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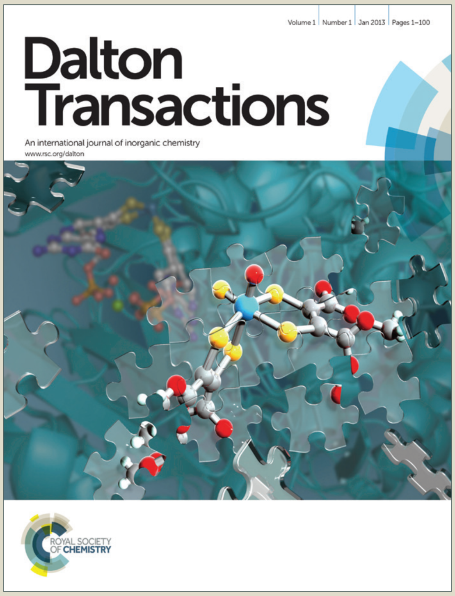

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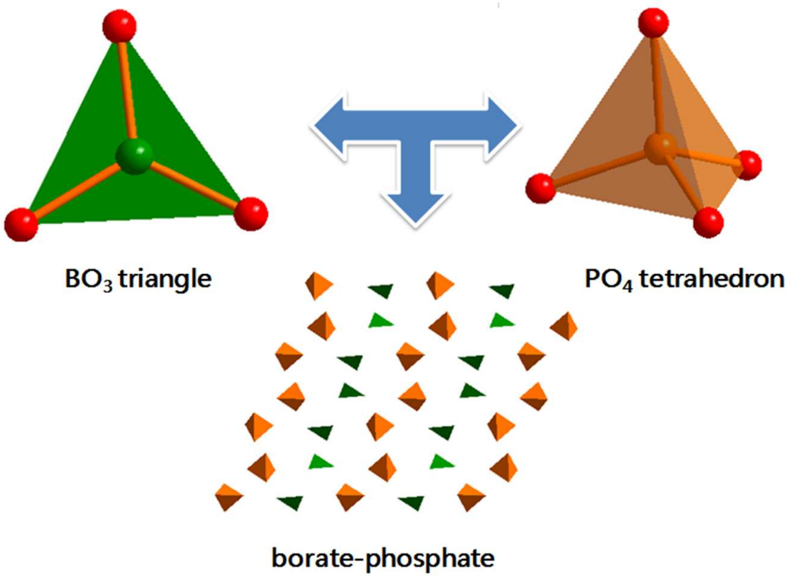

A principle to design new borate-phosphates has been proposed.

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Structural Insights for the Design of New Borate-phosphates: Synthesis, Crystal Structure and Optical Properties of $Pb_4O(BO_3)(PO_4)$ and $Bi_4O_3(BO_3)(PO_4)$ †

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Two new metal borate-phosphates, $Pb_4O(BO_3)(PO_4)$ (**1**) and $Bi_4O_3(BO_3)(PO_4)$ (**2**) have been successfully designed and synthesized. The structures of the title compounds were determined by single-crystal X-ray diffraction.The title compounds have similar crystal structures consisting of oxygen-centered (OPb_4) or (OBi_4) tetrahedra as well as isolated BO_3 and PO_4 groups. Structural comparison and the Madelung energy calculation indicate that the title compounds also exhibit strong correlation to known metal borates and phosphates. In addition, a strategy of BO_3-PO_4 substitution is proposed for designing new borate-phosphates. Thermal analyses, IR spectra and UV-vis-NIR diffuse reflectance spectra have also been performed.

Introduction

Borate and phosphate compounds have been widely studied over the past decades due to their rich structural chemistry and magnetic, optical, and electrical applications.[1] In recent years, many attempts have been made to explore new compounds containing both B-O and P-O groups, and a large number of useful functional materials have be obtained. For example, $M_2BP_3O_{12}$ (M= Fe, Cr) show interesting magnetic properties;[2] β-$Zn_3(BO_3)(PO_4)$,[3] $MBPO_5$ (M = Sr and Ba),[4] $Na_3Cd_3B(PO_4)_4$[5] and $AMBP_2O_8$ (A= K, M = Sr, Ba and A = K, Rb, M = Pb)[6] are potential nonlinear optical materials; The Eu^{2+}-doped $Ba_3BP_3O_{12}$ have been found an application as a new scintillation material.[7]

According to the classification proposed by R. Kniep et al,[8] there are two types of compounds containing both B-O and P-O groups but with obvious differences: a) borophosphates: the ones at least one BO_3 (or BO_4) group and one PO_4 tetrahedron share a common O atom; b) borate-phosphates: isolated character of BO_3/BO_4 and PO_4 anionic units. So far, a large number of borophosphates with quite different structures have been synthesized.[8-9] On the contrary, borate-phosphates are less common. To the best of our knowledge, $M_3(BO_3)(PO_4)$ (M = Ba, Co, Mg, Zn and Cd),[10] $SrCo_2(BO_3)(PO_4)$,[11] $Ln_7O_6(BO_3)(PO_4)_2$ (Ln= La, Pr, Nd, Sm, Gd, and Dy),[12] $K_3Ln[OB(OH)_2]_2[HOPO_3]_2$ (Ln = Yb and Lu),[13] $M_2(BO_4)(PO_4)$ (M = Th and U),[14] $Ba_5((UO_2)(PO_4)_3(B_5O_9))\ (H_2O)_{0.125}$[15] and the mineral Seamanite, $Mn_3(OH)_2[B(OH)_4][PO_4]$[16] are the only known borate-phosphates.

