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Second-harmonic generation of 400nm blue-violet light in $Gd_{1-x}R_xCa_4O(BO_3)_3$ (R = Lu, Sc) crystals through noncritical phase-matching

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The optical birefringence of $Gd_{1-x}R_xCa_4O(BO_3)_3$ (R = Lu or Sc) crystals can be controlled by changing the compositional parameter x. Two nonlinear crystals of $Gd_{0.884}Lu_{0.116}Ca_4O(BO_3)_3$ and $Gd_{0.952}Sc_{0.048}Ca_4O(BO_3)_3$ with large size and good quality have been grown by Czochralski method. According to our assumptions, the obtained results demonstrate that both crystals convert the near-infrared radiation of 800nm into blue-violet light (400nm) by type-I noncritical phase-matching (NCPM) second-harmonic generation (SHG) processes along Y axis.

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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. 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.

$GdCa_4O(BO_3)_3$ (GdCOB) has attracted great attention as a new biaxial NLO crystal for frequency generation since its earliest development. GdCOB crystal has a non centro-symmetric monoclinic structure with the space group Cm and combines some of the more attractive mechanical and optical properties in one crystal in comparison with the most commonly used NLO crystals (KDP, KTP, BBO, and LBO) [1]. GdCOB exhibits large nonlinear coefficients, a broad transmission band, a high damage threshold, and non-hygroscopic properties. In addition, the crystal melts congruently, so that large single crystals can be produced by the Czochralski melt-pulling technique [2]. Our previous researches showed that in GdCOB crystal, the Gd^{3+} cations can be partially substituted by smaller radius ions Sc^{3+} or Lu^{3+} in order to tune the chemical composition of the crystal [3 - 5]. It was demonstrated that by changing the compositional parameter x of $Gd_{1-x}R_xCa_4O(BO_3)_3$ (R = Lu, Sc) crystals, their optical birefringence can be controlled in order to achieve second-harmonic generation (SHG) in noncritical phase-matching (NCPM) conditions of specific near infrared laser emission wavelengths shorter than phase-matching cutoff wavelength of GdCOB crystal (824nm along Y axis and 963nm along Z axis at room temperature [2]). According to the ionic radii of R^{3+} ions ($r_{Lu} = 0.861$Å, $r_{Sc} = 0.75$Å), the effect on magnitude of optical birefringence is more stronger in case of substitution with Sc^{3+} ions and the optical birefringence increases with increasing of compositional parameter x.

For frequency conversion application, it is important to use NCPM along the principal axes due to the large angular acceptance and elimination of the walk-off between fundamental and harmonics lights, leading to the highest efficiency.

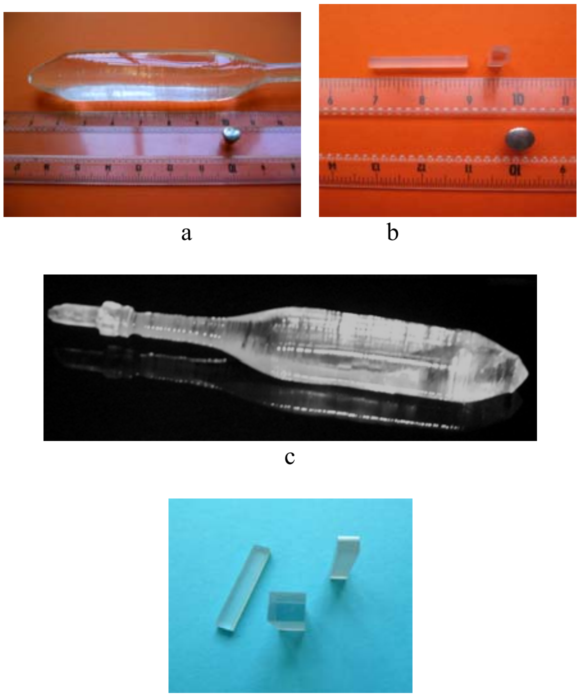
Since NCPM is achieved at a unique wavelength for each NLO process and determined by the birefringence, in the aim to obtain blue-violet (~ 400nm) laser radiation by type I NCPM SHG at room temperature of ~ 800nm AlGaAs laser diodes and Ti: Sapphire laser emission (the strongest emission of a Ti: Sapphire laser), crystal growth and NCPM frequency conversion properties of two new nonlinear crystals $Gd_{1-x}R_xCa_4O(BO_3)_3$ (R = Lu, Sc) are reported in this work.

