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Estimated immiscibility isotherms of the Li_2O–Al_2O_3–SiO_2 system

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Using the immiscibility temperature estimation method, recently developed by the present author and Tomozawa, immiscibility isotherms of the Li_2O–Al_2O_3–SiO_2 system were estimated. High reliability of the estimated immiscibility isotherms was confirmed by observing the morphologies of phase-separated glasses, and also by comparing the estimated and observed immiscibility temperatures at several compositions. The determined immiscibility isotherms revealed that, in the Li_2O–Al_2O_3–SiO_2 system, only composition regions near the Li_2O–SiO_2 and Al_2O_3–SiO_2 binary edges are phase-separable. In composition regions where base glasses for commercial glass–ceramics are located, the immiscibility temperatures were much lower than the glass transition temperatures, implying that no phase separation actually occurs. Accordingly the phase separation in practical glasses for producing glass–ceramics may be attributed to increased immiscibility resulting from various additives.

1. Introduction

Li_2O–Al_2O_3–SiO_2 based glasses are used for producing low thermal expansion glass–ceramics. Thus far a number of studies have been performed on their crystallization processes in connection with manufacturing such glass–ceramics [1]. The crystallization process studies strongly suggested that, in the glasses, phase separation takes place before crystallization and plays an important role in the formation of favourable glass–ceramics. To prove this, Nakagawa and Izumitani [2] investigated in detail the relationship between metastable phase separation and crystallization in Li_2O–Al_2O_3–SiO_2 based glasses.

In their study they determined the immiscibility boundary of the SiO_2–($Li_2O \cdot 1.34\ Al_2O_3$) pseudobinary system, and then confirmed the occurrence of metastable phase separation in the glasses by electron microscopic observation. Consequently it became an undoubted fact that Li_2O–Al_2O_3–SiO_2 glasses exhibit phase separation before crystallization. Here, however, it should be noticed that the glasses examined by Nakagawa and Izumitani [2] were not pure Li_2O–Al_2O_3–SiO_2 glasses but glasses developed for manufacturing commercial glass–ceramics, containing 2 wt% of TiO_2 and ZrO_2 as nucleating agents and 0.5 to 2 wt% of MgO, K_2O, BaO, and P_2O_5. Thus the findings might not necessarily represent the phase separation characteristics of pure Li_2O–Al_2O_3–SiO_2 glasses.

Li_2O–Al_2O_3–SiO_2 based glasses are of great practical value among silicate-system glasses, not only for making glass–ceramics but also as having various industrial applications. In connection with the development and processing of Li_2O–Al_2O_3–SiO_2 based glasses, therefore, elucidation of the phase separation characteristics of pure Li_2O–Al_2O_3–SiO_2 glass is very important. Nevertheless no work has so far been done on the immiscibility gap of the system.

The present author and Tomozawa [3] have recently developed a simple and reliable method of predicting the immiscibility boundary of a ternary silicate-glass system, by knowing the immiscibility boundaries of binary silicates. By employing this method, the immiscibility isotherms of the systems R_2O–R'_2O–SiO_2 (R and R′ are alkali metals) and R_2O–$R''O$–SiO_2 (R″ is an alkaline-earth metal) have been successfully

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determined in previous studies [4–6]. In the present study the prediction method was applied to the $Li_2O–Al_2O_3–SiO_2$ system to estimate the immiscibility isotherms, and to clarify the phase separation characteristics.

2. Outline of previously developed estimation method

As detailed in a previous paper [3] the estimation method is based on a superposition principle of immiscibility boundaries of silicate-glass systems. As shown in Fig. 1, the immiscibility boundary curves of silicate glasses can be superposed when the immiscibility temperature T_m, and the immiscibility composition C are normalized by the critical temperature T_c, and by the immiscibility composition C_m at $T_m/T_c = 0.8$, respectively.

It is assumed that this superposition is valid for any silicate glass system, and that one of the two separated phases is pure SiO_2 at 0 K. Consequently a master curve of the normalized immiscibility boundary can be drawn, as shown by a solid line in Fig. 1. This superposition principle suggests that the immiscibility boundaries of any silicate system and any pseudobinary system chosen along a tie line in a ternary silicate system can be superposed on this master curve. Thus, if the T_c and C_m values of a binary or pseudobinary system are available, the immiscibility boundary of the system can be estimated from this master curve.

