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SYNTHESIS AND MAGNETOELECTRIC PROPERTIES OF SINGLE CRYSTALS OF METASTABLE KC0PO4

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Single crystals of the metastable phase of KCoPO₄ (α -KCP) have been synthesized in a gel of tetramethoxysilane. The crystals have a hexagonal symmetry which belongs to space group P6₃ (cell parameters a = 18.206(1), c = 8.5135(8) [Å] and Z = 24). The crystals have been characterized by x-ray diffraction and by polarized light microscopy. The magnetoelectric properties of this compound have been studied at 4.4 K. No linear magnetoelectric effect has been detected and all coefficients of the tensor corresponding to the quadratic magnetoelectric effect (ME)_H have been determined at 4.4 K: $\beta_{123} = -\beta_{213} = 2.3 \ 10^{-18}$, $\beta_{113} = \beta_{223} = 7.1 \ 10^{-18}$, $\beta_{311} = \beta_{322} = 12.2 \ 10^{-18}$ and $\beta_{333} = 7.2 \ 10^{-18}$ in [s A⁻¹] (estimated error less than 5%). The absence of a linear magnetoelectric effect and the form of the tensor of the quadratic effect indicate that the magnetic symmetry of the crystal at this temperature must belong either to the antiferromagnetic magnetic point group 6' or to the paramagnetic one 61'. The pyroelectric effect was also measured confirming polar character of the structure.

Keywords: Quadratic magnetoelectric effect, KCoPO₄, pyroelectric effect, metastable phase.

1. INTRODUCTION

The compound KCoPO₄ exists in two different crystalline forms at room temperature. One of these forms, α -KCoPO₄ (α -KCP), belongs to space group P6₃, with the cell dimensions a = 18.206(1) [Å], c = 8.5135(8) [Å] and Z = 24 formular units per cell.¹ This form is obtained when crystals of KCP are grown in water solution. A crystalline powder can very easily be obtained by adding a solution of Co²⁺ to a concentrated solution of K₂HPO₄ at 70°C.^{1,2} Upon heating, α -KCoPO₄ undergoes a phase transition at 565°C to an orthorhombic structure (β -KCoPO₄)³; upon cooling, this orthorhombic structure transforms to a presumably monoclinic one, the structure of which we are still studying. This monoclinic phase is the stable form of KCoPO₄ at room temperature and which we call γ -KCoPO₄. Therefore the hexagonal structure represents a metastable phase.

As concerns the structure of α -KCoPO₄ several interesting features have to be noted. It belongs to the polar and chiral point group 6, therefore pyroelectricity, piezoelectricity, rotatory power, etc. are permitted. Furthermore, Co²⁺ being a paramagnetic ion, the possibility exists that the magnetic moments of Co order at low temperatures.¹ The two magnetic point groups 6 and 6' are possible. In case of such an ordering. Magnetic point group 6 allows a linear magnetoelectric (ME)_H effect with the coefficients $\alpha_{11} = \alpha_{22}$, $\alpha_{21} = -\alpha_{12}$ and α_{33} of the corresponding tensor being permitted. On the contrary, magnetic point group 6' does not allow a linear magnetoelectric effect. As concerns the quadratic magnetoelectric effect, 70/[418]

it is allowed in both magnetic point groups. The corresponding tensor has the same form for both of these magnetic point groups.

In the present paper we give a method for growing single crystals of α -KCoPO₄. The crystals have been characterized by X-ray diffraction and by polarized light microscopy. The magnetoelectric properties of these crystals at 4.4 K have been studied in order to obtain more information about the magnetic symmetry of these crystals at low temperature. The pyroelectric nature of the compound is also demonstrated.

2. GENERAL ASPECTS

The density of stored free enthalpy of a given crystal phase is a function dependent on the constraints of the system, temperature (T), electric field (E_i) , magnetic field (H_i) and mechanical stress (T_{ij}) :

$$g = g(T, E_i, H_i, T_{ij}),$$

the derivative of this function with respect to E_i is the polarization of the crystal. In our case, only the magnetic field applied to the crystal is changed, therefore the relevant total polarization P_i is given by the following expression:

$$P_i = P_i^0 + \alpha_{ij}H_i + \frac{1}{2}\beta_{ijk}H_jH_k + \cdots$$

where P_i^0 , is the spontaneous polarization and the second and third terms represent the linear and the quadratic magnetoelectric effect (ME)_H respectively.

