α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$: Polymorphism drives changes in structure and performance

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ABSTRACT Introducing Pb^{2+} cations with lone pair electrons in borates is efficient to form multiple crystalline forms. Here, we report two new compounds, α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, which exhibit different crystal forms from the previously reported lead borates, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α - $\text{Pb}_4\text{B}_6\text{O}_{13}$, respectively. Two sets of polymorphs: α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, exhibit completely different crystal structures and diverse optical properties. Thermal gravimetric and differential scanning calorimetry (TG-DSC) and variable-temperature powder X-ray diffraction (XRD) analyses were performed to study their thermodynamic stabilities. Structure-property relationships were discussed through first-principles calculation. Notably, the new phases, α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, have larger birefringence than their corresponding polymorphs due to the rearrangement of the functional groups in their structures.

Keywords: borate, polymorphism, birefringence, first-principles calculation

INTRODUCTION

Borates have been in the spotlight of research fields owing to their continuous extended structural diversity and various applications in the design of novel photonic and optoelectronic devices [1–12]. Especially, the optical properties such as ultraviolet (UV) and deep-UV non-linear optics (NLO), as well as birefringence [13–17], largely depend on the unique structures of borates. Therefore, understanding the structure-property relationship will help material scientists to explore more functional materials with better performances [18–21]. In the study of borates, polymorphism has attracted special interests because it boosts different structures with different properties and applications [22–26]. For example,

α - BaB_2O_4 with centrosymmetric structure is one of the most excellent birefringent materials, while β - BaB_2O_4 that crystallizes in the noncentrosymmetric space group is a famous NLO material [22,23]. Therefore, polymorphism can be utilized as an ideal system for the analysis of structure-property relationship [27–33].

Generally, the combination of the cations with a flexible coordination environment and the anion groups having variable architectures is favorable to form polymorphs [24]. It is well known that the anion groups in the crystal structure of borates, similar to silicates, can exist as isolated groups or condensate into complex rings, one dimensional (1D) chains, 2D layers, and 3D frameworks [34–38]. However, unlike the fixed coordination number of four for the Si atom in silicates (SiO_4 tetrahedra), the coordination number of the B atom in borates can be either three (BO_3 triangles) or four (BO_4 tetrahedra). As a result, the structure of borates is more complicated and variable than that of silicates [39–44]. For the cations, it was found that Pb^{2+} with lone pair electrons could exhibit variable coordination numbers from 2–10 and form diverse coordination polyhedra with holodirected or hemidirected geometries. Thereby, the synergistic regulation of the variable B–O groups and Pb^{2+} cations increases the incidence of borate polymorphism.

Herein, we report two new lead borates, α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, which exhibit completely different crystal structures in comparison with β - $\text{Pb}_4\text{B}_2\text{O}_7$ [45] and α - $\text{Pb}_4\text{B}_6\text{O}_{13}$ [46] (different polymorphic forms are denoted by letters, α , β , γ , depending on the sequence from low symmetry to high one of the crystal space group). The syntheses, crystal structures, thermal stabilities, Infrared (IR) and UV-vis-NIR diffuse reflectance spectroscopies were studied comprehensively. Specifically, the bi-

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refrigrant properties for the polymorphs, α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, were discussed. Combined with the first-principles calculation, the structure-property relationships of these two sets of polymorphs were investigated by analyzing the changes in the structure and performance.

EXPERIMENTAL SECTION

Syntheses of α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$

Single-crystals of α - $\text{Pb}_4\text{B}_2\text{O}_7$ were obtained by the high-temperature melt method. A mixture of PbO (4.464 g, 20 mmol) and B_2O_3 (0.348 g, 5 mmol) was loaded into a platinum crucible. The crucible was heated to 700°C in 10 h and held at this temperature for 10 h, and then quenched to 630°C . After that, the temperature was cooled to 450°C with a rate of 2°C h^{-1} , then cooled down to room temperature for 15 h. Colorless block-shaped crystals of α - $\text{Pb}_4\text{B}_2\text{O}_7$ were manually selected from the crucible. Powder samples for the related characterizations were obtained by grinding the prepared single crystals. By the conventional solid-state reaction of stoichiometric PbO and B_2O_3 , the polycrystalline sample β - $\text{Pb}_4\text{B}_2\text{O}_7$ [45] was synthesized rather than α - $\text{Pb}_4\text{B}_2\text{O}_7$.

