THE EFFECT OF DIFFERENT STARTING MATERIALS ON THE SYNTHESIS OF LITHIUM TRIBORATE

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Lithium triborate (LiB$_3$O$_5$) was synthesized using different starting materials. The effect of these materials on the phase purity of LiB$_3$O$_5$ was investigated in each case. Identification and characterizations of the products were carried out by powder X-ray diffraction (XRD) and infrared (IR) analyses. The present study showed that the starting materials play an important role in the synthesis of lithium triborate with respect to phase impurity.

Key words: lithium triborate, solid state, XRD analysis, IR analysis

INTRODUCTION

Lithium triborate, LiB$_3$O$_5$, is a newly developed nonlinear optical crystal which is chemically stable, mechanically robust and not hygroscopic. It shows thermoluminescence properties. The synthesis and characterization of lithium triborate (LiB$_3$O$_5$) have been investigated and reported in the literature (Mazetti 1926; Rollet and Bouaziz 1955; Sastry and Hummel 1958; König and Hoppe 1978; Betourne and Touboul 1997; Massot et al., 1989; Zhong and Tang 1996; Morcyc and Ptak 1999; Almedia et al., 2001). It is difficult to obtain LiB$_3$O$_5$ as a pure compound. During the synthesis stage, some lithium borate compounds like tetraborate (Li$_2$B$_4$O$_7$), pentaborate (LiB$_5$O$_8$), lithium octaborate (Li$_2$B$_8$O$_13$) can be present in the lithium triborate phase (Sabharwal et al., 2003, 2004; Özdemir et al., 2004; Arduçoğlu et al., 2006). The purity of lithium triborate is important in the usage of LiB$_3$O$_5$ as a thermoluminescent material, as the impurities may influence the intensity of glow curve.
In recent years, Özdemir et al. (2004) and Ardcıoğlu et al. (2006) studied the synthesis of LiB$_3$O$_5$ starting from a stochiometric mixture of the Li$_2$CO$_3$ and H$_3$BO$_3$ by heating at 750 °C for 7, 14, and 21 hours. They found that LiB$_3$O$_5$ can be produced by solid state reaction method at 750 °C for 14 hours, but they observed some impurities (e.g Li$_2$B$_4$O$_7$) in the XRD patterns.

In this present study, the effect of different starting materials on synthesis of LiB$_3$O$_5$ was investigated with respect to phase impurity.

**EXPERIMENTAL PROCEDURE**

Li$_2$CO$_3$ and H$_3$BO$_3$ powders were used as starting materials for the synthesis of LiB$_3$O$_5$. The powders, weighed in stoichiometric amounts, were ground in an agate mortar and pre-heated at 300 °C for 4 hours to remove water. Obtained material was reground and heated in a crucible at 750 °C for 14 hours. The procedure was based on the study carried out by Özdemir et al., (2004).

In the second series of tests, different starting materials were used for the synthesis of LiB$_3$O$_5$ to determine the possibility of its production without any impurity. The same synthesis conditions of previous test were applied during these tests. Four binary compounds, LiBO$_2$ – H$_3$BO$_3$, LiBO$_2$–B$_2$O$_3$, LiOH–H$_3$BO$_3$, LiOH–B$_2$O$_3$ respectively were used in the preparation of LiB$_3$O$_5$.

Typical reactions are given below:

\[
\text{Li}_2\text{CO}_3 + 6\text{H}_3\text{BO}_3 \rightarrow 2\text{LiB}_3\text{O}_5 + \text{CO}_2 + 9\text{H}_2\text{O}
\]

\[
\text{LiBO}_2 + 2\text{H}_3\text{BO}_3 \rightarrow \text{LiB}_3\text{O}_5 + 3\text{H}_2\text{O}
\]

\[
\text{LiBO}_2 + \text{B}_2\text{O}_3 \rightarrow \text{LiB}_3\text{O}_5
\]

\[
\text{LiOH} + 3\text{H}_3\text{BO}_3 \rightarrow \text{LiB}_3\text{O}_5 + 5\text{H}_2\text{O}
\]

\[
2\text{LiOH} + 3\text{B}_2\text{O}_3 \rightarrow 2\text{LiB}_3\text{O}_5 + 5\text{H}_2\text{O}
\]

In order to identify the phases of samples, a Rigaku MiniFlex X-ray Diffractometer was employed. All measurement were performed by using monochromatic Cu Kα (30 kV, 15 mA, λ=1.54051 Å) radiation at room temperature and XRD patterns were recorded from 5 ° <2θ <70 °. The measurements were made with 0.05 degree steps and 1 degree/ minute rate.

