Polarized light microscopy (PLM) of ferroelectric and ferroelastic domains in transmitted and reflected light

Schmid, Hans

N. Setter and E. L. Colla, Eds,

Ferroelectric Ceramics, Monte Verità, © Birkhäuser Verlag Basel, 1993

POLARIZED LIGHT MICROSCOPY (PLM) OF FERROELECTRIC AND FERROELASTIC DOMAINS IN TRANSMITTED AND REFLECTED LIGHT

Hans Schmid

The importance of polarized light microscopy (PLM) for the study of the domains and phase transitions of ferroelectric and ferroelastic single crystals is pin-pointed and the experimental set-ups for observations and measurements between 4 and 1600K are outlined. The contrast formation between domains by spontaneous birefringence and reciprocal rotatory power in transmission, and by bireflectance, specular reflection and etching in reflected light are considered. A symmetry classification for the birefringence and rotatory power contrast formation is proposed. The use of PLM for ceramic materials encounters difficulties, which can be overcome by enhancing grain growth and reducing sources of light scattering. Some examples are given, demonstrating the great power of PLM, if used in conjunction with other physical measurements.

1 Introduction

Ferroelectrics and other materials with phase transitions split up into "domains" (Březina et al., 1989) upon passage to the low symmetry phase. Their identification and the study of their optical properties by polarized light microscopy (PLM) is the main subject of this contribution. The resolution of a light microscope is in the most favourable case of the order of half a wavelength of light, whereas with a high resolution electron microscope one can see ranges of atoms, incommensurabilities and many more fine detail, including domains and domain walls. Information on the bulk and anisotropy properties may, however, get lost. Fortunately there exists a resolution range, spanning from about half a micrometer to the resolution of the bare human eye (about 100μm), which is most brilliantly covered for anisotropic crystals by the polarizing light microscope, permitting great penetration depths in the transmission regime, unequaled in electron microscopy. For PLM studies the availability of single crystals is of utmost importance.

Application of PLM to the ceramic state yields only limited information, but research and development of ceramics would greatly benefit from the preceding or simultaneous study of the corresponding single crystalline state. For studying domains by PLM, a good hold of macroscopic crystal optics and knowledge of the microscope functioning are required. Both topics - excluded in this review - are well covered by textbooks (Shubnikov, 1960; Wahlstrom, 1979; Bloss, 1961; Rinne-Berek, 1973; Beugnies, 1969; Burri, 1950; Galopin and Henry, 1972). This paper is intended to show that PLM is an indispensable tool for the study of ferroelectric and ferroelastic materials. It becomes *most powerful*, if used *in conjunction with other techniques*, such as X-ray, electron and neutron diffraction, ferroelectric or ferroelastic domain switching, e.g. with stroboscopic monitoring at high frequencies, electric field or mechanical stress induced phase transitions under simultaneous visual control, domain wall and symmetry considerations, quantitative crystal optical measurements of the single domain state by means of microspectroscopy and modern dynamic high resolution microphotometer techniques, including studies of spontaneous and induced birefringence, dichroism, rotatory power, bireflectance, and so forth.

2 Experimental set-up for studying domains between 4K and 1600K

Observations and measurements of domain properties are often desirable between 4K and 1300K. For work above room temperature and down to 80K, heating and cooling stages, which can be turned jointly with the turn-table of the microscope, can be found on the market. However, they may have to be modified, if electric, dielectric and optical measurements under simultaneous visual control are aimed at. If about 4K has to be reached - no commercial systems are available, i.e. own assemblies, constructions or adaptations become necessary. In the writers laboratory the following solutions have been adopted:

Polarizing light microscopes, easily commutable from transmission to reflection, equipped with normal, conoscopy and long working distance objectives (universal stage type), rotating (de Sénarmont, Laves-Ernst) and tilting (Berek) compensators, etc.

4K-300K: Helium flow cryostat with windows, mounted rigidly horizontally, operating under a polarizing light microscope, with turn-table removed. For compensating the lost faculty of turning the crystal on the turn-table, two devices are provided:

i) a sample holder inside the cryostat permitting rotation of a crystal plate in its plane and perpendicular to the microscope axis, e.g. between crossed polarizers. Moreover, the axis of the sample holder rod may be rotated, thus allowing tilting of the crystal plate and therefore allowing to some extent universal stage or spindle stage operations.

ii) for crystal-plates which cannot be rotated freely in their plane on the holder, e.g. because of rigid electrical contacts, a precision table permitting rotation of the entire microscope around its optical axis, as well as tilting of the microscope axis relative to the crystal platelet, are provided. This system allows synchronous rotation of the crossed polars relative to the fixed sample, i.e. replacing herewith the often required operation of turning the crystal between fixed crossed polars. This kind of operation is invaluable for the study of multi-extinction direction domain patterns and extinction dispersion versus temperature and wavelength. In addition, the crystal platelet may be ilted by rotation of the sample holder rod, thus permitting to decide whether the birefringence is due to an indicatrix principal cut or not.

80K-873K: Cooling (with N_2) and heating stage, covering continuously the room temperature range, allowing a limited rotation, solidarily with the turn-table.

300K-1600K: Hot stage for high temperature studies.

Microphotometers, operating in conjunction with a Babinet-Soleil compensator and a photoelastic modulator (Rivera et al., 1985), permitting to make birefringence and other optical measurements inside domains down to diameters of about 10μm. By connection of a monochromator via optical fiber, spectroscopy of domains is possible for wavelengths between 380 nm and 2000 nm.

Spindle stage (Bloss, 1981)*:* with room temperature operation, for refractive index measurements, domain control, X-ray sample preparation, etc.

3 How to obtain optical contrast between domains?

Since many ferroelectrics are also ferroelastic, *spontaneous linear birefringence* (Shubnikov, 1960; Vahlstrom, 1979; Bloss, 1961; Rinne-Berek, 1973; Beugnies, 1969; Burri, 1950) is the most important means for generating contrast between transparent *ferroelastic* domains, followed by *spontaneous, reciprocal optical rotatory power* (Shubnikov, 1960), which is also important for some kinds of non-ferroelastic ferroelectric and non-ferroelectric domains.

By birefringence contrast we mean the intensity and colour differences which may be obtained between crossed polars due to i) different extinction directions of birefringent domains, ii) different birefringence in inequivalent domain sections, iii) differences in path difference between domains produced by addition or subtraction of path difference by compensators, e.g. for domains with equal birefringence and extinction directions, but a 90° rotation between their indicatrix sections. All these phenomena are governed by Fresnel's relation describing the intensity transmitted for a birefringent plate between crossed polars (e.g. Ch.7,Eqs.7-33,7-35 in Wahlstrom, 1979)

$$I = I_o \sin^2 2\theta \cdot \sin^2\{(\pi d/\lambda)(n'' - n')\},$$

where I_o=intensity of incident light, θ=angle between plane of vibration of polarizer and vibration direction for n", λ=wavelength, d=thickness, n"-n'=birefringence, d·(n"-n')=path difference.

