CrystEngComm

COMMUNICATION

$BaPbSi_2O_6 \cdot BaSO_4$: the first mixed anionic compound synthesized *via* $BaSO_4$ salt-inclusion†

Cite this: *CrystEngComm*, 2014, **16**, 5993

Received 14th March 2014,
Accepted 14th April 2014

DOI: 10.1039/c4ce00527a

www.rsc.org/crystengcomm

Lingyun Dong,[ab] Shilie Pan,*[a] Ying Wang,[ab] Hongwei Yu,[ab] Qiang Bian,[ab]
Zhihua Yang,*[a] Hongping Wu[a] and Min Zhang*[a]

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

The design and synthesis of mixed anionic materials has attracted much attention not only because of their varied forms and novel structures, but also because of 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 a 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 an extremely short UV cut-off wavelength and a 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 which exhibit an interesting framework with mixed anionic groups.[4] Very recently, our group has discovered some noncentrosymmetric (NCS) materials by introducing relatively rigid MO_4 (M = P and Al) tetrahedra into the B–O framework, such as $Na_3Cd_3B(PO_4)_4$ (ref. 5) and $NaBa_4(AlB_4O_9)_2Br_3$.[6] Some compounds also have mixed SO_4 and SiO_4 groups, such as $Ca_5(SiO_4)_4SO_4$ (ref. 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. Regarding the synthesis method, S.-J. Hwu *et al.* firstly recognized salt-inclusion synthesis using metal halides in phosphates and arsenates.[9] Later compounds contained metal halides, which adopt new structure types and exhibit fascinating physical properties,[10] also proving 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* 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 a metallic cation and SO_4 anion by ionization. Consequently, $BaSO_4$ could be seen as an ionic lattice in the structure, and used as a molten-salt, which plays the role of a 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 their 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 the *Pnma* space group,[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 *Pnma* space group, which is different from that of the basic compound, $BaPbSi_2O_6$. To the best of our knowledge, the ${}^{1}_{\infty}[Si_2O_6]$ 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

---

[a] *Key Laboratory of Functional Materials and Devices for Special Environments of CAS, Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China. E-mail: slpan@ms.xjb.ac.cn*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

† Electronic supplementary information (ESI) available: 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 $BaPbSi_2O_6 \cdot BaSO_4$. CCDC 969031, 969032 for $BaPbSi_2O_6$ and $BaPbSi_2O_6 \cdot BaSO_4$, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00527a

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 presented. Theoretical calculations based on density functional theory (DFT) are also performed on the reported materials.[14]

Firstly, a polycrystalline powder sample of the basic compound, $BaPbSi_2O_6$, was prepared by standard solid-state reaction. Then, analytical grade orthorhombic $BaSO_4$ 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) patterns are in agreement with the calculated patterns based on the single-crystal crystallographic data of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$, respectively (Fig. S1, ESI†).

Colorless block crystals of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$ were grown by a spontaneous crystallization method. As we expected, the structure of $BaPbSi_2O_6{\cdot}BaSO_4$ can be viewed as an intergrowth of a $BaPbSi_2O_6$ [001] slab and a [100] slab of the orthorhombic sulfate, $BaSO_4$ (Fig. 1). Fig. 2 shows ball-and-stick diagrams of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$.

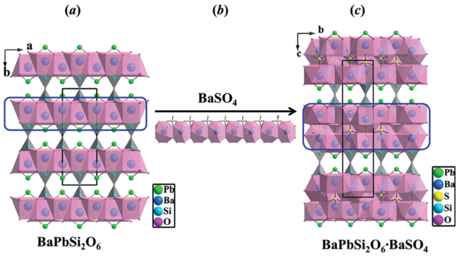

Fig. 1 Structure design of $BaPbSi_2O_6{\cdot}BaSO_4$.

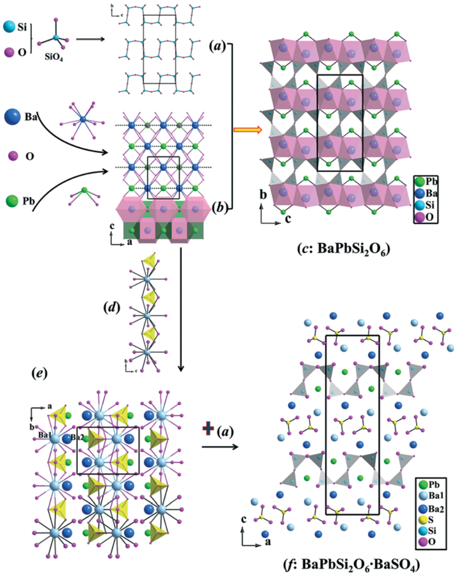

Fig. 2 Ball-and-stick diagrams of $BaPbSi_2O_6$ and $BaPbSi_2O_6{\cdot}BaSO_4$.

