Journal of the European Ceramic Society **18** (1998) 1131–1137
PII: S0955-2219(98)00003-X
0955-2219/98/$19.00 + 0.00

A New Criterion for the Stability of Glasses

Ren-Guan Duan,* Kai-Ming Liang and Shou-Ren Gu

Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

(Received 10 September 1997; accepted 19 December 1997)

Abstract

A new criterion for the stability of glasses, $k_D(T)$, $k_D(T) = v \cdot exp\ (-\frac{E}{RT} \cdot D)$, *where* $D = \frac{T_c(T_p - T_c)}{T_l(T_l - T_g)}$, was proposed, which included both the kinetic factor and the thermodynamic factor by means of bringing the correction factor, D, *into the crystallization kinetic parameter,* $k(T)$, $k(T) = v \cdot exp\ (-\frac{E}{RT})$. *The lower the value of* $k_D(T)$, *the more stable glass. The new criterion,* $k_D(T)$, *was not influenced by the heating rate of differential thermal analysis (DTA). Especially when the values of frequency factor* v *of glasses were near, the new criterion,* $k_D(T)$, *could accurately determine the stability of the glasses. The correctness of the new criterion,* $k_D(T)$, *had been verified through being used in the* $CaO–Al_2O_3–SiO_2$ *system glasses and the Nd doped fluorozirconate glasses.* *© 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

The stability of glasses have been defined as the resistance of glasses towards devitrification upon reheating (especially near or somewhat above the glass transition temperature, T_g).[1] Determining the stability of the glasses is very important for technological applications. For example, when optical fibers are prepared, if the glasses are not stable, then it will be difficult to draw fibers without glass crystallization. Also, when glasses are used for radioactive waste disposal applications, the long-term devitrification of glasses is harmful.[2,3]

Differential thermal analysis (DTA) can show the characteristic temperatures of glasses, such as glass transition temperature (T_g), beginning crystallization temperature (T_c), crystallization peak temperature (T_p), and liquification temperature (T_l). In the past, many criteria for the stability of glasses had been proposed on the basis of the characteristic temperatures measured by DTA. Uhlmann[4] proposed that the value of T_g/T_l could judge the stability of glasses. Gelsing[5] suggested that the critical cooling rate Q could judge the stability of glasses and that the low value of Q meant a good stability of glasses. Because the critical cooling rate Q is very difficult to measure precisely, the criterion, Q, cannot be applied extensively. Wakasugi[6] derived a linear relationship between T_c/T_l and $\log Q$, $\frac{T_c}{T_l} = -(0{\cdot}031 \pm 0{\cdot}006) \log Q + (0{\cdot}70 \pm 0{\cdot}05)$. The value of Q can be calculated according to the values of T_c and T_l. The above equation cannot be applied to all glass systems and only to some limited glass systems, such as $Na_2O–B_2O_3–Al_2O_3$ system. A quantitative measure of glass stability is $T_p - T_g$.[7–9] Because T_p is a function of heating rate of DTA, the value of $T_p - T_g$ can be influenced by the heating rate. Hruby[10] proposed a criterion, k_{gl}, $k_{gl} = \frac{T_c - T_g}{T_l - T_p}$. The low value of k_{gl} means a good stability. Iqbal[11] firstly combined the thermodynamic factor with kinetic factor and proposed a stable criterion (ST) for glasses, $ST = \frac{T_c - T_g}{Q}$. Because the value of Q is very difficult to measure precisely, its application is very limited. Surinach *et al.*[12] used the crystallization kinetic parameter, $k(T_g)$, to determine the stability of glasses, and suggested that the low value of $k(T_g)$ meant a good stability. Hu Lili *et al.*[13] suggested that the crystallization kinetic factor, $k(T)$ or $k(T_p)$, could judge the stability of glasses, and realized that the low value of $k(T)$ or $k(T_p)$ meant a good stability. The criterion, $k(T_g)$, $k(T)$ or $k(T_p)$, cannot accurately judge the stability of glasses, because they are severely influenced by heating rate of DTA. Their applications are also very limited. Yang Qiuhong *et al.*[14] brought the stability factor, A, $A = \frac{\Delta T}{T_l}$, where $\Delta T = T_c - T_g$, into the crystallization kinetic factor, $k(T)$, and proposed a criterion, $k_y(T)$, $k_y(T) = \nu \cdot \exp\ (-\frac{E}{RT} \cdot A)$. The low value of $k_y(T)$ means a good stability. $k_y(T)$ cannot determine the stability of glasses when either the frequency factor ν or the crystallization activation energy E among the studied glasses are near.

---

*To whom correspondence should be addressed.

The stability of glasses is connected to both thermodynamic factor and kinetic factor. The above stability criterions are limited because they only contain either the thermodynamic factor or kinetic factor, or they contain both the thermodynamic factor and kinetic factor but they are still influenced by the heating rate of DTA. Until now there is not a criterion which can be suitable for all glass systems. The purpose of this paper is to suggest a new criterion which can judge the stability of glasses more extensively. The CaO–Al_2O_3–SiO_2 system glasses are very universal and have been used in many fields. Because the CaO–Al_2O_3–SiO_2 system glasses are not easy to crystallize, it is very difficult to determine the difference of stability among the glasses with approximate compositions. This paper use them to verify the correctness of the newly proposed criterion. Simultaneously, this paper also use the Nd doped fluorozirconate glasses in the literature[14] to test the correctness of the new criterion. Of course, it is necessary to continue to use other system glasses to verify the correctness of the newly proposed criterion.

