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SYNTHESIS AND CHARACTERIZATION OF LITHIUM TRIBORATE

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Lithium triborate (LBO) is a newly developed ideal nonlinear optical (NLO) crystal used in laser weapon, welder, radar, tracker, surgery, communication and etc. In this study, lithium triborate was synthesized from the solid state reaction of Li_2CO_3 and H_3BO_3 at 750°C. X-ray diffractometer was used to characterize and identifiy the products. According to the experimental results conducted up to now, lithium triborate was produced successfully with minor amount of side products. The preliminary results of this study will be presented here, the studies for the removal of side products are underway.

Keywords: lithium triborate, synthesis, solid state reaction, non-linear optical material

INTRODUCTION

Research on borates provides distinctive opportunities for the discovery and identification of new compounds having certain physical properties that are unattainable with any other type of material. In large measure, these properties come from the unique crystal and electronic structures that result from the very small B atom in an oxide matrix (Keszler 1999).

Borates find widespread use as phosphors: $Eu:SrB_4O_7$ in UV-emitting medical lamps, $Ce,Tb:GdMgB_5O_{10}$ as the green-emitting component in high-efficacy fluorescent lamps and $Eu:(Y,Gd)BO_3$ as the red-emitting component in plasma display panels for high-definition television. Borate crystals such as β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), and $CsLiB_3O_5$ (CLBO) have made possible the reliable production of laser light at wavelengths and power levels that were preciously unattainable with solid-state systems. Due to these performance characteristics including excellent nonlinear

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properties as well as good mechanical and chemical parameters borates find widespread use in materials processing, medicine, and R&D (Keszler 1999; Moryc and Ptak 1999).

Ultraviolet lasers are viewed as clean energy sources for the synthesis and processing of materials. They have been strongly demanded for various applications such as high density optical disk mastering, photolithography, material processing and medical treatment. However, for many applications, no convenient source exists for the direct production of laser light having the proper frequency and power characteristics. For these uses, the requisite frequency and power may be generated by passing a laser beam through a suitable nonlinear optical crystal. Only an excimer laser (e.g. XeCl, KrF, and ArF) practically meets these requirements today. However, these bulky lasers use corrosive gases, require high voltage gaseous discharges and regular maintenance. A compact, maintenance free, all-solid-state alternative is therefore desired (Furukawa and Sato 1995; Sugawara et al. 1998; Takatomo et al. 2001; Mori et al. 2002)

High polarizability and excellent transparency in ultraviolet region of planar $[BO_3]^{3-}$ imply that borates are attractive candidates in the search for new nonlinear optical materials. The fundamental features of NLO borate materials are: i) a crystal structure with an advantageous arrangement of highly NLO active structural units, ii) suitable linear optical properties, and iii) the availability of crystals of sufficient optical quality and size through crystal growth processes. So a great deal of research interest has been focused on the synthesis and characterization of inorganic borates during the past decades (Becker 1998; He et al. 2002a).

$K[B_5O_6(OH)_4]\cdot 2H_2O$ (KB_5) (Dewey et al. 1975) is the first NLO crystal discovered in the series of borates in 1975. After that various borate crystals, including β-BaB_2O_4 (BBO) (Liebertz and Stahr 1983), LiB_3O_5 (LBO) (Chen et al. 1989), $Sr_2B_2Be_2O_7$ (SBBO) (Chen et al. 1995), BiB_3O_6 (BiBO) (Helwing et al. 1999), and the latest $Ca_4LnO(BO_3)_3$ (CLnOB) (Aka et al. 1996) have been studied as promising NLO crystals (Xue et al. 2000). A review on borate crystals is recently reported by Becker in 1998.

Although there are many reports on the applications of $Li_2B_4O_7$ and LiB_3O_5 in surface acoustic wave (SAW) and non-linear optical (NLO) devices, respectively, the data on the unit cell parameters, density, solubility in water, thermal stability and thermal expansion characteristics etc. of these compounds are incomplete and scantily reported. A detailed study on the Li_2O-B_2O_3 system were undertaken by Mathews et al., in 1998.

Recently LBO has been proposed to be a promising scintillator for neutron detection. The elements Li and B both have large neutron capturing capacity. This possibility has been reported mainly for glass and ceramic materials by Van Eijk with the details of adsorption and cross-section of neutrons, their different products and energies derived from these elements (Senguttuwan et al. 2002).

