Ferroelastic domain walls in the incommensurate phase of $\gamma$-KCoP$_0$$^4$

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Abstract

Ferroelastic domains in $\gamma$-KCoPO$_4$ were studied by polarized light microscopy and by x-ray methods. These domains appear upon cooling as a result of a phase transition at $\sim$449° from an orthorhombic normal (N) phase (with probable space group Pnma) to a incommensurate phase (IC) which is monoclinic and has a $\overline{a}$. structure isotypic with CsLiSO$_4$ with space group $\bar{P}2_1/c$. The modulation of the monoclinic structure decreases as the cell parameters change when the crystals are ground to a grain size of

Reference

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Ferroelectric domains in \( \gamma \)-KCoPO\(_4\) were studied by polarized light microscopy and by X-ray methods. These domains appear upon cooling as a result of a phase transition at about 449°C from an orthorhombic normal (N) phase (with probable space group \( \text{Pnma} \)) to an incommensurate phase (IC) which is monoclinic and has an average structure isotypic with \( \text{CsLiSO}_4 \) with space group \( \text{P2}_1/c \). The modulation of the monoclinic structure decreases and the cell parameters change when the crystals are ground to a grain size of less than 7 \( \mu \text{m} \) and heated and cooled several times through the phase transition. A Rietveld refinement of the structure of \( \gamma \)-KCoPO\(_4\) was achieved on a powder pattern. The cell parameters are:

\[
\begin{align*}
 a &= 5.3052(3), \\
b &= 8.5571(4), \\
c &= 10.3926(6), \\
\beta &= 120.833(2)^\circ
\end{align*}
\]

in [Å] and \( Z = 4 \).

Keywords: Domains, ferroelasticity, incommensurability.

1. INTRODUCTION

Many phosphate compounds of the type \( \text{M}'\text{M}''\text{PO}_4 \), where \( \text{M}' \) stands for an alkaline cation and \( \text{M}'' \) is a divalent transition element, are known at present. Most of these compounds have one or several phase transitions in the temperature range 6–1400 K and show ferroelectric and ferroelastic properties.\(^1\)–\(^4\) The structure of these compounds depends essentially on the size of the \( \text{M}' \) and the \( \text{M}'' \) ions. When \( \text{M}' \) is large (\( r_1 > 1.0 \)) and \( \text{M}'' \) is small (\( r_1 < 0.7 \)), the structure generally presents two types of tetrahedra formed by \( \text{PO}_4 \) and \( \text{M}''\text{O}_4 \) groups. In such a case the structure is closely related to the beryllonite and \( \beta \)-tridymite types. The differences are due only to different orientations of the tetrahedra. Another interesting feature of this type of compounds is that many of them have the same orthorhombic prototype phase at high temperature. It belongs to the centrosymmetric space group \( \text{Pnma} \) (e.g. \( \text{KBePO}_4 \), \( \text{RbBePO}_4 \), \( \text{CsBePO}_4 \), \( \text{CsZnPO}_4 \), \( \text{CsLiSO}_4 \), \( \text{NH}_4\text{LiSO}_4 \), etc.\(^5\)–\(^7\) ) The general sequence of phase transitions on cooling is \( \text{mmm} \rightarrow \text{mm2} \rightarrow \text{2/m} \) or 2. This sequence confers ferroelectric and ferroelastic properties to these compounds.

The compound \( \text{KCoPO}_4 \) (KCP) belongs to this crystal family. In a preceding work\(^8\) it was shown that KCP exists in two different structures at room temperature. One of them called \( \alpha \)-KCP has hexagonal symmetry with space group \( \text{P6}_3 \). In this structure the paramagnetic \( \text{Co}^{2+} \) ions are in tetrahedral sites surrounded by four oxygen atoms. This form is metastable, upon heating it undergoes a phase transition at 576°C to a phase which was found to be orthorhombic with cell dimensions \( a = 8.90, b = 5.31, c = 8.56 \) in [Å].\(^9\) Upon cooling the phase transition occurs at 449°C and the compound adopts a new structure called \( \gamma \)-KCP which is the stable form of KCP.

In the literature different descriptions are given for the structure of \( \gamma \)-KCP,\(^1\)\(^2\)\(^9\) but so far no complete structural determination has been done. This might be due to the fact that a very complicated pattern of ferroelastic domains appears on \( \gamma \)-KCP crys-
tals at the phase transition temperature during the cooling process. In this work a study of the ferroelastic domains of γ-KCP with polarized light microscopy and X-ray diffraction methods is presented. The crystal structure is also given, based on a Rietveld refinement of a powder diffraction pattern.