In order to determine the structure of the produced compounds, the infrared spectra (IR) was measured, using KBr pellets made from a mixture of samples by using VARIAN 1000FTIR Spectrometer (from 400 to 2000 cm$^{-1}$).
RESULTS AND DISCUSSION

Lithium triborates, which were synthesized by using different starting materials, such as Li₂CO₃ – H₃BO₃, LiBO₂ – H₃BO₃, LiBO₂ – B₂O₃, LiOH – H₃BO₃, LiOH – B₂O₃ at 750 °C for 14 hours, were evaluated by XRD and IR.

The phase identifications of the lithium triborates are shown in Fig. 1. Comparing these characteristic X-ray powder diffraction patterns of lithium triborates with each other, it was found that LiB₃O₅ obtained by a stoichiometric ratio of LiBO2 and H₃BO₃ (Fig. 1b) was in a good agreement with the XRD pattern of LiB₃O₅ synthesized by using Li₂CO₃ and H₃BO₃ (Fig. 1a). Analysis of the powder X-ray diffraction data showed that the compounds contained LiB₃O₅ as a major phase (JCPDS File No 77-0774). The reflection at 21.8°, 25.55°, and 33.6° (2θ) confirmed the presence of Li₂B₄O₇ (JCPDS File No 18-717) and also, lithium triborate lines match exactly the peak values reported in the literatures (Betourne and Touboul 1997, Sabharwal et al., 2003, 2004, Özdemir et al., 2004, Ardiçoğlu et al., 2006).

However, in the XRD patterns of LiB₃O₅ obtained from LiBO₂–B₂O₃ (Fig. 1c), LiOH–H₃BO₃ (Fig. 1d) and LiOH–B₂O₃ (Fig. 1e), the intensities of lines belonging to LiB₃O₅ were lower and signal to noise ratios of Li₂B₄O₇ pattern were higher. Especially, in Fig. 1e (LiOH–B₂O₃ powders as starting materials), Li₂B₄O₇ appeared as a dominant phase.

The IR spectra of lithium triborates are shown in Fig. 2. In the literature, it was observed that 400–2000 cm⁻¹ region was enough to determine the structure of lithium borates, because of existence of many clear intensive bands, sensitive to the boron
substitutions in this region (Morcyc and Ptak 1999, Almedia et al., 2001). Therefore, in the present study, the IR spectra of lithium triborates were measured from 400 to 2000 cm\(^{-1}\) region.

When the IR spectra were compared, no major change was observed in the infrared bands except LiB\(_3\)O\(_5\) synthesized by using LiOH–B\(_2\)O\(_3\) as the starting materials. The strong bands observed in the frequency range of 1200–1600 cm\(^{-1}\) in the spectra were consistent with the existence of trigonal coordination, while the bands in the frequency range of 850–1100 cm\(^{-1}\) were characteristic of tetrahedral coordination. The weaker bands in the region 700–800 cm\(^{-1}\) attributed to scissor vibrations of B-O-B bridges in the boron oxygen network (Massot et al., 1989a, Zhong and Tang 1996, Morcyc and Ptak 1999, Almedia et al., 2001).

Analysis of IR spectra of LiB\(_3\)O\(_5\) synthesized using LiOH–B\(_2\)O\(_3\) (Fig. 2e) showed that this combination caused changes in the absorption band. Its IR spectra showed a great similarity with that of Li\(_2\)B\(_4\)O\(_7\) (Tsvetkova et al., 2006).

Under the light of XRD and IR analyses, it was found that none of the starting materials except LiBO\(_2–H_3BO_3\) were superior over Li\(_2\)CO\(_3\) and H\(_3\)BO\(_3\). However, LiBO\(_2\) is much more expensive than Li\(_2\)CO\(_3\). Therefore, it was concluded that the combination of Li\(_2\)CO\(_3\) and H\(_3\)BO\(_3\) was good starting materials for LiB\(_3\)O\(_5\) synthesis.

CONCLUSIONS

The starting materials play an important role in the synthesis of lithium triborate. Among the reagents used, the Li\(_2\)CO\(_3\) and H\(_3\)BO\(_3\) combination was found the most suitable for the synthesis of LiB\(_3\)O\(_5\) in respect to phase impurity as well as their costs.
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Syntezowano trójboran litu (LiB₃O₅) stosując różne materiały wyjściowe. Badano wpływ tych materiałów na końcową czystość LiB₃O₅. Identyfikowano i charakteryzowano produkty syntezy za pomocą dyfrakcji rentgenowskiej (XRD) oraz analizy spektroskopowej w podczerwieni (IR). Badania wykazały, że wyjściowe materiały grają ważną rolę w czystości syntezowanego trójboranu litu.