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Optical features of calcium neodymium oxyborate $Ca_4NdO(BO_3)_3$ doped by Yb^{3+}

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ABSTRACT

We have found that the $Ca_4NdO(BO_3)_3$ single crystals doped by Yb^{3+} (5 at.%) present promising materials for optical second harmonic generation and for the photoinduced effects. In particularly it is found that illumination by single pulsed Nd-YAG lasers with power about 1 GW/cm^2 causes substantial changes of the corresponding optical constants. The value of the efficient second order susceptibility is about 1.8 pm/V at wavelength 1064 nm.

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1. Introduction

The increasing variety of applications of nonlinear optical materials for second harmonic generation (SHG), sum or difference frequency mixing, optical parametric oscillation or amplification, have resulted in the development of inorganic nonlinear optical crystals [1]. The development of highly efficient nonlinear optical crystals for the ultraviolet region is extremely important for both laser spectroscopy and laser processing, including laser-tailoring of molecules and optical triggering. In particular the borate crystals are very useful for solid-state ultraviolet lasers [2–4] and infrared spectral range. The number of well-characterized solid rare earth borates is so far very small and includes the Sr^{2+}-containing phase $Sr_3R_2(BO_3)_4$ (see, e.g., Abdullaev and Mamedov [5]) and the Ba^{2+} containing phase [6] with similar compostion, $Ba_3R_2(BO_3)_4$, but with different structure [7]. Another family of oxyborates, with the composition $A_6MM'(BO_3)_6$ where A = Sr or Ba, have been found [8,9]. The metal ion M and M′ comprise several metal ions, whose sum of formal charges add up to +6. In general, rare earth borates containing, among others, Nd could be of great importance as they might be potential miniature laser material [6]. The nonlinear optical properties of the oxoborate family have been reported and appear to be comparable to those of β-BaB_2O_4 (BBO) for SHG [1], but they have one very important advantage—they can be doped with different rare earths [10]. By studying the structural characterization of the borate crystals we can understand why the borate crystals dominate in the field of the nonlinear optics. The boron atom has two types of hybridized orbitals, the planar sp^2 and the three dimensional sp^3, to coordinate three or four oxygen atoms forming $BO_3{}^{3-}$ or $BO_4{}^{5-}$ clusters. Further, these clusters can comprise several different typical B_xO_y groups, and therefore various types of borate crystals can be constructed based on these infrastructures, for example, the isolated BO_3 group in $NdAl_3(BO_3)_4$ (NAB) and $Ca_4ReO(BO_3)_3$ (CReOB), the B_3O_6 group in BBO, the B_3O_7 group in LBO, and the B_5O_{10} group in KB_3O_5. This is a very attractive phe-

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nomenon discovered in inorganic borate crystals. Therefore, it is very interesting to study the influence of these $BO_3{}^{3-}$ or $BO_4{}^{5-}$ clusters on second-order NLO response of various types of borate crystals, so that we can get some useful information in searching for new NLO materials [1].

The optical properties of solids are a major topic, both in basic research as well as for industrial applications. While for the former the origin and nature of different excitation processes is of fundamental interest, the latter can make use of them in many optoelectronic devices. These wide interests require experiment and theory. To the best of our knowledge there are no experimental measurements and also no first principles calculations of the linear and nonlinear optical properties of calcium neodymium oxyborate $Ca_4NdO(BO_3)_3$. Therefore we thought it is worthwhile to perform experimental study of this compound. It is necessary to point out that particular interest present only Yb doped NAB because for these types of crystals the photoinduced effects are observed only in the rare earth doped materials [11].

2. Experimental

2.1. Single crystal growth of ytterbium doped calcium neodymium oxoborate

Undoped and ytterbium doped calcium neodymium oxoborate single crystals $Ca_4NdO(BO_3)_3$—CNOB were grown by the Czochralski method using the Oxypuller 05-03 equipment made by Cyberstar (France). The inductive heating with Hüttinger generator was used.

The charge material was prepared on the basis of 4N purity $CaCO_3$, 5N purity Nd_2O_3, 4.5N purity Yb_2O_3, all from Metall Rare Earth Ltd., China and 4N purity B_2O_3 prepared at Institute of Electronic Materials Technology (Poland). The reagents were mixed according to stoichiometric formula and then heated in resistance furnace at 1100 °C for 12 h. After that the charge material was pressed isostatically. Ytterbium was substituted for neodymium.

