Effects of the moisture and thermal annealing on CLBO crystal

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Abstract

The effects of the moisture and thermal annealing on CLBO crystal have been investigated. CLBO has hydrated at high humidity condition, resulting in $5B_2O_3$•Cs_2O•$8H_2O$. The surface hydration seems to induce the cracking and the refractive index change in CLBO. The thermal annealing is effective to restore the changed index.

Keywords

Nonlinear optical materials, CLBO, Hydration

Introduction

$CsLiB_6O_{10}$ (CLBO) crystal has the advantages for UV generation by nonlinear optical (NLO) processes due to its smaller walk-off angle, lager angular, spectral and temperature bandwidths as compared to β-BaB_2O_4 (BBO).[1-3] Therefore CLBO is considered to be the most suitable material for fourth (FOHG) and fifth harmonic generations (FIHG) of Nd:YAG laser.[4] However, despite the excellent NLO property, CLBO exhibits disadvantages such as cracking and change of refractive index.[5] These characteristics seems to be related to the hygroscopic nature and fragility of CLBO. In this study, we have examined the effect of moisture on CLBO in order to find a clue to overcome these problems.

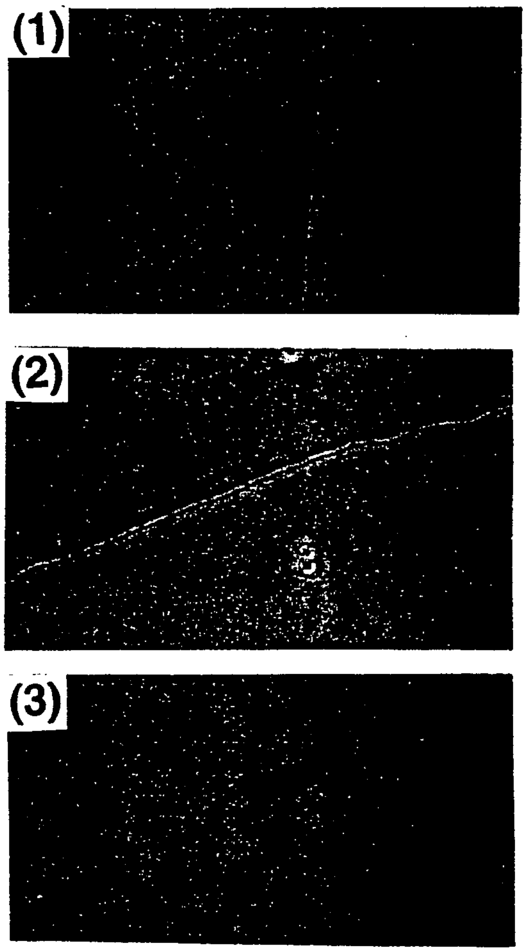

Figure 1. Optical microscope pictures of CLBO surfaces of, (1) as-polished, (2) after exposed to 70% humidity for 17 days and (3) polished sample kept in a desiccator for 14 days.

Result and discussion

Figure 1 shows the optical microscope pictures of CLBO surfaces of, (1) as-polished, (2) after exposed to 70%

humidity for 17 days and (3) polished sample kept in a desiccator for 14 days. These figures clearly indicate that atmospheric moisture caused the degradation of CLBO surface. Then we have investigated chemical reactions between moisture and CLBO. Powder X-ray diffraction (XRD) analysis was carried out on two CLBO powder samples; (1) kept in the desiccator (5% humidity) for 14 days and (2) exposed to 65% humidity for 14 days at room temperature (RT). Figures 2(a) and (b) show the XRD patterns of sample (1) and sample (2), respectively. New XRD peaks appeared as indicated in figure 2(b). These XRD peaks are attributed to $5B_2O_3{\bullet}Cs_2O{\bullet}8H_2O$, considered to be resulted in hydration of CLBO.

