

investigation [7] it is monoclinic, $P2_1/n$, which denies the possibility of ferroelectricity, otherwise quite frequent in similar compounds of glycine [8–10]. In the analogous H_2SeO_3 –alanine– H_2O system, no analogous compound was found [7].

The authors will send the programs on request.

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Phase Equilibria in the System $LiF-KF-B_2O_3-TiO_2$

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In the region of the primary crystallization of LiF in the ternary system $LiF-KF-B_2O_3$ a liquid miscibility gap is formed at the composition from 5 to 23 mole % B_2O_3 in the $LiF-B_2O_3$ boundary and up to 12 mole % KF in the ternary system. From the thermodynamic analysis of the binary systems it follows that the dissolution of boron oxide in molten lithium fluoride leads to the formation of $Li_2B_4O_7$, while in molten potassium fluoride the compounds KBF_4 and $K_2B_4O_7$ are formed. These compounds are most probably present also in the melts of the ternary system. By addition of TiO_2 into molten LiF or into molten $LiF-KF$ mixtures insoluble Li_2TiO_3 precipitates immediately from the melt. It may be therefore concluded that the rising of the temperature of primary crystallization in the melts of the system $LiF-KF-B_2O_3-TiO_2$ is due to the formation of Li_2TiO_3 with a relatively high melting point.

The melts of the system $LiF-KF-B_2O_3-TiO_2$ may be used as the electrolyte in the electrochemical synthesis of titanium diboride, especially when preparing well dispersed powders [1]. The use of this electrolyte is motivated by the effort to exclude special and expensive boron and titanium sources, such as fluoroborates and fluorotitanates, which moreover introduce surplus of alkali fluorides.

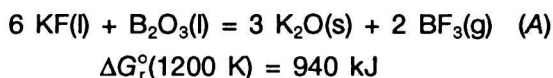
The system $LiF-KF-B_2O_3-TiO_2$ is a considerably complicated subsystem of the quinary reciprocal system $Li^+, K^+, B^{3+}, Ti^{4+}/F^-, O^{2-}$, in which a number of compounds are formed. The phase equilibria in the system $LiF-KF-B_2O_3-TiO_2$ have been investigated still unsatisfactorily. The existing phase equilibria studies are as follows.

The phase diagram of the binary system $LiF-B_2O_3$ was studied in [2, 3], especially in the range of high concentrations of LiF. It was found [3] that

two immiscible liquid phases are formed in the composition range 5–23 mole % B_2O_3 with the monotectic temperature of 836 °C and the upper critical temperature of 862 °C at ca. 14 mole % B_2O_3 . In the system $LiF-B_2O_3$ a number of chemical reactions between the components may be expected. From the X-ray powder diffraction analysis as well as the IR spectroscopy of quenched melts it follows that $LiBO_2$ and volatile BF_3 is formed up to ca. 5 mole % of B_2O_3 . At higher amounts of B_2O_3 lithium metaborate polymerizes into tetraborate. The system $LiF-B_2O_3$ seems to be thus a nonlinear projection of the $LiF-LiBO_2-B_2O_3$ joint.

The binary system $LiF-KF$ is a simple eutectic one with the coordinates of the eutectic point of 49 mole % KF and the eutectic temperature of 492 °C [4].

The phase diagram of the system KF–B₂O₃ is not known. According to the value of the reaction Gibbs energy of the metathetical reaction [5]



the system KF–B₂O₃ should be the stable diagonal of the ternary reciprocal system K⁺, B³⁺//F⁻, O²⁻. However, again a number of chemical reactions between components forming new compounds are possible. In the boundary binary system K₂O–B₂O₃ [6] the following congruently melting compounds are formed: K₂O · B₂O₃, $\theta_f = 950 \text{ }^\circ\text{C}$, K₂O · 2B₂O₃, $\theta_f = 815 \text{ }^\circ\text{C}$, and K₂O · 3B₂O₃, $\theta_f = 857 \text{ }^\circ\text{C}$. The next boundary system KF–BF₃ was studied only up to 50 mole % BF₃ [6], where a congruently melting compound KBF₄ with the melting temperature of 570 °C is formed. KF–KBF₄ is a simple eutectic system. In the ternary system KF–KBF₄–B₂O₃ the cross-section KF–B₃O₃F₃ up to 60 mole % B₃O₃F₃ [7] was studied. In this system the ternary compound K₃B₃O₃F₆ with the congruently melting point of 560 °C is formed.

