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Na₂PbB₆O₁₀SO₄ and Ca_{2.58}Pb_{0.42}B₆O₁₁SO₄: first borate–sulfates featuring 3D porous borate anionic frameworks†

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This study presents two new borate–sulfate compounds, Na₂PbB₆O₁₀SO₄ (I) and Ca_{2.58}Pb_{0.42}B₆O₁₁SO₄ (II). Both crystals form unique three-dimensional (3D) porous frameworks ³[B₆O₁₀]_∞ and ³[B₇O₁₃]_∞, composed of fundamental building blocks [B₆O₁₃] and [B₇O₁₇], respectively, with [SO₄] units embedded within the pores. These examples represent the first observation of 3D borate frameworks in borate–sulfates, thus expanding the structural diversity of borate–sulfate compounds. The relationship between the structure and birefringence was studied using first-principles calculations. This study uncovers new insights into the connectivity and structural properties of borate–sulfates.

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1. Introduction

Borates have attracted considerable scientific attention due to their remarkable structural diversity and exceptional optical properties.^{1–16} This structural diversity arises from the versatile coordination of the boron atom, which can form [BO₂], [BO₃], and [BO₄] units with two, three, or four oxygen atoms, respectively.^{17–28} These basic units can exist in isolation or assemble into complex fundamental building blocks (FBBs), which further polymerize into diverse borate structures, including 0D clusters, 1D chains, 2D layers, and 3D frameworks.^{29–34} From the perspective of optical properties, the B–O groups are characterized by a large HOMO–LUMO gap and are beneficial for developing ultraviolet (UV) materials with wide band gaps.³⁵ Specifically, the π-conjugated [BO₃] groups, known for their high hyperpolarizability and pronounced polarizability anisotropy, are highly desirable components for designing nonlinear optical (NLO) and birefringent materials.^{36–38}

In the realm of mixed anionic compounds, borosulfates and borate–sulfates are characterized by their rich structural chemistry and fascinating physicochemical properties.^{39–43} Borosulfates are characterized by condensed tetrahedral [BO₄] and [SO₄] units interconnected through B–O–S linkages, forming oxoanionic frameworks that resemble silicates.^{44–48} Since the first synthesis of K₅[B(SO₄)₄]⁴⁸ in 2012, over 50 borosulfates have been reported. In contrast, in borate–sulfates, the borate anions and sulfate anions are not directly connected.^{41,42,49–51} To the best of our knowledge, only 26 borate–sulfates have been identified (as summarized in Table S1†). As shown in Fig. 1, the S–O groups in borate–sulfates exist as isolated [SO₄] units, while the B–O groups can form isolated [BO₃] or [BO₄] units, one-dimensional B–O chains, or two-dimensional B–O layers. To date, no borate–sulfates with three-dimensional B–O frameworks have been reported.

Owing to the limited systematic exploration of structure–property relationships in borate–sulfates, expanding this family of compounds and uncovering their unique features are essential. In this study, we report two new borate–sulfate compounds, Na₂PbB₆O₁₀SO₄ (I) and Ca_{2.58}Pb_{0.42}B₆O₁₁SO₄ (II). These compounds represent the first reported examples of borate–sulfates featuring 3D porous borate anionic frameworks (structurally porous frameworks with crystallographically defined channels). The unique structures of the two compounds, as well as their structural changes, are thoroughly discussed. Pure phases were obtained, and their thermal, infrared, and UV-Vis-NIR diffuse reflectance spectroscopy properties were comprehensively characterized. First-principles calculations were employed to systematically analyze the optical properties of these compounds, revealing the intrinsic

