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High-temperature transformation in KH_2PO_4 and RbH_2PO_4 crystals

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Abstract

The high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 have been investigated by differential thermal analysis, thermogravimetric methods, and thermo-polarizing microscopy. The thermal transformations which appear at $T_p = 196^\circ\text{C}$ in KH_2PO_4 and $T_p = 96^\circ\text{C}$ in RbH_2PO_4 are endothermic in addition to showing weight loss. On heating further to beyond T_p , the thermal transformation shows several endothermic peaks and there is weight loss in KH_2PO_4 and RbH_2PO_4 . It has been observed by thermo-polarizing microscopy that until T_p is exceeded, uniaxial interference figures are exhibited by crystals of KH_2PO_4 and RbH_2PO_4 , with cracks and chemical change at the surface of KH_2PO_4 near $T_p \sim 192^\circ\text{C}$ and RbH_2PO_4 near $T_p \sim 92^\circ\text{C}$. The high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 near T_p could indicate not changes from tetragonal to monoclinic structure but chemical decomposition at the surface of the crystals such as that described by $n\text{MH}_2\text{PO}_4 \rightarrow \text{M}_n\text{H}_2\text{P}_n\text{O}_{3n+1} + (n-1)\text{H}_2\text{O}$ ($\text{M} = \text{K}, \text{Rb}$)

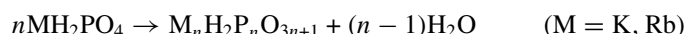
1. Introduction

KH_2PO_4 and RbH_2PO_4 are members of the KDP family of H-bonded crystals. There has been, for a long time, some dispute regarding whether the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 crystal indicate high-temperature phase transitions (HTPTs) or thermal decomposition [1–27]. Most investigators have considered the high-temperature anomaly exhibited by KH_2PO_4 and RbH_2PO_4 near T_p as indicating a structural phase transition; these investigators used various experimental methods [1–15], e.g., optical observations and measurements of thermal properties, x-ray diffraction, dielectric constants, Raman scattering, electrical conductivity, infrared reflectivity, nuclear magnetic resonance (NMR), and nuclear quadrupole resonance (NQR).

But the T_p -values are scattered widely over a temperature range and there are considerable differences in the published reports as regards the high-temperature behaviour [1–23]. After prolonged heat treatment above T_p , crystals of the KDP family turn milky white, and there are

numerous microscopic cracks [1–4]. Mechanical shaking, removal of a very fine surface layer by scratching or grinding, and exposure to water vapour transform the metastable monoclinic phase back to the stable tetragonal phase at room temperature [2–7]. The transition rate seems to depend strongly on the experimental conditions.

Recently, Lee and Park reported that the high-temperature phenomenon is not a structural phase transition but an effect of thermal decomposition at the surface in KH_2PO_4 and RbH_2PO_4 ; their report was based on dielectric constant, thermal analysis, and thermo-microscopy data [16–19]. Ortiz *et al* supported the assertion that the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 are effects of thermal decomposition on the basis of their x-ray, thermogravimetric analysis (TGA), and DSC results [20–22]. They concluded that the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 near T_p are related not to a physical change like a structural phase transition but to a chemical change caused by thermal decomposition such as



that sets in around T_p (see figure 5 of reference [16] for the actual phase interrelations of KH_2PO_4 and RbH_2PO_4 and their thermal products), and claimed that the high-temperature anomaly should be interpreted as an *onset of partial polymerization at reaction sites at the surface of solids*. The condensation of phosphates has been the subject of much investigation in crystal chemistry, and a few excellent reviews have already appeared [23, 24].

But there is still controversy regarding whether it is the existence of a structural phase transition (tetragonal $\rightarrow T_p \rightarrow$ monoclinic) or thermal decomposition that gives rise to the high-temperature anomalies exhibited by KH_2PO_4 and RbH_2PO_4 . Moreover, it is not known as yet what form the so-called high-temperature phase of KH_2PO_4 and RbH_2PO_4 takes, although many investigators have assumed monoclinic crystal systems above T_p . Therefore, we decided to investigate the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 by means of thermal analyses and thermo-polarizing microscopy.