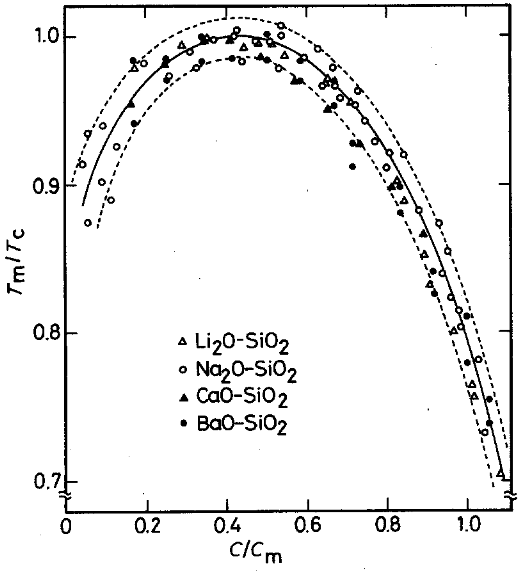

Figure 1 Normalized immiscibility boundaries of the systems Li_2O–, Na_2O–, CaO–, and BaO–SiO_2 and a master curve of immiscibility boundary (solid line). This figure is reproduced from [3].

The evaluation of these T_c and C_m values of a pseudobinary system in the $Li_2O–Al_2O_3–SiO_2$ ternary system is explained. In a pseudobinary system with a composition $a Li_2O \cdot b Al_2O_3 \cdot (100 - a - b) SiO_2$ with a constant a/b ratio, the critical temperature in the immiscibility boundary, T_c, can be given by

$$T_c = y(T_c)_{Li} + (1-y)(T_c)_{Al} - y(1-y)(T_c)_{Li-Al} \qquad (1)$$

where $(T_c)_{Li}$, $(T_c)_{Al}$ and $(T_c)_{Li-Al}$ are the critical temperatures in the immiscibility boundaries of the binary systems $Li_2O–SiO_2$, $Al_2O_3–SiO_2$ and $Li_2O–Al_2O_3$ respectively, and y and $(1-y)$ are the normalized mole ratios of Li_2O and Al_2O_3 respectively. The y value is given by

$$y = [a/(C_m)_{Li}] / [a/(C_m)_{Li} + b/(C_m)_{Al}] \qquad (2)$$

where $(C_m)_{Li}$ and $(C_m)_{Al}$ are values for the systems $Li_2O–SiO_2$ and $Al_2O_3–SiO_2$, respectively.

The value of $(T_c)_{Li-Al}$, which is required to obtain the T_c value from Equation 1, is determined experimentally by the procedure described in the next paragraph. On the other hand, C_m in the immiscibility boundary can be given by the additivity of C_m of the binary systems $Li_2O–SiO_2$ and $Al_2O_3–SiO_2$, that is

$$C_m = y(C_m)_{Li} + (1-y)(C_m)_{Al} \qquad (3)$$

Therefore, if the immiscibility boundaries of the binary systems $Li_2O–SiO_2$ and $Al_2O_3–SiO_2$ are known, then the immiscibility isotherms of the system $Li_2O–Al_2O_3–SiO_2$ can be determined by the procedure explained in the previous paper [3].

The $(T_c)_{Li-Al}$ evaluation is done as follows. First a glass with a given composition which falls on an a/b = constant line of $a Li_2O \cdot b Al_2O_3 \cdot (100 - a - b) SiO_2$ is prepared, and the immiscibility temperature of the glass $(T_m)_{exp}$ is measured. Next the C/C_m value of the glass is calculated by

$$C/C_m = (a+b) / [y(C_m)_{Li} + (1-y)(C_m)_{Al}] \qquad (4)$$

and the T_m/T_c value of the glass is found from the master curve of normalized immiscibility boundary (a solid line in Fig. 1), which provides a graphical relationship between C/C_m and T_m/T_c.

The T_m/T_c value obtained is

$$T_m/T_c = (T_m)_{exp}/[y(T_c)_{Li} + (1-y)(T_c)_{Al} - y(1-y)(T_c)_{Li-Al}] \qquad (5)$$

so that the $(T_c)_{Li-Al}$ value can be calculated.

