JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 1, February 2006, p. 91 - 94

Growth and optical properties of $GdCa_4O(BO_3)_3$:RE crystals (RE=Sc^{3+} or Lu^{3+}) as new nonlinear materials

L. GHEORGHE, V. LUPEI, A. ACHIM*, G. AKA[a], C. VARONA[a]
National Institute R&D for Lasers, Plasma and Radiation Physics, Bucharest R-012577
[a]*Laboratoire de Chimie Appliquée de l'Etat Solide, ENSCP, Paris, France*

The optical birefringence of $Gd_xRE_xCa_4O(BO_3)_3$ (RE=Sc^{3+} or Lu^{3+}) crystals can be controlled by changing the compositional parameter x. Single crystals of $Gd_{1-x}RE_xCa_4O(BO_3)_3$ were grown by Czochralski method. The limits of solubility of RE ions in the GdCOB crystals were determined. The refractive indices of crystals were measured. The non-critical phase-matching (NCPM) condition for second harmonic generation (SHG) in the range 790-940 nm was obtained.

(Received October 14, 2005; accepted January 26, 2006)

Keywords: $GdCa_4O(BO_3)_3$:RE crystal, Nonlinear material, Optical properties, Second harmonic generation

1. Introduction

Highly efficient, compact, visible laser sources are desirable in various applications. In particular, diode-pumped solid state lasers operating in the blue range are of interest for various applications including high-density data storage, photo-therapy, medical diagnosis, etc. The current approach to achieve efficient blue emission is by second harmonic generation (SHG) in nonlinear optical crystals of diode-pumped solid state laser ~0.9 μm emission, in non-critical phase matching (NCPM) conditions. The advantage of NCPM is the lack of beam walk-off so that the beam pattern is not distorted and the crystal can be made longer in order to improve efficiency. In addition, the angular acceptance, as well as temperature acceptance is larger during the SHG process.

The rare-earth calcium oxoborate crystals $RCa_4O(BO_3)_3$ - RCOB (R = La, Gd, Y) are congruent melting nonlinear materials allowing the growth of large dimension crystals to be used as frequency converter in solid state laser systems. In $Gd_4Ca_4O(BO_3)_3$ (GdCOB) crystal, the Gd^{3+} ions can be partially substituted by Sc^{3+} or Lu^{3+}, in order to tune the chemical composition of the crystal. The optical birefringence of $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ (GdScCOB) or $Gd_{1-x}Lu_xCa_4O(BO_3)_3$ (GdLuCOB) crystals can be controlled by changing the compositional parameter x. Therefore, it is possible to achieve NCPM, with efficient d_{eff} coefficient, in the range of 780-963 nm during second harmonic generations. Because $ScCa_4O(BO_3)_3$ and $LuCa_4O(BO_3)_3$ crystals do not exists, cannot be grown, the main problem is to establish the growth conditions and the solubility limit of Sc^{3+} respectively Lu^{3+} ions in GdCOB crystal.

Single crystals of $Gd_{1-x}RE_xCa_4O(BO_3)_3$ with large size and good quality have been grown by Czochralski method. The limits of solubility of RE (RE=Sc^{3+} or Lu^{3+}) in the GdCOB crystals were also determined. The chemical compositions of the grown crystals have been determined by microprobe analysis. The X-ray diffraction measurements have been carried out to characterize the structural changes with compositional parameter x. The refractive indices were measured by minimum deviation method. Sellmeir equations for GdScCOB and GdLuCOB were established. The experimental phase matching results are compared with theoretical predictions and discussed.

2. Experimetnal

The $Gd_{1-x}RE_xCa_4O(BO_3)_3$ compounds were prepared by classical solid state reaction. Single crystals of $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ and $Gd_{1-x}Lu_xCa_4O(BO_3)_3$, with x = 0.1 respectively x = 0.13 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 Siemens D5000 diffractometer with Co Kα radiation (λ = 1.78897 Å). Chemical compositions of the crystals grown were determined by microprobe analysis. Differential thermal analyses were performed on the $Gd_{1-x}RE_xCa_4O(BO_3)_3$ compounds, with various compositional parameter x, in order to determine the solubility limits of RE ions in GdCOB crystals. The refractive indices of grown crystals were measured. Phase matching properties were measured with a continuous waved (CW) Ti: sapphire laser.