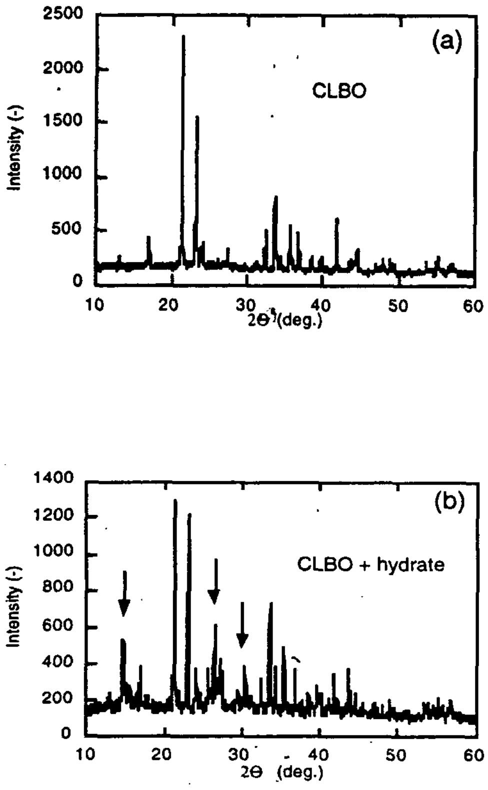

Figure 2. XRD spectra obtained for (a) CLBO and (b) CLBO after hydration.

Figure 3 shows the dependence of hydration rate on the humidity. Three CLBO powder samples were prepared by using 280 mesh and kept in the following conditions at RT for 7 days, respectively; (1) in the desiccator (~5% humidity), (2) 45% humidity and (3) 65% humidity. The hydration rate was determined from the ratio of the initial weight of the sample and the measured gross weight of the sample at various time. The hydration did not occur in the sample kept in the desiccator. The hydration rate of CLBO at 65% humidity condition is more than 10 times than that at 45% humidity case.

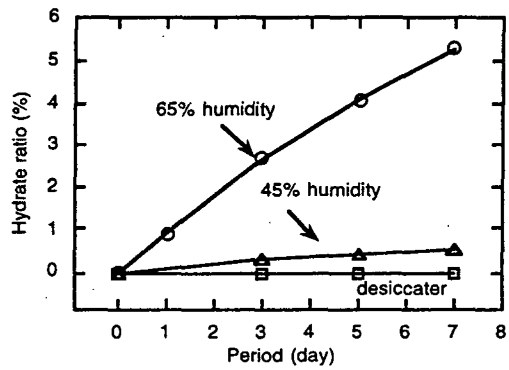

Figure 3. Dependence of the hydration rate on the humidity.

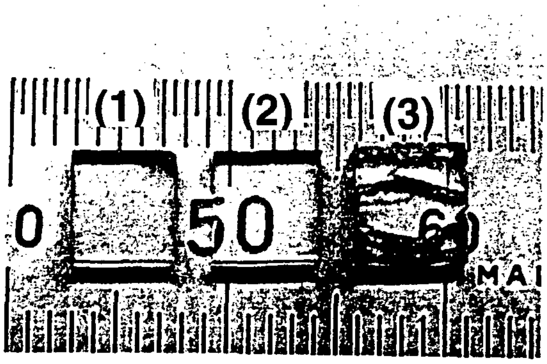

Figure 4. Pictures of CLBO samples kept in the three different conditions at RT for 5 days, respectively; (1) in the desiccator (~5% humidity), (2) 45% humidity and (3) 65% humidity.

