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Calculation of subliquidus miscibility gaps in the Li_2O–B_2O_3–SiO_2 system

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Abstract

A thermodynamic approach of predicting the binary and ternary subliquidus miscibility gaps of the Li_2O–B_2O_3–SiO_2 system is described. For the binary B_2O_3–SiO_2, Li_2O–B_2O_3, and Li_2O–SiO_2 systems, according to the shape of liquidus and the location of subliquidus miscibility gaps, a simple model such as regular, quasi-regular, and subregular solution models is applied to describe the liquid phase. The present calculations agree with experimental data available in the literature. The ternary subliquidus miscibility gaps with tie lines were calculated by applying the Toop–Muggianu method which uses the binary systems. In the present calculations, the isothermal sections of the subliquidus miscibility gaps in the ternary systems were reasonable in the aspect of the development of both the tie lines and the critical points according to changing the temperature. Also, the composition range was calculated where spinodal decomposition is possible. © 2000 Published by Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

While most phase equilibria have been and continue to be determined by experimental techniques, there is a growing trend toward calculating multi-component equilibria from thermodynamic data. There are various experimental methods to investigate phase separations in the glass-forming oxide systems. Techniques such as electron microscopy give direct information on the number, shape, and dimensions of the dispersed phase in the matrix. On the other hand, indirect techniques such as small-angle X-ray scattering are based on physical property measurements and have been used to deduce information on phase separations. In complex systems such as oxide melts, there exist many controversies between the results from the different techniques. Especially, the metastable immiscibility in boric oxide–silica and alkali borate systems has been repeatedly investigated by various methods. So far, however, there is no final solution of the problem of the nature of the inhomogeneous structure of these glasses and the presence or absence of liquid–liquid phase separation [1]. Recently, Tomozawa [2] suggested the change of local glass structure around boron with heat-treatment temperature to explain the apparent discrepancies between the reported miscibility gap data in borate and borosilicate glass systems. Therefore, if possible, the thermodynamic calculation is one of the best ways to understand the behavior of liquid phases in those systems precisely.

In case the phase equilibria in oxide melts show contradictory behavior, the simple mixture models might not be adequate for describing the behavior of oxide melts. Therefore, numerous thermodynamic models have been proposed to account for the thermodynamic behavior of oxide melts. Recently, Saunders and Miodownik [3] have published a review of various models for ionic liquids. Until recently, there have been few attempts to calculate the subliquidus miscibility gaps in ternary glass-forming systems, compared to those in the binary systems. Charles [4] has tried to estimate thermodynamically the metastable subliquidus miscibility in the Li_2O–BaO–SiO_2 system on the basis of the calculated silica activities obtained from binary and pseudobinary systems. He treated lines of constant BaO/Li_2O ratio as pseudobinaries, assuming that one of the tie-line compositions for two liquid phases would generally be located in the silica corner of ternary composition triangle. Burnett and Douglas [5] have

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reported an empirical correlation for the form of the miscibility gap in the Na_2O–CaO–SiO_2 system. Their method is based on the correlation between miscibility temperature and composition, that is, the reciprocal of the miscibility temperature for a constant silica section increases linearly as the soda is replaced by lime. Kawamoto and Tomozawa [6] have developed a simple empirical method in order to predict the subliquidus miscibility gaps of ternary silicate glasses from the subliquidus miscibility gaps experimentally determined in binary silicate systems. Their method is based on the similarity in shape observed in subliquidus miscibility gaps of binary alkali silicate systems. Like Charles' treatment [4], they regarded lines of constant ratio of two alkali and/or alkaline earth oxides as pseudobinaries in a ternary system and assumed that ternary alkali and/or alkaline earth silicate glasses separate into two phases, one of which is nearly pure SiO_2 and that tie lines would generally radiate from the silica corner of the ternary diagram. A regular solution model was applied to describe the ternary liquid solutions for the pseudo-binaries of a ternary system. However, as Strnad et al. [7,8] pointed out, such an assumption is not accurate thermodynamically because the location of tie lines generally depends on the temperature so that the composition of the high silica phase may be considerably different from pure silica, particularly at high temperature. From the thermodynamic viewpoint, the above approaches are insufficient in determining the compositions of coexisting phases and the shape of subliquidus miscibility gaps.

Strnad and Strnad [7] and Strnad and McMillan [8] have presented a more general method for calculating the metastable two-liquid tie lines and spinodal curves in ternary systems showing two-liquid phase separation by using the Newton numerical iterative method. Their calculation is based on the thermodynamic relations obtained by equating the chemical potentials of the components in the region of two-liquid phase equilibrium. They attempted to apply the quasi-regular solution model to the liquid phase in the binary silicate systems which show the asymmetrical miscibility gaps. Therefore, like Kawamoto and Tomozawa's treatment, they had to symmetrize the miscibility gaps in binary oxide systems by properly choosing the chemical compositions of end-members for the assumed solution because the asymmetrical shape of miscibility gaps in most binary alkali silicate systems cannot be obtained with the quasi-regular solution model. The excess Gibbs free energies of the ternary liquid solutions in this calculation were obtained by simply adding three binary excess free energy terms without using a ternary correction term.