The β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ crystals were grown by the high-temperature solution method in the PbO - H_3BO_3 system. A mixture of PbO (4.464 g, 20 mmol) and H_3BO_3 (1.237 g, 20 mmol) was ground evenly and preheated to 450°C for 24 h, then loaded into a platinum crucible. The crucible was heated to 650°C in 10 h and held at this temperature for 10 h. After that, the temperature was cooled to 430°C with a rate of 2°C h^{-1} , then cooled down to room temperature for 24 h. Colorless block-shaped crystals were separated manually from the crucible for structure determination. The polycrystalline samples of β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ were obtained by the conventional solid-state reaction techniques. Stoichiometric reagents of PbO and H_3BO_3 were ground and loaded into a fused-silica crucible. After that, the temperature was gradually raised to 400°C for the compound with several intermediate grindings, and the polycrystalline samples of β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ were obtained and confirmed by the powder X-ray diffraction (XRD) measurements.

Single-crystal XRD

The single-crystal XRD data were collected on a Bruker SMART APEX II 4K charge-coupled device (CCD) diffractometer using $\text{Mo K}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at room temperature. Data integration, cell refinement, and absorption correction were carried out with the program

SAINT [47]. The structures were solved by the direct methods and refined on F^2 by the full-matrix least-squares techniques using the program suite SHELXTL [48]. Solutions were checked for missed symmetry using PLATON [49]. Table 1 gives the details of the crystal data and structure refinements. Tables S1–S3 in the Supplementary information (SI) summarize the equivalent isotropic displacement parameters and atomic coordinates. Bond valence sum calculations were performed for all atoms of the asymmetric units (Pb, 1.8–2.3; B, 2.9–3.1; O, 1.8–2.3), and the values were consistent with the expected valences and confirmed the reliability of the structures (Table S1). Herein, bond valence sum for all atoms was calculated with the following formula: $V_i=\sum_j s_{ij}$ and $s_{ij}=\exp[(d_0-d_{ij})/b]$, where s_{ij} is the valence of bond i – j , and d_0 and b are bond valence parameters, with values 1.963 and 0.49 for Pb–O bonds and 1.371 and 0.37 for B–O bonds, respectively [50].

Powder XRD

Powder XRD data were collected with a Bruker D2 PHASER diffractometer ($\text{Cu K}\alpha$ radiation with $\lambda=1.5418 \text{ \AA}$, $2\theta=5^\circ$ – 70° for β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ and 10° – 70° for α - $\text{Pb}_4\text{B}_2\text{O}_7$, respectively, scan step width= 0.02° , and counting time= 1 s step^{-1}).

Infrared spectroscopy

IR spectra measurements were carried out on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 400 – 4000 cm^{-1} range.

Thermal analysis

Thermal gravimetric (TG) and differential scanning calorimetry (DSC) analyses were carried out on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument in a flowing N_2 atmosphere. The samples were placed in platinum crucibles and heated from 40 – 800°C at a rate of 5°C min^{-1} , respectively.

UV-vis-NIR diffuse reflectance spectroscopy

UV-vis-NIR diffuse reflectance spectroscopy data in the wavelength range of 200 – 2600 nm were recorded at room temperature by using the powder samples of α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ on a Shimadzu SolidSpec-3700DUV spectrophotometer.

