Nanoporous Crystalline Material CsLiB₆O₁₀

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Abstract—CsLiB₆O₁₀ crystals up to $60 \times 40 \times 20$ mm in dimensions were prepared by top-seeded solution growth, and their interaction with water was studied. The crystals were found to be subject to hydration followed by hydrolysis, during which water leaches Cs from the structural channels to yield Cs₂B₁₀O₁₆ · 8H₂O as the final product. The channel dimensions are not large enough to incorporate ethanol or acetone molecules.

INTRODUCTION

The crystal growth, structure, and nonlinear optical properties of cesium lithium borate, $CsLiB_6O_{10}$ (CLBO), a new noncentrosymmetric crystal (tetragonal system, sp. gr. I4 2d), were first reported in 1995 [1–3]. CLBO finds rather wide application in nonlinear optics for frequency conversion-in particular, for conversion of visible light to UV radiation-through second and higher (up to fourth or fifth) harmonic generation [1– 11]. Moreover, CLBO crystals have a laser damage threshold as high as 26 GW/cm², which is several times higher than that of β -BaB₂O₄ (BBO), a widely used nonlinear optical material. Accordingly, in going from BBO to CLBO, the mean incident UV power can be raised by an order of magnitude. In addition, CLBO is superior to BBO in that less stringent requirements are imposed on phase mismatch, which allows one to employ CLBO crystals for efficient higher harmonic generation using industrial multimode lasers with a beam divergence of up to 3-5 mrad/cm [12].

However, a serious problem arises because CLBO crystals are subject to embrittlement in the course of postgrowth storage and may collapse into powder as a result of mechanical processing. The purpose of this work was to establish the reason for the degradation of CLBO crystals during storage.

EXPERIMENTAL

As starting materials, we used extrapure-grade Li_2CO_3 , Cs_2CO_3 , B_2O_3 and MoO_3 .

CLBO crystals up to $60 \times 40 \times 20$ mm in dimensions were prepared by top-seeded solution growth in the Li_2CO_3 - Cs_2CO_3 - B_2O_3 -MoO₃ system using platinum crucibles [6, 8].

Thermal analysis (DTA + TG) was carried out in air with a MOM Q-1500 system at a heating rate of 10 or 20° C/min, using 300- to 500-mg samples placed in platinum crucibles. The thermocouples were calibrated against the melting points of ground NaCl (800°C) and LiF (845°C) crystals.

X-ray diffraction (XRD) studies were performed on HZG-4 and AFV-202E diffractometers (Cu K_{α} radiation, external silicon standard). In data processing, we used the Profit and Powder 2 application programs.

RESULTS AND DISCUSSION

Our XRD data for CLBO (Fig. 1) were similar to those presented in [13] (tetragonal structure with a = 10.48 Å and c = 8.92 Å).

The thermal analysis results are displayed in Fig. 2. During the first heating, the endothermic peak due to melting occurred at $852 \pm 5^{\circ}$ C. During subsequent cooling to 400°C and a second heating to 1000°C, thermal effects were missing. Therefore, the melt solidified without crystallization. After cooling, the sample appeared as transparent glass. The crucible was washed with water.

The melting point of CLBO determined in this study agrees well with those reported earlier: 848° C in [1] and $859 \pm 2^{\circ}$ C in [9].

One possible reason for the cracking of CLBO crystals as a result of mechanical processing is the stressinduced low-temperature polymorphism of this compound ("tin pest" effect). To check this assumption, we took XRD patterns from a crystal which was ground for



Fig. 1. Powder XRD patterns of CsLiB₆O₁₀ after (a) dry grinding and (b) grinding with ethanol for many days.



Fig. 2. Thermal analysis of $CsLiB_6O_{10}$ (sample weight of 0.268 g).

several hours in a jasper mortar fitted with a mechanical drive. Long-term grinding of CLBO, dry or with ethanol and acetone, caused no changes in the XRD pattern (Fig. 1), indicating that our assumption was wrong.

According to earlier studies [5, 8], CLBO is hydrated at high humidity. We studied the interaction of CLBO with atmospheric moisture by XRD. A powdered CLBO sample was placed over a water surface in a closed vessel, in which the room-temperature (20–25°C) humidity of air was close to 100%, and its XRD patterns were taken at regular intervals. The results are presented in Fig. 3. The XRD pattern of moist CLBO contained peaks from an additional phase. The XRD pattern from the surface layer of CLBO powder pressed

INORGANIC MATERIALS Vol. 38 No. 12 2002



Fig. 3. XRD patterns of hydrolyzed CLBO samples: (a) after storage in air at ambient humidity for many days, (b, c) after storage at 100% humidity for 3 and 7 days, respectively, (d) final hydrolysis product.

into a holder and stored in humid air showed no peaks from CLBO. The additional peaks could be assigned to $Cs_2B_{10}O_{16} \cdot 8H_2O$ [14], in line with previous results [5].