Since there exist experimental difficulties in the phase analysis in the phase separation region, there have been few experimental studies on the subliquidus miscibility gaps in alkali borosilicate systems except the extensive works in the sodium borosilicate system. So far, there are no calculations of subliquidus miscibility gaps in the alkali borosilicate systems. In the present work, the experimental data determined by direct methods were chosen as inputs to calculate binary and ternary metastable subliquidus miscibility gaps in the lithium borosilicate system and the thermodynamic properties of their liquid phases were computer-modeled. Regular, quasi-regular, and subregular solution models were applied to describe the SiO_2- and/or B_2O_3-rich regions of binary liquid solutions. In the Li_2O–SiO_2 and B_2O_3–SiO_2 systems, multiple linear regression method was used to determine the interaction parameters of liquid solutions from silica liquidus data. In the Li_2O–B_2O_3 system, the interaction parameters of the liquid solution was determined from subliquidus miscibility data. To calculate the subliquidus miscibility gaps in the Li_2O–B_2O_3–SiO_2 system, the Toop–Muggianu method was applied to describe the Gibbs free energy of the ternary liquid solution by using the binary interaction parameters. Using the interaction parameters in the Gibbs free energy expression for liquid phases in both binary and ternary systems, the metastable subliquidus miscibility gaps were calculated by determining the tie lines with a Newton-Raphson numerical iterative method. Also, the spinodals were calculated for both binary and ternary systems. The calculated results were compared and discussed with available data from the literature.

2. Thermodynamic methodology

At constant temperature and pressure, the equilibrium compositions in multicomponent systems can be calculated with the Gibbs free energies for each phase as a function of composition. The equilibrium state of the phases in a system possesses the lowest Gibbs free energy for the phases. Simultaneously, this requirement satisfies the condition that equilibrium occurs when the chemical potentials (i.e. partial molar Gibbs free energies) of each component are equal in all phases. In the mathematical treatment of phase equilibria, this concept provides a useful relationship between the phases.

2.1. Binary systems

In the present calculation, the components in liquid solutions were Li_2O, B_2O_3, and SiO_2. When the standard states are solid phases (s) of pure component i and pure component j, the Gibbs free energy of a liquid phase (l) in the $i-j$ system is given by:

$$G_m^l = y\Delta G_i^{s\to l} + x\Delta G_j^{s\to l} + RT[y\ln y + x\ln x] + G_{ij}^{\mathrm{E}} \tag{1}$$

where y and x are mol fractions of components i and j, $\Delta G_i^{s\to l}$ and $\Delta G_j^{s\to l}$ are the difference in Gibbs free energies between the s phase and the l phase of pure components i and j, respectively, G_{ij}^{E} is the excess Gibbs free energy of the binary system. The excess Gibbs free energy for a subregular solution is expressed as

$$G^{\mathrm{E}} = yx\left[A^0 + A^1(y - x)\right] \tag{2}$$

where A^0 and A^1 are the interaction parameters of the liquid phase which do not depend on the composition. In this work the interaction parameters are expressed as a linear function of temperature. If A^1 is zero, the solution model is reduced to a regular solution when A^0 is independent of temperature and a quasi-regular solution when A^0 is a linear function of temperature. These solution models can be used when only the miscibility gaps are symmetric with respect to the two components. When the binary systems show asymmetric miscibility gaps, the excess Gibbs free energies of liquid solution phases should be expressed at least using a subregular solution model. The partial molar Gibbs free energies of components i and j for the l phase are given by

$$\overline{G}_i^l = \Delta G_i^{s\to l} + RT\ln(1 - x) + x^2\left[A^0 + A^1(3 - 4x)\right] \tag{3a}$$

$$\overline{G}_j^l = \Delta G_j^{s\to l} + RT\ln x + (1 - x)^2\left[A^0 + A^1(1 - 4x)\right] \tag{3b}$$

where x is the mol fraction of the solute.

In many ceramic systems, including the alkali silicate and borate systems, there is no solubility between the two components in the solid phases. In this case, the equilibrium condition between the liquid and the solid phases can be solved easily because the equilibrium composition of the solid phase is already known. In such a binary system, the interaction parameters of the liquid phase can be evaluated relatively easily by using the experimental liquidus in phase diagram. The liquidus boundaries in many binary oxide systems are well established experimentally [9] and can be used to represent the Gibbs free energies of the liquid phases. Additionally, basic data such as specific heat, melting point, and heat of fusion are required. The specific heat data, however, are available for only a few oxides and are sometimes inaccurate. In the present calculation, therefore, only the melting points and heats of fusion of components were used in order to calculate the interaction parameters of the liquid phase. If the small heat capacity corrections to the enthalpy and the entropy of fusion are neglected, then

$$\Delta G_i^{s\to l} = \Delta H_{\mathrm{f},i}\left(1 - \frac{T}{T_{\mathrm{m},i}}\right) \tag{4a}$$

$$\Delta G_j^{s\to l} = \Delta H_{\mathrm{f},j}\left(1 - \frac{T}{T_{\mathrm{m},j}}\right) \tag{4b}$$

where $T_{\mathrm{m},i}$, $T_{\mathrm{m},j}$, $\Delta H_{\mathrm{f},i}$, and $\Delta H_{\mathrm{f},j}$ are the melting points and the enthalpies of fusion of the components i and j, respectively.

In the present work, three approaches were used to determine the interaction parameters of the liquid phases in the binary systems. In the first method described below, the interaction parameters were determined from the equilibrium liquidus data. The subliquidus miscibility gaps can then be calculated by extending the interaction parameters to the metastable range at the lower temperatures.

