

MS15-O2 Crystal chemistry of layered Pb hydroxycarbonate minerals

Oleg I. Siidra¹, Diana O. Zinyakhina¹, Anatoly N. Zaitsev¹, Rick Turner², Mike Rumsey³, Igor V. Pekov⁴, Nikita V. Chukanov⁵, Sergey V. Krivovichev¹, Erik Jonsson⁶

1. Saint-Petersburg State University
2. Imbuia Holdings
3. Natural History Museum
4. Moscow State University
5. Institute of Problems of Chemical Physics
6. Geological Survey of Sweden, Department of Mineral Resources

email: o.siidra@spbu.ru

Oleg Siidra, Diana Zinyakhina, Anatoly Zaitsev, Rick Turner, Mike Rumsey, Nikita Chukanov, Sergey Krivovichev, Igor Pekov, Erik Jonsson.

Pb carbonate minerals containing additional hydroxyl groups receive considerable attention due to their importance to the environment. These phases widely form as lead corrosion technological products. Majority of Pb hydroxycarbonates demonstrate layered structural architectures and include: hydrocerussite, plumbonacrite and recently discovered grooffonteinite, abellaite and NaPb₃(OH)₃(CO₃)₄ mineral phase from Lavrion slags. There were several reports on hydrocerussite physical properties and chemistry previously (e.g. Anthony *et al.*, 2003; Olby, 1966). Structural data on powdery synthetic samples of '2PbCO₃·Pb(OH)₂' were reported in Marinetto *et al.*, 2002. However single-crystal X-ray data for natural samples of layered Pb hydroxycarbonates were unavailable till very recent time. We have worked with many samples of "hydrocerussite" from several localities within our ongoing projects on Pb²⁺ oxysalts crystal chemistry: Merehead quarry, England; Långban, Sweden; Lavrion, Greece; Kombat, Namibia. Structural studies allowed identification of grooffonteinite from Kombat and unknown yet as a mineral NaPb₃(OH)₃(CO₃)₄ from Lavrion slags. Several different polytypes for hydrocerussites from Merehead were also identified. Each of above mentioned Pb hydroxycarbonates demonstrates unique but related structure type, which in turn can be transformed via various mechanisms one to each other.

This work was supported by St. Petersburg State University through the internal grant 3.38.238.2015 and RFBR 15-35-20632.

Keywords: lead, carbonates, minerals, layered materials, oxysalts

MS15-O3 Phase diagrams of Ba₂M²⁺Te⁶⁺O₆: insight into the interplay between crystal structure and magnetic dimensionality

Alexandra S. Gibbs^{1,2,3}, Kevin S. Knight¹, Paul J. Saines^{4,5}, James R. Hester⁶, Hidenori Takagi^{2,3,7}

1. ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, OX11 0QX, United Kingdom
2. Department of Physics, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-0033 Japan
3. Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany
4. School of Physical Sciences, University of Kent, Canterbury, CT2 7NH, United Kingdom
5. Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, United Kingdom
6. Bragg Institute, ANSTO, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia
7. Institute for Functional Materials and Quantum Technologies, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

email: alexandra.gibbs@stfc.ac.uk

Ba₂M²⁺Te⁶⁺O₆ (M²⁺=Ni, Cu, Zn) adopt structures composed of triplets of face-sharing TeO₆ and MO₆ octahedra linked by corner-sharing TeO₆ octahedra [1,2]. This leads to a crystal structure composed of 1D chains along the *c*-axis and a 2D network in the *ab*-plane. We will present detailed high resolution neutron diffraction studies of the thermal phase diagrams of all three compounds, focusing on the relationship between crystal structure and magnetic dimensionality in this family.

At ambient temperature, Ba₂NiTeO₆ and Ba₂ZnTeO₆ crystallise in space group *R*-3 \bar{m} whilst Ba₂CuTeO₆ has a distorted monoclinic *C2/m* structure² (Figure 1). Ba₂CuTeO₆ and Ba₂NiTeO₆ display clear differences in magnetic dimensionality. Ba₂NiTeO₆ is a strongly frustrated antiferromagnet with $T_N=8.5$ K [3]. Ba₂CuTeO₆, on the other hand, shows quasi-1D two-leg *S*=1/2 spin ladder behaviour above *T*~25 K followed by 'marginal' magnetic ordering at *T*_{mag}=16 K. Our previous work implies that the system is in close proximity to a quantum critical point induced by inter-ladder coupling [2].

It could be easily assumed that the different crystal structure of Ba₂CuTeO₆ compared to Ba₂NiTeO₆ and nonmagnetic Ba₂ZnTeO₆ at ambient temperature is related to the Jahn-Teller effect of the Cu²⁺ ion. However, using high-resolution neutron diffraction the phase diagrams of the three compounds have been mapped by us and reveal a more complex and interesting picture [3]. The phase diagram of Ba₂CuTeO₆ reveals a high-temperature Jahn-Teller transition and unexpected low-temperature monoclinic-to-triclinic transition undetectable by specific heat measurements. Ba₂NiTeO₆ shows no structural phase transitions down to *T*=1.8 K whereas in Ba₂ZnTeO₆, a transition to *C2/m* below *T*~165 K is found. The discovery of an intrinsic structural instability towards the *C2/m* phase displayed by Jahn-Teller inactive Ba₂ZnTeO₆ (but not by Ba₂NiTeO₆) requires a re-examination of the interplay between crystal structure, Jahn-Teller distortions and magnetic dimensionality in these compounds opening up a new route to understanding the exotic magnetism present in this family.