2. Experiment

Crystals of KH_2PO_4 and RbH_2PO_4 were grown from aqueous solution at 45 °C by slow evaporation of the solvent. The DSC and TGA were performed in the temperature range from room temperature to 900 °C using a Dupont 910 differential scanning calorimeter in the open atmosphere. The heating rate was kept at 5 °C min⁻¹. Fragments of crystal were used in the DSC experiment. Optical observation was carried out in the temperature range from room temperature to above T_p by using a thermo-polarizing microscope (Olympus BH-2). Specimens were studied by transmission of light along the *c*-axis. The heating rate was kept at 5 °C min⁻¹. The thermal properties were investigated and optical observations made for samples grown in the same crystallizer.

3. Results and discussion

The DSC and TGA experiments were performed with heating rates of 5 °C min⁻¹ in the open atmosphere. As shown in figures 1(a) and 1(b) and figures 2(a) and 2(b), the thermal transformation shows an endothermic peak at $T_p = 196$ °C for KH_2PO_4 and $T_p = 96$ °C for RbH_2PO_4 ; the onsets of weight loss at $T_p = 190$ °C for KH_2PO_4 and at $T_p = 92$ °C for RbH_2PO_4 are taken to indicate the beginning of thermal decomposition. These temperatures may correspond to the so-called high-temperature transition temperature. On heating further, beyond T_p , the thermal transformations which occur at 289, 448, 645, and 801 °C in KH_2PO_4

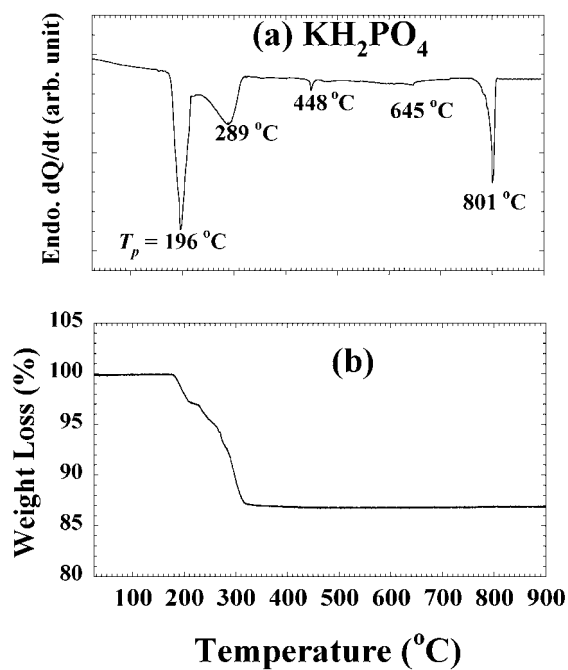


Figure 1. (a) DSC and (b) TGA curves for KH_2PO_4 heated in air to 900°C at a heating rate of $5^{\circ}\text{C min}^{-1}$.

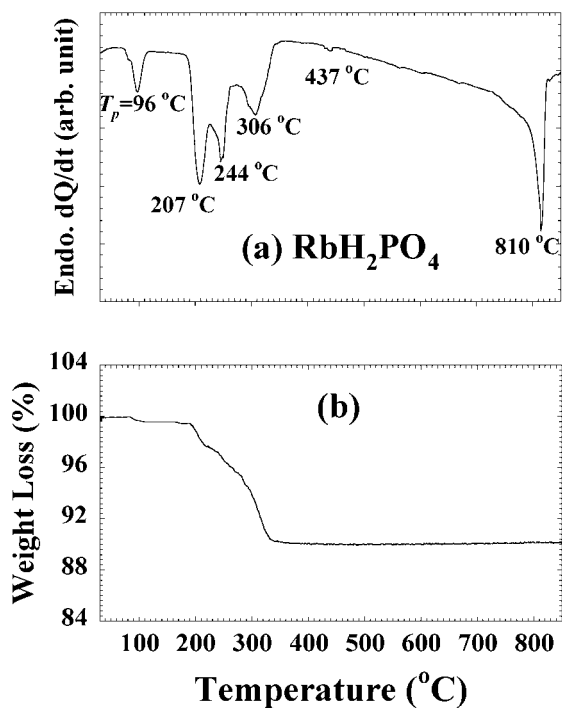
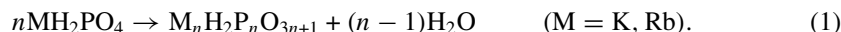


Figure 2. (a) DSC and (b) TGA curves for RbH_2PO_4 heated in air to 900°C at a heating rate of $5^{\circ}\text{C min}^{-1}$.

