx/dt, is proportional to the slopes of DTA curves, $d\Delta T/dT$. Correspondingly, eq 11 indicates that the crystallization rate, dx/dt, reaches its maximum at the inflection point temperature, T_f, on the DTA curves. Now it is clear that the temperature T_f in eq 5 is just the inflection point temperature on DTA curves.

Since both the formation of glasses and their crystallization are the kinetic processes, it is reasonable to evaluate the thermal stability of glasses by the kinetic parameter, $k(T)$. Furthermore, a thermodynamic factor, $T_p - T_f$, takes into account the strong dependence of the shape of a DTA curve on the heating rate. Therefore, a new criterion is finally defined as

$$k_f(T) = \nu \exp[-E/RT \cdot (T_p - T_f)/T_f] \qquad (12)$$

Similar to the existing $k(T)$ criteria, the greater values of $k_f(T)$, the poorer the stability of glasses.

3. Experimental Procedures

$Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 1.5SiO_2$ glasses were employed for this investigation. It is well known that the Li_2O-SiO_2 glass system exhibits strong bulk crystallization. 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 glasses were quenched by pouring them into a cold copper mold. The amorphous nature of the as-quenched glasses was confirmed by X-ray diffraction (XRD).

Glass powders of 200 ± 5 mg with an average size of 90 μm were employed for each DTA run with the reference material of alumina. Temperature calibrations of the instrument were performed by using the well-determined melting temperature of high-purity indium. The heating rates were carefully selected from 2 °C/min to 20 °C/min because the DTA curves show appropriate shapes for data analyses. The maximum peak temperature, T_p, was determined directly from DTA curves. To determine the inflection point temperature, T_f, DTA curves were differentiated and thereby derivative differential thermal analysis (DDTA) curves were generated. Then the inflection point temperature, T_f, was determined as the peak temperature on DDTA curves. A minimum of five samples was employed for each isothermal and nonisothermal determination.

4. Result and Discussion

The typical DTA and DDTA curves of $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 1.5SiO_2$ glasses at the heating rate of 10 °C/min are shown in Figure 2 and Figure 3, respectively. The glass transformation temperature, T_g, the crystallization starting temperature, T_x, the maximum peak temperature, T_p, and the melting point temperature, T_m, were directly determined from DTA curves. The inflection point temperature, T_f, was determined from the maximum peak temperature on the DDTA curve. All of these characteristic temperatures are summarized in Table 1.

Apparently, all of the characteristic temperatures of the studied glasses increase with the increasing heating rates. The glass transition temperature, T_g, and the maximum peak temperature, T_p, decrease with the increase of the ratio of Li_2O/SiO_2. In lithia-rich solid solutions, it is believed that the structure should consist of silicate sheets in which some of the constituent $[SiO_4]$ tetrahedra are replaced by $[LiO_4]$ tetrahedra; the sheets should be connected by the layers of lithium ions.[27] For the