The thermal system consisted of a 50 mm diameter and 50 mm high iridium crucible and an active after heater 50 mm in diameter and 80 mm in height placed on the crucible. The schematic view of the system is presented in Fig. 1.

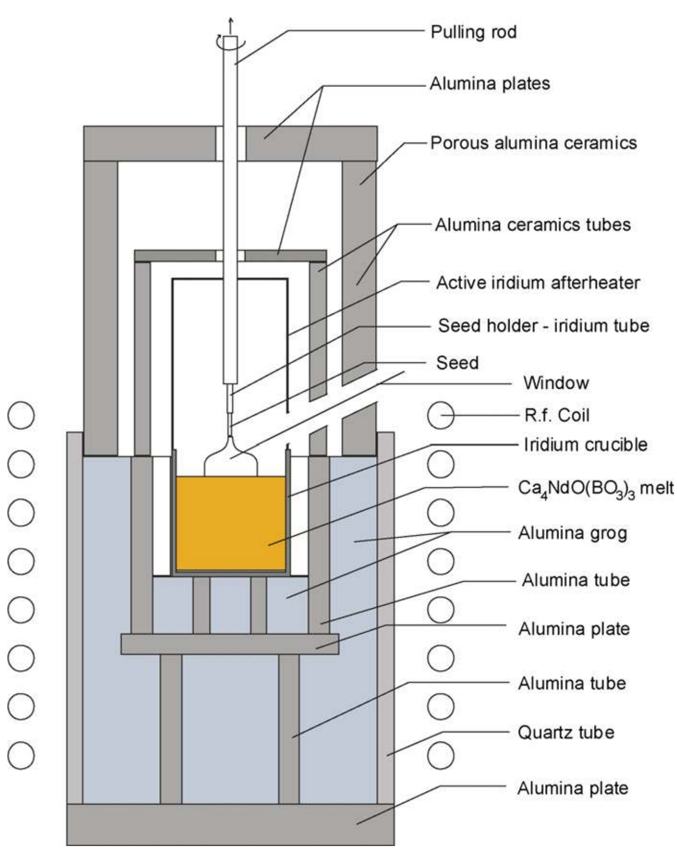

Fig. 1. Thermal system for the Czochralski growth of calcium neodymium oxoborate.

Fig. 2. Single crystals of $Ca_4NdO(BO_3)_3$: 5 at.% Yb.

The growing atmosphere consisted of nitrogen with 1.0 vol.% of oxygen. The following conditions of the growth process have been applied: growth rate 1.2–2.0 mm/h; rotation rate 15–30 rpm; cooling after growth—at least 24 h; growth direction [0 1 0] (*b*-axis).

The violet coloured single crystals with characteristic rhombus cross-section 21 mm × 24 mm and up to 50 mm in length were obtained. The ytterbium concentration in crystals was equal to 5 at.%.

The content of ytterbium in single crystals was determined with use of inductively coupled plasma-optical emission spectroscopy (ICP-OES) method. According to the obtained results the distribution coefficient of ytterbium in CNOB was estimated to be $k \approx 1.1$.

All the single crystals are transparent with homogeneous coloration but independently of growth conditions it is very difficult to obtain crack-free boules (Fig. 2).

3. Results and discussion

In the following Fig. 3, one can see the absorption spectrum of the investigated crystals without illumination and after illumination by one pulse of the 1 GW/cm^2 lasers. One can see the more remarkable changes are observed for the spectral line about 890 nm corresponding to $4F_{3/2}$ Yb transitions.

From the Table 1 one can see that the addition of the ytterbium substantially renormalize the principal Judd-Ofelt parameters.

The angle dependence of the SHG for the *XY* plane are presetned in the Fig. 4. One can see a relatively large output SHG at angle about 18° with respect to the *XY* plane. The performed investigation

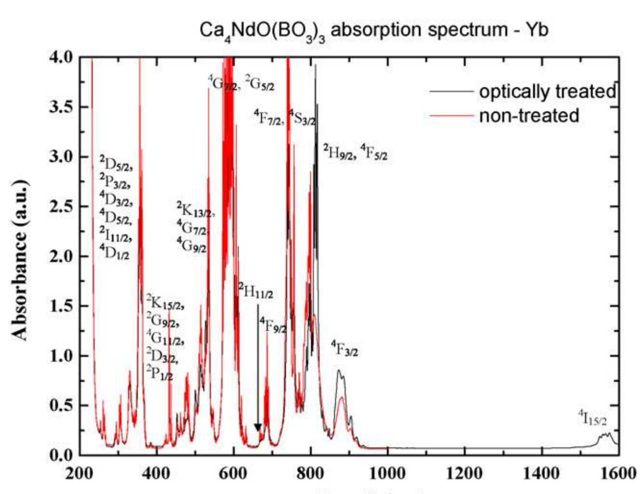

Fig. 3. The absorption spectra of the investigated crystals before and after the 1064 nm 1 GW/cm^2 pulse illumination.

