

# Nonlinear current-voltage and optical properties of $\text{Zn}_4\text{B}_6\text{O}_{13}$

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This paper reveals the nonlinear optical properties of  $\text{Zn}_4\text{B}_6\text{O}_{13}$  (ZBO). The samples were synthesized by solid state reaction. The formed polycrystalline phases were analyzed by X-ray diffraction. The nonlinear optical properties of prepared samples were investigated by measurements of second harmonic generation (SHG) intensity. The highest SHG intensity of ZBO was observed for the powder particle sizes of 40-70  $\mu\text{m}$ . The value of the intensity was estimated to be two times higher than that of  $\text{KH}_2\text{PO}_4$ . The nonlinearity coefficient of the current-voltage curve was calculated to be 2.14 in the current range of 2-4 nA.

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## 1. Introduction

Inorganic borates are of great interest due to their nonlinear optical (NLO), fluorescence, piezoelectric and ferroelectric properties. They have been widely used as UV transparent materials. A number of excellent NLO borate materials such as  $\text{M}_2\text{B}_{10}\text{O}_{14}\text{F}_6$  ( $\text{M} = \text{Ca}, \text{Sr}$ ) [1],  $\text{LiGeBO}_4$  [2],  $\text{NH}_4\text{B}_4\text{O}_6\text{F}$  [3],  $\text{CsLiB}_6\text{O}_{10}$  [4],  $\beta\text{-BaB}_2\text{O}_4$  [5], etc. have been investigated and reported. Recently, bismuth-tellurium-borate  $\text{Bi}_3\text{TeBO}_9$  (BTBO) was reported as a new NLO material possessing the largest second harmonic generation (SHG) effect among the known borate crystals [6]. The second harmonic generation (SHG) intensity of BTBO was reported to be 20 times that of  $\text{KH}_2\text{PO}_4$  (KDP). Third order nonlinear optical susceptibility was studied in titania modified sodium borate glasses [7]. In borate crystals, the boron atom may adopt triangular or tetrahedral oxygen coordination forming  $(\text{BO}_3)$  or  $(\text{BO}_4)$  groups, respectively. Furthermore, those boron groups can be connected in different ways to form typical  $\text{B}_x\text{O}_y$  infrastructures leading to rich physical properties. The existence of  $\text{Zn}_4\text{B}_6\text{O}_{13}$  (ZBO) was suggested by Smith, et. al [8]. In the same year, the structure was reported by S. Terol and Maria J. Oterio [9]. Then, the structural properties in more detail were determined by Smith, Garcia-Blanco, and Rivoir in 1964 [10] and redetermined by Smith-Verdier and Garcia-Blanco in 1980 [11] using three-dimensional diffractometer data to obtain more accurate parameters. ZBO belongs to the cubic system with space group  $I43m$  and the dimensions of the unit cell are  $a=b=c=7.4659(3)$  Å. The experimental density is  $4.22$  g/cm<sup>3</sup>. A lot of researches have been devoted to discovering the unique properties of ZBO. The ZBO cubic crystals were grown in a glass and their luminescence properties were reported in [9]. Also, large single crystals were grown by the Czochralski method

[12]. The crystals were of optical quality and exhibited a plain growth face (100). Later, the photoluminescence, thermo-luminescence, and electron paramagnetic resonance properties of the single crystals were studied [13]. The sol-gel method was applied to synthesize ZBO crystals as well [14]. At a crystallization temperature of 850 °C, ZBO cubic crystals with a size of 400–600 nm were obtained. The density functional theory calculations showed that the crystal belongs to the semiconductors with an indirect energy bandgap of about 3.289 eV. Note that ZnO based materials are promising candidates for varistor applications as well. Especially, zinc oxide nanopowders [15] and doped materials [16] have shown promising varistor properties.

In this paper, the nonlinear electrical and optical properties of ZBO are presented. The polycrystalline samples were synthesized by solid state reaction and analyzed by X-ray diffraction. The current-voltage (I-V) characteristic of ZBO was studied. The nonlinear optical properties were investigated by measurements of second harmonic generation (SHG) intensity in powders with different particle sizes.