In the case of a hexagonal crystal, the co-ordinates have to be defined to which the indices *i*, *j* and *k* refer. Following the recommendations of Reference 4, we have taken 1||a-axis, 3||c-axis and $2 \perp$ to the a^c plane.

The magnetic point group of the crystal determines which of the coefficients of the α_{ij} and β_{ijk} tensor are permitted. The linear magnetoelectric effect is permitted in the ferromagnetic magnetic point group 6, with the tensor coefficients mentioned before. No linear effect is permitted in the antiferromagnetic magnetic point group 6'. The tensor corresponding to the quadratic effect has the same form as the piezoelectric one, therefore it has the same form for magnetic point groups 6 and 6'. Seven coefficients are allowed and among them four are independent: $\beta_{123} = -\beta_{213}$, $\beta_{113} = \beta_{223}$, $\beta_{311} = \beta_{322}$ and β_{333} .^{5,6}

3. EXPERIMENTAL

3.1. Crystal Growth of α -KCoPO₄

In order to study the physical properties of α -KCP, the synthesis of large enough single crystals is essential. This was achieved by optimising a method already described¹ where crystals of α -KCP are grown in a gel of tetramethoxysilane (TMS).

A gel containing 5% TMS was prepared by adding 2.66 gr. of TMS to 49 ml of a solution containing 50 mg/ml of $CoCl_2 \cdot 6H_2O$ and 5mM of EDTA (ethylene-

diaminetetraacetate). The two liquids were intensively mixed with a magnetic stirrer until only a single phase was visible; 4 test tubes of 30 ml were filled with 12 ml of the resulting solution and left at room temperature until gelling was completed. Then the tubes were placed into a water bath at 70°C and 12 ml of a solution containing 4 M of K_2HPO_4 and 5mM of EDTA was added on top of the gel of each tube, taking care of not damaging the gel. The tubes were covered with a laboratory film (Parafilm®) avoiding evaporation of the solvent.

After a few days crystals of α -KCP begin to grow, seven weeks later, deep blue crystals were separated from the gel mechanically. The largest crystals had a size of $3 \times 1 \times 1$ mm³ and hexagonal shape as shown on Figure 1.



FIGURE 1 Crystals of α -KCoPO₄ obtained after a 7 weeks growth in a gel of tetramethoxysilane 5%.



FIGURE 2 a) Morphology of α -KCoPO₄ single crystals. The system of co-ordinates chosen for the description of the tensor of the magnetoelectric effect is indicated together with the orientation of the hexagonal cell relative to the crystal's natural facets. b) Cuts prepared for the (ME)_H measurements.

a)

3.2. Crystal Characterization

The crystals obtained were studied by x-ray diffraction and polarized light microscopy. Precession photographs allowed to determine the orientation of the hexagonal cell within the crystals. The morphology of the crystals and the coordinate system chosen for the description of the magnetoelectric effect tensor are shown on Figure 2a.

Three different cuts were prepared by polishing having their large surfaces parallel to the x = 0, y = 0 and z = 0 planes (c.f. Figure 2b). The three cuts were examined by polarized light microscopy and appeared to be uniaxial optically negative crystals. This is consistent with the hexagonal symmetry of the cell. The crystals often present some gel inclusions near the surface, though they have very well developed facets. The principal birefringence measured at 405, 436 and 478 nm (where the absorption is not too strong) was 0.0312, 0.0312 and 0.0315, respectively. No ferroelastic transition was detected when a x = 0 crystal cut was examined by polarized light microscopy from room temperature down to 6 K.

3.3. Measurement of the Magnetoelectric Effect $(ME)_{H}$.

The three cuts prepared for the optical characterization were also used for the magnetoelectric measurements. Gold electrodes were evaporated on the large surfaces of the crystals. The edges where polished off to ensure complete insulation of the two surfaces. The area of the electroded surfaces was measured on photographs. The contacts were realized by means of epoxy-silver paste and gold wires. A complete description of all the crystals prepared and their dimensions is given in Table I. Several y = 0 cuts were prepared with a view to finding a good quality crystal exempt from inclusions, but unfortunately this was not achieved, hence two y = 0 cuts were electroded to compare the results obtained.

