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

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Lithium triborate (LiB_3O_5) was synthesized using different starting materials. The effect of these materials on the phase purity of LiB_3O_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_3O_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_3O_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_3O_5 as a pure compound. During the synthesis stage, some lithium borate compounds like tetraborate ($Li_2B_4O_7$), pentaborate (LiB_5O_8), lithium octaborate ($Li_2B_8O_{13}$) can be present in the lithium triborate phase (Sabharwal et al., 2003, 2004; Özdemir et al., 2004; Ardıçoğlu et al., 2006). The purity of lithium triborate is important in the usage of LiB_3O_5 as a thermoluminescent material, as the impurities may influence the intensity of glow curve.

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In recent years, Özdemir et al. (2004) and Ardıçoğlu et al. (2006) studied the synthesis of LiB_3O_5 starting from a stochiometric mixture of the Li_2CO_3 and H_3BO_3 by heating at 750 ^oC for 7, 14, and 21 hours. They found that LiB_3O_5 can be produced by solid state reaction method at 750 ^oC for 14 hours, but they observed some impurities (e.g $Li_2B_4O_7$) in the XRD patterns.

In this present study, the effect of different starting materials on synthesis of LiB_3O_5 was investigated with respect to phase impurity.

EXPERIMENTAL PROCEDURE

Li_2CO_3 and H_3BO_3 powders were used as starting materials for the synthesis of LiB_3O_5. The powders, weighed in stoichiometric amounts, were ground in an agate mortar and pre-heated at 300 ^oC for 4 hours to remove water. Obtained material was reground and heated in a crucible at 750 ^oC 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_3O_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, $LiBO_2 - H_3BO_3$, $LiBO_2$–B_2O_3, $LiOH$–H_3BO_3, $LiOH$–B_2O_3 respectively were used in the preparation of LiB_3O_5.

Typical reactions are given below:

$$Li_2CO_3 + 6H_3BO_3 \rightarrow 2LiB_3O_5 + CO_2 + 9H_2O$$

$$LiBO_2 + 2H_3BO_3 \rightarrow LiB_3O_5 + 3H_2O$$

$$LiBO_2 + B_2O_3 \rightarrow LiB_3O_5$$

$$LiOH + 3H_3BO_3 \rightarrow LiB_3O_5 + 5H_2O$$

$$2LiOH + 3B_2O_3 \rightarrow 2LiB_3O_5 + 5H_2O$$

In order to identify the phases of samples, a Rigaku MiniFlex X-ray Diffractometer was employed. All measurement were performed by using monochomatic Cu Kα (30 kV, 15 mA, λ=1.54051 Å) radiation at room temperature and XRD patterns were recorded from 5 º <2θ <70 º. 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 $Li_2CO_3 - H_3BO_3$, $LiBO_2 - H_3BO_3$, $LiBO_2 - B_2O_3$, $LiOH - H_3BO_3$, $LiOH - B_2O_3$ at 750 ^oC 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 LiB_3O_5 obtained by a stoichiometric ratio of $LiBO_2$ and H_3BO_3 (Fig. 1b) was in a good agreement with the XRD pattern of LiB_3O_5 synthesized by using Li_2CO_3 and H_3BO_3 (Fig. 1a). Analysis of the powder X-ray diffraction data showed that the compounds contained LiB_3O_5 as a major phase (JCPDS File No 77-0774). The reflection at 21.8^o, 25.55^o, and 33.6^o (2θ) confirmed the presence of $Li_2B_4O_7$ (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, Ardıçoğlu et al., 2006).

