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Study on crystallization of glass by differential thermal analysis. Effect of added oxide on crystallization of Li_2O–SiO_2 glasses

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Differential thermal analysis was made of 33.3 Li_2O·66.7 SiO_2·3 RO_n and 25 Li_2O·75 SiO_2·3 RO_n glasses, where RO_n is an added oxide. The exothermic temperatures, T_c, due to the precipitation of lithium disilicate crystal, were plotted against the ionic radius of the cation of the added oxide. It was possible to classify the added oxides into a few groups on the basis of the valency of the cation. Within each group, the T_c increased as the ionic radius of the cation increased. It was shown that the temperature, T_η corresponding to the viscosity of 10^{10} P also increased with increasing the radius of the cation. The relation between T_c and T_η was discussed using the theory on the rates of nucleation and crystal growth. The effect of phase separation on T_c was also discussed.

1. Introduction

Li_2O–SiO_2 glasses are bases for typical commercial glass-ceramics and, therefore, their crystallization behaviour has been studied by many investigators [1-6]. It is necessary for the production of glass-ceramics that the glass should crystallize at temperatures at which its viscosity is still high enough to retrain the shape of a formed article. Therefore, it is very important to study the crystallization temperatures of Li_2O–SiO_2 glasses in relation to the viscosity of the glasses.

In the present study the variation of the bulk crystallization temperature with the added oxide has been measured using the differential thermal analysis and the exothermic peak temperatures were correlated with the viscosity of the glass through the theory of crystal nucleation and growth. Although the effect of the added oxide on the crystallization of Li_2O–SiO_2 glasses have attracted much attention [7-14], no systematic DTA studies have been made yet.

2. Experimental procedure

The compositions of glasses used were 33.3 Li_2O·66.7 SiO_2·3 RO_n and 25 Li_2O·75 SiO_2·3 RO_n in mole where R = Na, K, Cs, Mg, Ca, Sr, Ba, B, Al, In, Ge, Ti, Zr, P or V. These compositions were derived from the base compositions of Li_2O·2 SiO_2 and Li_2O· 3 SiO_2 by adding 3 mole of various oxides in the form RO_n to 100 mole of the two Li_2O–SiO_2 compositions. The raw materials used and the method of glass melting were described in the previous reports [7, 8].

Differential thermal analysis was made with a Shimadzu apparatus type DT-8 which has a platinum sample holder of 4 mm in inside diameter and 8 mm in depth. The bulk glass was used as the sample, instead of powder, in order to minimize the effect of the surface crystallization. To fill the sample holder with glass, the glass melt of 1.3 g was poured into it, remelted in an electric furnace at 1400°C for about 10 min, and allowed to cool in air. The heating rate in the DTA measurement was 10 deg min^{-1}.

3. Experimental results

The DTA curves for Li_2O·2 SiO_2 glass, 33.3 Li_2O·66.7 SiO_2·3 RO_n glasses, Li_2O·3 SiO_2 glass and 25 Li_2O·75 SiO_2·3 RO_n glasses are

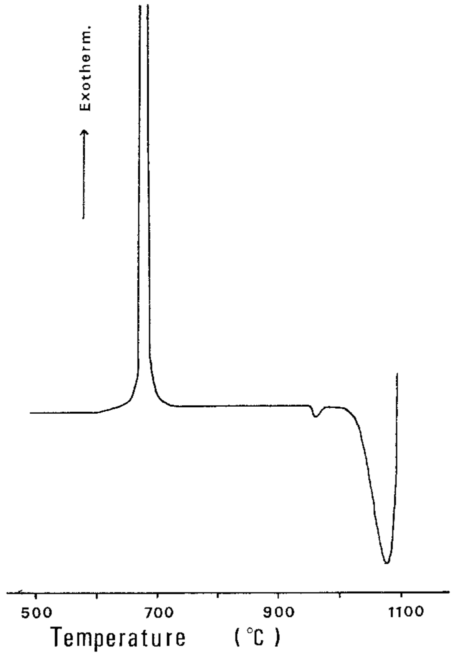


Figure 1 DTA curve for $Li_2O \cdot 2\ SiO_2$ glass.

