Inorganic Materials, Vol. 41, No. 4, 2005, pp. 393–396. Translated from Neorganicheskie Materialy, Vol. 41, No. 4, 2005, pp. 465–468.
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Second Harmonic Generation in Boracites

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Received July 8, 2004

Abstract—The $M_3B_7O_{13}X$ (M = Mg, Ni, Cd; X = Cl, Br, I) boracites were synthesized and characterized by x-ray diffraction and second harmonic generation. Their nonlinear optical susceptibility was estimated using the Phillips–Van Vechten–Levine model. The results demonstrate that the nature of the halogen has an insignificant effect on the second-order nonlinear response of the boracites.

INTRODUCTION

Mixed borates have recently been the subject of extensive studies. The results of those studies have been systematized in many reviews [1–6]. The interest in these compounds is motivated not only by their intriguing crystal chemistry, no less rich than that of silicates, but also by the exceptional potential of borates for nonlinear optical applications, where they are expected to be key materials for the conversion of UV radiation. One of the challenges in modern photonics is the development of short-wavelength optical technologies in connection with the need for a marked increase in recording density.

Direct lasing in the frequency range in question is difficult to achieve in solids because of the extremely short lifetime and the need for high excitation intensities. One effective way of producing such radiation is by using second harmonic generation (SHG) in nonlinear optical crystals to convert the output of conventional light sources.

Clearly, such crystals must be transparent throughout the working frequency range. This condition is only met by borates, which are currently regarded as the only candidate materials for the application field in question. In addition, borates offer high radiation hardness and often have noncentrosymmetric structures [1, 3]. Most borates, however, have relatively low nonlinear optical susceptibilities, which limits their application area.

In this context, the anomalously large second-order nonlinear response of microcrystalline $Pb_2B_5O_9Br$ [7] is of great practical interest. This bromoborate has a hilgardite-type framework structure made up of B_5O_9 groups, with the Pb and Br atoms sitting in infinite channels. Current approaches to establishing relationships between the structural basis and nonlinear optical properties of borates do not deal with framework phases [1]. Furthermore, detailed data on their nonlinear optical response are missing. Therefore, systematic SHG characterization of framework haloborates is of considerable scientific and technological interest.

One of the largest families of framework haloborates is constituted by boracites—phases with the general formula $M_3B_7O_{13}X$ (M = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Li; X = Cl, Br, I) [8–11]. The low-temperature forms of the boracites have pyroelectric space groups. The ferroelectric properties of these compounds have been studied in detail [9], whereas their nonlinear optical properties are essentially unexplored.

In this paper, we analyze the effect of chemical composition on SHG in the $M_3B_7O_{13}X$ (M = Mg, Cd, Ni; X = Cl, Br, I) boracites.

EXPERIMENTAL AND RESULTS

Synthesis of Mg, Ni, and Cd boracites. $Mg_3B_7O_{13}Cl$ and $Cd_3B_7O_{13}Cl$ were synthesized by the procedure that was successfully used by Li *et al.* [9] to prepare the M–Cl (M = Fe, Co, Ni) boracites. As starting chemicals, we used analytical-grade B_2O_3 and reagent-grade $MgCl_2 \cdot 6H_2O$ and $CdCl_2 \cdot 2.5H_2O$. Mixtures of B_2O_3 and one of the chlorides (weight ratio of 2 : 5) were dissolved in a small amount of distilled water, and then the solutions were boiled down to dryness. The resulting solid material was placed in an alundum boat and calcined in flowing nitrogen at 700°C for 2 h in a quartz reactor. During the calcination of the Cd-containing sample, we observed the formation of several transparent needlelike cadmium chloride crystals at the cold end of the reactor. After cooling, the reaction product was washed with a large amount of water and then dried at about 100°C.

$Ni_3B_7O_{13}Cl$ was synthesized by the reaction

$$2H_3BO_3 + 6B_2O_3 + 2NiO + 4NiCl_2 = 2Ni_3B_7O_{13}Cl + 6HCl.$$

The starting chemicals used were extrapure-grade H_3BO_3, analytical-grade B_2O_3, and reagent-grade NiO.