Thermal analysis of hydrated CLBO is illustrated in Fig. 4. The weight loss occurs in two steps: the first

begins at about 85°C and terminates around 130°C. The second step begins at \approx 176°C and terminates at \approx 210°C.

We also studied the interaction of CLBO with acetone and ethanol by exposing CLBO powder to vapors

INORGANIC MATERIALS Vol. 38 No. 12 2002

of these compounds for many days. No interaction was detected by XRD.

Water sorption by CLBO is closely related to its crystal structure. Figure 5 shows different projections of the CLBO structure (Diamand program) [3]. The structure contains three-membered rings, each built from two BO₃ triangles (sp^2 -hybridized boron) and one BO₄ tetrahedron (sp^3 hybridization). These rings (also present in LBO crystals) are responsible for the nonlinear optical properties of the crystals [15]. Each tetrahedron shares a corner (bridging oxygen) with one of the triangles of the neighboring ring so as to form infinite zigzag chains (Fig. 5d) which run along the body diagonals of the unit cell. In Fig. 5c, some of the chains are viewed from the side, and some from the front.

The structure contains spacious pores occupied by Cs. The pores (channels) are best seen in the *c*-axis projection (Fig. 5a), where the channels have an ellipsoidal cross section with minor and major axes of 4.16 and 6.4 Å (center-to-center distance between the projections of oxygen atoms). Note that the actual dimensions of the channels are larger since they are tilted. Therefore, the Cs ions would be expected to have a high mobility.

There are also channels running along the c axis (Fig. 5b) and having an approximately square cross section about 3.55 Å in size (center-to-center distance between the projections of oxygen atoms). These channels are also rather spacious; however, along this direction, the Cs ions alternate with Li ions, which seem to be rather strongly bonded to the boron–oxygen chains. Therefore, the cation mobility in this direction must be lower.

Proceeding from structural data, one can easily understand the mechanism of the interaction between CLBO crystals and water: the latter penetrates into the porous structure of CLBO and leaches Cs ions (hydration followed by hydrolysis).

Our results on the influence of moisture on CLBO crystals agree well with earlier findings [6]. According to IR spectroscopic data [11], there are four inequivalent positions of protons in the CLBO structure: adsorbed H₂O, H₂O in inclusions, H₃O⁺ and H₅O⁺₂ ions on the Cs site, and H₂O molecules in the form of H–O–H bridges between borate chains normal to the *c* axis.

The present and earlier reported data indicate that CLBO reacts with water according to the following overall equation:

$$2\operatorname{CsLiB}_{6}\operatorname{O}_{16} + 12\operatorname{H}_{2}\operatorname{O} \longrightarrow 2\operatorname{LiOH} + \operatorname{Cs}_{2}\operatorname{B}_{10}\operatorname{O}_{16} \cdot 8\operatorname{H}_{2}\operatorname{O} + 2\operatorname{H}_{3}\operatorname{BO}_{3}.$$
(1)

INORGANIC MATERIALS Vol. 38 No. 12 2002



Fig. 4. Thermal analysis of hydrated CLBO.

The initial steps of this process can be described by the equations

 $CsLiB_6O_{10} + xH_2O \Longrightarrow CsLiB_6O_{10} \cdot xH_2O, \quad (2)$

 $CsLiB_6O_{10} + 2H_2O \Longrightarrow Li(H_3O)B_6O_{10} + CsOH, (3)$

$$CsLiB_6O_{10} + 3H_2O \implies Li(H_5O_2)B_6O_{10} + CsOH. (4)$$

Equation (2) describes water sorption (hydration), and Eqs. (3) and (4) describe substitution of oxonium and hydroxonium ions for Cs. The compounds resulting from reactions (3) and (4) are polymeric acids.

Note that the hydration process must be anisotropic and must take place, for the most part, in directions perpendicular to the c axis.

To avoid water sorption, CLBO crystals should be stored in a dry atmosphere. According to DTA data, the first step of dehydration reaches completion at 130°C. Consequently, another way to prevent hydration followed by hydrolysis is to store CLBO above this temperature [7]. Accordingly, devices in which CLBO crystals are used must operate in a dry atmosphere or contain a thermostat.

CLBO crystals can be thought of as nanoporous, zeolite-like materials [16]. They would be expected to have a high ionic conductivity and good ion-exchange, sorptive, and catalytic properties. In particular, CLBO crystals should have a high cesium ion conductivity in directions perpendicular to the c axis. Since the size of the water molecule is close to the cross-sectional size of



Fig. 5. Crystal structure of CLBO: (a) *b*-axis projection, (b) *c*-axis projection, (c) projection along the body diagonal, (d) characteristic structural component; large circles represent Cs atoms, and small circles represent Li and B atoms.

the channels in the structure of CLBO, water is easy to incorporate into the channels. The acetone and ethanol molecules are substantially larger and cannot be inserted into the channels. CLBO would be expected to react with ammonia.

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