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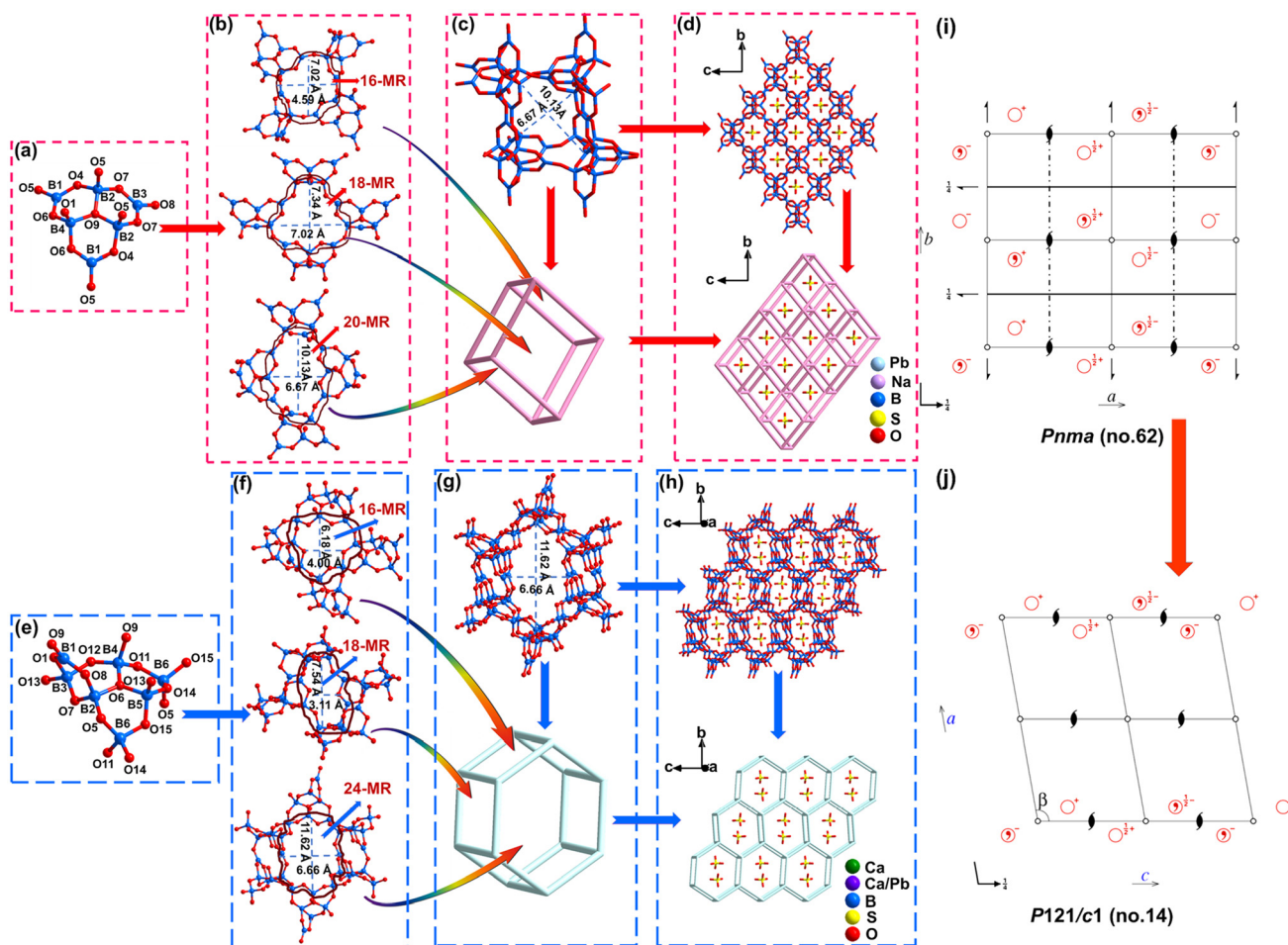


Fig. 2 (a and e) The $[B_6O_{13}]$ and $[B_7O_{17}]$ FBBs of structures I and II; (b and f) 16-, 18-, and 20-MRs formed by $[B_6O_{13}]$ in I; 16-, 18-, and 24-MRs formed by $[B_7O_{17}]$ in II; (c and g) frameworks constructed from interconnected ring structures in I and II; (d and h) view of the topology network in I and II; (i and j) spatial symmetry operation change from I [high symmetry $Pnma$ (no. 62)] to II [low symmetry $P2_1/c$ (no. 14)].

