

NaRb₆(B₄O₅(OH)₄)₃(BO₂) Featuring Noncentrosymmetry, Chirality, and the Linear Anionic Group BO₂[−]

Fenghua Ding, Kent J. Griffith, Weiguo Zhang, Shaoxin Cui, Chi Zhang, Yiran Wang, Kendall Kamp, Hongwei Yu, P. Shiv Halasyamani, Zhihua Yang, Shilie Pan, and Kenneth R. Poeppelmeier*



Cite This: *J. Am. Chem. Soc.* 2023, 145, 4928–4933



Read Online

ACCESS |



Metrics & More



Article Recommendations



Supporting Information

ABSTRACT: Noncentrosymmetric (NCS) structures are of particular interest owing to their symmetry-dependent physical properties, e.g., pyroelectricity, ferroelectricity, piezoelectricity, and nonlinear optical (NLO) behavior. Among them, chiral materials exhibit polarization rotation and host topological properties. Borates often contribute to NCS and chiral structures via their triangular [BO₃] and tetrahedral [BO₄] units and their numerous superstructure motifs. However, no chiral compound with the linear [BO₂] unit has been reported to date. Herein, an NCS and chiral mixed-alkali-metal borate, NaRb₆(B₄O₅(OH)₄)₃(BO₂), with a linear BO₂[−] unit in the structure was synthesized and characterized. The structure features a combination of three types of basic building units (BBUs), [BO₂], [BO₃], and [BO₄] with sp-, sp²-, and sp³-hybridization of boron atoms, respectively. It crystallizes in the trigonal space group R32 (No. 155), one of the 65 Sohncke space groups. Two enantiomers of NaRb₆(B₄O₅(OH)₄)₃(BO₂) were found, and their crystallographic relationships are discussed. These results not only expand the small family of NCS structures with the rare linear BO₂[−] unit but also prompt recognition to the fact that NLO materials have generally overlooked the existence of two enantiomers in achiral Sohncke space groups.

Centric coordination environments of anions are often leveraged for the design and synthesis of NLO crystals.^{1–3} Examples include distorted octahedral groups (e.g., TiO₆),^{4,5} rigid tetrahedral groups, (e.g., BO_{4–x}F_x^{(5–x)–} ($x = 1, 2, 3, 4$),^{6–11} PO_{4–x}F_x^{(3–x)–} ($x = 1, 2$)^{12,13}), and π -conjugated planar groups (e.g., BO₃^{3–}, CO₃^{2–}, NO₃[–], and C₃N₃O₃^{3–}).^{14–16} From a structure–property relationship perspective, these distorted three-dimensional groups and planar groups contribute a large microscopic second-order susceptibility,^{16–25} which is desirable for second-harmonic generation (SHG). Birefringence is another important parameter for NLO materials since proper birefringence is essential for the phase-matching of a crystal. A lower dimensional group is believed to have larger birefringence compared to a higher dimensional group, e.g., [BO₃] > [BO₄] due to larger polarizability anisotropy from the structure–property point of view.²⁶ With the report on the structure of K₅Ba₂(B₁₀O₁₇)₂(BO₂),²⁶ the linear group [BO₂] (sp-hybridization) was calculated to possess enhanced polarizability and moderate HOMO–LUMO gap compared with [BO₃] and [BO₄] units (sp²- and sp³-hybridization, respectively).²⁷ This inspires a new direction to enrich the structural diversity of the borate family of NLO materials. While nearly 1000 anhydrous borates have been reported, and the number is still growing,²⁸ there are very few reported borates containing [BO₂] units. These compounds include several apatite-type structures {M_{9+y}Na_x(PO₄)₆B_{x+2y}O₂ (M = Ca or Sr),²⁹ Sr₇La₃[(PO₄)_{2.5}(SiO₄)₃(BO₄)_{0.5}](BO₂),³⁰ and Sr₁₀[(PO₄)_{5.5}(BO₄)_{0.5}](BO₂)³¹} as well as Gd₄(BO₂)O₅F³² and K₅Ba₂(B₁₀O₁₇)₂(BO₂).²⁶ Moreover, none of these reported compounds adopt a noncentrosymmetric (NCS) point group (or space group).^{1,33,34} Therefore, synthesizing

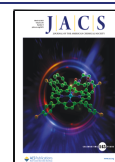
NCS structures featuring [BO₂] is a promising direction to push the boundaries of borate chemistry and NLO materials.

