High-pressure crystal structure investigations on K_2Te in DACs of modified Merrill-Bassett type.

K. Stöwe

Technische Chemie, Universität des Saarlandes, FR 8.1, C4.2, 66123 Saarbrücken, Germany

For the alkali metal monotelluride K_2Te the only information on crystal structure given in the past was by Zintl, Harder, Dauth in 1934 [1]: according to their investigations K_2Te is crystallizing in the anti-fluorite structure type with a = 815.2 pm. But from high-pressure and high-temperature investigations of the analogous rubidium monotelluride it is well-known that this type of compounds reveals a very rich structural chemistry with typical polymorphic transitions from anti-fluorite (CN = 8) into anti-cotunnite (CN = 9) and further on into Ni_2In type (CN = 11) [2,3]. According to this findings we also investigated K_2Te in DACs (self-made, modified Merrill-Bassett type) at beamline F1 at HASYLAB at DESY (λ = 40 pm, image plate). K_2Te was prepared from the elements in liquid ammonia with a small surplus of potassium, which was removed by a subsequent extraction with liquid ammonia in special designed glass-ware [4]. As pressure transmitting medium a low viscosity poly(dimethyl)siloxane and for pressure calibration the standard ruby fluorescence method was used. The image plate data were transformed into diffraction powder pattern by the program FIT2D (V12.034, A. Hammersley, ESRF, Grenoble, France) using calibration data from LaB_6 measurements (0.1mm silica capillaries). Subsequently the diffraction data were refined using the Rietveld program TOPAS (V2.1, Bruker AXS). A typical result of the powder pattern refinement is shown in Figure 1.

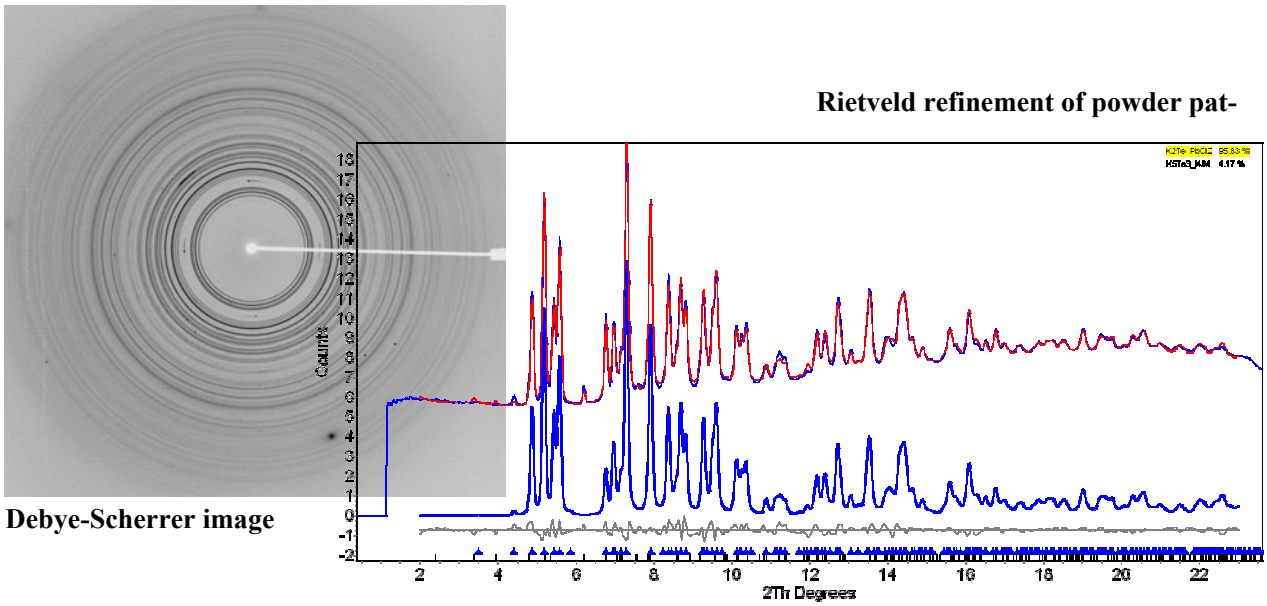

Figure 1: K_2Te in anti-cotunnite type at p = 0.84 GPa.

