High temperature phase transition in KH_2PO_4 crystal

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Abstract. DTA, weight loss, infrared and dielectric measurements have been performed on KH_2PO_4 (KDP) single crystal as well as on different particle size specimens. DTA result reveals two endothermic peaks. The lower peak at 180°C is particle size dependent and vanishes in specimen of particle size ≤ 0.1 mm. Dielectric measurements also show similar behaviour. No significant weight loss of the crystal was noticed when kept at 180°C . We are inclined to believe that fragmentation of crystal is likely to be responsible for the transition rather than PO_4 -group rotation or decomposition of KDP.

Keywords. DTA; weight loss; IR; dielectric behaviour; phase transition; potassium dihydrogen phosphate; particle-size dependence.

1. Introduction

Imry and co-workers (Imry *et al* 1965) in the theory of the fluctuating double minimum potential well predicted two correlated phase transitions in KH_2PO_4 -type crystals. The lower transition point was identified as the Curie point and the higher one was suggested to be the melting or dissociation point, where some of the H-bonds break. Since the prediction of high temperature phase transition, a lot of interest has been developed in the study of high temperature phase transition in the hydrogen bonded solids of KDP-type materials (Grinberg *et al* 1967; O'Keefe and Perrino 1967; Blinc *et al* 1968, 1969; Pereverzeva *et al* 1972; Viswanath and Miller 1979). The investigations have been carried out employing various techniques which are based on NMR (Blinc *et al* 1968, 1969; Adriaenssens and Bjorkstom 1971) and vibrational spectroscopy (Grinberg *et al* 1972; She and Pan 1975; Shapira *et al* 1978; Viswanath and Miller 1979), thermal analysis (Blinc *et al* 1968, 1969; Rapoport 1970), X-ray and neutron scattering (Blinc *et al* 1968, 1969; Efron *et al* 1971), and dielectric and conductivity (Grinberg *et al* 1967, 1972; Pereverzeva *et al* 1972; Perrino and Wentercek 1974) measurements. It was shown that KDP crystal has a phase transition at around 182°C . Sharp changes in the dielectric constant and in the IR spectrum were observed at the transition point. At the same time the crystal became opaque and no significant change in crystal weight was seen.

Blinc *et al* (1968) investigated the thermal decomposition of KDP by means of TGA and DTA on samples of crystallites of 0.1–0.3 mm. TGA showed that the decomposition begins around 220°C , and also a small weight loss if the sample was held for more than 24 h at 180°C . DTA data revealed two endothermic peaks. The first endothermic minimum occurred at 188°C which, according to Blinc *et al* (1968), corresponds to a structural change and the higher one at 265°C corresponds to decomposition.

The microscopic nature of the high temperature phase transition in KDP is still not completely understood. Different authors have observed different phenomena and their interpretations are not identical. The difficulty is that the transition occurs

very close to the region where thermal decomposition sets in and the two effects overlap to a certain extent.

In view of the fact that KDP-type crystals represent one of the simplest disordered hydrogen-bonded systems and that an understanding of what is happening at high temperatures might help us to determine the low temperature ferroelectric properties, it seemed worthwhile to look for high temperature transitions in KDP in more detail.

2. Experimental

Single crystals of KDP were grown from aqueous solution by slow evaporation at room temperature and by seeding technique. Large transparent crystals of good morphology were obtained. These crystals were oven dried and then powdered thoroughly using a ballmill. The powdered mass was separated into different particle sizes: (a) 0.01 mm to 0.1 mm; (b) 0.5 mm to 1.0 mm; (c) 1.0 mm to 1.5 mm; and (d) 1.5 mm to 2.0 mm.

2.1 Differential thermal analysis (DTA)

From each batch of the sample 30 mg was taken in an aluminium crucible. The standard sample was 30 mg of Al_2O_3 . The heating rate was $600^\circ\text{C}/\text{h}$ for the samples. The apparatus used for DTA measurement was DTA Model 30, Shimadzu Corporation, Japan.