2. Crystal growth

Based on our previous results [3,4], the calculation regarding the relationship between the compositional parameter x and the NCPM wavelengths along Y axis, revealed that is possible to obtain room temperature type I NCPM SHG at of an 800nm wavelength using GdCOB crystals doped with small amounts of Sc or Lu ions. In this order, two single crystals of $Gd_{0.882}Lu_{0.118}Ca_4O(BO_3)_3$ and

$Gd_{0.872}Sc_{0.128}Ca_4O(BO_3)_3$ (for starting melts) were grown by using the conventional Czochralski method with iridium crucibles and inductive radio frequency (RF) heating. The crystals were grown under a nitrogen atmosphere, and the diameters of the crystals were controlled by a computer through the feedback of weight measurement. The typical pulling rate was 0.6 - 0.8 mm/h, and the rotation rate was 30–45 rpm. In all growth processes <010> oriented single crystal samples of pure GdCOB were used as seeds. As much as 25% of the melt was converted into a single crystal in approximately one week. The growth temperatures were about 1480±10°C. The crystals were cooled to room temperature at a rate of 0.5K/min. The grown crystals are colorless, highly transparent, nonhygroscopic, and chemically stable. The crystals have good mechanical properties, which make them easier for cutting and polishing. Figure 1 shows the as-grown crystals and examples of polished crystals cut from the grown crystals. Typically they are 25mm in diameter and 120mm long. We have examined the compositional uniformity along the growth direction by means of inductively coupled plasma (ICP) atomic emission spectroscopy, on the samples exerted from the beginning, middle, and end of each grown crystal. It was found that the crystals had a high uniformity of composition because they were pulled from a large amount of the melt charge. The chemical compositions of grown crystals were determined and they were found to be $Gd_{0.884}Lu_{0.116}Ca_4O(BO_3)_3$ and $Gd_{0.952}Sc_{0.048}Ca_4O(BO_3)_3$, respectively. The segregation coefficients (*k*) of the Lu and Sc ions in the GdCOB grown crystals were also calculated. The values are found to be 0.99 and 0.38, respectively.

From the X-ray powder diffraction patterns of grown single crystals, the unit cell parameters for both crystals were also calculated. The X-ray spectra were performed using a X'Pert PANalytical diffractometer with Cu Kα radiation (λ = 1.5406 Å). The lattice parameters of the grown crystals are given in Table 1.



a b

c

d

Fig. 1. $Gd_{1-x}R_xCa_4O(BO_3)_3$ as-grown crystals: (a) $Gd_{0.884}Lu_{0.116}Ca_4O(BO_3)_3$ crystal, (b) Y-cut polished $Gd_{0.884}Lu_{0.116}Ca_4O(BO_3)_3$ crystal samples, (c) $Gd_{0.952}Sc_{0.048}Ca_4O(BO_3)_3$ crystal, (d) Y - cut polished $Gd_{0.952}Sc_{0.048}Ca_4O(BO_3)_3$ crystal samples.

Table 1. Lattice parameters of $Gd_{1-x}R_xCa_4O(BO_3)_3$ grown crystals.

Crystal	Lattice parameters (± 0.001Å)
$Gd_{0.884}Lu_{0.116}Ca_4O(BO_3)_3$	a = 8.092, b = 16.015, c = 3.553, β = 101.24°
$Gd_{0.952}Sc_{0.048}Ca_4O(BO_3)_3$	a = 8.086, b = 15.999, c = 3.544, β = 101.25°

3. Nonlinear properties

NCPM SHG experiments on $Gd_{0.884}Lu_{0.116}Ca_4O(BO_3)_3$ and $Gd_{0.952}Sc_{0.048}Ca_4O(BO_3)_3$ crystals were performed at room temperature. All crystals samples were cut in Y-direction (which was the direction for NCPM) with a typically length of 20mm, and their faces were polished and uncoated. By using an optical parametric oscillator (OPO) tunable from 420 to 2000nm as laser source, the NCPM wavelengths were determined by tuning the OPO wavelength around 800nm to find the wavelength yielding the maximum harmonic conversion efficiency (maximum blue-violet output power).

The input light was linearly polarized and it was irradiated along Y axis of the crystals samples. According to our assumptions, the obtained results demonstrate that both crystals convert the near-infrared radiation of 800nm into blue-violet light (400nm) through type-I noncritical phase-matching at room temperature. Figures 2 and 3 show the dependence of the NCPM wavelength on the compositional parameter x for type I SHG at room temperature in Y-cut $Gd_{1-x}Lu_xCa_4O(BO_3)_3$ and $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ crystals, respectively. In both figures, the left ends of the curves (the open circles) represent the situation of pure GdCOB.

