Abstract

For the investigation of crystal structures and the phase transitions of TlH_2PO_4 (TDP), single crystals have been synthesized. TDP (TDP II) crystallizes at room temperature in the space group $P1\frac{2_1}{a}1$ (Z = 4) with the lattice parameters a = 14.4062(6) Å, b = 4.5308(2) Å, c = 6.5338(2) Å and β = 91.46(4) °. By the slow evaporation of the solution, large single crystals of $Rb_{0.5}Tl_{0.5}H_2PO_4$, which are proper to the neutron investigations and small single crystals of $Rb_{0.7}Tl_{0.3}H_2PO_4$ have been obtained. During the synthesis of TlH_2PO_4 Tl_2HPO_4, single crystals could be isolated and their structure was solved (Oh et al., 2004). The crystal structure of TDP II was newly solved at room temperature by neutron scattering and refined. In this way, the data obtained by Rios (1997) was perfect reproduced. In the phase TDP II two of three hydrogen atoms are disordered at room temperature. For the investigation of the behaviour of the disordered hydrogen atoms in the vicinity of phase transition, a further structure analysis was accomplished at 240 K. Also at this temperature, the two hydrogen atoms are disordered yet. As to be expected, the average temperature factors of all atoms are around a factor smaller, which corresponds to the relationship of the different measuring temperature ($\frac{295K}{240K} = 1.23$). In the comparison with the structure at room temperature, the PO_4 – bond of the tetrahedron is only little changed. The difference between the P – O3 and P – O4 becomes little larger, that indicates an increased anisotropy of O3 – H3 ... O4 bond. The O3 – H3 distance is reduced from 1.175(3) Å at room temperature to 1.150(6) Å at 240 K, during the H3 ... O4 distance is increased from 1.338(3) Å to 1.357(6) Å. The distance between thallium ions and oxygen ions is at 240 K little smaller than at room temperature.

The crystal structure of low temperature phase of TDP (TDP III) was completely determined and refined at 210 K for the first time by neutron scattering. From this investigation, the space group $P\bar{1}$ and the enlarged elementary cell were confirmed. The U_{iso} – values at 210 K are generally smaller than at 240 K. The values of the H – atoms are compared with the values of the H3 – atoms at 240 K in the asymmetric O3 – H3 ... O4 bond. In the phase TDP – III all atoms occupy general positions. The H1 and H2 atoms of TDP – II structure freeze in one of their split positions. Thus all hydrogen bonds become asymmetric. TDP – III shows a completely ordered state of H – atoms. These ordered hydrogen atoms and formation of the portion of the covalent O – H bond cause a change of the electron density, which leads to a strong distortion of PO_4 – groups.

During the phase transition, no new domains were observed. The colour change means a change of optical double reflection of crystal at T_c. For the investigation of the phase transition TDP II – III with X – ray the high resolved powder diffractometer X'Pert PRO by Philips was used. No evidence indicating an additional phase transition was observed at low temperature. The TDP III structure remains until 7.7 K. By the observation of the split of the reflex (reflex broadening) the temperature of the phase transitions of 229.5 ± 0.5 K was determined. In the measurement no hysteresis was observed.

With neutron the temperature dependence measurement on a single crystal was accomplished. Under the phase transition temperature T_c, a reflex broadening (Splitting) was observed, which is attributed to the formation of the twin due to the symmetry reduction from monocline to tricline with 2 twin states. The splitting of the reflex due to the twinning goes completely back for $T > T_c$. The intensity of the strong reflexes increases on cooling at T_c precipitously by more than 100%. This observation was also on heating completely reversible. The huge change of reflex intensity is attributed at T_c to the decrease of the extinction. By the precipitous change of the reflex intensity the phase transition temperature could be exactly determined: $T_c = 229.5 \pm 0.5$ K. No evidence for the hysteresis was found on the phase transition of first order.

Between the point groups of phases II and III of TDP exists group – subgroup relation of index 2 $(\frac{2}{m} - t \rightarrow \bar{1})$. Due to the point group relation two ferroelastic domains are possible. Additional there is a "klassengleich" group – subgroup relation of index 2 ($P\bar{1} - k2 \rightarrow P\bar{1}$), whereby a doubling of a – and b – axes arises. So that also two anti – phase domains are possible in the phase III, which have been not observed however so far yet.

In this work the structures of the $(Tl_{1-x}Rb_x)H_2PO_4$ – mixed crystals were investigated for the first time not only by X – ray but also by neutron at room temperature. The mixed crystals for x = 0.5 and x = 0.7 crystallize in the space group $P1\frac{2_1}{a}1$ of the TDP II phase. The Tl^+ – ions behave isotropically in the TDP – II phase. On the other hand, the Tl / Rb – positions in the mixed crystals posses anisotropic temperature factors, that point out little different positions of the Tl^+ and Rb^+ ions. Also in the Tl – Rb mixed crystals a partial H – ordering has been discovered. The protons show a dominant thermal vibration in the bond direction. The first type of hydrogen atom links each PO_4 – groups in zigzag – like chains parallel to the c axis, while the second type links these chains along the a axis. Hydrogen bonds form a two – dimensional network parallel to the ac plane. The Tl^+ – and/or Rb^+ – ions lie between the zigzags – chains. The structure is composed of independent layers packed perpendicular to the b axis and linked together by Coulombic interactions with Tl^+ and Rb^+ ions.

With this work the polymorphism of TDP / DTDP was determined to a large extent. Only the phase transition of the deuterated form DTDP has been known at 127 K and the crystal structure of DTDP at low temperature has not been yet determined until now.