In order to enrich the borate-phosphate family, we are trying to figure out an efficient way to design and synthesize borate-phosphates with novel properties. After carefully analyzing the known borate-phosphates, first of all, we noticed that the ratio of borate to phosphate units equals one (B/P ratio = 1) in most borate-phosphates, which suggests that borate-phosphates can be synthesized by the reaction of stoichiometric metal borates and phosphates. For example, stoichiometric $Mg_3(BO_3)_2$ and $Mg_3(PO_4)_2$ were used as precursors for preparing $Mg_3(BO_3)(PO_4)$.[10d] Moreover, according to J. G. Fletcher et al, the BO_3 groups can occupy PO_4 sites of the apatite $Ca_5(PO_4)_3F$, leading to the new compound $Ca_5(BO_3)_3F$.[17] Inspired by that finding, we analyzed the structures of all known borate-phosphates. Interestingly, in some case, the structure of borate-phosphates could be viewed as a borate in which half of BO_3 triangles are replaced by PO_4 tetrahedra, or a phosphate in which fifty percent of PO_4 tetrahedra are substituted by BO_3 triangles. Fig. S1 in the ESI† illustrates an example of the substitution relationship of BO_3-PO_4 groups and the structural similarities among $Co_3(BO_3)_2$,[18] $Co_3(PO_4)_2$,[19] and $Co_3(BO_3)(PO_4)$.[10b] Therefore, we suppose that new borate-phosphates may be obtained by mutual replacement between BO_3 triangles and PO_4 tetrahedra in known borates or phosphates.

Leaving those insights, we pay much more attention on metal borates or phosphates for discovering new borate-phosphates. Recently, a series of oxosalts, $Pb_4B_2O_7$,[20] $Pb_4O(PO_4)_2$,[21] $Bi_4O_3(BO_3)_2$[22] and $Bi_{4+x}(PO_4)_2O_{3+3x/2}$ ($0.175 \leq x \leq 1$)[23] have been reported. We have, therefore, investigated the Pb-B-P-O and Bi-B-P-O system. Two new borate-phosphates: $Pb_4O(BO_3)(PO_4)$ (**1**) and $Bi_4O_3(BO_3)(PO_4)$ (**2**) have been obtained. As we expected, the two compounds show some structural similarities with corresponding metal borate and phosphate. Herein, we report the synthesis and characterization of the two compounds with a focus on the structural relationship among borate, phosphate and borate-phosphate.

Experimental

Synthesis

All commercially available chemicals are of reagent grade and used as received. Single crystals of compounds **1** and **2** were grown from a high temperature solution. A mixture of 1.115 g (5.00 mmol) of PbO, 0.062 g (1.00 mmol) of H_3BO_3, and 0.115 g (1.00 mmol) of $NH_4H_2PO_4$ for compound **1** and a mixture of 1.631 g (3.50 mmol) of Bi_2O_3, 0.062 g (1.00 mmol) of H_3BO_3, and 0.230 g (2.00 mmol) of $NH_4H_2PO_4$ for compound **2** were thoroughly ground. The respective mixtures were prepared in a platinum crucible and held at 850 °C (950 °C for compound **2**) for 12 h in a programmable temperature electric furnace. The homogenized solutions then slowly cooled down to 700 °C at a rate of 3 °C/h, and finally cooled down to room temperature at a rate of 50 °C/h. Colorless block crystals were separated from the crucible for structural characterization (estimated yield: 10-15% for compound **1** and 5–10% for compound **2**, based on the P contents). It should be mentioned that side products were also observed. For compound **1**, $Pb_4O(PO_4)_2$ has been found, and for compound **2**, the side product is Bi_3PO_7. The ratio of main products/side products for both compounds is about 1:1 as observed by naked eye and single crystal diffraction measurement.

After structural analysis, polycrystalline samples of the two compounds were prepared by conventional solid-state methods. Separate stoichiometric mixture of PbO/Bi_2O_3, H_3BO_3 and $NH_4H_2PO_4$ was initially ground well. The samples were placed in alumina crucibles and heated to 600 ° C (670 ° C for compound **2**), held for 3 days, and then cooled to room temperature. The purity of the polycrystalline samples was confirmed by subsequent powder X-ray studies.

