BaPbSi2O6•BaSO4: The first mixed anionic compound synthesized via BaSO4 salt-inclusion

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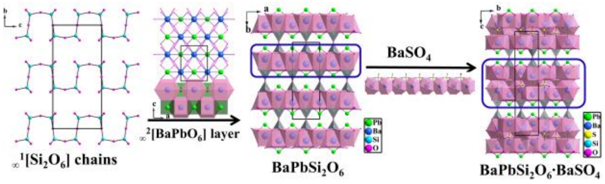

The novel silicate and sulfate compound, $BaPbSi_2O_6$ $BaSO_4$, has been synthesized via $BaSO_4$ salt-inclusion.

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$BaPbSi_2O_6{\cdot}BaSO_4$: The first mixed anionic compound synthesized via $BaSO_4$ salt-inclusion

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Exploring mixed anions materials is an ongoing challenge because of their important characteristics. However, there is no better way to guarantee the connection modes of anion groups and structures of mixed anions materials so far. We developed $BaSO_4$ as anion group provider and structure template to synthesize mixed anions materials.

Design and synthesis of mixed anionic materials have attracted much attention not only because of their varied forms and novel structures, but also their multifunctional physical and chemical properties.[1] For example, $A[ZnBP_2O_8]$ (A = NH_4, K, Rb, and Cs) show zeolite-like microporous structures,[2] and boron phosphate, BPO_4, has been proved to be a promising deep UV nonlinear optical (NLO) material.[3] The combination of B_4O_{10} group and SiO_4 group in $Cs_2B_4SiO_9$[1h] further expands the structural diversity of mixed anionic compounds, and also generates a potential deep-UV NLO material with extremely short UV cut-off wavelength and relatively large NLO response. The first borosulfate, $K_5[B(SO_4)_4]$,[1f] in which a central borate tetrahedron shares all its corners with four sulfate tetrahedra, gives a glance into the exciting new world of borosulfates. More recently, a new family of alkali borosulfates were synthesized and exhibit interesting framework with mixed anionic groups.[4] Very recently, our group has discovered some noncentrosymmetric (NCS) materials by introducing the relatively rigid MO_4 (M = P and Al) tetrahedra into the B-O framework, such as $Na_3Cd_3B(PO_4)_4$[5] and $NaBa_4(AlB_4O_9)_2Br_3$.[6] Some compounds also have mixed SO_4 and SiO_4 groups, such as $Ca_5(SiO_4)_4SO_4$[7] and $Ag_6(SO_4)(SiO_4)$.[8] Because of the interesting structures and potential applications of these materials containing mixed anionic groups, we focus on the subset of mixed anionic compounds. About the synthesis method, S.-J. Hwu et al. firstly recognized the salt-inclusion synthesis using metal halides in phosphates and arsenates.[9] The later appeared compounds containing metal halides, which adopt new structure types and exhibit fascinating physical properties,[10] also prove that salt-inclusion is a valid tool for a broad range of synthetic chemistry.[11] These discoveries have opened doors to novel material synthesis via the utilities of salt-inclusion chemistry (SIC). By a broad definition, salt-inclusion solids (SISs) are compounds made of a hybrid framework exhibiting integrated covalent and ionic lattices.[12] According to the traditional definition of ionic compounds, sulfates would be metallic cation and SO_4 anion by ionization. Consequently, $BaSO_4$ could be seen as ionic lattice in the structure, and used as molten-salt, which plays the role of structure template. In addition, sulfates will provide SO_4 tetrahedra, which could be combined with other anionic groups showing fascinating structural and physical properties associated with features. Based on the above idea, the basic compound, $BaPbSi_2O_6$, which we firstly synthesized by solid-state reaction at 845 °C, melts in the orthorhombic $BaSO_4$ salt crystallizing in *Pnma*,[13] and we have obtained a complex silicate and sulfate compound, $BaPbSi_2O_6{\cdot}BaSO_4$, for the first time. Because of the $BaSO_4$ salt-templating effect, $BaPbSi_2O_6{\cdot}BaSO_4$ crystallizes in the space group of *Pnma*, which is different from that of the basic compound, $BaPbSi_2O_6$. To the best of our knowledge, the ${}_{\infty}{}^{1}[Si_2O_6]$ chains, in which the periodic four SiO_4 tetrahedra are connected through corners forming open-rings, have not been found in any other complex silicate and sulfate compounds. Here, the synthesis of $BaPbSi_2O_6{\cdot}BaSO_4$ via $BaSO_4$ salt-inclusion is reported. The crystal structures and UV-Vis-NIR diffuse reflectance spectra of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$ are represented below. Theoretical calculations based on density functional theory (DFT) method are also performed on the reported materials.[14]

