JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Communication

$NaRb_6(B_4O_5(OH)_4)_3(BO_2)$ Featuring Noncentrosymmetry, Chirality, and the Linear Anionic Group BO_2^-

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Cite This: J. Am. Chem. Soc. 2023, 145, 4928–4933
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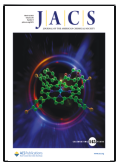
ABSTRACT: Noncentrosymmetric (NCS) structures are of particular interest owing to their symmetry-dependent physical properties, e.g., pyroelectricity, ferroelectricity, piezoelectricity, and nonlinear optical (NLO) behavior. Among them, chiral materials exhibit polarization rotation and host topological properties. Borates often contribute to NCS and chiral structures via their triangular [BO_3] and tetrahedral [BO_4] units and their numerous superstructure motifs. However, no chiral compound with the linear [BO_2] unit has been reported to date. Herein, an NCS and chiral mixed-alkali-metal borate, $NaRb_6(B_4O_5(OH)_4)_3(BO_2)$, with a linear BO_2^- unit in the structure was synthesized and characterized. The structure features a combination of three types of basic building units (BBUs), [BO_2], [BO_3], and [BO_4] with sp-, sp^2-, and sp^3-hybridization of boron atoms, respectively. It crystallizes in the trigonal space group *R*32 (No. 155), one of the 65 Sohncke space groups. Two enantiomers of $NaRb_6(B_4O_5(OH)_4)_3(BO_2)$ were found, and their crystallographic relationships are discussed. These results not only expand the small family of NCS structures with the rare linear BO_2^- unit but also prompt recognition to the fact that NLO materials have generally overlooked the existence of two enantiomers in achiral Sohncke space groups.

Acentric coordination environments of anions are often leveraged for the design and synthesis of NLO crystals.[1−3] Examples include distorted octahedral groups (e.g., TiO_6),[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., BO_3^{3-}, CO_3^{2-}, NO_3^-, and $C_3N_3O_3^{3-}$).[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., [BO_3] > [BO_4] due to larger polarizability anisotropy from the structure−property point of view.[26] With the report on the structure of $K_5Ba_2(B_{10}O_{17})_2(BO_2)$,[26] the linear group [$BO_2$] (sp-hybridization) was calculated to possess enhanced polarizability and moderate HOMO−LUMO gap compared with [BO_3] and [BO_4] units (sp^2- and sp^3-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 [BO_2] units. These compounds include several apatite-type structures $\{M_{9+y}Na_x(PO_4)_6B_{x+2y}O_2$ (M = Ca or Sr),[29] $Sr_7La_3[(PO_4)_{2.5}(SiO_4)_3(BO_4)_{0.5}](BO_2)$,[30] and $Sr_{10}[(PO_4)_{5.5}(BO_4)_{0.5}](BO_2)$[31]$\}$ as well as $Gd_4(BO_2)O_5F$[32] and $K_5Ba_2(B_{10}O_{17})_2(BO_2)$.[26] Moreover, none of these reported compounds adopt a noncentrosymmetric (NCS) point group (or space group).[1,33,34] Therefore, synthesizing NCS structures featuring [BO_2] 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, $NaRb_6(B_4O_5(OH)_4)_3(BO_2)$, containing the rare linear BO_2^- 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 $NaRb_6(B_4O_5(OH)_4)_3(BO_2)$ 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 $NaRb_6(B_4O_5(OH)_4)_3(BO_2)$ 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 $NaRb_6(B_4O_5(OH)_4)_3(BO_2)$ confirmed the phase purity of the crystalline fraction of the samples (see