shown, respectively, in Figs. 1 to 4. The large exothermic peak, observed below 900°C on each curve was found to be due to the precipitation of lithium disilicate ($Li_2O \cdot 2\ SiO_2$) crystal from the X-ray diffraction analysis except for the 33.3 $Li_2O \cdot 66.7\ SiO_2 \cdot 3\ ZrO_2$ glass. The exothermic peak observed at 840°C in this glass was attributed to the precipitation of lithium metasilicate ($Li_2O \cdot SiO_2$) and α-quartz crystals and the endothermic peak observed at 985°C to the formation of lithium disilicate crystal from lithium metasilicate and α-quartz crystals. The endothermic peaks at about 1000°C found in all glasses were attributed to the fusion of lithium disilicate crystal. The exothermic peak temperatures, T_c, are listed in Table I, together with the ionic radius of added cation and the temperature corresponding to the viscosity of 10^{10} P [7, 8].

4. Discussion

4.1. Effect of added oxide on crystallization of $Li_2O \cdot 2\ SiO_2$ glass

When the glass is heated at a constant rate, $dT/dt = \alpha$, from room temperature, T_r, the total number, N, and the radius, R, of grown crystal particles are expressed by the equations

$$N = \frac{1}{\alpha} \int_{T_r}^{T} I dT \qquad (1)$$

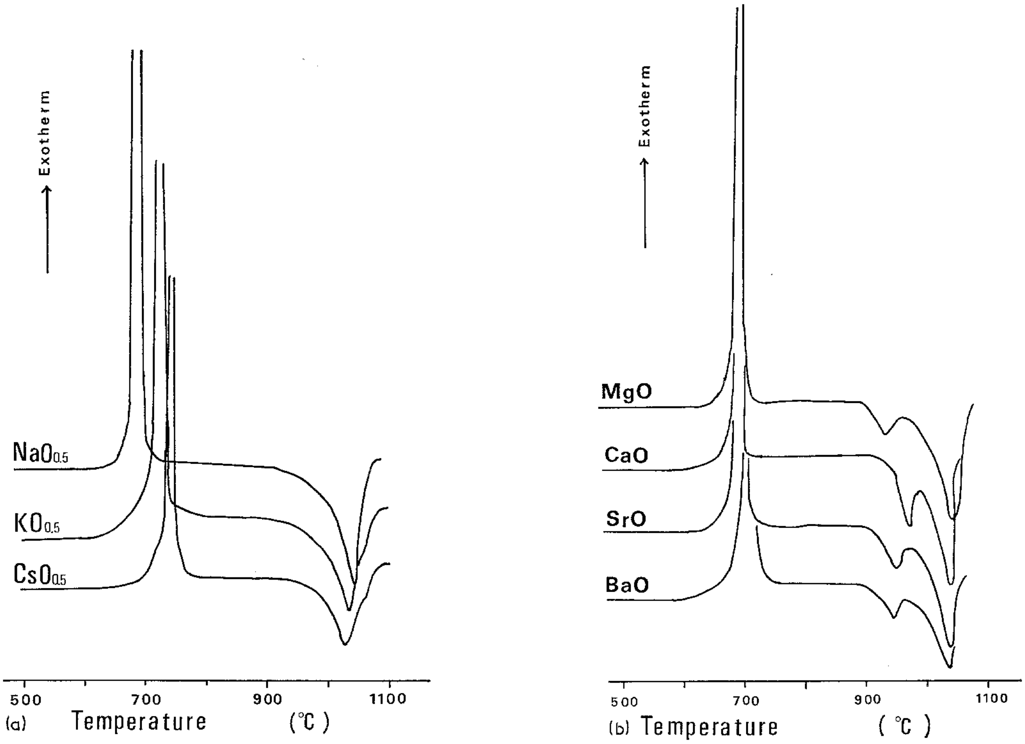
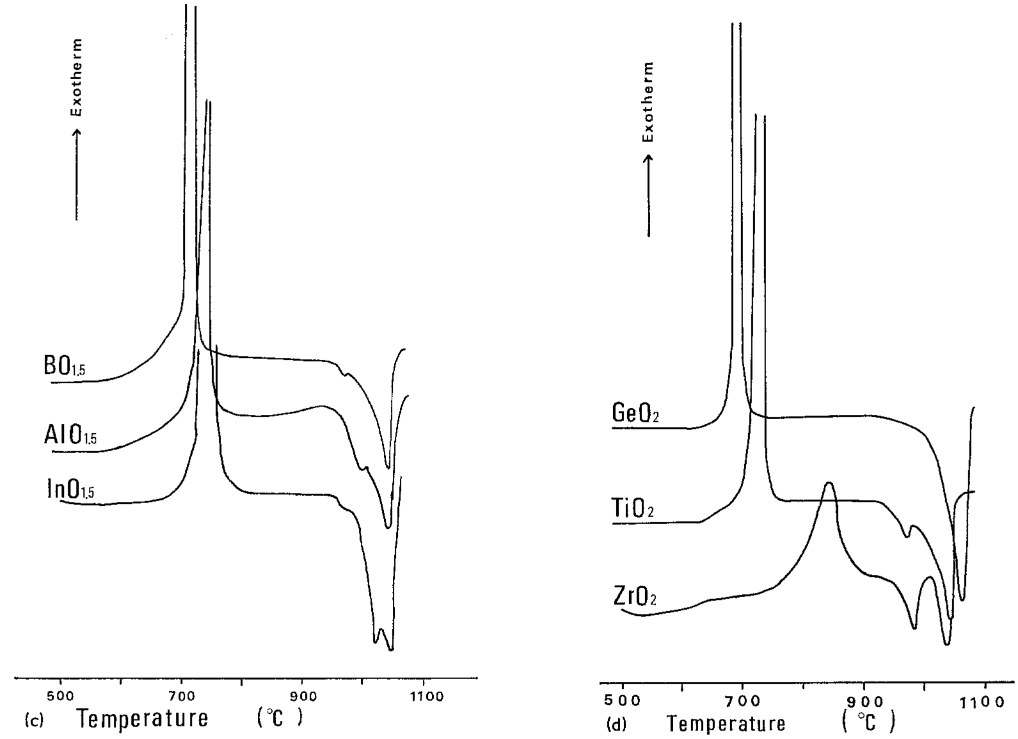


Figure 2 DTA curves for 33.3 $Li_2O \cdot 66.7\ SiO_2 \cdot 3\ RO_n$ glasses. (a) R = Na, K or Cs; (b) R = Mg, Ca, Sr or Ba; (c) R = B, Al or In; (d) R = Ge, Ti or Zr; (e) R = P or V.



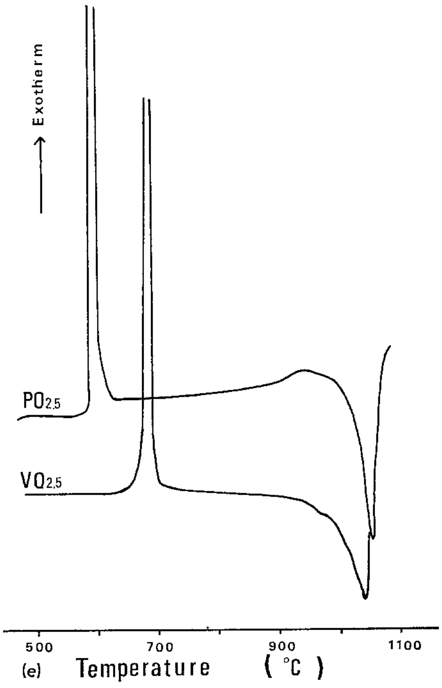


Figure 2 continued.