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 ${}^{1}_{\infty}[Si_2O_6]$ chains with open rings (Fig. 2a). The ${}^{1}_{\infty}[Si_2O_6]$ chains are stacked with a coplanar orientation along the [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 ${}^{2}_{\infty}[BaPbO_6]$ layer (Fig. 2b). Then, the ${}^{1}_{\infty}[Si_2O_6]$ chains are bridged with the adjacent layers, forming the whole structure of $BaPbSi_2O_6$ (Fig. 2c).

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 ${}^{2}_{\infty}[BaPbO_6]$ layers are not firm enough because of the weaker ionic bonds. Hence the ${}^{2}_{\infty}[BaPbO_6]$ layers can be easily disconnected, and the [100] slab of orthorhombic $BaSO_4$ (Fig. 2d) can insert into the ${}^{2}_{\infty}[BaPbO_6]$ layers, forming the stronger ${}^{2}_{\infty}[BaPbSO_{10}]$ layers (Fig. 2e). As shown in Fig. 2e, the ${}^{1}_{\infty}[BaSO_4]$ chains insert into the ${}^{2}_{\infty}[BaPbO_6]$ 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 the 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 ${}^{1}_{\infty}[Si_2O_6]$ chains with four SiO_4 tetrahedra forming open rings are not found in any other sulfosilicates, from 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 partially replaces the Ba^{2+} cation in $BaSiO_3$. The ${}^{1}_{\infty}[Si_2O_6]$ chains exhibit different bond tendencies owing to the different cation size and the coordination environment, resulting in ${}^{1}_{\infty}[Si_2O_6]$ chains with a repeat interval of two SiO_4 tetrahedra in $BaSiO_3$ and ${}^{1}_{\infty}[Si_2O_6]$ chains with open rings formed by four SiO_4 tetrahedra in $BaPbSi_2O_6$ (Fig. S2, ESI†).

As shown in Fig. S3, ESI,† only one clear endothermic peak at 1048 °C and one sharp endothermic peak at 1174 °C are observed in 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 the SO_4 group, $BaPbSi_2O_6{\cdot}BaSO_4$ has higher thermal stability than $BaPbSi_2O_6$.

The pure polycrystalline samples of the two compounds were put in a platinum crucible, heated to 1050 °C, and then slowly cooled down to room temperature. 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. S4a, ESI†). However, $BaPbSi_2O_6{\cdot}BaSO_4$ did not decompose (Fig. S4b, ESI†), which further suggests that $BaPbSi_2O_6{\cdot}BaSO_4$ has higher thermal stability than $BaPbSi_2O_6$. Next, $BaPbSi_2O_6{\cdot}BaSO_4$ 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 $BaSi_2O_5$, $BaSO_4$ and SiO_2, as well as some unidentified products (Fig. S4b, ESI†). Therefore, it is necessary to use the flux method to grow large single crystals of the two compounds.

In order to specify and compare the coordination of silicon and sulfur in both compounds, the IR spectra were measured, and they display similar features (Fig. S5, ESI†). The main IR absorption region between 1200–450 cm^{-1} reveals several absorption bands on account of the stretching and bending vibrations of the Si–O and S–O groups, which are similar to those of other metal silicates and sulfates.[1f,h,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 the two compounds.

Fig. S6, ESI† shows the optical diffuse reflectance spectra of the two compounds, which were converted from UV-vis-NIR diffuse reflectance spectra using the Kubelka–Munk function.[21] The UV cut-off edges of the two compounds are all below 300 nm. From the $F(R)$ *versus* E(eV) plots, 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 that the introduction of the SO_4 group has not apparently influenced the band gap, which will be explained well using the theoretical calculations as discussed below.

