



Article Cd₄InO(BO₃)₃: A New Nonlinear Optical Crystal Exhibiting Strong Second Harmonic Generation Effect and Moderate Birefringence

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Abstract: A new noncentrosymmetric cadmium indium borate, $Cd_4InO(BO_3)_3$ (CIBO) has been successfully developed via a standard solid-state reaction. Its crystal structure was confirmed by the single crystal X-ray diffraction, which shows that CIBO belongs to the non-centrosymmetric and polar space group *Cm*. Its structure contains the distorted InO_6 and CdO_n (n = 6, 8) polyhedra, which link together by sharing an edge or corner to build a three dimensions framework with BO₃ triangles accommodated in tunnels. Benefiting from the approximately parallel configuration of BO₃ triangles, CIBO exhibited a strong second harmonic generation (SHG) effect (3 × KDP), and moderate birefringence of 0.077@1064 nm. Further optical and thermal characterizations suggest that CIBO possesses a wide transparent window and good thermal stability. Theoretical calculation reveals that the macroscopic SHG coefficients of CIBO results from the synergistic effect of the parallel arrangement of BO₃ groups and d^{10} Cd²⁺ cation.

Keywords: borates; crystal growth; birefringence; nonlinear optical crystal

1. Introduction

Nonlinear optical (NLO) crystals that can expand the wavelength of a solid-state laser by second-harmonic generation (SHG) have been applied at the forefront of scientific and technological research, such as medicine, scientific research, civil industries, etc. [1–4]. However, an available NLO crystal must satisfy some structure and performance requirements. Structurally, only non-centrosymmetric (NCS) crystalline materials can exhibit the SHG response [5,6]. As for the properties, NLO crystals also need to possess a large SHG response and moderate birefringence, which are essential to realize phase-matching (PM) in the desired wavelength range and obtain high laser conversion efficiency [7–9]. However, it was exceptionally challenging to simultaneously maximize these two optical parameters [10,11]. For example, BPO₄ [12], LiGeBO₄ [13], and SrB₄O₇ [14] all exhibited strong SHG responses, originating from the aligned arrangements of tetrahedral BO₄ units, but they suffered from a too-small birefringence to achieve a PM condition in transmittance regions. On the contrary, Li₂B₄O₇ and KB₅O₈·4H₂O possessed moderate birefringence and wide transmission range, unfortunately, their weak SHG responses hindered practical applications [15,16]. Therefore, exploring new NLO materials with a large SHG response and moderate birefringence were consequently of enormous current academic and commercial interest.

Traditionally, inorganic planar π -conjugated systems, including borates [17–19], cyanurates [20,21], carbonates [22,23], and nitrates [24,25], were excellent candidates for NLO materials because their delocalized π -conjugated groups, such as (BO₃)^{3–}, (C₃N₃O₃)^{3–},



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). $(CO_3)^{2-}$, and $(NO_3)^-$. Generally, these units possessed high NCS possibility, strong SHG responses, wide transmittance window, and strong anisotropy [26–28]. For instances, KBe₂BO₃F₂ (KBBF) [29], Ca₃(C₃N₃O₃)₂ [30], and β -Sr₃(C₃N₃O₃)₂ [31], etc. all exhibited a large birefringence and/or strong SHG coefficients due to the π -conjugated of anionic groups [32,33]. However, it should also be noted that most cyanurates, carbonates, and nitrates were not thermally stable [34]. They often tended to decompose at a high temperature. Therefore, π -conjugated (BO₃)³⁻ groups were preferred as the most ideal structural motif for the design of new NLO materials, and a wide range of compounds with the π -conjugated (BO₃)³⁻ groups as the basic building units have been synthesized, including KBe₂BO₃F₂ [29], Pb₂Ba₃(BO₃)₃Cl [35], Cd₄BiO(BO₃)₃ [18], Li₄Sr(BO₃)₂ [36], Bi₃TeBO₉ [37], and BaYBO₄ [38], etc.