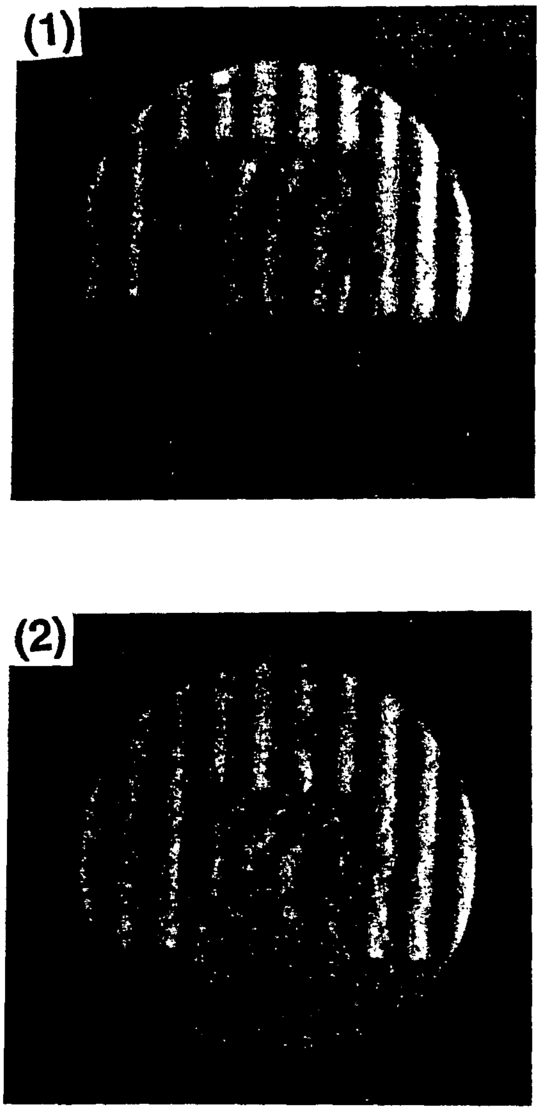

Figure 5. Laser transmission interferogram of CLBO for (1) as-prepared and (2) sample after 16 days outside the desiccator.

We have investigated the effect of the hydration on the cracking of CLBO. Three CLBO bulk samples used in this experiment were roughly polished. These samples have been kept in the three different conditions at RT for 5 days, respectively; (1) in the desiccator (~5% humidity), (2) 45% humidity and (3) 65% humidity. As shown in fig. 4, the cracking was observed only in the sample exposed to 65% humidity. This means that the surface hydration seems to be the reason of the crystal cracking.

It has been pointed out that the refractive index of CLBO varied from the edge of the sample, resulting in the lensing effect for the laser beam.[6] This index change is considered to be resulted in changing in the lattice constant induced by some unknown factor. In this work the effect of the moisture on the refractive index change has been investigated. Laser transmission interferogram of CLBO for (1) as-prepared and (2) sample after 16 days outside the desiccator are shown in fig. 5. As shown in the figure, the refractive index started to change from the edge after 16 days.

On the other hand, CLBO sample kept in the desiccator for 16 days did not showed refractive index change as shown in fig. 6(a) and (b). The gross weight of the CLBO samples as refered to atmosphere humidity at various time are shown in fig. 7. This figure indicates that CLBO sample increased in weight due to the surface hydration when the humidity was above 40%.

The index change of CLBO are thought to be closely related to its crystal structure. The CLBO unit cell in the (010) plane (Figure 8) shows large vacant space for the upper and the lower sides of two isolated Cs ions.[7] It is conceivable from the figure that the zigzag chains of the rhombic borate network may move in opposite directions between the a- and c-axis, due to the stretching of pantograph-like motion. The stress induced by surface hydration seems to cause this motion, resulting in the variation of lattice constants.

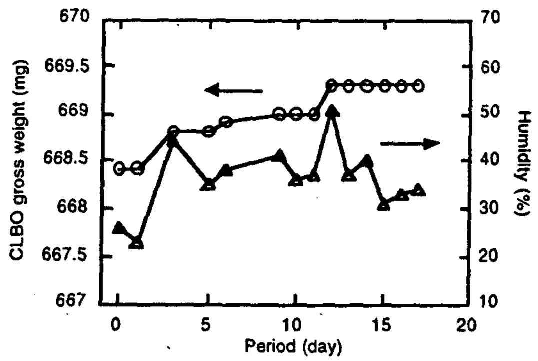

Figure 7. The gross weight of the CLBO samples outside the desiccator refered to atmosphere humidity at various time.

We have found that the changed refractive index can be restored by thermal annealing above ~130 °C. The laser interferogram of changed index shown in fig. 5 (2) could become to like that shown in fig. 5 (1). It is interesting that the restoration of index could not be observed by the low temperature annealing below ~100 °C, suggesting the existence of the threshold temperature between 100 to 130 °C. Though the reason for this phenomenon is not cleared yet, it seems to be explained by the following experiment. Figure 9 shows the differential thermal analysis (DTA) and thermogravimetry (TG) curves obtained for the CLBO powder sample exposed to 65% humidity for 5 days. The TG-DTA graph indicates the decomposition of hydrate at 120 °C. It must be noted that no change in TG-DTA curves was observed for the CLBO powder sample without hydrate. There is a good agreement between the decomposition temperature of hydrate and the threshold temperature for the restoration of index. We consider that the stress induced by hydration would hinder the restoration of changed index.