X-ray Crystallography

Single crystal data were collected at room temperature on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The reductions of data were carried out with the Bruker Suite software package. The numerical absorption corrections were performed with the SADABS program and integrated with the SAINT program.[24] All calculations were performed with programs from the SHELXTL crystallographic software package.[25] The structures were solved by direct methods, and all of the atoms were refined using full-matrix least-squares techniques with anisotropic thermal parameters and final converged for $F_o^2 \geq 2\sigma(F_o^2)$. The structures were examined using the *Adsym* subroutine of PLATON,[26] and no additional symmetry could be applied to the models. Crystallographic data and structural refinements for the two compounds are summarized in Table 1. The atomic coordinates and isotropic displacement coefficients are listed in Table S1 in the ESI†. Important bond lengths are listed in Table S2 in the ESI†.

Table 1. Crystal Data and Structural Refinements for the two compounds.

compound	**1**	**2**
formula weight ($g\cdot mol^{-1}$)	998.54	1037.70
crystal system	Monoclinic	Orthorhombic
space group	$P2_1/c$	*Pbca*
a (Å)	10.202(2)	5.536(6)
b (Å)	7.0047(1)	14.102(1)
c (Å)	12.921(4)	22.62(2)
β (deg)	113.057(1)	
volume (Å^3)	849.6(4)	1766(3)
Z	4	8
D_{calcd} ($g\cdot cm^{-3}$)	7.807	7.807
absorption coeffient (mm^{-1})	79.227	79.715
GOF on F^2	1.059	1.011
R_1, wR_2 $[F_o^2>2\sigma(F_o^2)]^a$	0.0508, 0.1258	0.0365, 0.0806
R_1, wR_2 (all data) ^{a}	0.0566, 0.1288	0.0539, 0.0884
Largest diff. peak and hole (e·Å^{-3})	3.551 and -4.948	3.088 and -3.155

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

Powder X-ray Diffraction (XRD)

Powder XRD patterns of polycrystalline materials were obtained on a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10-70° with a step size of 0.02° and a fixed counting time of 1 s/step.

Thermal Analysis

Thermal analysis were carried out on NETZSCH STA 449C instrument at a temperature range of 30-1000 °C with a heating rate of 10 ºC·min^{-1} under a constant flow of nitrogen gas.

Vibrational Spectroscopy

IR spectra were recorded on a Shimadzu IR Affinity-1 spectrometer in the 400-4000 cm^{-1} range with a resolution of 2 cm^{-1}. The sample was mixed thoroughly with dried KBr. (5 mg of the sample and 500 mg of KBr).

UV-Vis-NIR Diffuse-Reflectance Spectroscopy

The UV-Vis-NIR diffuse reflectance spectra of crystalline samples were collected with a Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected using fluororesin as a standard in the wavelength range from 250 to 2600 nm at room temperature. Reflectance spectra were converted to absorbance using the Kubelka-Munk function.[27]

Madelung Energy calculation

Madelung (electrostatic, coulomb) energy of a crystal was calculated using the Fourier methods.[28] The calculation utilizes a subroutine MADEL embedded in the VESTA program. [29] At first, electrostatic potential at i position (ϕ_i), is computed by

$$\phi_i = \sum_{j \neq i} \frac{eZ_j}{4\pi\epsilon_0 l_{ij}},$$

where e (=1.6022×10^{-19} C), Z_j is the number of charges of the jth ion, ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8.854188\times10^{-12}$ Fm^{-1}), and lij is the distance between the ith and the jth ion; the summation is carried out over all the ions j ($j \neq i$) in the crystal. Then, the Madelung energy (E_{M}) per asymmetric unit is calculated by using the formula:

$$E_M = \frac{1}{2}\sum_i \phi_i Z_i W_i,$$

$$\text{with } W_i = \frac{(\text{occupancy})\times(\text{number of equivalent positions})}{(\text{number of general equivalent positions})}$$

The summation in the above equation is carried out over all the sites in the asymmetric unit. It must be multiplied by the number of general equivalent positions to obtain the Madelung energy for the unit cell.

Results and discussion

Generalized Description

Single crystals of compounds **1** and **2** were grown through spontaneous nucleation method from high temperature solution of PbO/Bi_2O_3-B_2O_3-P_2O_5 mixtures. In general, the two compounds possess similar fundamental building units (FBUs): isolated BO_3 triangles and PO_4 tetrahedra. It is worth noting that both compounds do not contain any B-O-P linkage, and this feature distinguishes them from borophosphates. In addition, there are two types of O atoms in both compounds: those that belong to borate or phosphate groups (BO_3/PO_4) and those that do not. The latter ones are considered as “additional” oxygen atoms, *i.e.* atoms that do not participate in strong covalent B-O or P-O bonds. Therefore, the two compounds also belong to oxoborate-phosphates. The oxysalts containing additional O atoms may be considered as consisting of oxygen-centered (OM_4) (M = metal cations) tetrahedra, which appears to be more simple and elegant for understanding the whole structures.[30]

