Silikáty *XXIII*, s. 1—8 (1979)

Původní práce

CALCULATION OF LIQUIDUS CURVES IN GLASS-FORMING TWO-COMPONENT SYSTEMS OF ALKALI BORATES

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Dedicated to the 25th anniversary of the Institute of
Inorganic Chemistry of the Slovak Academy of Sciences

Received 6. 4. 1978

Liquidus curves of glass-forming two-component systems of alkali borates were calculated by means of the Le Chatelier–Schreder equation. Activities of components in solutions were obtained by the formal use of the Haases approach. An analogy of the structure of the crystalline phase with that of the melt was considered in the calculation. The liquidus curves obtained by calculation were compared with the experimental ones and a satisfactory agreement was found.

INTRODUCTION

Structural research of vitreous and molten boron trioxide made with the aid of X-ray techniques has shown that the substance comprises BO_3 triangles joined by their apexes into an irregular three-dimensional network [1], [2]. The low electric conductivity value and the high viscosity of molten B_2O_3 close to its melting point indicate that the three-dimensional covalent network is retained in the structure even after fusion.

Richter and coworkers [3] on the basis of X-ray analysis first suggested that the BO_3 groups are not planar, forming flat tetrahedrons with the boron atom at the apex. Grjotheim and Krogh-Moe [4] pointed out that the structure of boron oxide glass is similar to that in its hexagonal crystalline form and that it consists of two types of irregular BO_4 tetrahedrons. The first one is a hybride between triangular and tetrahedral configuration with the boron situated much closer to the three oxygen atoms. The other is a distorted tetrahedron with various lengths of the B—O bond. The mean co-ordination number of boron in the B_2O_3 melt, 3.1 as determined by Biscoe and Warren [5], does not provide explicit evidence of any change in boron co-ordination according to the authors of study [4]. However, more recent measurements of nuclear magnetic resonance have confirmed the Warren's X-ray diffraction measurements.

In the glass-forming binary systems of alkali borates it is possible to observe a change in the trend of a number of physico-chemical properties in the concentration range of approx. 20 mole % of alkali oxide. For instance, Gooding and Turner [6] found that expansion of sodium borate glasses decreases with increasing content of alkali oxides up to about 16 mole %, increasing again above this concentration. Shartsis et al. [7] found that the viscosity of borate melts first decreases with increasing concentration of alkali oxide, then increases and attains a maximum in the region of about 20 mole % of alkali oxide. These phenomena, called 'boric acid anomaly' in literature, are due to a change in the structure of the B_2O_3 melt caused by the alkali oxide addition and are related to the ability of boron to change its co-ordination number.

Biscoe and Warren [5] studied X-ray diffraction of sodium borate glasses and for the first time established a change in the co-ordination of some boron atoms from 3 to 4 in the low Na_2O concentration range. Abe [8] assumed a maximum concentration of four-co-ordinated boron at a concentration of 16.7 mole % Na_2O. Krogh-Moe [9], on the basis of a similarity between the infrared spectra of crystalline and glassy alkali borates, has come to the conclusion that the change in the co-ordination number of boron from 3 to 4 takes place up to a content of 33 mole % of alkali oxide, which corresponds to a maximum concentration of 50 % of four-co-ordinated boron. This assumption has been explicitly confirmed experimentally by the measurements of nuclear magnetic resonance carried out by Silver and Bray [10] and by Bray and O'Keefe [11]. These authors found that within the concentration range of $x = 0$—30 mole % of alkali oxide the concentration N_4 of four-co-ordinated boron may be quite accurately expressed by the relation

$$N_4 = \frac{x}{100 - x} \,. \tag{1}$$

Equation (1) may be interpreted so that each oxygen added will change the co-ordination of two boron atoms from the triangular to the tetrahedral one. As a result of this there are no non-bridging oxygen atoms present within this concentration range. This fact has also been confirmed by X-ray structural analyses of various crystalline borates described in study [9] where it is also pointed out that equation [1], which primarily holds for alkali borate glasses, may likewise be applied to crystalline alkali borates.