$$R = \frac{1}{\alpha}\int_{Tr}^{T} U \mathrm{d}T \qquad (2)$$

where I and U are the rates of nucleation and crystal growth respectively. Neglecting the overlap of crystal particles, the total volume fraction of crystal, V, is approximately expressed by the following equation

$$V = \frac{4}{3}\pi R^3 N. \qquad (3)$$

As the volume fraction, V, increases, the heat of

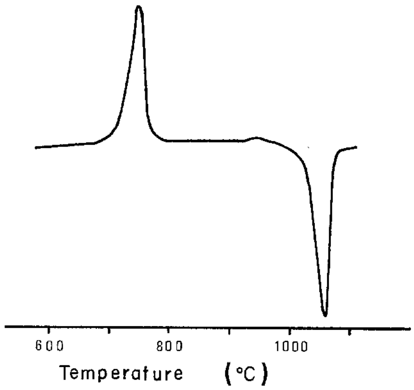
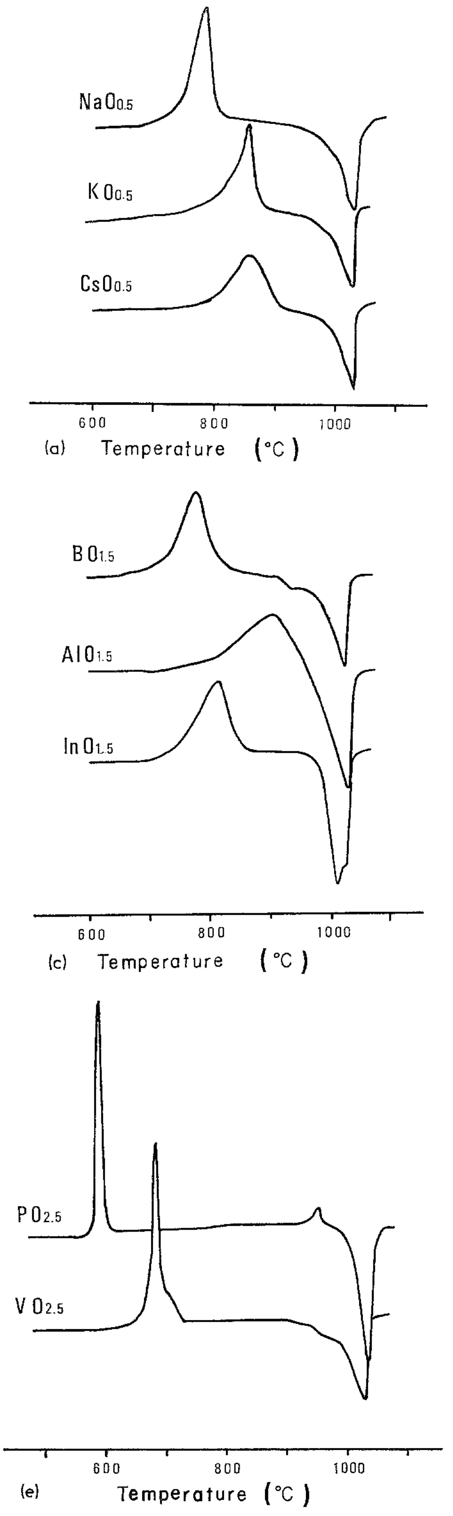


Figure 3 DTA curve for $Li_2O \cdot 3\ SiO_2$ glass.



