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UNIAXIAL STRESS-INDUCED PHASE TRANSITION, PIEZO-OPTICAL EFFECT AND OPTICAL DOMAIN STUDIES IN Cr-CI BORACITE

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Uniaxial stress was applied to the single crystals of $Cr_3B_7O_{13}Cl$ [Cr-Cl] boracite along $\langle 110 \rangle_{cub}$ directions by means of a special rod constructed in our laboratory and adapted to low temperature polarized light microscopy. Evidence for a stress-induced first-order phase transition from the cubic $\overline{4}3m$ or the tetragonal $\overline{4}2m$ phase to the orthorhombic mm2 phase has been obtained by *in situ* observations of the ferroelastic/ferroelectric domains. The domain structure and the birefringence have been analyzed and correlated to the crystal symmetry of the initial and the induced phase. For a mechanical stress below the threshold strength, the piezo-optical effect has been disclosed, leading to a linear and reversible birefringence, e.g. $\Delta n = 4.8 \times 10^{-4}$ under a stress of about 22×10^7 N/m² (22.4×10^2 kg/cm²) at 285 K. The piezo-optical coefficient π_{44} in the $\overline{4}3m$ and $\overline{4}2m$ phases was found to be 1.5×10^{-12} m²/N (T = 264 K). In the spontaneous mm2 phase the application of a uniaxial stress gave rise to ferroelastic "poling" (mechanical detwinning) of the orthorhombic lamellar polydomain state, hence to ferroelectric poling due to fully ferroelastic/fully ferroelectric coupling of the domains.

Keywords: Boracite Cr₃B₇O₁₃Cl, induced phase transition, piezo-optical effect, ferroelastic/ ferroelectric domains, birefringence.

1. INTRODUCTION

Chromium-chlorine boracite $Cr_3B_7O_{13}Cl$ (Cr-Cl) is an unusual member of the crystal family of boracites which includes more than 20 isomorphous compounds with the general formula $M_3B_7O_{13}X$ [M-X], where M stands for divalent metal ions (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd) and X for halogen ions (F, Cl, Br or I). It is known to undergo the following sequence of structural phase transitions¹:

$$\overline{4}3m \xleftarrow{T_1 = 264 \text{ K}} \overline{4}2m \xleftarrow{T_2 = 160 \text{ K}} mm2,$$

where the tetragonal non-polar $\overline{4}2m$ phase (space group $P\overline{4}2_1c^2$) is the first and so far unique one in the boracite family. Interesting properties related to the presence of the $\overline{4}2m$ phase of Cr-Cl were disclosed recently³⁻⁵: i) in the temperature interval of the tetragonal phase (160 K < T < 264 K), application of an electric field E// $\langle 001 \rangle_{cub} (E > 8 \times 10^4 \text{ V/cm})$ can induce a polar mm2 phase, giving rise to double hysteresis loops of "antiferroelectric" behaviour; ii) during the first order transition from the cubic to the tetragonal phase at $T_1 = 264$ K, domains of the mm2 phase were found to be induced transiently by internal stress generated at the mechanically non-matching $\overline{4}3m/\overline{4}2m$ phase boundary. At low temperatures, anomalies of the spontaneous polarization and birefringence were also reported and ascribed to magnetic ordering.⁵ The recent studies of the linear and quadratic magnetoelectric effects allowed to suggest the nature of the magnetic ordering and the symmetry of the magnetic phase, i.e., antiferromagnetic mm2 for T < 14 K and weakly ferromagnetic m'm'2 for T < 10 K.^{6.7}

In thermodynamical terms, the astonishing and ephemeral presence of the polar mm2 phase at the $\overline{43m}/\overline{42m}$ phase boundary, i.e., the coexistence of the $\overline{43m}$, $\overline{42m}$ and mm2 phase,³ can be understood only by admitting the presence of internal stress during the first-order $\overline{43m} \leftrightarrow \overline{42m}$ phase transition, which introduces an additional external constraint variable and hereby increases the number of degrees of freedom by one. From the symmetry point of view both the cubic $\overline{43m}$ and the tetragonal $\overline{42m}$ phase can be transformed to the ferroelectric/ferroelastic mm2 phase by stress components acting along $\langle 110 \rangle_{cub}$ -directions. Therefore the purpose of this work was to investigate, by means of simultaneous optical studies of the ferroelastic/ferroelastic/ferroelastic, by means of subsequently induced, in order to prove the thermodynamic and symmetry considerations.