In this procedure the composition of a glass prepared has to be chosen such that the C/C_m value of the glass corresponds to the master curve. Once the $(T_c)_{Li-Al}$ value is evaluated, then it is possible to calculate the T_c value of pseudobinary systems with different y values, i.e. glasses with different a/b ratios, using Equation 1. Consequently the immiscibility dome of the entire ternary composition can be determined. From this the immiscibility isotherms of the ternary $Li_2O-Al_2O_3-SiO_2$ system can be constructed.

3. Experimental procedure

3.1. Glass preparation

Nine kinds of glass, the compositions of which are given in Table I were prepared from acid-washed quartz sand, reagent grade Li_2CO_3, and chemical grade $Al(OH)_3$. Batches of 100 to 150 g were melted in platinum/rhodium crucibles at 1450 to 1600° C for 3 to 4 h and then quenched together with the crucibles in water.

3.2. Determination of immiscibility temperature

The immiscibility temperatures of the prepared glasses were determined by replica electron microscopy for Glasses 1 and 9, and by an opalescence method for Glasses 2 to 8. Chunks of the glasses, 10 mm x 10 mm x 15 mm in size, were held at various temperatures for half an hour to several days, depending on glass composition, in an electrical furnace temperature-controlled to within ± 1° C. The samples quenched after the heat-treatment were subjected to phase separation observation. The opalescence observation was made visually on samples dipped in water, while the replica electron microscopic observation was carried out by a platinum/palladium preshadowed carbon replication technique on freshly fractured and HF-etched surfaces. In Glasses 5 and 8, surface devitrification proceeded at high speed during the heat-treatment so that the immiscibility temperature determination was impossible.

TABLE I Compositions and immiscibility temperatures of prepared glasses

Glass No.	Composition (mol %)			Immiscibility temperature (°C)
	Li_2O	Al_2O_3	SiO_2	
1	13.3	1.7	85.0	797
2	12.5	2.5	85.0	703
3	17.8	2.2	80.0	766
4	16.7	3.3	80.0	668
5	15.0	5.0	80.0	–
6	20.0	2.5	77.5	730
7	23.6	1.4	75.0	755
8	24.0	3.0	73.0	–
9	9.3	12.6	78.1	*

* No phase separation was observed.

3.3. Determination of volume ratio of two phases in phase-separated glass

For Glass 1 phase-separated at 764 and 744° C, the volume ratios of two phases (droplet and matrix) were determined by observing the phase separation morphologies with replica electron microscopy. The replication technique was the same as that described in the preceding section.

4. Results and discussion

4.1. Estimation of immisicibility isotherms of the $Li_2O-Al_2O_3-SiO_2$ system

In order to estimate the immiscibility temperatures of $Li_2O-Al_2O_3-SiO_2$ glasses using the estimation method outlined in Section 2, the immiscibility boundary data of the Li_2O-SiO_2 and the $Al_2O_3-SiO_2$ systems are required. The immiscibility boundary of the Li_2O-SiO_2 system has been well established and varies little between investigators [7–9]. In the present estimation the result of Haller *et al.* [7] was employed.

On the location of the immiscibility boundary in the $Al_2O_3-SiO_2$ system, on the contrary, there is large disagreement between workers. In the extreme case, even no presence of immiscibility has been reported [10, 11]. Until now, four immiscibility boundaries have been reported by MacDowell and Beall [12], Galakov *et al.* [13], Risbud and Pask [14], and Jantzen and Herman [15]. Among them the boundary of MacDowell and Beall [12] seems more reliable at the present stage. For instance, it is supported by recent STEM analysis of a phase-separated $Al_2O_3-SiO_2$ glass [16]. Their data was therefore adopted in this work. Thus the T_c and C_m values of the Li_2O-SiO_2 and the $Al_2O_3-SiO_2$ immiscibility boundaries are 1000° C and 27.5 mol%, and 1640° C and 53 mol%, respectively. On the other hand, the immiscibility temperature, 730° C, of Glass 6 was taken as the experimental T_m of an