The comparison of results of nuclear magnetic resonance studies [10], [11] and those of the glass forming ability of alkali borates indicate that the limit glassforming concentration is only slightly higher than that at which non-bridging oxygen atoms are formed. This implies that at the limit glassforming concentration the degree of latticing in alkali borate systems is much higher than for instance in silicate systems. However, this difference in structure will obviously decrease with increasing temperature as a result of the lower stability of BO_4 groups at higher temperatures [8].

In a previous work [13] the present authors suggested a thermodynamic model of silicate melts in the systems MeO — SiO_2, based on an analogy of the crystalline structure and that of the melt. On the basis of the facts mentioned above one may reasonably expect an analogy between the structures of the crystalline phase and of the liquid one also in the alkali borate systems. This assumption has been verified in the present study in the calculation of liquidus curves in alkali borate systems while a approach similar to that employed in study [13] has been used in the formulation of the thermodynamic model of borate melts.

THEORETICAL

The structure of alkali borate melts can be assumed to be a three-dimensional network of apex-joined BO_3 triangles and BO_4 tetrahedrons where the cations are situated in the free spaces. The properties of such a melt will obviously depend on the numerical representation of boron in the individual co-ordinations, on the amount of alkali cations and bridging oxygens, and at higher concentrations of the alkali oxide also on the amount of nonbringing oxygens present.

Let us consider a two-component system Me_2O — B_2O_3 containing a moles Me_2O and b moles B_2O_3. The total number of boron moles in the mixture is $2b$. When assuming that each oxygen atom of alkali oxide changes the co-ordination of two boron atoms from 3 to 4, then the number of moles of four-co-ordinated boron atoms in any mixture will be $2a$ and the number of moles of three-co-ordinated boron atoms $2b — 2a$. The total number of oxygen atoms in any arbitrary mixture will be equal to $3b + a$. The total number of boron co-ordinations is $6b + 2a$. The number of moles of bridging oxygens will be $6b + 2a — (3b + a) = 3b + a$, so that all the oxygen atoms present will be the bridging ones. For example, in the compound Na_2O . $4B_2O_3$ there will be two boron atoms in tetrahedral co-ordination, six boron atoms in triangular co-ordination and all the oxygen atoms will be the bridging ones.

As follows from the results of work [10], [11] such a trend is maintained up to a concentration of approx. 30 mole % of alkali oxide. Above this concentration in melt, nonbridging oxygen atoms arise as a result of reverse transition of some boron atoms from tetrahedral co-ordination into the triangular one. According to [11], Na_2O . $2B_2O_3$ melt contains by about 7 % less boron in tetrahedral co-ordination than would correspond to equation [1]. In the melt there are therefore about 7 % atoms of non-bridging oxygen, which formally corresponds to 0.5 non-bridging oxygen atoms per formula unit. When further alkali oxide is added the representation of boron in the tetrahedral co-ordination remains at first unchanged (at about 50 %) but then it decreases and falls down to zero at 70 % of the alkali oxide [11]. In metaborate melts it is possible to assume the presence of approximately 40 % non-bridging oxygen atoms which corresponds roughly to 1.5 atom of non-bridging oxygen per formula unit. It should be noted, however, that within the concentration range above 33 % of alkali oxide only scarce experimental data are available so that the picture of the structure of these melts is only approximate. Larger differences between the liquid and the crystalline phase can likewise be expected in this concentration range.

The Haase's approach was used in the calculation of activities of the individual components [14]. Chemical potential of the component in solution was determined as a sum of chemical potentials of cations, three- and four-coordinated boron and that of bringing and non-bridging oxygen atoms. The derivation of the expression for the activity of a component based on the theory mentioned above, as well as the assumptions under which the activity of a component was calculated, have been dealt with in the preceding study [13].