3. Results and discussion

$RCa_4O(BO_3)_3$ crystals have a non centro-symmetric monoclinic structure, with the space group Cm [1,2]. RCOB structure contains a rare earth site of C_s symmetry, two types of calcium sites $Ca^{2+}(1)$ and $Ca^{2+}(2)$ and two distinct $(BO_3)^{3-}$ groups. The unit cell parameters for GdCOB are a = 8.095 Å, b=16.018 Å, c=3.558 Å and $\beta = 101.28^0$. Six close oxygen ions, two B^{3+} ions and two O^{2-} at larger distances than borons coordinate the R^{3+} ion. Two nearest oxygen ions to the R^{3+} cation, labeled O(1), do not belong to the borate groups, while the other six oxygen ions are members of these groups. Ca^{2+} occupy two sites of C_1 symmetry, $Ca^{2+}(1)$ in a sixfold O^{2-} coordination and $Ca^{2+}(2)$ in a distorted eightfold O^{2-}

coordination and with two B^{3+} ions intercalated between the first six O^{2-} and the other two. Since the ionic radii of R^{3+} are close to Ca^{2+} ions [3] a degree of inversion or non-stoichiometry that increases with decreasing of the R^{3+} ionic radii has been reported [1,2].

The GdScCOB and GdLuCOB starting materials were prepared by solid state reaction of 4N Gd_2O_3, $CaCO_3$, B_2O_3, Sc_2O_3 and Lu_2O_3 powders in stoichiometric proportions. The mixtures were heated at 950 ^oC for 18 h, cooled and ground, and then heated again at 1350 ^oC for 24 h. The X-ray diffraction patterns confirmed that the solid state reactions were complete. Two crystals of $Gd_{0.87}Lu_{0.13}Ca_4O(BO_3)_3$ and $Gd_{0.90}Sc_{0.10}Ca_4O(BO_3)_3$ were grown by the Czochralski pulling method. The growths were performed in an iridium crucible (50mm diameter and 50mm height) and were computer monitored by a weight-and-diameter control system. A neutral atmosphere was provided with a continuous argon flow. The typical growth rate was 0.5 – 1.5 mm/h. In all growth processes rectangular <001> oriented single crystalline seeds were used. The crystal was rotated at 30-45 rpm. As much as 40% of the melt was converted into a single crystal in approximately one week. The growth temperatures, determined by an infrared pyrometer, were about 1480 ± 15 °C. The temperature gradient just above the melt was 30-40 °C/cm. The crystals were cooled to room temperature at a rate of 40 ºC/h. Both crystals obtained are colorless, with a good optical quality, not hygroscopes, and chemically stables. They are shown in Figs. 1a and 1b. Typically they are 25 mm in a diameter and 120 mm long. The crystals present good mechanical properties, permitting easy polishing.

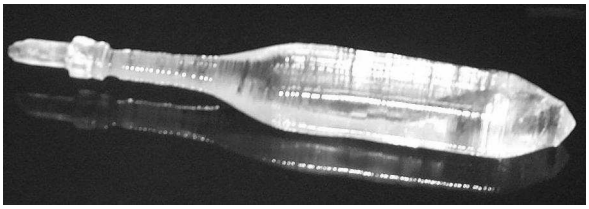

Fig. 1a. $Gd_{0.90}Sc_{0.10}Ca_4O(BO_3)_3$ single crystal.

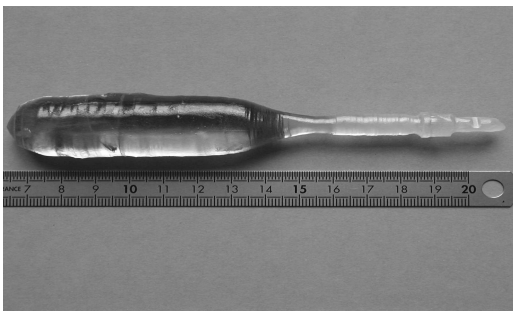

Fig. 1b. $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ single crystal.