and 207, 244, 306, 437, and 810 °C in RbH₂PO₄ give rise to several endothermic peaks. The transformation temperatures corresponding to the peaks of the DSC signals indicating weight losses are commonly believed to indicate high-temperature phenomena caused by thermal decompositions such as



For comparison with TGA results and theory, the possible products are calculated on the basis of equation (1), and are shown in table 1 for (a) KH₂PO₄ and (b) RbH₂PO₄. The ratio of the changed products (polymerization) and escaped products (H₂O) are related to the chemical changes in KH₂PO₄ and RbH₂PO₄ for the various possible *n*-values as follows:

- the case of *n* = 2, 2KH₂PO₄ → K₂H₂P₂O₇ + H₂O:

$$\text{ratio of changed product} : \frac{M(\text{K}_2\text{H}_2\text{P}_2\text{O}_7)}{M(2\text{KH}_2\text{PO}_4)} \times 100 = 93.38\%$$

$$\text{ratio of escaped product} : \frac{M(\text{H}_2\text{O})}{M(2\text{KH}_2\text{PO}_4)} \times 100 = 6.62\%$$

- the case of *n* = 10, 10KH₂PO₄ → K₁₀H₂P₁₀O₃₁ + 9H₂O:

$$\text{ratio of changed product} : \frac{M(\text{K}_{10}\text{H}_2\text{P}_{10}\text{O}_{31})}{M(10\text{KH}_2\text{PO}_4)} \times 100 = 88.09\%$$

$$\text{ratio of escaped product} : \frac{M(9\text{H}_2\text{O})}{M(10\text{KH}_2\text{PO}_4)} \times 100 = 11.9\%$$

- the case of *n* ≫ 1, *n*KH₂PO₄ → *n*K_{*n*}H₂P_{*n*}O_{3*n*+1} + (*n* - 1)H₂O:

$$\begin{aligned} \text{ratio of changed product} : & \frac{M(\text{K}_n\text{H}_2\text{P}_n\text{O}_n)}{M(n\text{KH}_2\text{PO}_4)} \times 100 \\ & = \frac{M(\text{KPO}_3)_n}{M(n\text{KH}_2\text{PO}_4)} \times 100 = \frac{M(\text{KPO}_3)}{M(\text{KH}_2\text{PO}_4)} \times 100 = 86.76\% \end{aligned}$$

Table 1. For various *n*-values, the masses of the possible products in (a) KH₂PO₄ and (b) RbH₂PO₄ crystals. The possible products are calculated on the basis of equation (1).

| (a) KH ₂ PO ₄ | | | | | | | | |
|--------------------------------------|---------|--|--|-----|--|-----|--|-------------------------|
| Atom | Mass | <i>n</i> = 1 KH ₂ PO ₄ | <i>n</i> = 2 K ₂ H ₂ P ₂ O ₇ | ... | <i>n</i> = 10 K ₁₀ H ₂ P ₁₀ O ₃₁ | ... | <i>n</i> ≫ 1 (KPO ₃) _{<i>n</i>} | H ₂ O |
| K | 39.10 | K: 39.10 | K: 39.10 | ... | K ₁₀ : 391 | ... | K: 39.10 | |
| H | 1.0079 | H ₂ : 2.0158 | H ₂ : 2.0158 | | H ₂ : 2.0158 | | | H ₂ : 2.0158 |
| P | 30.9737 | P: 30.9737 | P ₂ : 61.9475 | | P ₁₀ : 309.9731 | | P: 30.9737 | |
| O | 15.9994 | O ₄ : 63.9976 | O ₇ : 111.9958 | | O ₁₃ : 495.9815 | | O ₃ : 47.9982 | O: 15.9994 |
| | | 136.0871 | 254.1591 | ... | 1198.7348 | ... | (118.0713) _{<i>n</i>} | |
| (b) RbH ₂ PO ₄ | | | | | | | | |
| Atom | Mass | <i>n</i> = 1 RbH ₂ PO ₄ | <i>n</i> = 2 Rb ₂ H ₂ P ₂ O ₇ | ... | <i>n</i> = 10 Rb ₁₀ H ₂ P ₁₀ O ₃₁ | ... | <i>n</i> ≫ 1 (RbPO ₃) _{<i>n</i>} | H ₂ O |
| Rb | 85.4678 | Rb: 85.4678 | Rb ₂ : 170.935 | ... | Rb ₁₀ : 854.678 | ... | Rb: 85.4678 | |
| H | 1.0079 | H ₂ : 2.0158 | H ₂ : 2.0158 | | H ₂ : 2.0158 | | | H ₂ : 2.0158 |
| P | 30.9737 | P: 30.9737 | P ₂ : 61.9475 | | P ₁₀ : 309.9731 | | P: 30.9737 | |
| O | 15.9994 | O ₄ : 63.9976 | O ₇ : 111.9958 | | O ₁₃ : 495.9815 | | O ₃ : 47.9982 | O: 15.9994 |
| | | 182.4549 | 346.8947 | ... | 1662.4128 | ... | (164.4397) _{<i>n</i>} | |