When equilibrium between the liquid and the pure solid of component j is considered, the Eq. (3b) must be equal to zero since in the standard state of the pure solid there is no solubility of component i in the solid phase of component j. Therefore,

$$\Delta G_j^{s\to l} + RT\ln x + (1 - x)^2\left[A^0 + A^1(1 - 4x)\right] = 0. \tag{5}$$

Rearranging the above equation gives

$$\begin{aligned} &-\left(\Delta G_j^{s\to l} + RT\ln x\right)/(1 - x) \\ &\quad = A^0(1 - x) + A^1(1 - x)(1 - 4x). \end{aligned} \tag{6}$$

This expression can be considered as a linear combination, i.e.,

$$Y = A^0X_1 + A^1X_2 \tag{7a}$$

where

$$Y = -\left(\Delta G_j^{s\to l} + RT\ln x\right)/(1 - x) \tag{8a}$$

$$X_1 = (1 - x) \tag{8b}$$

$$X_2 = (1 - x)(1 - 4x) \tag{8c}$$

The function X_1 is a decreasing straight line for all compositions, and the function X_2 decreases to about $x \approx 0.63$ and then increases. The linear relationships between Y and X_1, X_2 were confirmed in alkali silicate systems [10]. When the interaction parameters are given by a linear function of temperature, above Eq. (7a) is expressed as:

$$Y = A_1^0 X_1 + A_2^0 T X_1 + A_1^1 X_2 + A_2^1 T X_2 \tag{7b}$$

where $A^0 = A_1^0 + A_2^0 T$ and $A^1 = A_1^1 + A_2^1 T$.

Using experimental liquidus data (x and T), the interaction parameters in Eqs. (7a,b) can be determined through a multiple linear regression method. With these parameters, the equilibrium liquidus as well as the metastable subliquidus miscibility gap can be calculated by observing the Gibbs free energy behavior of the liquid phase as a function of temperature. In the present calculation, this approach was applied to the B_2O_3–SiO_2 system where subliquidus data are rare.

In the second method, the interaction parameters of liquid phase were determined from the metastable subliquidus miscibility gap data. The equilibrium liquidus can be determined by extending the lower temperature behavior of the liquid to the higher temperature behavior of the liquid. In the Li_2O–B_2O_3 system where the equilibrium liquidus curve of boric oxide are not available, this method was applied to determine the interaction parameters of the liquid phase in this system and is described below. A subregular solution model was used to describe the asymmetric subliquidus miscibility gap in this system. To determine the interaction parameters of Eq. (2) the properties at the top of the subliquidus miscibility gap are used. That is, the second and third derivatives of the Gibbs free energy function, with respect to composition, must be zero at the critical point, i.e.

$$\frac{\partial^2 G_m^l}{\partial x^2} = RT_c\left[\frac{1}{1-x_c} + \frac{1}{x_c}\right] - 2A^0 - 6(1-x_c)A^1 = 0 \tag{9a}$$

$$\frac{\partial^3 G_m^l}{\partial x^3} = RT_c\left[\frac{1}{(1-x_c)^2} - \frac{1}{x_c^2}\right] + 12A^1 = 0 \tag{9b}$$

where T_c and x_c are the temperature and composition at the critical point. Furthermore, below the critical point, the equilibrium condition for the coexistence of two phases requires equality of the partial molar Gibbs free energies of each component. Therefore, two more equations are obtained.

$$\begin{aligned} &RT\ln(1-x_1) + x_1^2\left[A^0 + A^1(3-4x_1)\right] \\ &\quad = RT\ln(1-x_2) + x_2^2\left[A^0 + A^1(3-4x_2)\right] \end{aligned} \tag{10a}$$

$$\begin{aligned} &RT\ln x_1 + (1-x_1)^2\left[A^0 + A^1(1-4x_1)\right] \\ &\quad = RT\ln x_2 + (1-x_2)^2\left[A^0 + A^1(1-4x_2)\right] \end{aligned} \tag{10b}$$

where the x_1 and x_2 are two equilibrium compositions on the subliquidus miscibility gap at temperature T. The two interaction parameters, expressed as a linear function of temperature, can be obtained from these four equations. As the number of interaction parameters increases, their values can be determined by choosing additional temperatures and the appropriate compositions to develop a set of simultaneous equations of the form (10a,b). In the present calculation, with the interaction parameters of the liquid phase, subliquidus miscibility gaps at lower temperature were reproduced and confirmed by comparing with the experimental data.

The third method is a combination of the above two approaches and was used when both the equilibrium liquidus and subliquidus miscibility gap data are available. In many cases, the miscibility gaps calculated by the first approach were located at much higher temperature than the observed ones like in Charles' results [4,11]. Therefore, as used by Eliezer et al. [12], the available subliquidus miscibility gap data were added to equilibrium liquidus data to obtain the interaction parameters of the liquid phase in the Li_2O–SiO_2 system.

Having determined the Gibbs free energy expressions for the three binary systems, the Li_2O–SiO_2, Li_2O–B_2O_3, and B_2O_3–SiO_2 systems, it then becomes possible to calculate subliquidus miscibility gaps in the ternary system. The methodology for these calculations is described in detail in the next section.

2.2. Ternary system

For an i–j–k ternary system, Gibbs free energy of the l phase in choosing all pure solid phases as a standard state can be expressed as

$$\begin{aligned} G_m^l &= z\Delta G_i^{s\to l} + x\Delta G_j^{s\to l} + y\Delta G_k^{s\to l} \\ &\quad + RT[z\ln z + x\ln x + y\ln y] + G_{ijk}^{\mathrm{E}} \end{aligned} \tag{11}$$

where z, x, and y are mole fractions of components i, j, and k, respectively, and $\Delta G_i^{s\to l}$, $\Delta G_j^{s\to l}$, and $\Delta G_k^{s\to l}$ are the difference in Gibbs free energies between the s phase and the l phase of pure components i, j, and k, respectively, and G_{ijk}^{E} is the excess Gibbs free energy for the ternary system.