2 Experimental Procedure

2.1 Preparing samples

The compositions of glasses are listed in Table 1. The glasses were prepared by melting analytical grade reagents, $CaCO_3$, Al_2O_3, SiO_2, Na_2CO_3 and TiO_2, in the alumina crucibles in an electric furnace with $SiMo_2$ elements for 4 h, in the temperature range 1450∼1500°C. The melts were quenched in air and then annealed at 700°C for 18 h.

2.2 Differential thermal analysis

Differential thermal analysis was carried out by an instrument of Model Dupont 2100, and Al_2O_3 powders were the reference material, which was conducted at a rate of 5, 8, 10 and 15°C min^{-1}, respectively.

2.3 Measuring stability of glasses

The glasses were heat-treated at the different temperatures and times and the stability of glasses were measured.

3 Theoretical analysis

The JMA equation[15,16] is usually applied to study the nucleation and growth of crystals in glasses by using the method of DTA. The isothermal JMA equation can be written in the form:

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

where x is the volume fraction of crystals at time t; n is numerical constant which is related to the crystallization mechanism ($n = 1$ means surface domination crystallization, and $n = 3$ means bulk crystallization from a constant number of nuclei); k is the crystallization kinetic parameter. The relationship between k and temperature T can be written as

$$k = \nu \cdot \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where ν is frequency factor; E is the crystallization activation energy; R is the universal gas constant, and T is temperature (K).

For a non-isothermal process of DTA:

$$T = T_0 + \alpha t \tag{3}$$

$$\mathrm{d}T = \alpha \mathrm{d}t \tag{4}$$

where T_0 is the beginning temperature and T is a temperature at the time t. α is the heating rate of DTA. The non-isothermal MA equation can be written as

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

At the crystallization peak temperature, T_p, the crystallization rate, $\mathrm{d}x/\mathrm{d}t$, reach the maximum value.

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2}\Big|_{T=T_p} = 0 \tag{6}$$

Let $T \gg T_0$, after a series of calculations[17] the following equation can be obtained:

Table 1. Compositions and kinetic parameters of CaO–Al_2O_3–SiO_2 system glasses

Glass no.	*Compositon (wt%)*					*Kinetic parameter*	
	CaO	*Al_2O_3*	*SiO_2*	*Na_2O*	*TiO_2*	*E ($kJ mol^{-1}$)*	*(νmin^{-1})*
1	13∼17	20∼24	61∼65	0	0	338·96	$2{\cdot}748\times10^{12}$
2	13∼17	20∼24	61∼65	1∼3	0	443·39	$1{\cdot}441\times10^{17}$
3	13∼17	20∼24	61∼65	0	3∼5	441·47	$1{\cdot}521\times10^{17}$
4	13∼17	20∼24	61∼65	1∼3	3∼5	240·69	$6{\cdot}595\times10^{8}$

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \ln\left(\frac{E}{R}\right) - \ln \nu + \frac{E}{RT_p} \qquad (7)$$

According to the results of DTA at different heating rate α, we can obtain different values of T_p. Plot the curve of $\ln(T_p^2/\alpha)$ versus $1/T_p$, we can acquire a straight line whose slope is E/R. After the values of E and ν are evaluated, the equation, $k(T) = \nu{\cdot}\exp(-\frac{E}{RT})$, can be obtained.

Because the forming process of glasses is a kinetic one, it is reasonable to use the crystallization kinetic parameter $k(T)$ to judge the stability of glasses. The structures of glasses are very particular and there are a series of characteristic temperatures. At same characteristic temperatures there are some properties that are nearly same for different glasses, such as at the transition temperature, T_g, there being almost the same viscosity, 10^{12} pa·s, for different glasses. So, in order to compare the stability of different glasses, it is reasonable to compare the crystallization kinetic parameter, $k(T)$, at some characteristic temperatures, such as $T = T_g, T_c, T_p$ and T_l. These characteristic temperatures, in particular T_g, are severely influenced by the heating rate of DTA, so the criterion, $k(T)$, is also severely influenced by the heating rate. In order to avoid or decrease the influence of heating rate of DTA, on the basis of the $k(T)$ this paper propose a new criterion, $k_D(T), k_D(T) = \nu{\cdot}\exp(-\frac{E}{RT}.D)$, by bringing the correction factor, D, $D = \frac{T_c(T_p-T_c)}{T_l(T_l-T_g)}$, into the crystallization kinetic parameter $k(T)$. The effect of heating rate of DTA on E/RT is negative and the effect on the correction factor D is positive, which leads to that the heating rate has a very slightly or no effect on $(E/RT){\cdot}D$. The criterion of $k_D(T)$ includes both thermodynamic factor and kinetic factor, which cannot be influenced or is influenced very slightly by the heating rate of DTA. It can be applied more extensively.

