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EFFICIENT SECOND HARMONIC GENERATION OF BLUE-VIOLET LIGHT IN NONCRITICAL TYPE-I PHASE MATCHING

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Abstract
Single crystals of $Y_{1-x}R_xCa_4O(BO_3)_3$ (R = Sc or Lu) of good quality have been grown from the melt by the Czochralski pulling method. The chemical compositions of the grown crystals were determined. Type-I noncritical phase matching (NCPM) wavelengths for second harmonic generation (SHG) in $Y_{1-x}R_xCa_4O(BO_3)_3$ grown crystals were also determined.

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. At this time, the availability of laser frequencies in the visible and UV is limited by laser materials and pump sources. Frequency conversion of solid-state lasers operating in the near infrared range by nonlinear optical (NLO) crystals has become the most available method to obtain shorter wavelength lasers with high beam stability, low cost and compactness. Thus, the reliance on nonlinear methods of frequency generation demonstrates the need for new nonlinear harmonic crystals with the ability to frequency convert a wide variety of laser wavelengths.

$YCa_4O(BO_3)_3$ (YCOB) has attracted great attention as a new NLO crystal for frequency generation since its earliest development [1]. YCOB is a congruent melting nonlinear material allowing the growth of large dimensions and high optical quality crystals to be used as frequency converters in solid-state laser systems [1-4]. Our previous researches [5-7] showed that in YCOB crystal, the Y^{3+} ions can be partially substituted by smaller radius ions

Sc^{3+} or Lu^{3+} (r_{Lu} = 0.861Å, r_{Sc} = 0.745Å, r_Y = 0.9Å [8]) in order to tune the chemical composition of the crystal. By changing the compositional parameter x of $Y_{1-x}R_xCa_4O(BO_3)_3$ (R = Lu, Sc) crystals, their optical birefringence can be controlled in order to perform noncritical phase matching (NCPM) second harmonic generation (SHG) of specific near infrared laser emission wavelengths shorter than phase matching cut-off wavelength of YCOB crystal (724 nm along Y axis and 832 nm along Z axis at room temperature [9]).

For biaxial crystals like YCOB family compounds, NCPM is the phase matching along one principal axis of the crystal, and for frequency conversion applications, NCPM is advantageous because of its large angular acceptance and because it eliminates walk-off between fundamental and harmonic radiations which leads to the highest efficiency.

Since NCPM is determined by the optical birefringence and is accomplished to an unique wavelength for each NLO process, the objective of this study is to evaluate the potential of $Y_{1-x}R_xCa_4O(BO_3)_3$ crystals as frequency converters for the laser emissions around 800 nm (AlGaAs laser diodes and the strongest emission of Ti: Sapphire laser) and about 700 nm (red laser diodes) in order to obtain visible or near-UV laser radiations by type-I NCPM SHG processes at room temperature. In this aim, crystal growth and NCPM frequency conversion properties of $Y_{1-x}R_xCa_4O(BO_3)_3$ new nonlinear crystals are reported in this work.

2. Method and samples

$Y_{1-x}R_xCa_4O(BO_3)_3$ compounds were prepared by classical solid state reaction. Chemicals of Y_2O_3, $CaCO_3$, B_2O_3, Lu_2O_3, and Sc_2O_3 of 99.99% purity were used as starting materials. The oxide mixtures, weighing in stoichiometric ratio, were ground, mixed and pressed into tablets, then heated at 900°C for 15h to decompose $CaCO_3$ completely. They were then ground, mixed and pressed again, and then heated at 1350°C for 36h. Single crystals of $Y_{1-x}Lu_xCa_4O(BO_3)_3$ and $Y_{1-x}Sc_xCa_4O(BO_3)_3$, with x = 0.2, 0.3 and 0.4 respectively x = 0.2 and 0.3 in the synthesized materials, were grown using the conventional radio frequency (RF) heating Czochralski method from iridium crucibles under nitrogen atmosphere. Determination of lattice parameters of the grown crystals were performed using a X'Pert PANalytical diffractometer with Cu Kα radiation (λ = 1.5406 Å). Chemical compositions of the grown crystals were determined by means of inductively coupled plasma (ICP) atomic emission spectroscopy. For experimental determination of the doubled frequencies, an optical parametric oscillator (OPO) pumped at 355nm (triple harmonic of a 10Hz, 7ns Q-switched YAG: Nd laser) was used as pump source.

