Crystal growth and characterization of 4 in. YCa₄O(BO₃)₃ crystal

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1. Introduction

Rare earth calcium oxyborate single crystals ReCa₄O(BO₃)₃ (Re-rear earth elements such as Gd, La, Y, Sm, and so on) were studied for second-harmonic generation (SHG) in the past two decades [1], because of several advantages, such as: easy to grow, small birefringence, effective NLO coefficient and high stability (not hygroscopic) [2]. Among this series of crystals, YCa₄O(BO₃)₃ (YCOB) crystal has gained great attention in the past few years. Prominent nonlinear-effect, thermo-optic effect, mechanical characteristic and large aperture make YCOB a main alternative for laser amplification in high-energy ultra-short laser systems [3]. Besides, YCOB can also be used in the automotive and aerospace industries due to their excellent high temperature piezoelectric properties according to recent research [4].

YCOB compound was produced by Norrestam [5] in 1992 using high-temperature solid-state reactions. Five years later, YCOB single crystal was obtained by conventional Czochralski method and congruent melting behavior was observed [6,7]. After that, YCOB crystals attracted broad interest of worldwide researchers. At present, YCOB crystals with large aperture (larger than 75 mm × 75 mm × 18 mm) and high quality are required for high-power ultra-short laser system and high temperature piezoelectric applications. However, to the best of our knowledge, successful growth of YCOB crystal with large size and high quality was seldom reported. In this work, 4 in. YCOB crystals without inclusions and cleavages were grown successfully. These YCOB crystals exhibit excellent nonlinear optical properties, and have been used in high-energy and high-power ultra-short laser systems successfully.

2. Crystal growth

2.1. Starting material synthesis

Before growth, it is necessary to obtain a proper starting melt composition [8]. Y₂O₃, CaCO₃ and H₃BO₃ with 99.99% purity were used as starting powders. Y₂O₃ and CaCO₃ powders were heated at 250 °C for 10 h to remove absorbed water before weighing (stoichiometric). An extra amount of H₃BO₃ (~ 1 wt%) was added to compensate the volatilization during crystal growth. The mixture was pressed into blocks after completely mixed. Then the block was sintered in a muffle furnace and the chemical reaction can be described with the following elemental formula:

\[
Y_2O_3 + 8CaCO_3 + 6H_3BO_3 \rightarrow 2YCa_4O(BO_3)_3 + 9H_2O + 8CO_2
\]

First, the block was heated at 350 °C during 5 h in order to ensure the complete transformation of H₃BO₃ to B₂O₃. Then, the block was heated at 900 °C during 5 h to decompose CaCO₃ into CaO. Finally, the pure starting YCOB material was obtained after a 10 h hearting at 1300 °C in air. In this research, CaCO₃ and H₃BO₃ were chosen as the starting powders because of their relatively stable properties compared with CaO and B₂O₃ (both hygroscopic). All of those steps are necessary to get accurate melt composition, which is a key point to get high quality crystals without inclusions.
2.2. Crystal growth technology

YCOB crystals (Figs. 1 and 2) were grown by the conventional Czochralski technology using a RF induction generator (8 KHz). The feedstock was heated to melting point for several times in order to cram the iridium crucible considering the higher density of the crystal than the porous feedstock. The growing atmosphere was nitrogen mixed with 1 vol% oxygen. The starting composition was stabilized at 30–40 K above the melting point for 10 h in order to reach a stable and homogeneous melt. A seeding crystal with [0 1 0] direction is then lowered into the crucible until it touches the surface of the melt after lowering the melt temperature to 2–3 K above the melting point. Pulling up was started after stabilization of the seeding (crystal weight does not change any more). An up-weighing system with Auto Diameter Control program was used for the growth of the single crystals.

Crystals were pulled directly from the congruent melt. Typical pulling rate is about 0.5–2 mm/h, while rotation rate varied from 5 rpm to 15 rpm. The as-grown crystal was 100 mm in diameter and 150–160 mm in length. Typically, Ir crucible with 170 mm in diameter and 170 mm in height was used to grow crystal of 4 in. We are able to convert less than 50% of the melt to high quality crystals. Based on observations of large amount growth results, we found that fiber-like inclusions often formed at the bottom of the as-grown crystal if the melt to crystal conversion ratio is over than 50%. Therefore, higher melt to crystal conversion ratio was not used in order to reach the best crystal quality. Three issues are responsible for these inclusions. First, the growth composition is off from the melt of congruent. During the melting process, YCOB decompose into two liquid phase with different composition. Under the condition of slow cooling and without stirring, the two liquids remain unmixed and cool separately, and three new crystalline phases will form [8]. These new crystalline phases may enter into YCOB crystal and form inclusions under inadequate flow. Second, since the solid–liquid interface moves down to the bottom of the Ir crucible due to the melt converting to high quality crystal, the temperature gradient would become smaller. As a result, the driving force of crystal growth would turn smaller, resulting in smaller critical growth rate. Fiber-like inclusions would form when growing rate is larger than critical growth rate. If the growing rate were larger than the critical growth rate, there were not enough time for heat and mass transfer in the interface. Then the forced growth would occur, and many types of defect such as: inclusions, bubbles and dislocations will be introduced into the crystal. Third, convex or a concave interface plane often cause the formation of ununiformed properties, inclusions and other defects. Therefore, it is important to keep the interface shape uniform and flat (or tiny convex) during crystal growth, neither too convex nor too concave. Crystal rotation rate should be adapted during the whole growing process. In general, high rotation rate may achieve a flat interface and help to eliminate some defects, however, is difficult to achieve in YCOB, due to YCOB is colorless. We were successfully achieved a stable tiny convex interface by varied the rotation rate from 5 to 15 rpm during the growth of a single crystal ingot. According to our experience, the last two issue are the main reasons, and inclusions can be reduced by lowering growth rate (no faster than 0.8 mm/h) and adapting the rotation rate to obtain stable tiny convex interface.

