

## X-Ray Scattering Studies of the Metastable Ferroelectric Phase in KDP Induced by Static Electric Field

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Potassium dihydrogen phosphate presents a ferroelectric phase below 122 K and a paraelectric phase for  $T > 122$  K. X-ray scattering measurements were performed in order to verify the mechanism of the phase transition from point group  $C_{2v}^{19}$  to  $C_{2v}^{j \neq 19}$  at 119 K induced by DC electric field; in other words, a change of the local site symmetries of the phosphate group occurs from  $C_2$  site in the  $C_{2v}^{19}$  point group to  $C_s$  in the  $C_{2v}^{j \neq 19}$  point group. This phenomenon was shown by analyzing the behavior of the integrated intensity of the (800), (080), (1600), (0160), (400) and (040) reflections. The curve fitting of these reflections showed the occurrence of a rotation of the phosphate group around the [010] crystallographic direction during the phase transition. This study confirms the observation of this metastable phase obtained by Raman spectroscopy.

**Keywords:** KDP, metastable phase, X-ray

### 1. Introduction

Many works developed with the objective of studying the physical properties of ferroelectric materials had already promoted discoveries with valuable contribution to technology. Although it has already been sufficiently studied, the Potassium Dihydrogen Phosphate (KDP) is a ferroelectric material that attracts the attention of many researchers because of its technological applications, such as Ferroelectric Devices for Random Access Memory (FDRAM). The KDP crystals undergo a phase transition at a temperature of 122 K<sup>1</sup>. This crystal presents an orthorhombic symmetry (ferroelectric phase) at temperature below 122 K, belonging to the Fdd2 ( $C_{2v}^{19}$ ) space group, while above this temperature it presents a tetragonal symmetry (paraelectric phase), belonging to the I42d ( $D_{2d}^{12}$ ) space group. The KDP crystal undergoes two metastable transitions induced by uniaxial pressure:  $D_{2d}^{12} \rightarrow C_{2v}^{j \neq 19}$  and  $C_{2v}^{19} \rightarrow D_{2v}^{j \neq 19}$ . According to the literature an explanation for these transitions is based on the changing of the local site symmetry of the phosphate ions: in the ferroelectric phase, the phosphate ions change their local site symmetry from  $C_2$  to  $C_s$ , maintaining the same factor group  $C_{2v}$ , but modifying the space group.

These changes are due to the rotation of the phosphate ions around the [010] direction of the orthorhombic structure<sup>2</sup>. Other works in the literature discuss the reversibility criteria of this new metastable phase<sup>3</sup>. The phase diagram for the KDP transitions on the plane ( $\sigma_6$ , T) for temperature in the range from 110 to 130 K explains the appearance of the metastable  $C_{2v}^{j \neq 19}$  phase based on the Gibbs free energy density of the system<sup>4</sup>.

Raman scattering experiments show that the potassium dihydrogen phosphate crystals undergo a metastable ferroelectric phase induced by a static electric field near the Curie point<sup>5</sup> taking advantage of the fact that the ferroelectric phase presents piezoelectricity. In other words, due to the converse piezoelectric effect a DC electric field applied along the [001] direction should induce a phase transition ( $C_{2v}^{19} \rightarrow C_{2v}^{j \neq 19}$ ) in KDP crystals similarly to that induced by pressure with the force applied along the shear direction.

Hence, the main goal of this work is to use X-ray diffraction measurements to confirm the assumption that the DC electric field applied along the ferroelectric c-axis forces the appearance of a metastable ferroelectric phase transition at 119 K, and that this transition is related to the rotation of the dipoles around the [010] direction of the

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orthorhombic structure leading to a change in the local site symmetry of the phosphate ions.

## 2. Experimental

Single crystals of KDP with good optical quality and good crystalline perfection used in the experiments were grown by the slow cooling method. These samples were cut in parallelepipeds with dimensions  $(0.87 \times 3 \times 5) \text{ mm}^3$ . The parallelepiped faces were orthogonal to the [100], [010] and [001] crystallographic directions of the tetragonal structure. Silver electrodes were painted on the larger faces which are perpendicular to the ferroelectric [001] direction. A Keithley instrument model 246 was used as the DC voltage source.

