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Growth and characterization of $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ single crystal for nonlinear optical applications

A. ACHIM*, L. GHEORGHE, S.GEORGESCU, F. VOICU
National Institute R&D for Laser, Plasma and Radiation Physics, Laboratory of Solid-State Quantum Electronics,
P.O. Box MG 36, 077125, Bucharest-Magurele, Romania

The nonlinear optical (NLO) crystal $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ (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 determined to be a = 0.80601(5) nm, b = 1.59946(8) nm, c = 0.35210(7) nm and β = 101.165(1)°. 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

NLO crystals play a very important role in the nonlinear optics field because they can perform frequency doubling, optical parametric oscillations (OPO) and optical parametric amplification (OPA). With the invention of new NLO crystals, the applications of nonlinear optics are also widespread. Now, NLO crystals are basic materials of the photoelectronic industry. For example, the properties of diode pumped solid-state lasers have been greatly improved and the output laser wavelengths have also made widespread by using NLO crystals such as KTP ($KTiOPO_4$), LBO (LiB_3O_5), and BBO (β-BaB_2O_4) [1-4]. So, the invention of new NLO crystals is a very interesting and important task in material research.

The requirements for the excellent NLO crystal includes high nonlinear coefficient, moderate birefringence for phase matching, high transparency for the wavelength of interest, non-hygroscopic nature, high laser damage threshold, good mechanical properties. Experimental results show that borate crystals are a very vast and useful family for NLO crystal research [5]. Borate crystals have relatively high resistance against laser-induced damage and high transparency in the visible and ultraviolet (UV) regions; NLO crystals with B-O bonds are often employed for high power UV and visible light generation. In recent 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) [5-11]. Among them, the monoclinic rare earth calcium oxoborate (RECOB) can be grown with large dimensions and high optical quality by the Czochralski method, and are efficient NLO crystals with a large transparent range, high damage threshold and non-hygroscopicity (other borate nonlinear crystals are grown by the flux method). The experiments show that RECOB crystals are efficient NLO crystals in second harmonic generation (SHG) and third harmonic generation (THG) [12-16].

Previously, it was found that the substitution of the trivalent RE cations with smaller radius cations lead to larger optical birefringence [17-18]. In YCOB crystal, the Y^{3+} ions can be partially substituted by smaller Sc^{3+} ions (r_Y = 0.9 Å, r_{Sc} = 0.745 Å [19]). As a consequence, by changing the compositional parameter x of $Y_{1-x}Sc_xCa_4O(BO_3)_3$ crystals, their optical birefringence can be controlled in order to achieve SHG in noncritical phase matching (NCPM) conditions of the specific near infrared laser emission wavelengths, shorter than phase matching cutoff wavelengths of YCOB crystal (724 nm along Y axis and 832 nm along Z axis at room temperature [20]).

For biaxial nonlinear crystals like RECOB, NCPM is the phase matching along one principal axis of the crystal. Compared to critical phase matching, NCPM has two major advantages: the larger angular acceptance, and the absence of the walk-off between fundamental and harmonics light. Thus, large angular acceptance bandwidths can be obtained and longer crystals can be used to increase the frequency conversion efficiency.

$ScCa_4O(BO_3)_3$ compound doesn't have congruent melting and single crystals with this composition cannot be grow from the melt. Therefore in the YCOB structure Sc^{3+} ions can only partially substitute Y^{3+} ions and according to the ionic radii of Y^{3+} and Sc^{3+} ions, the optical birefringence of $Y_{1-x}Sc_xCa_4O(BO_3)_3$ 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 [21] showed that the solubility limit of Sc^{3+} ions in YCOB crystal is close to 20 at% (x close to 0.2).

In this paper, the growth from the melt by the Czochralski method of $Y_{1-x}Sc_xCa_4O(BO_3)_3$ crystal with a compositional parameter x = 0.3 extended over the solubility limit of Sc^{3+} ions, and some structural properties of the grown crystal are reported.