Kim et al. studied the growth of the nonlinear optical crystals of lithium triborate and beta barium borate in 1997. The crystal growth and optical properties of rare earth aluminum borates were investigated by Lee et al., in 1998.

In 2001, He et al., synthesized a new compound, $LiAlB_2O_5$, by solid state reaction and they give hint for researcher exploring new non-linear optical materials (He et al. 2001a).

A new compound, dilithium aluminum pentaborate, $Li_2AlB_5O_{10}$ has been synthesized by solid state reaction and its structure determined by single crystal X-ray diffraction by He et al. in 2001(b).

The ternary system, Li_2O-Al_2O_3-B_2O_3 have been investigated by many researchers. However they left a lot of uncertainties in their work. In order to synthesize new borates and search for new optical materials, He et al., reinvestigated this system with solid state reaction and X-ray powder diffraction technique to clarify some long-standing uncertainties (He et al. 2002a).

$Li_3AlB_2O_6$ is another new compound synthesized by solid state reaction. Its structure was also solved and refined from single-crystal and powder X-ray diffraction data (He et al. 2002b).

LITHIUM TRIBORATE (LBO, LiB_3O_5)

Lithium triborate, LiB_3O_5, is one of the most known lithium borates. It is a newly developed nonlinear optical crystal. It offers the following advantages: extremely high damage threshold, large phase matching acceptance angle, very wide transparency range and chemical stability. So it is particularly useful for making doubler or tripler for such as Nd: YAG lasers where high power density, high stability, and long time operation are required. It is an ideal nonlinear optical crystal used in laser weapon, welder, radar, tracker, surgery, communication and etc..

LiB_3O_5 was first discovered in 1926 by Mazzetti and Carli, Rollet and Bouaziz (1955) and it was found that it crystallizes according to the phase diagram of the Li_2O-B_2O_3 system by a peritectic reaction at 834°C (Sastry et al. 1958). The structure of LBO was discovered by Konig and Hoppe (1978) 20 years later. Chen discovered the possible application of LBO crystals in nonlinear optics in 1989.

According to Konig and Hoppe, LiB_3O_5 crystallizes in the orthorhombic system with the space group $Pna2_1$-C_{2v}. The unit cell parameters are given as: a = 8.446 Å, b = 5.13 Å, c = 7.38 Å. At 595°C, LiB_3O_5 decomposes to $Li_2B_4O_7$ and $Li_2B_8O_{13}$, but this reaction is reported to take long period of time, so crystals of LiB_3O_5 cooled at moderate rates (30-40 °C/h) remain stable. The first successful growth of small crystals was achieved by the solid-state reaction of B_2O_3 glass covered with LiF powder and reaction at 750°C for 10 h by Konig and Hoppe in 1978.

Zhong and Tang studied the growth units and morphology of lithium triborate crystals in 1996. They have investigated the solution structures for compositions with different ratios of Li_2O and B_2O_3 using Fourier infrared-spectrum analysis of samples quenched in liquid nitrogen.

In 1997, Betourne and Touboul attempted to obtain LiB_3O_5 starting from a stochiometric mixture of the hydrated borates $LiB_2O_3(OH)\cdot H_2O$ and $LiB_5O_8\cdot 5H_2O$. LiB_3O_5. Cell parameters have been refined from those known using the X-ray powder diagram: a = 8.456 Å, b = 7.376 Å, c = 5.133 Å, the space group is $Pna2_1$.

Moryc and Ptak studied the infrared absorption spectra of lithium triborate (LBO) in the form of polycrystalline sample. The LiB_3O_5 samples were made from lithium carbonate, natural boric acid, boric acid containing isotope ^{10}B (94.4%) and ^{11}B (98.4%) and hydrated lithium hydroxide with ^{6}Li isotope.

Effect of highest temperature invoked on the crystallization of LiB_3O_5 from boron rich solution was studied in 2003 by Sabharwal et al. The polycrystalline LBO was synthesized by solid-state sintering method. The same authors were carried out investigations on the growth of LiB_3O_5 by top-seeded solution growth technique in 2004 (Sabharwal et al. 2004).