Firstly, polycrystalline powder sample of the basic compound, $BaPbSi_2O_6$, was prepared by standard solid-state reaction. Then, the orthorhombic $BaSO_4$ with analytical grade was added into $BaPbSi_2O_6$. A pure polycrystalline sample of $BaPbSi_2O_6{\cdot}BaSO_4$ was synthesized in air by standard solid-state reaction, according to the following formula,

$$BaPbSi_2O_6 + BaSO_4 \rightarrow BaPbSi_2O_6{\cdot}BaSO_4.$$

The experimental X-ray diffraction (XRD) data patterns are in agreement with the calculated ones based on the single-crystal crystallographic data of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$, respectively (Fig. S1 in the ESI†).

Colorless block crystals of $BaPbSi_2O_6$ and $BaPbSi_2O_6 \cdot BaSO_4$ were grown by spontaneous crystallization method, respectively. As we expected that the structure of $BaPbSi_2O_6 \cdot BaSO_4$ can be viewed as an intergrowth of $BaPbSi_2O_6$ [001] slab and [100] slab of the orthorhombic sulfate, $BaSO_4$ (Fig. 1). Fig. 2 is the ball-and-stick diagram of $BaPbSi_2O_6$ and $BaPbSi_2O_6 \cdot BaSO_4$. The asymmetric unit of the basic compound, $BaPbSi_2O_6$, contains one crystallographically independent Ba atom, one independent Pb atom, one independent Si atom, and three independent O atoms. In the structure, the only crystallographically independent Si atom coordinates to four O atoms to form SiO_4 tetrahedra, which are further connected through corner-sharing forming the $_{\infty}^{1}[Si_2O_6]$ chains with open-rings (Fig. 2*a*). The $_{\infty}^{1}[Si_2O_6]$ chains are stacked with coplanar orientation along [100] direction and the Si-O bond lengths are in the range from 1.603(4) to 1.629(3) Å, which are consistent with those observed in other compounds.[15] The BaO_{10} polyhedra and PbO_4 tetrahedra are connected alternatively to form the $_{\infty}^{2}[BaPbO_6]$ layer (Fig. 2*b*). Then, the $_{\infty}^{1}[Si_2O_6]$ chains are bridged the adjacent layers forming the whole structure of $BaPbSi_2O_6$ (Fig. 2*c*).

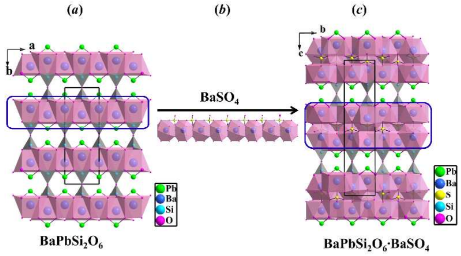

Fig. 1 Structure design of $BaPbSi_2O_6 \cdot BaSO_4$.