The crystals were cooled down to 4.4 K in an Inox liquid helium dewar. A quasistatic method was used to detect the magnetic field induced polarization,⁷ a Keithley electrometer (model 642, special low noise) in the charge mode served to measure the charges produced on the crystal surfaces. An electromagnet with linear sweep of magnetic field H vs. time, up to 20 [KOe] was used for applying the magnetic field. The orientation of the magnetic field relative to the crystal could be rotated by 360° in a horizontal plane. The intensity of the magnetic field

TABLE I
Crystal cuts and dimensions of crystals prepared for measurements of
the magnetoelectric effect on α -KCP

Crystal	Cut	Surface [mm ²]	Thickness [µm]	Cryst. Quality
КСРХ	x = 0	1.157	92	no inclusions
КСРҮа	y = 0	0.571	95	gel inclusions
КСРУЪ	y = 0	0.852	100	gel inclusions
KCPZ	z = 0	0.547	110	no inclusions

applied was measured independently with a Hall effect Gaussmeter. The temperature of the sample holder was monitored with a calibrated carbon glass resistor. The temperature was stable within ± 0.04 K.

For all the crystals prepared, a magnetic field of 23.1 [KOe] was applied parallel to the *c*-axis during the cooling operation, in an attempt to detect a linear $(ME)_H$ effect but no linear signal was measured on any of the crystals prepared, only a quadratic effect is present and there was no significant difference of the quadratic signal between field cooling and zero field cooling experiments. Therefore, the crystals were placed in different positions relative to the plane of rotation of the magnetic field in such a way that all the coefficients of the tensor corresponding to the quadratic effect could be measured. For each crystal position the angular variation of the $(ME)_H$ signal was measured by changing the orientation of a static magnetic field by steps of 10°. The intensity of the magnetic field applied was the same for all crystals and was about 23.1 [KOe]. Measurements of the $(ME)_H$ signal with a linear variation of *H* vs. time were also made to illustrate the fact that the signal is quadratic.

3.4. Measurement of the Pyroelectric Effect

The polarization of the crystal was measured on a x = 0 cut as a function of temperature between 4.4 and 300 K. The same set-up used for the magnetoelectric measurements allowed us to determine the change of polarization of the crystal vs. temperature. The crystal was first cooled to 4.4 K and thereafter the system was left to heat up by closing the liquid helium input. Above 40 K, heating of the sample was achieved by means of an internal heating system. A complete measurement took about 12 min.

4. RESULTS AND DISCUSSION

No linear $(ME)_H$ effect was detected at 4.4 K on any of the crystals measured. Therefore, the compound either does not have a magnetic order at that temperature, in which case the magnetic Shubnikov space group is P6₃1', or it has a magnetic order with antiferro-magnetic space group P6₃'. In both cases only the quadratic magnetoelectric effect is allowed.

Former measurements of the quadratic effect and a theoretical model showed that the quadratic $(ME)_H$ effect decreases as T^{-2} with temperature.⁸⁻¹⁰ A maximum is observed at 3 K in the case of NiSO₄·6H₂O. Therefore, in order to detect a measurable quadratic effect, the measurements of this effect are preferably carried out at low temperature.

Given that the magnetic field induced polarization in α -KCP is due only to the quadratic effect, the following relations describe this effect on the different cuts prepared for a crystal belonging to magnetic point group 61' or 6':

$$P_{1} = \beta_{113}H_{1}H_{3} + \beta_{123}H_{2}H_{3},$$

$$P_{2} = \beta_{223}H_{2}H_{3} + \beta_{213}H_{1}H_{3},$$

$$P_{3} = \frac{1}{2} (\beta_{311}H_{1}^{2} + \beta_{322}H_{2}^{2} + \beta_{333}H_{3}^{2}),$$



FIGURE 3 Angular variation of the quadratic magnetoelectric $(ME)_H$ signal on α -KCoPO₄ at 4.4 K. Crystal KCPX, x = 0 cut, H = 23.1[KOe]. a) $H \perp y$ is applied and the orientation of H is changed relative to the z direction. The signal is due to the β_{113} coefficient. b) $H \perp x$ is applied and the orientation of H is changed relative to the z direction. The signal is due to the β_{113} coefficient. b) $H \perp x$ is applied and the orientation of H is changed relative.

from these relations, it is easy to see that a favourable orientation of the different cuts relative to the applied field allow the determination of all the β_{ijk} coefficients. For example, to determine β_{113} we put a x = 0 cut (crystal KCPX) with $H \perp y$ and the orientation of the field is changed in the x^2 plane. Therefore, $H_2 = 0$ and the angular variation of the induced polarization is given by:

Coefficient	Crystal	Orientation	Value [s A ⁻¹]
β ₁₁₃	КСРХ	Ĥ⊥у	7.14 10 ⁻¹⁸
β ₁₂₃	КСРХ	Ĥ⊥x	2.35 10 ⁻¹⁸
β ₂₁₃	КСРҮЬ	Ĥ⊥y	2.30 1 0 ⁻¹⁸
β ₂₂₃	КСРҮЬ	Ĥ ⊥ x	5.44 10 ⁻¹⁸
β ₂₂₃	КСРҮа	Ĥ⊥x	8.35 10 ⁻¹⁸
β ₃₁₁	KCPZ	Ĥ⊥y	12.21 10 ⁻¹⁸
β333	KCPZ	Ĥ⊥y	7.15 10 ⁻¹⁸

TABLE II Determined coefficients of the β_{ijk} tensor at 4.4 K and corresponding crystals and crystal orientations utilized

$$P_1 = \beta_{113}H_1H_3 = \beta_{113}H\sin\theta H\cos\theta = \frac{1}{2} \beta_{113}H^2\sin 2\theta,$$

where θ is the angle between **H** and the z direction, hence the signal is proportional to sin 2 θ . The measured values are shown on Figure 3a. These are fitted by the least squares method with the expression,

$$P_1 = \beta_{113} \mathbf{H}^2 \cos(\theta - \phi) \sin(\theta - \phi),$$

where ϕ is the phase of the signal that takes into account a possible misorientation of the crystal relative to the z direction of the measuring system. The numerical value of the β_{113} coefficient was obtained from this fitting. The difference between the measured values and the fitting curve is also shown. The measurement of the β_{123} coefficient was made on the same crystal, therefore the position of the crystal relative to the former position had been changed by a simple 90° rotation around the z direction, in such a way that $\mathbf{H} \perp x$. All the connections remained in the same position and the already described procedure was followed. The measured values are plotted on Figure 3b, together with the fitting curve from which β_{123} was determined and the difference between the measured values and the fitting curve. From Figures 3a and 3b we can see that the sign of the β_{113} and β_{123} coefficients is the same for the enantiomer corresponding to the crystal KCPX. The same procedure was followed for the determination of all other coefficients and the numerical values, crystals used and crystal orientations are detailed in Table II. The estimated errors are in all cases less than 5%.

On Figure 4 we give the results of the measurements on crystal KCPYb (y = 0 cut) from which the coefficients β_{213} and β_{223} were determined. It can be seen that the coefficients β_{213} and β_{223} have the same sign. For symmetry reasons the signs of these coefficients should be opposite if the KCYb crystal was the same enantiomer as crystal KCPX. Therefore crystal KCPYb must be the other enantiomer. On Figure 5 we give the results of the measurements on crystal KCPZ (z = 0 cut). The coefficients $\beta_{311} = \beta_{322}$ and β_{333} have been determined on this crystal from a



FIGURE 4 Angular variation of the quadratic magnetoelectric $(ME)_H$ signal on α -KCoPO₄ at 4.4 K. Crystal KCPYb, y = 0 cut, H = 23.1 [KOe]. a) $H \perp y$ is applied and the orientation of H is changed relative to the z direction. The signal is due to the β_{213} coefficient. b) $H \perp x$ is applied and the orientation of H is changed relative to the z direction. The signal is due to the β_{213} coefficient. b) $H \perp x$ is applied and the orientation of H is changed relative.

single measurement of the angular variation of the quadratic magnetoelectric signal. In this case, $H \perp y$ and the measured values have been fitted with the expression:

$$P_{3} = \frac{1}{2} \mathbf{H}^{2} [\beta_{311} [\cos(\theta - \phi)]^{2} + \beta_{333} [\sin(\theta - \phi)]^{2}],$$

where θ is the angle between H and the x direction. On Figure 5 we can see that the signs of β_{311} and β_{333} are opossite. This is also demonstrated on Figure 6b; the



FIGURE 5 Angular variation of the quadratic magnetoelectric $(ME)_H$ signal on α -KCoPO₄ at 4.4 K. Crystal KCPZ, z = 0 cut. A constant magnetic field of H = 23.1 [KOe] $\perp y$ is applied and the orientation of H is changed relative to the x direction. The signal is due to the β_{311} and β_{333} coefficients.

sign of the signal changes when the applied field is rotated by 90° from a position where H||x| to a position where H||z|.