2. EXPERIMENTAL PROCEDURE

2.1 Crystal Orientation

Single crystals of Cr-Cl boracite were grown by the chemical vapour transport technique.^{8,9} Rectangular platelets were cut with the largest facets parallel to $(001)_{cub}$ and the border facets parallel to $(110)_{cub}$, and finely polished on all facets. The crystallographic orientations of the $(001)_{cub}/(110)_{cub}$ platelets are shown in Figure 1 with typical dimensions of $l = 660 \ \mu m$, $w = 200 \ \mu m$, $t = 110 \ \mu m$. Such an orientation permitted to apply a uniaxial stress along $\langle 110 \rangle_{cub}$ and to make simultaneous optical observation of domains and measurements of birefringence along $\langle 001 \rangle_{cub}$, i.e. perpendicular to the stress direction.

2.2 Low Temperature Uniaxial Stress Application Device

Stress was applied by means of a Low Temperature Uniaxial Stress Application Device, constructed in our laboratory on the basis of the experience gained with



FIGURE 1 Crystallographic orientation of the rectangular $(001)_{cub}/(110)_{cub}$ platelets of Cr-Cl boracite used for stress application experiments.

a previously built microscope hot-stage equipped with a micro-anvil, permitting among other things the study of ferroelastic detwinning of the superconductor $YBa_2Cu_3O_{7-\delta}$.¹⁰ The detailed technical description of these two systems constitutes the subject of a forthcoming publication.¹¹

Figure 2 gives a schematic representation of the low temperature system and setup allowing stress-application, optical observation and measurements between 4-300 K of ferroelectric/ferroelastic single crystals. The device is composed of the following parts: 1) A pressure-anvil, consisting of two ceramic guide rails equipped with sapphire jaws (i) and placed in a metallic case. Openings in the case allow optical observation and measurements in transmission and in reflection of the sample (h) situated on a quartz glass (o) and between two sapphire jaws. 2) A hollow main rod (f) connecting the pressure anvil-system to the load cell case (a). A screw (c), twisted in this case, provides a uniaxial stress to the crystal (h) through the load cell (b) and the transmitting rod (g). The maximum applied force is limited to about 1000 grams* (9.8 N).

The temperature was measured by means of a carbon-glass resistor (m), fixed near to the sample on the pressure anvil case. The load cell case is placed outside the cryostat in order to keep it at room temperature. The electric input/output signals of the load-cell are transmitted by an amphenol connector (d). The device is mounted on a special optical He-flow cryostat (e) adapted to a polarized light microscope. The crystal samples were placed between sapphire micro-jaws, with the stress being applied along $\langle 110 \rangle_{cub}$ -directions, as shown in Figure 3.

3. PIEZO-OPTICAL EFFECT

Application of a stress to crystals can in general give rise to a slight, thermodynamically reversible distortion of the crystal lattice and thereby to an anisotropic deformation of the optical indicatrix, leading to a small induced birefringence. Similarly to the electro-optical effect, the change of the refractive index caused by the applied stress is called photoelastic effect or piezo-optical effect. The small change of refractive index can more precisely be specified by giving the small changes in the relative dielectric impermeability tensor B_{ij} (at optical frequencies) whose components form the coefficients of the optical indicatrix (an ellipsoid),

$$\Delta B_{ii} = \pi_{iikl} \sigma_{kl} \ (i, j, k, l = 1, 2, 3), \tag{1}$$

where σ_{kl} is the applied stress and π_{ijkl} is the fourth-rank tensor of the linear piezooptical effect.¹² By means of conventional matrix notation, Equation (1) can be written as

$$\Delta B_{\mu} = \pi_{\mu\nu}\sigma_{\nu} (\mu, \nu = 1, 2, 3, 4, 5, 6). \tag{2}$$

The number of independent coefficients $\pi_{\mu\nu}$ depends on the symmetry of the crystal (cf. Table 15 of Reference 12). In the case of the cubic $\overline{43m}$ phase of Cr-Cl boracite, changes in the refractive index can be expressed, to the 1st-order approximation, as

$$\Delta n_{\mu} = -(1/2)(n_{o})^{3} \Delta B_{\mu}, \qquad (3)$$



FIGURE 2 Schematic representation of the Low Temperature Uniaxial Stress Application Device: (a) Load cell case; (b) Load cell (10 N); (c) Screw for stress transmission; (d) Input/output connections; (e) He-flow cryostat; (f) Main rod; (g) Pressure transmitting rod; (h) Crystal sample; (i) Sapphire jaws; (k) Guide rail, mobile; (l) Guide rail, fixed; (m) Carbon-glass resistor; (n) Windows; (o) Quartz glass; (p) Polarized light microscope; (q) Light source.