## 2. Experimental

Polycrystalline samples of ZBO were synthesized by solid state reaction from the stoichiometric mixture of ZnO and  $\text{H}_3\text{BO}_3$ . The mixture was pressed into a pellet and heated up in a “Nabertherm” furnace. Z. Zhan synthesized ZBO at firing temperature of 900 °C [17]. To find an optimized synthesis condition at lower temperatures, we started the thermal treatment process from 750 °C. For achieving a significant amount of ZBO, additional different temperature treatments were also performed. The four thermal treatment regimes of sample preparation are

presented in Table 1. The synthesized phases produced by the reaction were analyzed by powder X-ray diffraction (XRD) using a DRON-3 diffractometer (CuK $\alpha$  radiation, Ni-filter). Detected crystalline phases were identified by JCPDS-ICDD PDF release 2008 database [18]. The I-V characteristics of prepared samples were measured by a high resistance meter (4339B, Agilent). The intensity of second harmonic generation (SHG) was measured by the Kurts and Perry powder method [19]. A Q-switched Nd<sup>3+</sup>:YAP laser with radiation at 1067 nm was used as a radiation source. For the investigation of SHG, the powders of synthesized materials were hand-pressed into a 7 mm diameter pellet. Also, the powder of well-known optical material KH<sub>2</sub>PO<sub>4</sub> (KDP) was used as a reference sample.

Table 1. Sample preparation regimes

Name of sample	Temperature and duration
Sample_#1	750°C-12h plus 800°C-24h
Sample_#2	800°C-24h
Sample_#3	800°C-96h
Sample_#4	800°C-96h plus 850°C-96h

### 3. Results and discussion

Firstly, sample\_#1 was prepared by heating the mixture of precursors at 750 °C for 12 h and, then, 800 °C for 24h. The XRD analysis of the sample detected ZnB<sub>4</sub>O<sub>7</sub>, Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, and ZBO phases (see Fig. 1). To understand the temperature influence, sample\_#2 was prepared by heating the mixture at 800 °C for 24 h. As can be seen from Fig. 1 the amounts of ZnB<sub>4</sub>O<sub>7</sub>, Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phases in sample\_#2 are decreased. This can show that the formation of ZnB<sub>4</sub>O<sub>7</sub>, Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phases at 750 °C is more preferable to 800 °C. To understand the influence of the duration of synthesis, sample\_#3 was prepared by heating the mixture at 800 °C for 96 h. In this case, the amounts of the above mentioned two phases are slightly decreased in comparison with sample\_#2. Consequently, the longer the duration, the less the amounts of ZnB<sub>4</sub>O<sub>7</sub> and Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub>. Note, the amount of ZBO increases and no other phases appears from sample\_#1 to sample\_#3. Thus, at the initial stage, the mentioned two phases are formed but, later, ZBO is formed due to their interaction. One of the ways to obtain a pure ZBO sample is the synthesis at 800 °C, but it may take a few additional days. Another way is the synthesis at a higher temperature which will allow us to reduce the synthesis duration. We decided to continue the synthesis process of sample\_#3 at 850°C. As shown in Fig. 1, pure ZBO phase was obtained at 800°C for 96h and 850°C for 96h (sample\_#4 in the figure). The I-V characteristic of sample\_#4 is presented in Fig. 2. The nonlinearity of the I-V curve shows the possibility of the utilization of high voltage varistors based on ZBO. The operation voltage region of sample\_#4 as a varistor is above 38 V where the nonlinearity is observed. In this region, the I-V relation can be empirically described by the power law,  $I = kV^\alpha$ , where k is a constant and  $\alpha$  is the nonlinearity constant. The nonlinearity coefficient is an

important parameter for varistors and can be determined from the formula  $\alpha = \log[I_2/I_1]/\log[V_2/V_1]$ , where  $I_1$  and  $I_2$  are the currents corresponding to the voltages  $V_1$  and  $V_2$  (operation voltages), respectively. By using this formula, the nonlinearity coefficient of sample\_#4 was found to be 2.14 for the current range of 2-4 nA. The I-V behavior becomes linear (ohmic) below 38 V. The linear portion of the I-V curve is clearly shown in the inset of Fig. 3. In this region the resistance of the sample is  $3 \times 10^{11} \Omega$ .