The rotatory power (Shubnikov, 1960; Hecht and Zajac, 1976) parallel to an optical axis depends on the circular birefringence (n_{left}-n_{right}), wavelength λ and thickness d. For a thickness d the angle through which the plane of vibration of linearly polarized light rotates in one domain is

$$b = (\pi d/\lambda)(n_{left}-n_{right}).$$

Hence maximum contrast between opposite domains is achieved at $2b=\pi/2$ for a fixed wavelength and extinction in one of the domains.

In the general case the extinction directions between unequal ferroelastic domains differ. Therefore contrast formation with crossed polars alone is possible in principle. The study of the extinction directions and their dispersion is not only important for contrast generation between ferroelastic domains but it may also be helpful for determining the correct point symmetry of the ferroic phase. For example it is well known that in the monoclinic indicatrix principal section (perpendicular to the b-axis) dispersion of the extinction direction with temperature and wave length is allowed. Less well known - although pointed out by Burri (1950) - is the fact that indicatrix general sections of orthorhombic crystals and domains have oblique extinction and permit also dispersion of the extinction angle, both with temperature and wavelength. Such cuts of orthorhombic domains are often encountered in crystals with cubic prototype. They should not be misinterpreted with a symmetry lower than orthorhombic!

Another property of the optical biaxial indicatrix which may give rise to misinterpretations of symmetry is the fact that close to the optical axes the angles of extinction change very rapidly and drastically for tiny changes of the direction of observation. This important behaviour has been described in detail by Burri (1950) (pages 293-296) for the example of an orthorhombic crystal, using stereographic projection of equi-extinction angle curves. This property of the biaxial indicatrix is usually ignored in non-german-language textbooks of optical crystallography, but may give rise - if ignored - to misinterpretations of symmetry. Striking examples are the pseudocubic (100)-cuts of orthorhombic domains of boracites with the spontaneous polarization in that (100) plane (Schmid, 1967). The domains have parallel extinction, but because of one optical axis forming an angle of only about 10 degrees with the vertical, slight misorientations of the crystal give rise to pronounced oblique extinction. Even by peeping into the microscope tube in a slightly oblique manner, strongly oblique extinction is observed and may erroneously give rise to "finding" a symmetry lower than orthorhombic!

In the reflection regime only the ferroelastic domains can be more or less easily detected. Here *bireflectance* is most important, followed by *reflection dichroism*, and by *specular reflection* contrast of "living" and "fossil" ferroelastic domains, which may produce a puckered surface.

For ferromagnetic ferroelectric and non-ferroelectric transparent materials we have to add *spontaneous non-reciprocal optical rotatory power* (=spontaneous Faraday effect) in the transmission case and the magneto-optical Kerr effects in the reflection case for revealing ferromagnetic domains. This topic will, however, be excluded from the present report, but it will be treated in a forthcoming paper.

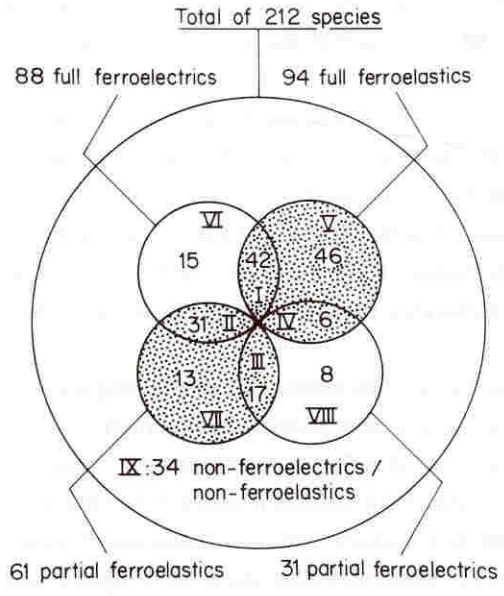
A major question is the following: *is polarized light of any use for generating contrast between ferroelectric domains with antiparallel spontaneous polarization* $\mathbf{P_s}$ *and is it capable of revealing the sign of* $\mathbf{P_s}$ *in such domains ?* The answer is unfortunately no in many cases, except for *fully ferroelectric/fully ferroelastic species* (Aizu, 1970; Schmid and Schwarzmüller, 1976) and *electro-ambidextrous species*. (Shuvalov and Ivanov, 1964; Newnham and Cross, 1974; Newnham, 1973) However, because many ferroelectrics are ferroelastic, the study of their ferroelastic domains is of major importance.

Because the complex permittivity - governing the complex indicatrix at optical frequencies - and spontaneous deformation are symmetric second rank tensors, coupled by symmetry, contrast by birefringence, transmission dichroism, bireflectance or reflection dichroism is in principle always possible between ferroelastic domains. Inversely, if domains are revealed by birefringence (etc.) contrast , we can conclude that the material is ferroelastic. The latter reasoning requires caution, however, because growth sectors (=growth pyramids) often show birefringence and dichroism contrast, too (Schmid, 1967). But with some experience true ferroelastic domains are readily distinguished from sectors.

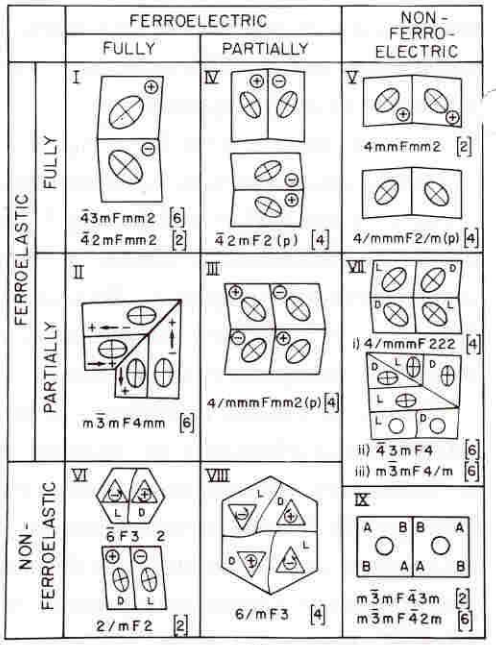
4 Classification of birefringence and rotatory power contrast formation for ferroelectric and ferroelastic domains

In order to obtain an idea of the different symmetry conditioned possibilities of contrast formation between ferroelectric and ferroelastic domains by using birefringence and reciprocal rotatory power , it appears useful to split up the 212 grey point group pairs, so called species (Aizu, 1970; Shuvalov, 1970), relating the prototype to the ferroic phase, into ensembles I to IX, characterized by different combinations of *fully ferroelectric, fully ferroelastic, partially ferroelectric, partially ferroelastic, non-ferroelectric and non-ferroelastic* (see Table I). "Fully ferroelectric" means that an electric field can in principle command all ferroelectric domain states, i.e. that it is capable of switching one domain state into any of all the other possible ones, at least in principle.