From the X-ray powder diffraction patterns of $Gd_{0.87}Lu_{0.13}Ca_4O(BO_3)_3$ and $Gd_{0.90}Sc_{0.10}Ca_4O(BO_3)_3$ single crystals grown, we calculated the unit cell parameters for both crystals. The lattice parameters and chemical compositions of the grown crystals are given in Table 1.

Table 1. Chemical composition and lattice parameters of GdScCOB and GdLuCOB single crystals.

Starting Composition	Formulas deduced from compositional analyses	Lattice parameters (± 0.001 Å)
$Gd_{0.87}Lu_{0.13}Ca_4O(BO_3)_3$	$Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$	a = 8.094 b = 16.012 c = 3.552 β = 101.241^O
$Gd_{0.90}Sc_{0.10}Ca_4O(BO_3)_3$	$Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$	a = 8.083 b = 15.996 c = 3.549 β = 101.253^O

In order to determine the limits of solubility of RE ions (RE = Sc^{3+} or Lu^{3+}) in the GdCOB crystals, the compounds of $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ with x = 0.07, 0.08, 0.10, respectively $Gd_{1-x}Lu_xCa_4O(BO_3)_3$ with x = 0.22, 0.23, 0.24, 0.27 were prepared by solid state reaction. The differential thermal analyses performed on the synthesized materials are presented in the Figs. 2a, 2b, 2c and 2d. These experiments revealed that the solubility limits of RE^{3+} ions in GdCOB crystals is 7% for Sc^{3+} respectively 23% for Lu^{3+} ions. Up to these doping values the compounds have a congruent melting character.

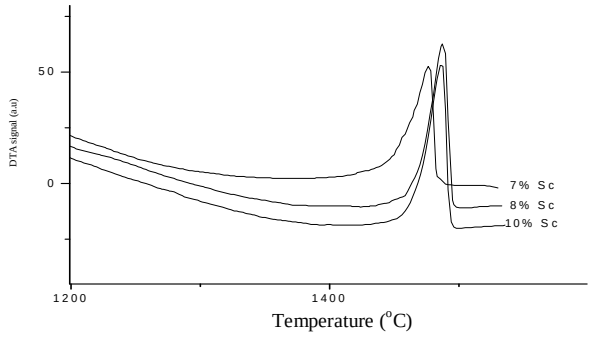

Fig. 2a. DTA traces of $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ upon heating.

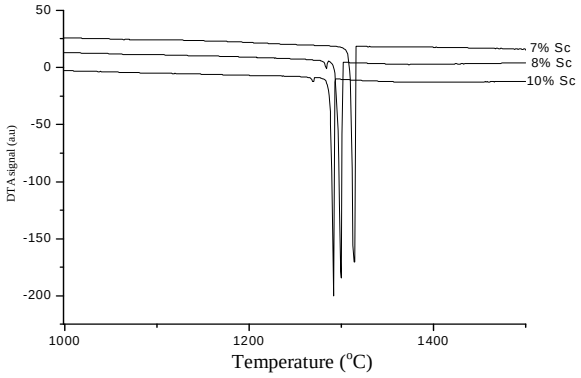

Fig. 2b. DTA traces of $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ upon cooling.

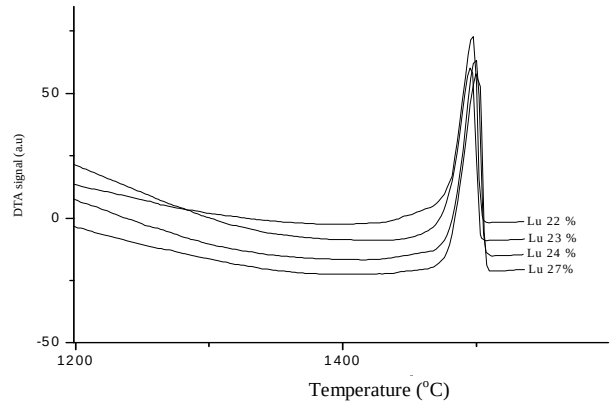

Fig. 2c. DTA traces of $Gd_{1-x}Lu_xCa_4O(BO_3)_3$ upon heating.

