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Ferroelastic symmetry changes in the perovskite $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$

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Abstract. The ferroelastic symmetry changes of the lead-based complex perovskite $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ are investigated by means of single crystal x-ray diffraction and observations in polarized light microscopy at different temperatures. The position of the 400 and 222 cubic reflections is followed between 80 K and 300 K. Results indicate the presence of two structural transitions at about 270 K and 220 K. Such temperatures define the stability range of three different phases. The high-temperature phase ($T > 270$ K) is the *optically anomalous* paraelectric prototype, the optical symmetry of which is uniaxial (tetragonal) in spite of the diffractometric (pseudo)cubic symmetry. The intermediate derived phase ($270 \text{ K} > T > 220 \text{ K}$) is tetragonal. This tetragonal phase coexists with a monoclinic one for $220 \text{ K} > T > 200 \text{ K}$. Below 200 K only the monoclinic phase is stable. The (pseudo)cubic-to-tetragonal transition seems to be of the second order. The tetragonal-to-monoclinic one is of the first order.

1. Introduction

$\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PFT), prepared as ceramics by Smolenskii *et al* [1] in 1959, belongs to the wide family of lead-based oxides with general formula $\text{PbB}'_{0.5}\text{B}''_{0.5}\text{O}_3$, compounds in which two cationic species occupy the B-site lattice of the perovskite structure ABO_3 . Materials of this kind typically undergo a sequence of temperature-induced ferroic phase transitions, which from the structural point of view consist in small modifications of a highly symmetric and ideally undistorted parent structure, which is called the *aristotype* or *prototype*. From this ideally undistorted phase all the less symmetric *ettotypes* are derived. The crystallographic point symmetry groups of the prototype and the ferroic (equitranslational) derived phase are related in such a way that the former is a supergroup of the latter.

The sequence of phases of PFT one finds in *Landolt-Börnstein* [2], determined for ceramic samples, is at first sight quite simple: at room temperature the geometry of the x-ray powder diffraction pattern was reported to be cubic, space group $Pm\bar{3}m$ and a lattice parameter of about 4 Å, corresponding to Fe^{3+} and Ta^{3+} statistically distributed over B sites. Below a transition smeared around 243 K, a derived equitranslational ferroelectric phase was identified, the most likely symmetry of which was inferred to be rhombohedral $R\bar{3}m$ from the geometry of the x-ray powder diffraction pattern [3, 4]. Accordingly, PFT was assigned to the ferroic species $m\bar{3}mF3m$, in the Aizu notation [5].

However, as we mentioned in a previous paper [6], this simple picture has become more complicated since single crystals were synthesized [7]. The main points open to discussion are briefly recalled in the following.

A subtle crystallographic problem suddenly appeared in studying the *cubic* room temperature phase: it was found that crystals of PFT grown from PbO flux, which always display the {100} cubic form, are actually composed of six pyramidal growth sectors which are uniaxial, and more specifically tetragonal, from the point of view of the optical symmetry [8]. The six vertex-sharing growth pyramids have the six (100) faces of a cube-shaped crystal as their bases and define three different orientations of the uniaxial indicatrix, with unique axes along the [100] cubic directions. The *anomalous* birefringence, characterized by very sharp extinctions, is small (of the order of 10^{-4}) and thus the tetragonal distortion from cubic, if any, must be expected to be small. The experiments we carried out to investigate the possible structural etiology of the optical anomaly, i.e. to prove the presence of a spontaneous strain in this *so-called* cubic phase, gave the following results: (i) the effect of mechanical loading on differently oriented growth sectors clearly indicated the presence of long-range uniaxial strain within each sector [8]; (ii) a weak gain, with respect to cubic, was obtained in refining the structure of single sectors as tetragonal [6]. Since no transition was observed above room temperature towards an optically isotropic phase, then, in principle, the recognized tetragonal optical symmetry of growth sectors would be taken as the prototype for PFT. Under this assumption, the assessed rhombohedral symmetry of the ferroelectric phase appears to be unlikely for the lacking of group–subgroup relations between tetragonal and rhombohedral groups [9].

The second important point emerged from dielectric measurements and observations under polarized light versus temperatures carried out on single crystals: such experiments evidenced, already in 1987, the likely presence of *two* structural transitions, taking place respectively at about 250 K and 210 K. As result, a new phase was suggested to be stable between the high-temperature paraelectric phase and the already known ferroelectric phase. The transition at 250 K was assessed to be of second order, while the one at 210 K of (weakly) first order. Unfortunately, these results, widely discussed in a thesis [10], were never published.

Results of the aforementioned studies encourage a reinvestigation of the whole sequence of phases in PFT. With the aim of definitely clarifying the number of phase transformation and the symmetry change occurring at each transition, high-resolution single-crystal x-ray diffraction was carried out as a function of temperature. Results will be presented and compared with observations in polarized light microscopy versus temperature performed on oriental crystal sections.