4 Results

The values of various kinetics criteria for the stability of Nd doped fluorozirconate glasses in the literature[9] were calculated and listed in the Table 2. Figure 1 shows the DTA curves of CaO–Al_2O_3–SiO_2 system glasses at $\alpha = 10°C\,min^{-1}$. Plot the curve of $\ln(\frac{T_p^2}{\alpha})$ versus $\frac{1}{T_p}$ (Fig. 2) according to the equation of $\ln(\frac{T_p^2}{\alpha}) = \ln(\frac{E}{R}) - \ln\nu + \frac{E}{RT_p}$. Calculate the crystallization activation energy E and frequency factor ν of various samples of CaO–Al_2O_3–SiO_2 system glasses and list them in Table 1. The values of the characteristic temperatures of CaO–Al_2O_3–SiO_2 system glasses at different heating rates of DTA and the values of A and D which are

Table 2. Values of various kinetic criterions for the stability of Nd doped fluorozirconate glasses at various heating rates

Sample no.	$K(T_g)$	$K(T_p)$	$K_y(T_g)$	$K_y(T_c)$	$K_y(T_p)$	$K_D(T_g)$	$K_D(T_c)$	$K_D(T_p)$
$\alpha = 4°C\,min^{-1}$								
1	$2{\cdot}45\times10^{-3}$	0·377	$3{\cdot}65\times10^{10}$	$5{\cdot}87\times10^{10}$	$6{\cdot}20\times10^{10}$	$3{\cdot}87\times10^{11}$	$4{\cdot}55\times10^{11}$	$4{\cdot}63\times10^{11}$
2	$2{\cdot}17\times10^{-3}$	0·351	$6{\cdot}26\times10^{8}$	$1{\cdot}08\times10^{9}$	$1{\cdot}16\times10^{9}$	$6{\cdot}11\times10^{9}$	$7{\cdot}51\times10^{9}$	$7{\cdot}70\times10^{9}$
3	$2{\cdot}64\times10^{-3}$	0·252	$6{\cdot}71\times10^{6}$	$1{\cdot}11\times10^{7}$	$1{\cdot}19\times10^{7}$	$3{\cdot}99\times10^{7}$	$4{\cdot}96\times10^{7}$	$5{\cdot}12\times10^{7}$
4	$3{\cdot}45\times10^{-4}$	0·683	$2{\cdot}44\times10^{14}$	$4{\cdot}32\times10^{14}$	$5{\cdot}23\times10^{14}$	$1{\cdot}56\times10^{14}$	$2{\cdot}92\times10^{14}$	$3{\cdot}60\times10^{14}$
5	$3{\cdot}12\times10^{-4}$	0·299	$5{\cdot}74\times10^{9}$	$1{\cdot}19\times10^{10}$	$1{\cdot}39\times10^{10}$	$3{\cdot}23\times10^{10}$	$5{\cdot}07\times10^{10}$	$5{\cdot}57\times10^{10}$
6	$5{\cdot}99\times10^{-4}$	0·293	$2{\cdot}80\times10^{9}$	$3{\cdot}80\times10^{9}$	$4{\cdot}74\times10^{9}$	$1{\cdot}80\times10^{8}$	$3{\cdot}32\times10^{8}$	$5{\cdot}18\times10^{8}$
$\alpha = 8°C\,min^{-1}$								
1	$4{\cdot}36\times10^{-3}$	0·597	$3{\cdot}76\times10^{10}$	$6{\cdot}01\times10^{10}$	$6{\cdot}34\times10^{10}$	$3{\cdot}75\times10^{11}$	$4{\cdot}41\times10^{11}$	$4{\cdot}50\times10^{11}$
2	$2{\cdot}72\times10^{-3}$	0·533	$6{\cdot}17\times10^{8}$	$1{\cdot}07\times10^{9}$	$1{\cdot}18\times10^{9}$	$2{\cdot}95\times10^{9}$	$4{\cdot}05\times10^{9}$	$4{\cdot}27\times10^{9}$
3	$3{\cdot}64\times10^{-3}$	0·405	$5{\cdot}67\times10^{6}$	$9{\cdot}91\times10^{6}$	$1{\cdot}08\times10^{7}$	$3{\cdot}52\times10^{7}$	$4{\cdot}52\times10^{7}$	$4{\cdot}70\times10^{7}$
4	$6{\cdot}18\times10^{-4}$	0·767	$2{\cdot}58\times10^{14}$	$4{\cdot}52\times10^{14}$	$5{\cdot}26\times10^{14}$	$4{\cdot}48\times10^{14}$	$7{\cdot}34\times10^{14}$	$8{\cdot}39\times10^{14}$
5	$4{\cdot}05\times10^{-4}$	0·705	$6{\cdot}20\times10^{9}$	$1{\cdot}26\times10^{10}$	$1{\cdot}60\times10^{10}$	$4{\cdot}76\times10^{9}$	$1{\cdot}01\times10^{10}$	$1{\cdot}30\times10^{10}$
6	$9{\cdot}05\times10^{-4}$	0·692	$1{\cdot}89\times10^{9}$	$2{\cdot}81\times10^{9}$	$3{\cdot}64\times10^{9}$	$9{\cdot}16\times10^{7}$	$1{\cdot}99\times10^{8}$	$3{\cdot}33\times10^{8}$
$\alpha = 10°C\,min^{-1}$								
1	$4{\cdot}12\times10^{-3}$	0·703	$3{\cdot}21\times10^{10}$	$5{\cdot}34\times10^{10}$	$5{\cdot}67\times10^{10}$	$3{\cdot}39\times10^{11}$	$4{\cdot}08\times10^{11}$	$4{\cdot}17\times10^{11}$
2	$2{\cdot}87\times10^{-3}$	0·717	$6{\cdot}10\times10^{8}$	$1{\cdot}05\times10^{9}$	$1{\cdot}20\times10^{9}$	$1{\cdot}21\times10^{9}$	$1{\cdot}89\times10^{9}$	$2{\cdot}10\times10^{9}$
3	$3{\cdot}17\times10^{-3}$	0·585	$4{\cdot}89\times10^{6}$	$9{\cdot}00\times10^{6}$	$1{\cdot}02\times10^{7}$	$2{\cdot}05\times10^{7}$	$2{\cdot}93\times10^{7}$	$3{\cdot}15\times10^{7}$
4	$6{\cdot}71\times10^{-4}$	0·862	$2{\cdot}45\times10^{14}$	$4{\cdot}38\times10^{14}$	$5{\cdot}08\times10^{14}$	$6{\cdot}30\times10^{14}$	$9{\cdot}99\times10^{14}$	$1{\cdot}12\times10^{15}$
5	$4{\cdot}60\times10^{-4}$	0·893	$5{\cdot}60\times10^{9}$	$1{\cdot}17\times10^{10}$	$1{\cdot}51\times10^{10}$	$4{\cdot}26\times10^{10}$	$9{\cdot}34\times10^{9}$	$1{\cdot}22\times10^{10}$
6	$1{\cdot}01\times10^{-3}$	0·644	$2{\cdot}47\times10^{9}$	$3{\cdot}44\times10^{9}$	$4{\cdot}42\times10^{9}$	$6{\cdot}02\times10^{7}$	$1{\cdot}30\times10^{8}$	$2{\cdot}32\times10^{8}$
$\alpha = 16°C\,min^{-1}$								
1	$5{\cdot}16\times10^{-3}$	1·548	$2{\cdot}42\times10^{10}$	$4{\cdot}39\times10^{10}$	$4{\cdot}80\times10^{10}$	$2{\cdot}05\times10^{11}$	$2{\cdot}67\times10^{11}$	$2{\cdot}81\times10^{11}$
2	$3{\cdot}77\times10^{-3}$	0·891	$5{\cdot}49\times10^{8}$	$9{\cdot}81\times10^{8}$	$1{\cdot}10\times10^{9}$	$1{\cdot}44\times10^{9}$	$2{\cdot}15\times10^{9}$	$2{\cdot}42\times10^{9}$
3	$3{\cdot}62\times10^{-3}$	0·791	$4{\cdot}99\times10^{6}$	$9{\cdot}01\times10^{6}$	$1{\cdot}06\times10^{7}$	$7{\cdot}15\times10^{6}$	$1{\cdot}21\times10^{7}$	$1{\cdot}41\times10^{7}$
4	$9{\cdot}29\times10^{-4}$	1·704	$1{\cdot}86\times10^{14}$	$3{\cdot}55\times10^{14}$	$4{\cdot}21\times10^{14}$	$3{\cdot}29\times10^{14}$	$5{\cdot}82\times10^{14}$	$6{\cdot}76\times10^{14}$
5	$6{\cdot}71\times10^{-4}$	1·169	$3{\cdot}00\times10^{9}$	$7{\cdot}61\times10^{9}$	$9{\cdot}23\times10^{9}$	$1{\cdot}42\times10^{10}$	$2{\cdot}72\times10^{10}$	$3{\cdot}11\times10^{10}$
6	$1{\cdot}43\times10^{-3}$	1·060	$2{\cdot}71\times10^{9}$	$3{\cdot}15\times10^{9}$	$4{\cdot}13\times10^{9}$	$4{\cdot}05\times10^{7}$	$9{\cdot}40\times10^{7}$	$1{\cdot}78\times10^{8}$