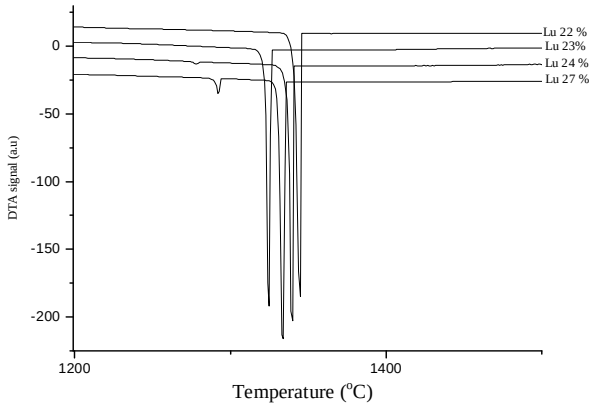

Fig. 2d. DTA traces of $Gd_{1-x}Lu_xCa_4O(BO_3)_3$ upon cooling.

The refractive indices of $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ and $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ grown crystals were measured by the minimum-deviation technique. Two prisms for each crystal, with crytalophysics axes Y (X) and X (Z) parallel to the bisector of (along) the transverse section apex, were cut and polished. The two prisms permit measurement of the all three refractive indices. The accuracy of the measurement is estimated to be 4×10^{-4} and permits a sufficiently accurate prediction of the phase-matching directions owing to the large birefringence. The two prisms permitted two independent measurement of n_X. The values obtained with one prism were not significantly different from those obtained with the other. Table 2 and 3 lists the parameters of Sellmeier equation that give the best fit for the three $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ respectively $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ refractive indices. The parameters were obtained by least-squares fits to the experimental data.

Table 2. Sellmeier Equation Coefficients for $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$.

Sellmeier Coefficients	n_X	n_Y	n_Z
A	2.80691	2.90342	2.93547
B	0.02141	0.02064	0.02167
C	0.01924	0.02914	0.02386
D	0.00622	0.01432	0.01575

Table 3. Sellmeier Equation Coefficients for $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$.

Sellmeier Coefficients	n_X	n_Y	n_Z
A	2.81268	2.90365	2.93852
B	0.02196	0.02302	0.02255
C	0.01844	0.01577	0.02078
D	0.00588	0.01054	001362

Types I and Types II phase-matching internal angles (θ_{PM} and φ_{PM}) of $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ respectively $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ were calculated. The phase matching angle expressions derive from the general equations given by Dmitriev et al. [4].

Second harmonic generation phase matching curves, when the fundamental wavelength direction is taken in each of the three principal planes, are given in Fig. 4 for $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ crystal respectively in Fig. 5 for $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ crystal. Calculation give the phase matching angles for which θ_{PM} and φ_{PM} is equal to 0 ° or 90 ° (non critical phase matching condition – NCPM), as function of the principal plane. For $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ crystal these particular phase matching angle values are obtained for type I angles in both the ZX (θ = 0 °, φ = 0 °, at λ = 934 nm) and the YZ (θ = 90 °, φ = 90 °, λ = 802 nm) planes. Type II phase matching occurs in the YZ (θ = 0 °, φ = 90 °, at λ = 2135 and 1505 nm) and the XY (θ = 90 °, φ = 90 °, at λ = 1170 nm) planes. For $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ crystal the particular phase matching angle values are obtained for type I angles in both the ZX (θ = 0 °, φ = 0 °, at λ = 921 nm) and the YZ (θ = 90 °, φ = 90 °, λ = 792 nm) planes. Type II phase matching occurs only in the YZ (θ = 0 °, φ = 90 °, at λ = 2358 and 1159 nm).