Measurement of birefringence

The birefringence (Δn) of β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ crystal was characterized by using the polarizing microscope (ZEISS Axio Scope. A1) equipped with Berek compensator. The wa-

Table 1 Crystal data and structure refinements of α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$

Parameters	α - $\text{Pb}_4\text{B}_2\text{O}_7$	β - $\text{Pb}_4\text{B}_6\text{O}_{13}$
Formula weight	962.38	1101.62
Wavelength ($\text{\AA}$)	0.71073	0.71073
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a ($\text{\AA}$)	7.068(4)	12.842(5)
b ($\text{\AA}$), β ($^\circ$)	11.656(7), 92.756(6)	13.557(6), 104.956(5)
b ($\text{\AA}$)	9.913(6)	7.103(3)
Z	4	4
Volume ($\text{\AA}^3$)	815.7(9)	1194.7(9)
Density (calc.) (g cm^{-3})	7.837	6.125
Absorption coefficient (mm^{-1})	82.305	56.271
$F(000)$	1576	1848
Theta range for data collection ($^\circ$)	2.70–27.78	2.225–27.469
Limiting indices	$-9 \leq h \leq 7$, $-9 \leq k \leq 15$, $-11 \leq l \leq 12$	$-16 \leq h \leq 11$, $-16 \leq k \leq 17$, $-8 \leq l \leq 9$
Reflections collected/unique	4929/1907 [$R(\text{int})=0.0249$]	3669/1374 [$R(\text{int})=0.0472$]
Completeness to θ	27.78°, 99.3%	27.469°, 99.8%
Goodness-of-fit on F^2	1.008	1.039
Final R indices [$I > 2\sigma(I)$] ^a	$R_1=0.0394$, $wR_2=0.0839$	$R_1=0.0346$, $wR_2=0.0871$
R indices (all data) ^a	$R_1=0.0535$, $wR_2=0.0915$	$R_1=0.0412$, $wR_2=0.0908$
Extinction coefficient	0.00463(17)	0.00047(6)
Largest diff. peak and hole ($\text{e \AA}^{-3}$)	3.492 and -2.384	3.528 and -3.249

a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Wavelength of the light source was 546 nm. The boundary lines of the first-, second- and third-order interference color are clear enough to reduce the relative error. Transparent lamellar crystal of β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ was selected and the thickness (d) of the crystal was measured under the microscope (Fig. S1a). The corresponding optical path difference (R) was obtained from the Michal Levy chart based on the maximum interference color observed under the cross-polarized light (Fig. S1b), i.e., $R=700$ nm. The formula for calculating the birefringence is

$$R = |N_e - N_o| \times d = \Delta n \times d,$$

where N_e and N_o represent the refractive indexes of light through a crystal.

Because the obtained crystal did not meet the test conditions, the birefringence of α - $\text{Pb}_4\text{B}_2\text{O}_7$ was not measured.

Computational methods

First-principles calculations were performed for α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, respectively. The electronic structures and optical property calculations were per-

formed by employing Cambridge Sequential Total Energy Package (CASTEP), a plane-wave pseudopotential package based on the density functional theory (DFT) [51]. During the calculation, geometry optimization was performed using the BFGS minimization technique. The geometry optimization was converged under the following criteria: the residual forces on the atoms were less than $0.01 \text{ eV \AA}^{-1}$, the displacements of atoms were less than $5.0 \times 10^{-4} \text{ \AA}$, and the energy change was less than $5.0 \times 10^{-6} \text{ eV atom}^{-1}$. Norm-conserving pseudopotentials (NCP) [52,53] were used with the following valence electron configurations: Pb $5s^2 5p^6 5d^{10} 6s^2 6p^2$, B $2s^2 2p^1$, O $2s^2 2p^4$. Meanwhile, the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was exerted [54,55]. The plane-wave energy cutoff was set at 910.0 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of $5.0 \times 10^{-7} \text{ eV atom}^{-1}$ on the total energy. The Monk-horst-Pack k -point separations for each material were set as $2 \times 1 \times 2$ (α - $\text{Pb}_4\text{B}_2\text{O}_7$), $2 \times 2 \times 1$ (β - $\text{Pb}_4\text{B}_2\text{O}_7$), $3 \times 3 \times 3$ (α - $\text{Pb}_4\text{B}_6\text{O}_{13}$), and $3 \times 3 \times 4$ (β - $\text{Pb}_4\text{B}_6\text{O}_{13}$) in the Brillouin zone corresponding to the primitive cell. The other cal-

calculation parameters and convergent criteria were set by the default values of the CASTEP code.