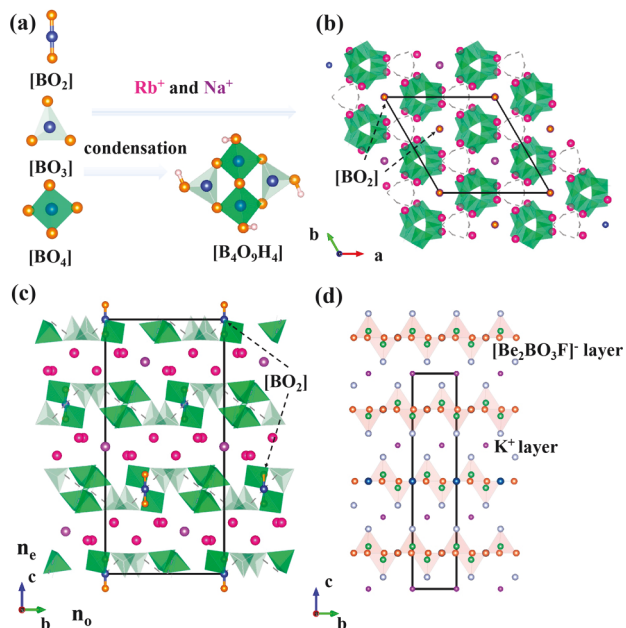
From the synthetic point of view, low-temperature methods favor a phase with low symmetry and low enthalpy. At the same time, high-temperature processes tend to form a solid phase with high symmetry and high entropy. The hydrothermal/solvothermal method possesses the advantage of relatively lower temperatures and has been widely used to synthesize NCS structures.^{35–37} Herein, we reported the first synthetic NCS borate, NaRb₆(B₄O₅(OH)₄)₃(BO₂), containing the rare linear BO₂[−] unit. Single crystals of the compound were grown by the solvothermal method and both enantiomers of the chiral structure were identified. Nonlinear and linear optical properties of the compound were characterized and the birefringence was calculated with DFT.

Single crystals of NaRb₆(B₄O₅(OH)₄)₃(BO₂) were synthesized by a solvothermal method (see more details in the Supporting Information). A representative bulk crystal is shown in Figure S1. The crystal structure of NaRb₆(B₄O₅(OH)₄)₃(BO₂) was determined with single-crystal X-ray diffraction. The crystal data and structure refinement are listed in Table S1. The measured powder XRD patterns of NaRb₆(B₄O₅(OH)₄)₃(BO₂) confirmed the phase purity of the crystalline fraction of the samples (see

Received: November 14, 2022

Published: February 22, 2023

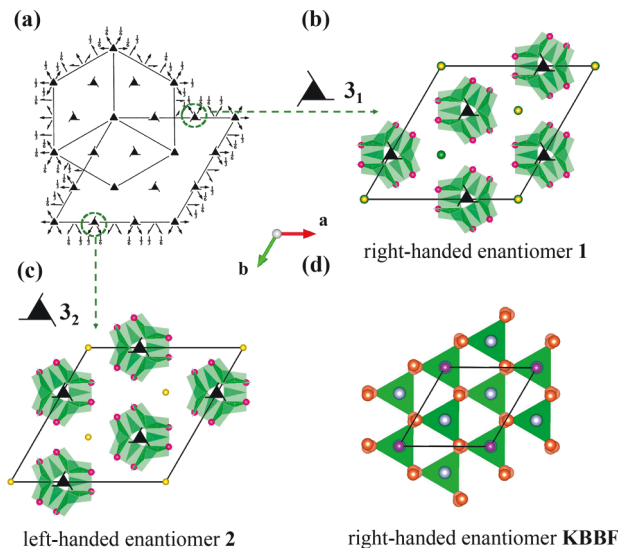


[illegible][illegible]

1. 本報告係根據本公司及子公司於民國 102 年 12 月 31 日止，依證券交易法第 36 條之規定，編製之財務報告，業經會計師查核竣事，除已將查核報告刊登於 103 年 3 月 10 日之公開資訊觀開系統外，並刊登於 103 年 3 月 10 日之公開資訊觀開系統，特此公告。

[illegible][illegible][illegible]

В соответствии с требованиями к содержанию отчета о деятельности организации, в котором должны быть указаны все существенные факты, влияющие на финансовое положение, результаты деятельности и денежные потоки организации, в том числе факты, влияющие на понимание заинтересованными сторонами деятельности организации, в отчете о деятельности организации за 2023 год, в частности, в разделе «Сведения об организации» и в разделе «Сведения об управлении организацией» раскрыты следующие сведения:

[illegible]