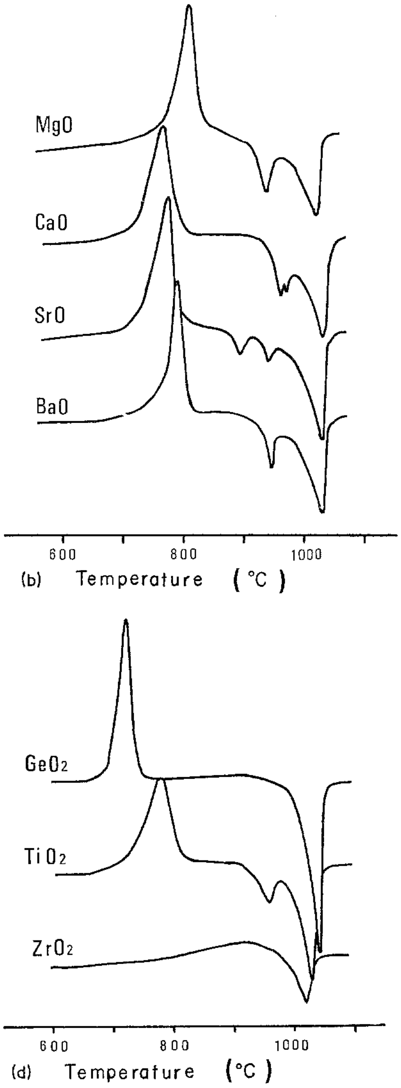


Figure 4 DTA curves for 25 $Li_2O \cdot 75\ SiO_2 \cdot 3\ RO_n$ glasses. (a) R = Na, K or Cs; (b) R = Mg, Ca, Sr or Ba; (c) R = B, Al or In; (d) R = Ge, Ti or Zr; (e) R = P or V.

crystallization is evolved and the exothermic peak appears on the DTA curves. Therefore, the exothermic peak temperature, T_c, may be a measure of the ease of crystallization; the lower T_c is, the more easily crystallization occurs. The relation between T_c and the ionic radius of the added cation, r, is shown in Fig. 5a. T_c of $Li_2O \cdot 2\ SiO_2$ glass containing no added oxide is shown by a broken line. The temperatures, T_η, corresponding to the viscosity of 10^{10} P taken from the previous papers [7, 8] are also plotted. It should be noted that the glasses can be classified into groups on the basis of the valency of the cations of the added oxide. In each group, T_c increases with increasing radius of the cation. The same tendency is found for the relation

TABLE I Data of differential thermal analysis and viscosity

		$33.3\ Li_2O{\cdot}66.7\ SiO_2{\cdot}3\ RO_n$		$25\ Li_2O{\cdot}75\ SiO_2{\cdot}3\ RO_n$	
R	r (Å)	T_c (°C)	T_η (°C)	T_c (°C)	T_η (°C)
Base glass		680	483	745	504
Na	0.94	685	463	785	500
K	1.33	720	475	850	510
Cs	1.67	740	488	860	530
Mg	0.67	695	474	810	497
Ca	0.99	695	471	770	495
Sr	1.12	695	471	780	497
Ba	1.34	705	478	795	500
B	0.23	715	484	780	502
Al	0.51	740	487	905	526
In	0.81	745	503	815	531
Ge	0.53	690	479	725	497
Ti	0.68	730	498	780	519
Zr	0.79	840	516	925	548
P	0.35	590	483	595	510
V	0.59	685	469	685	474

r = Ionic radius (Ahrens).
T_c = Exothermic peak temperature in DTA curve.
T_η = Temperature corresponding to viscosity of 10^{10} P [7, 8].

between T_η and the ionic radius, except for the glass containing P_2O_5.

The striking resemblance of the above two relationships can be explained from the close connection of the rates of nucleation and crystal growth with the viscosity of glass. As reported previously [7], N in $33.3\ Li_2O{\cdot}66.7\ SiO_2{\cdot}3\ RO_n$ glass is inversely proportional to the viscosity of the glass at a definite temperature except for the glasses containing P_2O_5, V_2O_5 and GeO_2, and U is also inversely proportional to the viscosity, so that T_c should be a function of the viscosity of the glass. It should be noted that the viscosity of glass has a stronger effect upon T_c through U than through N because, in Equations 1 to 3, V is proportional to the first power of N but to the third power of U. The difference in T_c observed in the present experiment is mainly caused by the viscosity of glass through U except for the glass containing P_2O_5 for which N value is extraordinarily large [7, 8].