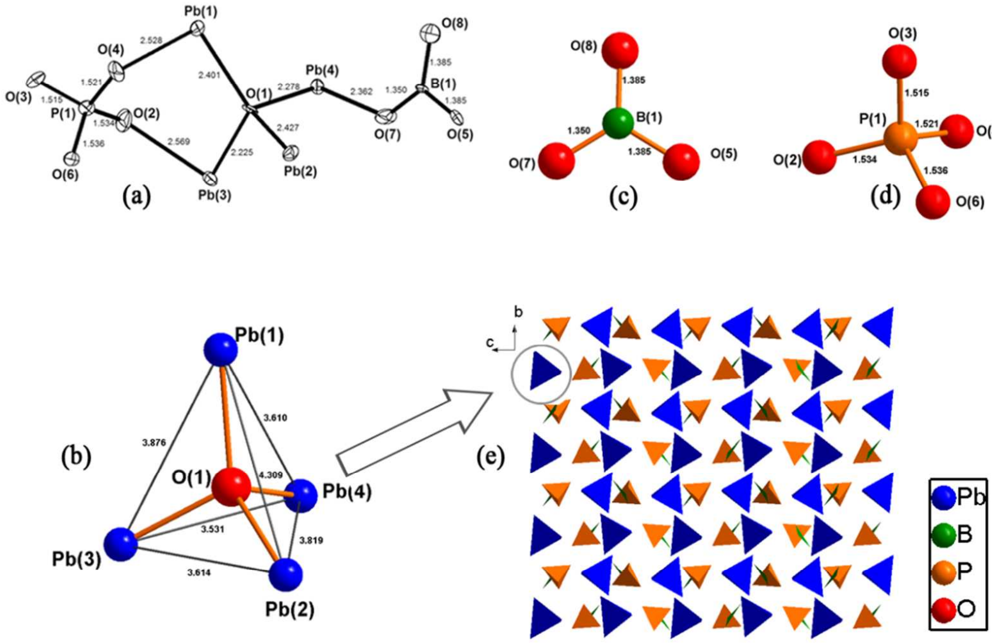

Fig. 1 View of crystal structure of compound 1. (a) ORTEP view of the asymmetric unit of 1, showing the atom-labeling scheme and 50% thermal ellipsoids; (b) ball-and-stick representation of the (OPb_4) tetrahedron; (c) the BO_3 triangle; (d) the PO_4 tetrahedron; (e) polyhedral view of 3D crystal structure of compound 1((OPb_4) tetrahedra, blue; BO_3 triangles: green; PO_4 terehedra, yellow).

Structure of $Pb_4O(BO_3)(PO_4)$ (1)

Compound **1** crystallizes in the space group *P*2$_1$/*c* with an asymmetric unit including four unique lead atoms, one unique boron atom, one unique phosphorus atom and eight unique oxygen atoms (Fig. 1a). The structure of compound **1** could be described as (OPb_4) tetrahedra linked by adjacent BO_3 triangles and PO_4 tetrahedra (Fig. 1e). In the structure, the O(1) atom are coordinated only to four different lead atoms (average O-Pb bond length = 2.333 Å) so that it can be described as a central atom for the (OPb_4) tetrahedron (Fig. 1b). It is reasonable to consider (OPb_4) tetrahedron as a kind of FBU because the Pb-Pb distances in this oxocentered unit is rather short (3.531 Å for the shortest one), which could be comparable to the Pb-Pb distance in Pb metal. To data, the (OPb_4) tetrahedron has been found in many lead-containing inorganic compounds.[30] Using the method suggested by Balic-Žunic and Makovicky,[31] the deviation of one tetrahedron from the idealized tetrahedral symmetry can be qualified. The result indicates that this (OPb_4) tetrahedron is strongly distorted (deviation value is 5.92%). The irregular tetrahedron may be caused by the lone-pair 6s electron effect of Pb^{2+} ions. In addition, the arrangement of (OPb_4) tetrahedra in the crystal structure possesses isolated characteristics: each (OPb_4) tetrahedron does not share its Pb−Pb edges with others, which can be classified as zero-dimensional (0 D) finite clusters. In addition, each B atom is coordinated to three O atoms with the B-O bond lengths ranging from 1.350(3) to 1.390(3) Å. Although the BO_3 groups are not equilateral triangles, the three O-B-O angles around B are close to 120°, indicating that the BO_3 groups are regular. The P atom is in a tetrahedral geometry with P–O distances ranging from 1.515(16) to 1.536(14) Å. The deviation of PO_4 tetrahedron from the ideal tetrahedral symmetry is only 0.2 %, which suggests that PO_4 tetrahedra may be classified as regular (deviation less than 1%). Bond valence calculations[32] result in values of 1.73 −1.96, 2.98, and 4.93 for Pb^{2+}, B^{3+}, and P^{5+}, respectively.