Beyond the π -conjugated systems, introducing some polar distorted polyhedra were also favorable for a large SHG response and birefringence, including the polyhedra with the canter of d^{10} cations (such as Zn^{2+} , Cd^{2+} , and Hg^{2+}) [11,17,39,40], d^0 cations (such as V^{5+} , Mo^{6+} , W^{6+} , Ti^{4+} , etc.) [41–44], and stereo-chemical active lone pair (SCALP) cations (such as, Bi^{3+} , Te^{4+} , Sn^{2+} Pb²⁺, I^{5+} , etc.) [18,35,42,45–47]. These cations with second-order Jahn– Teller (SOJT) effects could enhance the birefringence and SHG effect of NLO materials. For example, $Sn_2B_5O_9Cl$ [48] exhibited lager birefringence (0.168@546 nm) than $Ba_2B_5O_9Cl$ [49] (0.010@546 nm) due to the unique [SnO₇Cl₂] polyhedra with SCALP. Cd₄BiO(BO₃)₃ [18] (6.0 × KDP) and Bi₃TeBO₉ [37] (20.0 × KDP), displayed extremely strong SHG responses due to the synergistic effects of the BiO₆, CdO_n (n = 6, 7)/TeO₆ polyhedra and the π conjugated BO₃ groups. Thus, the incorporation of the above asymmetric chromophores into borates was a fruitful strategy for designing high-performance NLO crystals.

Inspired by the above ideas, we assembled the π -conjugated BO₃ triangles with polar displacement of d^{10} Cd²⁺ cations to explore new NLO materials, and successfully synthesized a new NLO crystal, Cd₄InO(BO₃)₃ (CIBO), which exhibited a strong SHG effect (3.0 × KDP), moderate birefringence (0.077@1064), suitable band gap, and wide transparent range. Herein, the synthesis, crystal structure, thermal behavior, spectrum, and NLO properties of CIBO were reported. Theoretical calculations have also been carried to elaborate the relation between its structure and performance. It manifested that CIBO was a promising candidate as new NLO material.

2. Experiment Sections

2.1. Syntheses and Crystal Growth

2.1.1. Reagents

The raw materials of In_2O_3 (Aladdin Chemistry Co., Ltd., 99.9%), CdO (Tianjin Fu Chen Chemical Co., Ltd., 99%), PbO (Tianjin Fu Chen Chemical Co., Ltd., 99%), and H_3BO_3 (Aladdin Chemistry Co., Ltd., 99%) were used.

2.1.2. Single Crystal Preparation

Single crystals of CIBO were prepared using the high-temperature solution method. A mixture of In_2O_3 , H_3BO_3 , CdO, and PbO at a molar ratio of 0.25:3.5:4:2 was placed into a Φ 20 × 20 mm platinum (Pt) crucible. Then, the crucible was placed in the center of the furnace, and heated slowly to 300 °C in order to release H_2O . Then, the temperature was slowly raised to 960 °C and maintained 24 h to form a homogeneous melt. Subsequently, the homogeneous melt was cooled to 860 °C at a rate of 3 °C/h, and then cooled to room temperature by turning off the furnace. Thus, some colorless and transparent single crystals were obtained for the structure determination.

2.1.3. Polycrystalline Synthesis

The powder sample of CIBO was prepared by conventional solid-state reactions. A mixture of CdO, In_2O_3 , and H_3BO_3 with a molar ratio of 4:0.5:3 was grounded homogeneously in an agate mortar and transferred into a crucible placed into a programmable furnace. The mixtures were preheated at 350 °C for 10 h to decompose the boron acid, then

sintered at 850 °C and maintained for 72 h with several intermediate grindings. The pure phase of CIBO was obtained and characterized by a powder X-ray diffraction method.

2.1.4. Powder X-ray Diffraction

The Smart Lab 9 KW X-ray diffractometer was used to collect the Powder-XRD (PXRD) at room temperature. Data were collected in the 2θ ranging from 10° to 70° using monochromatized Cu-K α radiation ($\lambda = 1.5418$ Å) with a step size of 0.02° and a step time of 2 s. The theoretical XRD patterns were well agreement with experimental PXRD patterns. Mercury software was used for the simulation of the CIBO PXRD pattern.

2.1.5. Single Crystal X-ray Diffraction

A colorless single crystal suitable for the determination of the CIBO compound was mounted on a Bruker D8 Venture APEX II CCD diffractometer with Mo K α (λ = 0.71073 Å) radiation at 298(2) K. The dates were integrated by the SAINT program [50]. The crystal structure was solved by direct methods SHELXs and refined on F² by full-matrix leastsquares techniques using the program SHELXTL [51]. The structure was checked for missing symmetry elements using PLATON [52]. Details of crystal parameters, data collection, and structure refinement were listed in Table S1. The atom coordinates, the related anisotropic displacement parameters, and bond valance sums (BVSs) are listed in Tables S2 and S3 [53], and the selected bond lengths and angles are presented in Table S4.