Table I: Subdivision of the 212 grey point group pairs (species into nine ensembles, representing different possibilities of contrast formation in polarized light for ferroelectric ferroelastic domains). a) Overview of intersecting and non-intersecting ensemble; b) Examples of domain pattern of ensembles I-IX; c) Species of ensemble II; d) Species of ensemble VI.



(a)



(b)

II 31 FULLY-FERROELECTRIC/ PARTIALLY FERROELASTIC SPECIES

ELECTRO-AMBIDEXTROUS (12 Species)					
Species	No of states	Species	No of states	Species	No of states
2/mF1	4	3̄mF2	6		
mmmF1	8	6/mF1	12		
4/mF1	8	6/mmmF1	24		
4/mmmF1	16	m3F1	24		
3̄F1	6	m3F3	8		
3̄mF1	12	m3mF1	48		
ELECTRO-PSEUDO-AMBIDEXTROUS (15 Species)					
mmmFm	4	3̄mFm	6	m3Fm	12
4/mFm	4	6/mFm	6	m3Fmm2	6
4/mmmFm(p)	8	6/mmmFm(p)	12	m3̄mFm(p)	24
4/mmmFm(s)	8	6/mmmFm(s)	12	m3̄mFm(s)	24
4/mmmFmm2(s)	4	6/mmmFmm2(s)	6	m3̄mFmm2(ps)	12
NON-ELECTRO-AMBIDEXTROUS (4 Species)					
432F1	24	m3̄mF3m	8		
432F4	8	m3̄mF4mm	6		

(c)

VI 15 FULLY-FERROELECTRIC/ NON-FERROELASTIC SPECIES

ELECTRO-AMBIDEXTROUS (6 Species)						
Species	No of states	examples				
		compound	Tc (°C)	ρ (deg mm⁻¹)	T (°C)	λ (mm)
1̄F1	2					
2/mF2	2	TGS	49	0.05 // O.A.	26	632.8
4/mF4	2					
3̄F3	2					
6̄F3	2	$Pb_5Ge_3O_{11}$	177	5.6	25	550
6/mF6	2					
ELECTRO-PSEUDO-AMBIDEXTROUS (2 Species)						
2/mFm	2	$LiH_3(SeO_3)_2$	70	1.7 // O.A.	23	589
mmmFmm2	2	$NaNO_2$	163	15.7 // O.A.	R.T.	632.8

NON-ELECTRO-AMBIDEXTROUS (7 Species)			
Species	No of states	Species	No of states
422F1	8	622F6	2
4/mmmF4mm	2	6̄m2F3m	2
32F3	2	6/mmmF6mm	2
3̄mF3m	2		

(d)

"Fully ferroelastic" means that elastic stress is capable for symmetry reasons to transform one ferroelastic domain state into any of all the other possible ones. "Partially" means that electric field and stress lack full command over some of all possible ferroelectric and ferroelastic domain states, respectively (Aizu, 1970). In the following we shall discuss the ensembles from the point of view of birefringence and rotatory power contrast and give some examples. Useful species for passive display and light gate applications have been discussed earlier (Schmid and Schwarzmüller, 1976). Examples of domain pattern for the ensembles I to IX are shown in Table I(b).

ENSEMBLE I: Fully ferroelectric/fully ferroelastic (42 species)

Because ferroelectric and ferroelastic domains are identical in this ensemble, unique properties are allowed:

i) An electric field has full command over all possible ferroelectric, and herewith all possible ferroelastic domain states. ii) Stress has full command over all ferroelastic domains and owing to the coupling, equally over all ferroelectric states. iii) Birefringence contrast is allowed between all of the possible domain states. iv) If the sense of the spontaneous polarization, $\mathbf{P}_s$, and the orientation of the optical indicatrix have been correlated to the absolute structure by some sort of label (etch pattern, growth hillock, pyroelectric response, etc.), simple visual inspection allows to find optically not only the orientation of the ferroelastic/ferroelectric domain, but also the absolute sense of $\mathbf{P}_s$. Examples are:

$\bar{4}$2mFmm2[2]*: KH_2PO_4(KDP)-type (Landolt-Börnstein, 1969), $Gd_2(MoO_4)_2$-type (Landolt-Börnstein, 1969) compounds, TANANE (Bordeaux et al., 1973)

$\bar{4}$3mFmm2[6]: Boracite crystal family (Schmid and Tippmann, 1978), $RbLiMoO_4$ (Melnikova and Voronov, 1990)

$\bar{4}$3mFm[12]: Boracite crystal family (Schmid and Tippmann, 1978), $CsLiMoO_4$, $CsLiWO_4$, $RbLiMoO_4$ (Melnikova and Voronov, 1990)

$\bar{4}$3mF3m[4]: Boracite crystal family (Schmid and Tippmann, 1978), $CsLiMoO_4$, $CsLiWO_4$, $RbLiMoO_4$ (Melnikova and Voronov, 1990)

Species $\bar{4}$2mFmm2[2] and $\bar{4}$3mFmm2[6] are outstanding in the sense that they allow in the "diagonal" position between crossed polars 100% transmission in one domain state (if reflection losses are disregarded) and zero transmission for the domain with opposite sense of $\mathbf{P}_s$ and if a compensator is used. That is why they are of interest for static or dynamic domain studies, and for potential applications as light gates (Schmid and Schwarzmüller, 1976). In ceramics the effect is canceled by symmetry (Schmid and Schwarzmüller, 1976).

*The number between [ ] indicates the possible number of domain states.

ENSEMBLE II: Fully ferroelectric/partially ferroelastic (31 species)

In species of ensemble II every ferroelastic domain may contain 180°-polar domains, invisible in polarized light, except in the 12 electro-ambidextrous species and the 15 electro-pseudo-ambidextrous species, in which contrast by rotatory power is in principle possible (see below and Table I(b,c)), so that only four species (432F1[24], 432F3[8], $m\bar{3}$mF3m[8], $m\bar{3}$mF4mm[6]) remain, which do not allow any kind of optical contrast between their 180°-domains of $\mathbf{P_s}$. Examples :

Total absence of electro-ambidexterity:

Species $m\bar{3}$mF4mm[6]: perovskite family, e.g.$BaTiO_3$ (Forsberg, 1956); Species $m\bar{3}$mF3m[8]: perovskite family, e.g. $BaTiO_3$, Pb_2FeNbO_6 (Brunskill et al., 1981), Pb_2FeTaO_6 (Brixel et al., 1988), $BiFeO_3$ (Tabares-Munoz et al., 1985).