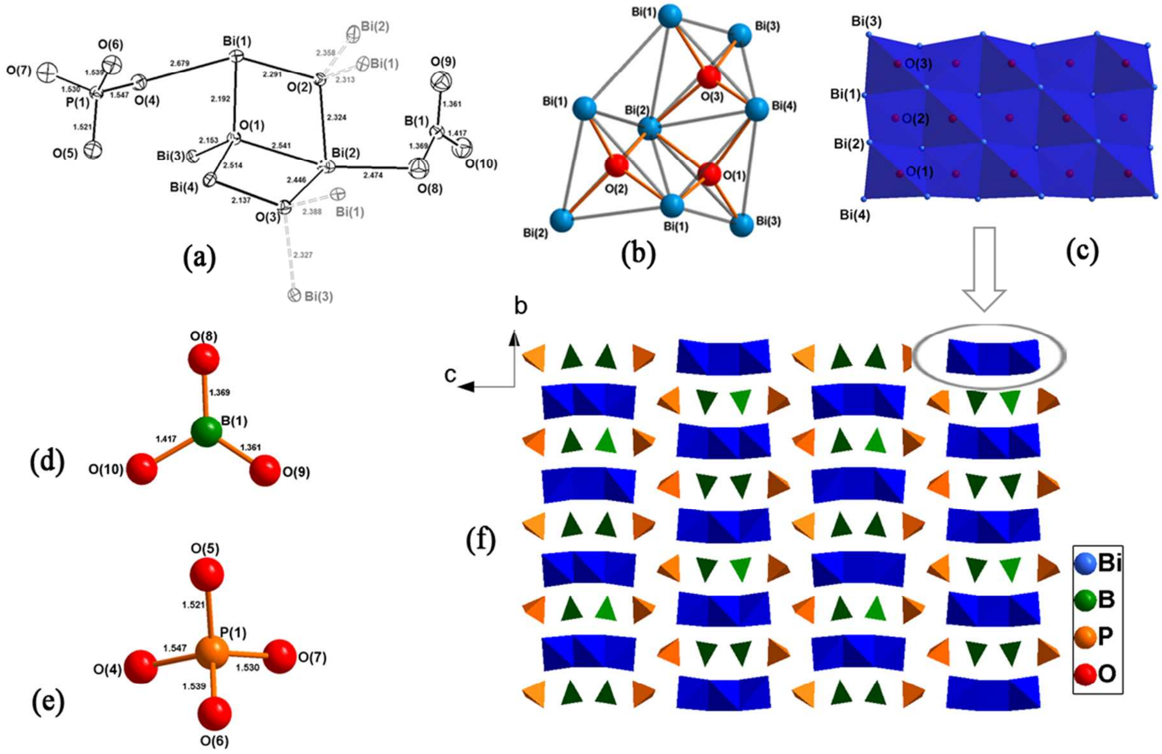

Fig. 2 View of crystal structure of compound 2. (a) ORTEP view of the asymmetric unit of 2, showing the atom-labeling scheme and 50% thermal ellipsoids; (b) ball-and-stick representation of three edge-sharing (OBi_4) tetrahedra; (c) the [O_3Bi_4] ribbon composed of *trans*-edge-sharing (OBi_4) tetrahedra; (d) the BO_3 triangle; (e) the PO_4 tetrahedron; (f) polyhedral view of 3D crystal structure of compound 2 ([O_3Bi_4] ribbons, blue; BO_3 triangles: green; PO_4 terehedra, yellow).

Structure of $Bi_4O_3(BO_3)(PO_4)$ (2)

Compound **2** belongs to the space group *Pbca*, and represents the first bismuth borate-phosphate. Four unique bismuth atoms, one unique boron atom, one unique phosphorus atom, and ten unique oxygen atoms are in an asymmetric unit (Fig. 2a). In compound **2**, the O(1), O(2) and O(3) atoms are the “additional” oxygen atoms that only connect with four crystallographic independent Bi atoms (Fig. 2b). The average length of O-Bi bonds in (OBi_4) tetrahedra is 2.332 Å, as long as that of O-Pb bonds in (OPb_4) tetrahedron. However, the three (OBi_4) tetrahedra are less distorted (distortion values in the range from 0.29 to 1.44%) than (OPb_4) tetrahedron. Besides, the three (OBi_4) tetrahedra are not isolated but share their Bi-Bi edges forming a single chain, in contrast to the 0 D (OPb_4) cluster in compound **1**. Moreover, three single chains of (OBi_4) tetrahedra are further linked up together (*trans*-edge-sharing) forming a [O_3Bi_4] ribbon (Fig. 2c). The [O_3Bi_4] ribbons in the structure are arranged in an anti-parallel manner as viewing along *a* axis, surrounded by BO_3 triangles and PO_4 tetrahedra (Fig. 2f). Many Bi inorganic compounds containing 1D chains or ribbons composed of *trans*-edge-sharing (OBi_4) tetrahedra are reported,[30] however, to our knowledge, this type of [O_3Bi_4] ribbons has not been observed in bismuth oxosalts. Interestingly, very similar cases, [O_3Pb_4] and [O_3La_4] ribbons, are observed in the structures of ([Pb_4O_3]-$C_2H_2(CO_2)_2(H_2O)_{0.5}$)[33] and $La_4O_3(AsS_3)_2$,[34] respectively. Besides, each B atom is coordinated by three oxygen atoms in compound **2**, while each P atom is coordinated by four oxygen atoms in a tetrahedral geometry. The distances of B-O and P-O bonds are ranging from 1.360(2) to 1.420(2) Å, and from 1.519(11) to 1.547(11) Å, respectively, and all are well within the normal limits. Moreover, by using the same analysis methods as in compound **1**, the BO_3 triangles and PO_4 tetrahedra are all regular. Bond valence calculations[32] result in values of 2.78 −3.02, 2.91, and 4.84 for Bi^{3+}, B^{3+}, and P^{5+}, respectively.