2. EXPERIMENTAL

Single crystals of γ-KCP were grown from a KCl flux following the method given in Reference 8. The deep blue crystals have the form of elongated prisms. Different cuts were prepared by polishing for optical examination with polarized light microscopy. The crystals are strongly absorbent, therefore it was necessary to prepare very thin plates (≈20 µm) for a convenient optical study. A Leitz polarized light microscope and a Linkam heating stage were used to follow the transition optically.

Buerger precession X-ray photographs of single crystals were made along different zone axes using a Cu Kα (λ = 1.5418 Å) radiation source. Powder X-ray diffraction patterns were measured on a Philips diffractometer with a Bragg-Brentano geometry and with a Co Kα (λ = 1.7903 Å) radiation source. Scans were made in the 2θ range of 10°–100°, in steps of 0.04° and 15 s per step. Powder patterns were also measured on films with a Guinier camera with Co Kα, radiation for controlling the purity of the sample and to follow the transformations of the structure after grinding and thermal treatments. Rietveld refinements were made with a modified version of the program DBW32.S.10

3. RESULTS AND DISCUSSION

3.1. Optical Studies

The morphology of γ-KCP crystals obtained from a KCl flux is shown on Figure 1. An orthogonal axis system is also indicated. We will refer to this system to describe the cuts prepared for optical examinations and to give the orientation of the ferroelastic domains walls relative to the facets of the crystal. The z direction is defined parallel to the long side of the crystals and the x direction is taken parallel to the bisector of the acute angle of a z = 0 cut. The same morphology is found for crystals of the related compound KNiPO4, synthesized by a similar method. The orientation of the orthogonal system defined is the same as the orientation of the orthorhombic cell of KNiPO4.11

FIGURE 1  Morphology of the γ-KCoPO4 crystals obtained from a KCl flux. An orthogonal axis system is also defined and which is used as a reference to describe the cuts prepared and the orientation of the ferroelastic walls.
FIGURE 2  Ferroelastic domains in \( \gamma \)-KCoPO\(_4\). Cut perpendicular to the monoclinic axis. Two different areas of the same crystal are seen with crossed polarizers; each area is shown in two different extinction positions. Only two domain states are present; the orientation of their corresponding optical indicatrix is indicated. Three types of wall are seen: [100], [001] and [102]. The orientation of the two monoclinic sublattices relative to the crystal as determined by X-rays is given on the upper part of the figure.

Ferroelastic domains are clearly seen on \( y = 0 \) cuts only. A very complicated "tweed" pattern, typical of modulated structures is seen (cf. Figure 2). The boundaries are very irregular and curved in some areas. Near the edges of the crystal the wall density decreases. Figures in the form of isosceles triangles are distinguishable (the angle between the two equal sides is \( 61.0 \pm 0.1^\circ \)). Three types of ferroelastic domain walls are visible, parallel to \( x = 0 \), \( x = (\sqrt{3} - \delta)z \) and \( x = - (\sqrt{3} - \delta)z \) planes with \( \delta = 0.038 \). Only two domain states are present as can be seen on Figure 2. These ferroelastic domains are not visible on \( x = 0 \) and \( z = 0 \) cuts, this means...
that the section of the index ellipsoid parallel to these planes is the same for the two ferroelastic domains. Domains are also visible on $x = \sqrt{3}z$ cuts, however, in order to achieve this it is necessary to use a compensator as the section of the index ellipsoid has in this case the same orientation but different birefringence. The domains appear as stripes of slightly different colour (blue/purple with white light) which run through the whole crystal parallel to the $y$ direction defined above. No domain wall is seen perpendicular to the $y$ direction. From these observations the orientation of the optical indicatrix of the two domains was derived and it is indicated on Figure 2. Both indicatrix cross sections have one principal axis parallel to the $y$ direction and are rotated around this axis by about $21.2^\circ$ in opposite directions relative to the $x$ direction. Therefore we can conclude that the domains correspond to two monoclinic crystallographic orientations with the monoclinic axis parallel to the $y$ direction. This was confirmed by X-ray studies.

The different cuts were heated up to above the phase transition under optical examination. The ferroelastic domains disappear completely at about $608^\circ$C upon heating, but the crystals begin to transform at about $590^\circ$C. Upon cooling the transformation begins at about $560^\circ$C, where inhomogeneities appear in certain areas of the crystal. At about $450^\circ$C, a phase boundary becomes visible and the crystal transforms rapidly, within a few degrees. It is interesting to note that the appearing phase does not nucleate at the areas where the first inhomogeneities began, the phase boundary starts at the edges of the crystal. As the coexistence of two phases is seen, this phase transition must be of first order. This unusually large hysteresis is also observed in DTA studies of this compound but the temperatures at which the transformations occur are somewhat different. The crystals normally crack after a few cycles of heating and cooling, this fact and the large hysteresis observed indicate that, on cooling, the transition must bring about some internal stress.