3. Results and Discussions

$Y_{1-x}R_xCa_4O(BO_3)_3$ single crystals with starting melt compositional parameter x = 0.2, 0.3, 0.4 and x = 0.2, 0.3 for $Y_{1-x}Lu_xCa_4O(BO_3)_3$ and $Y_{1-x}Sc_xCa_4O(BO_3)_3$ compounds respectively, were grown by the conventional Czochralski technique. The growths were performed by pulling from melts contained in iridium crucibles 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 of 40 - 50°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 processes rectangular <010> oriented single crystal samples of pure YCOB were used as seed. The growth temperatures were about 1510 ± 10°C. The crystals were cooled to room temperature at a rate of 40°C/h. In order to eliminate the residual stress inside the crystals, they were annealed further in air atmosphere. The crystals were heated to 1350°C at the rate of 50°C/h, held at this temperature for 36h and finally cooled to room temperature at the rate of 20°C/h. The obtained crystals are colorless, highly transparent, nonhygroscopic, chemically stable and they have good mechanical properties, which make them easier for cutting and polishing. Typically they have ~ 15mm in diameter and about 30mm in length (Fig. 1).

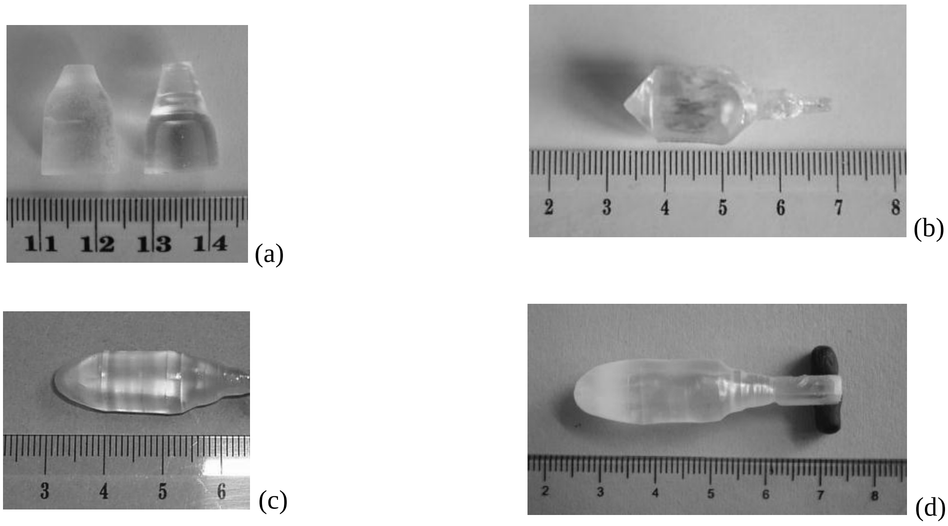

Fig. 1. $Y_{1-x}R_xCa_4O(BO_3)_3$ as-grown crystals: (a) $Y_{0.8}Lu_{0.2}Ca_4O(BO_3)_3$ and $Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$ crystals, (b) $Y_{0.7}Lu_{0.3}Ca_4O(BO_3)_3$ crystal, (c) $Y_{0.8}Sc_{0.2}Ca_4O(BO_3)_3$, (d) $Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$ crystal.

The chemical compositions of the grown crystals were determined by microprobe analysis, and the obtained results are given in Table 1. The segregation coefficients (k) of the

Lu and Sc ions in $Y_{1-x}R_xCa_4O(BO_3)_3$ grown crystals were also calculated. The values were found to be 0.97 ± 0.01 and 0.35 ± 0.01, respectively.