4.2. Effect of added oxide on crystallization of $Li_2O{\cdot}3\ SiO_2$ glass

$Li_2O{\cdot}3\ SiO_2$ glass is known to phase-separate easily into two liquids prior to its crystallization [1, 8]. The phase separation would affect the rates of nucleation and crystal growth and make crystallization mechanism more complicated in this glass than in $Li_2O{\cdot}2\ SiO_2$ glass which does not phase-separate [1].

The plots of T_c and T_η against the ionic radius of the added cation for $25\ Li_2O{\cdot}75\ SiO_2{\cdot}3\ RO_n$ glasses are shown in Fig. 5b. T_c and T_η of $Li_2O{\cdot}3\ SiO_2$ containing no added oxide are shown by the broken lines.

It is found that these glasses can also be classified into groups on the basis of the valency of the added cation. In each group T_c increases with increasing ionic radius except for the glasses containing In_2O_3 and MgO. The same tendency is found for the relation between T_η and the ionic radius except for the glass containing P_2O_5. It should be noted that the lines shown in Fig. 5b are steeper than those of corresponding lines shown in Fig. 5a. Since N and U in $25\ Li_2O{\cdot}75\ SiO_2{\cdot}3\ RO_n$ glasses are affected by liquid-liquid phase separation [8], T_c should also be affected by the phase separation.

This is examined in Fig. 6 by plotting ΔT_c against the miscibility temperature of $25\ Li_2O{\cdot}75\ SiO_2{\cdot}3\ RO_n$ glass. ΔT_c is the difference in the exothermic temperature, T_c, between $25\ Li_2O{\cdot}75\ SiO_2{\cdot}3\ RO_n$ glass and $33.3\ Li_2O{\cdot}66.7\ SiO_2{\cdot}3\ RO_n$ glass. The miscibility temperatures are taken from the previous work [8]. The miscibility temperature of the glass containing Cs_2O could not be obtained and, therefore,

