

THE REPORTED STRUCTURAL HIGH-TEMPERATURE PHASE TRANSITION ON KH_2PO_4 DOES NOT EXIST

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Resumen. Difracción de rayos X, análisis termogravimétrico (TGA) y calorimetría diferencial de barrido (DSC) se usaron para estudiar la reportada transición estructural a $T_p = 180 \pm 10^\circ C$ en muestras cristalinas y policristalinas de $KH_2PO_4(KDP)$. Nuestros resultados muestran evidencias contundentes de que la reportada transición de fase a T_p no es una transición estructural de la fase tetragonal a la monoclinica. En cambio encontramos que la anomalía térmica detectada a T_p esta relacionada con el inicio de un proceso de polimerización parcial en sitios reactantes distribuidos sobre la superficie del espécimen y por lo tanto la fase tetragonal estable a temperatura ambiente se mantiene hasta su descomposición final.

Palabras claves: Polimerización Parcial, Transición Estructural, KDP , KH_2PO_4 .

Abstract. $X - ray$ diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the reported structural high-temperature phase transition (HTPT) at $T_p = 180 \pm 10^\circ C$ in $KH_2PO_4(KDP)$. Our results show forceful evidence that the earlier reported phase transition at T_p is not a structural transition of the tetragonal phase to a monoclinic modification. Instead we have found that the thermal anomaly detected at T_p is related with the onset of partial polymerization at reaction sites distributed on the surface of the specimen and therefore the room temperature tetragonal phase is stable up to the final decomposition.

Keywords: Partial Polymerization , Structural Phase Transition, KDP , KH_2PO_4 .

1 Introduction

From thermogravimetric (TGA) and differential thermal analysis (DTA) on KDP , R. Blinc et al.[1] conclude that the endothermic DTA anomaly with offset at $171^\circ C$ are not associated with decomposition, because no weight loss was detected; instead it was related with structural changes. Later, using $X - ray$ diffraction measurements, K. Itoh et al. [2] conclude that on heating through

187°C (normally noted as T_p), a structural phase transition from tetragonal to monoclinic symmetric takes place. The lattice parameters at 195°C for this high-temperature modification were given as $a = 7.47\text{Å}$, $b = 7.33\text{Å}$, $c = 14.49\text{Å}$, $\alpha = \beta = 90^\circ$ and $\gamma = 92.2^\circ$. Moreover, it has been reported that the monoclinic phase of *KDP* is metastable at temperatures below T_p and that it reverts to the stable tetragonal phase after being kept some days in air at room temperature [3,4].

Many theories have been proposed in order to explain the mechanisms of the phase transitions in this material. The single particle approximation model of Imry, Pelah and Wiener [5], where the effective potential for the proton in the hydrogen bond is an asymmetric double-minimum potential well, is especially interesting because it predicts an additional phase transition at high temperature, T_p . According to this dynamical model an abrupt change occurs in the hydrogen bond at the temperature T_p . Proton tunneling almost stops and the hydrogen approaches one of the oxygens in the hydrogen bond. As a result, the bond is drastically weakened, and thus the bonding of the PO_4 tetrahedron to its neighbours is weakened, and it might turn around its c-axis. This should be reflected as an anomaly in the dielectric constant at T_p . In fact, measurements of the dielectric constant (ε) in *KDP* show an anomaly near 453K [3]. Furthermore, Grünberg et al. [3] reported that the room temperature infrared spectrum measured after a very fine surface layer was removed from the *KDP* single-crystal, which had previously been heated, was identical to that of the “ordinary” tetragonal phase. Here we report a very different point of view of the high-temperature nature of the *KDP* compound.

2 Results and Discussion

The temperature dependence of the water weight loss of a fresh *KDP* crystal, for the whole temperature range from 50 to 500°C, is plotted in the insert of Figure 1a. The marked first mayor variation on the inset is enlarged on the figure. Figure 1b displays the TGA derivative curve shown on Figure 1a. Figure 1c shows the DSC thermogram of a fresh *KDP* crystal sample from the same batch and with the same heating rate as that of the TG measurement (2.5°C/min).

The main reason why it has been suggested for *KDP* that a tetragonal \rightarrow monoclinic structural phase transition takes place at T_p is because above this temperature a new diffraction pattern seems to appear in *X-ray* diffraction measurements [2] while no change has been recorded in the sample weight at the transition [1]. In contrast with this result our TGA measurements show that the high-temperature phase transition of *KDP* at T_p is accompanied with a small weight loss, which indicates some chemical decomposition. Our results might thus be due to formation of the decomposition product, Kurrol’s salt C, $K_n H_2 P_n O_{3n+1}$ ($n \gg 1$) $\approx (KPO_3)_n$, at reaction sites on the surface of the *KDP* sample. To test this, we performed *X-ray* diffraction.

