

# Growth and structural characterization of $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$ new nonlinear crystal

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The nonlinear optical (NLO) crystal  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  (starting composition) of good quality has been grown from the melt by the Czochralski pulling method. X-ray diffraction experiments show that the structure of grown crystal belongs to the monoclinic system with space group  $Cm$  and its unit cell parameters have been measured to be  $a = 0.80711(2)nm$ ,  $b = 1.60132(1)nm$ ,  $c = 0.35230(8)nm$  and  $\beta = 101.166(1)^\circ$ . The crystal possesses a wide transmission range from UV to IR, which is advantageous for applications as new NLO material for frequency doubling of solid state lasers operating in the near infrared range.

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## 1. Introduction

In recent years, there has been a growing demand for specific visible and ultraviolet laser sources in medicine, industrial processing, remote sensing, laser printing, optical displays, and other areas. One of the best ways to obtain such coherent beams is by using frequency doubling of diode pumped solid state lasers operating in the near infrared range, especially through noncritical phase matching (NCPM) in nonlinear optical (NLO) crystals. The major advantage of NCPM is less beam walk-off so that the beam profile will be less distorted and the crystal can be made longer to improve efficiency. In addition, the angular acceptance is larger during the second harmonic generation (SHG) process.

Experimental results show that borate crystals are a vast and useful family for NLO crystal research [5]. Borate crystal has relatively high resistance against laser-induced damage and high transparency in the visible and UV regions. In the last years, many kinds of new borate NLO crystals have been developed, such as  $CsLiB_6O_{10}$  - CLBO,  $BiB_3O_6$  - BiBO,  $K_2Al_2B_2O_7$  - KABO,  $KBe_2BO_3F_2$  - KBBF,  $RECa_4O(BO_3)_3$  - RECOB (RE = Gd, Y, La) [1 - 7]. Among them, the monoclinic rare earth calcium oxoborate (RECOB) can be grown easily by the Czochralski method, and are efficient NLO crystals with a large transparent range, high damage threshold and non-hygroscopicity.

Previously, it was found that the substitution of the trivalent RE cations with smaller radius cations lead to larger optical birefringence [8, 9]. In YCOB crystal, the  $Y^{3+}$  ions can be partially substituted by smaller  $Lu^{3+}$  ions. As a consequence, by changing the compositional parameter  $x$  of  $Y_{1-x}Lu_xCa_4O(BO_3)_3$  crystals, their optical birefringence can be controlled in order to achieve SHG in NCPM conditions of specific near infrared laser emission

wavelengths shorter than phase-matching cutoff wavelength of YCOB crystal (724nm along Y axis and 832nm along Z axis at room temperature [10]).

$LuCa_4O(BO_3)_3$  compound doesn't have congruent melting and single crystals with this composition cannot be grown from the melt. Ilyukhin and Dzhurinskii [11] made structural investigations of  $LuCa_4O(BO_3)_3$  tiny crystals, grown from a PbO flux. Therefore in the YCOB structure  $Lu^{3+}$  ions can only partially substitute  $Y^{3+}$  ions and according to the ionic radii of  $Y^{3+}$  and  $Lu^{3+}$  ions ( $r_Y = 0.9\text{\AA}$ ,  $r_{Lu} = 0.861\text{\AA}$  [12]) the optical birefringence of  $Y_{1-x}Lu_xCa_4O(BO_3)_3$  new nonlinear crystals increases with increasing of the substitution degree (compositional parameter  $x$ ), giving us the possibility to tune the NCPM wavelength for SHG. Our recent results [13] showed that the solubility limit of  $Lu^{3+}$  ions in YCOB crystal is close to 40 at% ( $x$  close to 0.4).

In this paper, the  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  crystal growth and some structural properties of the grown crystal are reported.

## 2. Experimental

To synthesize the  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  compound, the solid state reaction technique was used. A single crystal of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  (starting composition) was grown using the conventional radio frequency (RF) heating Czochralski method from iridium crucible under nitrogen atmosphere. Further growth details will be described below. The range of optical transparency was determined in a Y-cut  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  sample with a thickness of 2mm. The transmission spectrum was measured using a Cary 5 spectrophotometer at room temperature in the range of 200-3000nm. X-ray powder diffraction (XRPD) experiments were performed with a

Bruker AXS D8 ADVANCE X-ray diffractometer (Cu  $K_{\alpha 1}$  = 1.5406 Å). The measurements were carried out at room temperature between  $10^\circ$  and  $70^\circ$  in  $2\theta$  using a flat rotating sample holder. The angular resolution of the apparatus was better than  $0.014^\circ$ . The XRPD data were analyzed with the Rietveld profile refinement method [14] using TOPAS V2.1 software [15].