The calculations of the linear optical properties described in terms of the complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, were performed. After the electronic structures were obtained, the imaginary parts of the dielectric constant can be calculated from the electronic transition between the occupied and unoccupied states. And the real part of the dielectric function was determined by the Kramers-Kronig transform, from which the refractive index n was obtained [56,57].

RESULTS AND DISCUSSION

α - $\text{Pb}_4\text{B}_2\text{O}_7$ crystallizes in the monoclinic space group $P2_1/n$ with four crystallographically independent Pb atoms, two B atoms and seven O atoms in its asymmetric unit. In its structure, all B atoms are coordinated with three O atoms forming the isolated BO_3 triangles, and the BO_3 triangles are arranged quasi-parallelly to the ac plane (Fig. 1a). The B–O bond lengths of these BO_3 triangles range from 1.361–1.412 Å (Table S3). The four different Pb atoms bond to O atoms, forming distorted PbO_n polyhedra (two PbO_4 and two PbO_6 polyhedra) due to the lone pair electrons of the lead(II) cations (Fig. S2). These PbO_n polyhedra are further linked *via* sharing O atoms to form the 3D framework. Remarkably, there is a centered “additional” atom O1, which only connects with four adjacent Pb atoms to form a distorted OPb_4 tetrahedron (Fig. 1b), where the Pb–O bond lengths vary from 2.192–

2.979 Å (Table S3). Thus the structure of α - $\text{Pb}_4\text{B}_2\text{O}_7$ can be described as consisting of two basic units: the isolated BO_3 triangles and distorted OPb_4 tetrahedra (Fig. 1c). Generally, the OPb_4 tetrahedra could exist as isolated groups or further connect with each other forming complex polyions with various structure types and dimensionalities. While in β - $\text{Pb}_4\text{B}_2\text{O}_7$ [45], three OPb_4 tetrahedra connect with each other to form the isolated trimer O_3Pb_8 by edge-sharing (Fig. 1e) and the bond lengths of Pb–O vary from 2.204 to 2.284 Å. In addition, the isolated B_2O_5 and BO_3 groups stack alternately along the a -axis (Fig. 1d). The final structural framework can be described as isolated B_2O_5 and BO_3 groups as well as O_3Pb_8 trimers (Fig. 1f). β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ crystallizes in the monoclinic space group $C2/c$, and there are two crystallographically independent Pb atoms, three B atoms and seven O atoms in the asymmetric unit. In the structure, the Pb1 and Pb2 atoms bond with O atoms to form the distorted PbO_6 and PbO_4 polyhedra, respectively, owing to the stereoactivity of the lone electron pairs on the Pb^{2+} cations (Fig. S3). The B1 atom is coordinated with four O atoms, forming the BO_4 tetrahedra, and the B2 and B3 atoms are coordinated with three O atoms, respectively, forming the BO_3 triangles. Two BO_3 triangles and one BO_4 tetrahedron are connected *via* corner-sharing to form the B_3O_7 ring, and two B_3O_7 rings are face-to-face connected *via* O2 atom to form the isolated B_6O_{13} double ring (Fig. 1g). Along the c -axis, the double rings B_6O_{13} show a “U”-shape and arrange alternately along the a -