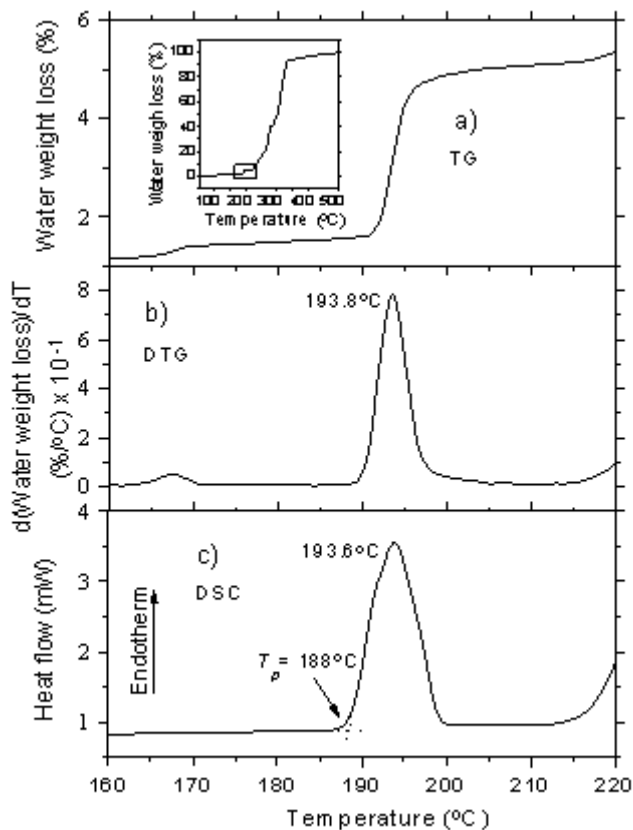


Figure 1. TGA (a), DTG (b) and DSC (c) curves of a fresh KDP crystal

Figure 2a shows the superposition of the X-ray patterns from two different single phases: the dotted line corresponds to the fresh *KDP* sample and the continuous line correspond the Kurrol's salt C, that is the polyphosphate $(KPO_3)_n$. This salt was produced by tempering fresh powdered *KDP* at 400°C during 25 hours [6]. The X-ray diffraction measurements were done at room temperature under dry conditions. Figure 2b shows the pattern for a *KDP* sample after being heat treated at 210°C for 24 hours, which clearly corresponds to a mixture of two phases: *KDP* and Kurrol's salt C. In figure 2b the intensity of the *KDP* peaks has been reduced because part of the *KDP* at the surface of the sample, was dehydrated and transformed to Kurrol's salt C.

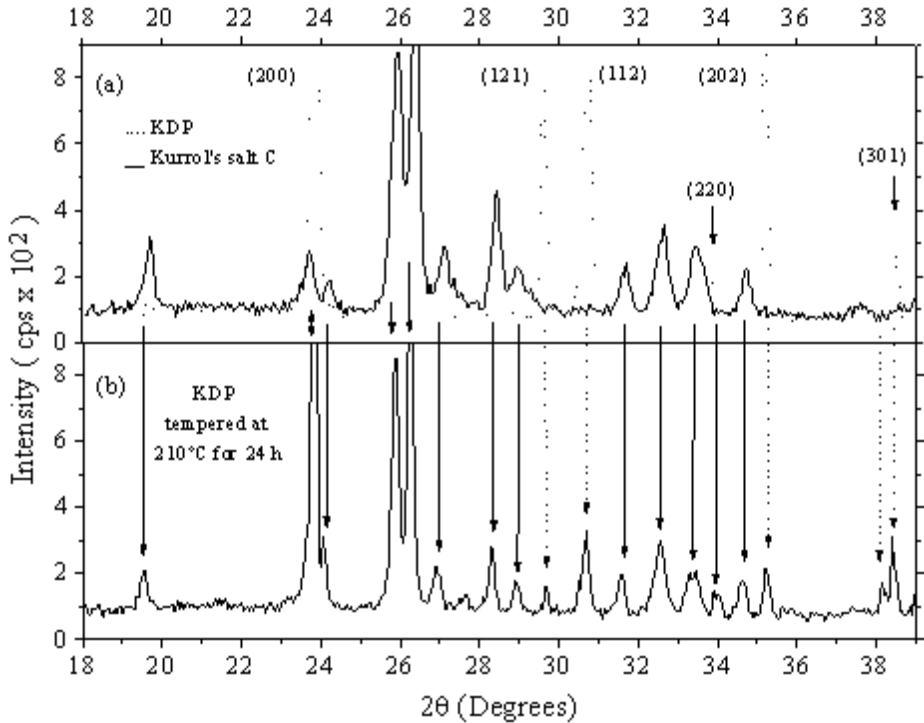


Figure 2. X – ray diffraction pattern at 20°C for: a) tetragonal fresh *KDP* (dotted curve) and Kurrol's salt C (continuous curve); b) *KDP* treated at 210°C for 24 hours. The indicated Miller indices correspond to the peaks of fresh *KDP*. The dotted and continuous line arrows show the peaks associated with the tetragonal fresh *KDP* and the monoclinic Kurrol's salt C respectively; the double arrow shows a peak associated with both phases.

3 Conclusion

The previously proposed third crystalline modification above T_p of *KDP* with monoclinic symmetry does not exist. Furthermore, on cooling a sample from above T_p to room temperature, the supercooled metastable high-temperature phase transforms back to the *KDP* phase with a very slow reaction rate, indicating the hydrolysis or depolymerization of Kurrol's salt C instead of a monoclinic \rightarrow tetragonal structural phase transition of *KDP*.

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