2019 年 12 月 31 日，公司总资产为 1,000,000,000.00 元，净资产为 500,000,000.00 元，营业收入为 1,200,000,000.00 元，净利润为 100,000,000.00 元。2020 年 1 月 1 日，公司总资产为 1,100,000,000.00 元，净资产为 550,000,000.00 元，营业收入为 1,300,000,000.00 元，净利润为 110,000,000.00 元。2020 年 2 月 1 日，公司总资产为 1,200,000,000.00 元，净资产为 600,000,000.00 元，营业收入为 1,400,000,000.00 元，净利润为 120,000,000.00 元。2020 年 3 月 1 日，公司总资产为 1,300,000,000.00 元，净资产为 650,000,000.00 元，营业收入为 1,500,000,000.00 元，净利润为 130,000,000.00 元。2020 年 4 月 1 日，公司总资产为 1,400,000,000.00 元，净资产为 700,000,000.00 元，营业收入为 1,600,000,000.00 元，净利润为 140,000,000.00 元。2020 年 5 月 1 日，公司总资产为 1,500,000,000.00 元，净资产为 750,000,000.00 元，营业收入为 1,700,000,000.00 元，净利润为 150,000,000.00 元。2020 年 6 月 1 日，公司总资产为 1,600,000,000.00 元，净资产为 800,000,000.00 元，营业收入为 1,800,000,000.00 元，净利润为 160,000,000.00 元。2020 年 7 月 1 日，公司总资产为 1,700,000,000.00 元，净资产为 850,000,000.00 元，营业收入为 1,900,000,000.00 元，净利润为 170,000,000.00 元。2020 年 8 月 1 日，公司总资产为 1,800,000,000.00 元，净资产为 900,000,000.00 元，营业收入为 2,000,000,000.00 元，净利润为 180,000,000.00 元。2020 年 9 月 1 日，公司总资产为 1,900,000,000.00 元，净资产为 950,000,000.00 元，营业收入为 2,100,000,000.00 元，净利润为 190,000,000.00 元。2020 年 10 月 1 日，公司总资产为 2,000,000,000.00 元，净资产为 1,000,000,000.00 元，营业收入为 2,200,000,000.00 元，净利润为 200,000,000.00 元。2020 年 11 月 1 日，公司总资产为 2,100,000,000.00 元，净资产为 1,050,000,000.00 元，营业收入为 2,300,000,000.00 元，净利润为 210,000,000.00 元。2020 年 12 月 1 日，公司总资产为 2,200,000,000.00 元，净资产为 1,100,000,000.00 元，营业收入为 2,400,000,000.00 元，净利润为 220,000,000.00 元。2020 年 12 月 31 日，公司总资产为 2,300,000,000.00 元，净资产为 1,150,000,000.00 元，营业收入为 2,500,000,000.00 元，净利润为 230,000,000.00 元。

$O(\frac{1}{\epsilon})$ iterations. For each iteration, we first sample n points $\{x_i\}_{i=1}^n$ from $\mathcal{X}$ and n points $\{y_i\}_{i=1}^n$ from $\mathcal{Y}$. Then, we compute the empirical covariance matrix $\hat{\Sigma} = \frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})(x_i - \bar{x})^T + \frac{1}{n} \sum_{i=1}^n (y_i - \bar{y})(y_i - \bar{y})^T$, where $\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i$ and $\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i$. We then compute the eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_d$ of $\hat{\Sigma}$ and the corresponding eigenvectors $v_1, v_2, \dots, v_d$. We then compute the principal components $z_i = v_i^T (x_i - \bar{x})$ for $i = 1, 2, \dots, d$. Finally, we compute the principal component scores $\{z_i\}_{i=1}^d$ for each point x_i .

Figure 1 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

Figure 2 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

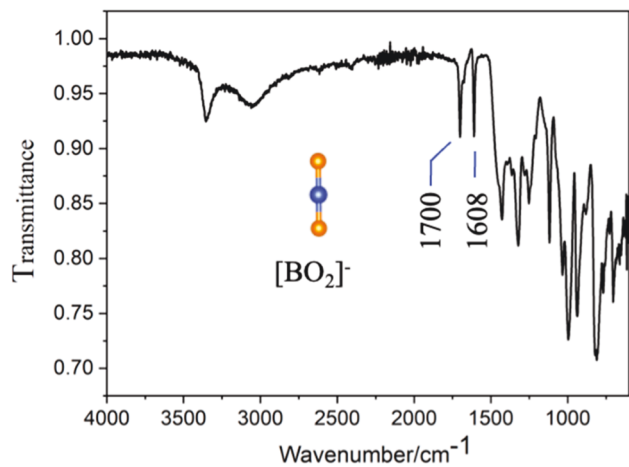


Figure 1. Calculated IR spectrum of the BO_2^- ion.