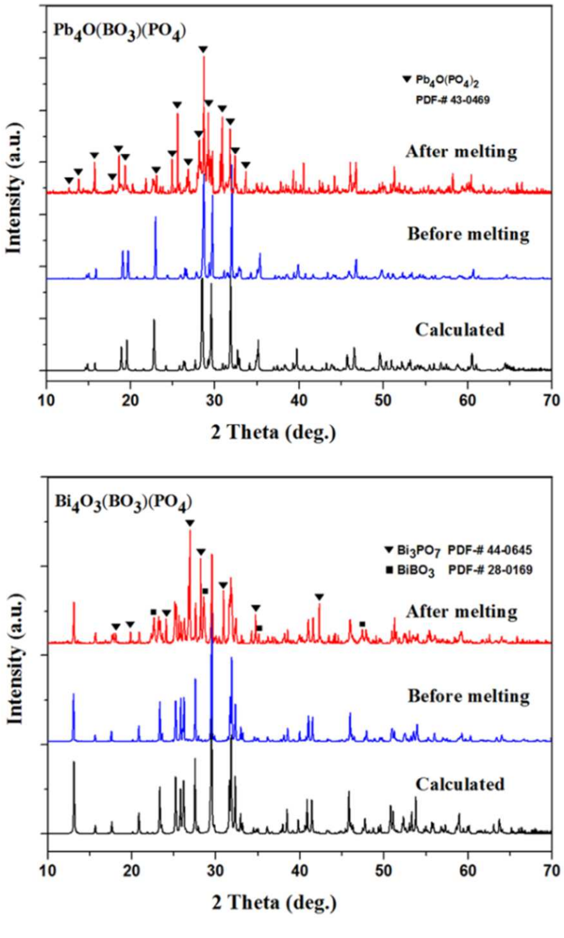

Fig. 3 Powder XRD patterns of calculated, before melting and after melting.

Thermal Analysis

Thermal gravimetric analysis (TGA) and differential scanning calarmeutry (DSC) curves of compounds 1 and 2 are presented in Fig. S3 in the ESI†. The TGA curves of both compounds exhibit nearly no weight loss up to 900 °C. In addition, for each one, only one endothermic peak (692 °C for compound 1 and 821 °C for compound 2) is observed from the heating curve of DSC results. The endothermic peaks were later pointed out to be the melting points of compounds **1** and **2**, respectively. In $Pb_4O(PO_4)_2$, and no other crystalline compounds were found, which may indicate the presence of amorphous boron-containing components; as for compound **2**, both Bi_3PO_7 and $BiBO_3$ were obtained beside initial phase (Fig. 3). In one sense, these results demonstrate that the two compounds are less stable than corresponding metal borate and phosphate compounds at high temperature. On the other hand, from the crystallization thermodynamical point of view, both of the two compounds melt incongruently so that the flux method is necessary for growing crystals.

Optical Properties

The IR spectra of compound **1** and **2** are similar (Fig. S2 in the ESI†). The main IR absorption region between 1240–540 cm^{-1} reveal several absorption bands on account of stretching and bending vibrations of the B-O and P-O groups, which are similar to those of other borate-phosphates. [10*d*, 12-13] There are no typical B-O-P absorption bands (around 850 or 750 cm^{-1}) as observed in other borophosphates,[6, 35] indicating the isolated characteristic of BO_3 and PO_4 groups. UV-Vis-NIR diffuse reflectance spectra were collected for compound **1** and **2** (Fig. S4 in the ESI†). It clearly reveals that their UV absorption edges are around 377 nm and 358 nm, respectively.

