THERMOGRAPHIC AND X-RAY PHASE STUDIES OF UNDOPED AND DOPED LITHIUM TETRABORATE

S.S.Krafchik, S.D.Chepur, B.M.Hunda, P.P.Puga, I.I.Turok, A.M.Solomon

Institute of Electron Physics, Ukrainian National Academy of Sciences,
Universytetska St. 21, Uzhhorod, 88016, Ukraine
e-mail: iep@iep.uzhgorod.ua

Using the thermogravimetric method the conditions of lithium tetraborate (LTB) synthesis from the initial component have been studied. Based on the results obtained, the use of a stepwise synthesis method has been recommended. It has been found that depending on the thermal prehistory one may obtain the vitreous, crystalline LTB samples as well as those with coexisting both vitreous and crystalline phases. Using the X-ray phase and thermogravimetric methods the effect of deviation from stoichiometry on the LTB phase composition has been found and would be applied to estimate the value of such deviation.

Lithium tetraborate is a promising material for acousto- and optoelectronics, while doped LTB – for the production of tissue-equivalent structures capable of detection of ionizing radiation doses based on thermoluminescence (TSL). It is well known [1,2] that the TSL efficiency to a great extent depends on the LTB matrix phase state, deviation from stoichiometry as well as on the dopant nature and quantity. Due to the necessity of development of optimal synthesis conditions for doped and undoped LTB in different phase states with controlled composition and reproducible TSL parameters, the thermogravimetric and X-ray phase studies of doped and undoped LTB is actual.

In the present work, using the thermogravimetric method the conditions of LTB synthesis from initial components (B_2O_3 and Li_2CO_3) by melting at 5 deg/min heating rate were studied by means of a MOM derivatographer.

In accordance with the thermogravimetric data for the initial components (B_2O_3 and Li_2CO_3), we have found that the boron oxide dehydration takes place within the 90–220°C temperature range, melting – at 450°C, while lithium carbonate destruction into the lithium oxide (Li_2O) and carbon dioxide (CO_2) – within the 620–650°C temperature range. The boron oxide dehydration takes place with strong melt foaming and material entrance from container, that in the LTB synthesis by initial component melting results in the stoichiometry violation. To avoid this, the boron oxide as well as the lithium carbonate before the LTB synthesis must be annealed at 300 °C. No endothermic dehydration effect is revealed in the annealed boron oxide thermogram.

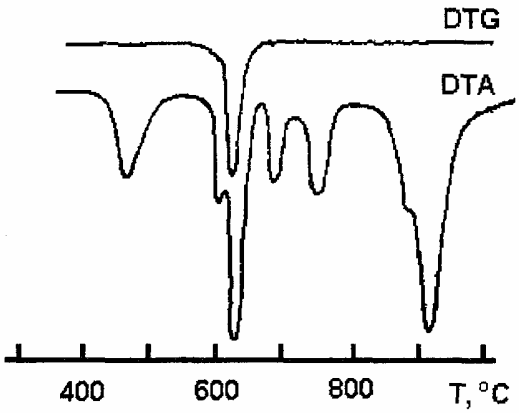

Fig. 1. LTB synthesis derivatogram
(DTA – differential thermal analysis curve;
DTG – sample mass change curve)

Figure 1 shows the derivatogram of the LTB synthesis from the initial components (B_2O_3 and Li_2CO_3) by their melting at the quasistationary heating at the 5 deg/min rate. As is seen from Fig.1, LTB synthesis from the initial components has rather compli-

cated character. One may distinguish in the synthesis thermogram (DTA curve) the following principal stages: the endothermic effect of boron oxide melting at 450°C; the endothermic effect of lithium carbonate destruction into the lithium oxide and carbon dioxide within the 620–650°C; two endothermic effects at 640 and 745°C, which, probably, correspond to the lithium tetraborate production in two stages, as well as endothermic effect of lithium tetraborate melting at 910°C. LTB production at synthesis is confirmed by the X-ray phase analysis. Thus, it has been found that the LTB synthesis proceeds in several stages: after the boron oxide melting, simultaneously with the lithium carbonate destruction, the melt starts to react with the lithium oxide producing LTB. Based on the obtained data the use of the stepwise LTB synthesis method has been suggested.

It is well known that LTB can be produced both in the vitreous and in crystalline states. Using the thermogravimetric method we have studied the influence of LTB thermal prehistory on the possibility of LTB production in various phase states. The vitreous LTB samples produced by quenching the melt at 950°C by spilling it onto the cold massive stainless steel plate (sample a). The polycrystalline LTB samples were produced by more slow cooling of the melted LTB in the oven-off mode (sample b), as well as by the protracted annealing of the crystallized LTB sample at 650°C (sample c).