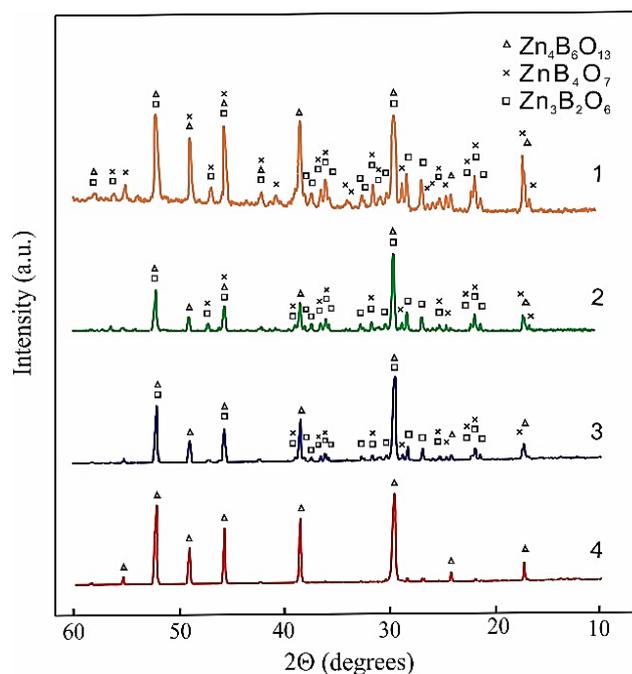


Fig. 1. XRD patterns of the prepared samples. 1 - Sample\_#1, 2 - Sample\_#2, 3 - Sample\_#3 and 4 - Sample\_#4 (color online)

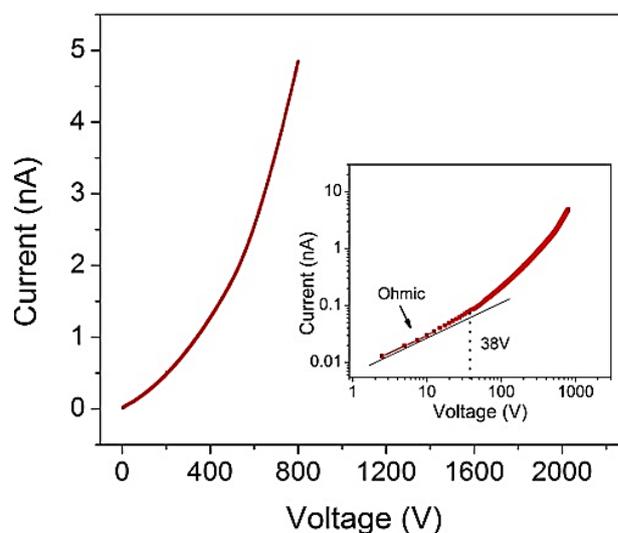


Fig. 2. I-V characteristic of sample\_#4. The inset illustrates the I-V characteristic in logarithmic scale (color online)

Next, it was our interest to study the second order optical nonlinearity of ZBO. First, we measured the intensity of SHG in the four prepared samples. The measurements were performed for different ranges of

particle sizes. According to Kurtz's method [18], this allows predicting the possibility of phase-matched interaction in a

material. The measurement results of SHG intensity are presented in Fig. 3.

