Complex ferroelastic domain patterns in Pb$_2$CoWO$_6$ (=PCW) observed with the polarized-light microscope

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Abstract

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Reference

COMPLEX FERROELASTIC DOMAIN PATTERNS IN Pb₂CoWO₆ (=PCW)
OBSERVED WITH THE POLARIZED-LIGHT MICROSCOPE

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Abstract

Polarized-light microscopy of Pb₂CoWO₆ in transmitted light reveals complex domain patterns in the transition range from the monoclinic/incommensurate phase to the orthorhombic one. As long as both phases coexist, a domain state with unique compensation properties appears.

1. Introduction

Thin plates of Pb₂CoWO₆ (=PCW)-crystals are investigated with a polarized-light microscope 'LEITZ Orthoplan' in transmitted light, in conjunction with a 'LINKAM' cooling stage. The great number of possible domain states (e.g. 12 for mcl. ferroelastic), the connected different extinction positions and the change of Newton interference colours due to absorption render the interpretation of the domain patterns very difficult. Moreover, owing to a polishing stress effect, combined with unfavourable ratios of lattice parameters, not all principal sections of the mcl. and orthorhombic indicatrix can be obtained.

2. Experimental methods at the phase transitions

Cube shaped PCW-crystals of about 0.5 to 2 mm size are sawn parallel {100} and {110} with respect to their cubic perovskite mother phase. They are polished on both sides, with an average thickness between 20 and 40 µm. Special interest is focussed on the phase transitions at about 300 K (+27°C) and 235 K (-38°C). At 300 K the cubic high temperature phase I transforms to an incommensurate

Figure 1: Path difference of the coexisting monoclinic incommensurate and orthorhombic domains (phase II and III) of PCW for different wavelengths upon cooling.
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The incommensurate phase transforms at 235 K to an orthorhombic low temperature phase III, but in some samples this phase transition was observed to be shifted to lower temperatures. If the principal vibration directions of phase II and III in the $b_{\|}/c_{\|}$- or $b_{m}/c_{m}$-plane are oriented parallel to the diagonals of the polarized-light microscope reference system, the path difference of both phases is measured simultaneously with a 'BEREK'-tilting compensator for different wavelengths of the visible range. A 'LINKAM' cooling stage enables optical measurements at the phase transition II $\leftrightarrow$ III under accurate temperature ($\pm 1$ deg.) control. At slow cooling rates ($< 5$ deg./min.) phase II and III coexist in the temperature range 220 to 190K, where the path difference of phase II is significantly higher than that of phase III (fig.1).

3.1 Domain patterns observed on (100)$_{c}$-cuts

The observation and interpretation of the domain patterns have been restricted in the present paragraph i) to the principal cut of the orthorhombic indicatrix, having 45° extinction with respect to the [100]$_{c}$-directions (lattice parameters $a_{c} = a_{0}$ perpendicular to the cut) and ii) to the transition between domain states maintaining 45° extinction in both phases. Such a transition between phases keeping $a_{c}$ parallel to $a_{0}$, was also observed by electron-microscopy. Under this condition the orientation of the orthorhombic principal vibration directions in differently oriented domains of the same phase can be explained by a twinning model (fig.2). The twin individuals (1) to (4) of Figure 4 correspond to the twinning model of ferroelastic domains in the superconducting crystals of YBa$_2$Cu$_3$O$_{7-\delta}$. Extinctions parallel to [110]$_{c}$ and [100]$_{c}$-directions are essential for this model and agree with the experiment on {100}$_{c}$-sections. Following successively the reorientation of the cubic mother cell by twinning, a characteristic pattern of rhomb shaped fields spreads out over the {100}$_{c}$-face (fig.3). The orthorhombic deformation finally leads to twin boundaries of mutually perpendicular orientation (fig.4). The

![Figure 2: Twinning model of PCW on {100}$_{c}$](image-url)
remaining shear angle of about 4 minutes, which is calculated from the lattice parameters\(^3\) is too small to be measurable with the polarized-light microscope.

3.2 Domain patterns observed on \{110\}_c\)-cuts

In the \(\alpha\)-rhombic phase two kinds of domain with parallel extinction (indicatrix principal cuts) and 4 kinds of domain with only one kind of oblique extinction (indicatrix general cuts) can appear. However, in the monoclinic phase three kinds of oblique extinction angles are permitted on \(\{110\}_c\), where one of them corresponds to a domain with the \(b_m\)-axis \(\perp\) to \(\{110\}_c\) (indicatrix principal-cut). Experimentally three kinds of oblique extinction angle have in fact been observed at 16°, 25° and 33° for the mcl.inc. phase and at a single angle of 24°, for the orthorhombic phase.