Figure 2 shows the thermograms for the vitreous, polycrystalline and monocrystalline LTB samples. As is seen from Fig. 2a, at the vitreous sample heating with the 5 deg/min rate, within the 400–450°C interval the devitrification process occurs with the transition of LTB from the vitreous to the softened viscosity-fluid state, then in the 500–570°C interval the LTB crystallization takes place from the devitrification state and, finally, LTB melts at 910°C. The similar pattern is also observed for the polycrystalline LTB sample (Fig. 2b), however, comparing the ΔT jump value at devitrification, which is proportional to the specific heat capacity jump (ΔC_p) at devitrification, one may conclude that in the polycrystalline LTB sample produced by slow melt cooling in the oven-off mode, alongside with the crystalline phase the considerable part of the vitreous phase is seen. And, finally, the protracted annealing of LTB (Fig. 2c) results in the almost polycrystalline sample with no vitreous phase. For comparison, Fig. 2d shows the thermogram for the monocrystalline LTB sample grown by the Czochralski method. Thus, the studies show that depending on the method of LTB sample production from melt (quenching, quenching rigidity, annealing, etc.) one may obtain the vitreous, crystalline LTB samples as well as the samples, which combine both the vitreous and the crystalline phases, that is essential at the production of the LTB samples with preset properties.

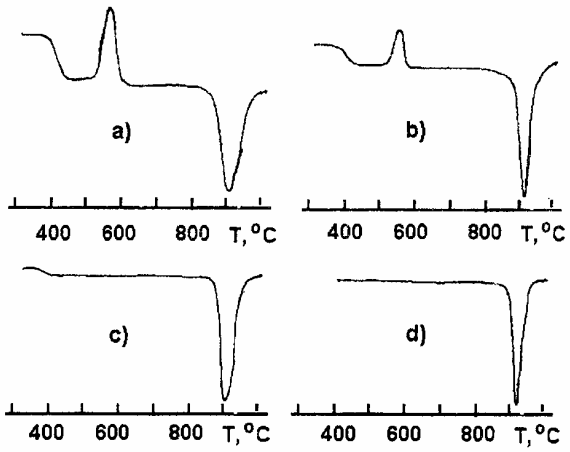

Fig. 2. LTB sample thermograms (a – vitreous sample, b and c – polycrystalline sample, d – monocrystalline sample).

We have studied the influence of dopant concentrations on the temperature transitions (devitrification, crystallization and melting) in LTB by the thermogravimetric method. The vitreous LTB samples doped by different terbium amounts (0.05; 0.1; 1 and 5 mol.%). It has been found that the dopant concentration increase has no essential influence on the crystallization and melting temperatures, however, at doped sample devitrification a tendency of the devitrification temperature increase with the dopant concentration is observed (for the LTB sample

doped with 5.0 mol.% of terbium, this increase is about 10°C). This is, probably, related to the fact that the dopant introduction and interaction with the LTB matrix result in the decrease of the elasticity of the LTB near-order structural fragments responsible for the devitrification process and, respectively, to the devitrification temperature increase.

It is known [3-5] that in the Li_2O–B_2O_3 system, according to the phase diagram, the formation of 5 compounds with the $Li_2O{\cdot}nB_2O_3$ general formula (n = 1–5) is possible. Each of these compounds is characterized by its own structure. The most stable of them are lithium tetraborate $Li_2B_4O_7$ with tetragonal structure $I4_1cd$ and lithium triborate LiB_3O_5 with the rhombic structure *Pna*21. LTB exists constantly within a narrow concentration interval that does not exceed 0.35 mol.% both towards Li_2O and B_2O_3. This interval neighbors the areas of existence of other compositions. In this relation, when synthesizing LTB, depending on the production conditions, the formation of the final product with coexisting compounds is possible. In this paper, using the XPA and thermogravimetric methods the influence of deviation from LTB stoichiometry on the phase composition of the final synthesis product has been studied.