2.1.6. Thermal Behaviors

The NETZCH STA 449F3 simultaneous analyzer was used to collect the thermal gravimetric (TG) and differential scanning calorimetry (DSC) data of CIBO. About 10 mg of CIBO samples was placed in the Pt crucibles, and heated at a rate of 5 °C/min in the range of 40–1100 °C under a nitrogen atmosphere.

2.1.7. UV-Vis-NIR Diffuse Reflectance Spectrum

The UV-Vis-NIR diffuse-reflectance data of the sample was obtained on a Hitachi UH4150 UV-vis-NIR spectrophotometer with $BaSO_4$ as the standard of 100% reflectance in the wavelength of 240–2500 nm. The reflectance spectra were converted to absorbance using the Kubelka–Munk function $F(R) = (1 - R)^2/2R = K/S$, where R, K, and S are the reflectance, absorption, and scattering, respectively [54].

2.1.8. Infrared Spectrum

The Fourier transform infrared (FTIR) spectra of CIBO were measured in the range of 4000–400 cm⁻¹ using a Nicolet iS50 Fourier transform infrared spectrometer with a smart orbit attenuated total reflectance (ATR) accessory.

2.1.9. Birefringence Measurement

Birefringence of CIBO was captured on a Nikon Eclipse polarizing microscope E200MV POL with a visible light filter. On the basis of the crystal optics, the birefringence was calculated from the following formula:

$$\mathbf{R} = (|\mathbf{N}\mathbf{e} - \mathbf{N}\mathbf{o}|) \mathbf{d} = \Delta \mathbf{n} \times \mathbf{d} \tag{1}$$

where R, Δn , and d are retardation, birefringence, and thickness, respectively [55].

2.1.10. Powder SHG Measurement

The powder second-harmonic generation (SHG) responses of CIBO were carried out on a Kurtz-NLO system with a 1064 nm Q-switched Nd: YAG laser. According the method of Kurtz and Perry, the SHG intensity was strongly dependent on the particle size of the samples, so the polycrystalline samples of CIBO and KH_2PO_4 (KDP) were ground and sieved into different particle size ranges (54–75, 76–106, 107–120, 121–150, and 151– 180μ m) and KDP served as the reference. The measurements were performed on a 1064 nm Q-switched Nd: YAG laser under the same voltage. [56]

2.1.11. Computational Method

To investigate the relationship between the electronic-structure and optical properties of CIBO. The calculations of the band structure and density of state (DOS) of CIBO were performed by CASTEP based on density functional theory (DFT) [57]. During the calculation, the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) function was selected to describe the exchange correlation energy. Under the normconserving pseudopotentials (NCP) [58], the valence electrons were set as follows: Cd- $4d^{10}5s^2$, In- $5s^25p^1$, B- $2s^22p^1$, and O- $2s^22p^4$. The kinetic energy cutoff of 850 eV and the Monk-horst Pack k-point meshes with a density of (4 × 4 × 7) points in the Brillouin zone were adopted. The cell parameters and atomic positions are optimized using the quasi-Newton method. The linear optical properties of CIBO were calculated by the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The $\varepsilon_2(\omega)$ were deduced from the matrix elements that describe the electronic transitions between the occupied and unoccupied states in the CIBO compound. Accordingly, the refractive indices and birefringence (Δ n) can be calculated.

3. Results and Discussion

3.1. Crystal Structure of CIBO

CIBO crystallizes in the monoclinic crystal system with an acentric and polar space group of *Cm*. In the asymmetric unit, CIBO contains one independent In, two Cd, six O, and two B atom(s), respectively. Two different B atoms, B(1) and B(2), coordinated three oxygen atoms to form planar BO_3 triangles with B–O bond lengths ranging from 1.330(2) to 1.390(2) Å. The B(1)O₃ and B(2)O₃ groups were almost oriented parallel to the ab plane, which contributed a large SHG effect and birefringence, as shown in Figure 1. The $In(1)^{3+}$ cations were six-fold coordinated to form an $In(1)O_6$ octahedra with bond lengths in the range of 2.110(2)–2.226(14) Å. The two types of Cd^{2+} ions, $Cd(1)^{2+}$ and $Cd(2)^{2+}$ cations, were six-fold and eight-fold coordinated to form distorted $Cd(1)O_6$ and $Cd(2)O_8$ polyhedra, respectively. For the Cd-O bonds, their bonds lengths in the range of 2.248(10)–2.801(3) Å. In the structure, $Cd(1)O_6$ and $Cd(2)O_8$ polyhedra interconnect to construct a 1D $[Cd_2O_{12}]$ double-chains via edge-sharing and corner-sharing. The In(1)O₆ polyhedra also linked with each other via corner-sharing to form the 1D [InO₆] single-chain, as shown in Figure 1a. Furthermore, the 1D $[Cd_2O_{12}]$ double-chains and $[InO_6]$ single-chain connect together by sharing common oxygen atoms to form a 3D framework with the BO_3 triangles filled in the tunnels (Figure 1b).