The aim of the present work was to determine the solidus–liquidus equilibria in the system LiF–KF–B₂O₃–TiO₂ in the composition region interesting from the point of view of the electrochemical synthesis of TiB₂, i.e. up to 20 mole % B₂O₃ and 5 mole % TiO₂ [1].

EXPERIMENTAL

The temperature of primary crystallization was determined by means of the thermal analysis method registering the cooling and heating curves of the investigated mixtures. The samples (ca. 40 g) were placed in a platinum crucible in the resistance furnace with an adjustable cooling rate. The temperature was measured using a Pt–PtRh10 thermocouple calibrated to the melting points of well defined simple salts. The hot end of the thermocouple was immersed directly in the melt. The measured temperatures of primary crystallization were reproducible in the range of 3 °C.

All chemicals used were of reagent grade purity. The liquidus temperatures in the ternary system LiF–KF–B₂O₃ up to the content of 20 mole % B₂O₃ and a cross-section of the quaternary system LiF–KF–B₂O₃–TiO₂ with a constant content of 5 mole % TiO₂, i.e. the region interesting in the electrochemical synthesis of TiB₂, were determined. Most experimental difficulties brought samples with increased B₂O₃ content, which show considerable evaporation and an increased tendency to undercooling. Careful adjustment of the cooling rate

and registration of the heating curves were used in such cases, especially in the concentration region of immiscibility.

The phase composition after melting of the investigated mixtures was determined by means of the X-ray powder diffraction analysis and of the IR spectroscopy method. Infrared spectra of the quenched molten mixtures were measured using the spectrometer 9836 (Perkin–Elmer). The mid-infrared spectra were recorded at 300 K using KBr pellets. Quenched samples of investigated melts were used for examination. It was supposed that the chemical composition of the melt after intense cooling was sufficiently conserved.

RESULTS AND DISCUSSION

System KF–B₂O₃

The experimental temperatures of the primary crystallization of KF in the system KF–B₂O₃ up to 20 mole % B₂O₃ are shown in Fig. 1. The calculated liquidus curve of KF is also shown for comparison. The calculation was performed according to the Le Chatelier–Shreder equation ($\Delta H_f(\text{KF}) = \text{const.}$). The activity of KF was expressed using the "universal model"

$$a(\text{KF}, \text{l}) = x^k(\text{KF})$$

where $x(\text{KF})$ is the true mole fraction of KF in the mixture and k is the number of new particles which

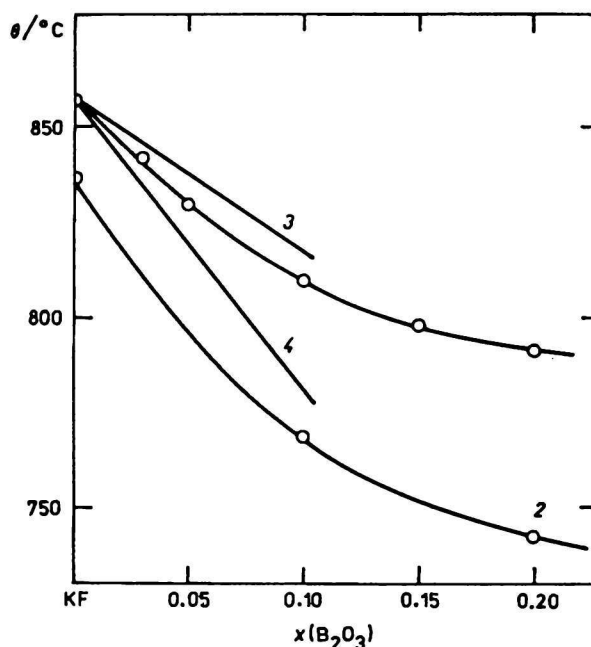
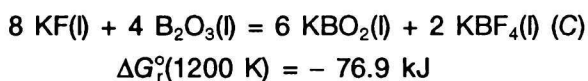
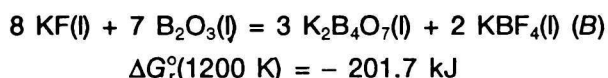