The experimental results obtained for all the crystals follow very well the theoretical expressions derived for each case, as can be seen on Figures 3 to 5. This shows that the signal is mainly due to a quadratic effect. The form of the tensor corresponds to magnetic classes 6' or 61'. In some cases (see Figures 3a, 4a and 5), the difference between the measured values and the fitted curve is proportional to sin 40 or cos 40. This modulation must be due to an intrinsic property of the crystal as no measurement artefact could give such a modulation. In one case (see Figure 3b) an anomaly is observed when the applied magnetic field is parallel to the *c*-axis of the crystal.

The variation of the magnetoelectric signal $(ME)_H$ when the applied field is changed linearly and periodically with time is shown on Figure 6. We can see that the signal is really quadratic and the sign of the signal does not depend on the sign of the magnetic field. This also shows that there is no linear magnetoelectric effect superposed.

Among all the coefficients determined only four are independent. For symmetry reasons $\beta_{123} = -\beta_{213}$, this has been verified experimentally as can be seen in Table II. It is important to stress that the two coefficients were determined on two different crystal cuts, KCPX and KCPYb. The difference between these two coefficients is about 2% only. Likewise, for symmetry reasons, $\beta_{113} = \beta_{223}$. The experimentally determined values, also on crystals KCPX and KCPYb, corresponding to these coefficients are significantly different (about 24%). The β_{223} coefficient has been determined twice on two different crystals (KCPYa and KCPYb), the values ob-

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FIGURE 6 Quadratic magnetoelectric signal on α -KCoPO₄ crystals. a) Crystal KCPX (x = 0 cut). A magnetic field is applied: $H \perp y$ and at 45° from the z direction. The intensity of the magnetic field applied is varied linearly and periodically with an amplitude of 20.5 [KOe] as shown below. Note that the signal does not depend on the sign of the magnetic field as expected. The signal is due to the β_{113} coefficient. b) Crystal KCPZ (z = 0 cut). As above a variable magnetic field with an amplitude of 11.25 [KOe] is applied first: $H \parallel x$ (Pos 0°) and the $H \parallel z$ (Pos. 90°), by a 90° rotation of the magnetic field around the y direction. The signal is due to the β_{311} and β_{333} coefficients. Note that the signs of these coefficients are opposite.



FIGURE 7 Change of Polarization vs. Temperature measured on a z = 0 crystal cut of α -KCoPO₄.

tained are also different. We have not been able to explain this difference but it may be due to the gel inclusions that are present in these crystals and which were unfortunately unavoidable. The more reliable numerical values are therefore those determined on crystals KCPX and KCPZ.

The crystal KCPZ was used for a measurement of the pyroelectric effect on α -KCP. A total change of polarization of $\Delta P = 8 \ 10^{-4} [\text{C m}^{-2}]$ was measured between 4.4 K and 300 K. The polarization changes steadily in this temperature range, only an anomaly is seen at 6 K where there is a change of sign of $\partial P/\partial T$ (see Figure 7). This measurement confirms that α -KCP belongs to a polar point group. The absence of any discontinuity or anomaly of the curve obtained shows that there is no phase transition in this temperature range as was also concluded from the optical study.

5. CONCLUSION

All the seven coefficients for the tensor corresponding to the quadratic magnetoelectric effect have been determined at 4.4 K on single crystals of the metastable phase of KCoPO₄(α -KCP). The relative sign of some of the coefficients was also determined. The magnitude of these coefficients is about 1/10 of the values determined for the quadratic effect of cobalt perovskite Pb₂CoWO₆¹¹ and it is about 3 times larger than the values found for Co-I Boracite.¹²

The fact that no linear effect was detected implies that there is no magnetic ordering of the Co magnetic moments corresponding to magnetic point group 6.

However there still remains the possibility of a magnetic ordering belonging to magnetic point group 6'. According to K. Aizu¹³ this should be an antiferromagnetic structure and if we examine the structure closely, the cobalt atoms are located at the corners of equilateral triangles, therefore the antiferromagnetic structure should be frustrated. Another possibility is that the crystal remains paramagnetic, possibly also due to frustration. Nevertheless, the anomaly seen at 6 K on the P vs. T measurement may indicate a magnetic transition as observed on KNiPO₄ crystals.¹⁴

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