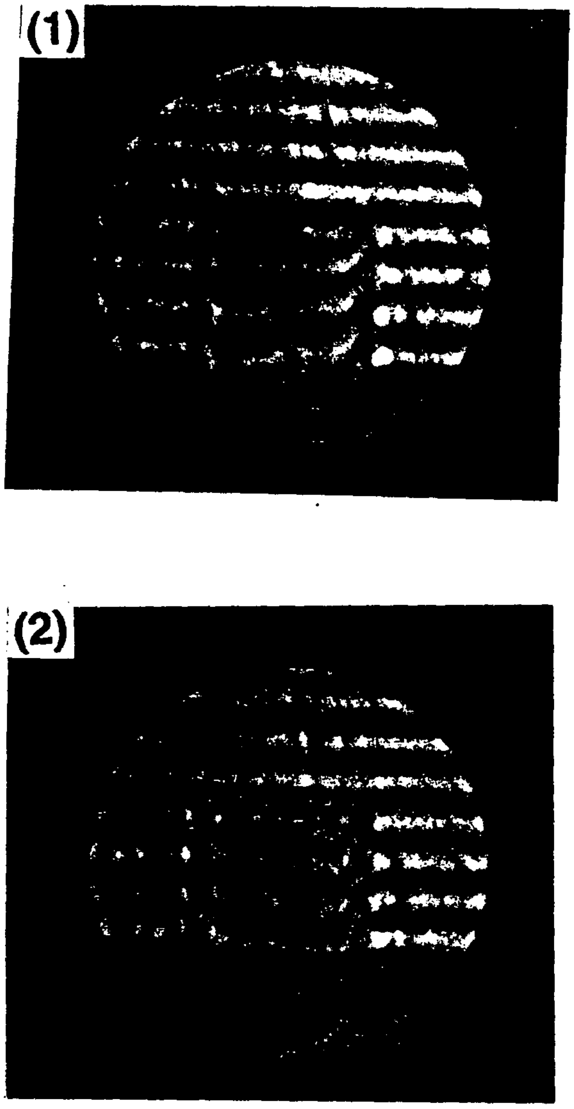

Figure 6. Laser transmission interferogram of CLBO for (1) as-prepared and (2) sample after 16 days in the desiccator.

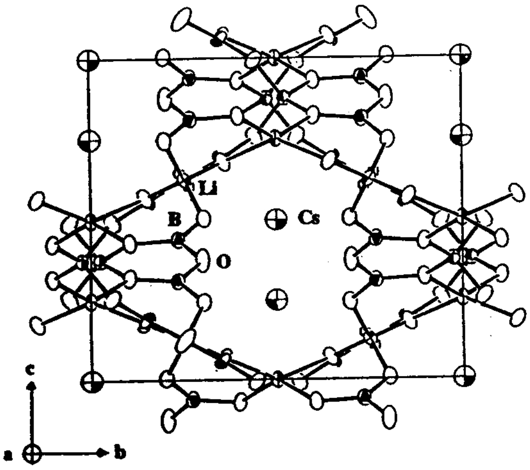

Figure 8. The CLBO unit cell in the (010) plane.

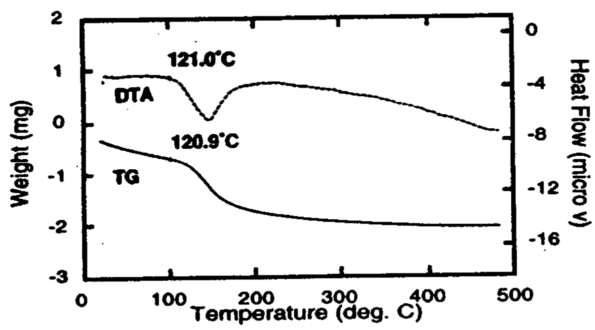

Figure 9. The differential thermal analysis and thermogravimetry curves obtained for the CLBO powder sample exposed to 65% humidity for 5 days.

Conclusion

We have investigated the effects of the moisture on CLBO. The CLBO surface hydrated at high humidity, resulting in $5B_2O_3 \cdot Cs_2O \cdot 8H_2O$. The hydration rate of CLBO depended on the humidity. At 65% humidity condition CLBO hydrated more than 10 times faster than that at 45% humidity case and the hydration could be suppressed at low humidity condition. The surface hydration caused the cracking and the refractive index change in CLBO. The changed index was restored by the thermal annealing > 130 °C.

Reference

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