Figure 1 The structures of α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$. The structure of α - $\text{Pb}_4\text{B}_2\text{O}_7$: (a) BO_3 triangles arranged quasi-parallel to the ac plane; (b) OPb_4 tetrahedron; (c) isolated BO_3 triangles and distorted OPb_4 tetrahedra arranged alternately on the ac plane. The structure of β - $\text{Pb}_4\text{B}_2\text{O}_7$ [45]: (d) arrangement of the B_2O_5 and BO_3 groups viewing along the c -axis; (e) O_3Pb_8 trimer; (f) spatial arrangement of B_2O_5 and BO_3 groups as well as O_3Pb_8 trimer along the b axis. The structure of β - $\text{Pb}_4\text{B}_6\text{O}_{13}$: (g) B_6O_{13} double ring; (h) the arrangement of the B_6O_{13} double rings viewing along the c -axis. The structure of α - $\text{Pb}_4\text{B}_6\text{O}_{13}$ [46]: (i) $[\text{B}_6\text{O}_{14}]$ FBB; (j) $^\infty[\text{OPb}_2]$ chain; (k) the integral structural framework.

axis, and the Pb^{2+} cations are located in the spaces to compensate for the negative charges (Fig. 1h). The bond lengths of Pb–O and B–O vary from 2.187–2.888 Å and 1.340–1.509 Å, respectively (Table S3). While in $\alpha\text{-Pb}_4\text{B}_6\text{O}_{13}$ [46], the “8”-shaped-ring B_5O_{12} and BO_3 triangle connect *via* sharing O8 atom forming the B_6O_{14} fundamental building block (FBB) (Fig. 1i), and the FBBs are further linked by sharing four-terminal atoms (two O2 and two O4 atoms), forming the $\infty^2[\text{B}_6\text{O}_{12}]$ 2D branched layers. In addition, there is an “additional” atom O1, which only bonds with nearby Pb1 and Pb2 atoms to form an OPb_4 tetrahedron, and the OPb_4 tetrahedra further connect each other *via* edge-sharing to generate the $\infty^1[\text{OPb}_2]$ chains (Fig. 1j). Thus, the final framework of $\alpha\text{-Pb}_4\text{B}_6\text{O}_{13}$ is made up of the $\infty^2[\text{B}_6\text{O}_{12}]$ 2D branched layers and $\infty^1[\text{OPb}_2]$ chains and Pb cations located in the interstitial voids (Fig. 1k).

The IR spectra of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ and $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$ are shown in Fig. S4. Clearly, the absorption peaks in the IR spectrum of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ are mainly attributed to the stretching (1253, 1203, 1165, 906 and 758 cm^{-1}) and bending vibrations (731, 709 and 630 cm^{-1}) of the B–O bonds in the BO_3 units [58,59], which is consistent with the crystal

structure analysis of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ that only isolated BO_3 units were formed for the B atoms. In the IR spectrum of $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$, the peaks of B–O vibrations for the BO_3 (1392, 1319, 1211, 727 and 684 cm^{-1}) and BO_4 units (1007, 972 and 878 cm^{-1}) were both observed [60,61]. This result also matches pretty well with the crystal structure analysis. The concrete assignment of the absorption bands is shown in Table S4.

TG-DSC measurements were performed to study the thermal stabilities of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ and $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$. Fig. 2a shows the thermal behavior of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$. It is clear that there is no evident weight loss during the heating process and a distinct endothermic peak at 546°C is observed. To identify the thermal behavior of this peak, the powder sample of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ was put into a platinum crucible and calcined at different temperatures. It is found that the sample begins to melt at about 540°C . The analysis of the powder XRD pattern of the solidified melt reveals that the main phase is $\beta\text{-Pb}_4\text{B}_2\text{O}_7$ (Fig. 2b). Therefore, we speculate that the peak observed at 546°C corresponds to the melting temperature of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ and also the phase transition temperature from α - to $\beta\text{-Pb}_4\text{B}_2\text{O}_7$. TG-DSC curves for $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$ are shown in Fig. 2c. It is observed