There is a considerable need to predict the thermodynamic properties of ternary phase diagram from the properties of its binary components. There exist numerous methods and they have been reviewed by Ansara [13]. Later, Wang et al. [14] presented many three-factor and multi-factor regular-type models for ternary systems. Some of the models applied are based on a theoretical description while others may be characterized as empirical. Experience shows that the analytical expressions which are obtained in predicting ternary properties from binary ones can be used for the representation of ternary experimental data. Therefore, it is important to choose the method of prediction with this purpose in mind, as well.

There are several practical numerical methods of predicting ternary properties from binary ones. The question is from what point on the binary side one should take the numerical value which will be allowed to contribute to the value in ternary system. According to the ways to choose weighting factors, there exist two methods: a symmetric and an asymmetric method. While the weighting factors in a symmetric method are same for all binary systems, those in an asymmetric method are different for the binary systems.

In the Li_2O–B_2O_3–SiO_2 system, the liquid solution contains two network formers, that is, boric oxide and silica. While the calculated miscibility gap in the B_2O_3–SiO_2 system shows a symmetric subliquidus miscibility gap, the other two binary systems show asymmetric subliquidus miscibility gaps. Therefore, an asymmetric method was applied to describe the liquid solution of the Li_2O–B_2O_3–SiO_2 system. Also, by using the experimental data in the literature the ternary interaction parameter was introduced in order to describe the behavior of the ternary liquid solutions precisely.

When one of the asymmetric methods called the Toop–Muggianu model [15] is applied to the subregular solution model, the following result is obtained,

$$\begin{aligned} G^{E}_{ijk} &= zx\left[A^{0}_{ij} + A^{1}_{ij}(z - x - y)\right] \\ &\quad + zy\left[A^{0}_{ki} + a^{1}_{ki}(z - y - x)\right] \\ &\quad + xy\left[A^{0}_{jk} + A^{1}_{jk}(x - y)\right]. \end{aligned} \tag{12}$$

Furthermore, if ternary experimental data are available, ternary correction terms can be introduced in order to describe ternary solution behavior more accurately.

$$G^{E}_{ijk} = A^{0}_{ijk}zxy \tag{13}$$

In the simplest case, A^{0}_{ijk} can be equal to be a constant. In the present calculations, by using the Toop–Muggianu model with a ternary correction term, the metastable subliquidus miscibility gaps in the ternary systems were calculated and compared with the data available from the literature. Also, the tie lines in the ternary systems were calculated in order to estimate the rotation of the tie lines about the original composition as the temperature decreases. The spinodal surfaces which represent the boundary between the stable and the unstable region were calculated in order to predict the composition range where spinodal decomposition may occur.

3. Results and discussion

In Figs. 1, 3, and 4, the cross and filled circles indicate the experimental liquidus and subliquidus data taken from the literature, respectively. The solid, dashed, and dot curves show the calculated liquidus, subliquidus miscibility gap, and spinodal curves, respectively.

3.1. B_2O_3–SiO_2 system

In the present calculation, the B_2O_3–SiO_2 phase diagram of Fig. 2353 of Ref. [9] was used to describe the behavior of the liquid solution. This system shows strong flattening of the liquidus curve of the SiO_2-rich side and a very short liquidus curve of the B_2O_3-rich side. Furthermore, by using electron microscopy [16], subliquidus immiscibility data have been identified experimentally. Therefore, a positive excess free energy function is expected for the liquid phase. Since this system shows a simple eutectic without any intermediate compounds, it is expected that the behavior of the liquid

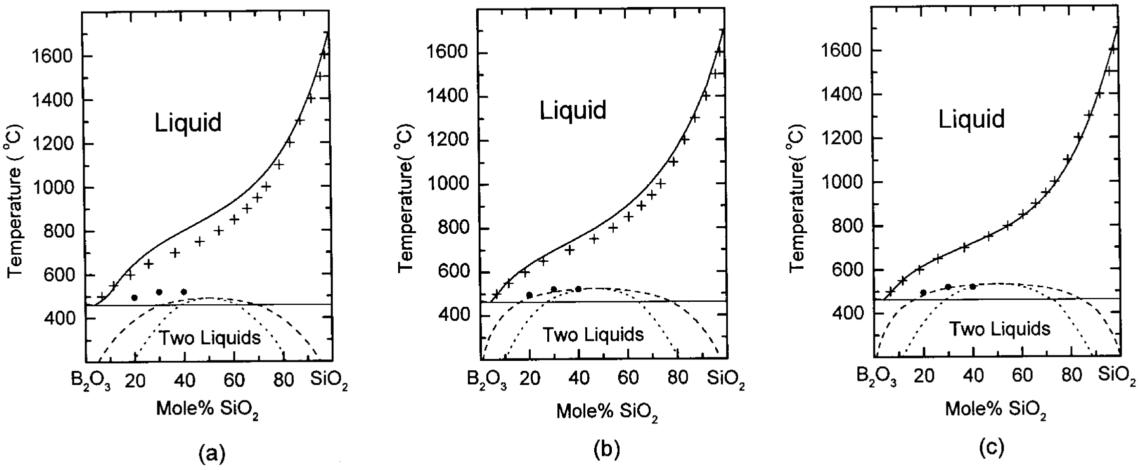

Fig. 1. Calculated subliquidus gaps and liquidus in B_2O_3–SiO_2 system according to various models: (a) regular solution; (b) subregular solution; (c) quasi-regular solution (+ experimental liquidus; ● experimental subliquidus).

solution in this system is simpler than that in the other systems. Therefore regular, subregular, and quasi-regular solution models were used to model the behavior of the liquid solution.

