Thermal decomposition of Cs_2PdCl_6

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Cs_2PdCl_6 crystallizes in the K_2PtCl_6 structure type [1]. According to [2] Cs_2PdCl_6 decomposes on heat treatment in air at 350°C corresponding

$$Cs_2PdCl_6 \rightarrow Cs_2PdCl_4 + Cl_2$$

In previous investigations we studied the phase transitions and thermal expansion as well as the crystal structure of Cs_2PdCl_4 [3-5]. Up to now, two modifications of Cs_2PdCl_4 are known: one crystallizes in the K_2PtCl_4 [6] structure type, the other in the Cs_2PtCl_4 [7] structure type. Furthermore, we have indications of the existence of a third Cs_2PdCl_4 modification or of yet unknown decomposition products. There is no information about the structural properties of the decomposition product of Cs_2PdCl_6 given in [2]. Therefore, we performed high-temperature X-ray diffraction experiments.

The measurements were performed with the powder diffractometer at the beamline B2, HASYLAB. For the high-temperature measurements a Stoe-high-temperature-chamber for Debye-Scherrer geometry was used. The powder of Cs_2PdCl_6 (prepared according to [8]) was filled in a quartz capillary ($\varnothing_{outside} = 0.3$ mm) in air. The diffraction patterns were recorded with an image plate detector in the 2θ range of 10° – 65°. We employed a wavelength of $\lambda = 0.908063$ Å.

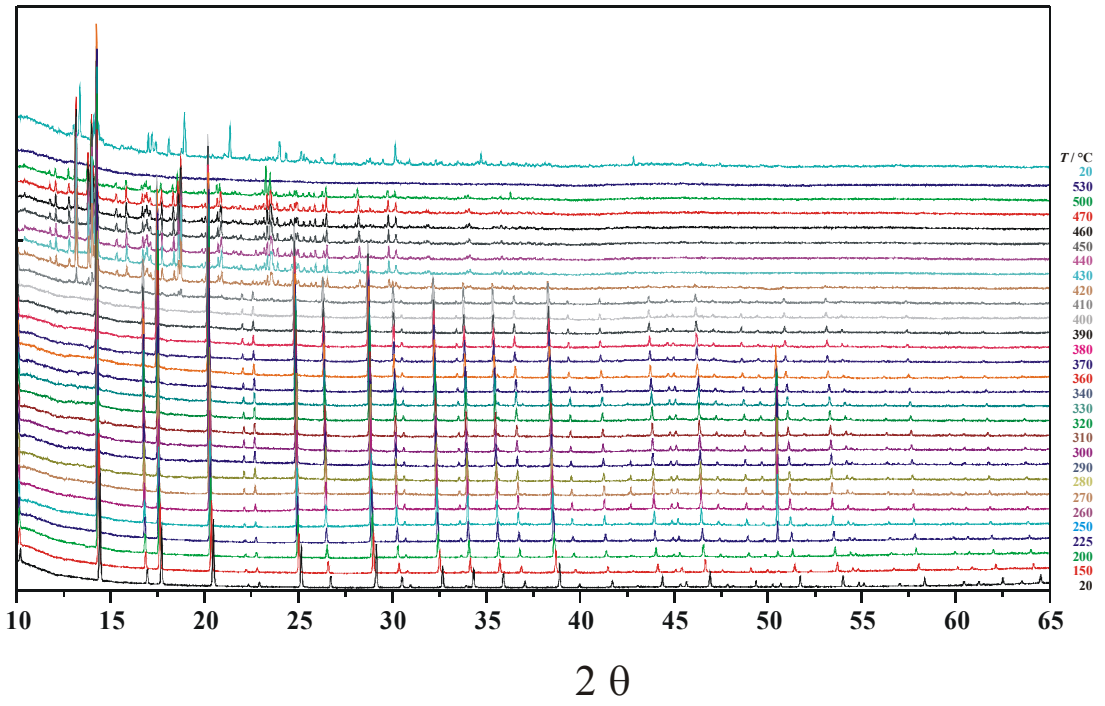

Figure 1: Diffraction patterns of Cs_2PdCl_6 and its decomposition products at different temperatures

According to the X-ray powder diffraction measurements at different temperatures the cubic phase Cs_2PdCl_6 exists in the temperature range from $T = 20$°C to $T = 400$°C. At 410°C a mixture of Cs_2PdCl_6 and the decomposition product is observed. The decomposition product melts at about 530°C as can be seen in the pattern and is in agreement with DSC measurements [3]. The product

shows a different diffraction pattern after melting and being allowed to reach ambient temperature. The reflections of the decomposition product of Cs_2PdCl_4 do not belong to the structurally known polymorphs of Cs_2PdCl_4 – neither to the orthorhombic (Cs_2PtCl_4 structure type) nor to the tetragonal (K_2PtCl_4 structure type). But the observed peaks correspond to those obtained from high temperature X-ray powder diffraction experiments on Cs_2PdCl_4 at $T \geq 310$°C [3]. These reflections presumably belong to a third modification or to a yet unknown decomposition product.

$$Cs_2PdCl_6 \xrightarrow{\approx 410°C} \text{"}Cs_2PdCl_4\text{"} + Cl_2\uparrow \xrightarrow{\approx 530°C} \text{melt}$$

$$Cs_2PdCl_4 \text{ (orthorhombic)} \xrightarrow{68°C} Cs_2PdCl_4 \text{ (tetragonal)} \xrightarrow{\approx 310°C} \text{"}Cs_2PdCl_4\text{"}$$

For the detailed determination of the lattice parameter of Cs_2PdCl_6 the peak positions were extracted and fitted with the program ProFit (Philips) [9], the unit cell parameter was refined with the program UnitCell [10]. The cubic unit cell parameter of Cs_2PdCl_6 increases linearly in the temperature range from $T = 20$°C to $T = 400$°C. The thermal expansion coefficients α_a of the lattice parameter is calculated according to the formula

$$\alpha_a = \frac{\Delta a}{a_0 \cdot \Delta T} = \frac{a_1 - a_0}{a_0 \cdot (T_1 - T_0)}$$

leading to $\alpha_a = 4.10 \cdot 10^{-5}$ K^{-1}.

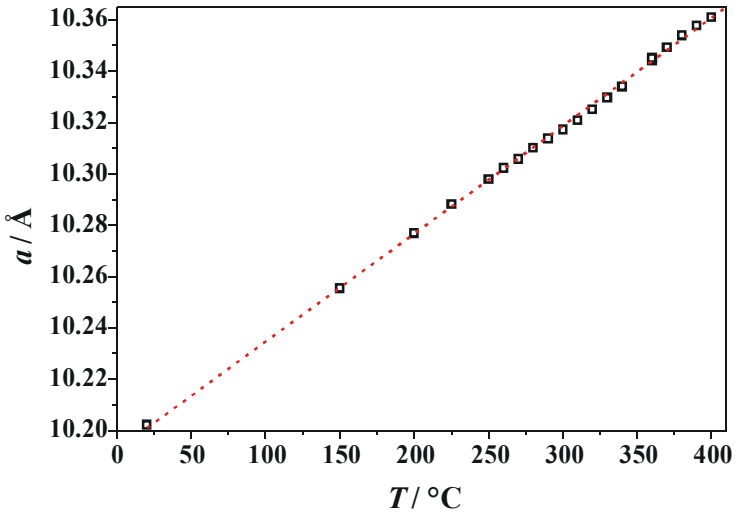

Figure 2: Dependence of the cubic unit cell parameter of Cs_2PdCl_6 on the temperature

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