Phase Diagram of the System LiF—B$_2$O$_3$

M. CHRENKOVÁ and V. DANĚK
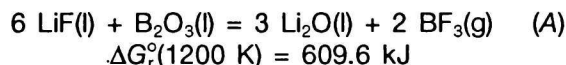
Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava

The phase diagram of the system LiF—B$_2$O$_3$ in the composition range up to 30 mole % B$_2$O$_3$, which is important from the TiB$_2$ electrochemical synthesis point of view, was measured. The system LiF—B$_2$O$_3$ is a quasi-binary one with a liquid immiscibility in the interval of 5—23 mole % B$_2$O$_3$. Up to ca. 5 mole % B$_2$O$_3$ LiF reacts with B$_2$O$_3$ under formation of LiBO$_2$ and BF$_3$, which escapes from the system, while at higher B$_2$O$_3$ content lithium tetraborate is formed. The investigated system is obviously the projection of the nonlinear LiF—LiBO$_2$—B$_2$O$_3$ cross-section into the LiF—B$_2$O$_3$ joint.

The study of the phase diagram of the system LiF—B$_2$O$_3$ is a part of the complex physicochemical investigation of the quaternary system LiF—KF—B$_2$O$_3$—TiO$_2$, which may be used as electrolyte for the electrochemical synthesis of titanium diboride in fused salts, especially when dispersed powders are to be obtained [1].

The system LiF—B$_2$O$_3$ is a part of the ternary reciprocal system Li$^+$, B^{3+} // F$^-$, O^{2-}. According to the value of the reaction Gibbs energy of the metathetical reaction [2]

$$6 \text{ LiF(l)} + \text{B}_2\text{O}_3\text{(l)} = 3 \text{ Li}_2\text{O(l)} + 2 \text{ BF}_3\text{(g)} \quad (A)$$
$$\Delta G_r^\circ(1200 \text{ K}) = 609.6 \text{ kJ}$$

the system LiF—B$_2$O$_3$ is a stable diagonal of the ternary reciprocal system.

The phase diagram of the system LiF—B$_2$O$_3$ in the composition range up to 55 mole % B$_2$O$_3$ was studied in [3]. According to this source the congruently melting compound LiF · B$_2$O$_3$ with the temperature of fusion of 840 °C is formed in this system. In the composition interval 5—23 mole % B$_2$O$_3$ the liquidus curve is parallel to the composition axis at temperature of 835 °C, probably due to the existence of immiscibility in the liquid state.

Beside the system LiF—B$_2$O$_3$ in the reciprocal system Li$^+$, B^{3+} // F$^-$, O^{2-} the phase equilibria in the binary system Li$_2$O—B$_2$O$_3$ were studied [4]. Two congruently melting compounds are formed in this system: LiBO$_2$ with the temperature of fusion of 849 °C and Li$_2$B$_4$O$_7$ with the melting point of 917 °C. Beside these compounds several incongruently melting compounds are formed. In the ternary system LiF—Li$_2$O—B$_2$O$_3$ the phase diagram of the pseudobinary system LiF—LiBO$_2$ is known [4]. The ternary compound 2LiF · 3LiBO$_2$ with a congruent melting point of 755 °C is formed in this system.

The aim of the present work was to verify the phase diagram of the system LiF—B$_2$O$_3$, namely in the composition range up to 30 mole % B$_2$O$_3$, which is important from the TiB$_2$ electrochemical synthesis point of view.

EXPERIMENTAL

The phase diagram of the investigated system was studied by means of the thermal analysis method registrating 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 defined simple salts. The measured temperatures of primary crystallization were reproducible in the range of 2 K. All chemicals used were of reagent grade purity. Samples with increased B$_2$O$_3$ content, which show considerable evaporation and an increased tendency to undercooling caused most experimental difficulties. Careful adjustment of the cooling rate and registration of the heating curves were used in such cases.

The composition of the investigated melts was elucidated on the basis of the thermodynamic calculations, the X-ray powder diffraction analysis, and the IR spectroscopic measurements of the quenched samples. Infrared spectra of the quenched molten mixtures were measured using a Perkin—Elmer 9836 spectrophotometer. The mid-infrared spectra were recorded at 300 K using KBr pellets. Quenched samples of investigated melts were used for examination. A part of the melt was taken up by means of a platinum spoon and thrown in a steel block. It was supposed that the chemical composition of the melt after intense cooling was sufficiently preserved.