Table 3. Characteristic temperatures (K) and value of *A* and *D* of CaO–Al_2O_3–SiO_2 system glasses at various heating rates

Sample no.	T_g	T_c	T_p	T_l	*A*	*D*	T_g	T_c	T_p	T_l	*A*	*D*
$\alpha = 5°C\,min^{-1}$							$\alpha = 8°C\,min^{-1}$					
1	1173	1298	1324	1493	0·08372	0·07064	1181	1303	1349	1511	0·08074	0·1202
2	1133	1253	1290	1476	0·08130	0·09157	1153	1253	1303	1478	0·06766	0·1304
3	1158	1258	1283	1482	0·06748	0·06550	1161	1253	1288	1483	0·06204	0·09184
4	1133	1201	1274	1486	0·04576	0·1671	1141	1201	1302	1512	0·03968	0·2162
$\alpha = 10°C\,min^{-1}$							$\alpha = 15°C\,min^{-1}$					
1	1183	1318	1358	1514	0·08917	0·1052	1188	1323	1369	1523	0·08864	0·1193
2	1159	1255	1311	1481	0·06482	0·1474	1163	1259	1323	1483	0·06473	0·1903
3	1163	1248	1287	1484	0·05728	0·1022	1166	1263	1303	1480	0·06554	0·08153
4	1141	1203	1307	1519	0·04082	0·2179	1143	1208	1339	1533	0·04240	0·2647

used to calculate the value of $k_y(T)$ and $k_D(T)$, respectively, are listed in Table 3. The values of various kinetics criteria for the stability of CaO–Al_2O_3–SiO_2 system glasses are listed in Table 4. Other criteria for the stability of CaO–Al_2O_3–SiO_2 system glasses are listed in Table 5.