Generally, a highly electronegative element (e.g., O, F, Cl) tends to form ionic bonding (electrostatic interactions) with a highly electropositive element (e.g., alkali metal, alkaline-earth metal, and rare-earth metals).[16] The $_{\infty}^{2}[BaPbO_6]$ layers are not firm enough because of the weaker ionic bonds. So the $_{\infty}^{2}[BaPbO_6]$ layers can be easily disconnected, and the [100] slab of orthorhombic $BaSO_4$ (Fig. 2*d*) can insert into the $_{\infty}^{2}[BaPbO_6]$ layers forming the stronger $_{\infty}^{2}[BaPbSO_{10}]$ layers (Fig. 2*e*). As shown in Fig. 2*e*, the $_{\infty}^{1}[BaSO_4]$ chains insert into the $_{\infty}^{2}[BaPbO_6]$ layer along the [010] direction. Obviously, the "salt templating" effect has resulted in a new centric solid. This work affirms the utility of molten $BaSO_4$ salt for the high-temperature synthesis of mixed anionic materials.

The S-O bond lengths are in the range from 1.447(8) to 1.475(5) Å, which are consistent with the orthorhombic $BaSO_4$ and other compounds.[17] There are two crystallographically independent Ba atoms, and both of them are in eleven coordination environments with the Ba-O bond distances ranging from 2.342 (11) to 3.285 (11) Å. The results of bond valence calculations[18] for two compounds (Ba, 1.940-2.052; Pb, 2.256-2.274; Si, 4.125-4.250; S, 6.109) indicate that the Ba, Pb, Si and S atoms are in oxidation states of +2, +2, +4 and +6, respectively.[19]

The $_{\infty}^{1}[Si_2O_6]$ chains with four SiO_4 tetrahedra forming open-rings have not been found in any other sulphosilicates in the ICSD data. The adjacent SiO_4 tetrahedra are pulled closely to hold the smaller PbO_4 tetrahedra forming the open-rings. For example, from the formulae of $BaPbSi_2O_6$ and $BaSiO_3$ (which can be seen as $Ba_2Si_2O_6$),[20] the Pb^{2+} cation replaces the Ba^{2+} cation partially in $BaSiO_3$. The $_{\infty}^{1}[Si_2O_6]$ chains exhibit different bond tendency owning to the different cation size and the coordination environment, resulting in the $_{\infty}^{1}[Si_2O_6]$ chains with a repeat interval of two SiO_4 tetrahedra in $BaSiO_3$ and the $_{\infty}^{1}[Si_2O_6]$ chains with open-rings forming by four SiO_4 tetrahedra in $BaPbSi_2O_6$ (Fig. S2 in the ESI†).

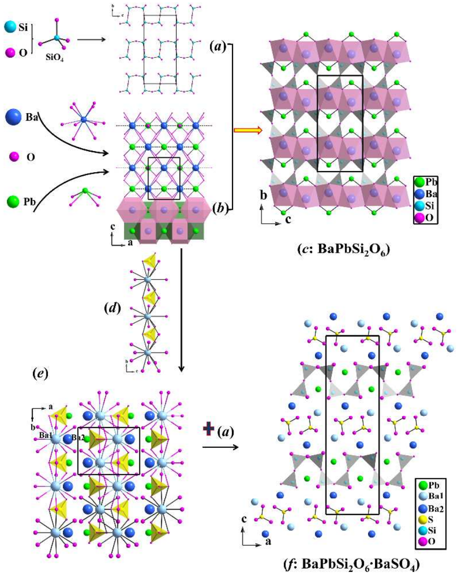

Fig. 2 Ball-and-stick diagram of $BaPbSi_2O_6$ and $BaPbSi_2O_6 \cdot BaSO_4$.