Figure 2 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

Figure 3 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

Figure 4 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

Figure 5 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

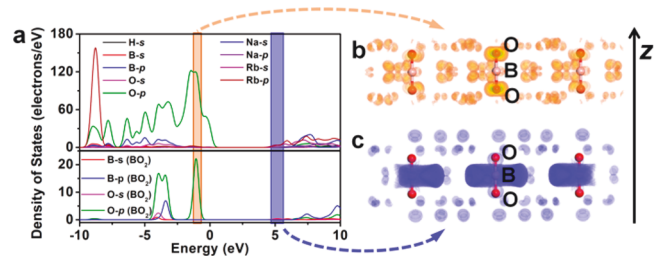


Figure 6. Calculated IR spectrum of the BO_2^- ion.

Figure 7 shows the calculated IR spectra of the BO_2^- ion. The x-axis represents the wavenumber in cm^{-1} , ranging from 4000 to 1000. The y-axis represents the transmittance, ranging from 0.70 to 1.00. The spectrum shows several characteristic absorption bands, with prominent peaks at 1700 and 1608 cm^{-1} . An inset shows the chemical structure of the BO_2^- ion, consisting of a central boron atom bonded to two oxygen atoms in a linear arrangement.

- (40) Sang, Y.; Yu, D.; Avdeev, M.; Piltz, R.; Sharma, N.; Ye, N.; Liu, H.; Wang, J. X-ray and neutron diffraction studies of flux and hydrothermally grown nonlinear optical material $\text{KBe}_2\text{BO}_3\text{F}_2$. *CrystEngComm*. **2012**, *14*, 6079–6084.
- (41) Nespolo, M.; Aroyo, M. I.; Souvignier, B. Crystallographic shelves: space-group hierarchy explained. *J. Appl. Crystallogr.* **2018**, *51*, 1481–1491.
- (42) Fecher, G. H.; Kübler, J.; Felser, C. Chirality in the Solid State: Chiral Crystal Structures in Chiral and Achiral Space Groups. *Mater.* **2022**, *15*, 5812.
- (43) Nespolo, M.; Benahsene, A. H. Symmetry and chirality in crystals. *J. Appl. Crystallogr.* **2021**, *54*, 1594.
- (44) Kopsky, V. c.; Litvin, D. B. *International tables for crystallography*. Wiley Online Library: 2010.
- (45) Mei, L.; Huang, X.; Wang, Y.; Wu, Q.; Wu, B.; Chen, C. Crystal structure of $\text{KBe}_2\text{BO}_3\text{F}_2$. *Z. Kristallogr. Cryst. Mater.* **1995**, *210*, 93–95.
- (46) Zhang, W.; Wei, Z.; Yang, Z.; Pan, S. Cation modulation on the crystal structure and band gap of fluorooxoborates $\text{A}_3\text{B}_3\text{O}_3\text{F}_6$ (A = alkali and mixed alkali metal). *Inorg. Chem.* **2019**, *58*, 13411–13417.
- (47) Brese, N.; O'keeffe, M. Bond-valence parameters for solids. *Acta Crystallogr. B* **1991**, *47*, 192–197.
- (48) Sohncke, L. *Entwicklung einer Theorie der Krystallstruktur*; Teubner, B. G.; Leipzig, 1879.
- (49) Müller, U. *Symmetry relationships between crystal structures: applications of crystallographic group theory in crystal chemistry*; OUP Oxford, 2013.

Recommended by ACS

$\text{Ba}_{1.09}\text{Pb}_{0.91}\text{Be}_2(\text{BO}_3)_2\text{F}_2$: The First Pb-Containing Beryllium Borate Fluoride with Trigonal Prismatic PbO_6 and 2D $[\text{Be}_3\text{B}_3\text{O}_6\text{F}_3]_\infty$ Layers

Ruixin Guo, Xiaoyang Wang, *et al.*

FEBRUARY 20, 2023
INORGANIC CHEMISTRY

READ 

$\text{C}(\text{NH}_2)_3(\text{I}_3\text{O}_8)(\text{HI}_3\text{O}_8)(\text{H}_2\text{I}_2\text{O}_6)(\text{HIO}_3)_4 \cdot 3\text{H}_2\text{O}$: An Unprecedented Asymmetric Guanidinium Polyiodate with a Strong Second-Harmonic-Generation Response and a Wi...

Dong Yan, Shu-Fang Li, *et al.*

JANUARY 19, 2023
INORGANIC CHEMISTRY

READ 

Strain-Driven Solid–Solid Crystal Conversion in Chiral Hybrid *Pseudo*-Perovskites with Paramagnetic-to-Ferromagnetic Transition

Haining Zheng, Kian Ping Loh, *et al.*

FEBRUARY 02, 2023
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

Inversion of Molecular Chirality Associated with Ferroelectric Switching in a High-Temperature Two-Dimensional Perovskite Ferroelectric

Wen-Feng Deng, Jun Tao, *et al.*

FEBRUARY 24, 2023
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

Get More Suggestions >