In order to obtain the Gibbs free energy expression for the liquid phase, the interaction parameters for the three kinds of solution models were determined by using the liquidus data of the silica-rich side. First, the equilibrium liquidus was calculated from the regular solution model and is shown in Fig. 1(a). This figure also shows a subliquidus miscibility gap where the critical point is located at $T_c = 503°C$ and $x_c = 0.5$. For both the liquidus and the subliquidus, however, there is a large difference between the calculated values and the experimental data ([16], Fig. 2353 of Ref. [9]). For this model, the interaction parameter obtained from the present work (12.9144 kJ/mol) is in good agreement with that of Hervig and Navrotsky (12.5±0.96 kJ/mol) [17], which was obtained from the measurement of enthalpies of solution of glasses and liquids in molten $PbO{\cdot}2B_2O_3$ at 974 K. However, the regular solution model proved to be the worst model to describe the liquid solution for this system.

Fig. 1(b) shows the equilibrium liquidus calculated from the subregular solution model. This figure also shows a slightly asymmetric subliquidus miscibility gap where the critical point is located at $T_c = 537°C$ and $x_c = 0.47$. The calculated values show a good agreement with the experimental data for the subliquidus miscibility gap but a little deviation for the liquidus curve. For the liquidus curve, the present deviation is similar to the result of Danilenko et al. [18] at higher temperature that was calculated with a subregular solution model. The shape of the subliquidus miscibility gap from the subregular solution model is almost the same as one ($T_c = 520°C$ and $x_c = 0.5$) that was estimated by Charles and Wagstaff [16].

Third, the equilibrium liquidus was calculated from the quasi-regular solution model and is shown in Fig. 1(c). This figure also shows a subliquidus miscibility gap where the critical point is located at $T_c = 541°C$ and $x_c = 0.5$. There is the best agreement between the calculated values and the experimental data for both the liquidus and the subliquidus miscibility gap. Therefore, this interaction parameter was chosen to calculate the ternary subliquidus miscibility gaps later.

Table 1 shows the interaction parameters of the liquid solution in the B_2O_3–SiO_2 system determined from above three models. The positive interaction parameter of the regular solution model or the quasi-regular solution model below 1306°C reflects the flattening of the liquidus curve and develops a subliquidus miscibility gap at low temperature. Boike et al. [19] estimated the excess Gibbs free energy of the liquid phase in the B_2O_3–SiO_2 system as a function of composition at 1475 K by using the activities of B_2O_3 which were studied by Knudsen effusion mass spectroscopy. Their result is shown in Fig. 2 and compared with the present results. It is found that it is located between the results for the quasi-regular and subregular models. Therefore, the present results from the quasi-regular and subregular models prove to be quite reasonable in order to describe the behavior of the liquid phase in the B_2O_3–SiO_2 system.

3.2. Li_2O–B_2O_3 system

The liquidus curve of the boric oxide-rich side in this system has not yet determined and its length would be very short like that of the B_2O_3–SiO_2 system. The observed subliquidus miscibility gap in the Li_2O–B_2O_3 system is located asymmetrically near the boric oxide [20]. Therefore, a subregular solution model was applied in order to obtain a reasonable subliquidus gap.

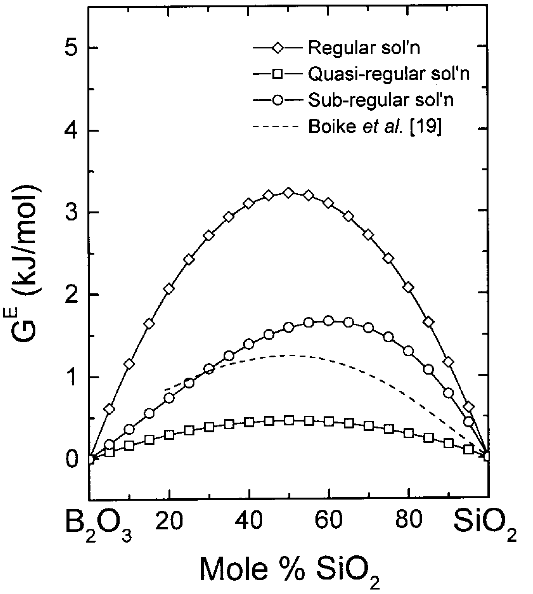

Fig. 2. Comparison of the calculated excess Gibbs free energies with an experimental one for the liquid phase in B_2O_3–SiO_2 system at 1475 K.

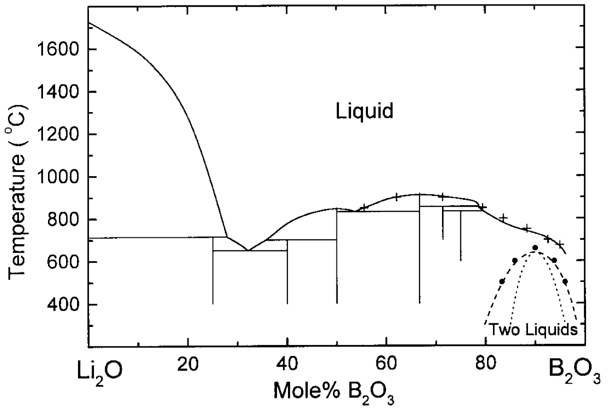

Fig. 3. Calculated subliquidus gaps and liquidus in Li_2O–B_2O_3 system (+ experimental liquidus; ● experimental subliquidus).

