Crystal structure analysis of Rb$_{0.5}$Tl$_{0.5}$H$_2$PO$_4$ at room temperature by neutron diffraction

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TH$_3$PO$_4$(TDP) and RbH$_2$PO$_4$(RDP) belong to the large family of A(H,D)PO$_4$- type (A = K',Rb',Cs',Tl' 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' and Rb' 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$_4$-groups with tetragonal symmetry (space group I-4d2), the monoclinic TDP-structure (space group: P21/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$_{0.5}$Tl$_{0.5}$)H$_2$PO$_4$ 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 $\lambda = 0.8724Å$ at the DIDO-reactor, FZ-Jülich, Germany. (Rb$_{0.5}$Tl$_{0.5}$)H$_2$PO$_4$ crystallizes in the monoclinic space group P21/a1 with lattice parameters: a=14.36(2)Å, b=4.524(3)Å, c=6.50(1)Å, and $\beta = 91.8(1)^{\circ}$. Its crystal structure is isotypic to that of TDP showing H-ordering 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$_{1-x}$Tl$_x$)H$_2$PO$_4$ 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-pairs electrons of the Tl' ions.

Keywords: hydrogen bond, neutron diffraction, crystal structure analysis

Crystal chemistry of (oxo)-nitridosilicate host lattices for rare-earth doped phosphors

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Owing to their suitability as host lattices for rare-earth doped phosphors in light-emitting diodes, (oxo)-nitridosilicates like MSi$_2$N$_2$ and MSi$_2$O$_2$N$_2$ (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$_2$Si$_3$N$_5$ to a new related phase with a sharper emission band of doping Eu$^{2+}$. The framework of BaAl$_2$N$_4$ consists of highly condensed layers of Si,N,O tetrahedra that are interconnected by less condensed silicate rings, whereas similar layers are directly interconnected in (Ca, Sr)$_2$(Si,Al)$_4$(N, O)$_7$. As Si$_2$N$_2$ and Al$_2$N$_2$ tetrahedra can share edges, unusual structural motifs become possible, such as rods of edge-sharing tetrahedra embedded in a framework in the compound SrAl$_2$N$_4$ [2]. Traces of oxygen lead to SrAl$_2$O$_2$(OH, 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$_2$O$_2$N$_2$, 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.


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

Crystal chemistry of natural and synthetic Pb(II) oxyhalides

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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$_2$O$_2$Cl$_2$, (1), Pb$_2$O$_2$Br$_2$, (2), Pb$_2$O$_2$Cl$_2$Br$_2$, (3), Pb$_2$O$_2$Cl$_2$Br, (4), Pb$_2$O$_2$Cl$_2$Br$_2$, (5), Pb$_2$O$_2$Cl$_2$Br$_2$, (6), Pb$_2$O$_2$Cl$_2$Br$_2$, (7), Pb$_2$O$_2$Cl$_2$Br$_2$, (8), Pb$_2$O$_2$Cl$_2$Br$_2$, (9), Pb$_2$O$_2$Cl$_2$Br$_2$, (10), Pb$_2$O$_2$Cl$_2$Br$_2$, (11), Pb$_2$O$_2$Cl$_2$Br$_2$, (12), Pb$_2$O$_2$Cl$_2$Br$_2$, (13), Pb$_2$O$_2$Cl$_2$Br$_2$, (14), Pb$_2$O$_2$Cl$_2$Br$_2$, (15), Pb$_2$O$_2$Cl$_2$Br$_2$, (16), Pb$_2$O$_2$Cl$_2$Br$_2$, (17). All of these mineral crystal structures were solved and refined: merrheidite Pb$_2$O$_2$Cl$_2$Br$_2$ (20), chloroxiphite Pb$_2$O$_2$Cl$_2$Br$_2$ (21). All of these compounds and minerals are based upon OPb$_x$ oxocentered tetrahedra. In all studied Pb(II) oxyhalides with additional O atoms, lone electron pairs on the Pb$^{2+}$ cations are stereochemically active. The compound 1 contains [OPb$_5$]$^{2+}$ chains of trans-edge-sharing OPb$_x$ tetrahedra. The compounds 2-17 contain double [OPb$_5$]$^{2+}$ chains. The structures of compounds 16-17 are based upon [OPb$_x$La]$^{2+}$ chains of mixed-metal OPb$_x$L$_y$n 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$_2$Pb$_3$]$_{20}$ complex chains form the structure of 18. The layer in the structure of 19 can be derived from the [OPb$_5$]$^{2+}$ tetrahedral layer that has been observed in the structure of PbO. The [O$_2$Pb$_3$]$^{20}$ layer in the structure of 14 is remarkable of its exceptional topological complexity. Exceptional [O$_2$Pb$_3$]$^{20}$ framework was found in the structure of 15.

Keywords: lead, oxocentered tetrahedra, crystal structure

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