Table 1. Lattice parameters of $M_3B_7O_{13}X$ boracites (sp. gr. $Pca2_1$)

M	a, b, c, Å		
	Cl	Br	I
Mg	$a = 8.529(3)$	$a = 8.537(3)$	
	$b = 8.487(3)$	$b = 8.501(8)$	–
	$c = 12.102(2)$	$c = 12.101(3)$	
Ni	$a = 8.501(4)$	$a = 8.521(1)$	$a = 12.0341(7)$*
	$b = 8.503(1)$	$b = 8.522(5)$	
	$c = 12.018(3)$	$c = 12.04(1)$	
Cd	$a = 8.817(1)$	$a = 8.841(1)$	$a = 8.879(5)$
	$b = 8.842(1)$	$b = 8.8478(7)$	$b = 8.872(5)$
	$c = 12.473(1)$	$c = 12.513(2)$	$c = 12.566(3)$

* Sp. gr. $F\bar{4}3c$.

Table 2. SHG signal intensity and calculated average nonlinear optical susceptibility of $M_3B_7O_{13}X$ boracites

M	$I_{2\omega}/I_{2\omega}(SiO_2)$ (±0.1)			d_{av}		
	Cl	Br	I	Cl	Br	I
Mg	6	8	–	0.24	0.27	–
Ni	0.2	0.4	0.3	0.06	0.03	0.06
Cd	14	4	8	0.19	0.12	0.11

$NiCl_2$ was prepared by direct chlorination of reagent-grade Ni powder at 700–750°C. A stoichiometric mixture of the reagents was loaded into an alundum crucible, which was then sealed in a silica tube. The sample weight and tube volume were chosen so that the concentration of the water released from the boric acid was 0.5 mg/cm^3 [11]. The tube was pumped down to 10 Pa, sealed off, and placed in a two-zone (780 and 800°C) furnace so that the sample was situated in the cold zone. During firing for two days, no significant mass transport took place: only a few green $Ni_3(BO_3)_2$ crystals were found on the tube wall. Most of the reaction products remained in the crucible.

The Br boracites were synthesized according to the general scheme

$$MBr_2 \cdot xH_2O + 5MO + 7B_2O_3 \longrightarrow 2M_3B_7O_{13}Br + xH_2O$$

$$(M = Mg, Cd, Ni),$$

with $x = 4$ for M = Cd and $x = 6$ for M = Mg and Ni. The starting bromides were prepared by dissolving appropriate metal oxides in an excess of hydrobromic acid. After filtration, the solution was boiled down until crystallization began.

Intimately ground stoichiometric bromide–oxide mixtures were loaded into silica tubes and calcined under a dynamic vacuum of ≈40 Pa first at 100–200°C for 3–4 h and then at 400°C for an additional 1 h in order to prevent pyrohydrolysis. In the synthesis of the Mg boracite, the sample was then heated to 720–750°C and fired for 2 h. In the syntheses of the Cd and Ni compounds, the tube was cooled and sealed off under vacuum. Next, the sample was fired at 700–750°C for 4–6 h.

$Ni_3B_7O_{13}I$ and $Cd_3B_7O_{13}I$ were synthesized according to the general scheme

$$MI_2 + 5MO + 7B_2O_3 = 2M_3B_7O_{13}I \ (M = Ni, Cd).$$

NiI_2 was prepared by reacting a stoichiometric mixture of metallic Ni and crystalline iodine in an evacuated silica tube at 400°C for five days. The reaction product had the form of dark crystals. CdI_2 was prepared by boiling an aqueous suspension of freshly precipitated cadmium and iodine with a reflux condenser. The amount of cadmium was in slight excess of the stoichiometric value. After the solution became colorless, it was filtered and boiled down until crystallization began. The precipitated crystals were collected on a filter and dried at about 100°C.

To synthesize the Ni and Cd boracites, stoichiometric iodide–oxide mixtures were reacted in evacuated silica tubes at 750°C for 48 and 14 h, respectively.