TABLE 1: Characteristic Parameters of Li₂O·2SiO₂ and Li₂O·1.5SiO₂ Glasses

glass	β/K·min^{-1}	T_g/°C	T_x/°C	T_p/°C	T_f/°C	T_m/°C	ΔT/°C	H_r	H'	S	E/RT_p
Li₂O·2SiO₂	2	443	530	587	560	1020	87	0.201	0.122	6.93	32.7
	4	452	541	602	574	1024	89	0.211	0.123	7.49	32.2
	8	458	556	619	590	1027	98	0.240	0.134	8.45	31.6
	10	462	561	626	596	1031	99	0.244	0.135	8.76	31.3
	12	467	567	633	603	1033	100	0.250	0.135	8.92	31.1
	15	473	574	640	609	1037	101	0.254	0.135	8.94	30.8
	20	481	582	647	616	1042	101	0.256	0.134	8.71	30.6
Li₂O·1.5SiO₂	2	425	514	569	543	1126	89	0.160	0.128	7.01	33.4
	4	433	527	584	557	1130	94	0.172	0.133	7.59	32.9
	8	440	539	599	571	1135	99	0.185	0.139	8.33	32.3
	10	444	545	606	577	1139	101	0.189	0.141	8.59	32.0
	12	449	551	610	581	1143	102	0.191	0.141	8.34	31.9
	15	454	557	616	586	1147	103	0.194	0.142	8.36	31.7
	20	460	564	623	593	1152	104	0.197	0.142	8.37	31.4
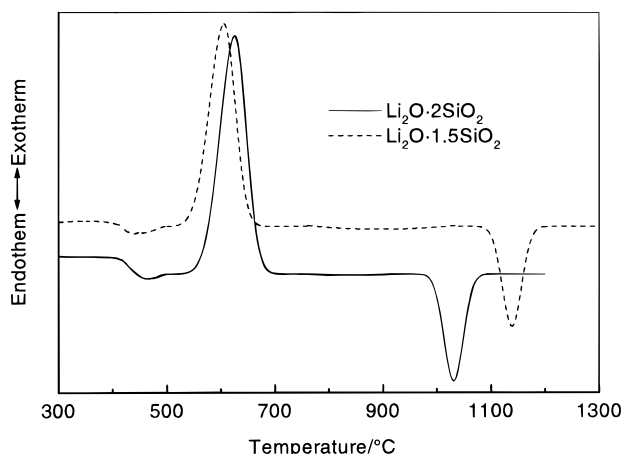
Figure 2. DTA curves of Li₂O·2SiO₂ and Li₂O·1.5SiO₂ glasses at various heating rates.
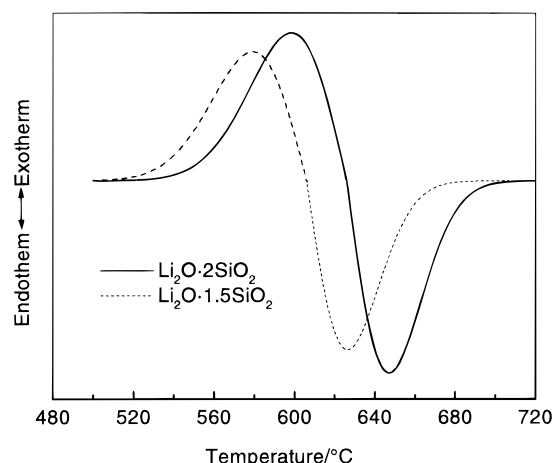
Figure 3. DDTA curves of Li₂O·2SiO₂ and Li₂O·1.5SiO₂ glasses at various heating rates.

Li₂O·1.5SiO₂ glass which contains 60 mol % SiO₂, its composition is beyond the range where complete Li₂O·2SiO₂ solid solution can be found, more lithium ions are expected to be at the interstitial sites of the network as glass modifier, which contributes the decrease of T_g and T_p. The melting point temperature, T_m, of the Li₂O·1.5SiO₂ glass is higher than that of Li₂O·sSiO₂ because its composition deviates from the stoichiometry of Li₂O·2SiO₂.[19]

To determine the kinetic parameters of the crystallization, the plot of $\ln(T_f^2/\beta)$ versus $1/T_f$ is given in Figure 4. On the basis of eq 5, the activation energy, E, and the frequency factor,
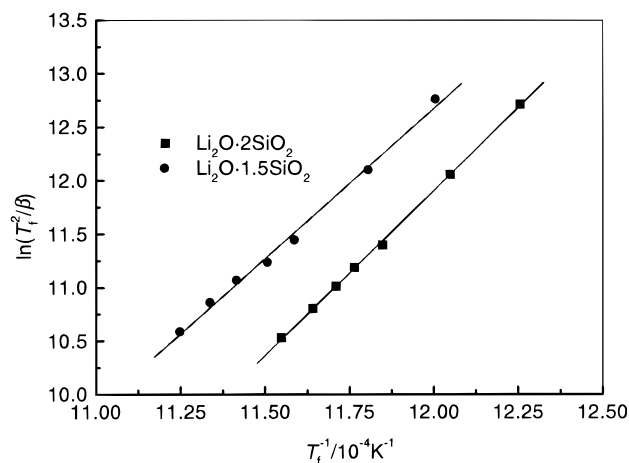
Figure 4. Plots of $\ln(T_f^2/\beta)$ versus $1/T_f$.