$$\begin{aligned} \text{ratio of escaped product: } & \frac{M((n-1)\text{H}_2\text{O})}{M(n\text{KH}_2\text{PO}_4)} \times 100 \\ & \approx \frac{M(n\text{H}_2\text{O})}{M(n\text{KH}_2\text{PO}_4)} \times 100 = \frac{M(\text{H}_2\text{O})}{M(\text{KH}_2\text{PO}_4)} \times 100 = 13.24\% \end{aligned}$$

- the case of $n = 2$, $2\text{RbH}_2\text{PO}_4 \rightarrow \text{Rb}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}$:

$$\text{ratio of changed product: } \frac{M(\text{Rb}_2\text{H}_2\text{P}_2\text{O}_7)}{M(2\text{RbH}_2\text{PO}_4)} \times 100 = 95.06\%$$

$$\text{ratio of escaped product: } \frac{M(\text{H}_2\text{O})}{M(2\text{RbH}_2\text{PO}_4)} \times 100 = 4.94\%$$

- the case of $n = 10$, $10\text{RbH}_2\text{PO}_4 \rightarrow \text{Rb}_{10}\text{H}_2\text{P}_{10}\text{O}_{31} + 9\text{H}_2\text{O}$:

$$\text{ratio of changed product: } \frac{M(\text{Rb}_{10}\text{H}_2\text{P}_{10}\text{O}_{31})}{M(10\text{RbH}_2\text{PO}_4)} \times 100 = 91.11\%$$

$$\text{ratio of escaped product: } \frac{M(9\text{H}_2\text{O})}{M(10\text{RbH}_2\text{PO}_4)} \times 100 = 8.89\%$$

- the case of $n \gg 1$, $n\text{RbH}_2\text{PO}_4 \rightarrow n\text{Rb}_n\text{H}_2\text{P}_n\text{O}_{3n+1} + (n-1)\text{H}_2\text{O}$:

$$\begin{aligned} \text{ratio of changed product: } & \frac{M(\text{Rb}_n\text{H}_2\text{P}_n\text{O}_n)}{M(n\text{RbH}_2\text{PO}_4)} \times 100 \\ & = \frac{M(\text{RbPO}_3)_n}{M(n\text{RbH}_2\text{PO}_4)} \times 100 = \frac{M(\text{RbPO}_3)}{M(\text{RbH}_2\text{PO}_4)} \times 100 = 90.13\% \end{aligned}$$

$$\begin{aligned} \text{ratio of escaped product: } & \frac{M((n-1)\text{H}_2\text{O})}{M(n\text{RbH}_2\text{PO}_4)} \times 100 \\ & \approx \frac{M(n\text{H}_2\text{O})}{M(n\text{RbH}_2\text{PO}_4)} \times 100 = \frac{M(\text{H}_2\text{O})}{M(\text{RbH}_2\text{PO}_4)} \times 100 = 9.87\%. \end{aligned}$$