When defining the true molar fraction of i-th particle in pure I-th component and in mixture by means of equations

$$y^{\circ}_{i,I} = \frac{n_{i,I}}{\Sigma\, n_{i,I}}, \qquad y_i = \frac{\Sigma\, n_{i,\,I}\, x_I}{\Sigma\,(x, \Sigma n_{i,\,I})}, \tag{2}$$

where x_I is the molar fraction of I-th component in mixture and $n_{i,I}$ is the number of i-th particles (e.g. alkali ions) in the I-th component, then the activity of I-th component in solution is given by the relationship

$$a_I = \prod_{i=1}^{k} \left(\frac{y_i}{y^{\circ}_{i,I}}\right)^{n_{i,I}}. \tag{3}$$

The same relations also hold for the other component. The liquidus curves of two-component borate systems were calculated by means of the simplified LeChatelier-Schreder equation (ΔH^f = const.)

$$\ln a = \frac{\Delta H^f}{R}\left(\frac{1}{T^f} - \frac{1}{T}\right), \tag{4}$$

where ΔH^f and T^f are enthalpy and temperature of fusion of the pure component respectively.

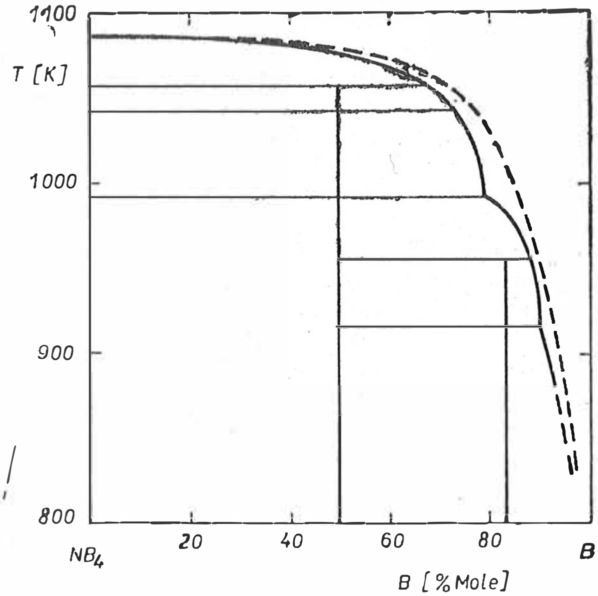

Fig. 1. Phase diagram of the system B_2O_3 — $Na_2B_8O_{13}$; - - - - *calculated.*

THE RESULTS OF CALCULATION AND DISCUSSION

The liquidus curves were calculated in the binary systems B_2O_3(B) — $Na_2B_8O_{13}$(NB_4), NB_4—$Na_2B_4O_7$(NB_2), NB_2—$Na_2B_2O_4$(NB), $Li_2B_4O_7$(LB_2)—$Li_2B_2O_4$(LB) and $K_2B_4O_7$(KB_2) — $K_2B_2O_4$(KB) (Figs. 1—5).
The necessary values of enthalpy and temperature of fusion are listed in Table I. As the values of enthalpy of fusion of NB_4 and KB are not known, they were estimated from known values of entropy of fusion of NB, NB_2 and oxides using the formulas

$$
\begin{aligned}
\Delta S^{N+B} &= \Delta S^{f}_{NB} - \Delta S^{f}_{N} - \Delta S^{f}_{B}\\
\Delta S^{NB+B} &= \Delta S^{f}_{NB_2} - \Delta S^{f}_{NB} - \Delta S^{f}_{B}\\
\Delta S^{f}_{NB_4} &= \Delta S^{f}_{NB_2} + 2\,\Delta S^{f}_{B} + 2\,\Delta S^{NB+B}\\
\Delta S^{f}_{KB} &= \Delta S^{f}_{K} + \Delta S^{f}_{B} + \Delta S^{N+B}
\end{aligned}
\tag{5}
$$

The calculation has shown that due to the relatively high values of enthalpy of fusion of the components in question an error of ± 10 % in the estimated value does not play any significant role and may cause an error of only a couple of degrees in the calculated temperature on the liquidus curve. The presence of the incongruently melting NB_3 compound has been taken into account in the calculation of the liquidus curve of the system $NB_4 - NB_2$. The primary crystallization curve for NB_3 was calculated on the basis of estimated hypothetical melting point of 1045 K, and the enthalpy of fusion was estimated similarly to the case of NB_4.