FIGURE 3 Photograph showing the orientation of stress and that of the crystal between the sapphire jaws. (See Color Plate V).

where the refractive index n_o at zero stress, if not easily measurable, can be calculated by means of the Gladstone-Dale relationship.¹³ According to the direction of uniaxial stress and that of observation, it is possible to calculate the coefficients $\pi_{\mu\nu}$ by measuring the birefringence produced by the piezo-optical effect. By means of a transformation of cubic axes, the birefringence $\Delta n = n_{\parallel} - n_{\perp}(n_{\parallel}, n_{\perp})$ being the index parallel and perpendicular to stress) induced by a stress applied along $\langle 110 \rangle_{cub}$ and observed along $\langle 001 \rangle_{cub}$, i.e. perpendicular to the stress direction, is given by

$$\Delta n = n_{\parallel} - n_{\perp} = -(1/4)(n_o)^3 \pi_{44} \sigma_{(110)}, \qquad (4)$$

where π_{44} is one of the three independent piezo-optical coefficients of the $\overline{43m}$ phase. The symmetry of the cubic crystal will therefore degenerate under stress to

orthorhombic mm2 with two of the axes of the optical indicatrix parallel to $\langle 110 \rangle_{cub}$ -directions.

The piezo-optical effect was actually observed in the cubic $\overline{4}3m$ and the tetragonal 42m phase of Cr-Cl boracite. Figure 4 shows the appearance of optical birefringence induced in the $\overline{4}3m$ phase by mechanical stress up to $22 \times 10^7 \text{ N/m}^2$. The extinction directions are parallel to $(110)_{cub}$, indicating well a symmetry lowering from cubic to orthorhombic. However, this orthorhombic symmetry due to piezo-optical effect remains reversible with stress and must be distinguished from the mm2 phase induced in the 42m phase by stress giving rise to a first-order phase transition (see later). The fact that only the top part of the crystal became birefringent was simply due to a not-completely close contact between the sapphire jaws and the crystal surfaces, because of a slight lack of parallelism of the larger (110)_{cub} border facets. The bottom part of the crystal will serve as an (unexpected) reference place in which the phase transitions take place at zero stress (see later). The applied stress was calculated according to the effective area of contact. A birefringence of $\Delta n =$ $n_{\parallel} - n_{\perp} = -4.8 \times 10^{-4}$ was obtained by the application of a stress of 22×10^{7} N/m². Δn changed weakly with temperature between 265 and 285 K. Figure 5 shows the variation of the induced birefringence versus the applied stress in the cubic



FIGURE 4 Photographs (a, b) and schematics (a', b') showing the piezo-optical effect in the cubic $\overline{43m}$ phase (285 K): (a, a') Isotropy at zero-stress; (b, b') Piezo-optical birefringence $(n_{\parallel} - n_{\perp})$ with the reversible (mm2) symmetry. The bottom part of crystal, free from stress, remains isotropic. (See Color Plate VI).



FIGURE 5 Linear and reversible variation of the induced birefringence due to the piezo-optical effect as a function of applied stress.

phase at 285 K, which remains linear and reversible. According to Equation (4), the piezo-optical coefficient π_{44} is found to be $1.5 \times 10^{-12} \text{ m}^2/\text{N}$ in the $\overline{43}$ m phase and to be nearly temperature-independent ($\lambda = 542 \text{ nm}$, $n_o = 1.79$). This value presents the same order of magnitude as those previously measured for the coefficients $\pi_{\mu\nu}$ of some other cubic crystals (see e.g. Table 17 in Reference 12). The piezo-optical effect in the tetragonal phase is discussed hereafter.

