Crystal chemistry of layered Pb hydroxocarbonate minerals

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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 NaPb3(OH)5(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 hydroxocarbonates 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 grootfonteinite from Kombat and unknown yet as a mineral NaPb3(OH)5(CO3)4 from Lavrion slags. Several different polytypes for hydrocerussites from Merehead were also identified. Each of above mentioned Pb hydroxocarbonate demonstrates unique but related structure type, which in turn can be transformed via various mechanisms one to each other.

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

Phase diagrams of Ba2M2+Te6+O66−, insight into the interplay between crystal structure and magnetic dimensionality

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Ba2M2+Te6+O66− (M2+=Ni, Cu, Zn) adopt structures composed of triplets of face-sharing TeO6 octahedra 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-3m whilst Ba2CuTeO6 has a distorted monoclinic C2/m structure (Figure 1). Ba2CuTeO6 and Ba2NiTeO6 display clear differences in magnetic dimensionality. Ba2NiTeO6 is a strongly frustrated antiferromagnet with Tc=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 Tm=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.


Figure 1. The room temperature structures of (a) Ba₂NiTeO₆ and Ba₂ZnTeO₆ and (b) Ba₂CuTeO₆.

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

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The crystal chemistry of A⁺⁺B⁺⁺X⁴⁻O₄ (A⁺⁺ = alkali ion, B⁺⁺ = alkali-earth ion, X = P, V, As) is very rich and leads to numerous polymorphic phases which belong to 8 different structures types: olivine, arcanite, glaserite, tridymite, α-K₂SiO₄, β-Na₂SO₄ and γ-Na₂SO₄ [1]. Among the various families (X = 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 A⁺⁺B⁺⁺X⁴⁻O₄ (A, B = Ca, Sr, Eu; Ba; X = Si, Ge, Ti) [4]. Upon doping on the A, B and X sites, some alcaline ions can be incorporated into the structure giving rise to belite [5] and flamite [6].

NaSrVO₄ 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 A⁺⁺B⁺⁺X⁴⁻O₄. 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.


Keywords: larnite, belite, vanadate, powder diffraction, NaSrVO₄