As shown in figures 1(a) and 1(b) and figures 2(a) and 2(b), this weight loss is indicative of the formation of various polymeric intermediates, during the course of dehydration to the final formation of KPO_3 and RbPO_3 . The final products can be changed from KH_2PO_4 to KPO_3 (weight loss 11.9%) above 320 °C and from RbH_2PO_4 to RbPO_3 (weight loss 9.8%) above 340 °C, because for the final products the calculated value and the measured weight loss are the same. Also, the onsets of weight loss at 185 °C in KH_2PO_4 and at 85 °C in RbH_2PO_4 are taken as indicating the beginning of thermal decomposition. These temperatures may correspond to the so-called high-temperature transition temperature. On further heating, one finds a semi-plateau region, accompanied by about 3% weight loss between 200 °C and 250 °C in KH_2PO_4 and about 3.4% weight loss between 150 °C and 200 °C in RbH_2PO_4 . For any given n -value, the weight losses at the semi-plateau are not the same as the values calculated for the intermediate products. But the temperature regions (KH_2PO_4 : 196 °C–350 °C; RbH_2PO_4 : 96 °C–350 °C) over which the weight loss changes in KH_2PO_4 and RbH_2PO_4 are difficult to explain, since the processes of polymerization are strongly dependent on temperature and the changed product is unstable. If we respect the realistic phase relationships of equation (1), the HTP slightly above T_p is not a single phase of MH_2PO_4 , but a mixture consisting mainly of MH_2PO_4 and $\text{M}_2\text{H}_2\text{P}_2\text{O}_7$. The temperature regions of changing weight loss in KH_2PO_4 and RbH_2PO_4 could be relating to mixed phases. We think that the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 near T_p should be interpreted as indicating the *onset of a partial polymerization at reaction sites on the surface of solids*, such as that represented by equation (1).

Many investigators reported that on heating above T_p the crystal symmetry seems to change from tetragonal with space group $I\bar{4}2d$ – D_{2d}^{12} to monoclinic with space group $P2_1$ – C_2^2

or $P2_1/m-C_{2h}^2$ for KH_2PO_4 and $P2_1-C_2^2$ or $P2_1/m-C_{2h}^5$ for RbH_2PO_4 [2, 3, 5, 7]. However, detailed structural analyses including atomic coordinates have not been thoroughly established. On the other hand, the crystal structures of possible intermediate and final products obtained by heat treatment have been reported also to be monoclinic with space group $C2/c-C_{2h}^6$ for $\text{K}_2\text{H}_2\text{P}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$, $P2_1/a-C_{2h}^5$ for $(\text{KPO}_3)_n$, and $P2_1/n-C_{2h}^5$ for $(\text{RbPO}_3)_n$ [25]. Also, for KH_2PO_4 and RbH_2PO_4 , mechanical shaking, removal of a very fine surface layer by scratching or grinding, and exposure to water vapour transform the metastable monoclinic phase back to the stable tetragonal phase at room temperature, as shown in figure 3.

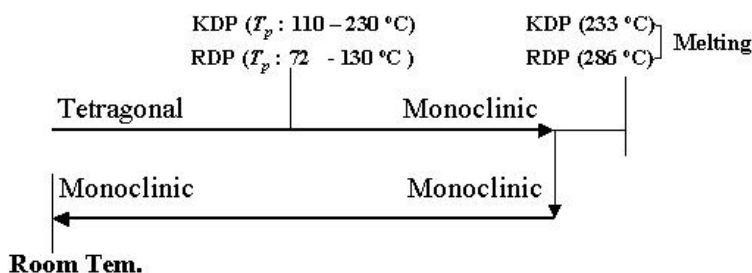


Figure 3. A schematic representation of the phase transformation in KH_2PO_4 and RbH_2PO_4 .

In order to clarify whether the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 at around T_p are due to the structural phase transition or due to partial thermal decomposition, optical observation was carried out by using a polarizing microscope. Figures 4 and 5 are (a) micrographs of the surface and (b) polarizing micrographs of interference figures in KH_2PO_4 and RbH_2PO_4 crystal along the c -axis. It has been observed by thermo-polarizing microscopy that until T_p is exceeded, uniaxial interference figures are seen for the crystals of KH_2PO_4 and RbH_2PO_4 . So, the crystal systems of KH_2PO_4 and RbH_2PO_4 above T_p cannot be monoclinic phases because monoclinic crystal will show not uniaxial interference figures but biaxial interference figures under conoscopic observation. A few cracks and spots appeared abruptly at the surfaces of KH_2PO_4 and RbH_2PO_4 near T_p . As the temperature is increased further, these cracks merge together, giving rise to a number of cracks.

Microcracks appearing upon heating above T_p have already been seen (see references [1–4]). After prolonged heat treatment near T_p , the sample changes from transparent and colourless to milky white. Recently, Park *et al* reported that microcracks appeared at the surface of KH_2PO_4 near 180°C (T_p) [18], and the appearance of cracks near 112°C (T_p) in RbH_2PO_4 [19] is similar to that near 180°C in KH_2PO_4 .