2. Experimental

To synthesize the $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ compound, the solid state reaction technique was used. A single crystal of $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ (starting composition) was grown using the conventional radio frequency (RF) heating Czochralski method from iridium crucible under air atmosphere. Further growth details will be described below. The range of optical transparency was determined in a Y-cut $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ sample with a thickness of 2 mm. The transmission spectrum was measured using a Cary 5 spectrophotometer at room temperature in the range of 200-3000 nm. X-ray powder diffraction (XRPD) experiments were performed with a Bruker AXS D8 ADVANCE X-ray diffractometer (Cu $K_{\alpha 1}$ = 1.5406Å). The measurements were carried out at room temperature between 10° and 70° in 2θ using a flat rotating sample holder. The angular resolution of the apparatus was better than 0.014°. The XRPD data were analyzed with the Rietveled profile refinement method using TOPAS V2.1 software.

3. Results and discussion

The $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ starting material was prepared by solid state reaction of 4N Y_2O_3, $CaCO_3$, B_2O_3, and Sc_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°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°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°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 $Y_{0.7}Sc_{0.4}Ca_4O(BO_3)_3$. It contains a major phase isostructural with monoclinic YCOB and two minor extra phases of $Ca_3B_2O_6$ [22] and CaO [23]. The peaks characteristics to $Ca_3B_2O_6$ and CaO phases are marked with full rhombus and circle, respectively. The presence of the minor parasitic phases confirms that the solubility limit of Sc^{3+} ions in YCOB structure is smaller than 30 at%.

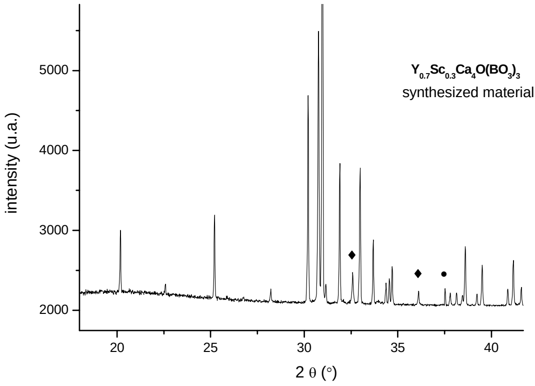
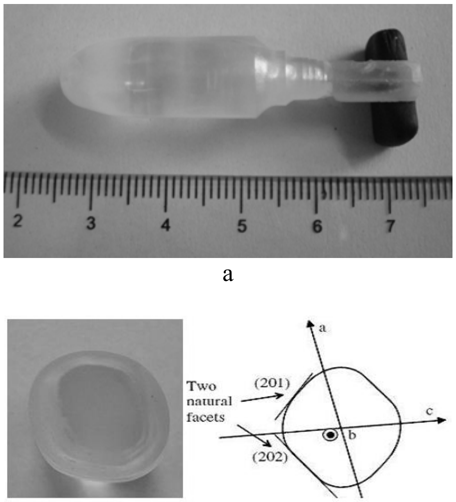


Fig. 1. Room temperature XRD pattern of $Y_{07.}Lu_{0.3}Ca_4O(BO_3)_3$ synthesized material. The peaks marked with rhombus and circle belong to $Ca_3B_2O_6$ and CaO parasitic phases, respectively.

$Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ 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 °C higher than the melting point was required. Then, the temperature was reduced to the growth temperature. The typical pulling rate was 0.6 - 0.8mm/h and the rotation rate was 30 - 40 rpm. In the growth process rectangular <010> oriented single crystal sample of pure YCOB with dimensions of 3×3×15 mm^3 was used as seed. The growth temperature, determined by an infrared pyrometer, was about 1510 ± 10 °C. The temperature gradient just above the melt was 30 - 40°C/cm. As much as 25% of the melt was converted into a single crystal in approximately three days. The crystal was cooled to room temperature at a rate of 40 °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 °C at the rate of 50 °C/h, held at that temperature for 36h and finally cooled to room temperature at the rate of 20 °C/h. Fig. 2a shows the obtained $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal. The grown crystal is highly transparent, colorless, non-hygroscopic and chemically stable. Its dimensions are about 15 mm in diameter and 30 mm in length. The crystal has good mechanical properties, which make it easier for cutting and polishing. The *b-axis* grown crystal shows two sets of natural facets parallel to the *b-axis*, which provides critical morphology information for crystal orientation (Fig. 2b).