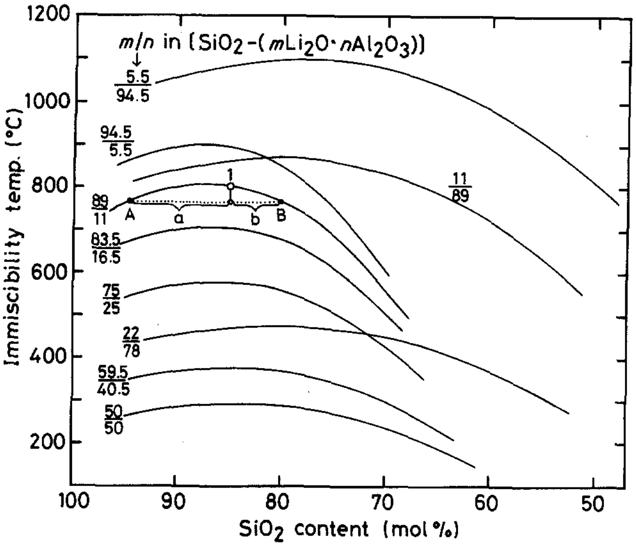

Figure 2 Estimated immiscibility boundaries of SiO_2–($m\text{Li}_2\text{O}\cdot n$ Al_2O_3) pseudobinaries.

$a\text{Li}_2\text{O}\cdot b\text{Al}_2\text{O}_3\cdot(100-a-b)\text{SiO}_2$ glass which is required to calculate the $(T_\text{c})_{\text{Li-Al}}$ value from Equation 1.

Following the procedure explained in Section 2 the immiscibility boundaries for the SiO_2–($m\text{Li}_2\text{O}\cdot n\text{Al}_2\text{O}_3$) pseudobinaries were calculated. Fig. 2 shows those for the pseudobinaries with $m/n = 94.5/5.5$, 89/11, 83.5/16.5, 75/25, 59.5/40.5, 50/50, 22/78, and 5.5/94.5. On the basis of the immiscibility boundaries of pseudobinaries, the immiscibility isotherms of the Li_2O–Al_2O_3–SiO_2 system were drawn and are shown in Fig. 3. Furthermore, immiscible (temperature–composition) regions in the Li_2O–Al_2O_3–SiO_2 system are illustrated schematically and three-dimensionally in an insertion in Fig. 3.

4.2. Reliability of estimated immiscibility isotherms

In principle the present immiscibility isotherm estimation is based on an assumption that Li_2O–Al_2O_3–SiO_2 glass phase separates into SiO_2-rich and SiO_2-poor phases. First the validity of the assumption, that is the correctness of immiscibility boundaries for the SiO_2–($m\text{Li}_2\text{O}\cdot n\text{Al}_2\text{O}_3$) pseudobinaries, was examined. The examination was made on an immiscibility boundary estimated for the SiO_2–($89\text{Li}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$) pseudobinary. If the estimated boundary curve is correct, Glass 1 lying on the SiO_2–($89\text{Li}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$) pseudobinary should phase-separate into two phases A and B, and the volume ratio of the two phases should be given by $b/d_\text{B} : a/d_\text{A}$, as shown in Fig. 2, where

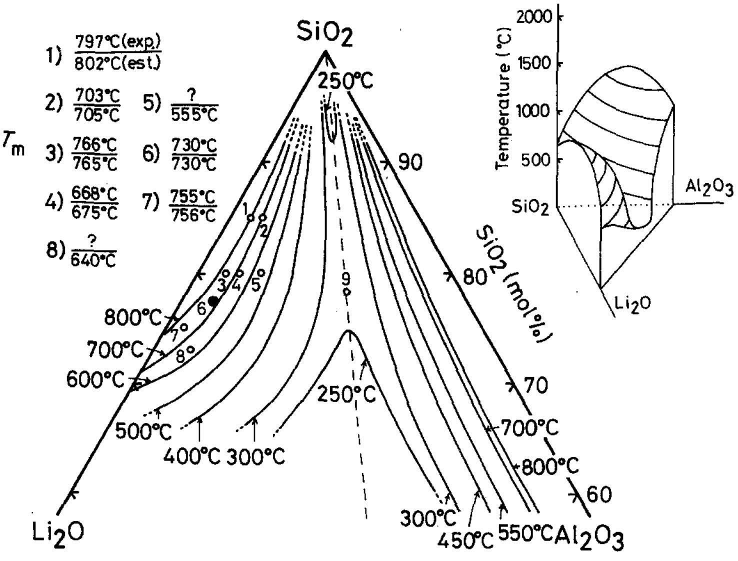

Figure 3 Estimated immiscibility isotherms of the Li_2O–Al_2O_3–SiO_2 system. A small figure inserted shows a schematic immiscibility dome in the Li_2O–Al_2O_3–SiO_2 system.