Pseudo-electro-ambidexterity allowed: for a fixed $<110>_{cub}$-direction of species $m\bar{3}$mFmm2(ps)[12],** i.e. for $\mathbf{P_s}$ //<110>: $BaTiO_3$, $Sr_8[Al_{12}O_{24}](CrO_4)_2$ (Rossignol et al., 1988).

ENSEMBLE III: Partially ferroelectric/Partially ferroelastic (17 species)

In this ensemble of species neither an electric field alone nor mechanical stress alone are able to transform a polydomain single crystal into a single domain, whereas an appropriate combination of electric field and stress may, however, be able to do so. In 7 out of the 17 species the electric field is unable to reorient ferroelastic domains to directions other than related by 180°. They are the following: mmmF2[4] (example: $BaMnF_4$ (Sciau et al., 1989) in the incommensurate phase, average symmetry 2), 4/mF2[4], 4/mmmF2(p)[8], 4/mmmFmm2(p)[4], 6/mF2[6], 6/mmmF2(p)[12], 6/mmmFmm2(p)[6].

In the remaining ten species an electric field is in principle able to reorient $\mathbf{P_s}$ both by 180° and to directions other than 180°. They are the following: 4/mmmF2(s)[8], 6/mmmF2(s)[12], m3F2[12], $\bar{4}3$mF3[8], $m\bar{3}$mF2(p)[24], $m\bar{3}$mF2(s)[24], $m\bar{3}$mFmm2(pp)[12] (example (Ye et al., 1991): pyrochlore , $Cd_2Nb_2O_7$), $m\bar{3}$mFmm2(ss)[12], $m\bar{3}$mF4[12], $m\bar{3}$mF3[16].

ENSEMBLE IV: Partially ferroelectric/Fully ferroelastic (6 species)

In species 432F2(p)[12] and $\bar{4}3$mF2[12] an electric field may not only reverse $\mathbf{P_s}$ by 180°, but also reorient it to other directions, involving ferroelastic switching. In the four remaining species, $\mathbf{P_s}$ cannot reorient to directions other than related by 180°: 422F2(p)[4], $\bar{4}2$mF2(p)[4], 622F2(p)[6], $\bar{6}$m2F2[6]. No examples seem to be known.

**For nomenclature see K.Aizu (1970).

ENSEMBLE V: Non-Ferroelectric/Fully ferroelastic (46 species)

For the 46 species of this ensemble Aizu's tables (1970) may be consulted. There exist six among them which have a polar/polar phase transition, but they are not ferroelectric, because neither a 180°-reversal nor a reorientation of $\mathbf{P_s}$ is allowed: mm2F2[2], 4F2[2], 4mmFmm2[2], 6F2[3], 6mmF2[6], 6mmFmm2[3]. In order to distinguish experimentally from a ferroelectric species, the combination of birefringence contrast with the etching technique may be employed. This was successfully done for germanium fresnoite (Schmid et al., 1978) $Ba_2TiGe_2O_8$ with species mmFmm2[2], where the observation of equal polarity in both ferroelastic domains (no etching speed differences) allowed to exclude prototype $\bar{4}2m$, in case of which the observation of a sign reversal of $\mathbf{P_s}$ would have been required, as is the case of GMO and KDP. (Landolt-Börnstein, 1969) - Some examples of the remaining 40 fully ferroelastic/non-ferroelectric species with non-polar ferroic phase are the following:
4/mmmF2/m(s)[4] (VO_2 in its semiconducting state below the metal/semiconductor transition at 68°C; ferroelastic domains observable by bireflectance and by transmission dichroism for thin layers) (Schmid and Tippmann, 1968), 4/mmmFmmm[2] ($YBa_2Cu_3O_{7-x}$ below its chemo-topotactical transition of about 650°C) (Schmid et al., 1988), $\bar{4}3mF\bar{4}2m[3]$ ($Cr_3B_7O_{13}Cl$, example of an antiferroelectric, transformable by an electric field or by stress into a ferroelectric with species $\bar{4}3mFmm2[6]$) (Ye et al., 1991).

ENSEMBLE VI: Fully ferroelectric/Non-ferroelastic (15 species)

Ferroelectrics of this category would in principle appear ideal for memory applications because of the impossibility of domain switchings involving ferroelastic reorientations, which give rise to fatigue, initiated by micro-cracking (Schmid and Schwarzmüller, 1976).

Because of the centrosymmetry and identical orientation of the optical indicatrix of polar 180°-domains, no birefringence contrast is possible for non-ferroelastic ferroelectrics. However, as shown in Table I(c), there exist 6 species among the total of 15 which are *electro-ambidextrous*, i.e. optical contrast formation is possible due to an interchange between enantiomorphous twin states upon 180°-reversal of the ferroelectric domains, giving rise to a true sign reversal of reciprocal rotation. For practical applications, e.g. page composers, light gates, as well as static or dynamic domain studies, the most interesting species are the four ones with an uniaxial indicatrix, avoiding the superposition of birefringence and rotatory power: 4/mF4[2], 3F3[2], 6F3[2] and 6/mF6[2]. It seems that the intensely studied $Pb_5Ge_3O_{11}$ (Newnham, 1973; Shur, 1989) with species 6F3[2] is sofar the only known example.

There exist two more species in the ensemble, 2/mFm[2] and mmmFmm2[2], which may be called *"electro-pseudo-ambidextrous"* (Newnham and Cross, 1974). They allow an interchange between left and right hand rotation along a given direction of the crystal matrix upon polarization

reversal. In this case the sign reversal of rotation is, however, only apparent because of the non-enantiomorphic character of the ferroelectric phase. In the optically biaxial symmetries m and mm2 the rotatory power will usually be observable for the eye only along the optical axes, because the superposition of birefringence decreases very much the effective rotation and renders the entering linearly polarized light elliptical upon passage through the crystal. In the known examples $LiH_3(SeO_3)_2$ (2/mFm[2]) and $NaNO_2$ (mmmFmm2[2]) (Schmid and Schwarzmüller, 1976) the rotatory power along the optical axes has been measured (see Table I(d)) and would be sufficient for contrast formation for cuts perpendicularly to these axes (Schmid and Schwarzmüller, 1976). However, no attempts seem to have been made to reveal 180°-polar domains.