4. UNIAXIAL STRESS-INDUCED PHASE TRANSITION

The sequence of the stress-induced $\overline{4}2m \rightarrow mm2$ phase transition is shown in Figure 6. In the tetragonal $\overline{4}2m$ phase, application of a small uniaxial stress (about 5 \times 10^7 N/m^2) along $\langle 110 \rangle_{\text{cub}}$ gave rise at first to a ferroelastic detwinning of the domains. The isotropic tetragonal domain with optical axis perpendicular to the observed (001)_{cub} plane was favoured at the expense of the ones with the optical axis lying in the plane because of the lattice parameters $a_{tet.} < c_{tet.}^2$. The vertical (110)_{cub}-type walls were eliminated and the inclined $(110)_{cub}$ walls move through the crystal to the bottom. The piezo-optical birefringence $(n_{\parallel} - n_{\perp})$ appeared thereafter on this domain with extinction directions along $(110)_{cub}$ (Figure 6a, b), giving rise to a coefficient $\pi_{44} = 1.5 \times 10^{-12} \text{ m}^2/\text{N}$ (T $\leq 264 \text{ K}$). When the applied stress was higher than 12×10^7 N/m², domains of the mm2 phase were found to be induced in some regions of the crystal, which were characterized by the extinction directions $(n_{\rm y} - n_{\rm a})$ oriented parallel to $\langle 110 \rangle_{\rm cub}$, i.e. parallel to the orthorhombic axes, instead of $(100)_{cub}$ in the tetragonal $\overline{4}2m$ phase (Figure 6c). The orientation of the birefringence due to the piezo-optical effect was rotated by 90° in the induced mm2 phase. An abrupt increase of birefringence was observed, from $\Delta n = n_{\parallel} - n_{\perp} =$ -3×10^{-4} for the piezo-optical birefringence or $\Delta n = n_E - n_O = -3.6 \times 10^{-4}$ for the principal birefringence of the $\overline{4}2m$ phase, to $\Delta n = 6 \times 10^{-3}$ for the induced



FIGURE 6 Sequence of the stress-induced $\overline{4}2m \rightarrow mm2$ phase transition: (a, a') Tetragonal phase with three orientations of domain states at zero-stress; (b, b') Ferroelastic detwinning of the $\overline{4}2m$ domains under stress ($<12 \times 10^7 \text{ N/m}^2$) with movement of the (110)_{cub}-walls, leading to the isotropic domain and then to the birefringent state (here in extinction position) due to the piezo-optical effect; (c, c') Appearance of the stress-induced mm2 phase (with birefringence $n_{\gamma} - n_{\alpha}$) due to a symmetry breaking. (See Color Plate VII).

phase ($\lambda = 542$ nm). Figure 7 gives the dependence of the induced birefringence upon the applied stress, where the discontinuous jump of birefringence indicates a breaking of the crystal symmetry, leading to an induced mm2 phase. The orientation of the optical indicatrix and the value of birefringence are well consistent with the properties of the ferroic species $\overline{43m1'Fmm21'}$, confirming the symmetry of the induced phase.^{3,5} The slight decrease of the birefringence with increasing stress in the mm2 phase is due to the presence of the piezo-optical birefringence $(n_{\parallel} - n_{\perp})$ which partially compensated the birefringence $(n_{\gamma} - n_{\alpha})$ of the induced phase (see Section 6 and Figure 9).

The cell parameters of the (spontaneous) mm2 phase of Cr-Cl are a = 8.5647(2)Å, b = 8.6125(2) Å and c = 12.1453(3).¹⁴ Since the optical character of the mm2 phase in Cr-Cl shows the A-type indicatrix with $n_{\beta}/(\langle 001 \rangle_{cub} (c-axis)^5$ and a compressing stress usually induces such domains having the shortest orthorhombic axis parallel to the stress direction ($\langle 110 \rangle_{cub}$), it is possible to correlate the indicatrix axes to the crystallographic ones, namely, n_{γ} parallel to a and n_{α} parallel to b, as indicated in Figure 6c'. According to the polar properties of the mm2 phase, the



FIGURE 7 Variation of the stress-induced piezo-optical birefringence $(n_{\parallel} - n_{\perp})$ in the range of $\overline{4}2m$ phase at zero stress and superposition of piezo-optical $(n_{\parallel} - n_{\perp})$ and structural $(n_{\gamma} - n_{\alpha})$ birefringence of the induced mm2. The discontinuous jump indicates a first-order phase transition.

applied stress necessarily induces simultaneously a polarization along the *c*-axis, as was detected in the case of the internal stress-induced phase transition.³