Table 1. Chemical compositions of $Y_{1-x}R_xCa_4O(BO_3)_3$ grown crystals.

Starting composition	**Formulas deduced from compositional analyses**
$Y_{0.8}Lu_{0.2}Ca_4O(BO_3)_3$	$Y_{0.81}Lu_{0.19}Ca_4O(BO_3)_3$
$Y_{0.7}Lu_{0.3}Ca_4O(BO_3)_3$	$Y_{0.71}Lu_{0.29}Ca_4O(BO_3)_3$
$Y_{0.6}Lu_{0.4}Ca_4O(BO_3)_3$	$Y_{0.61}Lu_{0.39}Ca_4O(BO_3)_3$
$Y_{0.8}Sc_{0.2}Ca_4O(BO_3)_3$	$Y_{0.93}Sc_{0.07}Ca_4O(BO_3)_3$
$Y_{0.7}Sc_{0.3}Ca_4O(BO_3)_3$	$Y_{0.89}Sc_{0.11}Ca_4O(BO_3)_3$

Type-I NCPM SHG experiments on $Y_{1-x}R_xCa_4O(BO_3)_3$ grown crystals were performed at room temperature. From each crystal, one cube of 6 mm x 6 mm x 6 mm oriented in the cristallophysic axes (X, Y, Z), was cut and polished, and used for experimental determination of the doubled frequencies along Y and Z cristallophysic axes (NCPM conditions). By using an OPO tunable from 420 to 2000 nm as laser source, the NCPM wavelengths were determined by tuning the OPO wavelength around 800 nm (for NCMP along Z axis) and 700 nm (in the case of NCMP along Y axis), in order to find the wavelengths yielding the maximum harmonic conversion efficiency (maximum blue or near-UV output power). The obtained values are summarized in Table 2. For a better comparison, the NCPM wavelengths characteristics of YCOB crystal [9] are also mentioned.

Table 2. Type-I phase matching wavelengths for NCPM SHG in $Y_{1-x}R_xCa_4O(BO_3)_3$ crystals.

Crystal	**Along Y axis (nm)**	**Along Z axis (nm)**
$YCa_4O(BO_3)_3$	724	832
$Y_{0.81}Lu_{0.19}Ca_4O(BO_3)_3$	708.7	812.2
$Y_{0.71}Lu_{0.29}Ca_4O(BO_3)_3$	700.6	801.8
$Y_{0.61}Lu_{0.39}Ca_4O(BO_3)_3$	692.6	791.4
$Y_{0.93}Sc_{0.07}Ca_4O(BO_3)_3$	710.6	813.9
$Y_{0.89}Sc_{0.11}Ca_4O(BO_3)_3$	702.9	803.6

These results demonstrate that in $Y_{1-x}R_xCa_4O(BO_3)_3$ crystals, NCPM wavelengths can be adjusted continuously by varying the compositional parameter x, and SHG can be achieved at room temperature for virtually any wavelength between the NCPM wavelengths of pure YCOB (724 nm along Y axis and 832 nm along Z axis) and at least 692.6 nm along Y axis and 791.4 nm along Z axis, respectively.

Conclusions

Five new nonlinear crystals of $Y_{1-x}Lu_xCa_4O(BO_3)_3$ and $Y_{1-x}Sc_xCa_4O(BO_3)_3$, with x = 0.19, 0.29, 0.39 and x = 0.07, 0.11, respectively, of good quality with no cracks and bubbles have been grown by Czochralski method, and their NCPM properties were investigated. We have demonstrated that efficient room temperature type-I NCMP SHG of any wavelength from 692.6 - 724 nm and 791.4 - 832 nm spectral ranges, can be achieved in $Y_{1-x}R_xCa_4O(BO_3)_3$ crystals by tuning the composition. This result has very important implications for many of today's tunable solid-state lasers (Ti: Sapphire, Cr: LiSAF, Cr: LiCAF, Alexandrite) and laser diodes (AlGaAs, AlGaInP) with emission in these spectral ranges, in order to obtain specific blue and/or near-UV laser emisions.

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