ENSEMBLE VII: Non-Ferroelectric/Partially Ferroelastic (13 species)

This ensemble splits up into *i)* seven *"Partially ambidextrous"* species because of their ferroic phase being both optically active and enantiomorphic (i.e. in one ferroelastic domain there may dwell two possible nonferroelastic domains related by a true sign reversal of rotation): 4/mmmF222[4], 6/mmmF222[6], m3F222[6], $m\bar{3}$mF222(pp)[12], $m\bar{3}$mF222(ss)[12], $m\bar{3}$mF422[6], $m\bar{3}$mF32[8], *ii)* four *"partially pseudo- ambidextrous"* species, because of their ferroic phase being optically active but not enantiomorphic (the two possible non-ferroelastic domains inside a ferroelastic one are related by an apparent sign reversal of rotatory power): $\bar{4}3$mF4[6], $m\bar{3}$mF4[12], $m\bar{3}$m$F\bar{4}2$m(ps)[6], $m\bar{3}$m$F\bar{4}2$m(sp)[6] and *iii)* two species with *non-ambidextrous* ferroic phases because being neither optically active nor enantiomorphic: $m\bar{3}$mF4/m[6], $m\bar{3}$mF32[8]. - No representative of ensemble VII seems to be known.

ENSEMBLE VIII: Partially Ferroelectric/Non-Ferroelastic (8 species) (Aizu, 1970)*:*

Among the eight species there is *i)* one which is *non-electro-ambidextrous:* 6/mmmF3m[4] and *ii)* seven ones which we may call *"Partially electro-ambidextrous":* 4/mmmF4[4], 3mF3[4], 6/mF3[4], 622F3[4], $\bar{6}$m2F3[8], 6/mmmF6[4]. For example, species "6/mmmF3[8]" with 8 states means that there is a 1:1 probability that an electric field being applied to one of the two right hand or two left hand domains with same polarity will switch the crystal to a polar 180°-domain with right hand *or* left hand gyration. However, since two possible domain states with same sign of gyration are allowed for one polarity, observation with uncrossed polars will give us a *"partial reply"* (!) only. - No representatives of ensemble VIII seems to be known!

ENSEMBLE IX: Non-Ferroelectric/Non-Ferroelastic (34 species) (Aizu, 1970)*:*

Within this category of ensemble materials with secondary ferroic domains may be found, a subject which will be treated in more detail elsewhere. Such domains need the simultaneous application of two constraints (e.g. stress + electric field) for poling and an induced property (e.g.

electro- or elasto-optic effect) for generating contrast between domains. Examples are: alpha-quartz (622F32[2]) and NH_4Cl ($m\bar{3}mF\bar{4}3m[2]$) (Newnham, 1973).

5 Contrast formation between domains in reflected light

5.1 Some particular features of PLM in reflected light

It seems worthwhile to point out some particularities of PLM in reflected light compared with the transmission regime (Rabe, 1983; Rabe et al., 1989; Azzam and Bashara, 1987; Schmid et al, 1988; Rabe et al., 1990; Schmid, 1991):

Crossing of polarizer and analyser. If the crystallographic principal axes of a ferroelastic domain have to be determined from their extinction directions between crossed polars, perfect crossing of polarizer and analyser is necessary because very slight uncrossing may lead to "run away" (in German "Verschlagen") of the extinction directions, with the danger of mimicking lower symmetry (Rabe, 1983). Test materials with a high bireflectance (e.g. Niccolite NiAs, pyrrhotite $Fe_{1-x}S$ or a-b-cuts of the orthorhombic phase of $YBa_2Cu_3O_{7-x}$) (Schmid et al., 1988) may be used for achieving perfect crossing.

Light level. When working with crossed polars, the light level is normally much lower in the diagonal position than in transmission, thus necessitating strong microscope lamps (tungsten/halogen or even Xenon-lamps).

State of reflected polarized light. Whereas in the transmission regime without absorption, linearly polarized light impingement at 45° to the birefringence extinction directions ("diagonal rientation") produces in the general case elliptically polarized light at the exit from the crystal, with the principal axes of the ellipse forming an angle of 45° with the extinction directions, in the reflection case, with anisotropic absorption, linearly polarized light impingement with the E-vector at 45° to the principal reflectivity directions is generally reflected in an elliptical state with the major axis of the ellipse invariably rotated by an angle η towards the axis of higher reflectivity: $\eta = (1/2)\ \mathrm{arctg}[(R_1-R_2) / (2\ (R_1R_2)^{1/2}\ \cos\delta_{12})]$ (Rabe, 1983). Here R_1, R_2 are the principal reflectivities and δ_{12} is the phase difference between the components of the waves along axes 1 and 2. - This behaviour is useful for finding easily the direction of higher reflectivity of the reflectivity ovaloid cross sections and for making contrast between ferroelastic 90°-domains without using compensators (with polarizer and uncrossed analyser alone) (Schmid et al., 1988), but it renders the interpretation of ferroelastic domain patterns and the determination of the orientation of the real and imaginary parts of the complex indicatrix, particularly of monoclinic and triclinic phases, rather difficult. An analogous rotation of the polarization ellipse occurs in

transmission when the crystal is strongly (e.g. $YBa_2Cu_3O_{7-x}$) (Schmid et al., 1988) and even weakly dichroic (e.g. $KNiPO_4$)! (Beugnies, 1969; Rivera)

Compensators. Both for qualitative and quantitative (e.g. ellipsometry! Azzam and Bashara, 1987) PLM in reflection it is important that the microscope allows the use of rotating (de Sénarmont, Laves-Ernst) and tilting compensators. Astonishingly, this is not the case for all "modern" commercial polarized light microscopes for episcopy.

"Form bireflectance". Intriguing "domains" have been discovered during polarized light studies of the ferroelastic $YBa_2Cu_3O_{7-x}$ (4/mmmFmmm[2]) which were characterized by principa reflectivity axes rotated by 45° with respect to the true orthorhombic ones, herewith mimicking a symmetry, inconsistent with the X-ray results. They were finally identified as stacks of lamellar orthorhombic domains with a high density of walls per unit length and wall distances close to or shorter than the resolution of the microscope (Schmid et al., 1988a; Rabe et al., 1989; Schmid et al., 1988b). It has been tried to explain the observations by extending the well known phenomenon and concept of "form birefringence" of the transmission case (Born and Wolf, 1980) to "form bireflectance" for opaque materials, by admitting that the complex refractive index of the wall was slightly different from that of the domains (Rabe et al., 1990). An alternative explanation is obtained, when we remember that the structure of the walls is orthorhombic (mm2) (Janovec). Thus with increasing volume percentage of walls the principal reflectivities will necessarily align parallel/perpendicular to the walls.