Received: November 14, 2022
Published: February 22, 2023



https://doi.org/10.1021/jacs.2c12069
J. Am. Chem. Soc. 2023, 145, 4928−4933

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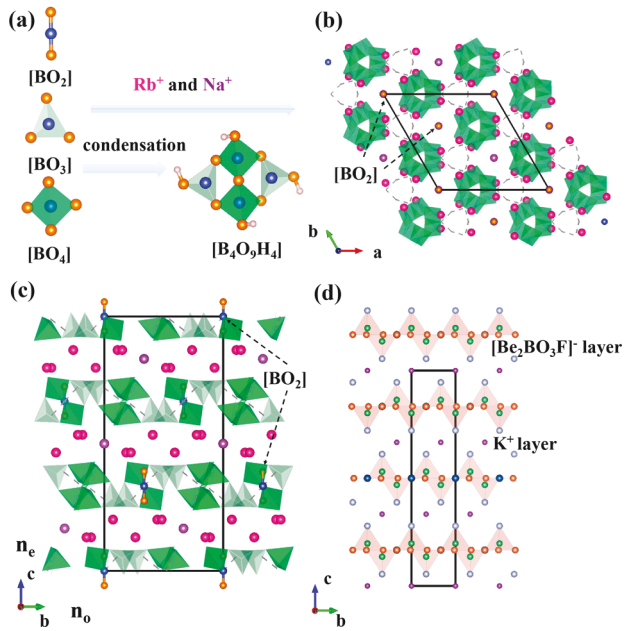
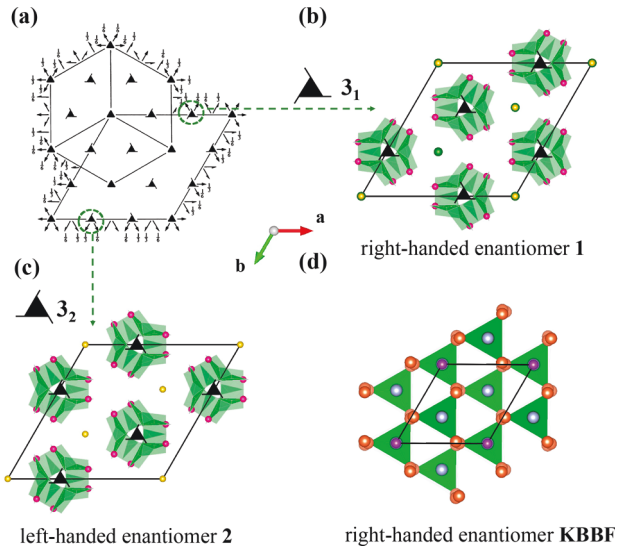
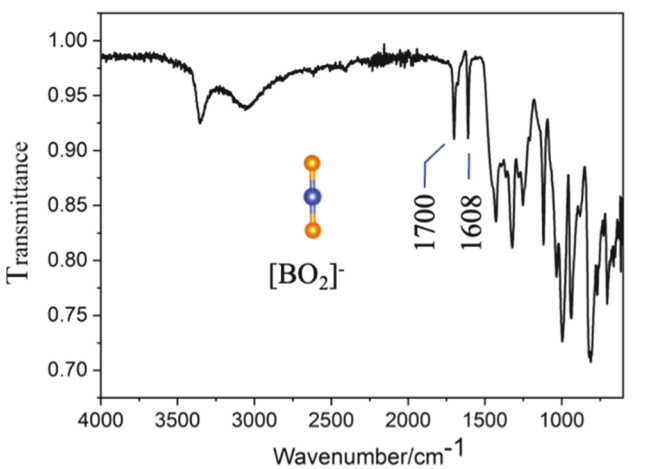

(a)
[BO2]
Rb+ and Na+
condensation
[BO3]
[BO4]
[B4O9H4]
(b)
[BO2]
b
a
(c)
[BO2]
ne
c
b
no
(d)
[Be2BO3F]- layer
K+ layer
c
b

[illegible]


(a)
(b)
31
a
b
right-handed enantiomer 1
(c)
32
(d)
left-handed enantiomer 2
right-handed enantiomer KBBF

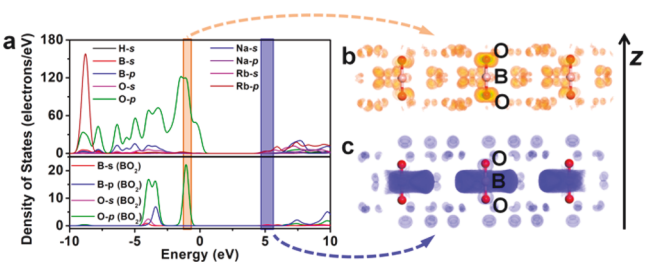
[illegible]

[illegible]


1.00
0.95
0.90
0.85
0.80
0.75
0.70
Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumber/cm-1
1700
1608
[BO2]-

[illegible]

[illegible]


a
b
c
z
O
B
O
H-s
B-s
B-p
O-s
O-p
Na-s
Na-p
Rb-s
Rb-p
B-s (BO2)
B-p (BO2)
O-s (BO2)
O-p (BO2)
Density of States (electrons/eV)
Energy (eV)

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

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[illegible]

[illegible]

[illegible]

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J. Am. Chem. Soc. 2023, 145, 4928−4933