According to Lee [16], this can be accounted for as being due to the formation and liberation of water molecules. The dehydration may start at reaction sites distributed on the surface of solids. As the temperature rises above T_p or the sample is tempered at constant temperature above T_p , more monomers are reacted and internal pressure due to water molecules may increase. As H_2O molecules formed near the surface or in the interior migrate to the surface, the increased water vapour pressure can cause the surface to become microcracked. The physical origin of this may be the hydrogen-bond breaking occurring due to the thermal decomposition. The bond breaking occurs where the energy deficiency is supplied by thermal activation. This phenomenon can be understood in terms of formation and growth of cracks and according to chemical reactions such as that described by equation (1). Numerous observations confirm that decomposition of solid reactants is generally initiated in defective regions of the crystal such as at the surface or, more specifically, at points of emergence of dislocations at the surface. Likewise, nuclei of solid product, $\text{M}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$ ($\text{M} = \text{K}, \text{Rb}$), are thus formed,

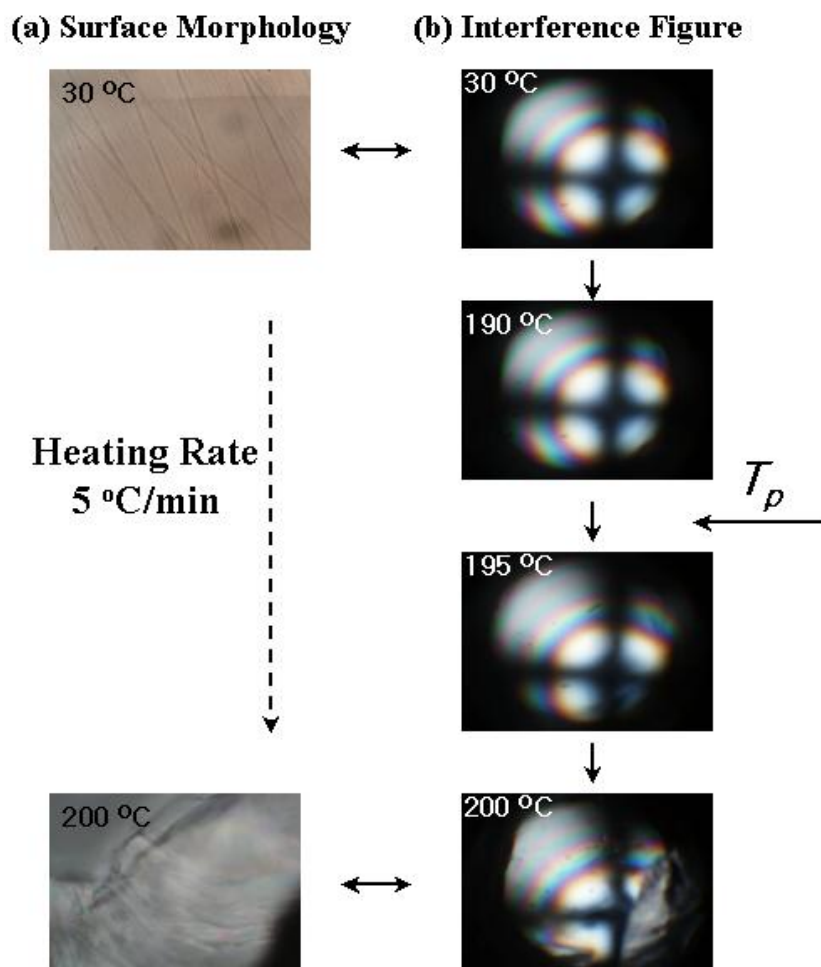
KH_2PO_4 -*c* axis

Figure 4. The effects of heat treatment on (a) the surface morphology and (b) the interference figure of KH_2PO_4 along the *c*-axis. The heating rate was kept at $5\text{ }^\circ\text{C min}^{-1}$.

the gaseous product escapes, and the resulting disruption causes strain in the neighbouring regions of unreacted MH_2PO_4 ($M = \text{K, Rb}$) and internal pressure due to $\text{M}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$ ($M = \text{K, Rb}$) polymer may increase. The interpretation is similar to that in the cases of thermal decomposition of TiH_2PO_4 [26] and $(\text{NH}_4)_2\text{SO}_4$ [27] crystals. So, the monoclinic structures of the HTP might stem partly from the monoclinic structures of intermediate and/or final products.