EXPERIMENTAL

Lithium triborate was prepared from the starting materials Li_2CO_3 and H_3BO_3 both of analytical grade. After mixing appropriate quantities of these materials, they were finely powdered by agate mortar. Finally, the homogenized mixture was heated in a porcelain crucible at 750°C for 7, 14 and 21 hours.

In order to identify the compounds obtained at the end of each heat treatment period, powder XRD patterns were recorded by using monochromatic CoKα radiation on Philips X-ray Diffractometer, Model PW 1320. The obtained powders will also be examined by IR technique in future studies.

RESULTS

The XRD pattern of the LiB_3O_5 obtained from the solid state reaction of Li_2CO_3 and H_3BO_3 at 750°C, 7 hours is given in Figure1. It is clear that, at the end of 7 hours heat treatment, all the LiB_3O_5 line with respect to JCDPS File No: 32-549 were observed. The literature given by Betourne and Touboul (1997) confirmed this result also. Li_2CO_3 at this temperature turns into Li_2O which then reacted with H_3BO_3. Besides strong $Li_2B_4O_7$ (JCPDS File No: 18-717) lines, some weak lines of H_3BO_3 were still present in the pattern.

Figure 2 shows the XRD pattern of the LiB_3O_5 obtained from the solid state reaction of Li_2CO_3 and H_3BO_3 at 750°C, 14 hours. LiB_3O_5 lines were observed again together with the lines of H_3BO_3 and $Li_2B_4O_7$.

XRD pattern of LiB_3O_5 produced at 750ºC for 21 hours were given in Figure 3. It can be observed from this figure that, $Li_2B_4O_7$ lines were still present in the pattern but the intensities were very weak. All the lines of LiB_3O_5 with respect to JCPDS File No: 32-549 were produced successfully and confirmed by the literature (Betourne and Touboul 1997) also.

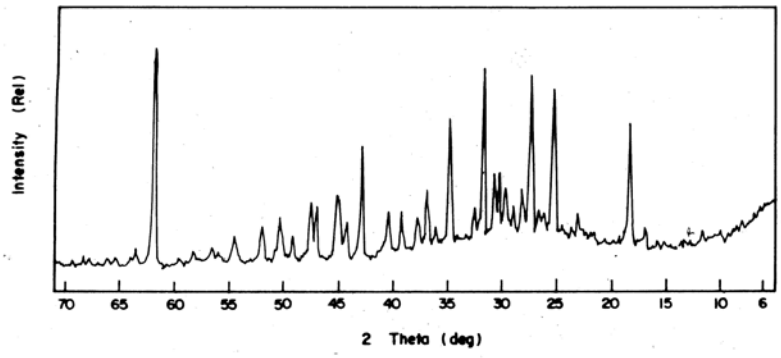

Fig. 1. The XRD pattern of LiB_3O_5 produced at 750°C for 7 hours (x: LiB_3O_5)

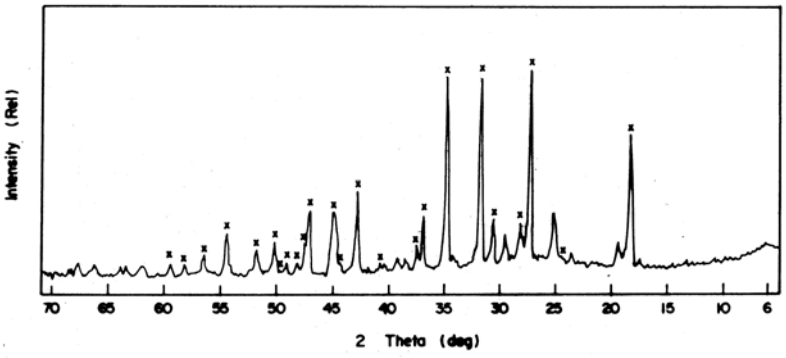

Fig. 2. The XRD pattern of LiB_3O_5 produced at 750°C for 14 hours (x: LiB_3O_5)

