

**P10.02.10***Acta Cryst.* (2008). **A64**, C493**Crystal structure analysis of Rb<sub>0.5</sub>Tl<sub>0.5</sub>H<sub>2</sub>PO<sub>4</sub> at room temperature by neutron diffraction**In-Hwan Oh<sup>1,3</sup>, Stefan Mattauch<sup>2</sup>, Gernot Heger<sup>3</sup>, Cheol Eui Lee<sup>1</sup>

<sup>1</sup>BK21 Initiative for Global Leaders in Physics, Korea University, Department of Physics, Asan Science Building, Room 626, Anam-dong Seongbuk-Gu, Seoul, Seoul, 136-701, Korea (S), <sup>2</sup>Institut fuer Festkoerperforschung, Juelich Centre for Neutron Science, Forschungszentrum Juelich, D-52425, Juelich, Germany, <sup>3</sup>Institut fuer Kristallographie, RWTH Aachen, Jaegerstr.17-19, D-52056, Aachen, Germany, E-mail: oh1905@korea.ac.kr

TlH<sub>2</sub>PO<sub>4</sub>(TDP) and RbH<sub>2</sub>PO<sub>4</sub>(RDP) belong to the large family of A(H,D)<sub>2</sub>PO<sub>4</sub>- type (A = K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Tl<sup>+</sup> etc) with remarkable ferroic properties and multiple structural phase transitions related to the ordering of the H,D atoms in short O-(H,D)-O hydrogen bonds of about 2.5Å. Although Tl<sup>+</sup> and Rb<sup>+</sup> have similar ionic radii(1.47Å), the crystal structures of RDP and TDP at room temperature are basically different. Whereas RDP exhibits a three-dimensional network of hydrogen bonded PO<sub>4</sub>-groups with tetragonal symmetry (space group *I-42d*), the monoclinic TDP-structure (space group: *P12<sub>1</sub>/a1*) is characterized by a two-dimensional network; both structures show disordered H-distributions[1,2]. In this work, we present a crystal structure analysis of (Rb<sub>0.5</sub>Tl<sub>0.5</sub>)H<sub>2</sub>PO<sub>4</sub> mixed crystal by neutron single crystal diffraction. Large, highly perfect crystals were grown from aqueous solution. At room temperature data collections were performed on the four-circle diffractometer SV28/1 with a wavelength of  $\lambda = 0.8724\text{\AA}$  at the DIDO-reactor, FZ-Jülich, Germany. (Rb<sub>0.5</sub>Tl<sub>0.5</sub>)H<sub>2</sub>PO<sub>4</sub> crystallizes in the monoclinic space group *P12<sub>1</sub>/a1* with lattice parameters  $a=14.36(2)\text{\AA}$ ,  $b=4.524(3)\text{\AA}$ ,  $c=6.50(1)\text{\AA}$ , and  $\beta=91.8(1)^\circ$ . Its crystal structure is isotypic to that of TDP showing H-disordering in the O-(H,D)-O hydrogen bonds. This result corresponds to NQR-investigations [3], where it was pointed out that the mixed crystals (Rb<sub>1-x</sub>Tl<sub>x</sub>)H<sub>2</sub>PO<sub>4</sub> show no phase transition at low temperatures for  $0.2 < x < 0.8$ . It may be very interesting to study this solid-solution more systematically in order to understand the role of the lone-pair electrons of the Tl<sup>+</sup> ions.

[1] S. Mattauch et al., *Cryst. Res. Technol.* 39,1027(2004) [2]I. H Oh et al., *Acta Cryst.*B62,719(2006) [3]J.Seliger & V. Zagar, *PRB* 52,1070(1995)

Keywords: hydrogen bond, neutron diffraction, crystal structure analysis

**P10.02.11***Acta Cryst.* (2008). **A64**, C493**Structural chemistry of (oxo)-nitridosilicate host lattices for rare-earth doped phosphors**

Oliver Oeckler, Juliane Kechele, Cora Hecht, Cordula Braun, Wolfgang Schnick

LMU Munich, Department of Chemistry and Biochemistry, Butenandtstr. 5 - 13 (D), Munich, 81377, Germany, E-mail: oliver.oeckler@gmx.de

Owing to their suitability as host lattices for rare-earth doped phosphors in light-emitting diodes, (oxo)-nitridosilicates like M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> and MSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> (M= Ca, Sr, Ba) have received remarkable attention [1]. Their crystal chemistry is very different from that of silicate minerals in many respects. As N atoms can connect three Si atoms, framework nitridosilicates can exhibit very high degrees of condensation. Their structures and properties strongly depend on reaction conditions and slight variations in composition. For example, at high pressure there is a reconstructive transition of Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> to

a new related phase with a sharper emission band of doping Eu<sup>2+</sup>. The framework of Ba<sub>2</sub>AlSi<sub>5</sub>N<sub>9</sub> consists of highly condensed layers of SiN<sub>3</sub>O tetrahedra that are interconnected by less condensed silicate rings, whereas similar layers are directly interconnected in (Ca,Sr)<sub>2</sub>(Si,Al)<sub>8</sub>(N,O)<sub>13</sub>. As SiN<sub>4</sub> and AlN<sub>4</sub> tetrahedra can share edges, unusual structural motifs become possible, such as rods of edge-sharing tetrahedra embedded in a framework in the compound SrAlSi<sub>4</sub>N<sub>7</sub> [2]. Traces of oxygen lead to SrAlSi<sub>6.5</sub>N<sub>7</sub>O, a 6-ring layer silicate that, in contrast to all layered oxosilicates, contains both edge and vertex sharing tetrahedra. Most layered structures, including MSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>, exhibit numerous real structure effects [3], which have been investigated in detail by means of high-resolution electron microscopy (HRTEM) complemented by the analysis of X-ray data including diffuse scattering and powder methods.