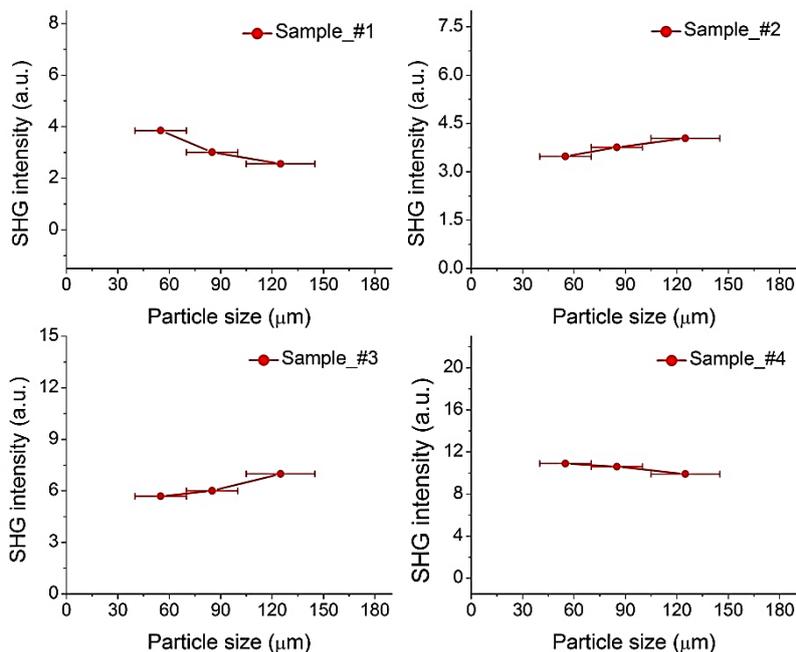


Fig. 3. SHG intensity dependence on particle size (color online)

In the case of sample\_#1, the decreasing behavior of the SHG curve rather indicates the absence of phase-matched interaction. This behavior could be attributed to the  $\text{ZnB}_4\text{O}_7$  and/or  $\text{Zn}_3\text{B}_2\text{O}_6$ . Note, sample\_#1 consists of three different compounds where the amount of ZBO is the least. As for sample\_#2, sample\_#3, and sample\_#4, the SHG curve more likely shows the character of phase-matched interaction. Taking into account that sample\_#4 consists of only ZBO, the obtained results could show the phase-matched interaction character of ZBO. However, more experimental data are needed to confirm this assumption. The ratio of SHG intensity of prepared samples to SHG intensity of KDP at different particle sizes is presented in Fig. 4.

As can be seen from the figure, the SHG intensity of sample\_#1 is lower than KDP in the ranges of 70-100 μm and 100-150 μm. In the case of sample\_#2 and sample\_#3, the intensity values slightly differ from KDP. The best result is obtained for sample\_#4. The highest value of SHG intensity is observed at particle sizes of 40-70 μm and two times higher than that of KDP. Also, the SHG characteristic of ZBO is comparable to that of  $\text{LiGeBO}_4$  [2].

#### 4. Conclusion

$\text{Zn}_4\text{B}_6\text{O}_{13}$  based samples were synthesized by solid state reaction from the stoichiometric mixture of ZnO and  $\text{H}_3\text{BO}_3$ . The results of XRD analysis showed that samples synthesized at different temperatures and duration contain mainly  $\text{ZnB}_4\text{O}_7$ ,  $\text{Zn}_3\text{B}_2\text{O}_6$ , and  $\text{Zn}_4\text{B}_6\text{O}_{13}$  phases. But, the sample prepared at 800°C-96h and 850°C-96h contains only  $\text{Zn}_4\text{B}_6\text{O}_{13}$ . The measurements revealed the nonlinear behavior of the I-V characteristic of that sample, which makes  $\text{Zn}_4\text{B}_6\text{O}_{13}$  an interesting material for varistor applications. The nonlinearity coefficient of the sample in the current range of 2-4 nA was calculated to be 2.14. The dependence of SHG intensity on particle size was investigated as well. It is shown that the SHG intensity of  $\text{Zn}_4\text{B}_6\text{O}_{13}$  is two times higher than that of KDP in the size range of 40 ÷ 70 μm.

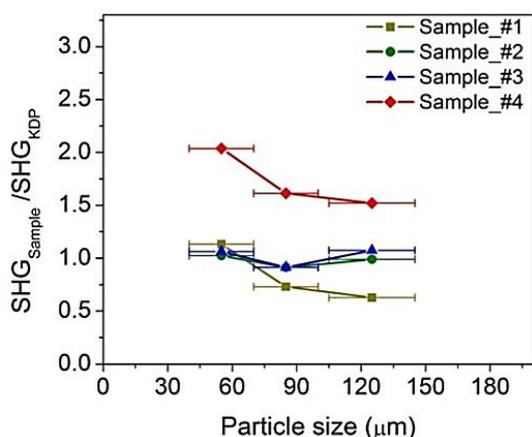


Fig. 4. Dependence of  $\text{SHG}_{\text{Sample}}/\text{SHG}_{\text{KDP}}$  on particle size (color online)

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