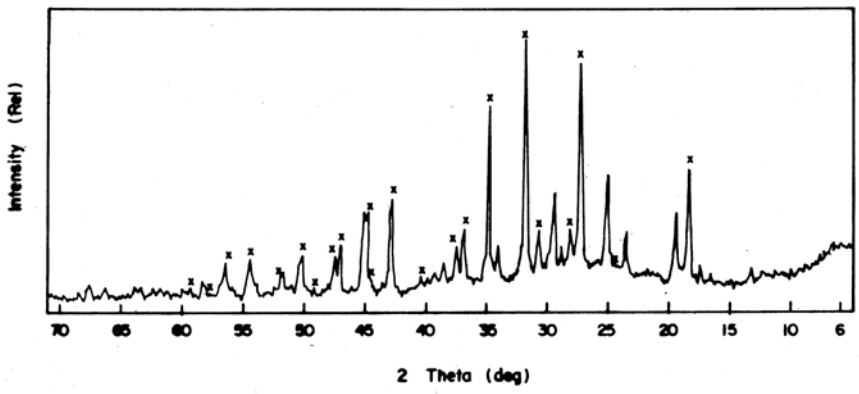

Fig. 3. The XRD pattern of LiB_3O_5 produced at 750°C for 21 hours (x: LiB_3O_5)

CONCLUSION

The interest in the use of borate crystals in nonlinear optics has increased during the past decade due to increase in the demand for solid-state short wave length lasers obtained with NLO. Lithium triborate is one of the most known lithium borates and it has become one of the most important crystals for NLO applications since it was first developed in 1989.

It was found from this study that, the LiB_3O_5 was produced successfully from the solid state reaction of Li_2CO_3 and H_3BO_3 at 750ºC together with a side product. Characterization of LiB_3O_5 and the side products will be completed by means of IR, DTA and TGA besides XRD in future studies.

REFERENCES

AKA G., HARARI K., VIVIEN D., BENIETZ J.M., SALIN F., GODARD J. J. (1996), Solid State Inorg. Chem 33, p. 727.

BECKER P. (1998), *Borate Materials in Nonlinear Optics,* Advanced Materials 10 (13), p. 979.

BETOURNE E., TOUBOUL M. (1997), *Synthesis of lithium borates (B/Li≥3) as LiB3O5 by dehydration of hydrated precursors,* Journal of Alloys and Compounds 255, p. 91.

CHEN C., U Y., JIANG A., BOCHANG Wu, , YOU G., LI R., LIN S. (1989), Journal of the Optical Society of America B: Optical Physics 6(4), p. 616.

CHEN C., WANG Y., WU B., WU K., ZENG W., YU L. (1995), Nature 373, p. 322.

DEWEY C.F., COOK Jr. W.R, HODGSON Jr. R.T., WYNNE J.J. (1975), Appl. Phys. Lett. 26, p. 714.

FURUKAWA Y., SATO M. (1995), *Lithium triborate and optical device using it*, Jpn. Kokai Tokkyo Koho 1995, 3 pp, Patent written in Japanese, Application JP 94-103966 19940518.

HE M., CHEN X.L., GRAMLICH V., BAERLOCHER Ch., ZHOU T., and HU B.Q. (2002b), *Synthesis, structure and thermal stability of* $Li_3AlB_2O_6$, Journal of Solid State Chemistry 163(2), pp. 369-376.

HE M., CHEN X.L., HU B.Q., ZHOU T., XU Y.P., and XU T. (2002a), *The ternary system* Li_2O-Al_2O_3-B_2O_3*: Compounds and phase relations*, Journal of Solid State Chemistry 165, pp. 187-192.

HE M., CHEN X.L., LAN C.H., LI H., and XU Y.P. (2001a). *Ab initio structure determination of new compound* $LiAlB_2O_5$, Journal of Solid State Chemistry 156, pp. 181-184.

HE M., LI H., CHEN X., XU Y., XU T. (2001b), $Li_2AlB_5O_{10}$, Acta Crystallographica Section C, Crystal Structure Communications, 57(Pt 9) 1010-1.

HELWING H., LIEBERTZ J., BOHATU L. (1999), Solid State Commun. 109, p. 249.

KESZLER D.A. (1999), *Synthesis, crystal chemistry, and optical properties of metal borates,* Current Opininon in Solid State and Materials Science 4, p. 155-162, 1999.

KIM H.G., KANG J.K., PARK S.J. (1997), *Growth of the nonlinear optical crystals of lithium triborate and beta barium borate*, Optical Materials (accepted).