RESULTS AND DISCUSSION

The phase diagram of the pseudobinary system LiF—B_2O_3 according to the present work is shown in Fig. 1. The temperatures of primary crystallization according to the previous work [3] are shown as well. From the figure it follows that both measurements are very close up to 23 mole % B_2O_3. Differences in the course of the liquidus curve of LiF are obviously due to the different measurements of the melting point of LiF (852 °C in [3], 847 °C in this work). A miscibility gap in the region 5—23 mole % B_2O_3 was found with the monotectic temperature of 836 °C and the upper consolute temperature of 862 °C at ca. 14 mole % B_2O_3. In the previous work [3] approximately the same monotectic temperature (835 °C) was found, however the immiscibility region is not shown. In fact, on the cooling curves of the investigated mixtures in the immiscibility region only one break at the temperature of 836 °C was observed. However, on the heating curves of these mixtures an additional break was found, which was ascribed to the upper temperature of the presence of two liquid phases. At higher content of B_2O_3 than 23 mole % the liquidus curve of LiF determined in this work lies above that given in [3]. It may be assumed that the values of the primary crystallization in the cited work were affected by the use of improper cooling rate and consequently the undercooling of the melts.

The course of the liquidus curve of LiF in the region of high concentration of LiF was verified with that calculated according to the simplified (ΔH_f = const., a(LiF, s) = 1) Le Chatelier—Shreder equation

$$T_{pc} = \frac{\Delta H_f T_f}{\Delta H_f - RT_f \ln a(\text{LiF, l})} \quad (1)$$

where ΔH_f and T_f are the enthalpy and temperature of fusion of LiF, respectively, and a(LiF, l) is the activity of LiF in the solution. The values ΔH_f(LiF) = 27.1 kJ mol^{-1} and T_f(LiF) = 1121 K were used for the calculation [2]. Since the real composition and thus the activity of LiF in the dilute solution of B_2O_3 in LiF is not known, the activity of LiF was calculated according to the simple "universal model"

$$a(\text{LiF, l}) = x^k(\text{LiF}) \quad (2)$$

where x(LiF) is the true mole fraction of LiF and k is the number of foreign particles introduced into LiF by addition of one molecule of B_2O_3. The calculated course of the liquidus curve of LiF for k = 1 is shown in Fig. 1. From the figure it follows
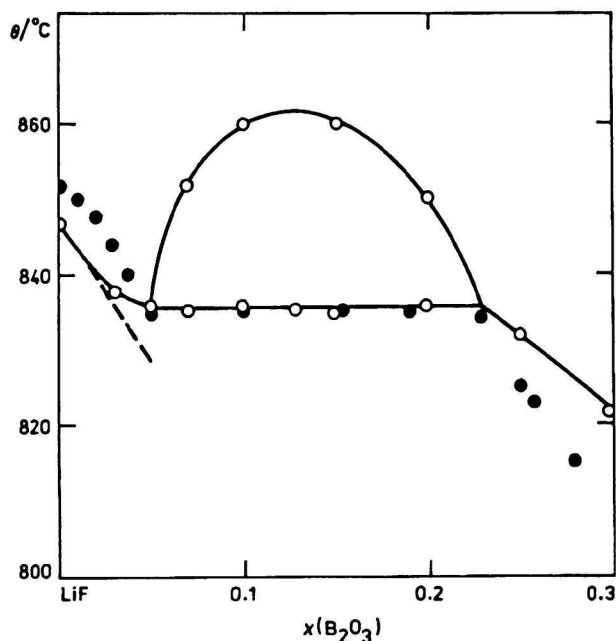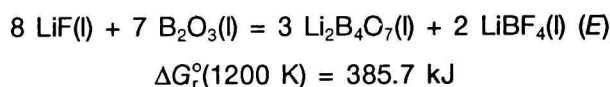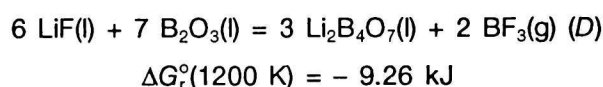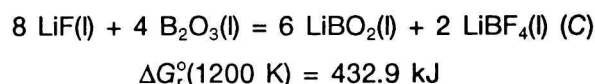