Figure 2 (a) TG-DSC curves of $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$; (b) powder XRD patterns of calculated and experimental $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$, and calculated $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$, respectively; (c) TG-DSC curves of $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$; (d) powder XRD patterns of calculated and experimental $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$, and calculated $\beta\text{-Pb}_6\text{B}_{10}\text{O}_{21}$ [62].

that there are two endothermic peaks at 482 and 578°C, respectively, without weight loss during the heating process. From the variable-temperature powder XRD patterns (Fig. 2d), we can see that the patterns for samples annealed at 400 and 450°C are consistent with the calculated data for β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, while at 500°C, the pattern for β - $\text{Pb}_6\text{B}_{10}\text{O}_{21}$ [62] is present. Therefore, it can be concluded that β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ decomposes to β - $\text{Pb}_6\text{B}_{10}\text{O}_{21}$ at 482°C. Upon heating, the β - $\text{Pb}_6\text{B}_{10}\text{O}_{21}$ begins to melt at 560°C, which is consistent with the endothermic peak at 578°C on the DSC curve. The XRD data of the solidified melt are identical to those of β - $\text{Pb}_6\text{B}_{10}\text{O}_{21}$ [62]. In the study of Dong *et al.* [46], the thermal analysis of the α - $\text{Pb}_4\text{B}_6\text{O}_{13}$ phase shows two endothermic peaks (around 478 and 564°C) on the DSC curve, and the solidified melt

also changes to β - $\text{Pb}_6\text{B}_{10}\text{O}_{21}$. Therefore, it is suggested that the temperature of the phase transition from α - to β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ is around the range of 478–482°C. Because the temperature of 478 is close to 482°C, the phase β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ was not detected in the thermal analysis of Dong *et al.* [46].

UV-vis-NIR diffuse reflectance spectra of α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ (Fig. S5) show that both compounds have wide UV transparency windows from UV to NIR with cutoff edges of 318 and 274 nm (corresponding to the bandgaps of 3.90 and 4.53 eV), respectively. In addition, the PBE calculation gives indirect bandgaps of α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ with the values of 2.88 and 3.63 eV (Fig. 3a and b), respectively, which are smaller than the experimental results. This underestimation mainly results

Figure 3 Calculated band structures of α - $\text{Pb}_4\text{B}_2\text{O}_7$ (a) and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ (b); total and partial density of states of α - $\text{Pb}_4\text{B}_2\text{O}_7$ (c) and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ (d).

from the discontinuity of exchange-correlation energy functional [63,64]. The partial densities of states for α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ are shown in Fig. 3c and d. The tops of valance bands of both compounds are mainly composed of O 2p orbitals and a small amount from the Pb 6p and B 2p orbitals. However, the bottoms of the conduction bands mainly consist of the Pb 6s, O 2p and B 2p orbitals. Therefore, we can conclude that the Pb–O and B–O interactions play a decisive role in determining the bandgaps of α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, which is similar to the results of β - $\text{Pb}_4\text{B}_2\text{O}_7$ [45] and α - $\text{Pb}_4\text{B}_6\text{O}_{13}$ [46].

The birefringence values of the two sets of polymorphs were calculated by using the first-principles calculations. As shown in Fig. 4, the calculated birefringences at 546 nm are 0.1278 and 0.0526 for α - and β - $\text{Pb}_4\text{B}_2\text{O}_7$, 0.0565 and 0.0725 for α - and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, respectively. Based on a proper crystal, the birefringence of β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ was measured by the cross-polarizing microscope (depicted in the Experimental Section). The experimental value of 0.070@546 nm is consistent with the calculated result, which verifies the rationality of the calculations.