The sequence of sample stability can be determined by keeping samples at a fixed temperature for different times and at a fixed time for different temperatures and then measuring the crystallization extent of samples. After experiment it can be determined that sample 3 is most stable and 4 is most unstable among the Nd doped fluorozirconate glasses in the literature.[14] According to the values listed in Table 2, the criterion of $k(T_g)$ cannot correctly judge the stability of the glasses. When the heating rates of DTA are 4, 8 and 16°C min^{-1}, respectively, $k(T_p)$ can correctly judge the stability of glasses, but when the heating rate is 10°C min^{-1}, it cannot correctly judge the stability. At the different heating rates, the criterion of $k(T_p)$ can lead to the different result of judgment. When $k_y(T)$ and $k_D(T)$ were used to judge the stability of the above glasses, they both can show the right judgement in spite of different heating rate α and different characteristic temperatures (T_g, T_c, T_p) of DTA. Table 6 shows that the frequency factors ν between samples 2 and 6 are near. Table 2 shows that the values of $k_y(T)$ between sample 2 and 6 are near but the values of $k_D(T)$ between them are very far. This means that when the frequency factors ν among the samples are near, the criterion of $k_D(T)$ has more advantages to judge the stability of glasses than $k_y(T)$.

Among the samples of CaO–Al_2O_3–SiO_2 system glasses in this paper, after measuring it can be known that the most stable sample is 4, and the sequence of stability is $4 > 1 > 2 > 3$. Table 4 shows that at any heating rate of DTA the criterion of $k(T_g)$ cannot correctly judge the stability of CaO–Al_2O_3–SiO_2 system glasses. The criterion of $k(T_p)$ can correctly judge the stability of the glasses only in the case that heating rate $\alpha = 5°C\ min^{-1}$. The criterion of $k_y(T)$ can supply a correct judgment for stability when $\alpha =$ 5, 8 and 10°C min^{-1}, respectively, but it cannot show a right result when $\alpha = 15°C\,min^{-1}$. According to the results of experiment, sample 3 is most unstable, but the criterion of $k_y(T)$ shows that sample 2 is most unstable. The criterion of $k_y(T)$ cannot correctly determine the stability of CaO–Al_2O_3–SiO_1 system glasses. Table 4 shows that the criterion of $k_D(T)$ is the uniquely right criterion for stability of CaO–Al_2O_3–SiO_2 system glasses in this paper.

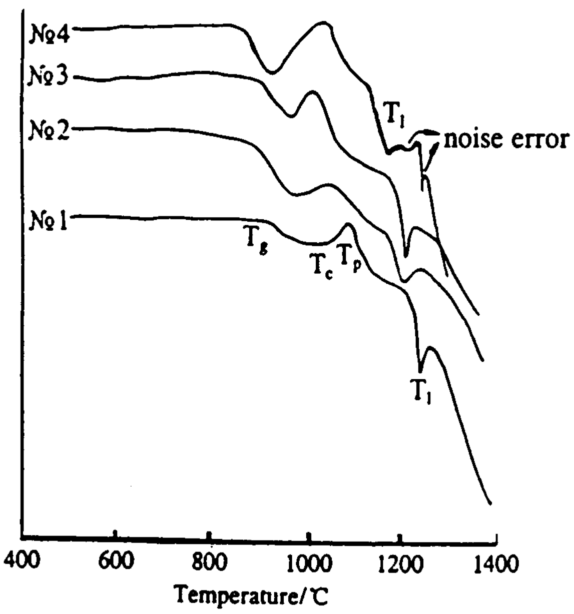

Fig. 1. DTA curves of CaO–Al_2O_3–SiO_2 system glasses.

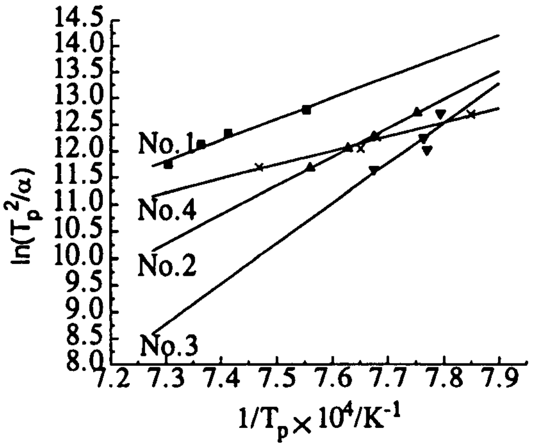

Fig. 2. Plots of $\ln(\frac{T_p^2}{\alpha}) - \frac{1}{T_p}$ for CaO–Al_2O_3–SiO_2 system glasses at $\alpha = 10°C\ min^{-1}$.

Table 4. Values of various kinetic criteria for the stability of CaO–Al_2O_3–SiO_2 system glasses at various heating rates of DTA