5.2 Specular reflection contrast, observable both in ordinary and polarized light

Beginners in PLM of ferroelectric and ferroelastic materials are often puzzled by observing domains in reflected light which sometimes do and sometimes do not correlate with the domai patterns seen in transmission or with those observed in polarized reflected light. This comes from the fact that the formation of ferroelastic domains, after passage through a phase transition, may lead to a puckered surface, observable even in unpolarized light owing to ordinary specular reflection contrast. In the latter case, where the crystal plate is supposed to have been polished in the non-ferroelastic high temperature phase, the domain pattern observed in reflection corresponds to that seen in transmission ("living domains"). After polishing the crystal plate in the ferroelastic phase, the initially flat surfaces may become puckered after transformation to the non-ferroelastic, e.g. cubic, phase and reveal a "fossil domain pattern". Repeated cycling through a phase transition may lead to a superposition of "living" and "fossil domains" in reflected light. - Whereas the puckering is usually a nuisance, it may also sometimes represent a means for revealing a ferroelastic domain pattern of an opaque material if the bireflectance of the domains is too small for revealing them in polarized light.

5.3 Etching contrast of polar domains

As was shown above, ferroelectric 180°-domains cannot be revealed in polarized light, except in the case of the coupled "full ferroelectrics / full ferroelastics" and in that of "electro-ambidextrous" ferroelectrics. Because of different etching speed of the plus and minus ends of polar domains, the domain patterns are obtained in the form of reliefs. As examples we may cite the classical work on $BaTiO_3$ (Fousek and Safrankova, 1965) and a more recent one on $BiFeO_3$ (Steiner et al., 1987). The latter compound was the subject of a more than twenty years' dispute, whether the material is ferroelectric or antiferroelectric. By combination of etching and PLM of the ferroelastic domains in transmission and reflection it was possible to solve the problem in the twinkling of an eye and to show that $BiFeO_3$ was in fact ferroelectric (Tabares-Munoz et al., 1985; Steiner et al., 1987). - An alternative way of monitoring polar domains consists in using the different width of etched polishing scratches on plus and minus ends of domains. For example the fully ferroelectric/fully ferroelastic domains of boracites (species $\bar{4}$3m/mm2[6]) have been characterized by combining PLM and etching (Schmid, 1967), and in a similar way the method has been used to verify species 4mm/mm2[2] of germanium fresnoite, for which the ferroelastic non-ferroelectric polar mm2-domains necessarily have to have same dipole direction for symmetry reasons (no change in width of etch pits) (Schmid et al., 1978).

6 PLM of domains and phase transitions of ceramics

The study of ferroelectric and ferroelastic domains by PLM in ceramics is evidently much more difficult than in single crystals. Nonetheless important information may often be obtained, if some precautions are taken.

Transmitted light. The major difficulties encountered in PLM of ceramics are the smallness of the grains and light scattering from the grain boundaries and domain walls, where different refractive indices meet. Pores give also rise to strong scattering and the superposition of grains and domains impedes any kind of helpful interpretation. The desirable reduction of light scattering may be achieved by

i)Reduction of the thickness of a ceramic platelet to a value which becomes comparable to the size of the grains and if possible to that of the ferroelastic domains so that superposition of grains and domains no longer occurs. ii)Increase of the grain size - if possible to 50 or 100 micrometer - by prolonged annealing at high temperature. Addition of tiny amounts of mineralizing agents (flux or gas phase transport agents) can be beneficial for speeding up the grain growth. iii)Elimination of the pores by prolonged annealing or efficient hot-pressing. iv)Oil immersion, reducing very much

the light scattering from pores (Kubel and Schmid).

The observation and correct interpretation of extinction directions and of the orientation of walls between ferroelastic domains requires the search for large ceramic grains with low index orientations, e.g. cubic (100)-, (110)- or (111)-cuts in case of a cubic prototype (perovskites, pyrochlores, sodalites, etc.), which facilitate very much the analysis. For example a pseudocubic (100)-cut is correctly oriented when the traces of mutually perpendicular (100)- or (110)-domain walls appear very sharp. Pseudocubic (110)-cuts are recognized by the typical rhombo-dodecahedral angles 35°/55° formed between the traces of walls, and (111)-cuts by 60°-intersections. Possibilities of orientation and observation of low index domain walls for a cubic prototype have been described (Schmid, 1967; 1970). - With some patience well oriented grains and domains with principal cuts of the optical indicatrix may be found and the birefringence or other optical properties may be measured versus temperature with a microphotometer. The study of phase transitions by means of a single crystalline ceramic grain comes close to the study of an isolated single crystal. This means that no smear-out of phase transition temperatures is observed and that the thermal hysteresis of first order transitions is usually well reproducible for an individual grain. Different grains may, however, differ in behaviour owing to inhomogeneities of local stress and/or concentration. In a recent study of the phase transitions of the sodalite $Ca_8[Al_{12}O_{24}](WO_4)$ the described technique has successfully been put to use (Kubel and Schmid).

Reflected light. The study of opaque ferroelastic ceramics by PLM in reflection is also facilitated after grain size enhancement as in the transmission case, whereas light scattering is negligible if the polishing was done correctly. The identification of the correct orientation of a grain by means of domain walls is more difficult than in the transmission case and can only be done approximately, because merely the sharp traces of the walls are visible, but without any perception in depth of the wall itself. - Ferroelastic twinning inside ceramic grains is easily detected in polarized light, provided the bireflectance is sufficiently important. As pointed out for single crystals, oil immersion may drastically enhance the contrast between ferroelastic domains, even with a polarizer alone. A ceramic of the ferroelastic high T_c superconductor $YBa_2Cu_3O_{7-x}$ is an excellent material for demonstrating the aforesaid, e.g. for teaching purposes (Schmid et al., 1988a).

7 Recognition of defects and anomalies

Growth sectors (= growth pyramids). All crystal growth methods permitting the development of free facets (solution growth, gas phase transport) with one or more kinds of (hkl) usually lead to

the development of growth pyramids which are often characterized by anisotropic physical properties, and which can differ very much from those of the ideal compound and among sectors having different (hkl). They can best be observed in the "cubic" phase of ferroelectrics or ferroelastics having grown in the cubic prototype phase. For example in boracites (Schmid, 1967) and perovskites (Rossignol et al., 1985) strong parasitic birefringence is observed in growth sectors. In boracites it may reach about 0.004, i.e. the order of magnitude of a true orthorhombic ferroelectric/ferroelastic phase of Fe-Iodine-boracite! By using birefringence contrast, the different growth pyramids of many boracite compositions have elegantly been shown to differ by up to ten degrees in phase transition temperature (Rossignol et al., 1985)! Without optical observation the origin of the related multiple peaking, e.g. of DTA curves at the phase transitions, would have remained obscure! Beginners in the field are often intrigued by the strong birefringence and dichroism in growth sectors. They are often confounded with genuine ferroelastic domains. Such birefringence can usually not be healed out by annealing and its origin is not clear. One possibility of explanation is that by "form birefringence" (Rabe et al., 1990; Rossignol et al., 1985), which may be generated by a periodic change of refractive index in growth layers parallel to the growth pyramid basis. Tiny changes in stoichiometry or in the impurity level may give rise to such oscillations of refractive index.

