Development of New NLO Borate Crystal $Gd_xY_{1-x}COB$

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Abstract

The interest in the use of borate crystals in ultraviolet (UV) nonlinear optics (NLO) has increased because all solid-state UV lasers obtained with NLO are in highly demand. Much effort has been spent on developing borates series, such as β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), and $CsLiB_6O_{10}$ (CLBO) in this decade. Recently another new borate crystals, $YCa_4O(BO_3)_3$ (YCOB) and $Gd_xY_{1-x}Ca_4O(BO_3)_3$ ($Gd_xY_{1-x}COB$) have been developed by the present authors. Here, the growth and NLO properties of YCOB and $Gd_xY_{1-x}COB$ crystal are reported and their properties are discussed in relation to those of other nonlinear optical crystals, such as LBO.

1. Introduction

In 1996, Aka *et al.* reported that $GdCa_4O(BO_3)_3$ (GdCOB) is an excellent candidate for practical NLO crystal for doubling the Nd:YAG laser output, because of ease in growth, and its stable chemical and mechanical properties.[1] The Sellmeier equations, however, predict the limit of phase matching (PM) wavelength to be 840 nm due to the small birefringnce of 0.033 at 1064 nm. Further efforts are necessary for developing the GdCOB families with larger birefringence in order to generate shorter wavelength.

In 1997, we have found that replacement of Gd by Y can lead to an increase in the optical birefringence from 0.033 to 0.041.[2] Therefore, the limits of PM wavelength can be shortened to 720 nm. YCOB can also generate the third harmonic of Nd:YAG fundamental, whereas not by GdCOB. Recently, we have succeeded to develop $Gd_xY_{1-x}Ca_4O(BO_3)_3$ ($Gd_xY_{1-x}COB$) crystal in order to control optical birefringence. This is important to achieve noncritical phase matching (NCPM) condition which can lead a significant improvement of frequency conversion efficiency. Here, the crystal growth and the characterization of $Gd_xY_{1-x}COB$ are discussed in details.

2. Crystal Growth

The $Gd_xY_{1-x}COB$ charge was prepared by solid state reaction with 4N Gd_2O_3, Y_2O_3, $CaCO_3$ and $3N^+$ B_2O_3 in various proportions ($0<x<1$). The mixture was heated at 1000 °C for 12 h, cooled and ground, and then heated again at 1200 °C for 24 h. Single crystals of $Gd_xY_{1-x}COB$ have been grown by the conventional Czochralski method. An atmosphere was provided with a continuous Ar flow. The $Gd_xY_{1-x}COB$ charge was melted in an iridium crucible 50 mm in diameter and 50 mm in height. The <010> oriented seed crystal was brought contact with the melt surface. The growth temperature determined by an infrared pyrometer to be about 1500 °C. The pulling rate was 3.0 mm/h and seed rotation rate was 30 rpm. The temperature gradient just above the melte was 30-40 °C/cm. The $Gd_xY_{1-x}COB$ crystals obtained were colorless without cracks and bubbles. Figure 1 shows the typical $Gd_xY_{1-x}COB$ crystal (x=0.23) with size of 24 mm in diameter and 60 mm in length.

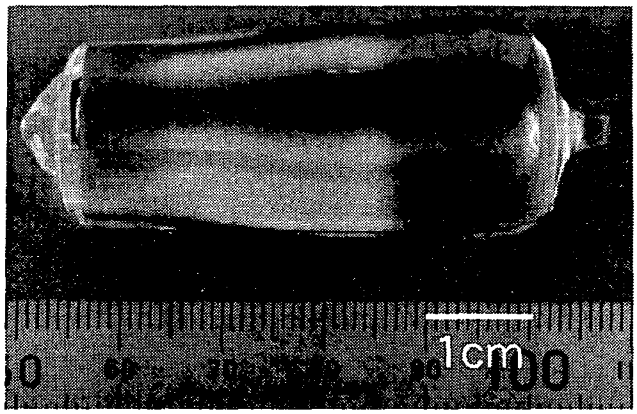

Figure 1. Typical $Gd_xY_{1-x}COB$ (x=0.23) crystal grown by the Czochralski method.