Fig. 1. The liquidus curve of KF in the system KF–B₂O₃ (1) and in the cross-section KF–B₂O₃ + 5 mole % TiO₂ (2). Calculated liquidus curve for $k = 1$ (3) and $k = 2$ (4).

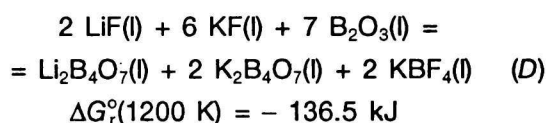
are introduced into pure molten KF by addition of one molecule of B_2O_3 . From the figure it follows that the investigated system fulfils the model used only in the region of diluted solutions of B_2O_3 in KF for $k = 2$. It means that the addition of one molecule of B_2O_3 into molten KF causes the formation of two new particles.

As it was mentioned above, a number of compounds are formed in the ternary reciprocal system K^+ , B^{3+}/F^- , O^{2-} . The values of the reaction Gibbs energies for different possible reactions are therefore calculated on the basis of the thermodynamic data [6]. Negative values of the reaction Gibbs energy were found for the following reactions



From the calculated ΔG_r° values it follows that the reaction (B) is the most possible reaction creating two complex compounds, KBF_4 and $K_2B_4O_7$. The presence of both compounds was confirmed also by means of the X-ray powder diffraction analysis and IR spectroscopy in the quenched molten mixtures. The two new particles introduced into

determination of the equilibrium temperature of primary crystallization (evaporization and undercooling effects) of melts with increased B_2O_3 content. From the figure it follows that in the region of the primary crystallization of LiF a liquid miscibility gap is formed at compositions from 5 to 23 mole % B_2O_3 in the LiF– B_2O_3 boundary and up to 12 mole % KF in the ternary system. From the thermodynamic analysis of the binary systems it follows that the dissolution of boron oxide in molten lithium fluoride leads to the formation of $Li_2B_4O_7$ [3] while in molten potassium fluoride the compounds KBF_4 and $K_2B_4O_7$ are formed. These compounds are most probably present also in the melts of the ternary system. This assumption is supported also by the negative value of the Gibbs energy of the reaction



System LiF–KF– B_2O_3 – TiO_2

Owing to the low solubility of titanium dioxide in alkali halides the phase equilibria study in the LiF–KF– B_2O_3 – TiO_2 system was performed only in the cross-section with constant content of 5 mole %

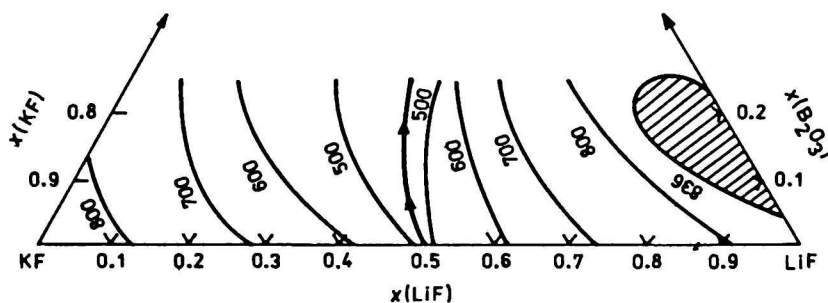


Fig. 2. The investigated part of the phase diagram of the system LiF–KF– B_2O_3 .

KF by addition of one molecule of B_2O_3 are the anions BF_4^- and $B_4O_7^{2-}$. The positive deviation of the real liquidus curve is most probably due to further polymerization of the borate species.