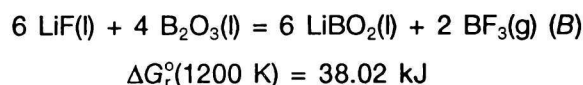**Fig. 1.** Investigated part of the phase diagram of the system LiF—B_2O_3.
○ This paper, ● according to [3], --- calculated (a(LiF, l) = x(LiF)).

that a good agreement of the experimental and calculated liquidus curve was found only at compositions up to 3 mole % B_2O_3. This result indicates that by addition of one molecule of B_2O_3 only one new particle is introduced into molten LiF. At higher content of B_2O_3 the LiF liquidus curve runs above the calculated one, which refers either to the polymerization of the melt or to the chemical reaction of both components.

As mentioned above a number of compounds are formed in the ternary reciprocal system Li$^+$, B^{3+} // F$^-$, O^{2-} From among the possible chemical reactions which lead to the compound formation in the investigated system the following four ones were considered to be probable

6 LiF(l) + 4 B_2O_3(l) = 6 LiBO$_2$(l) + 2 BF$_3$(g) (B)
$\Delta G_r^°$(1200 K) = 38.02 kJ

8 LiF(l) + 4 B_2O_3(l) = 6 LiBO$_2$(l) + 2 LiBF$_4$(l) (C)
$\Delta G_r^°$(1200 K) = 432.9 kJ

6 LiF(l) + 7 B_2O_3(l) = 3 Li$_2$B$_4$O$_7$(l) + 2 BF$_3$(g) (D)
$\Delta G_r^°$(1200 K) = − 9.26 kJ

8 LiF(l) + 7 B_2O_3(l) = 3 Li$_2$B$_4$O$_7$(l) + 2 LiBF$_4$(l) (E)
$\Delta G_r^°$(1200 K) = 385.7 kJ

The values of the reaction Gibbs energies were calculated from the data given in [2]. The value of the Gibbs energy of LiBF$_4$ formation was taken from [5].

From the values of the reaction Gibbs energies it follows that the equilibrium of the reactions (C) and (E) is shifted considerably to the left and the reactions do not take place. On the other hand, the reactions (B) and (D) with respect to the values of the reaction Gibbs energies can take place, especially when BF$_3$ escapes from the system, which shifts the equilibrium of both reactions fully to the right. Both reactions can also explain the determined number of introduced foreign particles. On escaping of BF$_3$ from the system, the only new particle is the BO$_2^-$ or B$_4$O$_7^{2-}$ anion.

To explain the structure of the LiF—B$_2$O$_3$ melts the composition of the quenched samples was determined by means of X-ray diffraction powder analysis and IR spectroscopy. Both methods eliminate the presence of LiBF$_4$ in the mixtures. On the other hand, the presence of LiBO$_2$ up to 5 mole % B$_2$O$_3$ and of Li$_2$B$_4$O$_7$ at higher content of B$_2$O$_3$ was confirmed. In dilute solution of B$_2$O$_3$ in molten LiF the reaction (B) obviously takes place, whereas at higher B$_2$O$_3$ content lithium metaborate polymerizes into more condensate polyanions. The repulsive effect of both present anions, F$^-$ and B$_4$O$_7^{2-}$ leads at a certain content of B$_2$O$_3$ to liquid separation into a LiF-like melt with a limited solubility of Li$_2$B$_4$O$_7$ and a B$_2$O$_3$-like one creating an immiscibility region.

From the obtained results it may be concluded that the system LiF—B$_2$O$_3$ is a quasi-binary one. In fact, the system is the projection of the LiF—LiBO$_2$—B$_2$O$_3$ nonlinear cross-section into the LiF—B$_2$O$_3$ diagonal. The congruently melting compound LiF · B$_2$O$_3$ found in [3] is obviously only a distectic point on this cross-section.

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Translated by V. Daněk