In order to investigate the origin of the changes for the optical performances derived by the polymorphism, the electron localization function (ELF) analysis and real-space atom-cutting (RSAC) method [65–68] were employed to examine the contributions of the constituent functional groups for the two sets of polymorphs. As

shown in the ELF diagrams (Fig. S6), it is clear that the regions with maximal density, i.e., main contributors to the optical properties, are the atoms involving in the B–O groups and the $\text{Pb}^{2+}/\text{OPb}_4$ tetrahedra. Based on the RSAC method, the contribution of the functional groups to birefringence was obtained by cutting the wave functions of the cation groups $\text{Pb}/\text{Pb}+\text{O}_a$ (O_a atoms were coordinated solely by the Pb atoms) and the B–O groups, respectively. The results are shown in Table S5. Specifically, from α - to β -phase, the arrangements of the functional groups have different contributions to optical properties, which lead to the changes of the birefringence in the polymorph compounds.

CONCLUSIONS

Two lead borates α - $\text{Pb}_4\text{B}_2\text{O}_7$ and β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ were synthesized for the first time, and their crystal structures were defined by single-crystal and powder XRD data, as well as IR spectra. TG-DSC and variable-temperature powder XRD analyses indicate that the phase transition from α - to β - $\text{Pb}_4\text{B}_2\text{O}_7$ maybe occur at about 546°C, and the phase transition temperature from α - to β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ is around the range of 478–482°C. Structurally, two sets of polymorphs: α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, exhibit completely different crystal structures. α - $\text{Pb}_4\text{B}_2\text{O}_7$ is composed of isolated BO_3 triangles and distorted OPb_4 tetrahedra, while β - $\text{Pb}_4\text{B}_2\text{O}_7$ consists of isolated B_2O_5 and BO_3 groups as well as O_3Pb_8 trimers; α - $\text{Pb}_4\text{B}_6\text{O}_{13}$ is

Figure 4 Calculated birefringence (Δn) curves α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ (a, b) and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ (c, d).

composed of the $\infty^2[\text{B}_6\text{O}_{12}]$ 2D branched layers and $\infty^1[\text{OPb}_2]$ chains and Pb^{2+} cations locate in the interstitial voids, while $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$ is made up of the “U”-shaped double rings B_6O_{13} and the Pb^{2+} cations located in the spaces to compensate the negative charges. In addition, the structure-property relations of the two sets of polymorphism, α -, $\beta\text{-Pb}_4\text{B}_2\text{O}_7$ and α -, $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$, were studied and analyzed by structure comparisons and first-principles calculations. It shows that the birefringences of the $\alpha\text{-Pb}_4\text{B}_2\text{O}_7$ and $\beta\text{-Pb}_4\text{B}_6\text{O}_{13}$ are larger than their polymorphs, caused by the synergistic effect of the B–O groups and the $\text{Pb}^{2+}/\text{OPb}_4$ tetrahedron with stereochemically active 6s lone pair electrons.

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α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ and α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$: 多态性驱动结构和性能变化

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摘要 在硼酸盐中引入带孤对电子的 Pb^{2+} 离子可以有效地形成多种结晶形态. 本文报道了两个新的结构, α - $\text{Pb}_4\text{B}_2\text{O}_7$ 和 β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, 这两个结构与已经报道的两例硼酸盐 β - $\text{Pb}_4\text{B}_2\text{O}_7$ 和 α - $\text{Pb}_4\text{B}_6\text{O}_{13}$ 具有不同的晶体形式. 两组多形体: α -, β - $\text{Pb}_4\text{B}_2\text{O}_7$ 和 α -, β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, 分别具有完全不同的晶体结构和光学性质. 采用热重-差示扫描量热法(TG-DSC)和变温粉末X射线衍射(XRD)分析对 α - $\text{Pb}_4\text{B}_2\text{O}_7$ 和 β - $\text{Pb}_4\text{B}_6\text{O}_{13}$ 的热力学稳定性进行了研究. 通过第一性原理计算讨论了结构与性质的关系. 值得注意的是, 由于结构中功能基团的重组, 两个新的相, α - $\text{Pb}_4\text{B}_2\text{O}_7$ 和 β - $\text{Pb}_4\text{B}_6\text{O}_{13}$, 具有比与之对应的多形体较大的双折射.