[1] Mueller-Mach, R., Mueller, G., Krames, M. R., Höpfe, H. A., Stadler, F., Schnick, W., Juestel, T., Schmidt, P., *Phys. Stat. Sol. A* 2005, 202, 1727. [2] Stadler, F., Ph. D. thesis, LMU Munich, 2006. [3] Oeckler, O., Stadler, F., Rosenthal, T., Schnick, W., *Solid State Sci.* 2007, 9, 205.

Keywords: silicate crystal structures, disordered systems, materials structure and characterization

**P10.02.12***Acta Cryst.* (2008). **A64**, C493**Crystal chemistry of natural and synthetic Pb(II) oxyhalides**Oleg I. Siidra<sup>1</sup>, Sergey V. Krivovichev<sup>1</sup>, Wulf Depmeier<sup>2</sup>

<sup>1</sup>Saint-Petersburg State University, Geological Faculty, Crystallography, University emb. 7/9 199034, Saint-Petersburg, Saint-Petersburg, 199034, Russia, <sup>2</sup>Universitaet zu Kiel, Institut fuer Geowissenschaften, Olshausenstrasse 40, 24118, Kiel, Germany, E-mail: siidra@mail.ru

In the course of our ongoing research in Pb(II) oxyhalide structural chemistry, 18 new lead oxyhalides have been prepared by high temperature solid-state reactions and hydrothermal syntheses. The structures of these compounds have been solved by direct methods. The following compositions were obtained: Pb<sub>2+x</sub>OCl<sub>2+2x</sub> (1), Pb<sub>3</sub>O<sub>2</sub>Br<sub>2</sub>(2), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>0.19</sub>Br<sub>1.81</sub>(3), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>0.46</sub>Br<sub>1.54</sub>(4), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>0.52</sub>Br<sub>1.48</sub>(5), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>0.81</sub>Br<sub>1.19</sub>(6), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>1.03</sub>Br<sub>0.97</sub>(7), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>1.09</sub>Br<sub>0.91</sub>(8), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>1.41</sub>Br<sub>0.59</sub>(9), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>1.61</sub>Br<sub>0.39</sub>(10), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>1.84</sub>Br<sub>0.16</sub>(11), Pb<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>(12), Pb<sub>7</sub>O<sub>4</sub>(OH)<sub>4</sub>Br<sub>2</sub>(13), Pb<sub>31</sub>O<sub>22</sub>Br<sub>10</sub>Cl<sub>8</sub>(14), Pb<sub>13</sub>O<sub>10</sub>Cl<sub>6</sub>(15), Pb<sub>6</sub>LaO<sub>7</sub>Br(16), Pb<sub>6</sub>LaO<sub>7</sub>Cl(17), Pb<sub>24</sub>O<sub>21</sub>I<sub>6</sub>(18). The following mineral crystal structures were solved and refined: mereheadite Pb<sub>47</sub>O<sub>24</sub>(OH)<sub>13</sub>Cl<sub>25</sub>(CO<sub>3</sub>)(BO<sub>3</sub>)<sub>2</sub> (19), unnamed mineral Pb<sub>7</sub>MgO<sub>4</sub>(OH)<sub>5</sub>Cl<sub>3</sub> (20), chloroxiphite Pb<sub>3</sub>O<sub>2</sub>Cu(OH)<sub>2</sub>Cl<sub>2</sub> (21). All of these compounds and minerals are based upon OPb<sub>4</sub> oxocentered tetrahedra. In all studied Pb(II) oxyhalides with additional O atoms, lone electron pairs on the Pb<sup>2+</sup> cations are stereochemically active. The compound 1 contains [OPb<sub>2</sub>]<sup>2+</sup> chains of trans-edge-sharing OPb<sub>4</sub> tetrahedra. The compounds 2-13, 20, 21 contain double [O<sub>2</sub>Pb<sub>3</sub>]<sup>2+</sup> chains. The structures of compounds 16-17 are based upon [O<sub>7</sub>Pb<sub>6</sub>La]<sup>+</sup> chains of mixed-metal OPbnLa<sub>4-n</sub> tetrahedra. The topology of the chains can be described as being based upon an arrangement of eight tetrahedra that all share the same central La atom. The unique [O<sub>21</sub>Pb<sub>24</sub>]<sup>6+</sup> complex chains form the structure of 18. The layer in the structure of 19 can be derived from the [OPb] tetrahedral layer that has been observed in the structure of PbO. The [O<sub>22</sub>Pb<sub>30</sub>]<sup>16+</sup> layer in the structure of 14 is remarkable of its exceptional topological complexity. Exceptional [O<sub>10</sub>Pb<sub>13</sub>]<sup>6+</sup> framework was found in the structure of 15.

Keywords: lead, oxocentered tetrahedra, crystal structure