Structural Comparison and Prediction of new Compounds

As we stated early, the two compounds are intentionally synthesized based on our preliminary speculation. In fact, compounds **1** and **2** show strong structural correlations to $Pb_4O(PO_4)_2$ and $Bi_4O_3(BO_3)_2$, respectively. On the one hand, except for one oxygen atom, the asymmetric units of these compounds contain almost the same number of atoms, and all of them share the same FBUs, including (OPb_4) or (OBi_4) tetrahedra, BO_3 triangles and PO_4 tetrahedra. On the other hand, considering the BO_3-PO_4 correlation, $Pb_4O(PO_4)_2$ and $Bi_4O_3(BO_3)_2$ can be viewed as prototype of the two compounds, respectively. As seen from Fig. 4, the relationship between compound **1** and $Pb_4O(PO_4)_2$ represent the case of substitution from PO_4 tetrahedron to BO_3 triangle, while comparison between $Bi_4O_3(BO_3)_2$ and compound 2 stands for the example from BO_3 triangle to PO_4 tetrahedron. In the former case, both compound **1** and $Pb_4O(PO_4)_2$ crystallize in the same space group $P2_1/c$. In these two compouds, all B and P atoms are located at general positions 4*e*. It can be seen that four equivalent P(2) atoms in $Pb_4O(PO_4)_2$ are replaced by four B(1) atoms in compound **1,** whereas P(1) atoms in two compouds remain unchanged (Fig. 4a and 4b). In the latter case, because compound **2** and $Bi_4O_3(BO_3)_2$ are quite different in space group and cell parameter, it seems that the BO_3-PO_4 substitution takes place randomly in each site. However, a long range order can be revealed if one notices the arrangement of BO_3 and PO_4 groups (Fig. 4c and 4d). In $Bi_4O_3(BO_3)_2$, BO_3 triangles are arranged alternately with two different orientations, which can be considered as two kinds of pseudo-layers. Thus, when BO_3-PO_4 substitution takes place, the PO_4 terehedra only occupy the sites of BO_3 triangles in every two "layers" in compound **2.** It is worth noting that only half of BO_3 or PO_4 groups are substituted in one unit cell (for compound **2**, the unit cell is doubled). Although the arrangement of these FBUs varies, a general rule is that the BO_3 triangles are tending to "stack" more tightly with other groups, that is to say, compounds with more BO_3 triangles have higher density. For instance, the density of BO_3 and PO_4 groups in one unit cell (number of groups / cell volume) follows such an order: $Pb_4O(PO_4)_2$ (0.0085) < compound **1** (0.0094), and compound **2** (0.0091) < $Bi_4O_3(BO_3)_2$ (0.0098). The reason for this is simple: PO_4 tetrahedron always occupies larger space than BO_3 triangle.

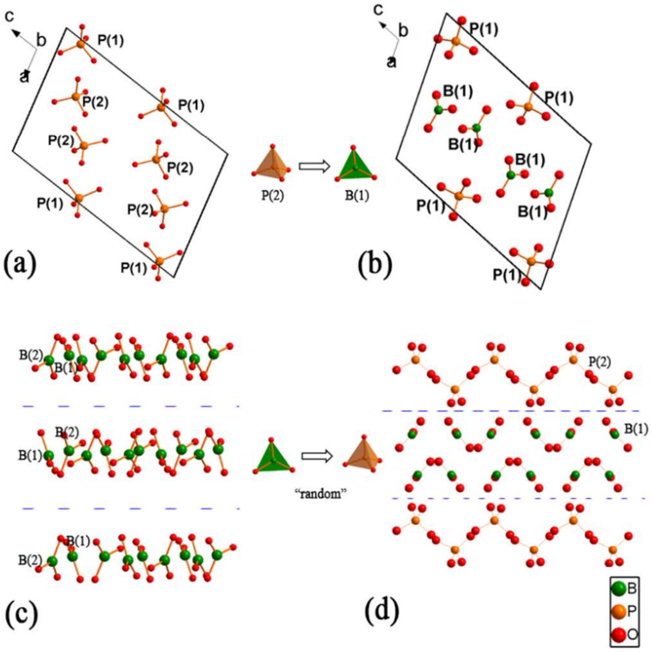

Fig. 4 Crystal structure comparisons of (a) $Pb_4O(PO_4)_2$; (b) compound 1; (c) $Bi_4O_3(BO_3)_2$; (d) compound 2 (Pb and Bi atoms are omitted for clarity).