TABLE 2: Least-Square Fitting to Evaluate the Plots of $\ln(T_f^2/\beta)$ vs $1/T_f$

| glass	$\ln(T_f^2/\beta)$	E/kJ·mol^{-1}	ν/s^{-1}	r^a
Li₂O·2SiO₂	$28159/T_f - 21.11$	234	6.9×10^{11}	0.9974
Li₂O·1.5SiO₂	$30889/T_f - 25.16$	257	4.3×10^{13}	0.9996

^{a} r is the correlation coefficient.

ν, are evaluated by the least-squares fitting method. The results of the calculations are summarized in Table 2.

The existing stability criterion parameters based on these characteristic temperatures are also listed in Table 1. The greater these parameters, the more stable the glass should be. Branda et al. suggested that E/RT_p could also be used to evaluate the stability of glasses. Higher values of E/RT_p imply greater devitrification tendency. According to E/RT_p criterion, glass Li₂O·2SiO₂ is more stable than glass Li₂O·1.5SiO₂, which is consistent with the evaluation of the H_r criterion. On the contrary, ΔT and H' criteria indicate that glass Li₂O·1.5SiO₂ is more stable than glass Li₂O·2SiO₂. The S criterion fails to evaluate the stability of these two glasses because it is not self-consistent, i.e., it gives contrary evaluations at the different heating rates. As discussed above, more lithium ions act as the network modifier in Li₂O·1.5SiO₂ glass than in Li₂O·2SiO₂ glass, so Li₂O·1.5SiO₂ glass should be easier to devitrify and therefore it should be less stable. As shown in Table 1, the values of ΔT, H', and S for the studied glasses are rather close and susceptible to the heating rate, so any error in determining the characteristic temperatures would have resulted in opposite evaluation on the stability of the glasses. The E/RT_p criterion fits with the experimental observation. However, as shown in Table 1, the values of E/RT_p for the studied two glasses are
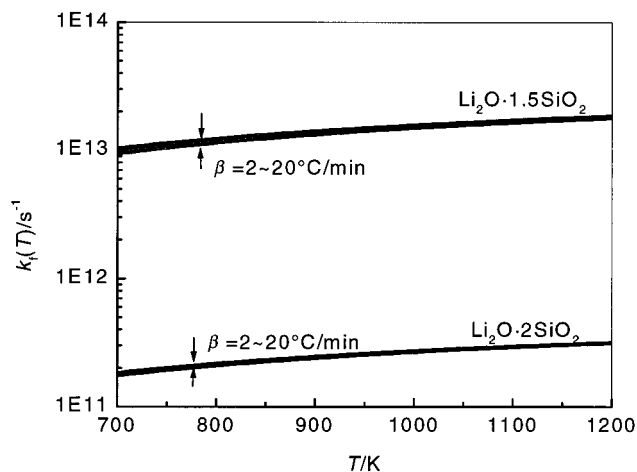
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TABLE 3: Kinetic Parameters $k(T)$, $k_y(T)$, $k_b(T)$, and $k_f(T)$ for $Li_2O\cdot2SiO_2$ and $Li_2O\cdot1.5SiO_2$ Glasses

