MS15-O2 Crystal chemistry of layered Pb hydroxocarbonate minerals

Oleg I. Siidra[1], Diana O. Zinyakhina[1], Anatoly N. Zaitsev[1], Rick Turner[2], Mike Rumsey[3], Igor V. Pekov[4], Nikita V. Chukanov[5], Sergey V. Krivovichev[1], Erik Jonsson[6]

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 hydroxocarbonates demonstrate layered structural architectures and include: hydrocerussite, plumbonacrite and recently discovered grootfonteinite, abellaite and $NaPb_5(OH)_3(CO_3)_4$ 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 '$2PbCO_3$·$Pb(OH)_2$' were reported in Marinetto *et al*., 2002. However single-crystal X-ray data for natural samples of layered Pb hydroxocarbonates were unavailable till very recent time. We have worked with many samples of "hydrocerussite" from several localities within our ongoing projects on Pb^{2+} oxysalts crystal chemistry: Merehead quarry, England; Långban, Sweden; Lavrion, Greece; Kombat, Namibia. Structural studies allowed identification of grootfonteinite from Kombat and unknown yet as a mineral $NaPb_5(OH)_3(CO_3)_4$ from Lavrion slags. Several different polytypes for hydrocerussites from Merehead were also identified. Each of above mentioned Pb hydroxocarbonates 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 $Ba_2M^{2+}Te^{6+}O_6$: insight into the interplay between crystal structure and magnetic dimensionality

Alexandra S. Gibbs[1,2,3], Kevin S. Knight[1], Paul J. Saines[4,5], James R. Hester[6], 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

$Ba_2M^{2+}Te^{6+}O_6$ (M^{2+}=Ni, Cu, Zn) adopt structures composed of triplets of face-sharing TeO_6 and MO_6 octahedra linked by corner-sharing TeO_6 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, Ba_2NiTeO_6 and Ba_2ZnTeO_6 crystallise in space group $R\bar{3}m$ whilst Ba_2CuTeO_6 has a distorted monoclinic $C2/m$ structure [2] (Figure 1). Ba_2CuTeO_6 and Ba_2NiTeO_6 display clear differences in magnetic dimensionality. Ba_2NiTeO_6 is a strongly frustrated antiferromagnet with T_N=8.5 K [3]. Ba_2CuTeO_6, 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 Ba_2CuTeO_6 compared to Ba_2NiTeO_6 and nonmagnetic Ba_2ZnTeO_6 at ambient temperature is related to the Jahn-Teller effect of the Cu^{2+} 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 Ba_2CuTeO_6 reveals a high-temperature Jahn-Teller transition and unexpected low-temperature monoclinic-to-triclinic transition undetectable by specific heat measurements. Ba_2NiTeO_6 shows no structural phase transitions down to T=1.8 K whereas in Ba_2ZnTeO_6 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 Ba_2ZnTeO_6 (but not by Ba_2NiTeO_6) 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.