Table 1
Judd-Ofelt analysis of the absorption spectrum.

Transitions from $^4I_{9/2}$ to	Wavelength (nm)	Energy (cm^{-1})	Experimental OS (10^{-6})	Calculated OS (10^{-6})
$^4I_{15/2}$	1576	6,345.00	0.0552	0.0717
$^4F_{3/2}$	873	11,454.0	1.0055	1.1678
$^2H_{9/2}$, $^4F_{5/2}$	812	12,315.0	2.3684	2.7253
$^4F_{7/2}$, $^4S_{3/2}$	740	13,513.0	2.5111	2.4558
$^4F_{9/2}$, $^2H_{11/2}$	687	14,556.0	0.2816	0.2805
$^4G_{5/2}$, $^2G_{7/2}$	586	17,064.0	8.3745	8.4249
$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	536	18,656.0	3.2329	2.5643
$^2K_{15/2}$, $^2G_{9/2}$	481	20,790.0	0.4643	0.3365
$^4G_{11/2}$, $^2D_{3/2}$	453	22,075.0	0.2149	0.2605
$^2P_{1/2}$, $^2D_{5/2}$	433	23,094.0	0.3075	0.3637
$^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$	357	28,011.0	5.8550	5.9585
$^2L_{15/2}$, $^2I_{13/2}$, $^2L_{17/2}$	331	30,211.0	1.0900	0.5038
$^4D_{7/2}$, $^2H_{9/2}$, $^2D_{3/2}$	307	32,573.0	0.4407	0.2446

$\Omega_2 = 1.473 \times 10^{-20}$; $\Omega_4 = 2.142 \times 10^{-20}$; $\Omega_6 = 1.406 \times 10^{-20}$; RMS = 0.320×10^{-6}.

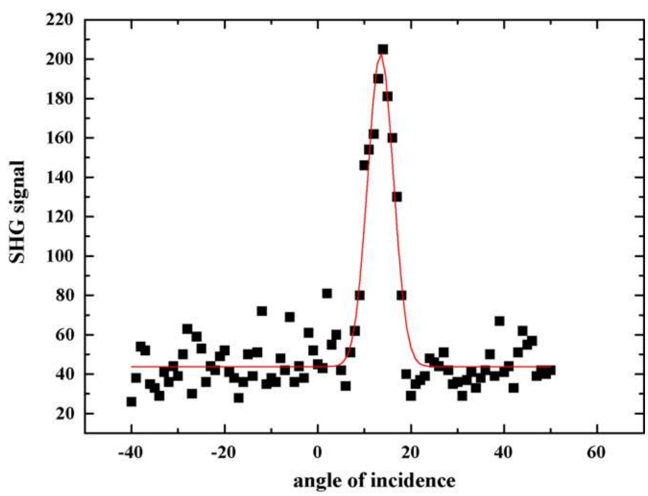

Fig. 4. Angle dependent optical SHG in the *XY* plane.

in the different directions allowed to evaluate an effective susceptibility about 1.8 pm/V. This value together with the possibility to operate by the absorption by single laser pulses allowed proposing these crystals as multifunctional materials for the optical second harmonic generation and for the photoinduced effects.

The observed photoinduced absorption may be a consequence of several photochromic effects due to presence of the ytterbium ions. The crystals possess high space homogeneities which allow proposing these crystals for effective optically operated switchers.

4. Conclusions

We have synthesized the $Ca_4NdO(BO_3)_3$ single crystals doped by Yb^{3+} (5 at.%). The performed investigation in the different directions allowed to evaluate an effective susceptibility about 1.8 pm/V. This value together with the possibility to operate by the absorption by single laser pulses allowed proposing these crystals as multifunctional materials for the optical second harmonic generation and for the photoinduced effects. The observed photoinduced absorption may be a consequence of several photochromic effects due to presence of the ytterbium ions. The crystals possess high space homogeneities which allow proposing these crystals for effective optically operated switchers.

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