glass	β/K·min^{-1}	$k(T_p)$/s^{-1}	$K_y(T_p)$/s^{-1}	$k_b(T_p)$/s^{-1}	$k_f(T_p)$/s^{-1}	$k_f(T_f)$/s^{-1}	$k_f(T_g)$/s^{-1}
$Li_2O\cdot2SiO_2$	2	4.16×10^{-3}	7.62×10^{10}	9.59×10^{8}	2.39×10^{11}	1.93×10^{11}	2.31×10^{11}
	4	7.29×10^{-3}	7.58×10^{10}	7.78×10^{8}	2.38×10^{11}	1.91×10^{11}	2.30×10^{11}
	8	1.35×10^{-2}	6.39×10^{10}	3.51×10^{8}	2.39×10^{11}	1.89×10^{11}	2.31×10^{11}
	10	1.72×10^{-2}	6.40×10^{10}	3.26×10^{8}	2.34×10^{11}	1.84×10^{11}	2.25×10^{11}
	12	2.19×10^{-2}	6.39×10^{10}	2.91×10^{8}	2.38×10^{11}	1.88×10^{11}	2.29×10^{11}
	15	2.78×10^{-2}	6.40×10^{10}	2.70×10^{8}	2.33×10^{11}	1.83×10^{11}	2.25×10^{11}
	20	3.52×10^{-2}	6.56×10^{10}	2.75×10^{8}	2.37×10^{11}	1.88×10^{11}	2.29×10^{11}
$Li_2O\cdot1.5SiO_2$	2	5.03×10^{-3}	4.19×10^{12}	1.22×10^{11}	1.34×10^{13}	1.05×10^{13}	1.29×10^{13}
	4	9.55×10^{-3}	3.84×10^{12}	8.68×10^{10}	1.33×10^{13}	1.04×10^{13}	1.28×10^{13}
	8	1.78×10^{-2}	3.56×10^{12}	6.19×10^{10}	1.33×10^{13}	1.02×10^{13}	1.28×10^{13}
	10	2.35×10^{-2}	3.48×10^{12}	5.51×10^{10}	1.30×10^{13}	0.99×10^{13}	1.25×10^{13}
	12	2.76×10^{-2}	3.46×10^{12}	5.32×10^{10}	1.31×10^{13}	1.01×10^{13}	1.26×10^{13}
	15	3.50×10^{-2}	3.46×10^{12}	5.09×10^{10}	1.28×10^{13}	0.98×10^{13}	1.23×10^{13}
	20	4.59×10^{-2}	3.47×10^{12}	4.90×10^{10}	1.30×10^{13}	1.00×10^{13}	1.25×10^{13}
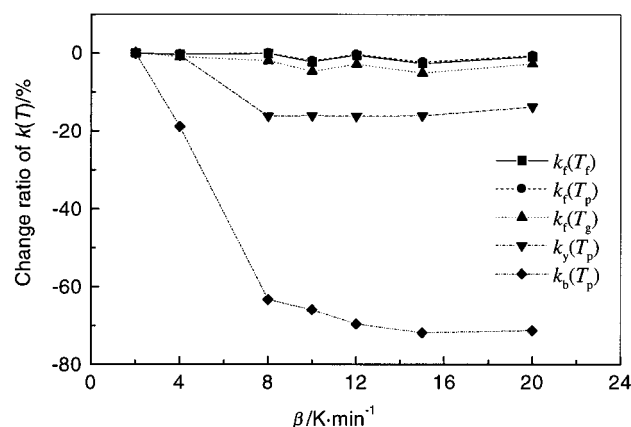
Figure 5. Susceptibility of $k_b(T)$, $k_b(T)$, and $k_f(T)$ on the heating rate of $Li_2O\cdot2SiO_2$.
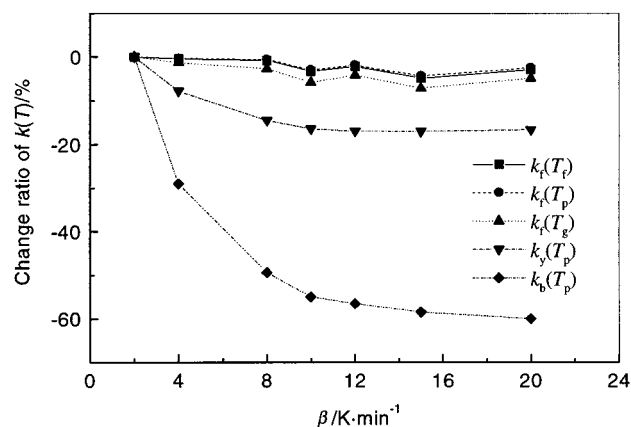
Figure 6. Susceptibility of $k_y(T)$, $k_b(T)$, and $k_f(T)$ on the heating rate of $Li_2O\cdot1.5SiO_2$.