2.2 Weight loss measurement

A sample of KDP was taken inside an air-tight weighing bottle. The weight of the bottle with the sample was taken in an electrical balance. The bottle with the sample was heated inside a furnace at 180°C for 3 h and then the weight taken. From the difference in weight, the loss was calculated. Following the same procedure four other samples were heated at 180°C for 36 h, at 200°C for 3 h, at 235°C for 72 h and at 280°C for 3 h. Weight loss was calculated in each case from the difference in weight at room temperature. The results are shown in table 1.

2.3 Infrared transmission spectral analysis

Infrared transmission spectra of an as-grown KH_2PO_4 sample at room temperature and another after heating at 200°C for 3 h and then cooling to room temperature

Table 1. Per cent weight loss at different temperatures.

Sample KDP	Fixed temp. at which the samples were heated	Duration of heating	% wt loss
1	180°C	3 h	0.11
2	180°C	36 h	0.31
3	200°C	3 h	0.58
4	235°C	72 h	2.36
5	280°C	3 h	7.5

were obtained in the spectral region $400\text{--}4000\text{ cm}^{-1}$. Samples were prepared by employing the KBr pellet technique and the spectra were recorded by using infrared spectrometer IR-470, Shimadzu, Japan.

2.4 Dielectric measurement

Both capacitance and loss tangent were measured using a Marconi Instruments Universal Bridge (TF 1313A) operating at 10 kHz. The dielectric constants and loss tangents were measured on single crystal as well as pellets of different particle sizes prepared in a hydraulic press.

3. Results and discussion

The DTA results are shown in figure 1. The figure in the inset shows the results of Blinc *et al* (1968). The figure shows two endothermic peaks, one at 180°C and the other at 213°C . It is interesting to note that the magnitude of the intensity of the endothermic minimum at 180°C reduces as the particle size decreases and finally

Figure 1. DTA curves of KDP of different particle size: (a) 1.5 mm–2.0 mm; (b) 1.0 mm–1.5 mm; (c) 0.5 mm–1.0 mm; (d) 0.01 mm–0.1 mm; (e) 1.0 mm–1.5 mm (2nd heating run); (f) 0.01 mm–0.1 mm (heating rate $5^\circ\text{C}/\text{min}$).

vanishes below the particle size of 0.01 mm to 0.1 mm. This peak also shifts towards higher temperature with decrease of particle size. The second peak which is much stronger than the first one covers the range of thermal decomposition. The decomposition of KDP is known to occur at 253°C (Duval 1963).

At the phase transition at 180°C the change in dielectric constant and the appearance of endothermic peak are accompanied by the appearance of a large number of microcracks. While looking through the microscope it was observed that these microcracks started originating at 175°C. The larger the size of the crystal, the more the cracks. The non-appearance of the endothermic peak at 180°C for particle size ≤ 0.1 mm and the absence of sharp dielectric anomaly at that temperature due to thermal cycling may be attributed to the fact that these phenomena are particle size dependent. It is reasonable to argue that as the transition temperature is approached, the internal stresses in the bulk crystal become enormous and the crystal gets shattered, but smaller crystals could accommodate these stresses. Similar behaviour has also been observed by Pereverzeva *et al* (1972) in RbH_2PO_4 crystals around 86°C. This large increase in the internal stresses is likely to be associated with thermal expansion of the crystal. The X-ray analysis on the as-grown crystal and after heating the crystal at 190°C for 24 h and at 240°C for 3 h reveals that there is no variation in the lattice parameters. It will be interesting to measure the thermal expansion and X-ray analysis at high temperature particularly near the transition temperature to elucidate the mechanism of the phase transition. Blinc *et al* (1968) also pointed out that the magnitude of the enthalpy of the transformation depended on the crystallinity of the sample.

In order to ascertain whether there was any decomposition we took infrared spectra of an as-grown sample at room temperature and another after heating at 200°C for 4 h and then cooling to room temperature. These spectra are shown in figure 2. From

Figure 2. Infrared transmission spectra of KDP: (a) as-grown crystal at room temperature and (b) after heating at 200°C and then cooling to room temperature.

the figure it is seen that there is no variation of $\nu_4(PO_4)$ band at 518 cm^{-1} ; indicating that there is no decomposition. It will be interesting to measure the spectra with variation of temperature particularly above the transition temperature.