Sample no.	*$K(T_g)$*	*$K(T_p)$*	*$K_y(T_g)$*	*$K_y(T_c)$*	*$K_y(T_p)$*	*$K_D(T_g)$*	*$K_D(T_c)$*	*$K_D(T_p)$*
$\alpha = 5°C\,min^{-1}$								
1	$2{\cdot}21\times10^{-3}$	0·1163	$1{\cdot}50\times10^{11}$	$1{\cdot}98\times10^{11}$	$2{\cdot}09\times10^{11}$	$2{\cdot}36\times10^{11}$	$2{\cdot}99\times10^{11}$	$3{\cdot}12\times10^{11}$
2	$5{\cdot}21\times10^{-4}$	0·1601	$3{\cdot}14\times10^{15}$	$4{\cdot}53\times10^{15}$	$5{\cdot}00\times10^{15}$	$1{\cdot}94\times10^{15}$	$2{\cdot}92\times10^{15}$	$3{\cdot}27\times10^{15}$
3	$1{\cdot}85\times10^{-3}$	0·1614	$6{\cdot}89\times10^{15}$	$8{\cdot}81\times10^{15}$	$9{\cdot}32\times10^{15}$	$7{\cdot}55\times10^{15}$	$9{\cdot}58\times10^{15}$	$1{\cdot}01\times10^{16}$
4	$5{\cdot}28\times10^{-3}$	0·0892	$2{\cdot}05\times10^{8}$	$2{\cdot}19\times10^{8}$	$2{\cdot}33\times10^{8}$	$9{\cdot}22\times10^{6}$	$1{\cdot}18\times10^{7}$	$1{\cdot}48\times10^{7}$
$\alpha = 8°C\,min^{-1}$								
1	$2{\cdot}80\times10^{-3}$	0·2059	$1{\cdot}69\times10^{11}$	$2{\cdot}20\times10^{11}$	$2{\cdot}40\times10^{11}$	$4{\cdot}33\times10^{10}$	$6{\cdot}39\times10^{10}$	$7{\cdot}27\times10^{10}$
2	$1{\cdot}18\times10^{-3}$	0·2419	$6{\cdot}30\times10^{15}$	$8{\cdot}09\times10^{15}$	$9{\cdot}04\times10^{15}$	$3{\cdot}46\times10^{14}$	$5{\cdot}60\times10^{14}$	$6{\cdot}93\times10^{14}$
3	$2{\cdot}09\times10^{-3}$	0·1895	$8{\cdot}91\times10^{15}$	$1{\cdot}10\times10^{16}$	$1{\cdot}18\times10^{16}$	$2{\cdot}28\times10^{15}$	$3{\cdot}10\times10^{15}$	$3{\cdot}45\times10^{15}$
4	$6{\cdot}31\times10^{-3}$	0·1454	$2{\cdot}41\times10^{8}$	$2{\cdot}53\times10^{8}$	$2{\cdot}73\times10^{8}$	$2{\cdot}74\times10^{6}$	$3{\cdot}60\times10^{6}$	$5{\cdot}39\times10^{6}$
$\alpha = 10°C\,min^{-1}$								
1	$2{\cdot}96\times10^{-3}$	0·2515	$1{\cdot}27\times10^{11}$	$1{\cdot}74\times10^{11}$	$1{\cdot}89\times10^{11}$	$7{\cdot}32\times10^{10}$	$1{\cdot}06\times10^{11}$	$1{\cdot}17\times10^{11}$
2	$1{\cdot}50\times10^{-3}$	0·3105	$7{\cdot}30\times10^{15}$	$9{\cdot}17\times10^{15}$	$1{\cdot}03\times10^{16}$	$1{\cdot}63\times10^{14}$	$2{\cdot}74\times10^{14}$	$3{\cdot}59\times10^{14}$
3	$2{\cdot}26\times10^{-3}$	0·1835	$1{\cdot}11\times10^{16}$	$1{\cdot}33\times10^{16}$	$1{\cdot}43\times10^{16}$	$1{\cdot}43\times10^{15}$	$1{\cdot}97\times10^{15}$	$2{\cdot}24\times10^{15}$
4	$6{\cdot}31\times10^{-3}$	0·1583	$2{\cdot}34\times10^{8}$	$2{\cdot}47\times10^{8}$	$2{\cdot}67\times10^{8}$	$2{\cdot}62\times10^{6}$	$3{\cdot}48\times10^{6}$	$5{\cdot}29\times10^{6}$
$\alpha = 15°C\,min^{-1}$								
1	$3{\cdot}43\times10^{-3}$	0·3201	$1{\cdot}31\times10^{11}$	$1{\cdot}79\times10^{11}$	$1{\cdot}96\times10^{11}$	$4{\cdot}58\times10^{10}$	$6{\cdot}96\times10^{10}$	$7{\cdot}87\times10^{10}$
2	$1{\cdot}75\times10^{-3}$	0·4491	$7{\cdot}41\times10^{15}$	$9{\cdot}29\times10^{15}$	$1{\cdot}06\times10^{16}$	$2{\cdot}34\times10^{13}$	$4{\cdot}55\times10^{13}$	$6{\cdot}72\times10^{13}$
3	$2{\cdot}54\times10^{-3}$	0·3046	$7{\cdot}69\times10^{15}$	$9{\cdot}67\times10^{15}$	$1{\cdot}05\times10^{16}$	$3{\cdot}71\times10^{15}$	$4{\cdot}94\times10^{15}$	$5{\cdot}49\times10^{15}$
4	$6{\cdot}60\times10^{-3}$	0·2688	$2{\cdot}25\times10^{8}$	$2{\cdot}39\times10^{8}$	$2{\cdot}64\times10^{8}$	$8{\cdot}08\times10^{5}$	$1{\cdot}16\times10^{6}$	$2{\cdot}17\times10^{6}$

Table 5. Values of other criteria for the stability of Cao–Al_2O_3–SiO_2 system glasses at various heating rates of DTA. (The values of Q are determined on the basis of the equation, $\frac{T_c}{T_l} = -0{\cdot}031 \log Q + 0{\cdot}70$, which was derived by Wakasugi[6])