### 3. Results and discussion

The  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  starting material was prepared by solid state reaction of 4N  $Y_2O_3$ ,  $CaCO_3$ ,  $B_2O_3$ , and  $Lu_2O_3$  in stoichiometric ratio. Considering the evaporation of  $B_2O_3$  during the growth process, an excess quantity of  $B_2O_3$  (less than 3%) was added to the starting material. In order to eliminate the absorbed water, the  $CaCO_3$  powder was preheated at  $400^\circ C$  for 10h. Then, the compounds were immediately weighed and mixed by milling in an agate mortar until fine powder was obtained. After that, they were cold-pressed into cylindrical pellets and prereacted by heating at  $900^\circ C$  for 15h in order to decompose  $CaCO_3$  completely. Subsequently, the obtained pellets were crushed, mixed, pressed again into pellets and annealed for 36h at  $1350^\circ C$ .

The room temperature X-ray powder diffraction pattern of the synthesized material was taken to examine whether the solid state reaction was complete. The pattern of Fig. 1 shows that the synthesized product is not single phases of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$ . It contains a major phase isostructural with monoclinic YCOB and two minor extra phases of  $Y_2O_3$  [16] and  $CaO$  [17]. The peaks characteristics to  $Y_2O_3$  and  $CaO$  phases are marked with full and open circles, respectively. The presence of the minor parasitic phases confirms that the solubility limit of  $Lu^{3+}$  ions in YCOB structure is smaller than 40 at% but is close to this value [13].

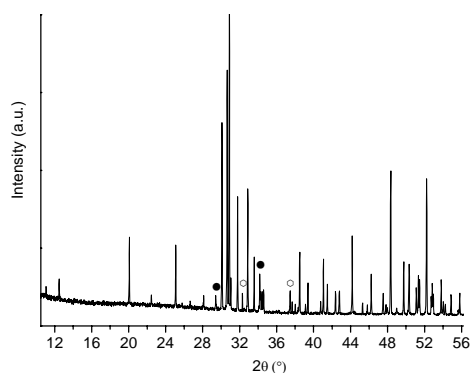


Fig. 1. Room temperature XRD patterns of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  synthesized material. The peaks marked with full and open circles belong to  $Y_2O_3$  and  $CaO$  parasitic phases, respectively.

$Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  single crystal was grown by the conventional Czochralski technique. The growth was performed by pulling from melt contained in an iridium

crucible of 30 mm diameter and 30 mm height, in a continuous  $N_2$  flow. In order to avoid the formation of polycrystals in the growth process, preheating at a temperature  $50$ - $60^\circ C$  higher than the melting point was required. Then, the temperature was reduced to the growth temperature. The typical pulling rate was  $0.6$  -  $0.8$  mm/h and the rotation rate was  $30$ - $45$  rpm. In the growth process rectangular  $\langle 010 \rangle$  oriented single crystal sample of pure YCOB with dimensions of  $3 \times 3 \times 25$  mm<sup>3</sup> was used as seed. The growth temperature, determined by an infrared pyrometer, was about  $1510 \pm 10^\circ C$ . The temperature gradient just above the melt was  $30$ - $40^\circ C/cm$ . As much as 25% of the melt was converted into a single crystal in approximately four days. The crystal was cooled to room temperature at a rate of  $40^\circ C/h$ . In order to eliminate the residual stress inside the crystal, it was annealed further in air atmosphere. The crystal was heated to  $1350^\circ C$  at the rate of  $50^\circ C/h$ , held at that temperature for 36h and finally cooled to room temperature at the rate of  $20^\circ C/h$ . Figure 2 shows the obtained  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  crystal and a polished crystal sample cut from the grown crystal. Excepting the crystal shoulder region where the crystal surface is covered by an opaque white polycrystalline thin layer, the grown crystal is highly transparent, colorless, nonhygroscopic and chemically stable. Its dimensions are about 15mm in diameter and 25mm in length. The crystal has good mechanical properties, which make it easier for cutting and polishing.

X-ray powder diffraction patterns of samples exerted from the polycrystalline thin layer and single crystal are shown in Fig. 3. The parasitic  $Y_2O_3$  and  $CaO$  phases exist only in the polycrystalline layer. The occurrence of the parasitic phases arises from noncongruent melting of the  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  synthesized material [13]. In the diffraction pattern of single crystal no parasitic phase is observed and the crystal is of good quality. This implies that the melt becomes congruent after segregation of the parasitic phases in the crystal shoulder region.