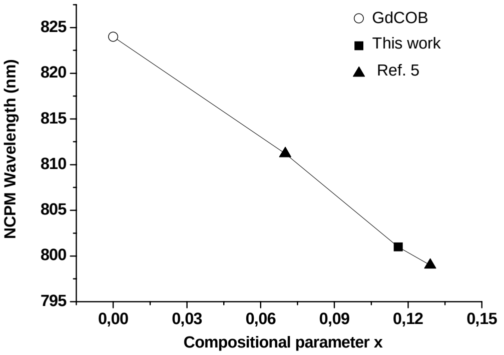


Fig. 2. Type-I NCPM wavelength for SHG in Y-cut Gd$_{1-x}$Lu$_x$Ca$_4$O(BO$_3$)$_3$ *versus compositional parameter x at room temperature.*

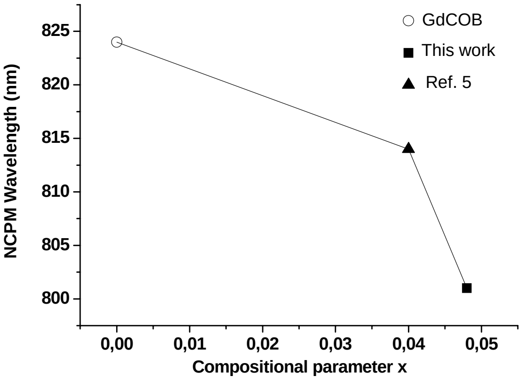


Fig. 3. Type-I NCPM wavelength for SHG in Y-cut Gd$_{1-x}$Sc$_x$Ca$_4$O(BO$_3$)$_3$ *versus compositional parameter x at room temperature.*

These two figures prove that NCPM wavelengths can be adjusted continuously by varying the compositional parameter x. In both crystals, SHG can be achieved at room temperature for virtually any wavelength between the NCPM wavelength of the pure GdCOB (824nm) and at least 800nm. No significant change in conversion efficiency at the NCPM wavelength was observed for the different compositions.

Wang et al. [6] have measured the NCPM for frequency doubling in different Gd$_{1-x}$Y$_x$COB crystals. It has been found that type I SHG in NCPM conditions (along the Y axis) of the 800 nm wavelength can be achieved in the crystals with a compositional parameter of x = 0.24 (Gd$_{0.76}$Y$_{0.24}$COB). In addition, Klimm et al. [7] have demonstrated that GdCOB-YCOB mixed crystals can be grown with low segregations. Our results revealed that we can obtain type-I NCPM SHG of an 800 nm wavelength (along the Y axis) using smaller amounts of Sc or Lu (x = 0.048 or 0.116, respectively) dopants in GdCOB crystals. Therefore we can affirm that the partial substitution of Gd ions with Sc or Lu ions in the GdCOB crystal is a more efficient solution to obtain 400nn blue-violet light through the NCPM SHG processes along Y axis.

4. Conclusion

Two nonlinear crystals of Gd$_{0.884}$Lu$_{0.116}$Ca$_4$O(BO$_3$)$_3$ and Gd$_{0.952}$Sc$_{0.048}$Ca$_4$O(BO$_3$)$_3$ with large size and good quality have been grown by Czochralski method and their NCPM properties were studied. We have demonstrated that efficient NCMP SHG can be achieved at room temperature for any wavelength between 824nm and at least 800nm using type-I phase-matching by tuning the composition of Gd$_{1-x}$R$_x$Ca$_4$O(BO$_3$)$_3$ crystals. In particular, we show that Gd$_{0.884}$Lu$_{0.116}$Ca$_4$O(BO$_3$)$_3$ and Gd$_{0.952}$Sc$_{0.048}$Ca$_4$O(BO$_3$)$_3$ crystals convert the near-infrared radiation of 800nm into blue-violet light (400nm) in type-I NCMP conditions along Y axis. This result has important implications for many of today's tunable solid-state lasers (Ti: Sapphire - with the strongest emission at ~ 800nm, Cr: LiSAF, Cr: LICAF, Alexandrite) and for AlGaAs laser diodes with emission at ~ 800nm. Our research shows that Gd$_{1-x}$R$_x$Ca$_4$O(BO$_3$)$_3$ crystals are suitable to design specific wavelength converters in noncritical configuration.

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