[1] P. Köhl and D. Reinen, *Z. Anorg. Allg. Chem* 409, 257-352 (1974).

[2] A. S. Gibbs, A. Yamamoto, A. N. Yaresko, K. S. Knight, H. Yasuoka, M. Majumder, M. Baenitz, P. J. Saines, J. R. Hester, D. Hashizume, A. Kondo, K. Kindo and H. Takagi, arXiv:1511.01477 (2015).

[3] A. S. Gibbs, K. S. Knight, P.J. Saines, J. R. Hester and H. Takagi, to be submitted.

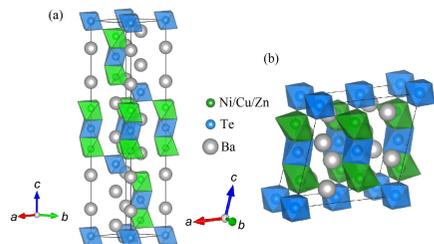


Figure 1. The room temperature structures of (a) $\text{Ba}_2\text{NiTeO}_6$ and $\text{Ba}_2\text{ZnTeO}_6$, and (b) $\text{Ba}_2\text{CuTeO}_6$.

Keywords: transition metal oxides, phase transitions, neutron diffraction, magnetism

MS15-O4 Crystal structure and polymorphism of NaSrVO_4 : the first $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{X}^{\text{V}}\text{O}_4$ larnite related structure from X-ray powder data

Gwilherm Nenert¹

1. PANalytical B. V., Lelyweg 1, 7602 EA Almelo, The Netherlands

email: gwilherm.nenert@panalytical.com

The crystal chemistry of $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{X}^{\text{V}}\text{O}_4$ (A^{I} = alkali ion, B^{II} = alkali-earth ion, $\text{X} = \text{P, V, As}$) is very rich and leads to numerous polymorphic phases which belong to 8 different structures types: olivine, arcanite, glaserite, tridymite, $\alpha\text{-K}_2\text{SO}_4$, $\beta\text{-Na}_2\text{SO}_4$ and $\gamma\text{-Na}_2\text{SO}_4$ [1]. Among the various families ($\text{X} = \text{P, V, As}$), the phosphates have been the most widely investigated. Besides the purely interest from a crystal chemistry point of view, the research activities related to this family of materials is driven mainly due to their ferroelectric and ferroelastic properties and possible applications as phosphors for LEDs [1,2].

Within the rich crystal chemistry of this family, no structural data have demonstrated the occurrence of the larnite/belite structure [3]. The larnite/belite structure has been widely investigated due to its importance for Portland cement and its rich polymorphism [4]. All the materials related to the larnite structural type have the general formula $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{X}^{\text{V}}\text{O}_4$ ($\text{A, B} = \text{Ca, Sr, Eu; Ba}$; $\text{X} = \text{Si, Ge, Ti}$) [4]. Upon doping on the A, B and X sites, some alkaline ions can be incorporated into the structure giving rise to belite [5] and flamite [6].

NaSrVO_4 has been mentioned in the past but with conflicting results and without providing any structural model [3, 7]. These contradicting results and the absence of report on the crystal structure motivated us to reinvestigate this material. We present here its crystal structure, as determined and refined from laboratory powder X-ray diffraction data. This is the first crystal structure reported among the larnite/belite structural type exhibiting the chemistry $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{X}^{\text{V}}\text{O}_4$. Similarly to other larnite structures, we observe a rich polymorphism in the temperature range 25 – 900°C and we report one polymorph which was not previously reported in the larnite family.

[1] V. A. Isupov, *Ferroelectrics*, **2002** 274:1, 203-283.

[2] S. Choi, *et al. Optical Letters*, **2013** 38, 1346-1348.

[3] S. Drai, *et al.*, **1974**. *Journal of Solid State Chemistry*, 10, 95-101

[4] H. F. W. Taylor, **1990** *Cement Chemistry*, Academic Press.

[5] M. Catti, *et al.* **1983**. *Acta Crystallogr., Sect. B: Struct. Sci.*, 39, 674-679; S. Deganello, **1973**. *Acta Cryst. B* 29,2593-2597; J. Felsche **1971**. *Die Naturwissenschaften*, 58, 218-219; C. M. Midgley **1952**. *Acta Cryst.* 5, 307-312.

[6] F. Gfeller, *et al.* **2015**. *European Journal of Mineralogy* 27, 755-769.

[7] R. Klement, P. Kresse **1961**. *Zeitschrift für anorganische und allgemeine Chemie*, 310, 53-68.

Keywords: larnite, belite, vanadate, powder diffraction, NaSrVO_4