

[o.m1.p15] Structure of the hydrated phase of RbD_2PO_4 (DRDP) : $\text{RbD}_2\text{PO}_4 \cdot \text{D}_2\text{O}$. S. Mattauch^a, W. Paulus^b, J. Glinnemann^a and G. Hege^a ^a*Inst. f. Kristallographie, RWTH Aachen*; ^b*LCSIM Université Rennes I*.
Keywords: ferro-electricity, NLO materials.

RbH_2PO_4 (RDP) and RbD_2PO_4 (DRDP) are known for a long time and belonging to the Hydrogen/Deuterium bonded ferroelectric. The best known representative of this family is KDP. In order to get a better understanding of the polymorphism of the KDP-family, especially with respect to the role of the hydrogen bonds and the H/D isotope effect, we have started a program focussed on the Rb- and Tl-compounds^{1,2}. The existing of the hydrated phase $\text{RbD}_2\text{PO}_4 \cdot \text{D}_2\text{O}$ was already mentioned by A. V. Mishenko et al.³ as early as 1972, but no information on the crystals structure with its lattice and spacegroup was given. By X-ray and neutron diffraction we were able to prove the existence of the mono-hydrate phase, the detailed crystal structure analysis of which is presented in the paper⁴.

For growing the single crystals of $\text{RbD}_2\text{PO}_4 \cdot \text{D}_2\text{O}$ the standard procedure for DRDP was used⁵:



Depending on the history of the solution DRDP or $\text{RbD}_2\text{PO}_4 \cdot \text{D}_2\text{O}$ crystals are obtained. Under a closed atmosphere which prevents also an exchange of $\text{D} \rightleftharpoons \text{H}$ the crystals are stable at room temperature. The structure was determined by combined neutron (5C2 ORPHEE Reactor, CE Saclay) and X-ray (Stoe IPDS) single crystal investigations at room temperature. The unitcell was found to be monoclinic with:

$$P 1 2_1/c 1, a = 7.262(1) \text{ \AA}, b = 7.746(1) \text{ \AA}, c = 9.481(1) \text{ \AA}, \beta = 104.91(1)^\circ, V = 515.36 \text{ \AA}^3, Z = 4.$$

The structure consists of double layers of PO_4 tetrahedra with respect to the fully ordered deuterium bonding. The double layers them self are linked by electrostatic bonds between the Rubidium atom and the PO_4 tetrahedrons. In between this double layer structure lies a D_2O plane, linked by a hydrogen bonds to the double layers.

Under heating $\text{RbD}_2\text{PO}_4 \cdot \text{D}_2\text{O}$ dehydrates below 329(5)K and undergoes a reconstructive phase transition to DRDP.

[o.m1.p16] Lifetime of small Nb^{4+} -Polarons in $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6:\text{Ce,Cr}$ and KNbO_3 . Th. Woike¹, D. Berben^{1,2}, M. Imlau¹, K. Buse², R. Pankrath², E. Krätzig², ¹*Institut für Kristallographie, Universität zu Köln, Zülpicherstr. 49b, 50674 Köln, Germany*, ²*Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49069 Osnabrück, Germany*.

Keywords: ferro-electricity, NLO materials.

The existence of small polarons in Niobate-crystals is of importance for both holographic data storage and frequency conversion such as second harmonic generation.

If doped single crystals of LiNbO_3 , KNbO_3 or $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ are illuminated with continuous light or short laser pulses with sufficiently high intensity in the visible spectral range, electrons are excited into the conduction band. These electrons can be trapped by Nb^{5+} -ions. The coulomb-interaction of a trapped electron distorts the crystal lattice, thus lowering the potential energy of the electron. The electron is now trapped inside its own potential hole. Because this localized state is only weakly bound, these polarons decay at room temperature after short lifetimes. However, they show an extremely broad absorption band. Its maximum lies in the near-infrared region, and it may extend well into the visible spectral range. This light-induced absorption can seriously influence second harmonic generation and holographic data storage.

We show the temperature-dependence of the lifetime and the non-exponential decay of small polarons in Cerium- resp. Chromium-doped SBN and nominally pure KNbO_3 after excitation with a short laser pulse of $\lambda=532$ nm. Further illumination with a pulse of $\lambda=1064$ nm after a delay of about 10 ns does not destroy the polarons, but causes a charge-transport. This mechanism is sensitive to the distance between the polaron and the next possible trapping-center. The result of this distance-dependent charge-transport is a polaron-hopping. With absorption spectra we show the influence of light-induced polaron-absorption on second harmonic generation.

This work was supported by the Deutsche Forschungsgemeinschaft: GRK549/1-99 'Azentrische Kristalle', Wo618/2-1 and SFB 225/C5

[1] Rios S. et al., "Isotope effect in TiH_2PO_4 and TiD_2PO_4 ", *Acta Cryst.*, (1998), **54**: 790-797

[2] Mattauch S. et al., "Polymorphism of RbH_2PO_4 (RDP)", *Physica B*, (1997), **234-236**: 40-42

[3] Mishenko A.V. et al., "Crystalization of rubidium dideuterium phosphate from solution in heavy water", *Soviet Physics Crystallography*, (1972), Vol. **16**, No.5: 940-942

[4] Mattauch S. et al., "Crystal structure of RbD_2PO_4 (DRDP) : A new hydrate phase of KDP-type compounds", *Cryst. Res. Technol.*, (2000), **35** 4: 501-509

[5] Wilke u. Bohm (1988), "Kristallzüchtung", VEB Deutscher Verlag der Wissenschaft, Berlin