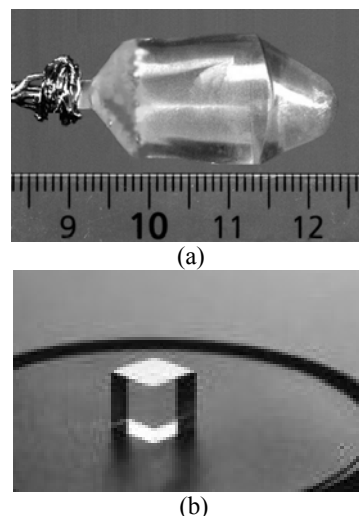


Fig. 2. Photographs of: (a)  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  single crystal and (b) polished crystal sample cut from the grown crystal.

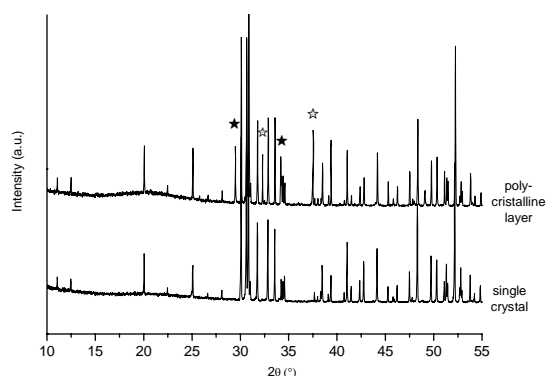


Fig. 3. Room temperature X-ray powder diffraction patterns of the polycrystalline thin layer and single crystal. The peaks marked with full and open stars are characteristics of the  $Y_2O_3$  and  $CaO$  parasitic phases, respectively.

$RECa_4O(BO_3)_3$  ( $RE = Gd^{3+}, Y^{3+}, La^{3+}$ ) compounds have a non centro-symmetric monoclinic structure, with space group  $Cm$  [11, 18]. Their structure contains a RE site of  $C_s$  symmetry, two types of calcium sites  $Ca^{2+}(1)$  and  $Ca^{2+}(2)$  and two distinct  $(BO_3)^{3-}$  groups. In the case of  $YCa_4O(BO_3)_3$ , the unit cell parameters are  $a = 0.80770(3)nm$ ,  $b = 1.60194(5)nm$ ,  $c = 0.35308(1)nm$  and  $\beta = 101.167(4)^\circ$  [19].  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  crystal structure was analyzed by Rietveld method and the structure refinement was initiated using the reported space group ( $Cm$ ) and the atomic coordinates for  $YCa_4O(BO_3)_3$  [19] with the substitutional Lu atoms incorporated into the Y atomic sites.

According to the ionic radii of  $Y^{3+}$  and  $Lu^{3+}$  ions the lattice parameters  $a$ ,  $b$  and  $c$  decrease by substitution of the  $Y^{3+}$  ions with smaller  $Lu^{3+}$  ions in YCOB structure, confirming the effective incorporation of the  $Lu^{3+}$  ions. Only the angle  $\beta$  remains practically constant. The founded values are  $a = 0.80711(2)nm$ ,  $b = 1.60132(1)nm$ ,  $c = 0.35230(8)nm$  and  $\beta = 101.166(1)^\circ$ . The unit cell volume of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  also decreases by insertion of  $Lu^{3+}$  ions.

Fig. 4 shows the unpolarized transmission spectrum of a Y-cut  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  crystal sample with a thickness of 2mm. From the figure, we can observe that there is a wide transmission range in the UV-IR region. The crystal has high transmission from 215nm (50%) to 2400nm (80%), which is comparable with the transmission of BBO and LBO crystals. For nonlinear optical devices, the 215-2400nm transparency window is suitable for frequency conversion and other parametric processes.

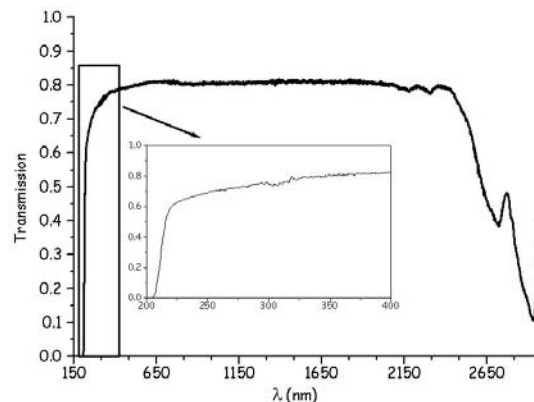


Fig. 4. Transmission spectrum of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  crystal.

#### 4. Conclusions

Single crystal of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  of good quality with no cracks and bubbles has been grown from the melt by the Czochralski method. To our knowledge, this is the first report on the growth and structural characterization of  $YCa_4O(BO_3)_3$  crystal type with substitutional  $Lu^{3+}$  ions incorporated into the  $Y^{3+}$  cationic sites.  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  crystal has a large transmission range suitable for generation of the specific wavelength laser emissions in UV-visible domain by NCPM SHG processes. Investigations of frequency conversion properties of  $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$  nonlinear optical crystal are now in progress.

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