Cracking mechanism in CLBO crystals at room temperature

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Abstract

Cesium lithium borate single crystals tend to crack at room temperature in an ambient air atmosphere, which has limited their use in device applications. This study shows that the cracking of high-quality CLBO crystals results from the anisotropic corrosive effect of water vapor in the ambient atmosphere. The directional attack by water molecules at the crystal surface was related to its crystal structure. The crystal quality of CLBO was found to influence the crack propagation velocity.

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1. Introduction

Cesium lithium borate CsLiB$_6$O$_{10}$ (CLBO) is a novel NLO crystal discovered in the 1990s [1–3]. It has excellent properties such as a high $d_{\text{eff}}$ in the UV region, a high optical damage threshold, etc. Unfortunately, CLBO crystals have a tendency to crack when left in air at room temperature, which has strongly limited their use in devices. In order to prevent the cracking, it is first necessary to understand the cracking mechanism.

A few attempts have been made to explain the reasons for the cracking phenomenon in CLBO crystals [4–6]. Ryu et al. [4] reported that crack nucleation occurred at “strain” defects such as voids and growth striae, and were parallel to the {100}. They also pointed out that cracking occurred much less frequently for high-quality crystals prepared using optimized growth procedures. Zhanget al. [5] claimed that the cracking was caused by the inclusion of glassy material into the crystal during the growth procedure. Taguchi et al. [6] found that the product of hydration of CLBO was Cs$_2$B$_{10}$O$_{16}$$\cdot$8H$_2$O, and that the hydration occurred faster with higher humidity (>45%). They also investigated the dependence of the hydration rate on the humidity and summarized that surface hydration seemed to cause crystal cracking.

This paper proposes a new mechanism for the cracking of CLBO crystals.

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2. Experiments and discussion

2.1. Phase transition assumption

The investigation first considered whether the cracking was due to the existence of a phase transition near room temperature. Differential scanning calorimetry (DSC) was used to examine the phase behavior of CLBO crystals at room temperature. Calorimetric measurements were performed on a Mettler-Toledo DSC821e instrument. A lamellar CLBO crystal weighing 7.7 mg was sealed in an aluminum pan under an infrared lamp to avoid the effect of water vapor, then scanned using the heating and cooling modes over a temperature range of \(-30^\circ\text{C}\) to \(80^\circ\text{C}\) with a scanning rate of 5 \(^\circ\text{C}/\text{min}\). No major thermal effects were observed during either heating or cooling process, as shown in Fig. 1. One minor endotherm at about \(0^\circ\text{C}\) had an enthalpy of only \(-8.29 \times 10^{-3} \text{J/g}\), too small to indicate any phase transition point.

2.2. Crystalline structure analysis

Taguchi et al. [6] suggested that the cracking of CLBO crystals was caused by surface hydration at room temperature. However, they did not explain this phenomenon in detail while surface hydration in air occurs with many crystals, such as KDP, LBO, or even CsB\(_3\)O\(_5\) (which is hygroscopic), none of them cracks like CLBO. Therefore, more information is needed to relate the cracking mechanism to surface hydration.

CLBO crystallizes in a tetragonal structure with space group I 42d and unit cell parameters \(a = 10.460\) and \(c = 8.955 \text{ Å}\) [1]. The borate anionic frame consists of a three-dimensional network made up of [B\(_3\)O\(_7\)]\(^5-\) six-membered rings which are approximately parallel to each other. Cesium and lithium cations alternate in the channels formed by the borate groups. The lithium ion is located in a tetrahedral cavity surrounded by four oxygen atoms with an average Li–O bond lengths of 1.960 Å. The cesium ion is located in a larger cavity surrounded by eight oxygen atoms, with an average Cs–O bond lengths of 3.160 Å in one oxygen tetrahedron and 3.546 Å in another. The projection of a unit cell along the \(c\) and \(a\) (or \(b\)) directions is shown in Fig. 2. Part (A) illustrates that the atoms in the crystal unit cell are densely arrayed along the \(c\)-axis. However, Part (B) shows that channels exist parallel to the \(a\) (or \(b\)) axis whose minimum width is 4.2 Å. Since H\(_2\)O molecules are 1.48 Å in length, the channels provide enough space for infiltration of water vapor molecules that can react with the Cs and Li ions.

2.3. Effect of defect and humidity

Two cubic crystals, one with high quality and one with many inclusions, were both polished and placed in a silicagel desiccator. No visible cracking.
was observed after several months. When both were exposed to an air atmosphere, the crystal with many inclusions cracked into pieces within several days, while the cracking in the high-quality crystal closely correlated with the humidity. Under

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Fig. 2. (A) CLBO crystal cell projection along the c direction; (B) CLBO crystal cell projection along the a (or b) direction.