Examination of the crystal cuts at $630^\circ$C allowed the determination of the orientation of the optical indicatrix in the orthorhombic phase. The principal axes of the indicatrix run parallel to the coordinates defined in Figure 1. This is also the orientation of the orthorhombic cell. The most probable space group of this phase is $Pnma$ by analogy with the same type of compounds given above.

### 3.2. X-Ray Studies

Buerger precession photographs were made along the $x$, $y$, and $z$ directions. Careful examination of the photographs allows the determination of two monoclinic sublattices. They can be clearly seen on photographs with the zone axis parallel to the $y$ direction. The lattice parameters measured from the photographs are: $a = 5.259(7)$, $b = 8.53(1)$, $c = 10.25(2)$ in [Å] and $\beta = 120.42(8)^\circ$. The orientation of the reciprocal lattices relative to the crystal is given in the upper part of Figure 2. Satellite reflections near the main Bragg reflections indicate that each monoclinic structure has a modulation vector $q = 0.093(2)a^*$. The $x = (\sqrt{3} - \delta)z$ and $x = -(\sqrt{3} - \delta)z$ domain walls are perpendicular to these modulation vectors. Systematic extinction of the main Bragg reflections $00l$ with $l \neq 2n$ and $0k0$ with $k \neq 2n$ is observed. Hence the parent structure of this phase belongs to space group $P2_1/c$. The precession photographs showed that the intensity of the satellite reflections and the cell parameters
were slightly dependent on the sample size, but the magnitude of the modulation vector was quite constant for all samples.

The three types of domain wall observed can be described on the basis of the monoclinic cell chosen as being parallel to the [100], [001] and [102] planes (cf. Figure 2). Assuming that the prototype phase has mmm point group, only two types of ferroelastic domain walls are allowed by symmetry, namely \( x = 0 \) and \( z = 0 \) (monoclinic axis parallel to \( y \)),\(^{12}\) therefore the [100] and [102] walls are mechanically stressed.

### 3.3. Effect of Thermal Treatment and Grain Size on the Modulation of the Structure

For a better understanding of the influence of the crystal size, crystals of \( \gamma \)-KCP were finely ground to a grain size of less than 7 \( \mu \)m. A powder X-ray diffraction was performed on this sample. A few weak reflections were present on the pattern that could not be indexed with the monoclinic cell given above. They may be satellite reflections due to the modulation of the structure (cf. Figure 3a). The same sample was then heated several times through the phase transition and a new powder diffraction pattern was taken (cf. Figure 3b). The main differences between the two patterns are indicated on Figure 3 with small arrows under the patterns. They mainly correspond to peaks that could not be indexed. The relative intensity of them decreases after the thermal treatment, but they do not disappear completely. This may indicate that the amplitude of the modulation also decreases or that the IC phase has disappeared in a fraction of the sample. It is also noticeable that the cell parameters change slightly, the more intense peak splitting into two because of these changes.

Taking into account 38 of the main reflections of the powder pattern between 26°-78° the pattern could be indexed with the automatic indexation program DICVOL91.\(^{13}\) The cell found was monoclinic with parameters \( a = 5.317(2), b = 8.570(2), c = 10.389(3) \) in [Å] and \( \beta = 120.72(2)^\circ \). The extinction law derived indicates also \( P2_1/c \) as the space group. Based on these data a search of isotypic structures gave CsLiSO\(_4\) as a possible one. This compound has orthorhombic structure with space group Pnma at room temperature and undergoes a Phase transition at \( T_c = 202 \) K to an incommensurate (IC) phase. At \( T_c = 160 \) K it undergoes a lock-in phase transition and becomes commensurate (C) with a monoclinic cell which has almost the same volume as the cell in the normal phase.\(^{14}\)

A Rietveld refinement was made using the powder pattern given on Figure 3b and the atomic positions of the monoclinic structure of CsLiSO\(_4\) as starting positions. For the refinement the cell parameters, the positions of the atoms and the displacement parameters were varied, but to have a stable refinement it was necessary to fix the values of the displacement parameters of the oxygen atoms. Plots of measured, calculated and the difference diffraction pattern are given in Figure 4. The final atomic positions, the cell parameters and goodness-of-fit factors are given in Table I. This refinement gives us only the average structure of the modulated structure. Considering the values of the goodness-of-fit parameters, which indicate a rather acceptable refinement, we can expect the deviations from the mean positions to be relatively small. A drawing of the structure projected down along the monoclinic axis is shown in Figure 5. The structure is very similar to the one of hexagonal \( \alpha- \)}}
FIGURE 3 Powder patterns of a $\gamma$-KCoPO$_4$ powder sample with grain size of less than 7 $\mu$m, (a) before and (b) after heating through the phase transition. The main differences between the patterns are indicated by small arrows under the patterns.