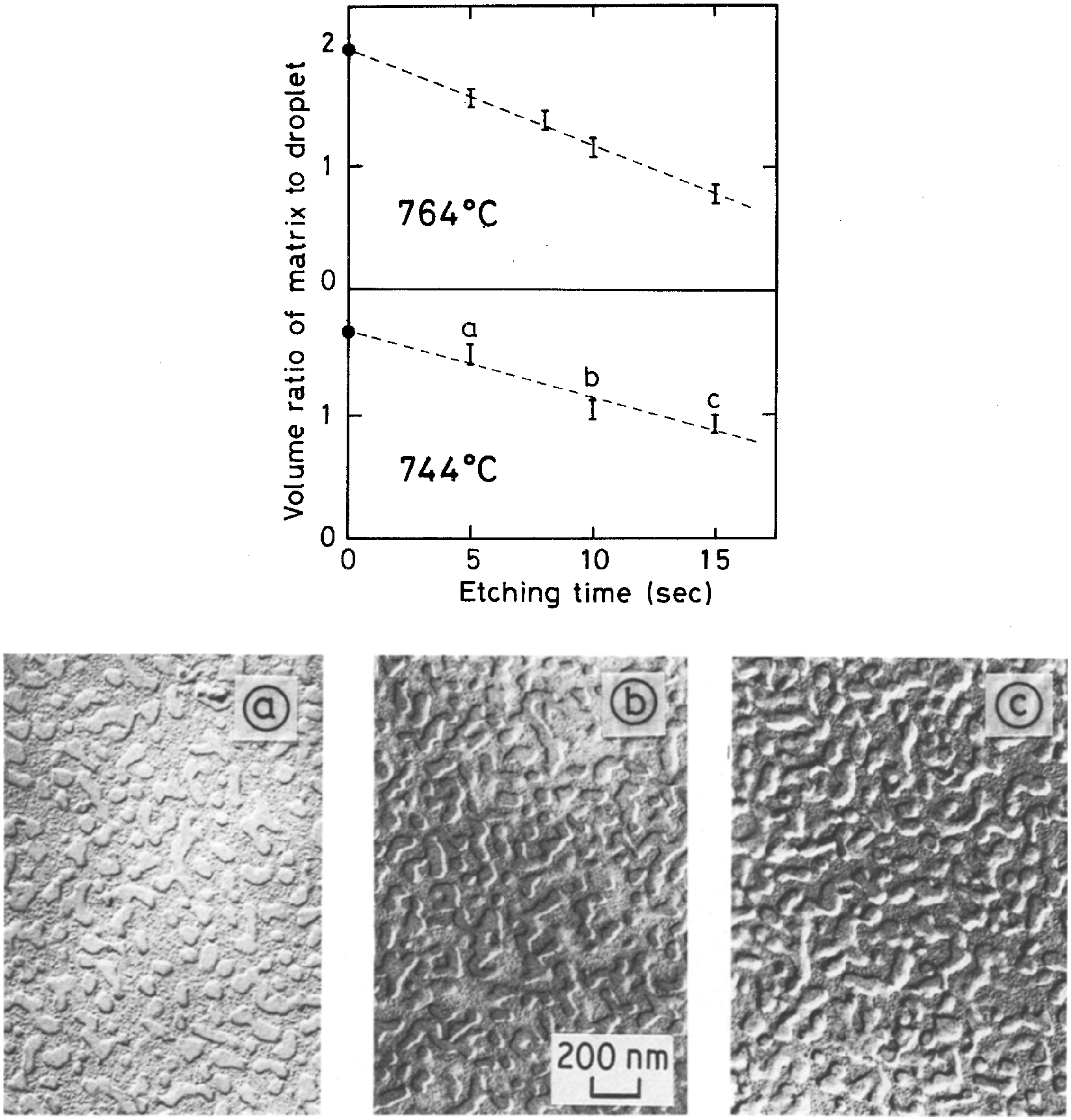

Figure 4 Volume ratios of two phases in Glass 1 phase-separated at 764 and 744° C. Micrographs show phase separation morphologies observed for etching times (a), (b) and (c) in the Figure.

d_A and d_B are the densities of the A and B phases and the values can be calculated by Huggins' method [17–22]. The calculated volume ratios at 764 and 744° C are indicated by closed circles in Fig. 4.