5. IDENTITY OF THE INDUCED AND SPONTANEOUS ORTHORHOMBIC PHASE

The induced mm2 phase and its orientation of $(n_{\gamma} - n_{\alpha})$ can be maintained upon further cooling under stress through the temperature of the spontaneous $\overline{4}2m \rightarrow$ mm2 phase transition at $T_2 = 160$ K, as shown in Figure 8. Below T_2 , domains of the spontaneous mm2 phase developed in the bottom part of crystal, which was free from stress. They appeared as stacks of dense lamellae, with P_s lying in the plane of the plate and perpendicular to the platelet with (100)_{cub}-type walls (Figure 8b; see also Figure 11 and Section 7). Once having been induced by stress, the domain orientation $(n_{\gamma} - n_{\alpha})$ remained stable in the whole temperature range of the mm2 phase. No elastic back-switching was observable when relieving the applied stress totally. In the temperature range of $\overline{42m}$ phase, the induced mm2 phase was found to subsist in the metastable state in some areas of the crystal after removal of stress, probably due to inhomogeneous internal stress. This permitted the measurement of the birefringence $(n_{\gamma} - n_{\alpha})$ at zero stress above T_2 (Figure 9, curve (b)). The temperature dependence of the birefringence under a stress of 22×10^7 N/m^2 is given by curve (a). The orientation and birefringence of the induced domain show a continuous variation through T_2 , indicating the identity of the induced and



FIGURE 8 Transformation of the domain structure from the partially induced mm2 phase (in the presence of the $\overline{4}2m$ phase) (a, a') to the spontaneous mm2 phase (b, b') upon cooling through $T_2 = 160$ K, with the induced $(n_{\gamma} - n_{\alpha})$ domain kept on and the development of the mm2 domains with other orientations. (See Color Plate VIII).

spontaneous mm2 phase. The value and variation of the birefringence in the mm2 phase agree well with those measured previously on single domains obtained after an electric field poling. The broad maximum of Δn near 30 K due to a precursor effect of magnetic ordering,⁵ was also reproduced.

The difference of the birefringence between curve (b) (at zero stress) and curve (a) (under stress) in Figure 9 results from the piezo-optical effect in the (induced or spontaneous) mm2 phase, which gives rise to a birefringence $(n_{\parallel} - n_{\perp})$ with sign opposite to that of $(n_{\gamma} - n_{\alpha})$. Therefore the birefringence (a) measured under stress corresponds in fact to the superposition of these two birefringences, i.e. $(n_{\gamma} - n_{\alpha}) + (n_{\parallel} - n_{\perp})$. It decreases with increasing stress strength (see also Figure 7). This decrease was found to be 4.5×10^{-4} under a stress of 22×10^7 N/m² and nearly temperature independent. Thus the piezo-optical birefringence of the mm2 phase presents the same orientation and value as that of the cubic and tetragonal phase. The related piezo-optical coefficient π_{44} also has the same value in the mm2 phase. Since the stress acts along the longest axis of the optical indicatrix (n_{γ}) , it appears to be effective in decreasing the elongation of the indicatrix, leading to a weaker anisotropy on the principal cross section. However, the elastic deformation of the crystal lattice rises with increasing stress applied along the short *a*-axis,



FIGURE 9 Temperature dependence of the birefringence $(n_{\gamma} - n_{\alpha})$ of the stress-induced $(T > T_2 = 160 \text{ K})$ or stress-oriented $(T < T_2)$ mm2 domain measured under stress (a) or after removal of stress (b). T_1 and T_2 indicate the zero-stress transition temperatures between $\overline{43}$ m, $\overline{42}$ m and mm2 phase. Data points of the curve (b) above T_2 are due to metastability of the induced phase in some areas of the sample.

once this domain state is induced. Therefore in the presence of the piezo-optical effect, the deformation of the optical indicatrix under the action of stress along the a-axis is opposite to that of the crystal lattice of the mm2 phase.

6. RELEASE OF THE INDUCED mm2 PHASE

Figure 10 gives the evolution of the stress-induced mm2 domain structure upon heating under stress. When passing through the tetragonal \rightarrow cubic phase transition temperature ($T_1 = 264$ K), domain walls linking the induced mm2 phase and the other orientation states began to move. On the bottom part of the crystal, free from stress, the $\overline{4}2m \rightarrow \overline{4}3m$ transition took place normally at T_1 , as was monitored by the disappearance of the $\overline{4}2m$ domains and appearance of the isotropic domain. During this phase transition, at the interface of these two phases, small domains of crescent form were observed with extinction parallel to $\langle 110 \rangle_{cub}$ -directions, corresponding to the appearance of the mm2 phase, which was induced here by the internal stress generated at the mechanically non-matching $\overline{4}2m/\overline{4}3m$ phase boundary. Therefore in Figure 10(b, b') there is coexistence of four phases: the cubic $\overline{4}3m$, the tetragonal $\overline{4}2m$, the uniaxial stress-induced mm2 and the internal stressinduced mm2 phase, but these two orthorhombic phases are not in equilibrium.