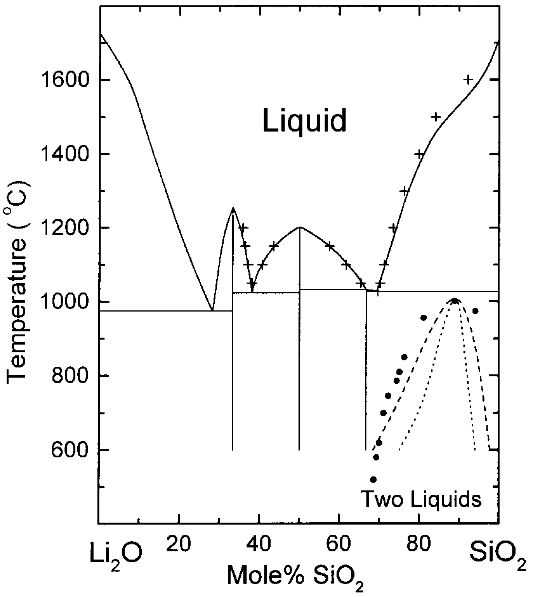

Fig. 4. Calculated subliquidus gaps and liquidus in Li_2O–SiO_2 system [10] (+ experimental liquidus; ● experimental subliquidus).

Table 1
Calculated interaction parameters of liquid phases in the B_2O_3–SiO_2, Li_2O–B_2O_3, and Li_2O–SiO_2 systems (kJ/mol).
Excess free energy: $G^E = x(1-x)[A^0 + A^1(1-2x)]$

Systems	Interaction parameters	
B_2O_3–SiO_2 ($x = x_{SiO_2}$)	A^0	12.9144
	A^0	27.9399–0.0177T/K
	A^0	22.0006–0.0106T/K
	A^1	4.7749–0.0052T/K
Li_2O–B_2O_3 ($x = x_{B_2O_3}$)	A^0	−131.4221 + 0.0228T/K
	A^1	−67.8520 + 0.0043T/K
Li_2O–SiO_2 ($x = x_{SiO_2}$)	A^0	89.4849–0.1566T/K
	A^1	18.7356–0.0699T/K

The interaction parameters of the liquid phases were determined by using the experimental subliquidus miscibility data at the critical temperature ($T_c = 660°C$) and the lowest temperature ($T_c = 500°C$). With the interaction parameters of the liquid phases, the subliquidus miscibility gap was reproduced at lower temperatures and shown in the Fig. 3. The calculated subliquidus miscibility gap shows excellent agreement with the experimental data [20]. Also, the liquidus curve was calculated by using the invariant reactions and compared with available experimental data in the literature [21]. The present calculation for the liquidus curve was also satisfactory. So far, there has been no report on the liquidus curve below 50 mol% B_2O_3 in the Li_2O–B_2O_3 system. Therefore, the liquidus curves in this range also were estimated by using the Gibbs free energy of liquid phase calculated from the subliquidus data. Table 1 summarizes the calculated interaction parameters of the liquid solution in the lithium borate system.

3.3. Li_2O–SiO_2 system

This section sums up the result of previous calculations on the liquidus and subliquidus phase equilibria in Li_2O–SiO_2 system [10]. In this calculation, the liquidus data of the silica-rich side were taken from Kracek's phase diagram (Fig. 182 of Ref. [9]) in order to obtain the Gibbs free energy expression for the liquid phase. The liquidus curve of the silica-rich side in this system shows the most extensive flattening among all the alkali silicate systems and a submerged subliquidus miscibility gap has been observed. Therefore, a large positive deviation from ideality is expected for the liquid solution.

The observed subliquidus miscibility gap in the Li_2O–SiO_2 system is located asymmetrically near the silica-rich side of the phase diagram. Two asymmetric subliquidus miscibility gaps near the silica are available in the literature: one by Moriya et al. ($T_c = 1002°C$, $x_c = 0.89$) [22] and the other by Galakhov and Alekseeva ($T_c = 910°C$, $x_c = 0.83$) [23]. These experimental results are the same at lower temperature but the latter is approximately 90°C below the result of the former in the region of the critical composition. However, it should be pointed out that the Moriya et al.'s result was confirmed experimentally by Haller et al. [24]. Furthermore, Galakhov et al. [25], one of the investigators of the latter data, used the result of Moriya et al. in a subsequent publication to investigate the phase separation in ternary silicate systems. Therefore, with the data of Moriya et al. the subregular solution model was applied to determine the interaction parameters of the liquid phase. This choice was tested in the previous work in order to obtain both the reasonable liquidus curve and subliquidus miscibility gap (Fig. 4) [10].

The equilibrium liquidus and the metastable subliquidus miscibility gap were calculated with the interaction parameters of the liquid phase and are shown in Fig. 4. The calculated critical point at $T_c = 1010°C$ and $x_c = 0.89$ agrees well with the experimental data at $T_c = 1002°C$ and $x_c = 0.89$ [24]. This result was much improved compared to Charles' result ($T_c = 1200°C$, $x_c = 0.92$) [11]. The calculated liquidus curves showed a reasonable agreement with the experimental data over most of the composition range. However, the calculated liquidus of Li_2O in the low silica region descends so rapidly that this result cannot agree with the Kracek's phase diagram where there is no report on the liquidus data of Li_2O but $2Li_2O{\cdot}SiO_2$ melts incongruently to Li_2O and liquid at 1255°C.