Fig. 3. Surfaces normal to the a- and b-axis of CLBO sample “1” were covered with glue while those of sample “2” were not. (A) Original crystals; (B) after 4 months with humidity over 40%, the corners of sample “2” cracked first and then the edges; (C) after 6 months; (D) after 7 months with the glue on sample “1” removed.
Fig. 4. (A) X-ray powder diffraction pattern of the hydrolytic products of a CLBO crystal; (B) X-ray powder diffraction pattern of a CLBO crystal.
humidity of 40% or less, the crystal did not crack for over 7 months. When the humidity was raised to 40%, cracks first occurred at the corners of the cube, then the edges, then propagated along planes vertical to the c-axis. The final result was that the crystal broke into a number of pieces. The whole process took place over a period of several months to over 1 year.

2.4. Effect of humidity and crystal orientation

Two cubic crystals with the same dimensions were cut from one as-grown high-quality CLBO crystal, then oriented and roughly polished. Four surfaces normal to the a- and b-axis of one crystal (labeled No. 1) were covered with glue while its other two surfaces (normal to the c-axis) were exposed to the ambient conditions. The second crystal was not covered with glue (labeled No. 2) so all six surfaces were exposed. The samples were studied at regular intervals. Fig. 3 illustrates the whole procedure for both crystals over a 7-month period. Letters A–D indicate 0, 4, 6 and 7 months of exposure to an air atmosphere, respectively. Under conditions of humidity over 40%, first the corners and then the edges of sample “2” cracked and the whole crystal became opaque after 4 months; but no obvious changes occurred in sample No. 1. After 6 months sample “2” cracked more seriously and the layered structure was quite clear. Sample “1” on the other hand was still intact except for a little opaqueness on parts of some corners and edges. This was seen more clearly after 7 months when the glue on sample “1” was removed.

Crystalline structure analysis result was proved by this experiment that water vapor molecules attack certain crystal faces (the faces parallel to the c-axis) more rapidly than those perpendicular to it. Therefore, the cracking always resulted in the development of opaque, strained layers parallel to the a–b faces.

The hydrolytic products found on CLBO crystals after exposure to air included α-Li₄B₂O₅ and H₃BO₃ besides Cs₂B₁₀O₁₆·8H₂O previously reported [6]. X-ray powder diffraction analysis was carried out on a Brüker D8 diffractometer with Cu Kα radiation. The result is shown in Fig. 4A along with the X-ray pattern for a CLBO crystal in Fig. 4B for comparison.

Comparison with the standard patterns in the ICDD PDF-2 database showed that the majority of hydrolytic products on the crystal surface were Cs₂B₁₀O₁₆·8H₂O, α-Li₄B₂O₅ and H₃BO₃. The major 2θ values in the standard patterns of each product are listed in Table 1. Therefore, the hydrolysis equation of CLBO crystal was deduced to be

\[
4\text{CsLiB}_6\text{O}_{10} + 19\text{H}_2\text{O} \rightarrow 2\text{Cs}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O} + \alpha\text{-Li}_4\text{B}_2\text{O}_5 + 2\text{H}_3\text{BO}_3.
\]

Besides the effect of hydrolysis, our experiments also showed that crystals with defects cracked more easily and rapidly. The defects included growth striae, inclusions, invisible cracks, and so on. A special type of tubular grown defect found in CLBO crystals is shown in Fig. 5. Tubular defects formed when faster growth rates were used and crystals containing these defects cracked quite quickly. These tiny tubes with an average diameter of 100–200 μm were always aligned along the a- or b-axis, i.e. in the growth directions.
3. Conclusions

The possibility of a phase transition was excluded as the cause of CLBO crystal cracking at room temperature. The main cause was found to be anisotropic corrosion by water vapor. The rate of crystal cracking was influenced by the environmental humidity level and the crystal quality. Under conditions of air humidity over 40%, the CLBO crystals were likely to crack. Crystals with greater defect concentrations cracked more easily and rapidly. The hydrolytic products of CLBO crystals were determined to be $\alpha$-Li$_4$B$_2$O$_5$ and H$_3$BO$_3$ besides Cs$_2$B$_{10}$O$_{16} \cdot 8$H$_2$O. Structural analysis and corrosion experiments showed that the water molecules attacked the crystal along the $a$- or $b$-axis much more easily than along the $c$-axis. Therefore, two ways should be considered to preclude the cracking of CLBO crystals: to improve the crystals quality and to isolate as-grown crystals from humid environments.

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References