4. Summary

In summary, the high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4 can be explained as follows. The high-temperature phenomena exhibited by KH_2PO_4 and RbH_2PO_4

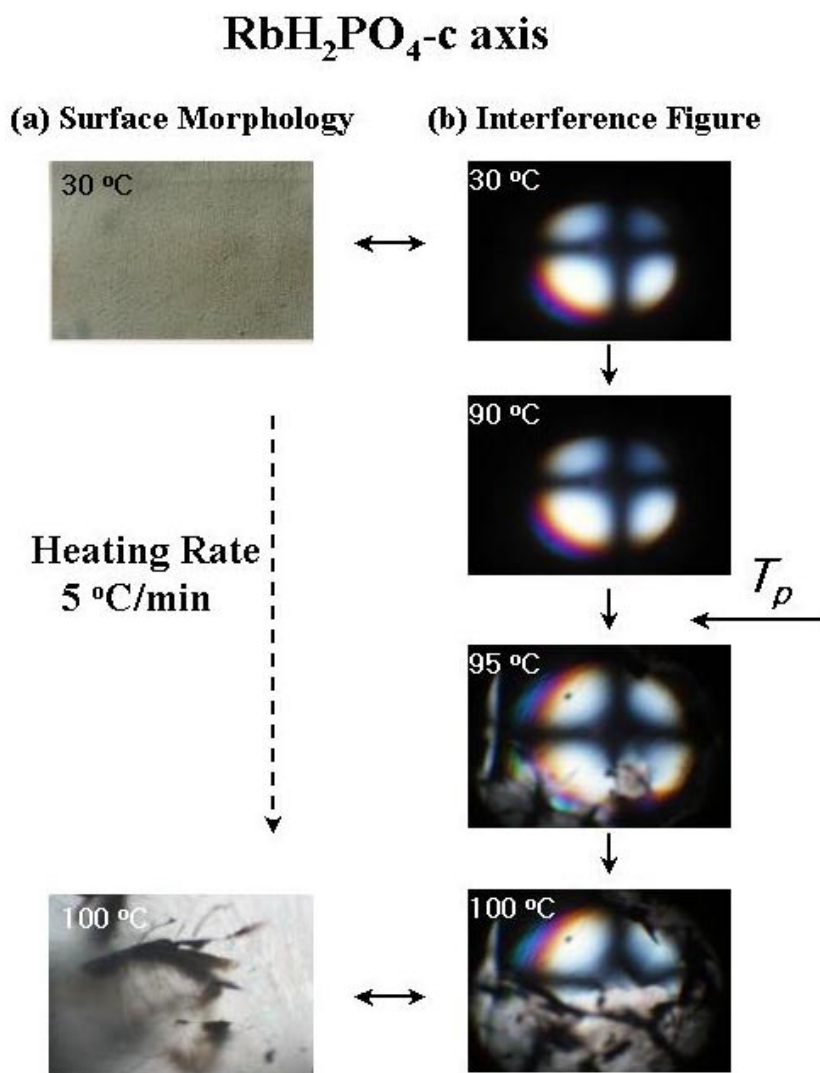


Figure 5. The effects of heat treatment on (a) the surface morphology and (b) the interference figure of RbH₂PO₄ along the *c*-axis. The heating rate was kept at 5 °C min⁻¹.

have been investigated by differential thermal analysis, thermogravimetric analysis, and thermo-polarizing microscopy. The thermal transformations which appear at $T_p = 196$ °C in KH₂PO₄ and $T_p = 96$ °C in RbH₂PO₄ are endothermic in addition to showing weight loss. Upon heating further, beyond T_p , the thermal transformation gives rise to several endothermic peaks and weight loss in RbH₂PO₄. It has been observed by thermo-polarizing microscopy that until T_p is exceeded, uniaxial interference figures are seen for the crystals of KH₂PO₄ and RbH₂PO₄, with cracks and chemical change at the surfaces of KH₂PO₄ near $T_p \sim 192$ °C and RbH₂PO₄ near $T_p \sim 92$ °C. The high-temperature phenomena exhibited by KH₂PO₄ and RbH₂PO₄ near T_p could indicate not a change from tetragonal to monoclinic structure but a chemical decomposition at the surface of the crystals such as $n\text{MH}_2\text{PO}_4 \rightarrow \text{M}_n\text{H}_2\text{P}_n\text{O}_{3n+1} + (n-1)\text{H}_2\text{O}$ ($M = \text{K}, \text{Rb}$).

Acknowledgments

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