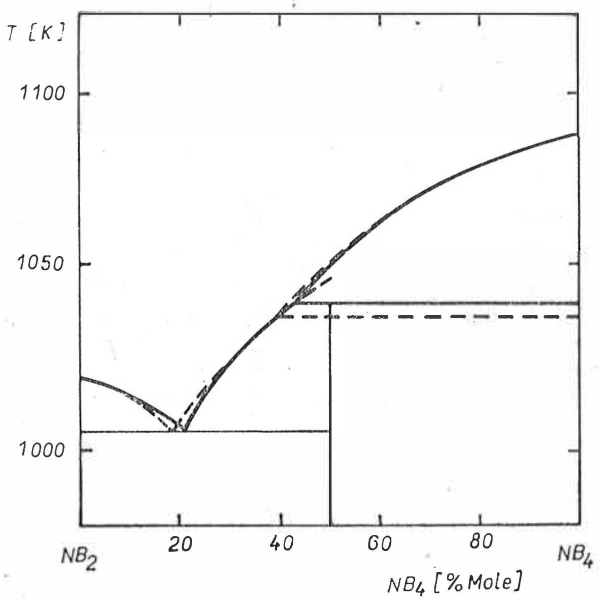

Fig. 2. Phase diagram of the system $Na_2B_8O_{13} - Na_2B_4O_7$; – – – – *calculated.*

Table II lists the numbers of particles in a formula unit of the pure components considered. The numbers of three- and four-co-ordinated boron atoms in the formula unit was calculated according to equation (1). In the case of metaborate the presence of 50 % tetrahedrally co-ordinated boron was assumed. The calculation of non-bridging oxygen atoms was based on experimental data given in [11]. For diborate the presence of 0.5 atom of non-bridging oxygen and 6.5 atoms of bridging oxygens was considered. The values of 2.5 bridging and 1.5 non-bridging oxygen atoms were adopted for metaborate.

Table I.
Thermodynamic data for pure components [18]

Component	T^f [K]	ΔS^f [J . mol^{-1} . K^{-1}]	ΔH^f [kJ . mol^{-1}]
B_2O_3	723	30.6	22.2
NB_4	1 088	122.6*	133.4*
NB_3	1 045	101.2*	105.7*
NB_2	1 016	79.8	81.1
KB_2	1 088	95.7	104.1
LB_2	1 190	101.2	120.4
NB	1 239	58.4	72.4
KB	1 223	53.0*	64.8*
LB	1 117	60.3	67.7
Na_2O	1 405	33.9	47.6
K_2O	1 154	28.5**	32.7**

* estimated values (see the text)
** [19]

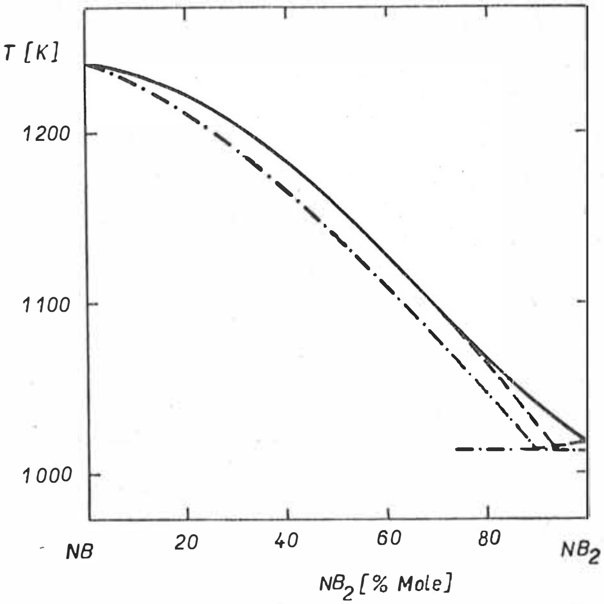

Fig. 3. Phase diagram of the system $Na_2B_4O_7$ — $Na_2B_2O_4$; ——— *Milman and Bouaziz [15, 1975],* –.–.– *Morey and Merwin [15, 1964],* – – – – *calculated.*