Concomitantly simulations of the phase transitions were performed by full crystal structure optimizations with the DFT plane-wave pseudo-potential program CASTEP (Materials Studio V2.2, Accelrys Inc., USA) as function of pressure revealing equation-of-state relations E(V) of the three polymorphs given above (functional GGA, norm-conserving potentials, optimized cut-off energy and k-point sets). The transition pressure anti-fluorite $\forall$ anti-cotunnite was determined by the steepest descent method $\partial E/\partial V = -p$. Since between the space groups of Ni_2In and anti-cotunnite type a group-subgroup relation exists, the second transition can be described in terms of a continuous transformation of the positional parameters in the subgroup Pnma. Accordingly the transition pressure can be directly taken from the E(V) or E(p) relation. Experimentally the first phase transition was observed at p_T = 0.9 GPa from anti-fluorite into anti-cotunnite type, the second at p_T = 1.7 GPa from anti-cotunnite into Ni_2In type. These transition pressures are in fair agreement with the

calculated ones of p_T = 0.85 GPa and 3.3 GPa, respectively. The results of the Rietveld refinements for K_2Te are given in Figure 2.

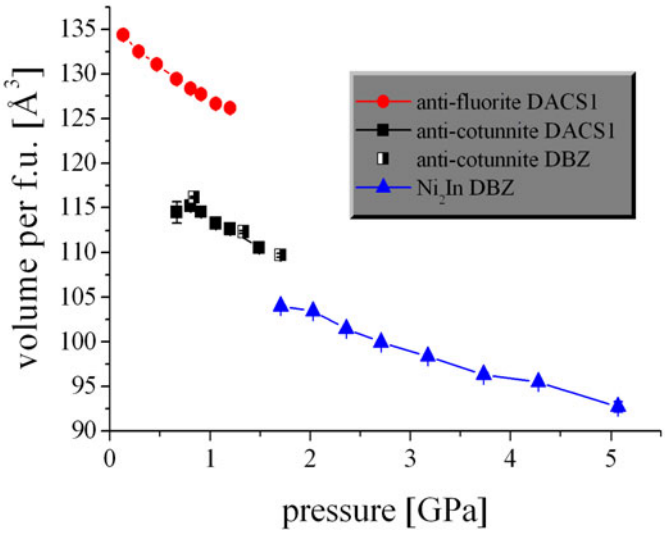

Figure 2: Volume per formula unit versus pressure for K_2Te from Rietveld refinements

Together with the high-temperature X-ray diffraction investigations on K_2Te we found all in all four new polymorphs of the compound, two HP and two HT forms: at elevated temperatures K_2Te transforms from the anti-fluorite into the anti-cotunnite type and further on into the γ-Ag_2Te type with a partially molten cation sublattice. Thus the structural richness of K_2Te is as versatile as already observed for Rb_2Te. By this investigations we have now completed our experimental and theoretical structural work on the alkali metal monotellurides Na_2Te, K_2Te and Rb_2Te. For the future additional investigations are planned for Cs_2Te and various interalkali metal tellurides such as CsNaTe.

Acknowledgement

The author is greatly indebted to Dr. R. Haberkorn, Dr. H. Kohlmann (Universität des Saarlandes, Anorganische und Analytische Chemie und Radiochemie) and Dr. C. Paulmann (Universität Hamburg, Mineralogisch-Petrographisches Institut) for their kind assistance during measurements.

References

[1] Zintl, Harder, Dauth, Z. Elektrochem. 40, 588 (1934)
[2] K. Stöwe, S. Appel, Angew. Chem.. Int. Ed. Eng. 41, 2725 (2002)
[3] K. Stöwe, Z. Kristallogr. 219, 359 (2004)
[4] K. Stöwe, S. Appel-Colbus, Z. Anorg. Allg. Chem. 625, 1647 (1999).