Stress fields, e.g. generated by growth dislocations or impurity-generated dislocations, may well be seen and studied by PLM. They often take on the surface symmetry of the growth pyramid basis and are typical of certain sectors (Schmid, 1967). For example traces of Al^{3+} ions, incorporated into boracites, generate innumerable defect centers with well recognizable strain fields, characterized by the surface symmetry.

Metastable phases. For example incommensurate phases have a great tendency to survive metastably in wide temperature ranges in coexistence with stable phases. Such a behaviour was observed in Pb_2CoWO_6 by PLM and helped to clarify "obscure" initial X-ray results (Sciau et al., 1992).

8 The power of PLM in combination with other techniques

8.1 Help for symmetry determinations

An X-ray crystallographer, used to determine easily any of the 230 spacegroups, may laugh at polarized light microscopy, when hearing that the 32 crystallographic (or morphological) point groups split up into only five so-called birefringence groups (Shubnikov, 1960), which characterize five types of refractive index ellipsoid (indicatrix) and which behave differently in

polarized light: spherical ∞∞∞m, uniaxial m∞/m, and the three biaxial groups mmm, 2/m and 1 ! If no reference framework and other property information would be available, indeed even not all the seven crystal systems could be distinguished! However, *in a ferroic material*, in which we can determine the prototype symmetry, an excellent reference framework - generating restrictions - is available. For example if the prototype is cubic, the choice of point groups for an uniaxial indicatrix can sensibly be trimmed down from the total 19 possibilities: i) the six hexagonal groups can be eliminated, because not forming a subgroup, ii) if extinction parallel to cubic <100>-directions with a single birefringence value is found, we are left with the seven tetragona point groups. If ferroelectricity is evidenced experimentally also, the choice is reduced to groups 4 and 4mm. May-be if rotatory power is observed, we are left with the single group 4. Herewith also the number of possible space groups is drastically reduced! Moreover, by isolating a ferroelastic single domain grain by optical control, and checking its polar single domain character by etching, we may prepare a successful X-ray structure determination.- By combining PLM with detection methods for non-centrosymmetry (second harmonic generation, piezoelectricity, Pockels effect, etc.,) and observation of orientation (Sapriel, 1975), number (Aizu, 1970; Sapriel, 1975) and types of domain and wall (Březina et al., 1989; Fousek and Janovec, 1969; Fousek, 1971; Shuvalov et al., 1985), we may also narrow the choice of symmetry groups.

8.2 Examples

i) X-ray analysis was unable to distinguish between group $\bar{4}3m$ and $m\bar{3}m$ of the cubic phase of the aluminate sodalite $Sr_8[Al_{12}O_{24}](CrO_4)_2$ (Depmeier et al., 1987). By combining PLM and electric switching experiments, $\mathbf{P_s}$ in the orthorhombic low temperature phase was unequivocally found to lie along cubic <110>, fixing the prototype and the species unequivocally to $m\bar{3}m$ an $m\bar{3}mFmm2(ps)[12]$, respectively (Rossignol et al., 1988).

ii)For the perovskite Pb_2CoWO_6 four different unit cell sizes, orientations and different symmetries had been "determined" by X-rays. Studies by PLM allowed to clarify the situation in less than a day's work by proving monoclinic symmetry and finding the b-axis to lie along cubic <110> (Brixel et al., 1985).

iii)In spite of numerous physical measurements realized on the pyrochlore $Cd_2Nb_2O_7$, the number and nature of its phase transitions remained obscure during about 20 years. By combining PLM with electric switching experiments, using transparent gold electrodes, the number of the transitions has been clarified. A stable ferroelectric phase with species $m\bar{3}mFmm2(pp)[12]$ and a field induced ferroelectric phase with species $m\bar{3}mFmm2(ps)[12]$ have rapidly been identified (Ye et al., 1991b).

iv) In Cr-Cl boracite an antiferroelectric tetragonal ($\bar{4}2m$) phase was recently discovered by PLM

and an anomalous "pyroelectric" signal has been explained by the observation of an "ephemeric" mm2-phase, occurring in a 1-2 degree temperature interval at the mechanically non-matching $\bar{4}3m/\bar{4}2m$ phase boundary (Ye et al., 1991a). Owing to the tiny volume percentage of the phase, it would have escaped detection by X-rays. In future more attention should be given to this phenomenon, which possibly occurs at first order phase transitions of many more materials.

9 Conclusion

It is hoped that the short report has shown to the young chemist and physicist that PLM is a privileged and indispensable complementary tool for studying domains and phase transitions and that it may bring rapidly abundant invaluable information, which often cannot be obtained by other techniques in an equally elegant way.

Acknowledgments

Thanks are due to Prof. N.Setter for proposing the subject, to Dr. J.-P.Rivera for critical reading and improving of the manuscript, but in particular for his painstaking task of transposing the manuscript from SAMNA to WORD 5.5, to Dr. H.Rabe for helpful discussions, to O.Hirth, E.Burkhardt and R.Cros for technical help, and the Swiss National Science Foundation for support.

References

Aizu, K., (1970): *Phys.Rev.*, **B2**, 757.

Azzam, R.M.A., and N.M.Bashara, (1987): *Ellipsometry and Polarized Light*, North Holland, Amsterdam.

Beugnies, A., (1969): *Microscopie des milieux cristallins*, Presses Académiques Européennes, Bruxelles and Dunod, Paris.

Bloss, F.D., (1981): *The Spindle Stage*, Cambridge University Press, Cambridge.

Bloss, F.D., (1961): *An Introduction to the Methods of Optical Crystallography*, Holt, New York.

Bordeaux, D., J.Bornarel, A.Capiomont, J.Lajzerowicz-Bonneteau, J.Lajzerowicz and F.F. Legrand, (1973): *Phys.Rev.Letters*, **31**, 314.

Born, M., and E.Wolf, (1980): *Principles of Optics*, Pergamon Press, Oxford, (Ch.14, §14.5.2), 6th ed..

Březina, B., and J.Fousek, in H.Arend and J.Hulliger, (1989): Eds., *Crystal Growth in Science and Technology*, NATO ASI Series, Ser.B: Physics, **210**, 185, Plenum Press, New York; see also: J.Fousek, this Summer School.

Brixel, W., J.-P.Rivera, A.Steiner and H.Schmid, (1988): *Ferroelectrics*, **79**, 201.