Figure 1. The structure of the CIBO: (**a**) The Cd–O double-chains, In–O single-chain, and the BO₃ units arrangement viewed along the c axis. (**b**) The whole 3D framework.

Structurally, CIBO was isostructural with the $Cd_4ReO(BO_3)_3$ (Re = Y, Gd, Lu), its structure can be considered as the Re³⁺ cation in $Cd_4ReO(BO_3)_3$ is replaced by the In³⁺ cations, and they all presented the classical apatite-like structure [59]. These indicated the feasibility of the substitution of In³⁺ for rare-earth cations during synthesizing new NLO

crystals. Besides, the bond valence sums results [53] were 1.871 to 2.124 for O^{2-} , 2.230 and 1.971 for Cd^{2+} , 3.031 for In^{3+} , and 2.920 and 3.124 for B^{3+} , (Table S2), which were very close to the ideal oxidation, indicating the correctness of the structure.

3.2. UV-Vis-NIR Diffuse Reflectance Spectrum

UV–vis–NIR diffuse reflectance spectrum of the synthesized polycrystalline samples was measured in the range of 240–2500 nm. It reveals that CIBO has a cut-off edge of approximately 313 nm (Figure S1), which is comparable with its isostructural compounds $Cd_4ReO(BO_3)_3$ (Re = Y, Gd, Lu) whose cut-off edges were approximately 320 nm [59]. Absorption (K/S) data were calculated from the Kubelka–Munk function and manifested that the optical band gap for CIBO was about 3.40 eV (Figure S1).

3.3. Infrared Spectrum

The Infrared Spectrum of CIBO is shown in Figure S2. The peaks at 1174 cm^{-1} and 933 cm⁻¹ can be assigned to the asymmetric stretching vibrations of the BO₃ group [60,61]. The peaks located at 707 cm⁻¹ and 583 cm⁻¹ were assigned as the bending vibrations of BO₃ groups. The assignments matched well with those of reported solids containing BO₃ groups in the literature [18,35].

3.4. Thermal Analysis

Thermal property of CIBO was performed on a TG–DSC instrument, as shown in Figure 2a. There was one endothermic peak observed at 963 °C on the DSC curve. Meanwhile, the weight loss can also be observed on the TG curve, indicating the CIBO should be an incongruently melting compound. In addition, the powder samples of CIBO were sintered at 1100 °C and cooled down to 900 °C with the rate of 10 °C/h, following a cooled to room temperature by turning off the furnace. The sample was analyzed by the XRD as shown in Figure 2b, which was completely different form the simulated one, further indicating that the compound melts incongruently around 963 °C. Thus, the CIBO single crystals must be grown using the flux growth technique.



Figure 2. (a) Thermal gravimetric (TG) and differential scanning calorimetry (DSC) curves of CIBO (b) XRD patterns of simulation, experiment, and after melting for CIBO.

3.5. Birefringence Measurements

The birefringence of CIBO was performed on a cross-polarizing microscope. As shown in Figure 3a, the observed interference color in cross-polarized light were the III-order green. According to the Michel–Levy chart, the retardation (R value) for CIBO was 1350 nm and its crystal thickness was measured as 18.1 μ m [62,63]. Thus, the birefringence of CIBO in the visible region can be calculated as 0.075 based on Equation (1) [55]. Furthermore, the birefringence of CIBO was also executed based on the theoretical calculation and the calculated result shows that CIBO exhibited a relatively large birefringence of about 0.077@1064 nm (Figure 3b). The experimental value was consistent with the calculated one and greater than that of Cd₅(BO₃)₃Cl (0.054@1064 nm) [64], Ca₄YO(BO₃)₃ (0.043@589 nm) [65], and $Ca_5(BO_3)_3F$ (0.043@589 nm) [65]. The large birefringence of CIBO was beneficial to phase



Figure 3. (a) The interference color observed for CIBO. (b) Birefringence curve of CIBO.