X–ray powder diffraction pattern of a sample exerted from $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal is shown in Fig. 3. The parasitic phases $Ca_3B_2O_6$ and CaO exist only in the synthesized material and are no observed in the diffraction pattern of the grown crystal.



a

b

Fig. 2. (a) The as-grown $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal, (b) the cross section of the b-axis growth $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal.

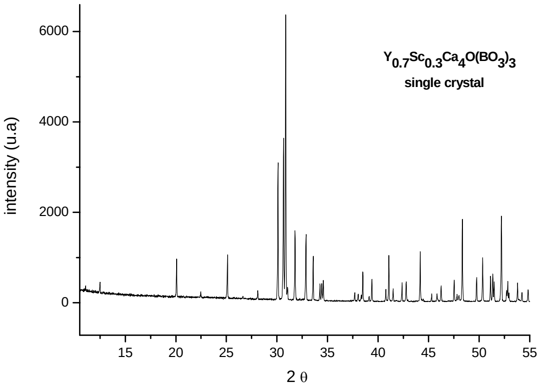


Fig. 3. Room temperature X-ray powder diffraction pattern of $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ single crystal.

$RECa_4O(BO_3)_3$ (RE= Gd^{3+}, Y^{3+}, La^{3+}) compounds have a non centro-symmetric monoclinic structure, with space group *Cm* [24, 25]. Their structure contains a RE site of *Cs* 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 β = 101.167(4)° [26]. $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal structure was analyzed by Rietveld method and the structure refinement was initiated using the reported space group (*Cm*) and the atomic coordinates for $YCa_4O(BO_3)_3$ [26] with the substitutional Sc atoms incorporated into the Y atomic sites. According to the ionic radii of Y^{3+} and Sc^{3+} ions the lattice parameters a, b and c decrease by substitution of the Y^{3+} ions with smaller Sc^{3+} ions in YCOB structure, confirming the effective incorporation of the Sc^{3+} ions. Only the angle β remains practically constant. The founded values are a = 0.80601(5) nm, b = 1.59946(8) nm, c = 0.35210(7) nm and β = 101.165(1)°. The unit cell volume of $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal also decrease by insertion of Sc^{3+} ions.

Fig. 4 shows the unpolarized transmission spectrum of a Y-cut $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal sample with a thickness of 2 mm. From the figure, we can observe that there is a wide transmission range in the UV-IR region. The crystal has high transmission from 215 nm (50%) to 2400 nm (80%), which is comparable with the transmission of BBO and LBO crystals. For nonlinear optical devices, the 215-2400 nm transparency window is suitable for frequency conversion and other parametric processes.

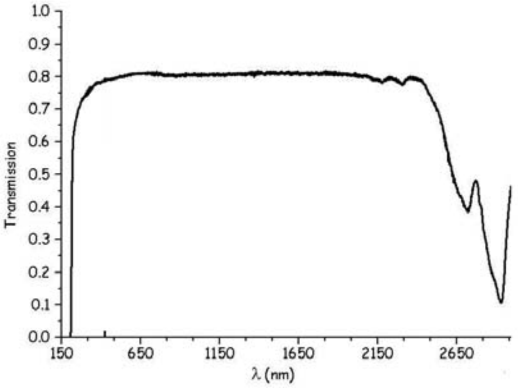


Fig. 4. Transmission spectrum of $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal.

4. Conclusions

Single crystal of $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ 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 $Y_{1-x}Sc_xCa_4O(BO_3)_3$ crystals type. $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ 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 $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ nonlinear optical crystal are now in progress.

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[*] Corresponding author: alexandru.achim@inflpr.ro