X-ray diffraction characterization. All of the reaction products were characterized by x-ray diffraction (XRD) using a Guinier focusing camera (Enraf Nonius, Delft) and germanium internal standard. Peak positions were determined with an IZA-2 comparator. The XRD data were processed using the Powder2 pack. In phase analysis, we used ICDD Powder Diffraction File data (PDF2) [12].

All of the synthesized compounds were XRD single-phase. Their lattice parameters (Table 1) agree with earlier data [12].

SHG characterization. The boracites were tested for SHG with a pulsed Nd:YAG laser ($\lambda = 1.064$ μm, 10-ns pulses with a repetition rate of 25 Hz) at room temperature using polycrystalline samples. The SHG signal ($\lambda = 0.532$ μm) was measured in reflection with an FEU-77 photomultiplier. As a standard, we used polycrystalline α-quartz with an average particle size of 3 μm. The results are summarized in Table 2.

DISCUSSION

In this work, $M_3B_7O_{13}X$ boracites were prepared and characterized by SHG for three metals differing in nature: Mg, the closest analog of the alkaline-earth metals forming hilgardite-structure haloborates; Ni, a 3*d* transition metal; and Cd, a Group IIB metal. This allows us to draw some tentative conclusions about the effects of cation and anion compositions on the conversion efficiency of the compounds under consideration. Note in this context that the nonlinear susceptibility (and, accordingly, the SHG signal) of a crystalline material is a tensor quantity, dependent on the crystallographic orientation. Therefore, SHG measurements on polycrystalline samples yield an average characteristic, which depends on the particle size of the material. The data presented in Table 2 were obtained on microcrystalline (3–5 μm) samples.

Taking into account the above observations, we infer from the data in Table 2 that the nature of the halogen has little effect on the second-order nonlinear response of the boracites studied, which is, at the same time, very sensitive to the nature of the metal. To establish the degree of generality of this conclusion, experimental data must be compared to theoretical predictions. Modern theories of nonlinear optical effects give no way of evaluating second-order nonlinear susceptibilities of multicomponent crystals in a first-principles manner. At the same time, components of the second-order nonlinear susceptibility tensor, d_{ijk}, can be calculated using the model developed in [13, 14], which represents the macroscopic property of interest here as a combination of contributions from all of the chemical bonds in the crystal. This approach was shown to be applicable to borates [15, 16] and hilgardite-structure haloborates [17]. The calculation procedure was described in detail in [17]. We used that model to calculate the d_{ijk} tensor for the boracites under consideration. To compare the calculation results and experimental data for polycrystalline samples, it is necessary to consider average susceptibilities d_{av} (Table 2). Given that all of the boracites studied, except $Ni_3B_7O_{13}I$, have the *mm*2 point group, d_{av} is related to d_{ijk} by [18]

$$d_{av}^2 = \frac{19}{105}d_{33}^2 + \frac{44}{105}(d_{32}^2 + d_{31}^2) + \frac{13}{105}(d_{31} + d_{32} + d_{33})^2.$$

For $Ni_3B_7O_{13}I$, we have

$$d_{av}^2 = \frac{5}{7}d_{14}^2.$$

At a given particle size, the relative SHG signal intensity $I_{2\omega}/I_{2\omega}(SiO_2)$ is proportional to d_{av}^2 (Table 2).

Both the experimental data and calculation results demonstrate that the Mg and Cd boracites have comparable nonlinear optical susceptibilities, which exceed those of the Ni boracites by an order of magnitude.

The nonlinear optical properties of borates are commonly interpreted in terms of the number of $[BO_3]$ groups per unit cell and their arrangement in the crystal structure [1]. In this approach, cations are thought of as stabilizers of the boron–oxygen subsystem [4]. Both the boracite and hilgardite phases have a rigid, difficult-to-deform framework. Nevertheless, in both borate families the nonlinear optical response depends strongly on the nature of the cation, which points to an intricate relationship between the composition and nonlinear optical properties of these borates. In this respect, the interpretation of experimental data in terms of the Phillips–Van Vechten–Levine model appears more reasonable.

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