3.6. Nonlinear Optical Properties

matching in the transparent region.

CIBO crystallizes in the NCS space group of *Cm*, so its NLO properties at 1064 nm fundamental light irradiation were also performed. As shown in Figure 4, the SHG effects become larger with the increasing particles size of the CIBO powders, which suggested that the CIBO is phase-matching according to the rule proposed by Kurtz and Perry [56,66,67]. CIBO has a powder SHG effect about three times of KDP. According to the anionic-group theory [68], the SHG response of NLO materials primary attributes to the anionic group, so the BO₃ groups play a key role in the structure [69]. As show in Figure 1b, the arrangement of the BO₃ units is approximately parallel to the (001) plane, which contributed to the large SHG effect. Additionally, the number density of BO₃ triangles (n/V) was 0.0144 per unit volume for CIBO, which was comparable to those of the reported Cd borates nonlinear optical material, such as $CdZn_2(BO_3)_2$ (0.0082 per unit volume) [70], and $Zn_3Cd_3(BO_3)_4$ (0.016 per unit volume) [71].



Figure 4. (a) Phase–matching curves for CIBO at 1064 nm and KDP (KH_2PO_4) serving as a benchmark sample. (b) The SHG (second harmonic generation) signals at 150–180 μ m particle sizes.

The dipole moment calculation of CIBO was also calculated by the bond valence model [72]. The CdO_n (n = 6, 8) polyhedra and BO₃ units were performed, respectively. As shown in Table S5, the total net dipole moment of BO₃ groups in the unit cell yield 1.025 Debey (D), which is approximately 54.45% of its optimal value. Meanwhile, the Cd-O polyhedra also contributes to the dipole moment of 0.878 D. Therefore, the synergistic effects of the NLO-active BO₃ groups and the d^{10} Cd²⁺ cations in CIBO endowed the material with a large SHG effect, which is comparable with LiB₃O₅ [60] and Cd₅(BO₃)₃F [73].

3.7. Electronic Structure

Theoretical calculations of CIBO were carried out by the plane-wave pseudopotential method performed on the CASTEP package based on the density functional theory [57].

CIBO exhibited an indirect band gap of 1.68 eV, as shown in Figure 5a, which was smaller than the experimental values because of the limitation of the GGA–PBE function [74]. Figure 5b shows that the density of states (DOS) and partial DOS of CIBO, which presented that the top of the valence band was mainly made up of the Cd-4d, O-2p orbitals with a mix of B-2p orbitals. The bottom of the conduction band mainly originates from the B-2p and O-2p orbitals. Therefore, the optical properties of CIBO mainly originate from the synergistic effect of BO₃ groups and the d^{10} cation Cd²⁺.



Figure 5. Electronic properties of CIBO: (a) Band structure; (b) total and partial DOS (density of states).

4. Conclusions

In conclusion, a new NLO material CIBO was reported. The title compound exhibited a 3D framework composed of CdO₆, CdO₈, and InO₆ polyhedra where the B atoms are located in the tunnels. CIBO exhibits a large SHG response about three times that of KDP and a moderate birefringence of 0.077@1064 nm, which mainly originated from the well arrangement and high density of BO₃ groups, as well as the d^{10} Cd²⁺ cation. The IR and UV–Vis–IR diffuse reflectance spectra indicated that CIBO possess BO₃ groups and a wide transparent region, respectively. TG–DSC manifests that the CIBO has good thermal stability up to 963 °C. We hope that these findings will shed valuable information on the development of new NLO materials.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/cryst12020266/s1. Figure S1: UV–Vis–NIR diffuse reflectance spectroscopy of CIBO. Figure S2: IR Spectroscopy of CIBO. Table S1: Crystal data and structure refinement for CIBO. Table S2: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for CIBO. Table S3: Bond lengths (Å) for CIBO. Table S4: Bond angles (°) for CIBO. Table S5. Dipole moments of BO₃ and CdO_n (n = 6, 8) polyhedra in the unit cell. Table S6: The assignments of the Infrared absorption peaks for CIBO.

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