A comparison of experimental [15] and calculated liquidus curves indicates that the calculation method describes satisfactorily the courses of liquidus curves in these complex glassforming melt systems. The explanation of the structure of borate melts conforms with experimental data obtained by both X-ray diffraction and nuclear magnetic resonance, and allows to characterize thermodynamic behaviour of the melt with satisfactory accuracy.

Table II.
Numerical representation of particles in formula unit of pure components

Component	Na^+	B^3	B^4	—O—	—O
B_2O_3	—	2	—	3	—
NB_4	2	6	2	13	—
NB_3	2	4	2	10	—
NB_2	2	2	2	6.5	0.5
NB	2	1	1	2.5	1.5

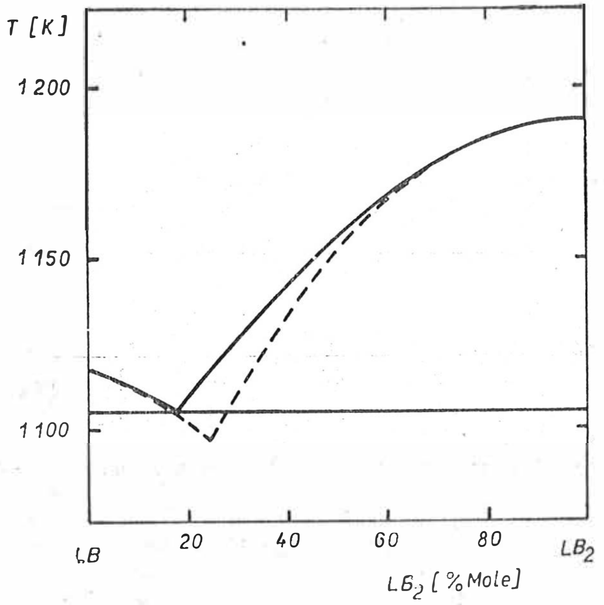

Fig. 4. Phase diagram of the system $Li_2B_4O_7$ — $Li_2B_2O_4$; - - - - *calculated.*

In the system NB_2 — NB the calculation has confirmed the course of the NB liquidus curve determined experimentally by Milman and Bouaziz [15, 1975] whereas the earlier results of the study by Morey and Merwin [15, 1964] can be considered incorrect because the limit relations are not fulfiled around the NB melting point. However, on the basis of the calculations submitted one may assume formation of an eutectic very close to the NB_2 compound.

A significantly less satisfactory agreement with experimental course of liquidus curves may be observed in the systems MeB_2 — MeB (where Me = Li and K) where the assumption of an analogy between the structures of the liquid and the crystalline phases will hold to a lesser degree. The effect of different polarizing effects of the individual alkali cations will also probably be more substantial in these systems. For example, according to [16], [17] the concentration of tetrahedral boron N_4 in the system K_2O — B_2O_3 decreases down to zero at 50 mole % K_2O. This means that in potassium metaborate all the boron atoms are in triangular co-ordination. This fact obviously results in an increase in the concentration of non-bridging oxygen atoms and consequently in a lower degree of latticing of the melt and thus in a steeper course of the KB liquidus curve in the system K_2B — KB (cf. Fig. 5).