Each $[B_7O_{17}]$ unit acts as a 5-connected node, linking to five neighboring clusters *via* shared O atoms (Fig. 2g). The resulting 3D framework adopts a *pcu* topology with the Schläfli symbol $(4^6 \cdot 6^4)$ (Fig. 2g). Furthermore, the $[B_7O_{17}]$ FBBs form a 3D structure of ${}^3\infty[B_7O_{13}]$ through the sharing of O atoms.

These linkages create a unique 3D porous borate anionic framework with open pores along the *bc* directions (Fig. 2h). The $[SO_4]^{2-}$ ions are embedded within the porous structure (Fig. 2h). The B–O bond lengths within the $[BO_3]$ triangles range from 1.353(3) to 1.369(3) Å, while those in the $[BO_4]$ tetrahedra range from 1.420(3) to 1.574(3) Å. The S–O bond lengths within the $[SO_4]$ tetrahedra vary from 1.4611(18) to 1.4861(19) Å. The O–B–O bond angles span from 102.36(17) to 120.8(2)°, while the O–S–O bond angles range from 107.40(10) to 111.89(12)°. The coordination environments of the Ca and Pb cations are shown in Fig. S2b of the ESI.† The Ca–O bond lengths range from 2.2844(15) to 2.877(2) Å, while the Pb–O bond lengths range from 2.4921(16) to 2.7899(19) Å. BVS calculations confirm the oxidation states of O, B, S, Pb, and Ca as -2 , $+3$, $+6$, $+2$, and $+2$, respectively, as summarized in Table S3

of the ESI.† and these oxidation states are consistent with the known oxidation states. Selected bond lengths and angles are provided in Table S4 of the ESI.†

3.2 Comparative structural analysis of compounds I and II

The structural comparison between I and II is primarily driven by the substitution of Na^+ with Ca^{2+} , resulting in significant changes in the crystal framework. Owing to the difference in cations, the structural comparison between I and II reveals a reduction in the symmetry of the space group, shifting from a higher-symmetry group ($Pnma$) to a lower-symmetry group ($P2_1/c$) (Fig. 2i and j). The Na^+ cations, with shorter coordination bonds (2.295–2.710 Å), support a compact and ordered framework.

In contrast, II incorporates Ca^{2+} , which exhibits stronger and more flexible coordination (Ca–O bond lengths: 2.284–2.877 Å), facilitating the formation of larger and more complex $[B_7O_{17}]$ clusters. The Ca^{2+} -driven transition also results in a shift from a 6-connected to 5-connected topology, along with longer B–O and S–O bond lengths and wider O–B–

O bond angles. Overall, the transition from **I** to **II** is attributed to the higher charge density and larger coordination capacity of Ca^{2+} , which enables increased structural flexibility, the formation of more complex clusters, and reorganization of the 3D porous borate anionic framework. This comparison highlights the critical role of cation substitution in tuning crystal topology and framework properties.

3.3 Characterization

Elemental analysis by energy-dispersive X-ray spectroscopy (EDS) revealed the presence of Na, Pb, B, S, and O in compound **I** and Ca, Pb, B, S, and O in compound **II** (see ESI Fig. S3a and b†). The purity of the polycrystalline sample was confirmed using powder XRD analysis (Fig. 3a and b). The IR spectra were recorded to confirm the coordination environment of B and S atoms, suggesting the presence of triangular $[\text{BO}_3]$, tetrahedral $[\text{BO}_4]$, and $[\text{SO}_4]$ groups. The absence of vibration bands near 3500 cm^{-1} confirms that hydroxyl groups are not present in the structure (Fig. 3c and d; Table S5†). Based on previous studies,^{46,53} the asymmetric (ν_{asym}) and symmetric (ν_{sym}) stretching vibrations of the $[\text{BO}_3]$ units are detected at $1300\text{--}1531$ and $910\text{--}945\text{ cm}^{-1}$, respectively. The vibrational peaks at $805\text{--}871$ and $528\text{--}592\text{ cm}^{-1}$ are attributed to the out-of-plane bending $[\delta(\text{O-B-O})]$ modes of the $[\text{BO}_3]$ groups. The ν_{sym} of the $[\text{BO}_4]$ tetrahedra are observed between 1103 and 1130 cm^{-1} . The very strong band at around $1195\text{--}1200\text{ cm}^{-1}$ can be ascribed to the ν_{asym} of the $[\text{SO}_4]$ units. The ν_{sym} of the $[\text{SO}_4]$ units are observed at around $505\text{--}509\text{ cm}^{-1}$. Detailed peak assignments for the IR spectra are provided in Table S5 of the ESI.† Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis was performed to study the thermal behavior. The results show that **I** and **II**