As shown in Fig. S3 in the ESI†, only one clear endothermic peak at 1048 ºC and one sharp endothermic peak at 1174 ºC are observed from the DSC heating curves for $BaPbSi_2O_6$ and $BaPbSi_2O_6 \cdot BaSO_4$, respectively, which suggests that after introducing stronger covalent bonds in SO_4 group, $BaPbSi_2O_6 \cdot BaSO_4$ has higher thermal stability than $BaPbSi_2O_6$. The pure polycrystalline samples of two compounds were put into a platinum crucible, heated to 1050 °C, and then cooled down to room temperature slowly. Analysis of the residue of $BaPbSi_2O_6$ in the platinum pan revealed that $BaPbSi_2O_6$ decomposed to $BaSi_2O_5$ and SiO_2 (Fig. S4*a* in the ESI†). However, $BaPbSi_2O_6 \cdot BaSO_4$ did not decompose (Fig. S4*b* in the ESI†), which further suggests that $BaPbSi_2O_6 \cdot BaSO_4$ has higher thermal stability than $BaPbSi_2O_6$. Then, $BaPbSi_2O_6 \cdot BaSO_4$ in the platinum crucible was heated to 1400 °C. Analysis of the residue in the platinum pan revealed that $BaPbSi_2O_6 \cdot BaSO_4$ decomposed to $BaSi_2O_5$, $BaSO_4$, SiO_2, as well as some unidentified products (Fig. S4*b* in the ESI†). Therefore, it is necessary to use the flux method to grow large single crystals of two compounds.

In order to specify and compare the coordination of silicon and sulfur in both compounds, the IR spectra were measured and display similar features (Fig. S5 in the ESI†). The main IR absorption region between 1200-450 cm^{-1} reveals several absorption bands on account of stretching and bending vibrations of the Si-O and S-O groups, which are similar to those of other metal silicates and sulfates.[1f,1h,18] The IR spectra further confirm the existence of SiO_4 and SO_4 tetrahedra, which are consistent with the results obtained from the single-crystal X-ray structural analysis of two compounds.

Fig. S6 in the ESI† shows the optical diffuse reflectance spectra of two compounds, which was converted from UV-Vis-NIR diffuse reflectance spectrum using the Kubelka-Munk function.[21] Obviously, the UV cut-off edges of two compounds are all below 300 nm. In a F(R) versus E (eV) plot, the band gap of $BaPbSi_2O_6$ is about 3.27 eV, and the band gap of $BaPbSi_2O_6{\cdot}BaSO_4$ is about 3.30 eV. That means the introduction of the SO_4 group has not apparently influenced the band gap, which will be explained well using the theoretical calculations as mentioned below.

The band structures of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$ along high symmetry points of the first Brillouin zone (BZ) are shown in Fig. S7 in the ESI†. Obviously, both compounds are indirect-gap materials. The calculated band gaps are 3.24 eV for $BaPbSi_2O_6$ and 3.29 eV for $BaPbSi_2O_6{\cdot}BaSO_4$, respectively, which are in good agreement with the values obtained from the diffuse-reflectance spectra. The partial density of states (PDOS) for two compounds are similar. As shown in Fig. S8 in the ESI†, the PDOS can be divided into three major distinct regions for both compounds. It is worth noting that the states near the band gap are mainly composed of Ba-5*p*, O-2*p* orbitals below the FL, and Ba-6*d*, Si-2*p* states at the bottom of conduction bands for both compounds. Accordingly, the absorption spectra near the UV cutoff edge can be assigned as the charge transfers from Ba-5*p* and O-2*p* to Ba-6*d* and Si-2*p* states, leading to the UV cutoff edge of both compounds locating at about 300 nm.

In conclusion, the synthesis of novel complex silicate and sulfate compound, $BaPbSi_2O_6{\cdot}BaSO_4$, is a result of inclusion of the $BaSO_4$ salt enroute to the $BaPbSi_2O_6$ framework. According to the electronic structure calculations, the absorption spectra near the UV cutoff edge can be assigned as the charge transfers from Ba-5*p* and O-2*p* to Ba-6*d* and Si-2*p* states, which means that the introduction of the SO_4 group has not apparently influenced the band gap. This is the first report of the synthesis of mixed anionic compound via $BaSO_4$ salt-inclusion. Further research on the mixed anionic compound via sulphates salt-inclusion is in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [CCDC reference numbers 969031, 969032 for $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$, respectively]. Experimental section; crystal data and structure refinements; atomic coordinates, equivalent isotropic displacement parameters (Å^2) and bond valence sum; selected bond lengths; experimental and calculated XRD patterns; DSC curves; IR spectra; UV-Vis-NIR diffuse reflectance spectra of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$. See DOI: 10.1039/c000000x/

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