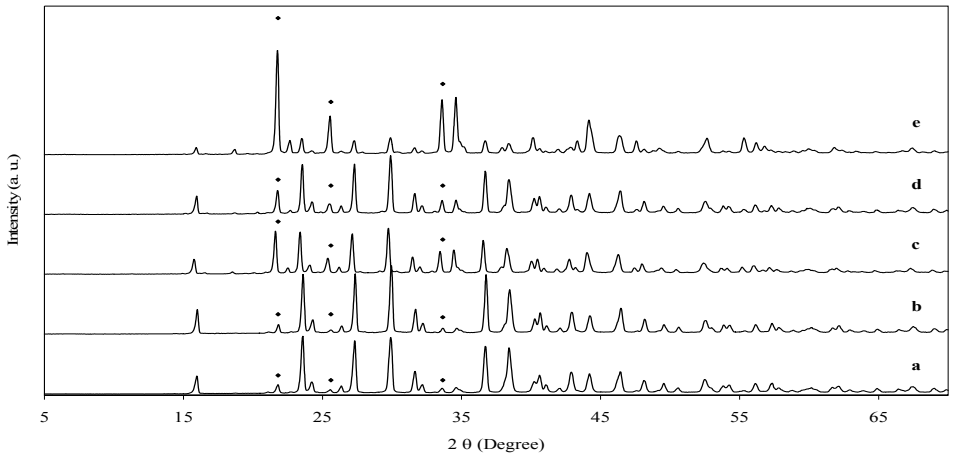

Fig. 1. Powder X-ray diffraction patterns recorded for the polycrystalline LiB_3O_5 materials obtained using different starting materials, a) Li_2CO_3 and H_3BO_3, b) $LiBO_2 - H_3BO_3$, c) $LiBO_2 - B_2O_3$, d) $LiOH - H_3BO_3$, e) $LiOH - B_2O_3$. The reflections marked by (♦) have been identified as $Li_2B_4O_7$, the remaining reflections belong to LiB_3O_5

However, in the XRD patterns of LiB_3O_5 obtained from $LiBO_2$–B_2O_3 (Fig. 1c), $LiOH$–H_3BO_3 (Fig. 1d) and $LiOH$–B_2O_3 (Fig. 1e), the intensities of lines belonging to LiB_3O_5 were lower and signal to noise ratios of $Li_2B_4O_7$ pattern were higher. Especially, in Fig. 1e ($LiOH$–B_2O_3 powders as starting materials), $Li_2B_4O_7$ 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.

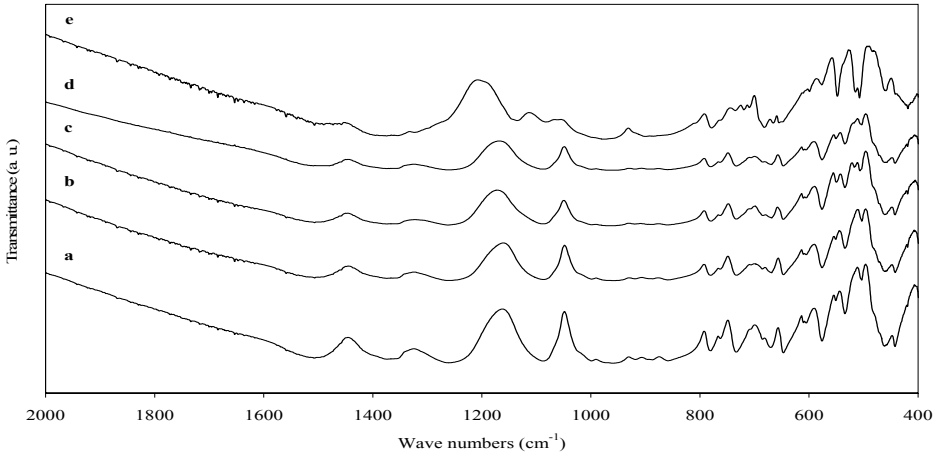

Fig. 2. IR spectra of LiB_3O_5 recorded for the polycrystalline LiB_3O_5 materials (a, b, c, d, e, are same as in Fig. 1)

When the IR spectra were compared, no major change was observed in the infrared bands except LiB_3O_5 synthesized by using $LiOH–B_2O_3$ 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_3O_5 synthesized using $LiOH–B_2O_3$ (Fig. 2e) showed that this combination caused changes in the absorption band. Its IR spectra showed a great similarity with that of $Li_2B_4O_7$ (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_2CO_3 and H_3BO_3. However, $LiBO_2$ is much more expensive than Li_2CO_3. Therefore, it was concluded that the combination of Li_2CO_3 and H_3BO_3 was good starting materials for LiB_3O_5 synthesis.

CONCLUSIONS

The starting materials play an important role in the synthesis of lithium triborate. Among the reagents used, the Li_2CO_3 and H_3BO_3 combination was found the most suitable for the synthesis of LiB_3O_5 in respect to phase impurity as well as their costs.

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Syntezowano trójboran litu (LiB_3O_5) stosując różne materiały wyjściowe. Badano wpływ tych materiałów na końcową czystość LiB_3O_5. Identyfikowano i charakteryzowano produkty syntezy za pomocą dyfrakcji rentgenowskiej (XRD) oraz analizy spektroskopowej w podczerwieni (IR). Badania wykazały, że wyjściowe materiały grają ważna rolę w czystości syntezowanego trójboranu litu.