X-ray scattering measurements were performed using a two-circle ( $\theta$ - $2\theta$ ) Rigaku diffractometer, with radiation source of  $\text{MoK}\alpha$  coupled with a low temperature chamber containing liquid nitrogen. The sample temperature was controlled with a fluctuation of  $\pm 0.5 \text{ K}$ . The high penetration feature of the X-ray beam ( $\lambda^{\text{MoK}\alpha} = 0.709 \text{ \AA}$ ) gives advantage to get diffraction from deeper planes. This reduces the diffraction from the crystal surface that is not affected by the electric field.

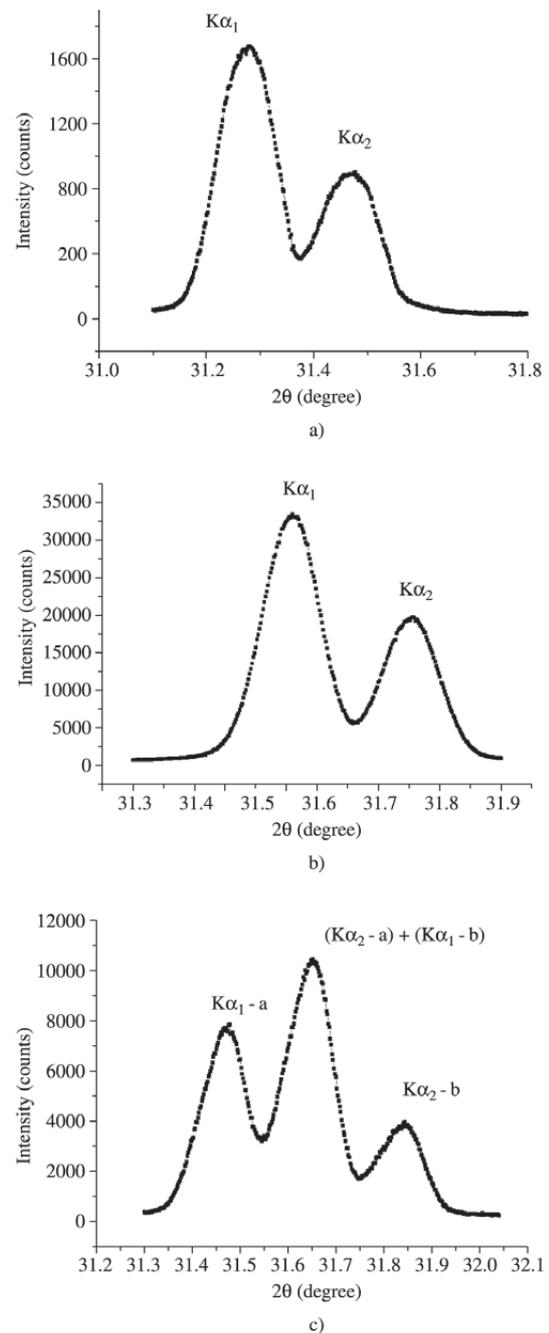
## 3. Results and Discussion

The crystal was aligned using the 440 reflection of paraelectric phase (tetragonal) and then cooled down to ferroelectric phase (orthorhombic). According to the space group of both phases, the extinction in the Miller indices for the reflections  $hh0$  ( $h = 2n$ ) in the tetragonal symmetry changes to  $h00$  ( $h = 4n$ ) in the orthorhombic symmetry.

Figure 1a shows the diffraction pattern for the 440 reflection at room temperature. The first peak corresponds to the scattering of the plane (440) for  $\text{K}\alpha_1$  radiation and the second one is the scattering of the same plane for  $\text{K}\alpha_2$  radiation. Figure 1b shows rocking curves for the 440 reflection at 125 K (near ferroelectric phase transition). The changes observed in Fig. 1b regarding to Fig. 1a are easily explained. The displacement of the peak position to higher angles occurs due to the reduction of the lattice parameters caused by thermal contraction. Its scattering intensity is related to the Debye-Waller factor.

Figure 1c shows the diffraction pattern below the transformation temperature. It shows three peaks where the first is the scattering of the  $\text{K}\alpha_1$  radiation by a domain we call *a*. The third peak is related to the diffraction of the  $\text{K}\alpha_2$  radiation by another domain that we call *b*. Finally the second peak is the overlap of  $\text{K}\alpha_2$  diffracted by the domain *a* and the  $\text{K}\alpha_1$  diffracted by the domain *b*<sup>6-9</sup>.