In addition to inclusions, cleavage planes along (2 0 2) and (2 0 1) (shown in Fig. 2) are also harmful for YCOB crystals, since they make crystals easy to crack during the process of cooling down to the room temperature, especially for larger size crystals. Reducing cooling rate and extending the separation time could minimize thermal shock and excess stress in crystals, as reported by Fei [9]. However, it cannot offset thermal stress in large size crystals. In this work, a small perpendicular temperature gradient and lower growth rate were applied to reduce thermal stress in YCOB single crystal. Therefore, 4 in. YCOB without inclusions and cleavages were grown successfully in such conditions.

3. Crystal properties

Rocking curve, transmittance and optical homogeneity of as-grown crystals were characterized. Nonlinear optical property has been investigated by OPCPA experiments and nanosecond OPA experiment.

Rocking curve was tested by D8 discover HRXRD (Bruker), and the result of a specimen with the size of 15 mm × 15 mm × 1 mm in [0 1 0] direction was shown in Fig. 3 (left). The FWHM (full width at half-maximum) value is 29.16 arcs, suggesting that the crystal has high quality and is without low-angle boundaries. Transmittance was tested by Cary 5000 UV–vis–NIR spectrophotometer (Agilent), and the result of polished specimen with the size of 14 mm × 14 mm × 2 mm in [0 1 0] direction was shown in Fig. 3 (right). The transmittance of the as-grown YCOB crystal reaches 87% in the range of 210 nm to 2500 nm, which is much larger than that of ever reported (80% in the range of 300 nm to 2400 nm). Two large infrared absorption peaks were observed at 2700 nm and 2900 nm, in consistent with Segon’s report [10]. The corresponding transmittance is around 78% and 65% respectively, which are also higher than reported results.
Optical homogeneity was tested by a 55 mm \(\times\) 55 mm \(\times\) 16.3 mm aperture, as shown in Fig. 1 (right). The tests were carried out in Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences (SIOM). The specimen had been finely polished before testing. The surface characterization and optical homogeneity results were shown in Fig. 4. The Ra roughness (Fig. 4 left) of the polished surface is 1.71 nm and optical homogeneity (Fig. 4 right) reaches 1.48 \(\times\) 10\(^{-6}\), as characterized by Vecco interferometer. These experiment tests justify the excellent optical properties of YCOB crystals grown during this work using our growth conditions.

The LIDT, OPCPA experiments and nanosecond OPA tests of YCOB crystals were also carried out in SIOM. Testing details were illustrated in our previous work [3,11,12]. The LIDT was tested at the wavelength of 1064 nm with pulse width of 12 ns. The result shows that the LIDT of YCOB crystal is higher than 29.1 J/cm\(^2\) when damage happened on the surface of the specimen. The collinear OPCPA experiment used a crystal with the size of 25 mm \(\times\) 25 mm \(\times\) 25 mm. From the experimental results, the \(D_{\text{eff}}\) was estimated to be 0.728 and 1.16 pm/V for the phase matching in orientation of (31.7°, 0°) and (31.7°, 180°), which is 92% and 85% percentage of theoretical value, respectively. In the non-collinear OPCPA experiment, signal pulse of 3.36 J with pulse duration of 44.3 fs was obtained at around 800 nm. To the best of our knowledge, this is the first time to demonstrate non-collinear OPCPA with YCOB as nonlinear crystal. The nanosecond OPA experiment used two pieces of YCOB crystal with the size of 10 mm \(\times\) 10 mm \(\times\) 20 mm, with the orientation of (0.0, 33.0°). The nanosecond OPA of pulses centered at 1572 nm was realized, and a saturated OPA gain of 2.4 was obtained. The experimental results show that the YCOB crystal is preferable as the gain medium in the power amplification stage of an OPA.

4. Conclusions

In this work, 4 in. YCOB crystals were grown by Czochralski method. High quality crystals without inclusions and cleavages have been gained by improving growth conditions including rotation rate, growth rate and temperature gradient. These YCOB crystals exhibit high transmittance, superior optical homogeneity and high LIDT. Using YCOB as nonlinear crystal, non-collinear OPCPA experiment centered at 800 nm and nanosecond OPA of pulses centered at 1572 nm were demonstrated successfully for the first time. Crystals with such excellent properties can satisfy the demand for high-peak and high-average power pulse generation in high-energy ultra-short laser systems. Moreover, grow technology concluded in this work could shed some light on the growth of some other crystals.

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References