Sample no.	*T_g/T_l*	*T_c/T_l*	*Q*	*$T_p - T_g$*	*K_{gl}*	*ST*	*$T_c - T_g$*
$\alpha = 5°C\,min^{-1}$							
1	0·7857	0·8694	$3{\cdot}432\times10^{-6}$	151	0·7396	$3{\cdot}642\times10^{7}$	125
2	0·7676	0·8489	$1{\cdot}573\times10^{-5}$	157	0·6452	$7{\cdot}629\times10^{6}$	120
3	0·7814	0·8489	$1{\cdot}573\times10^{-5}$	125	0·5025	$6{\cdot}357\times10^{6}$	100
4	0·7624	0·8082	$3{\cdot}234\times10^{-4}$	141	0·3208	$2{\cdot}103\times10^{5}$	68
$\alpha = 8°C\,min^{-1}$							
1	0·7816	0·8623	$5{\cdot}815\times10^{-6}$	168	0·7531	$2{\cdot}098\times10^{7}$	122
2	0·7801	0·8478	$1{\cdot}707\times10^{-5}$	150	0·5714	$5{\cdot}858\times10^{6}$	122
3	0·7829	0·8449	$2{\cdot}117\times10^{-5}$	127	0·4718	$4{\cdot}346\times10^{6}$	92
4	0·7546	0·7943	$9{\cdot}080\times10^{-4}$	161	0·2857	$6{\cdot}608\times10^{4}$	60
$\alpha = 10°C\,min^{-1}$							
1	0·7814	0·8705	$3{\cdot}162\times10^{-6}$	175	0·8654	$4{\cdot}269\times10^{7}$	135
2	0·7826	0·8474	$1{\cdot}759\times10^{-5}$	152	0·5647	$5{\cdot}458\times10^{6}$	96
3	0·7837	0·8410	$2{\cdot}829\times10^{-5}$	124	0·4315	$3{\cdot}005\times10^{6}$	85
4	0·7512	0·7920	$1{\cdot}077\times10^{-3}$	166	0·2925	$5{\cdot}757\times10^{4}$	62
$\alpha = 15°C\,min^{-1}$							
1	0·7800	0·8687	$3{\cdot}615\times10^{-6}$	181	0·8766	$3{\cdot}734\times10^{7}$	135
2	0·7842	0·8490	$1{\cdot}562\times10^{-5}$	160	0·6000	$6{\cdot}146\times10^{6}$	96
3	0·7878	0·8534	$1{\cdot}126\times10^{-5}$	137	0·5480	$8{\cdot}615\times10^{6}$	97
4	0·7456	0·7880	$1{\cdot}450\times10^{-3}$	196	0·3351	$4{\cdot}483\times10^{4}$	65

Table 6. Compositions (in mole) and kinetic parameters of Nd doped fluorozirconate glasses

Sample no.	*Glass composition (wt%)*						*Kinetic parameter*	
	ZrF_4	*BaF_2*	*LaF_3*	*AlF_3*	*NaF*	*NaCl*	*E ($kJ\,mol^{-1}$)*	*ν (min^{-1})*
1	57	34	5	4	0	0	163·18	$1{\cdot}29\times10^{12}$
2	53	20	4	3	20	0	133·57	$2{\cdot}39\times10^{10}$
3	56·04	21·16	4·32	3·13	0	15·13	112·56	$1{\cdot}55\times10^{8}$
4	53·18	20·08	4·10	2·97	18·25	1·42	205·82	$2{\cdot}37\times10^{16}$
5	55·21	20·85	4·26	3·08	5·29	11·31	156·79	$5{\cdot}23\times10^{11}$
6	54·65	20·64	4·22	3·05	9·16	8·28	141·77	$4{\cdot}17\times10^{10}$

Table 5 shows that at any heating rates of DTA the criterions, T_g/T_l, T_c/T_l, Q, $T_p - T_g$, k_{gl} and ST, cannot correctly determine the stability of CaO-Al_2O_3-SiO_2 system glasses.

5 Discussion

The stability of glasses is associated with both the thermodynamic factor and the kinetic factor. The values of characteristic temperatures of glasses, T_g, T_c, T_p and T_l, are influenced by measured methods, such as heating rate of DTA. They have different values at different heating rate. In particular the temperature T_p is influenced more severely by heating rate. The effect of the heating rate on the characteristic temperatures is different, so the criteria, T_g/T_l, T_c/T_l, $T_p - T_g$ and k_{gl}, which only contain the thermodynamic factor, are influenced by the heating rate of DTA, whereas the criteria Q and $k(T)$ are only connected to the kinetic factor. As the critical cooling rate Q is very difficult to measure precisely, the criterion Q cannot be applied extensively. The criterion, $k(T)$, are severely influenced by the heating rate of DTA. Its application are also very limited. The criteria, ST, $k_y(T)$ and $k_D(T)$, are connected to both the thermodynamic factor and the kinetic factor. They have more advantages to correctly judge the stability of glasses than other criteria. Because ST is connected to the critical cooling rate Q which is very difficult to measure precisely, its application is also very limited. The criterion $k_y(T)$ combine the thermodynamic factor with the kinetic factor by means of bringing the correction factor, A, $A = \frac{\Delta T}{T_l}$, where $\Delta T = T_c - T_g$, into the crystallization kinetic parameter, $k(T)$, $k(T) = \nu \cdot \exp(-\frac{E}{RT})$. $k_y(T)$ is influenced slightly by the heating rate of DTA. When the frequency factor ν or the crystallization activation energy E among the studied glasses are near, the criterion, $k_y(T)$, cannot correctly determine the stability. The reason is that the correction factor, A, cannot entirely correct the defect of $k(T)$.