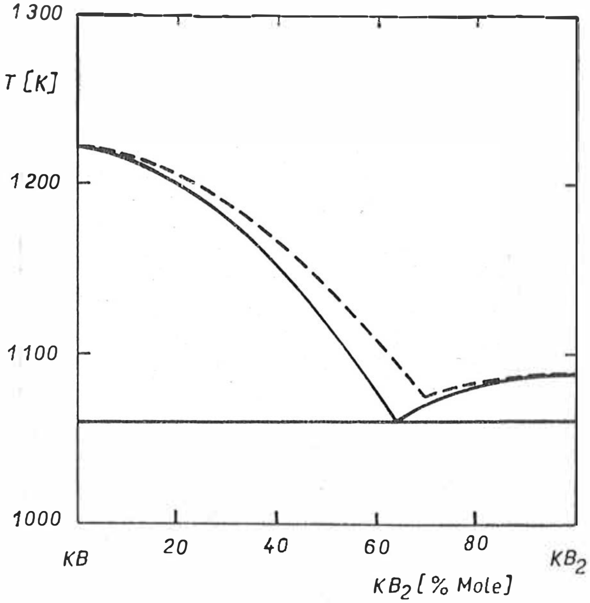

Fig. 5. Phase diagram of the system $K_2B_4O_7$ — $K_2B_2O_4$; - - - - *calculated.*

CONCLUSION

A thermodynamic model of silicate melts in the systems MeO — SiO_2 [13], based on an analogy between the structure of the cristalline phase and of the melt, was used in the calculation of activities and liquidus curves for two-component systems of alkali borates. The change in the co-ordination of boron atoms in dependence on alkali oxide concentration was taken into account in the calculations. The calculation is based on structural concepts obtained from experimental data of X-ray diffraction and nuclear magnetic resonance, and allows the liquidus curves of the given systems to be characterized with a satisfactory accuracy.

References

[1] Warren B. E., Biscoe J.: J. Amer. Ceram Soc. *21*, 257 (1938).
[2] Zarzycki J.: Proc. 4. th Int. Congress Glass, Paris *6*, 323 (1956).
[3] Richter H., Breitling G., Herre F.: Naturforschung *9a*, 390 (1954).
[4] Grjotheim K., Krogh-Moe J.: K. norske Vidensk. Selsk. Forh. *27*, No 18, 94 (1954).
[5] Biscoe J., Warren B. E.: J. Amer. Ceram. Soc. *21*, 287 (1938).

[6] Gooding E. J., Turner W. E. S.: J. Soc. Glass Technol. *18*, 32 (1934).
[7] Shartsis L., Capps W., Spinner S.: J. Amer. Ceram. Soc. *36*, 319 (1953).
[8] Abe T.: J. Amer. Ceram. Soc. *35*, 284 (1952).
[9] Krogh-Moe J.: Physics Chem. Glasses *1*, 26 (1960); Arkiv Kemi *12*, 475 (1958).
[10] Silver A. H., Bray P. J.: J. Chem. Phys. *29*, 984 (1958).
[11] Bray P. J., O'Keefe J. G.: Physics Chem. Glasses *4*, 37 (1963).
[12] Imaoka M.: in *Advances in Glass Technology*, Part I, p. 149. Plenum Press, New York 1962.
[13] Pánek Z., Daněk V.: Silikáty *21*, 97 (1977).
[14] Haase R.,: *Thermodynamic Properties of Gases, Liquids, and Solids* in Physical Chemistry Vol. 1, ed. H. Eyring, D. Henderson, W. Jost, p. 352. Academic Press, New York (1971).
[15] Levin E. M., Robbins C. R., McMurdie H. F.: *Phase Diagrams for Ceramists*, Am. Ceram. Soc., Columbus, Ohio 1964, 1975.
[16] Krogh-Moe J.: Physics Chem. Glasses *3*, 1 (1962).
[17] Svanson S. E., Forslind E., Krogh-Moe J.: J. Phys. Chem. *66*, 174 (1962).
[18] Barin I., Knacke O.: *Thermochemical Properties of Inorganic Substances*. Verlag Stahleisen, Düsseldorf 1973.
[19] *Thermodynamic Properties of Inorganic Substances* (in Russian). Atomizdat, Moscow 1965.