It should be pointed out that Kracek's phase diagram in the low silica region [26] is questionable since there are limited experimental data. And there exists an analogy with the incongruent melting of orthosilicate ($2Na_2O{\cdot}SiO_2$) in the Na_2O–SiO_2 system that was also determined by Kracek [27]. In this calculation, considering the Gibbs free energy behavior of the liquid solution, it is suggested that $2Li_2O{\cdot}SiO_2$ melts congruently at about 1255°C instead of melting incongruently as suggested by Kracek. The calculated liquidus at the low silica region shows that a eutectic point is located at 28.3 mol% and 975°C [10].

Although further experimental work is required to determine the liquidus curves in the low silica region precisely, these results show a reasonably good agreement between the calculated and the experimental values for both the liquidus curve and the subliquidus miscibility gap where data exist. Table 1 shows the calculated interaction parameter of the liquid solution in the Li_2O–SiO_2 system.

3.4. Li_2O–B_2O_3–SiO_2 system

The present calculation using excess Gibbs free energy data for three binary systems in the ternary Li_2O–B_2O_3–SiO_2 system has been extended to compute the ternary subliquidus miscibility gaps. In order to obtain reasonable subliquidus miscibility gap, a ternary interaction parameter was introduced. The ternary interaction parameter was established by comparing the experimental data [23] at several temperatures and estimated to be $G^{E}_{ijk} = zxy\,(-200.0224 + 0.1904\ T)$ kJ/mol.

In the Li_2O–B_2O_3–SiO_2 system, a subliquidus miscibility gap is developed below the calculated critical temperature of the Li_2O–SiO_2 system ($T_c = 1010$°C). Fig. 5 shows the development of the subliquidus miscibility gaps and the corresponding tie lines in the Li_2O–B_2O_3–SiO_2 system at several temperatures. Below the critical temperature of the Li_2O–SiO_2 system, a miscibility gap develops from the Li_2O–SiO_2 side. As the temperature decreases, its size increases and the critical point of the miscibility gap moves into the composition triangle. At the critical temperature of the Li_2O–B_2O_3 system ($T_c = 660$°C), another gap develops from the Li_2O–B_2O_3 side. The trend of developing tie lines and critical points from both the Li_2O–SiO_2 side and the Li_2O–B_2O_3 side to the inside of the composition triangle is quite reasonable.

At a temperature, such as 700°C in Fig. 5(c), the tie lines start from the binary tie line of the Li_2O–SiO_2 system. As B_2O_3 is added, the tie lines proceed into the composition triangle. They are no longer parallel to the Li_2O–SiO_2 side and rotate toward the B_2O_3–SiO_2 side. They become shorter and finally vanish at the critical point, where there exists a single phase liquid. From the present result of Fig. 5, it was shown that both of the tie-line compositions for two liquid phases develop into the composition triangle. Therefore, as Strnad et al. [7,8] pointed out, the assumption by Charles [4] and Kawamoto and Tomozawa [6] that tie lines would generally radiate from the silica corner of ternary silicate systems proved to be unreasonable. Since the spinodal region inside the miscibility gap is skewed near the B_2O_3–SiO_2 side, glasses with the lithia-poor composition could be phase-separated more favorably by spinodal decomposition.

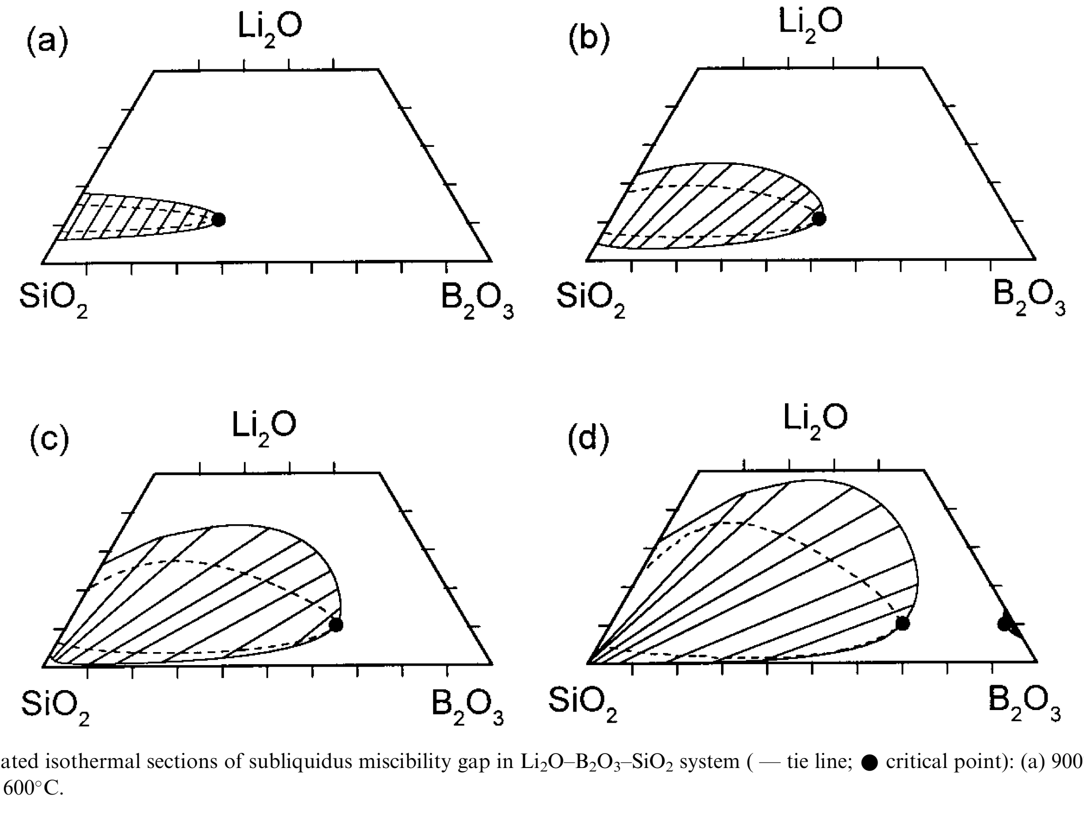

Fig. 5. Calculated isothermal sections of subliquidus miscibility gap in Li_2O–B_2O_3–SiO_2 system (— tie line; ● critical point): (a) 900°C; (b) 800°C; (c) 700°C; (d) 600°C.