The newly proposed criterion, $k_D(T)$, is not influenced by the heating rate of DTA. It can be applied more extensively. $k_D(T)$ contains both the thermodynamic factor and the kinetic factor by introducing the correction factor, D, into the crystallization kinetic parameter, $k(T)$. The correction factor D contain two parts, which are $\frac{T_c}{T_l}$ and $\frac{T_p-T_c}{T_l-T_g}$, respectively. Introducing the first part of $\frac{T_c}{T_l}$ can decrease the influence of the heating rate, α. Also $\frac{T_c}{T_l}$ can judge the stability of glasses to some extent.[6] The stability of glasses mainly means the resistance towards devitrification upon reheating. Below the transition temperature T_g, or above the melting temperature T_l, the glasses cannot crystallize. When the temperature is below T_g, the viscosity of glasses is very high and the crystallization of glasses is very difficult and when the temperature is above T_l, the glasses are in the state of liquid and cannot crystallize. The sole temperature region for crystallization of glasses is between T_g and T_l. The stability of glasses is associated with both the beginning crystallization temperature T_c, and the crystallization rate α. The faster the crystallization rate, the more unstable glasses. In order to correct the influence of the crystallization rate on the stability of glasses, this paper bring the second part, $\frac{T_p-T_c}{T_l-T_g}$, into the D. The possible crystallization time of glasses is $\frac{T_l-T_g}{\alpha}$ and the time from beginning crystallization to crystallization peak is $\frac{T_p-T_c}{\alpha}$, so the ratio of the time from beginning crystallization to crystallization peak to the time of all possible crystallization is $\frac{T_p-T_c}{T_l-T_g}$. The high value of $\frac{T_p-T_c}{T_l-T_g}$ means a good stability of glasses. Especially when the values of both E and ν are near, the criterion of $k_D(T)$ can precisely judge the difference of stability among the glasses. The lower the value of $k_D(T)$, the more stable glasses.

The correctness of new criterion, $k\hat{D}(T)$, has been tested through being used in the Nd doped fluorozirconate glasses and the CaO–Al_2O_3–SiO_2 system glasses. It is necessary to continue to verify the correctness of the new criterion through being applied to other glass systems.

6 Conclusions

1. A new criterion for stability of glasses, $k_D(T)$, $k_D(T) = \nu \cdot \exp(-\frac{E}{RT} \cdot D)$, is proposed in this paper, where D is the correction factor, $D = \frac{T_c(T_p-T_c)}{T_l(T_l-T_g)}$. The lower the $k_D(T)$, the more stable glass.
2. The new criterion combines the thermodynamic factor with the kinetic factor.
3. The heating rate of DTA has no effect on the new criterion $k_D(T)$.
4. Especially when the values of frequency factor ν of glasses are near, the new criterion, $k_D(T)$, can correctly judge the stability, whereas any other criteria cannot give the right judgment.

References

1. Weinberg, M. C., *J. Non-Cryst. Solids*, 1994, **167**, 81.
2. Andrews, M. K., Cicero, C. A., Marra, S. L., Beum, D. C. and Jantzen, C. M., In *Nucleation and Crystallization in Liquids and Glasses, Ceramic Transactions*, Vol. 30, ed. M. C. Weinberg. American Ceramic Society, Westerville, OH, 1983, p. 371.

3. Jain, V., Barnes, S., Joseph, I., Pye, L. D., Pegg, I. L. and Macedo, P. B., In *Nucleation and Crystallization in Liquids and Glasses, Ceramic Transactions*, Vol. 30, ed. M. C. Weinberg. American Ceramic Society, Westerville, OH, 1983, p. 367.
4. Uhlmann, D. R., *J. Non-Cryst. Solids*, 1972, **7**, 337.
5. Gelsing, R. J. H., Stein, H. N. and Stevels, J. M., *Phys. Chem. Glasses*, 1966, **7**(6), 185.
6. Wakasugi, T., Ota, R. and Fukunaga, J., *J. Amer. Ceram. Soc.*, 1992, **75**(11), 3129.
7. Bansal, N. P., Bruce, A. J., Doremus, R. H. and Moynihan, C. T., *J. Non-Cryst. Solids*, 1985, **70**, 379.
8. Drexhage, M. G., El-Bayoumi, O. H., Lipson, H., Moynihan, C. T., Bruce, A. J., Lucas, J. and Fonteneau, G., *J. Non-Cryst. Solids*, 1983, **56**, 51.
9. Cooper, E. I. and Angell, C. A., *J. Non-Cryst. Solids*, 1983, **56**, 75.
10. Hruby, A., *Czech. J. Phys.* 1972, **B22**, 1187.
11. Iqbal, T., Shahriari, M. R. and Sigel Jr, G. H., *Mater. Sci. Forum*, 1991, **67–68**, 225.
12. Surinach, S., Baro, M. D., Clavaguera-Mora, M. T. and Clavaguera, N., *J. Mater. Sci.*, 1984, **19**, 3005.
13. Hu Lili and Jiang Zhonghong, *J. Chin. Ceram. Soc.*, 1990, **18**, 315.
14. Yang Qiuhong and Jiang Zhonghong, *J. Chin. Ceram. Soc.*, 1994, **22**, 419.
15. Johnson, W. A. and Mehl, R. F., *Trans. AIME*, 1939, **135**, 416.
16. Avrami, M., *J. Chem. Phys.*, 1939, **7**, 1103.
17. Bansal, N. P., Doremus, R. H., Bruce, A. J. and Moynihan, C. T., *J. Amer. Ceram. Soc.*, 1983, **66**(4), 233.