are thermally stable up to 610 and $750\text{ }^\circ\text{C}$, respectively. Beyond these temperatures, decomposition occurs, accompanied by significant weight loss. This decomposition corresponds to the endothermic peaks at 640 and $774\text{ }^\circ\text{C}$ on the DSC curves (Fig. 3e and f). Therefore, **I** and **II** exhibit excellent thermal stability below 640 and $774\text{ }^\circ\text{C}$, making them suitable for use in a wide range of thermal applications. The UV-Vis-NIR spectra of compounds **I** and **II** show absorption ranges of $270\text{--}1200\text{ nm}$ and $300\text{--}1200\text{ nm}$, respectively. Fig. S4a and b† indicate that the UV cut-off edges are below 270 nm for **I** (with 5% reflectance) and below 300 nm for **II** (with 47% reflectance).

3.4 First-principles calculations

The electronic structures and optical properties were calculated by the first-principles method for **I** and **II**.

The band structure calculations performed using the generalized gradient approximation (GGA)⁵⁴ show a direct bandgap of 4.83 eV for **I** and an indirect bandgap of 4.48 eV for **II**, respectively (Fig. 4a and b). From the total and partial densities of states (DOS and PDOS) of **I** (Fig. 4c), the highest states of the valence bands (VBs) are primarily dominated by O 2p orbitals, while the lowest states of the conduction bands (CBs) are mainly derived from B 2p and Pb 6p orbitals, with a minor contribution from Na 3s and 3p orbitals. In the vicinity of the Fermi level in **II** (Fig. 4d), O 2p mostly occupies the VBs, while B 2p and Pb 6p orbitals dominate the CBs; additionally, the Ca 3d and S 3p orbitals contribute a minor portion. As O 2p and B 2p orbitals have apparent interactions in the VB and CB regions, it can be concluded that the band gap and linear optical performance are determined by the B-O framework in **I** and **II**.



Fig. 3 Performance of **I** and **II**. (a and b) Experimental and calculated XRD patterns; (c and d) IR spectra; (e and f) TG-DSC curves.