Brixel, W., M.L.Werk, P.Fischer, W.Bührer, J.-P.Rivera, P.Tissot and H.Schmid, (1985): *Jpn.J.Appl.Phys.*, **24**, Suppl. 24-2, 242.

Brixel, W., R.Boutellier and H.Schmid, (1987): *J.Cryst.Growth*, **82**, 396.

Brunskill, I.H., H.Schmid and P.Tissot, (1981): *Ferroelectrics*, **37**, 547.

Burri, C., (1950): *Das Polarisationsmikroskop*, Birkhäuser, Basel.

Depmeier, W., H.Schmid, N.Setter and M.L.Werk, (1987): *Acta Cryst.* **C43**, 2251.

Forsberg, P.W., (1956): "Piezoelectricity, Electrostriction and Ferroelectricity", in S.Flügge, *Handbuch der Physik*, Vol.XVII : Dielektrika, Berlin.

Fousek, J., (1971): *Czech. J.Phys.*, **B21**, 599.

Fousek, J., and M.Safrankova, (1965): *Jpn.J.Appl.Phys.*, **4**, 403.

Fousek, J., and V.Janovec, (1969): *J.Appl.Phys.*, **40**, 136.

Galopin, R., and N.F.Henry, (1972): *Microscopic Study of Opaque Minerals*, W.Heffers and Sons Ltd, Cambridge, and references therein.

Hecht, E., and A.Zajac, (1976): *Optics*, Addison-Wesley, Reading, MA..

Janovec, V., private communication.

Kubel, F., and H.Schmid,to be published.

Landolt-Börnstein, (1969): New Series, Group III, **Vol.3**, Springer, Berlin,etc..

Melnikova, S.V., and V.N.Voronov, (1990): *Ferroelectrics*, **111**, 307.

Newnham, R.E., (1973): *Amer.Mineralogist*, **59**, 121.

Newnham, R.E., and L.E.Cross, (1974): *Endeavour*, **33**, 18.

Rabe, H., (1983): *Fortschr.Miner.*, **61**, 243.

Rabe, H., E.Burkhardt, J.-P.Rivera, H.Schmid, E.Walker, W.Sadowski, M.G.Karkut, L.Antognazza, J.-M.Triscone and O.Fischer, (1989): *Ferroelectrics* **92**, 129.

Rabe, H., J.-P.Rivera, H.Schmid, J.-P.Chaminade and L.Nganga, (1990): *Matt.Sci.Eng.*, B5, 243.

Rinne-Berek, 1973: *Anleitung zur allgemeinen und Polarisations-Mikroskopie der Fest körper im Durchlicht*, 3.Aufl., Eds. H.Schumann und F. Kordner, Schweizerbart, Stuttgart.

Rivera, J.-P., F.-J.Schäfer, W.Kleemann and H.Schmid (1985): *Jpn.J.Appl.Phys.*, **24**, Suppl. 24-2, 1060 [for details and a review of the modulation techniques of the light polarization see ref. 10 (J.Badoz *et al*, *J. Optics* (Paris) **8**, 373 (1977)) and ref. 11 (J.Ferré and G.A.Gehring, *Rep. Prog. Phys.* **47**, 513 (1984)) of this paper].

Rivera, J.-P., "How to separate linear birefringence from linear biextinction with the polarized light microscope", ISFD-2, Nantes 7-10.7.92, *Ferroelectrics* (accepted).

Rossignol, J.-F., J.-P.Rivera and H.Schmid, (1985): *Jpn.J.Appl.Phys.*, **24**, Suppl. 24-2, 574.

Rossignol, J.-F., J.-P.Rivera, P.Tissot and H.Schmid, (1988): *Ferroelectrics*, **79**, 197.

Sapriel, J., (1975): *Phys.Rev.*, **B12**, 5128.

Schmid, H., (1967): *Rost Kristallov*, **7**,32 [*Growth of Crystals*, **7**, 25 (1969)].

Schmid, H., (1970): *phys.stat.sol.*, **37**, 209.

Schmid, H., (1991): *Phase Transitions*, **30**, 205.

Schmid, H., and H.Tippmann, (1968): unpublished.

Schmid, H., and H.Tippmann, (1978): *Ferroelectrics*, **20**, 21.

Schmid, H., and J.Schwarzmüller, (1976): *Ferroelectrics*, **10**, 283.

Schmid, H., E.Burkhardt, E.Walker, W.Brixel, M.Clin, J.-P.Rivera, J.-L.Jorda, M.François and K.Yvon, (1988a): *Z.Phys.B - Condensed Matter*, **72**, 305.

Schmid, H., J.-P.Rivera, M.Clin, A.Williams and E.Burkhardt, (1988b): *Physica* **C153-155**, 1688.

Schmid, H., P.Genequand, H.Tippmann, G.Pouilly and H.Guédu, (1978): *J.Materials Science*, **13**, 2257.

Sciau, Ph., G.Calvarin, B.N.Sun and H.Schmid, (1992): *phys. stat. sol.*(a) **129**, 309.

Sciau, Ph., J.-P.Rivera and H.Schmid, (1989): *Ferroelectrics* **9**, 293.

Shubnikov, A.V., (1960): *Principles of Optical Crystallography*, Consultants Bureau, New York

[Original: Institute of Crystallography, Acad. Sci. USSR Press, Moscow, (1958)].

Shur, V.Y., A.L.Gruverman, V.V.Letuchev, E.L.Rumyantsev and A.L.Subbotin, (1989): *Ferroelectrics*, **98**, 29.

Shuvalov, L.A., (1970): *J.Phys.Soc.Jpn.* **28** (suppl), 38.

Shuvalov, L.A., and N.R.Ivanov, (1964): *Kristallografiya*, **9**, 363.

Shuvalov, L.A., E.F.Dudnik and S.V.Wagin, (1985): *Ferroelectrics*, **65**, 143.

Steiner, A., C.Tabarez-Munoz and H.Schmid, (1987): *Helv.Phys.Acta*, **60**, 294.

Tabares-Munoz, C., J.-P.Rivera, A.Bezinges, A.Monnier and H.Schmid, (1985): *Jpn.J.Appl.Phys.*, **24**, Suppl.24-2, 1051.

Wahlstrom, E.E., (1979): *Optical Crystallography*, 5th ed., John Wiley, New York.

Ye, Z.G., J.-P.Rivera and H.Schmid, (1991a): *Ferroelectrics*, **116**, 251.

Ye, Z.G., N.N.Kolpakova, J.-P.Rivera and H.Schmid, (1991b): *Ferroelectrics*, **124**, 275.

Hans Schmid, University of Geneva, CH-1211-Geneva 4, Switzerland.