FIGURE 10 Evolution of domain structure upon heating under stress $(22 \times 10^7 \text{ N/m}^2)$ through the $\overline{42m} \rightarrow \overline{43m}$ phase transition temperature $T_1 = 264 \text{ K}$: (a, a') Uniaxial stress-induced mm2 phase $(n_{\gamma} - n_{\alpha})$ in the $\overline{42m}$ phase with piezo-optical birefringence $(n_{\parallel} - n_{\perp})$; (b, b') Ephemeral appearance of the internal stress-induced mm2 phase (crescent form) at the $42m/\overline{43m}$ phase boundary during the stress-free $\overline{42m} \rightarrow \overline{43m}$ transition at T_1 ; (c, c') mm2 phase maintained by stress above T_1 ; (d, d') Sharp release of the induced mm2 phase at $T'_1 = 275 \text{ K}$, leading to piezo-optical birefringence $(n_{\parallel} - n_{\perp})$ for the cubic phase. (See Color Plate IX).

As previously observed, the internal stress-induced phase appeared transiently and remained attached to the $\overline{43m/42m}$ phase boundary. It vanished above $T_1 = 264$ K as soon as the crystal transforms from one phase to the other.

The uniaxial stress induced mm2 phase can, however, be maintained in the temperature range of the (zero-stress) cubic phase above T_1 , because both in the $\overline{4}2m$ phase and the $\overline{4}3m$ phase the application of a stress along $\langle 110 \rangle_{cub}$ results in the same mm2 symmetry. This mm2 phase released only at $T'_1 = 275$ K under a stress of 22×10^7 N/m². The variation of birefringence (Figure 9) of the induced mm2 phase (above T_2) showed a continuous decrease up to $T'_1 = 275$ K, where a sharp fall of Δn was detected due to the abrupt disappearance of the induced mm2 phase. Above T'_1 the crystal is in the "cubic" phase but shows the slight piezo-optical birefringence under stress, as discussed in Section 3. When the stress was removed, the induced mm2 phase vanished totally at the $\overline{4}2m/\overline{4}3m$ phase transition temperature T_1 . Therefore the first-order phase transition from the stress-induced

mm2 to the cubic 43m phase can be shifted to higher temperature by increasing stress strength. In comparison with the stress-free $\overline{4}2m \rightarrow \overline{4}3m$ phase transition temperature $T_1 = 264$ K, the temperature of the induced mm2 $\rightarrow \overline{4}3m$ phase transition T'_1 was increased by 11 K under a stress of 22×10^7 N/m². An average pressure dependence of the transition temperature was thus found to be $(\Delta T_{ur}/dP)_{\rm or./cub.} = 5 \times 10^{-3}$ K/atm, which is to be compared with $(\Delta T_{ur}/dP)_{\rm or./tet.}$ $= 3.36 \times 10^{-2}$ K/atm, calculated from the thermodynamical analysis for the pressure dependence of the mm2/ $\overline{4}2m$ phase transition at $T_2 = 160$ K.¹⁵

7. FERROELASTIC "POLING"

The ferroelastic "poling" of the tetragonal $\overline{4}2m$ domains was shown in Figure 6, where the application of a $\langle 110 \rangle_{cub}$ stress gave rise to the movement of the $(110)_{cub}$ domain walls and thus to the detwinning of the birefringent domains with their optical axis lying in the plane of a $(001)_{cub}$ plate. A large single domain can be obtained with the optical axis perpendicular to be plane before the appearance of the piezo-optically induced birefringence and symmetry breaking. The detwining of the orthorhombic domains is discussed hereafter.

Upon cooling at zero stress, the spontaneous mm2 phase developed below $T_2 = 160$ K, which is characterized by six domain orientations with their spontaneous polarization parallel to $\langle 100 \rangle_{cub}$ -directions, as shown in Figures 11 and 12. The domains (I, II) with extinction parallel to $\langle 110 \rangle_{cub}$ have their spontaneous polarization P_s perpendicular to the $(100)_{cub}$ plate ("up" or "down"); those with extinctions along $\langle 100 \rangle_{cub}$ directions have P_s within the plane of the crystal plate (domains III-VI). The domains with antiparallel P_s are joined by $(100)_{cub}$ -type walls.