Two crystals (size: 7 mm × 7 mm × 7 mm) of $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ and $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$, polished and oriented along its crystallophysic axes (X, Y, Z), were used for experimental determination of the doubled frequencies along the crystallophyic axes (non critical phase matching condition) and directions around its. As one can see, we obtained a very reasonable fit with our calculated values. These phase-matching measurements provide a good test for Sellmeier coefficients and show that the coefficients given in Tables 2 and 3 are reasonably reliable.

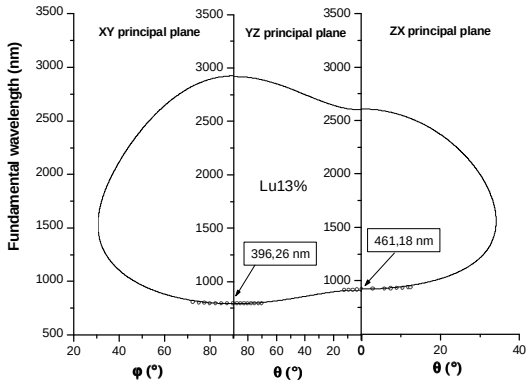

Fig. 4. Theoretical phase – matching curves of the fundamental wavelength in the $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ XY, YZ and ZX principal planes for SHG. Open circles are experimental points.

In $Gd_4Ca_4O(BO_3)_3$ crystal we can achieve second harmonic generation, in NCPM conditions, for radiations of 826nm along Y axis and 961nm along Z axis [5]. $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ and $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ crystals make its possible SHG (in NCPM conditions) for 792 respectively 802nm wavelength radiations along Y axis and 921 respectively 934 nm along Z axis. These results show that by changing the compositional parameter x of $Gd_{1-x}RE_xCa_4O(BO_3)_3$ crystals, it is possible to achieve NCPM, in the range of 780-963nm during second harmonic generations.

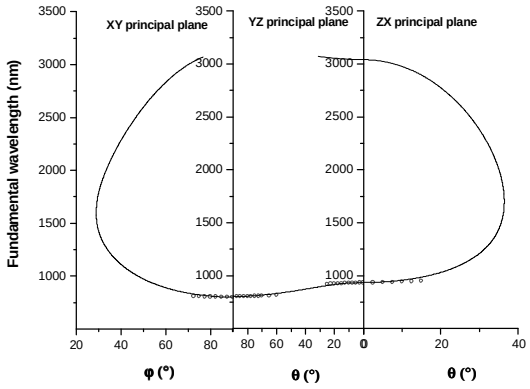

Fig. 5. Theoretical phase – matching curves of the fundamental wavelength in the $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ XY, YZ and ZX principal planes for SHG. Open circles denote the experimental points.

4. Conclusions

Single crystals of $Gd_{0.871}Lu_{0.129}Ca_4O(BO_3)_3$ and $Gd_{0.96}Sc_{0.04}Ca_4O(BO_3)_3$ with large size and good quality have been grown by Czochralski method. The optical birefringence of $Gd_{1-x}Sc_xCa_4O(BO_3)_3$ or $Gd_{1-x}Lu_xCa_4O(BO_3)_3$ crystals can be controlled by changing the compositional parameter x. Therefore, it is possible to achieve NCPM in the range of 780-963 nm during second harmonic generations. We have characterized new nonlinear crystals, GdScCOB and GdLuCOB, suitable to design specific wavelength converters in noncritical configuration.

References

[1] B. Ilyukhin, B. F. Dzhurinskii, Russian J. Inorg. Chem. **38**, 847 (1993).
[2] R. Norrestam, M. Nygren, J.O.Bovin, Chem. Mater. **4**, 738 (1992).
[3] R. D. Shanon, Acta Crystallogr. **32A**, 751 (1976).
[4] V. G. Dimitiev, G. G. Gurzadyan, D. N. Nikogosyan, Handbook of Nonlinear Crystals, Vol. 64 of Springer Series in Optical Science (Springer-Verlag, Berlin, 1991), 17.
[5] G. Aka, A. Kahn-Harari, F. Mougel, D. Vivien, F. Salin, P. Coquelin, P. Colin, D. Pelenc, J. L. Damelet, J. Opt. Soc. Am. **B14**, 2238 (1997).

* Corresponding author: achim@pluto.infim.ro