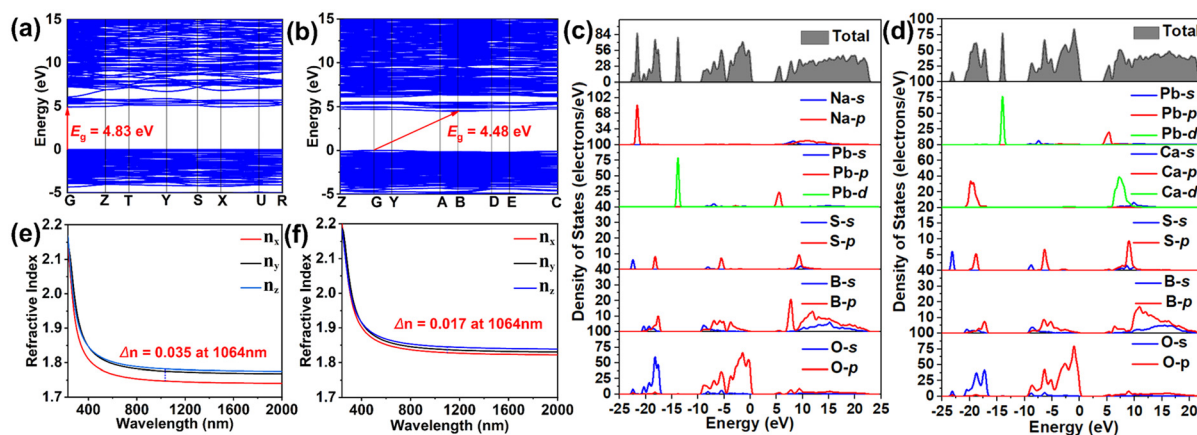


Fig. 4 Theoretical calculations of **I** and **II**. (a and b) Electronic band structures based on GGA. (c and d) Total and partial densities of states. (e and f) Calculated refractive index curves. (a, c, and e) and (b, d, and f) **I** and **II**, respectively.

The refractive indices of **I** and **II** were calculated using the first-principles method (Fig. 4e and f). The calculated birefringence is about 0.035 and 0.017 at 1064 nm for **I** and **II**, respectively. To further understand the structure–optical property relationship of the above-mentioned materials, the spatial density of the $[\text{BO}_3]$ groups was also calculated (Table S6[†]). The relationship between the birefringence of **I** and **II** with the density was determined. While comparing structures **I** and **II**, it can be seen that the anion $[\text{BO}_3]$ density in **I** is higher, resulting in greater birefringence in **I** than in **II**. The origin of birefringence was analyzed using the response electron distribution anisotropy (REDA) method.⁵⁵ As shown in Table S7,[†] the $[\text{BO}_3]$ units contribute significantly, with a proportion of 77.0%, while the $[\text{BO}_4]$, $[\text{SO}_4]$, $[\text{Na}_1\text{O}_8]$, $[\text{Na}_2\text{O}_6]$, and $[\text{PbO}_9]$ units contribute smaller proportions of −12.2, 3.0, 7.9, 10.7, and 13.7% in **I**, respectively. The contribution of the $[\text{BO}_3]$ units is 62.4%, and the contributions of the $[\text{BO}_4]$, $[\text{SO}_4]$, $[\text{Na}_1\text{O}_8]$, $[\text{Na}_2\text{O}_6]$, and $[\text{PbO}_9]$ units are 13.5, 9.6, 6.4, 13.5, and −5.4% for **II**, respectively. Since the $[\text{BO}_3]$ unit has larger polarizability anisotropy,³⁸ and the density of the $[\text{BO}_3]$ units in **I** is higher than that in **II**, the birefringence of **I** is greater than that of **II**.

4. Conclusion

In summary, two new borate–sulfates, $\text{Na}_2\text{PbB}_6\text{O}_{10}\text{SO}_4$ (**I**) and $\text{Ca}_{2.58}\text{Pb}_{0.42}\text{B}_6\text{O}_{11}\text{SO}_4$ (**II**), were successfully synthesized and characterized. Both compounds feature novel 3D porous borate anionic frameworks that incorporate isolated $[\text{SO}_4]$ groups. The transition from **I** to **II** is driven by differences in cationic radii, leading to distinct 3D porous borate anionic frameworks. First-principles calculations reveal that the birefringence of **I** is significantly greater than that of **II**, which can be attributed to the higher density of $[\text{BO}_3]$ units in **I**. These findings offer new insights into the structural diversity and connectivity of borate and sulfate groups, paving the way for

further exploration of their functional and structural properties.

Author contributions

Fangfang Zhang supervised the research and revision of the manuscript. Huan Pei designed and performed the experiments, wrote the first draft, and revised it. Shaohua Liu did the theoretical calculations. Zijian Li assisted with the experimental work. All authors participated in the discussion.

Data availability

Computational procedures, crystal data information, bond valence sum, selected bond lengths, and angles are available in the article and its ESI.[†]

Conflicts of interest

The authors declare no conflicts of interest.

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