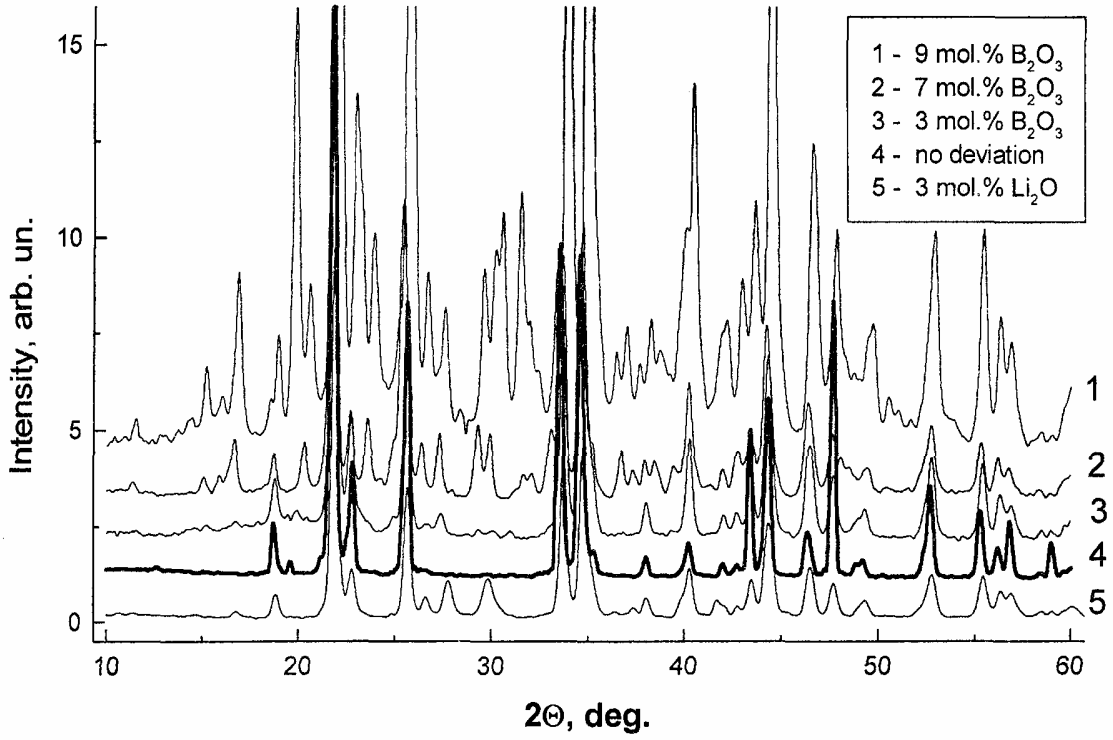

Fig. 3. Diffractograms of the LTB samples with stoichiometric and non-stoichiometric composition

The standard XPA was carried out by means of the diffractometer with the use of the X-ray tube with a copper anti-cathode and nickel filter. The studies show that the noticeable discrepancies between the diffractograms and thermograms of the stoichiometric and non-stoichiometric LTB samples are observed at the deviation from stoichiometry of order 3 and more mol.% both towards Li_2O and B_2O_3. Figure 3 shows the diffractograms of the LTB sample with stoichiometric composition and with different deviations from stoichiometry.

As is seen from Fig. 3, the deviation from stoichiometry results in the redistribution of the intensities of main LTB maxima and in the appearance of new maxima. At the same time the thermograms also reveal the appearance of additional endothermic effects. Analyzing the obtained results with the

use of the X-ray structural data for the pure compounds Li_2BO_2, $Li_2B_4O_7$, $Li_4B_{10}O_7$, LiB_3O_5, $Li_2B_8O_{13}$ and the data on the phase diagram for the Li_2O-B_2O_3 system, one may conclude that at the Li_2O excess mixed phase the $Li_2B_4O_7$-$LiBO_2$ is produced as the result of LTB synthesis, while at the B_2O_3 excess – the mixed phase $Li_2B_4O_7$-LiB_3O_5- $Li_2B_8O_{13}$. These results can be used to estimate the deviation from the LTB stoichiometry.

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ТЕРМОГРАФІЧНІ І РЕНТГЕНОФАЗОВІ ДОСЛІДЖЕННЯ НЕЛЕГОВНОГО І ЛЕГОВАНОГО ТЕТРАБОРАТУ ЛІТІЮ

С.С.Крафчик, С.Д.Чепур, Б.М.Гунда, П.П.Пуга, І.І.Турок, А.М.Соломон

Інститут електронної фізики НАН України,
вул. Університетська, 21, Ужгород 88016
e-mail: iep@iep.uzhgorod.ua

Використовуючи термогравіметричний метод, вивчено умови синтезу тетраборату літію (ТБЛ) з вихідних речовин та запропоновано метод покрокового синтезу. Встановлено, що в залежності від термічної передісторії можна отримати зразки ТБЛ у вигляді склоподібної, кристалічної та суміші кристалічної і склоподібної фаз. Використовуючи рентгенофазовий аналіз та термогравіметричні методи, вивчено вплив відхилень від стехіометрії ТБЛ на фазовий склад.