To further demonstrate the substitution relationship of BO_3-PO_4 groups, we have calculated the Madelung energy of the two title compounds and the corresponding $Pb_4O(PO_4)_2$ and $Bi_4O_3(BO_3)_2$. The value of the Madelung energy for compound **1** calculated with the structure parameters is −48464 kJ/mol, which is almost identical to the value of −48370 kJ/mol (difference Δ= 0.19%) of the Madelung energies: $Pb_4O(PO_4)_2$ −59270 kJ/mol,[21] B_2O_3 −21900 kJ/mol[36] and P_2O_5 −43700 kJ/mol,[37] with the formula: $Pb_4O(BO_3)(PO_4) = Pb_4O(PO_4)_2 + 1/2\ B_2O_3 - 1/2\ P_2O_5$. The calculated result of compound **2** is −62028 kJ/mol, which is also in good agreement with the value of −62048 kJ/mol (difference Δ= 0.03%) of the Madelung energies: $Bi_4O_3(BO_3)_2$ −51148 kJ/mol,[22] B_2O_3 −21900 kJ/mol[36] and P_2O_5 −43700 kJ/mol,[37] with the formula: $Bi_4O_3(BO_3)(PO_4) = Bi_4O_3(BO_3)_2 - 1/2\ B_2O_3 + 1/2\ P_2O_5$. It is noted that the Madelung energy for BO_3-PO_4 substitution is only 10900 kJ/mol, which is relatively small compared with those of other components. Because the Madelung energy is the principal contributor to the lattice energy of crystals; therefore, these results strongly indicate that this BO_3-PO_4 substitution is energetically feasible.

In addition, in view of the insight on BO_3-PO_4 correlation, the connection among borate, phosphate and borate-phosphate could also be established. It should be noted that corresponding lead borate $Pb_4B_2O_7$ have been reported and it contains additional B_2O_5 groups besides BO_3 triangles.[20] However, the good news is that a new phase (polymorphism of $Pb_4B_2O_7$) has been found by our group very recently (space group: $P2_1/n$, a = 7.060(2) Å, b = 11.644(4) Å, c = 9.915(3) Å, β = 92.731(4)°, CCDC 1005124), and it exhibits almost the same structure as those of $Pb_4O(PO_4)_2$ and $Pb_4(BO_3)(PO_4)$, in which isolated BO_3 triangles and (OPb_4) tetrahedra are observed (we will publish this work soon). The structure of the corresponding phosphate $Bi_4O_3(PO_4)_2$ has not been reported, and only non-stoichiometric $Bi_{4+x}(PO_4)_2O_{3+3x/2}$ ($0.175 < x < 1$)[23] were found with a new structural type related to the fluorite. Nevertheless, it encourages us to conduct systematic research in future research work.

After successfully synthesizing the two compounds, a tetrahedral-planar group substitution is proposed for designing new borate-phosphates. This principle has been verified in some known borate-phosphates, for example, $M_3(BO_3)(PO_4)$ (M = Mg, Ba, Zn and Co)[10] and $SrCo_2(BO_3)(PO_4)$.[11] This could happen because: Firstly, the two anion units have the same formal charge of -3, and therefore, no additional compensation of charge balance is needed. Conversely, the replacement of BO_4 and PO_4 are less possible because the BO_4 group has a high formal charge of -5 far from that of the BO_3 and PO_4 group, although it has similar coordinate environment as the PO_4 group. Secondly, the existence of isolated BO_3 or PO_4 groups is an important prerequisite. The BO_3-PO_4 replacement occurs only in borate-phosphates but not observed in borophosphates. Because there are many factors affecting the crystal formation, it speculates that the formation of FBUs containing B-O-B or B-O-P connections in borophosphates, limits the "free transformations" of the BO_3 or PO_4 groups so that the substitution is energy unfavorable. At last, the numbers of BO_3 and PO_4 groups are equal after replacement. In borophosphates, it has been demonstrated that B/P ratio plays an important role on crystal structures.[8-9] However, the known borate-phosphates comprise a very limit B/P ratio, either 1/2 or 1, in comparison to a large range of B/P ratio observed in borophosphates. This phenomenon could be closely linked to the observation in borophosphates,[8] that is: if B/P ratio > 1, the additional BO_3 or BO_4 groups are tending to form a B-O-B linkage; on the contrary, B-O-P linkages are likely formed with B/P ratio < 1.

Conclusions

In conclusion, two new metal borate-phosphates have been synthesized by the solid-state method. They are structurally related and constituted by oxygen-centered (OPb_4) or (OBi_4) tetrahedra as well as isolated BO_3 and PO_4 groups. These two compounds show strong structural correlations to known metal borates and phosphates. We work out a strategy to design new borate-phosphates: a half replacement of the BO_3 by PO_4 units or vice versa, based on known borates or phosphates, respectively. Two points should be satisfied: One needs first to choose a borate or phosphate that has isolated BO_3 or PO_4 units. And then, the B/P ratio equals one when half substitution takes place. This close relationship of borate-phosphate to typical borate and phosphate suggests some interesting options for further investigations. Furthermore, it is well known that the analogues among inorganic compounds containing isolated MO_4 groups (M= pentavalent cations, such as P^{5+}, As^{5+}, V^{5+}, Mo^{5+} and Cr^{5+}) are common. In this respect, the relationship between BO_3-MO_4 units also offers many possibilities for designing new compounds beyond borate-phosphates.

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Notes and references

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