On the other hand, the measured volume ratios obtained in Section 3.3 are plotted against etching time by bars in Fig. 4, where some electron micrographs employed for the volume ratio determination are also shown. Since etching gives significant errors in the volume-ratio determination with etched-surface replica-micrographs, accurate volume ratios have to be obtained by extrapolating the plot of measured volume ratio against etching time to zero etching time [23]. As can be seen from Fig. 4, the volume ratio values obtained by extrapolation agree very closely with the calculated values. This indicates that the immiscibility boundary estimated for each pseudobinary is valid, that is the tie line postulated for the phase separation of Li_2O–Al_2O_3–SiO_2 glasses is valid.

Next the accuracy of estimated immiscibility isotherms of the Li_2O–Al_2O_3–SiO_2 system was ascertained by comparing the observed and estimated immiscibility temperatures at several compositions. The comparison was made on compositions given in Table I and the result is shown in Fig. 3. Quite satisfactory agreement can be seen between the estimated and the observed values. This verifies the high reliability of the estimated immiscibility isotherms. Although such a comparison should be made on Al_2O_3–SiO_2 rich compositions also, it was impossible owing to difficulty in preparing the glasses.

4.3 Phase separation characteristics of the Li_2O–Al_2O_3–SiO_2 system

As seen from Fig. 3, the immiscibility temperature decreases steeply with the addition of Al_2O_3 to Li_2O–SiO_2 glasses, and also with the addition of Li_2O to Al_2O_3–SiO_2 glasses. The marked decrease in immiscibility temperature with increasing addition of Al_2O_3 to Li_2O–SiO_2 glasses agrees completely with an experimental result by Moriya *et al.* [8].

On the other hand, immiscibility temperatures in central composition areas of the Li_2O–Al_2O_3–SiO_2 system are far below glass transition temperatures, indicating that no phase separation takes place in the glasses. As indicated by a broken line in Fig. 3, SiO_2–($Li_2O \cdot 1.34\ Al_2O_3$) glasses in which the occurrence of phase separation was proved by Nakagawa and Izumitani [2] are situated in the central composition area. The present immiscibility isotherms reveal that the glasses do not exhibit phase separation. In fact no phase separation could be detected in Glass 9 when heat-treated at temperatures between 600° and 800° C for appropriate times.

As mentioned in the Introduction, a number of additives were contained in the Nakagawa and Izumitani glasses. Among them P_2O_5, TiO_2, and BaO are presumed to be components for increasing immiscibility, while ZrO_2 and MgO, may be components for decreasing immiscibility [24]. Accordingly the phase separation shown by these glasses, i.e. practical glasses for producing glass–ceramics, may probably be attributed to increased immiscibility resulting from the joint use of various additives. In other words, glasses for commercial glass–ceramics might be concluded to be designed with various additives so as to bring about phase separation before crystallization.

In alkali aluminosilicate glasses the compositional dependence at constant SiO_2 content of various physical properties such as density, refractive index, viscosity, alkali diffusion, and electrical conductivity exhibit minima or maxima at Al_2O_3/(alkali oxide + Al_2O_3) $\simeq$ 0.5 [25]. Of interest is that a similar phenomenon is observed in the present immiscibility isotherms. Fig. 5 shows the variation of immiscibility temperature at the 80 mol% SiO_2 content with the $Al_2O_3/(Li_2O + Al_2O_3)$ ratio. It can be seen that the compositional dependence exhibits a minimum at a ratio close to 0.5.