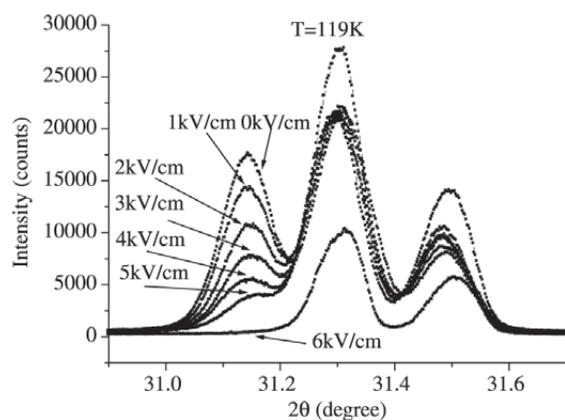
Before discussing X-ray results we need to show that under DC electric field, the KDP crystal undergoes a  $\text{C}_{2v}^{19} \rightarrow \text{D}_{2v}^{j \neq 19}$  phase transition. The idea of the experiment



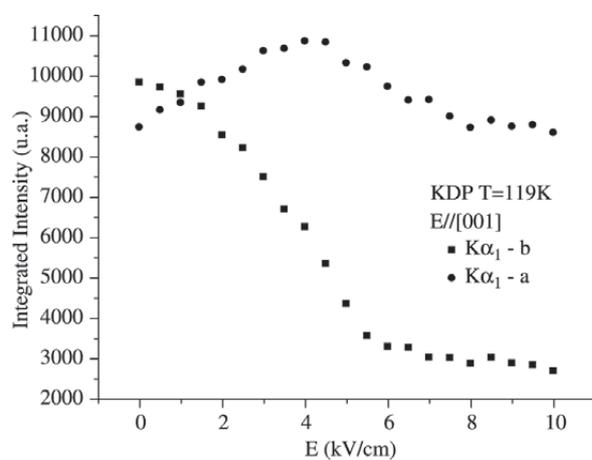
**Figure 1.** X-ray diffraction pattern for: a) (440) plane at room temperature; b) (440) plane near transition at 124 K; c) (800) plane for ferroelectric phase at 119 K.

is very simple: As the phosphate tetrahedron contributes with negative charge for the dipole, a variation in the integrated intensity for (800) plane, which is formed by oxygen and phosphor, should be observed by applying an electric field.

Figure 2 shows the diffraction patterns corresponding to the  $a$  and  $b$  domains in the orthorhombic structure as a function of the DC electric field up to 5 kV/cm at 119 K. The peaks emerge from the overlapping of the bands corresponding to the  $K_{\alpha 1}$  and  $K_{\alpha 2}$  lines of Mo radiation. By performing a spectral decomposition into Gaussian components, we can draw the variation of the integrated intensity of both reflections as a function of DC electric field, which is displayed in Fig. 3. It should be observed that the integrated intensity corresponding to the  $a$  domain decreases



**Figure 2.** X-ray diffraction pattern for KDP obtained in the ferroelectric phase under electric field from 0-6 kV/cm.



**Figure 3.** Integrated intensity for the  $a$  and  $b$  domains versus electric field.

with increasing the DC electric field up to 5 kV/cm, while the  $b$  domain increases. In addition, for the electric field of 6 kV/cm, the peak corresponding to the  $a$  domain disappears. These changes in the integrated intensity for the  $a$  domain until 5 kV/cm and the total disappearance of this peak at 6 kV/cm indicate essentially that oxygen atoms on these planes moved out. This can be attributed to the result of rotation of the phosphate tetrahedron around the [010] crystallographic direction relative to the  $C_{2v}^{19}$  orthorhombic structure.

## 4. Conclusion

We report here the mechanism which led to a conformational phase transition of KDP when an increase of DC electric field is applied along the orthorhombic  $c$ -axis. The huge variation in the integrated intensity of those peaks, corresponding to the  $a$  and  $b$  domains, indicated the occurrence of changes in the atom positions on (800) planes. These changes were attributed to the rotation of the phosphate tetrahedron around the  $b$ -axis, which also changes the local site symmetries of phosphate ions from  $C_2$  in the  $C_{2v}^{19}$  phase to  $C_s$  in the  $C_{2v}^{19}$  phase.

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