Phase transitions in mercallite, $KHSO_4$

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Acid sulphates and their electrical properties have been investigated since the middle of the last century. They are highly interesting materials for future applications for example as electrolytes in fuel cells. In contrast to other members of the family of alkali hydrogen sulphates, there is no hint for a super-protonic state in $KHSO_4$ at atmospheric pressure [1]. As there is a change of critical parameters leading to the super-protonic conductivity from K to NH_4 and Rb respectively [2, 3] we started to investigate these parameters from the structural point of view. The structure of $KHSO_4$ at ambient conditions was described in space group *Pbca* [4, 5]. The crystal structure consists of layers stacked along the *c*-axis of the orthorhombic lattice. The different layers are alternating planes of potassium ions, HSO_4 – dimers, and HSO_4 – chains running along the *a*-axis.

Synthetic samples of $KHSO_4$ were crystallised from aqueous solution and characterised prior to synchrotron experiments by DTA, TG, optical microscopy and powder X-ray diffraction. Single-crystal diffraction at ambient conditions was performed with a conventional four-circle diffractometer with Mo-$K\alpha$ radiation. High-temperature X-ray powder diffraction was performed at beamline B2 at HASYLAB at wavelenghts of 0.9088 Å resp. 1.1194 Å. The instrument was equipped with a Si(111) double-crystal monochromator without mirror and with the image plate detector OBI for fast temperature-dependent data acquisition. The lattice parameters were calculated via full pattern analysis with the Rietveld program fullprof. Oscillation photographs of single crystals were taken with an image plate detector at the four-circle diffractometer at beamline D3. One single crystal data set was obtained at 448K with a scintillation counter.

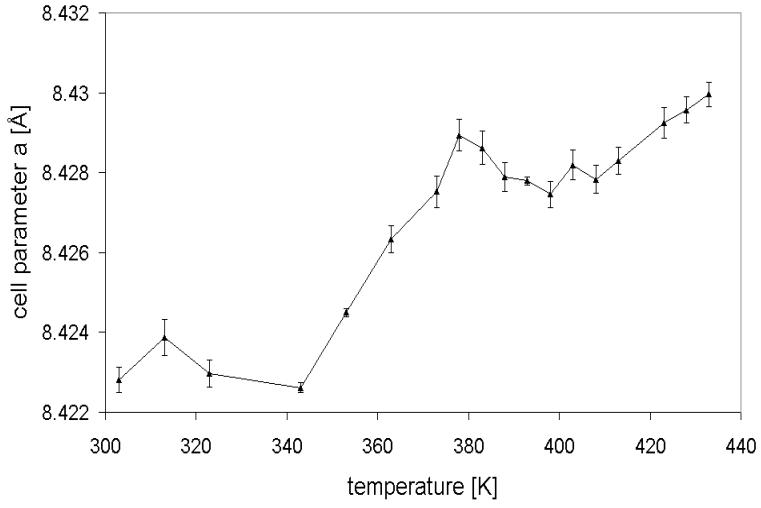

Figure 1: Temperature dependence of lattice parameter *a* of $KHSO_4$

According to our measurements, $KHSO_4$ undergoes four structural phase transitions between room temperature and the melting point at 483 K. Two phase transitions were found by the observation of the change of optical birefringence with temperature: One at 343 K which was not detected by DTA and another at 400 K, supported through an exothermic signal in the DTA. These results were confirmed by changes in the slope of the temperature dependence of the cell-parameter parallel [100] at 343 K, 378 K and 398 K (Fig.1). Note, that the hydrogen bonds run along this direction. No anomalies were found for the *b* – and *c* – directions (Fig.2)

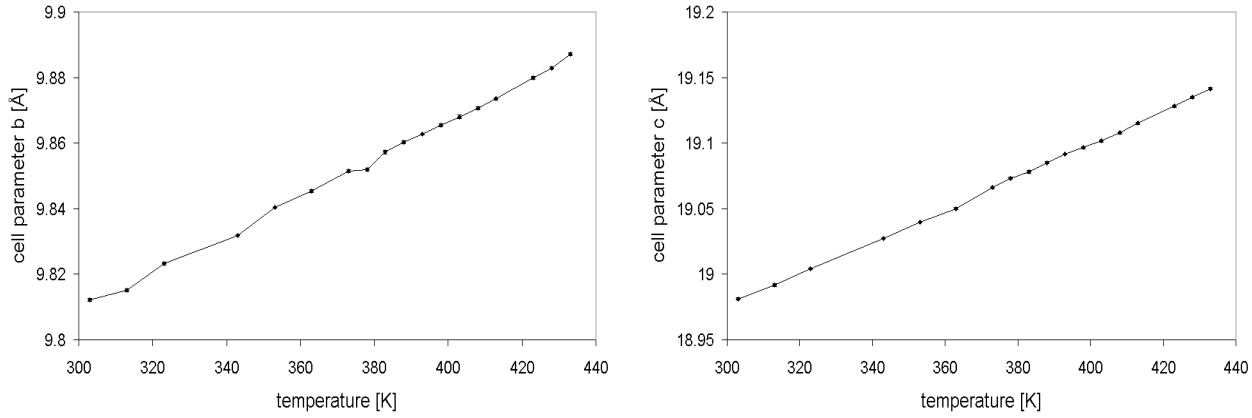

Figure 2: Temperature dependence of lattice parameters *b* and *c* of $KHSO_4$

To further evaluate this sequence of transitions single crystal investigations were performed. The oscillation photographs showed another effect, which occurred the first time in the photograph obtained at 398 K and was observed also for every temperature higher than 398 K. The positions of several reflections were moved and the associated reflecting planes rotated by a small angle. For all other reflections the orthorhombic metric remained unchanged until 453 K. Above this temperature the cracking of the crystal into small crystallites was observed. From powder diffraction data we could assign this to a reversible high temperature phase.

In house single crystal analysis of untreated samples approved the space group *Pbca* of the structure of $KHSO_4$ at ambient conditions.
In data sets obtained at ambient temperature from crystals heated at 343K for at least one hour, additional reflections breaking the symmetry of space group *Pbca* were clearly observed. Further on, many inconsistent equivalent reflections were observed for the Laue class *mmm*, which is an indication for the existence of twinning. The analysis of systematic extinctions led us to the monoclinic space group $P2_111$. No splitting of reflections was observed. The refined angles of the unit cell do not deviate significantly from 90°. Hence, the orthorhombic metric of the unit cell is preserved and the crystals are twinned by pseudomerohedry.
In one data set obtained after heating the crystal to 423 K no deviations from the space group *Pbca* were found any more, neither for the extinctions nor for the intensity distribution on the reciprocal lattice.
From analysis of systematic extinctions in the single crystal data set obtained at 448 K at HASYLAB we derived the space group $P2_12_12_1$, but with many inconsistent equivalents. This could be an indication for the formation of domains of lower symmetry at this temperature.
The high temperature phase obtained above 453 K could not be indexed yet.

Combining these results obtained with different methods a possible sequence of phase transitions is proposed for $KHSO_4$:

$$Pbca \xrightarrow[343\ K]{} P2_111 \xrightarrow[378\ K]{} Pbca \xrightarrow[398\ K]{} P2_12_12_1 \xrightarrow[453\ K]{} \text{unknown}$$

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