According to the density of the stored free enthalpy function G of a ferroic crystal (see e.g. References 16 and 17), we may find terms linear and quadratic in the elastic stress σ_{ij} :

$$-G = \cdots s_{ii}\sigma_{ii} + 1/2s_{iikl}\sigma_{ii}\sigma_{kl}, \qquad (5)$$



FIGURE 11 Schematic explanation of the ferroelastic "poling" of the orthorhombic mm2 domains in Cr-Cl: the application of the stress along $(110)_{cub}$ favours one of the six domains with n_{γ} parallel to the stress direction. Domains $\mathfrak{I}-\mathfrak{G}$ correspond to the domain states (I-VI) in the text.



FIGURE 12 Observation of the domain structure during the ferroelastic "poling" of the mm2 phase: (a) Domains of the orthorhombic phase upon zero-stress cooling down to 157 K; (b) Growth of the $(n_{\gamma} - n_{\alpha})$ domain under stress detwinning ($\sigma = 11 \times 10^7 \text{ N/m}^2$, T = 157 K); (c) Domain state during the mm2 $\rightarrow \overline{4}2$ m phase transition at $T_2 = 160 \text{ K}$ ($\sigma = 22 \times 10^7 \text{ N/m}^2$); (d) T = 175 K, with the bottom part transformed into the $\overline{4}2$ m phase and the top part maintained in the mm2 phase by stress. (See Color Plate X).

where s_{ij} stands for the spontaneous deformation of the ferroic phase relative to the prototype phase and s_{ijkl} for the elastic compliance of the ferroic phase. The linear term permitted by the symmetry species $\overline{43m1'Fmm21'}$ is responsible for ferroelastic domain switching and the bilinear term, which may give rise to ferrobielastic domain switching,^{18,19} can be neglected for our purpose. Application of a stress along $\langle 110 \rangle_{cub}$ -directions (i.e. the orthorhombic axes *a* and *b*) of Cr-Cl will favour one of the six ferroelastic/ferroelectric domains due to the differences in the stored free energy change, which are proportional to the difference in the spontaneous deformation, e.g.,

$$\Delta G(\mathbf{I}, \mathbf{II}) = (s_{22} - s_{11})\sigma_{11}, \tag{6}$$

for the two domain states with their spontaneous polarization perpendicular to the plane of the plate. $(s_{22} - s_{11})$ is given by $2(b_o - a_o)/(b_o + a_o) = 0.0056$. A schematic explanation of this ferroelastic "poling" of the mm2 domains is presented in Figure 11.

Figure 12 shows the experimental observations of the ferroelastic poling procedure in the mm2 phase. With increasing stress domains with extinction parallel to $\langle 100 \rangle_{cub}$ and \mathbf{P}_s lying in the plane were found to switch into one of the domains, which is energetically favoured, with extinction $(n_{\gamma} - n_{\alpha})$ parallel to $\langle 110 \rangle_{cub}$ and \mathbf{P}_s perpendicular to the surface of the plate (Figure 12 a, b). This domain state can thereafter be maintained, upon heating under stress, above the mm2 $\rightarrow \overline{4}2m$ transition at $T_2 = 160$ K (Figure 12 c, d). The mechanically "poled" domain became therefore an induced state in the temperature range of the $\overline{4}2m$ phase. It has the same orientation as the mm2 domain induced in the tetragonal phase, with the higher index n_{γ} parallel to the direction of stress and the orthorhombic *a*-axis.

8. CONCLUSIONS

By means of optical domain studies of Cr-Cl single crystals under uniaxial stress, it has been shown that the orthorhombic mm2 phase can actually be induced from

the tetragonal 42m phase or from the cubic $\overline{43m}$ phase by stress applied along $\langle 110 \rangle_{cub}$ -directions. This provides a direct proof that the mm2 phase can be induced by spontaneous internal stress generated during the first-order $\overline{43m}/\overline{42m}$ phase transition. The phase induction from the $\overline{43m}$ phase needs higher mechanical energy than from the $\overline{42m}$ phase. The stress induced mm2 phase is totally identical to the low temperature spontaneous orthorhombic phase.

The piezo-optical effect was observed in the $\overline{43m}$ and $\overline{42m}$ phase, and also in the induced and spontaneous mm2 phase. The piezo-optical coefficient was found to be of the same order of magnitude ($10^{-12} \text{ m}^2/\text{N}$) as the values measured previously for other elasto-optical materials. Therefore the elasto-optical properties of Cr-Cl may find potential applications with a view to realizing possible acoustooptical devices.