also very close. Extreme accuracy in determining the vaules of E and T_p is required for correct evaluations. Otherwise, contrary evaluation could have been given by E/RT_p criterion.

Criteria based on the crystallization rate constant, k, have also been proposed to evaluate the thermal stability of glasses. The greater the values of k, the poorer stability of glasses. The values of $k(T)$, $k_y(T)$, $k_b(T)$, and $k_f(T)$ criteria for $Li_2O\cdot2SiO_2$ and $Li_2O\cdot1.5SiO_2$ glasses are calculated and listed in Table 3. All of these criteria indicate that $Li_2O\cdot2SiO_2$ is more stable than $Li_2O\cdot1.5SiO_2$, which is consistent with the evaluation of the H_r criterion and experimental observation. It should be noted that $k(T)$ is much more significantly affected by the heating rate than $k_y(T)$, $k_b(T)$, and $k_f(T)$ criteria. Its values can vary one order in magnitude as the heating rates vary from 2 °C/min to 20 °C/min. For a further comparison of the dependence of $k_y(T)$, $k_b(T)$, and $k_f(T)$ on the heating rate, the ratios of the changes of $k_y(T)$, $k_b(T)$, and $k_f(T)$ values at various heating rates to those values at the heating rate of 2 °C/min are shown in Figure 5 and Figure 6 for $Li_2O\cdot2SiO_2$ and $Li_2O\cdot1.5SiO_2$ glasses, respectively. It is clearly shown that $k_f(T)$ is almost constant at various heating rates, while $k_y(T)$ and $k_b(T)$ changes with the heating rates. Comparison of values of $k_f(T)$ within a large temperature ranges for $Li_2O\cdot2SiO_2$ and $Li_2O\cdot1.5SiO_2$ glasses is made at various heating rates and is shown in Figure 7. Again, for each glass, its $k_f(T)$ curves at various heating rates overlap, which verifies that $k_f(T)$ is less affected by the heating rate. At a given temperature, the values of $k_f(T)$ for $Li_2O\cdot2SiO_2$ glass are much lower than that of $Li_2O\cdot1.5SiO_2$ glass, so the former is much more stable than the latter.

Figure 7. Plots of $k_f(T)$ versus T at various heating rates to verify the stable order.

5. Conclusions

A new criterion $k_f(T)$ has been proposed for evaluating the stability of glasses from DTA data. Not only the crystallization kinetic parameters such as activation energy, E, and frequency factor, ν, but also a thermodynamic factor $(T_p - T_f)/T_f$ are taken into account in the $k_f(T)$ criterion. A higher value of $k_f(T)$ indicates a poorer stability of glasses. The validity of the criterion is ascertained by applying it to evaluate the stability of $Li_2O\cdot2SiO_2$ and $Li_2O\cdot1.5SiO_2$ glasses. It is shown that the new criterion $k_f(T)$ is almost independent of the heating rate. It can be used to evaluate the thermal stability of glasses in a large range of temperature, while the existing criteria are either

affected by the heating rate or they are not suitable for evaluating the stability of these glasses at all. Finally, it is verified that the $Li_2O \cdot 1.5SiO_2$ glass is less stable than the $Li_2O \cdot 2SiO_2$ glass.

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