Grinberg *et al* (1972) in their measurements on KDP and DKDP observed that high temperature spectra above 175°C of both KDP and DKDP are identical and did not revert to the low temperature form when crystals were cooled to room temperature or even to liquid nitrogen temperature. The absorption spectra of KPO_3 powder at room temperature are identical to the reflection spectra of KDP and DKDP above 175°C . The above observations indicate that Grinberg's crystals were decomposed above 175°C ($KH_2PO_4 \rightarrow KPO_3 + H_2O$) and that is why spectra did not revert to the low temperature form when cooled and resemble KPO_3 spectra at room temperature. Grinberg *et al* (1972) observed only 0.15% weight loss in KDP and DKDP when heated for 30 min above the transition temperature. It is known that KDP starts decomposing above 180°C (Kiehl and Wallace 1927) very slowly. Because of this extremely slow rate of decomposition, Grinberg *et al* (1972) did not find any significant weight loss; but it is suspected that while taking IR spectra they kept the samples for a longer time and thus decomposition set in and the loss of weight might have been higher than they had assumed.

Dielectric constant (ϵ) and loss tangent ($\tan \delta$) for KDP along a and c -axes are shown in figures 3 and 4 respectively. It is seen from the figures that at 175°C both ϵ and $\tan \delta$ rise steeply with increasing temperature and above 180°C they flatten. While

Figure 3. Temperature dependence of dielectric constant and loss tangent of KDP crystals (along a -axis): $\circ$, heating run (as-grown crystal); $\bullet$, 1st cooling run; $\triangle$, 2nd heating run (after one day); $\square$, 3rd heating run (after three days); $\times$, heating run, 0.1 mm–0.5 mm (particle size).

Figure 4. Temperature dependence of dielectric constant and loss tangent of KDP crystals (along c -axis): ○, heating run (as-grown crystal); ●, 1st cooling run; △, 2nd heating run (after two days); □, 3rd heating run (after five days).

cooling the ϵ and $\tan \delta$ curves follow different paths. Second run on the same sample did not show any sharp rise at the transition temperature but showed monotonic increase of ϵ and $\tan \delta$ above 170°C. Repeated thermal cycling showed similar trend and the absolute magnitude near the transition showed smaller values. Dielectric constant of the sample of particle size 0.1 mm to 0.5 mm resembled the third thermal cycling run of the single crystal.

Pereverzeva *et al* (1972) measured dielectric constant and found a sharp fall along a -axis and no substantial change along c -axis at the transition point. Grinberg *et al* (1972) in their measurement observed a sharp fall (ϵ_a) and a sharp rise (ϵ_c) at the transition point. Both the groups have attributed that the rotation of PO_4 group may be responsible for the decrease in ϵ_a , but it is not clear how the increase or no change in ϵ_c can be explained by the PO_4 rotation. In the present measurement, dielectric constant and loss tangent show sharp increase for both a - and c -axis. We are inclined to believe that increase of ϵ_a and ϵ_c are associated with interfacial polarizability and shattering of crystal rather than PO_4 rotation. With successive thermal cycling more and more smaller crystals are fragmented and approach the condition of the powdered samples and the dielectric constant shows similar results as that of powdered samples. The change of colour of single crystal into milky white also justifies our explanation.

Electrical conductivity measurement was done. Preliminary result as shown in figure 5 on single crystal shows a sharp rise in conductivity at the transition temperature but the powdered sample does not show any sudden change. Conductivity

Figure 5. Temperature dependence of electrical conductivity of KDP crystals (along a -axis); ○, heating run (as-grown crystal); ●, 1st cooling run; △, 2nd heating run (after one day); □, heating run; 0.01 mm–0.1 mm (particle size).

measurement on different particle-size samples is in progress and will be reported elsewhere.

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