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

In conclusion, the synthesis of a novel complex silicate and sulfate compound, $BaPbSi_2O_6{\cdot}BaSO_4$, is a result of the inclusion of the $BaSO_4$ salt en route to the $BaPbSi_2O_6$ framework. According to the electronic structure calculations, the absorption spectra near the UV cutoff edge can be assigned as charge transfers from the Ba 5p and O 2p states to the Ba 6d and Si 2p 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 compounds *via* $BaSO_4$ salt-inclusion. Further research on the mixed anionic compound *via* sulfate salt-inclusion is in progress.

Acknowledgements

This work is supported by the 973 Program of China (grant no. 2012CB626803), the National Natural Science Foundation of China (grant no. U1129301, 51172277, 21201176, 21101168, 11104344), the Main Direction Program of Knowledge Innovation of CAS (grant no. KJCX2-EW-H03-03), The Funds for Creative Cross & Cooperation Teams of CAS, the Major Program of Xinjiang Uygur Autonomous Region of China during the 12th Five-Year Plan Period (grant no. 201130111), the High Technology Research & Development Program of Xinjiang Uygur Autonomous Region of China (grant no. 201116143, 201315103), and the Science and Technology Project of Urumqi (grant no. G121130002).

Notes and references

1 (*a*) Y. Wang, S. L. Pan, M. Zhang, S. J. Han, X. Su and L. Y. Dong, *CrystEngComm*, 2012, **18**, 12046; (*b*) J. L. Song, C. L. Hu, X. Xu, F. Kong and J. G. Mao, *Inorg. Chem.*, 2013, **52**, 8979; (*c*) R. E. Sykora, K. M. Ok, P. S. Halasyamani, D. M. Wells and T. E. Albrecht-Schmitt, *Chem. Mater.*, 2002, **14**, 2741; (*d*) J. Zhao and R. K. Li, *Inorg. Chem.*, 2012, **51**, 4568; (*e*) I. Boy, F. Stowasser, G. Schäfer and R. Kniep, *Chem. – Eur. J.*, 2001, 7, 834; (*f*) H. A. Höppe, K. Kazmierczak, M. Daub, K. Förg, F. Fuchs and H. Hillebrecht, *Angew. Chem., Int. Ed.*, 2012, **51**, 6255; (*g*) S. L. Pan, Y. C. Wu, P. Z. Fu, G. C. Zhang, Z. H. Li, C. X. Du and C. T. Chen, *Chem. Mater.*, 2003, **15**, 2218; (*h*) H. P. Wu, H. W. Yu, S. L. Pan, Z. J. Huang, Z. H. Yang, X. Su and K. R. Poeppelmeier, *Angew. Chem., Int. Ed.*, 2013, **52**, 3406.

2 (*a*) R. Kniep, G. Schäfer, H. Engelhardt and I. Boy, *Angew. Chem.*, 1999, **111**, 3857; (*b*) R. Kniep, G. Schäfer, H. Engelhardt and I. Boy, *Angew. Chem., Int. Ed.*, 1999, **38**, 3641.

3 (*a*) Z. H. Li, Z. S. Lin, Y. C. Wu, P. Z. Fu and Z. Z. Wang, *Chem. Mater.*, 2004, **16**, 2906; (*b*) S. G. Zhao, G. C. Zhang, K. Feng, J. Lu and Y. C. Wu, *Cryst. Res. Technol.*, 2012, **47**, 391.

4 M. Daub, K. Kazmierczak, P. Gros, H. Höppe and H. Hillebrecht, *Inorg. Chem.*, 2013, **52**, 6011.

5 Y. J. Shi, S. L. Pan, X. Y. Dong, Y. Wang, M. Zhang, F. F. Zhang and Z. X. Zhou, *Inorg. Chem.*, 2012, **51**, 10870.

6 H. W. Yu, S. L. Pan, H. P. Wu, Z. H. Yang, L. Y. Dong, X. Su, B. B. Zhang and H. Y. Li, *Cryst. Growth Des.*, 2013, **13**, 3514.

7 F. H. Irran, E. Tillmanns and G. Hentschel, *Mineral. Petrol.*, 1997, **60**, 121.

8 H. L. Keller and H. Mueller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1974, **408**, 121.

9 (*a*) Q. Huang, M. Ulutagay, P. A. Michener and S.-J. Hwu, *J. Am. Chem. Soc.*, 1999, **121**, 10323; (*b*) Q. Huang, S.-J. Hwu and X. Mo, *Angew. Chem., Int. Ed.*, 2001, **40**, 1690.