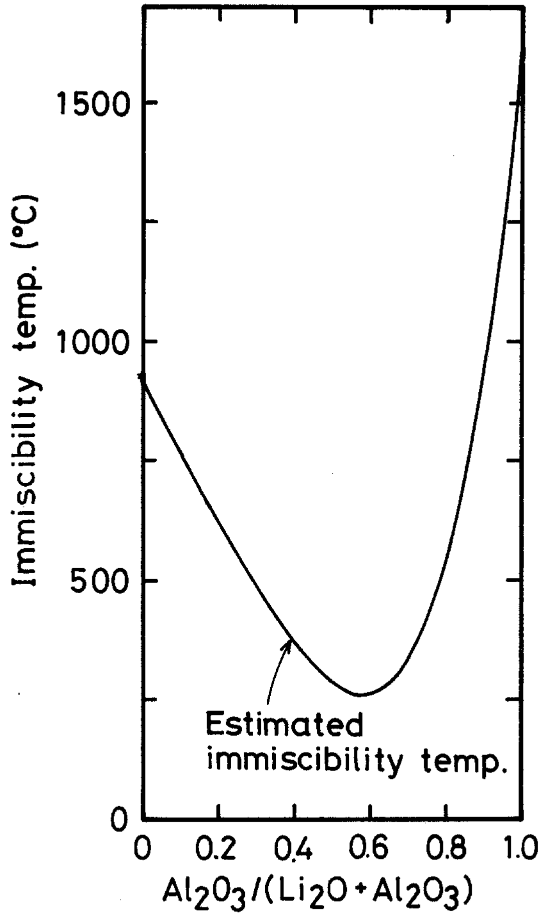

Figure 5 Variation of immiscibility temperature at 80 mol% SiO_2 content with $Al_2O_3/(Li_2O + Al_2O_3)$ ratio.

Finally it may be noted that successful estimation of the Li_2O–Al_2O_3–SiO_2 immiscibility isotherms in the present study demonstrates the MacDowell and Beall immiscibility boundary of the Al_2O_3–SiO_2 system to be highly reliable.

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References

1. P. W. McMILLAN, "Glass–Ceramics", 2nd edn. (Academic Press, New York, 1979).
2. K. NAKAGAWA and T. IZUMITANI, *Phys. Chem. Glasses* **13** (1972) 85.
3. Y. KAWAMOTO and M. TOMOZAWA, *ibid.* **22** (1981) 11.
4. *Idem*, *J. Amer. Ceram. Soc.* **64** (1981) 289.
5. *Idem*, *J. Non-Cryst. Solids* **43** (1981) 417.
6. *Idem*, *J. Mater. Sci. Lett.* **2** (1983) 42.
7. W. HALLER, D. H. BLACKBURN and J. H. SIMMONS, *J. Amer. Ceram. Soc.* **57** (1974) 120.
8. Y. MORIYA, D. H. WARRINGTON and R. W. DOUGLAS, *Phys. Chem. Glasses* **8** (1967) 19.
9. N. S. ANDREEV, D. A. GOGANOV, E. A. PORAI-KOSHITS and Y. G. SOKOLOV, "The Structure of Glass", Vol. 3, edited by E. A. Porai-Koshits (Consultant Bureau, New York, 1964) p. 47.
10. D. GANGULI and P. SAHA, *Mater. Res. Bull.* **2** (1967) 25.
11. T. TAKAMORI and R. ROY, *J. Amer. Ceram. Soc.* **56** (1973) 639.
12. J. F. MacDOWELL and G. H. BEALL, *ibid.* **52** (1969) 17.
13. F. YA. GALAKHOV, V. I. AVER'YANOV, V. T. VAVILONOVA and M. P. ARESHEV, *Sov. J. Glass Phys. Chem.* **2** (1976) 127.
14. S. H. RISBUD and J. A. PASK, *J. Amer. Ceram. Soc.* **60** (1977) 418.
15. C. M. JANTZEN and H. HERMAN, *ibid.* **62** (1979) 212.
16. S. H. RISBUD, *J. Non-Cryst. Solids* **49** (1982) 241.
17. M. L. HUGGINS, *J. Opt. Soc. Amer.* **30** (1940) 420.
18. *Idem*, *ibid.* **30** (1940) 495.
19. *Idem*, *ibid.* **30** (1940) 514.
20. *Idem*, *Ind. Eng. Chem.* **32** (1940) 1433.
21. *Idem*, *J. Amer. Ceram. Soc.* **26** (1943) 4.
22. *Idem*, *ibid.* **27** (1944) 10.
23. D. G. BURNETT and R. W. DOUGLAS, *Phys. Chem. Glasses* **11** (1970) 125.
24. Y. MORIYA, "Glass Handbook", edited by S. Sakka, T. Sakaino and K. Takahashi (Asakura Schoten, Tokyo, 1975) p. 793.
25. S. SAKKA, "Glass Handbook", edited by S. Sakka, T. Sakaino and K. Takahashi (Asakura Schoten, Tokyo, 1975) p. 859.

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