We have examined the compositional uniformity along the growth direction of $Gd_xY_{1-x}COB$ crystals, sampling at the position of 5, 20 and 35 mm from the seed crystal, by means inductively coupled plasma (ICP) atomic emission spectroscopy. The two samples of $Gd_xY_{1-x}COB$ (x = 0.13 and 0.48) single crystals with approximately 40 mm in lengths and 18 mm in diameters were used. It was found that the crystals showed high uniformity of composition with 13% and 48% of Gd, respectively, along the growth direction. We also measured the ratio of lattice constant (a/c, a/b) in $Gd_xY_{1-x}COB$ (x = 0, 0.48, 1) crystals by means of four-circle X-ray difractometer. The ratio of lattice constant a/c in $Gd_xY_{1-x}COB$ increased as compositional parameter x decreased. On the other hand, the a/b ratio decreased as x decreased. These results indicate that the birefringence of $Gd_xY_{1-x}COB$ can be controlled continuously by changing the compositional parameter x.

3. Nonlinear optical properties of $Gd_xY_{1-x}COB$ crystal

For frequency conversion applications, it is important to use NCPM along the principal axes due to the large angular acceptance and elimination of walk-off between fundamental and harmonics lights, leading to the higher efficiency. $Gd_xY_{1-x}COB$ achieves the phase-matching for third harmonic generation (THG) of a Nd:YAG laser. The phase-matching angles for THG in YCOB were found to be $(\theta, \phi) = (90°, 73.2°)$ and $(58.7°, 90°)$ in the xy and yz planes. We examined the phase matching angles in the xy and yz planes for various $Gd_xY_{1-x}COB$ compounds. Figure 2 shows the phase matching angles of θ and ϕ for THG as a function of a compositional parameter x in $Gd_xY_{1-x}COB$. We have found that noncritically phase-matched THG can be achieved in $Gd_{0.24}Y_{0.76}COB$ crystal. Table 1 shows values of effective nonlinear coefficient (d_{eff}), angular and temperature bandwidths and walk-off angle for frequency conversion process in the $Gd_{0.24}Y_{0.76}COB$, YCOB and LBO for 355-nm generations. $Gd_{0.24}Y_{0.76}COB$ possesses zero walk-off angle, and larger angular and temperature bandwidths compared to LBO. $Gd_{0.24}Y_{0.76}COB$ exhibits the better NLO properties compared to LBO.

4. Conclusion

New NLO crystals YCOB and $Gd_xY_{1-x}COB$ have been reported. These crystals showed the ease in growth without cracks and bubbles by the Czochralski method. $Gd_xY_{1-x}COB$ crystals had an uniformity of crystal composition along with growth direction so these crystals confirmed a substitutional solid solution of $Gd_xY_{1-x}COB$. We have succeeded to generate noncritical phase-matched THG of Nd:YAG laser (1064 nm) light in $Gd_{0.24}Y_{0.76}COB$.

Acknowledgments

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References

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2) M. Iwai, T. Kobayashi, H. Furuya, Y. Mori, and T. Sasaki, Jpn. J. Appl. Phys. 36 276-279 (1997).

Table 1. NLO properties of $Gd_{0.24}Y_{0.76}COB$, YCOB and LBO for 355-nm generation

	d_{eff} (pm/V)	Angular acceptance (mrad•cm)	Temperature acceptance (°C•cm)	Walk-off angle (mrad)
LBO	0.50	5.0	3.7	8.5
YCOB	0.52	3.5	10	9.3
$Gd_{0.24}Y_{0.76}COB$	0.54	9.0	10	0

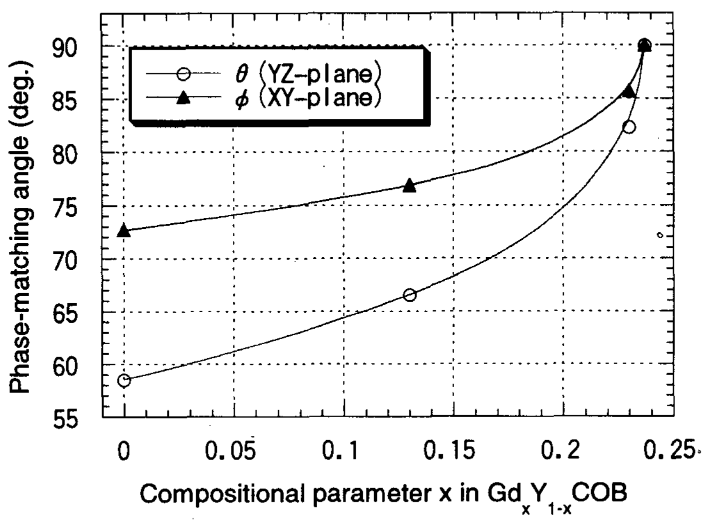

Figure 2. Phase-matching angles for THG in $Gd_xY_{1-x}COB$ in the xy and yz planes of $Gd_xY_{1-x}COB$ as a function of a compositional parameter x.