10 (*a*) Q. Huang, M. Ulutagay-Kartin, X. Mo and S.-J. Hwu, *Mater. Res. Soc. Symp. Proc.*, 2003, **755**, 459; (*b*) S.-J. Hwu, M. Ulutagay-Kartin, J. A. Clayhold, R. Mackay, T. A. Wardojo, C. T. O'Connor and M. Krawiec, *J. Am. Chem. Soc.*, 2002, **124**, 12404; (*c*) V. Gnezdilov, V. Bedarev, S. Gnatchenko, M. Pashchenko, Yu. Pashkevich, P. Lemmens, S. Zvyagin, X. Mo, W. Queen and S.-J. Hwu, *Low Temp. Phys.*, 2007, **33**, 684; (*d*) W. L. Queen, S.-J. Hwu and S. Reighard, *Inorg. Chem.*, 2010, **49**, 1316–1318.

11 (*a*) W. L. Queen, J. P. West, S.-J. Hwu, T. T. Tran, P. S. Halasyamani and D. VanDerveer, *Chem. Commun.*, 2012, **48**, 1665; (*b*) R. Vaidhyanathan, S. Natarajan and C. N. R. Rao, *Eur. J. Inorg. Chem.*, 2003, **9**, 1675; (*c*) A. Choudhury and P. K. Dorhout, *Inorg. Chem.*, 2006, **45**, 5245; (*d*) H. W. Yu, H. P. Wu, S. L. Pan, Z. H. Yang, X. Su and F. F. Zhang, *J. Mater. Chem.*, 2012, **22**, 9665.

12 J. P. West and S.-J. Hwu, *J. Solid State Chem.*, 2012, **195**, 101.

13 A. A. Colville and K. Staudhammer, *Am. Mineral.*, 1967, **52**, 1877.

14 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.

15 (*a*) S. J. Han, S. L. Pan, Z. H. Yang, Y. Wang, B. B. Zhang, M. Zhang, Z. J. Huang, L. Y. Dong and H. W. Yu, *Z. Anorg. Allg. Chem.*, 2013, **639**, 779; (*b*) W. H. Baur and T. Ohta, *J. Solid State Chem.*, 1982, **44**, 50; (*c*) R. A. Howie and A. R. West, *Nature*, 1976, **259**, 473.

16 A. H. Fang, F. Q. Huang, X. M. Xie and M. H. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 3260.

17 (*a*) J. Bruns, M. Eul, R. Pçttgen and M. S. Wickleder, *Angew. Chem., Int. Ed.*, 2012, **51**, 2204; (*b*) M. Reynauda, P. Barpanda, G. Rousse, J. N. Chotard, B. C. Melot, N. Recham and J. M. Tarascon, *Solid State Sci.*, 2012, **14**, 15; (*c*) U. Betke, W. Dononelli, T. Klüner and M. S. Wickleder, *Angew. Chem., Int. Ed.*, 2011, **50**, 12361.

18 (*a*) N. E. Brese and M. O¢Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 192; (*b*) I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244.

19 (*a*) H. P. Wu, H. W. Yu, Z. H. Yang, X. L. Hou, X. Su, S. L. Pan, K. R. Poeppelmeier and J. M. Rondinelli, *J. Am. Chem. Soc.*, 2013, **135**, 4215; (*b*) H. R. Tian, W. H. Wang, Y. E. Gao, T. T. Deng, J. Y. Wang, Y. L. Feng and J. W. Cheng, *Inorg. Chem.*, 2013, **52**, 6242; (*c*) M. A. Bredig, *J. Phys. Chem.*, 1942, **46**, 747; (*d*) S. J. Saint-Jean and S. Hansen, *Solid State Sci.*, 2005, **7**, 97; (*e*) H. W. Yu, S. L. Pan, H. P. Wu, W. W. Zhao, F. F. Zhang, H. Y. Li and Z. H. Yang, *J. Mater. Chem.*, 2012, **22**, 2105.

20 H. P. Grosse and E. Tillmanns, *Cryst. Struct. Commun.*, 1974, **3**, 603.

21 (*a*) P. Kubelka and F. Munk, *Z. Tech. Phys.*, 1931, **12**, 593; (*b*) J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721.