KCP. The principal monoclinic and the hexagonal axis are in the same direction and have very similar lengths. The main difference between them is the orientation of the PO$_4$ and CoO$_4$ tetrahedra. These form six-membered rings of alternating PO$_4$ and CoO$_4$ tetrahedra. In the hexagonal form two types of ring are present, in one type the neighbouring tetrahedra are pointing in opposite directions along the hexagonal
FIGURE 4 Result of the Rietveld refinement of $\gamma$-KCoPO$_4$ on the powder pattern shown on Figure 3b. (dotted-line = measured pattern, full line = calculated pattern and the difference is given below).
Atomic positions and cell parameters obtained from a Rietveld refinement of $\gamma$-KCoPO$_4$ at room temperature.

Space group $P2_1/c$ ($R_p = 5.2$, $R_w = 7.46$ and $R_{agg} = 11.0$).

(*) Fixed parameter.

Cell Parameters in [Å]:

$a = 5.3052(3)$, $b = 8.5571(4)$, $c = 10.3926(6)$, $\beta = 120.833(2)^\circ$

$Z = 4$, $V_m = 405.11(4)$, $\rho_s = 3.164$ g/cm$^3$

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<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>$U_{iso}$</th>
</tr>
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<td>Co</td>
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<td>0.3199(7)</td>
<td>0.426(1)</td>
<td>0.025(3)</td>
</tr>
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<td>-0.001(1)</td>
<td>0.2997(7)</td>
<td>0.024(4)</td>
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<tr>
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<td>0.214(2)</td>
<td>0.090(2)</td>
<td>0.022(7)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.090(7)</td>
<td>0.313(2)</td>
<td>0.041(3)</td>
<td>0.040(*)</td>
</tr>
<tr>
<td>O(2)</td>
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<td>0.049(3)</td>
<td>0.133(2)</td>
<td>0.040(*)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.424(7)</td>
<td>0.292(3)</td>
<td>0.487(4)</td>
<td>0.040(*)</td>
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<tr>
<td>O(4)</td>
<td>0.545(9)</td>
<td>0.260(3)</td>
<td>0.230(5)</td>
<td>0.040(*)</td>
</tr>
</tbody>
</table>

axis (UDUDUD) and in the other type, three adjacent tetrahedra are pointing in one direction and the other three in the opposite direction (UUUDD). In the monoclinic form only this second type of six-membered rings are found (UUUDD). As concerns the K atoms they have almost the same environment in both structures.

In the monoclinic structure of CsLiSO$_4$, the SO$_4$ tetrahedra are slightly tilted around the monoclinic axis by an angle of about $14^\circ$ from their position in the orthorhombic structure, upon cooling through the IC phase down to the C phase. Thus the distortion is rather small. In the case of $\gamma$-KCP the distortion is much more pronounced as can be seen in Figure 5.

4. CONCLUSIONS

The present results show that $\gamma$-KCoPO$_4$ has at room temperature an incommensurate ferroelastic phase. The average structure of the IC phase is isotypic with the monoclinic structure of CsLiSO$_4$. The prototype phase, that we should rather call the normal (N) phase, is optically orthorhombic consistent with preceding X-ray studies. Taking into account the cell dimensions given by Engel for the orthorhombic phase and the structural similarities of $\gamma$-KCP with CsLiSO$_4$, we can expect that it is isotypic with the normal phase of CsLiSO$_4$ with space group Pnma.

The ferroelastic domains observed are due to two monoclinic sublattices with opposite sign of the strain coefficient $u_s$. Each sublattice has a modulation vector parallel to the $a^*$ reciprocal axis. Three types of ferroelastic wall are present. Only one type of wall is mechanically unstrained considering that the symmetry lowering is mmm $\rightarrow$ 2/m. The other two types of wall are perpendicular to the modulation vectors as it is normally observed in the case of lock-in phase transitions. These ferroelastic walls must bring about mechanical stress. The cell dimensions and the strain were found to be dependent on the grain size of the samples.
FIGURE 5 Projection of the structure along the monoclinic axis. The small tetrahedra correspond to PO₄ and the large ones to CoO₆. Only one layer of tetrahedra is shown, it is related to a second layer by a 2,1 symmetry operation.

In the literature examples of ferroelastic incommensurate materials are rather scarce. In general the study of these structures is difficult because the deformations of the lattices are very small and high precision and high resolution instruments are necessary to detect them. Fortunately in this case the deformation is large enough to be seen on precession photographs. It is also visible with polarized light microscopy (this was essential to the understanding of the X-ray patterns). Therefore γ-KCP is a compound which presents some advantages for further study. For example switching of ferroelastic incommensurate domains and the reasons why a true lock-in phase transition does not occur in this kind of phase. Studies with T.E.M. of the incommensurate phase and neutron diffraction of the N phase are under way which will allow a more detailed explanation of the formation of the ferroelastic domain walls in γ-KCP.

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REFERENCES