System LiF–KF– B_2O_3

The experimentally determined part of the phase diagram of the system LiF–KF– B_2O_3 up to 20 mole % B_2O_3 is shown in Fig. 2. The phase equilibria investigation was limited to this concentration range because of the technological interest as well as the serious difficulties in the

TiO_2 . By addition of TiO_2 into molten LiF or into molten LiF–KF mixtures insoluble Li_2TiO_3 precipitates immediately from the melt. This is why the measurement of the temperature of primary crystallization was performed in the ternary cross-section KF– B_2O_3 – TiO_2 with constant content of 5 mole % TiO_2 (Fig. 1) and two cross-sections in the LiF–KF– B_2O_3 – TiO_2 system with constant content of 5 mole % TiO_2 and 10 and 20 mole % B_2O_3 , respectively (Fig. 3).

From Fig. 1 it follows that by addition of TiO_2 into the KF– B_2O_3 melt the temperature of primary crystallization decreases. However, by addition of LiF into the KF– B_2O_3 melt the liquidus temperature

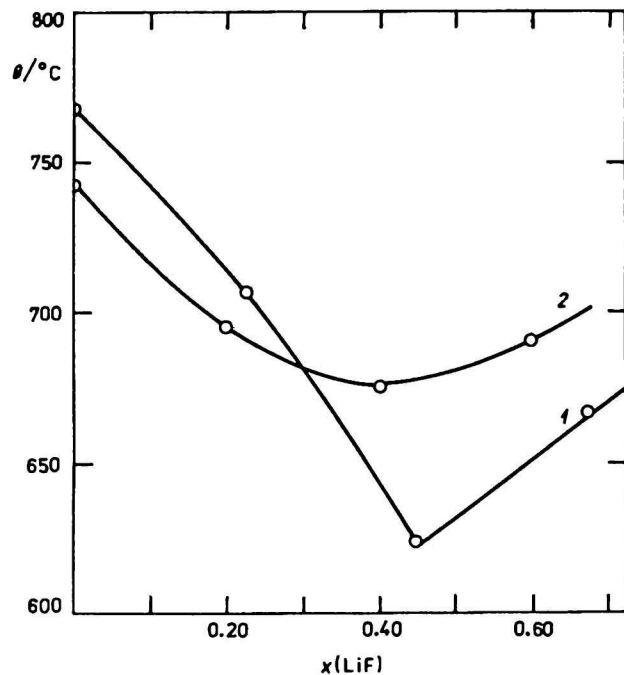
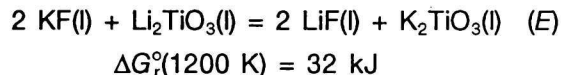


Fig. 3. Liquidus curves of the investigated cross-sections of the system LiF–KF–B₂O₃–TiO₂.
 1. Cross-section KF–LiF + 10 % B₂O₃ + 5 % TiO₂.
 2. Cross-section KF–LiF + 20 % B₂O₃ + 5 % TiO₂.

is higher, compared with that without the TiO₂ addition. For instance the liquidus temperature of the melt of the composition of 45 mole % LiF + 45 mole % KF + 10 mole % B₂O₃ is 482 °C, while by further addition of 5 mole % TiO₂ the liquidus temperature increases up to 623 °C. This observation is obviously due to the formation in the melt of titanates, namely of Li₂TiO₃, which exhibits relatively high melting point (1550 °C) and a very steep shape of the liquidus surface. The former measurement relates to the primary crystallization of LiF while the latter one responds to the

primary crystallization of Li₂TiO₃. The phase equilibria in the ternary reciprocal system Li⁺, K⁺//F⁻, TiO₃²⁻ were studied in [8]. The system was studied only up to ca. 40 mole % LiF, since above this amount Li₂TiO₃ precipitates from the melt. It was found that the system KF–Li₂TiO₃ is the stable diagonal of the reciprocal system. This finding is confirmed also by the thermodynamic calculation of the Gibbs energy of the metathetical reaction [9]



It may be therefore concluded that the rising of the temperature of primary crystallization in the melts of the system LiF–KF–TiO₂ is due to the formation of Li₂TiO₃.

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