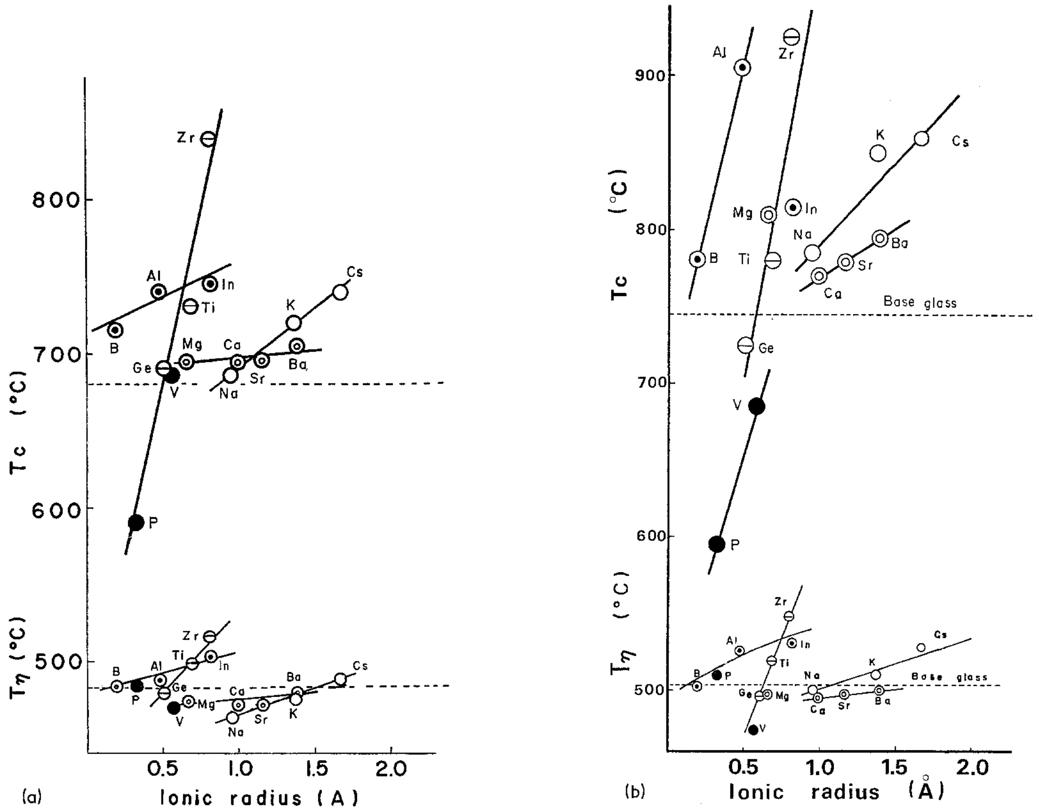


Figure 5 The exothermic temperature T_c and the temperature T_η corresponding to the viscosity of 10^{10} P versus the ionic radius of the added cation. (a) 33.3 $Li_2O \cdot 66.7\ SiO_2 \cdot 3\ RO_n$ glasses; (b) 25 $Li_2O \cdot 75\ SiO_2 \cdot 3\ RO_n$ glasses.

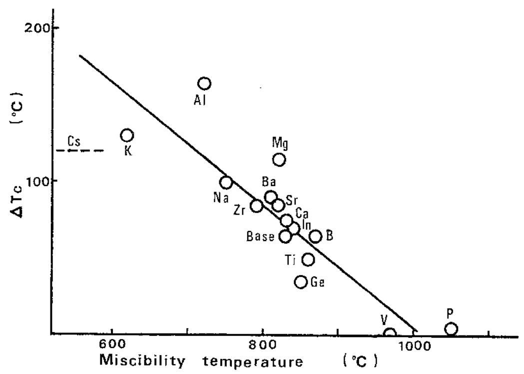


Figure 6 Difference in the exothermic temperature between 25 $Li_2O \cdot 75\ SiO_2 \cdot 3\ RO_n$ and 33.3 $Li_2O \cdot 66.7\ SiO_2 \cdot 3\ RO_n$ glasses versus the miscibility temperature of the former glass.

ΔT_c is shown by the broken line. It is seen from the figure that ΔT_c becomes smaller, as the miscibility temperature increases. This can be understood by referring to the previous finding that as the miscibility temperature increases, N and U in 25 $Li_2O \cdot 75\ SiO_2 \cdot 3\ RO_n$ glasses approach, respectively, those in 33.3 $Li_2O \cdot 66.7\ SiO_2 \cdot 3\ RO_n$ glasses [8]. It was also found previously that the value of N in the former glass is approximately the same as that in the latter glass, while U in the former glass is remarkably less than that in the latter glass [8]. Therefore, it may be considered that the phase separation has a stronger effect on ΔT_c through the change of U than through that of N.

5. Summary

The effects of added oxide on the crystallization of $Li_2O \cdot 2\ SiO_2$ and $Li_2O \cdot 3\ SiO_2$ glasses were studied using differential thermal analysis and correlated with the viscosities reported previously. The added oxides could be classified into a few groups on the basis of the valency of the cation. In each group, the exothermic temperature, T_c, due to the precipitation of lithium disilicate crystal and the temperature, T_η, at which the viscosity is 10^{10} P increased as the ionic radius of the added cation increases with a small number of exceptions. The relation between T_c and T_η was discussed on the basis of the theory on rates of nucleation and crystal growth. The effect of phase separation on the T_c was related to the change of the rates of nucleation and crystal growth caused by the phase separation.

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