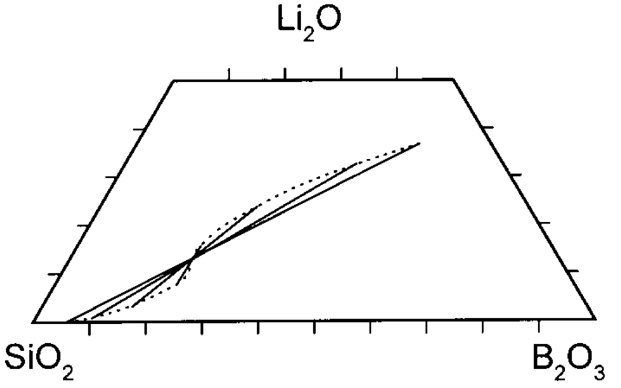

Fig. 6. The rotation of tie lines at the composition 13.1%Li_2O–21.7%B_2O_3–65.2%SiO_2 between 600 and 900°C.

Fig. 6 shows the calculated tie lines between 900 and 600°C as the liquid phase with the composition at 13.1% Li_2O–21.7% B_2O_3–65.2% SiO_2 is metastably cooled. It can be seen that there is a little rotation of the tie lines between 900 and 600°C. There have been no experimental data on the tie lines in this system but it is valuable to compare the present calculated tie lines with those determined experimentally in the Na_2O–B_2O_3–SiO_2 system [28]. The present calculation shows that the direction of the rotation of tie lines in the Li_2O–B_2O_3–SiO_2 system is similar to that of tie lines determined experimentally in the Na_2O–B_2O_3–SiO_2 system [28]. This similarity can be expected from the fact that the metal ions in these lithium and sodium oxides belong to the same alkali group.

Fig. 7 shows the isothermal sections through the subliquidus miscibility gap for the Li_2O–B_2O_3–SiO_2 system at 650, 700, 800 and 900°C. Superimposed on the same figure is the experimental result by Galakhov and Alekseeva [26]. The present calculation is satisfactory at 650 and at 700°C, reasonable at 800°C, and does not agree well with the data at 900°C. However, as discussed previously, it should be noted that while their experimental critical temperature in the Li_2O–SiO_2 system [26] is approximately 90°C below that of Haller et al. [24] and Moriya et al. [22] used in the present calculation, all those experimental data show no difference below 700°C. Therefore, the reason for the discrepancy in the ternary subliquidus miscibility gap at higher temperature is considered as a result of using the different binary data since the ternary miscibility gap in the present calculation was calculated by using the binary data. In order to remove the ambiguity of subliquidus miscibility gaps at higher temperatures, new experimental data should be collected near the critical point of the Li_2O–SiO_2 system in both the binary and the ternary systems.

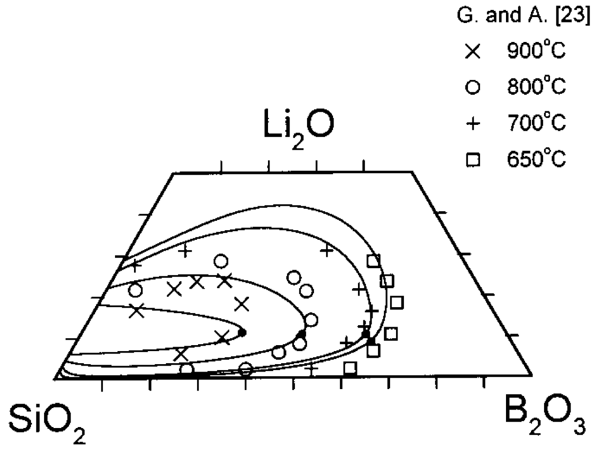

Fig. 7. Comparison of isothermal sections of subliquidus miscibility gap in Li_2O–B_2O_3–SiO_2 system (● critical point).

4. Conclusions

In the present calculations, the simple solution models such as quasi-regular and subregular solutions could describe well both the equilibrium liquidus and subliquidus miscibility data in the Li_2O–B_2O_3, Li_2O–SiO_2, and B_2O_3–SiO_2 systems. While the subliquidus miscibility gaps of the Li_2O–B_2O_3 and Li_2O–SiO_2 systems were located asymmetrically near B_2O_3 and SiO_2, respectively, that of the B_2O_3–SiO_2 system was shown symmetrically through the whole compositions. For these systems, the liquidus curves were reproduced with the obtained interaction parameters and also estimated for the unknown composition range.

By using the Toop–Muggianu method, the ternary subliquidus miscibility gaps were calculated. In the ternary system, the tie lines rotate from the Li_2O–SiO_2 system to the B_2O_3–SiO_2 system as the temperature decreases. In the present calculations, the isothermal sections of the subliquidus miscibility gaps in the ternary systems were quite reasonable, considering the development of both the tie lines and the isotherms of the subliquidus miscibility gap with critical points according to changing the temperature. The present results showed a good agreement with the experimental data when available in the literature. Also, the possible composition range was calculated where phase separation can occur by a spinodal decomposition process.

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