VÝPOČET KRIVIEK LIKVIDUS V SKLOTVORNÝCH DVOJZLOŽKOVÝCH SÚSTAVÁCH ALKALICKÝCH BORITANOV

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Vykonali sa výpočty kriviek likvidus sklotvorných dvojzložkových sústav alkalických boritanov pomocou rovnice LeChatelierovej-Šrederovej. Aktivity zložiek v roztoku sa získali formálnym použitím teórie konformných roztokov. Pre výpočet aktivít zložiek v roztoku sa použil termodynamický model silikátových tavenín sústav MeO — — SiO_2 [13], založený na analógii štruktúry kryštalickej fázy a taveniny, pričom sa zohľadnila zmena koordinácie atómov bóru v závislosti od koncentrácie alkalického kysličníka. Výpočty vychádzajú zo štruktúrnych predstáv, získaných na základe experimentálnych údajov rtg difrakcie a jadrovej magnetickej rezonancie. Vypočítané krivky likvidus sa porovnali s experimentálnymi. Zistilo sa, že uvedený spôsob výpočtu umožňuje s dostatočnou presnosťou charakterizovať krivky likvidus uvažovaných sústav.

РАСЧЕТ КРИВЫХ ЛИКВИДУС В СТЕКЛООБРАЗУЮЩИХ ДВУХКОМПОНЕНТНЫХ СИСТЕМАХ ЩЕЛОЧНЫХ БОРАТОВ

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Проводились расчеты кривых ликвидус стеклообразующих двухкомпонентных систем щелочных боратов с помощью уравнения Ле-Щательера—Шредера. Активности компонентов в растворе получались формальным использованием метода Хааса [14]. Для расчета активности компонентов в растворе применяли термодинамическую модель силикатных расплавов систем MeO—SiO_2 [13], основывающуюся на аналогии структуры кристаллической фазы и расплава, причем учитывается изменение координации атомов бора в зависимости от концентрации щелочного окисла. Расчеты выходят из структурных представлений, полученных на основании экспериментальных данных рентгеновской дифракции и ядерного магнитного резонанса. Далее сопоставлялись кривые ливквидус с экспериментальными кривыми. Было установлено, что приведенным способом расчета можно с достаточной точностью характеризовать кривые ликвидус рассматриваемых систем.

Рис. 1. Диаграмма фаз системы B_2O_3—$Na_2B_8O_{13}$; - - - - *расчет.*
Рис. 2. Диаграмма фаз системы $Na_2B_8O_{13}$—$Na_2B_4O_7$; - - - - *расчет.*
Рис. 3. Диаграмма фаз системы $Na_2B_4O_7$—$Na_2B_2O_4$; ▬▬ *Милман и Буазиз [15, 1975],*
-·-·- *Морей и Мервин [15, 1964],* - - - - *расчет.*
Рис. 4. Диаграмма фаз системы $Li_2B_4O_7$—$Li_2B_2O_4$; - - - - *расчет.*
Рис. 5. Диаграмма фаз системы $K_2B_4O_7$—$K_2B_2O_4$; - - - - *расчет.*

Obr. 1. Fázový diagram sústavy B_2O_3 — $Na_2B_8O_{13}$;
- - - - *výpočet.*
Obr. 2. Fázový diagram sústavy $Na_2B_8O_{13}$ — $Na_2B_4O_7$;
- - - - *výpočet.*
Obr. 3. Fázový diagram sústavy $Na_2B_4O_7$ — $Na_2B_2O_4$;
▬▬ *Milman a Bouaziz [15, 1975],* -·-·- *Morey a Merwin [15, 1964]*
- - - - *výpočet.*
Obr. 4. Fázový diagram sústavy $Li_2B_4O_7$ — $Li_2B_2O_4$;
- - - - *výpočet.*
Obr. 5. Fázový diagram sústavy $K_2B_4O_7$ — $K_2B_2O_4$;
- - - - *výpočet.*