Unfortunately it was not possible to identify among the three angles of oblique extinction the one corresponding to the mcl. principal section (\(b_m\perp\{110\}_c\)). The orientation of the PCW-domains depends on twinning due to the structural phase transition\(^5\), but it will also be influenced by a deformation of induced shear stress (mechanical twinning). This type of deforma-
tion can be described by an ellipsoid\(^6\)(fig.4), resulting from a sphere in an initially stress free crystal phase. In the case of PCW-plates, primary homogeneously extinguishing orthorhombic domains are interspersed by shear stress induced lamellar domains with different shear angles\(^6\) and twin-orientations. The shear vector \(\mathbf{s}\) advances parallel to the first circular section \((K1)\text{\textsuperscript{6}}\text{ident.}[0 1 \overline{1}])_{or} \equiv [001]_{c}\). The second circular section \((K2)\) coincides with the \([011]_{or} \equiv [010]_{c}\) directions. The orthogonal main axes \(\eta_1\) and \(\eta_3\) of the deformation ellipsoid follow nearly the \([011]_{c}\) directions. In Figure 6 the correspondence between the orthorhombic b- and c-axes of the twin-individuals "or" and "or*" and the shear vector \(\mathbf{s}\) has been represented.

On the microscopic structural level the situation may be far more complicated than described by the macroscopic homogeneous deformation. The domains may undergo multiple forward and backward shearing with oppositely aligned shear vectors as shown schematically in Figure 7.

Figure 5: The shear ellipsoid of PCW. The orthorhombic shear angle \(\varphi_0\) is strongly exaggerated.

Figure 6: Correspondence between the orthorhombic b- and c-parameters of the twin-individuals "or", "or*" and the shear vector \(\mathbf{s}\)
4. Domain states of short durability as observed on [100]c-cuts

Only visible close to the phase transition from mcl.inc. to o.-rhombic symmetry (i.e. only upon cooling), where both phases are coexisting, a "transition state" of short durability appears (fig.8). This unusual state attracts attention by compensation colours, which are different from those of the mcl.inc. and o.-rhombic phase. On crystal plates with homogeneous thickness three pairs of domain with same extinction directions coexist at equal temperature, each pair with domains having orthogonally oriented indicatrix sections. All pairs are well distinguishable due to different phase shifts. The phase boundary between the "transition state" and phase III is characterized by a saw-toothed front being dragged along the [011]c directions. Below the transition temperature, relics of mcl.inc. domains often remain frozen in, sometimes down to liquid He-temperature.

Figure 7: Scheme of multiple shearing with oppositely aligned shear vectors

Figure 8: Objective 20x/N.A.=0.40, crossed polars. T=231 K, left: eyepiece 10x, right: eyepiece 16x, photographically enlarged. Elongated domains of the "transition state" pointing along [100]c between coexisting mcl. inc. (phase II) and o.-rhombic domains (phase III). Remark: when replacing the eyepieces from 10x (left) to 16x (right), the shape of the "transition state" had already slightly changed.
5. Conclusions

Some of the present results merit further study: i) The nature of the observed "transition state" at the mcl. to o-rhombic transition requires clarification. Being separated by phase boundaries both from phase II and phase III and characterized by sharp extinction and a distinct birefringence value (situated between that of phases II and III), it has in principle the characteristics of a new phase. ii) The path difference, measured on phase II at several wavelengths and upon cooling, shows a kink at about 175 K, reminding of a 2nd order transition. Confirmation of reproducibility and correlation with X-ray data would be desirable.

For guidance of the experimentalist it is worth mentioning that repeated cycling of PCW-crystals through the cubic/monoclinic transition often leads to cracking. Since even spontaneous variations of room temperature may be responsible for that, storage of wafers and of as-grown crystals in a refrigerator is strongly recommended. In spite of a strong volume change occurring at the mcl.-inc./o-rhombic transition, cycling between these two phases is less dangerous.

Acknowledgements

The authors feel obliged to J.-P. Rivera for discussions on optical measurements and are grateful to E. Burkhardt and R. Cros for technical assistance, and to the Swiss National Science Foundation for support.

6. References

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