Ferroelastic detwinning has been performed by uniaxial stress both in the tetragonal and in the orthorhombic phase, giving rise to larger single domains useful for a variety of physical characterizations (optical measurements, structure determination, etc.). In the case of the mm2 phase, the ferroelastic "poling" by mechanical stress gives rise to a simultaneous ferroelectric poling, since the ferroelastic domains are totally coupled, i.e. identical to the ferroelectric ones for the ferroic species $\overline{43}$ m1'Fmm21'.²⁰ With electrodes deposited on the (001)_{cub} surfaces, the relationship between the electric displacement (polarization) and the applied stress may be established. Therefore the "cross-term" hysteresis loop resulting from the antiparallel switching of the spontaneous polarization under the mutually perpendicular stresses (along $\langle 110 \rangle_{cub}$ -directions) may be displayed.

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REFERENCES

- 1. Z.-G. Ye, J.-P. Rivera and H. Schmid, Ferroelectrics, 106, 87 (1990).
- 2. S.-Y. Mao, F. Kubel, H. Schmid and K. Yvon, Acta Cryst., B47, 692 (1991).
- 3. Z.-G. Ye, J.-P. Rivera and H. Schmid, Ferroelectrics, 116, 251 (1991).
- 4. Z.-G. Ye, J.-P. Rivera and H. Schmid, Phase Transitions, 33, 43 (1991).
- 5. Z.-G. Ye, J.-P. Rivera, E. Burkhardt and H. Schmid, Phase Transitions, 36, 281 (1991).
- 6. Z.-G. Ye, J.-P. Rivera, H. Schmid, M. Haida and K. Kohn, Ferroelectrics, 161, 99-110 (1994).
- 7. J.-P. Rivera, Ferroelectrics, 161, 165-180 (1994).
- 8. H. Schmid, J. Phys. Chem. Solids, 26, 973 (1965).
- 9. H. Schmid and H. Tippmann, J. Crystal Growth, 46, 723 (1979).
- 10. H. Schmid, E. Burkhardt, B.-N. Sun and J.-P. Rivera, Physica, C157, 555 (1989).
- 11. E. Burkhardt, Z.-G. Ye and H. Schmid, Rev. Sci. Instrum. (in press).
- 12. J. F. Nye, "Physical Properties of Crystals," Clarendon Press, Oxford, 1985, pp. 243-257.
- 13. J. A. Mandarino, Canadian Mineralogist, 14, 498 (1976); 16, 169 (1978); 17, 71 (1979); 19, 441 (1981).
- 14. S.-Y. Mao, F. Kubel, H. Schmid and K. Yvon, Ferroelectrics, 132, 239 (1992).
- 15. Z.-G. Ye, J.-P. Rivera, P. Tissot and H. Schmid, *Ferroelectrics*, **124**, 421 (1991) [Errata: p. 425, lines 1, 2, 3, 5, 6 & 8 from the bottom, $(\Delta V_u/dp)$ should be $(\Delta T_u/dp)$.
- 16. H. Schmid, Int. J. Magnetism, 4, 337 (1973).
- 17. R. E. Newnham, Amer. Mineral., 59, 906 (1974).
- 18. K. Aizu, J. Phys. Soc. Japan, 34, 121 (1973).
- 19. R. E. Newnham and L. E. Cross, Mat. Res. Bull., 9, 927, 1021 (1974).
- 20. K. Aizu, Phys. Rev., B2, 754 (1970).



COLOR PLATE IV. See A. G. C.-Guzman, J. C.-Molina and J. R.-Gomez, Figure 1. *FERROELECTRICS*, Volume 172 (1–4).



COLOR PLATE V. See Z.-G. Ye *et al.*, Figure 3. *FERROELECTRICS*, Volume 172 (1–4).



COLOR PLATE VI. See Z.-G. Ye *et al.*, Figure 4. *FERROELECTRICS*, Volume 172 (1–4).



COLOR PLATE VII. See Z.-G. Ye *et al.*, Figure 6. *FERROELECTRICS*, Volume 172 (1–4).



COLOR PLATE VIII. See Z.-G. Ye et al., Figure 8. FERROELECTRICS, Volume 172 (1-4).





COLOR PLATE IX. See Z.-G. Ye *et al.*, Figure 10. *FERROELECTRICS*, Volume 172 (1–4).



COLOR PLATE X. See Z.-G. Ye *et al.*, Figure 12. *FERROELECTRICS*, Volume 172 (1–4).