KÖNIG H., HOPPE R. (1978), Z.Anorg. Allg. Chem, R439 p. 71.

LEE S.M., CHOI D.Y., CHUNG S.J., KOR J. (1998), *Crystal growth and optical properties of rare earth aliminum borates*, Phys. Soc., Vol. 32, pp. 443-445.

LIEBERTZ J., STAHR S. (1983), Z. Kristallogr 165, p. 91.

MATHEWS M.D., TYAGI A.K., and MOORTHY P.N. (1998), *High temperature behaviour of lithium borates: Part I: Characterization and thermal stability*, Thermochimicia Acta 320, pp. 89-95.

MAZZETTI C., CARLI F.D. (1926), Gazz. Chim. Ital. 56, p. 146.

MORI Y., YAP Y.K., KAMIMURA T., YOSHIMURA M., Sasaki T. (2002), *Recent development of nonlinear optical borate crystals for UV generation, Optical* Materials 19, p.1.

MORYC U., and PTAK W.S. (1999), *Infrared spectra of* β-BaB_2O_4 *and* LiB_3O_5*: new nonlinear optical materials*, Journal of Molecular Structure 511-512, pp. 241-249, 1999.

Powder Diffraction File No. 18-717 JCPDS-ICDD, USA.
Powder Diffraction File No. 32-549 JCPDS-ICDD, USA.
ROLLET A.P., BOUAZIZ R. (1955), Comp. Rend. (Paris) 240, p. 2417.
SABHARWAL S.C., SANGEETA B. T. (2004), J. of Crystal Growth 263, p. 327.
SABHARWAL S.C., SANGEETA B.T. (2003), J. of Crystal Growth 249, p. 502.
SASTRY B.S.R., HUMMEL F.A. (1958), J. Am. Ceram. Soc. 41, p. 11.
SENGUUTUVAN N., ISHII M., SHIMOYAMA M., KOBAYASHI M., TSUTSUI N., NIKL M., DUSEK M., SHIMIZU H.M., OKU T., ADACHI T., SAKAI K., and SUZUKI J. (2002), Crystal growth and luminescence properties of Li2B4O7 single crystals doped with Ce, In, Ni, Cu and Ti ions, Nuclear Instruments and Methods in Physics Research A 486, pp. 264-267.
SUGAWARA T., KOMATSU R., and UDA S. (1998), *Linear and nonlinear optical properties of lithium tetraborate*, Solid State Communications 107, No.5, pp. 233-237, 1998.
TAKATOMO S., YUSUKE M., MASASHI Y. (2001), *Develeopment of new NLO borate crystals*, Journal of Nonlinear Optical Physics and Materials 10(2), pp. 249-263, 2001.
VAN EIJK C.W.E. (1997), *Proceedings of the International Conference on Inorganic Scintillators and Their Applications,* Shangai, Peoples Republic of China, September 22-25, p.3.
XUE, D., BETZLER K., HESSE H., and LAMMERS D. (2000), *Nonlinear optical properties of borate crystals,* Solid State Communications 114, pp. 21-25.
ZHONG W., TANG D. (1996)Journal of Crystal Growth 166, p. 91.

Özdemir Z., Özbayoğlu G., Kızılyallı M., Yılmaz A., *Synteza i charakterystyka trójboranu litu,* Physicochemical Problems of Mineral Processing, 38, (2004) 321-327 (w jęz. ang.).

Trójboran litu jest idealnie nieliniowym kryształem optycznym odkrytym w ostatnich latach. Jego szerokie zastosowanie obejmuje takie dziedziny jak broń laserowa, radary, spawalnictwo, chirurgia, komunikacja i wiele innych. Przeprowadzone w pracy badania dotyczyły syntezy trójboranu litu. Synteza została przeprowadzona w temperaturze 750^0C. Substartami były węglan litu (Li_2CO_3) i kwas borowy (H_3BO_3). Dla scharakteryzowania otrzymanego produktu zastosowano metodę dyfrakcji promieni X. Zgodnie z danymi eksperymentalnymi, synteza trójboranu litu zachodzi w sposób zadawalający z małą ilością produktów ubocznych. W pracy zostały przedstawione jedynie wstępne wyniki badań. W następnym etapie badań zostanie opracowany problem usuwania produktów ubocznych.