2. Experiment

2.1. Samples

Single crystals of $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ were grown from a PbO flux at the Departement de Chimie Minérale Analytique et Appliquée of the University of Geneva, in the group of Professor Hans Schmid. The studied crystals were as follows:

- CRY(111): an oriented (111) section. It is composed by a tiling of three growth sectors, as described in [8] and shown in figure 1. The section, 60 μm thick, was mechanically polished from an as-grown crystal shaped as a cube of edge about 500 μm . To relax possible residual mechanical stress, the section was annealed for several hours at 1000 K and then slowly cycled twice between 80 K and 1000 K.
- CRY(100)₁: a (100) section cut from inside a cube-shaped crystal of edge about 600 μm . The growth sectors composing the section are visible in figure 2. The section, 70 μm thick,



Figure 1. Crystal CRY(111) under crossed polarizers. At the bottom, one of the three sectors is in extinction. Sectors can be successively brought into extinction by rotation of 120° .

(This figure can be viewed in colour in the electronic version of the article; see <http://www.iop.org>)

was mechanically polished and subjected to the same annealing procedure as adopted for CRY(111). This sample was studied both by polarized light microscopy and x-ray diffraction. According to the crystal optics, CRY(100)₁ had both the a and c tetragonal parameters normal to the measured face during the x-ray experiments.

- CRY(100)₂: a natural cube-shaped crystal. One of the (100) faces was measured by x-ray diffraction. From the optical point of view, the unique tetragonal parameter c was normal to the measured face.

2.2. Polarized light microscopy

Observation under polarized light of CRY(100)₁ was performed with a Leitz Ortoplan microscope, equipped with a variable temperature sample holder. Temperature was measured with a thermocouple put near the crystal.

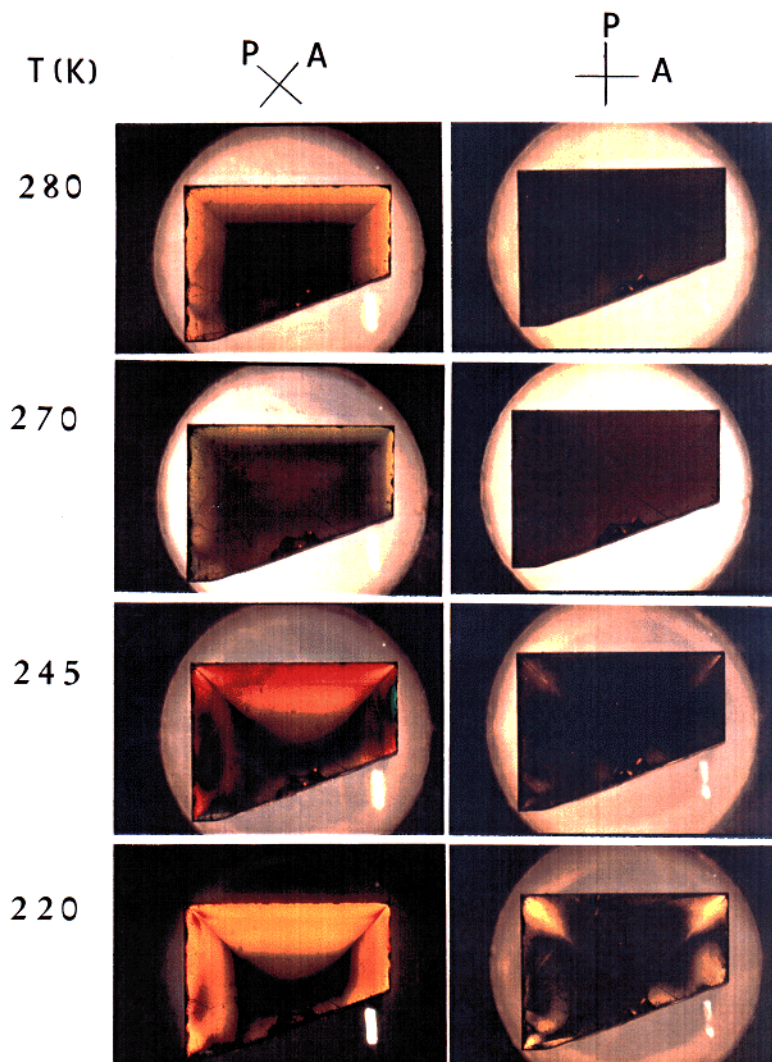


Figure 2. Crystal $\text{CRY}(100)_1$ under crossed polarizers. Right: polarizers parallel to $[110]_{\text{cub}}$; left: polarizers parallel to $[100]_{\text{cub}}$.

(This figure can be viewed in colour in the electronic version of the article; see <http://www.iop.org>)

2.3. The x-ray method

X-ray diffraction patterns were recorded on a prototype two-axis goniometer equipped with a Cu rotating anode generator of 18 kW [11]. Diffraction was performed in reflection mode on the oriented single crystals. Bragg angles 2θ and ω were accurately measured by means of incremental (10^{-4} degree) photoelectric encoders. Crystals were mounted in a cryostat and cooled by gaseous conduction, with a thermal stability of about 0.05 K. The precision on measured temperatures is better than 0.1 K.

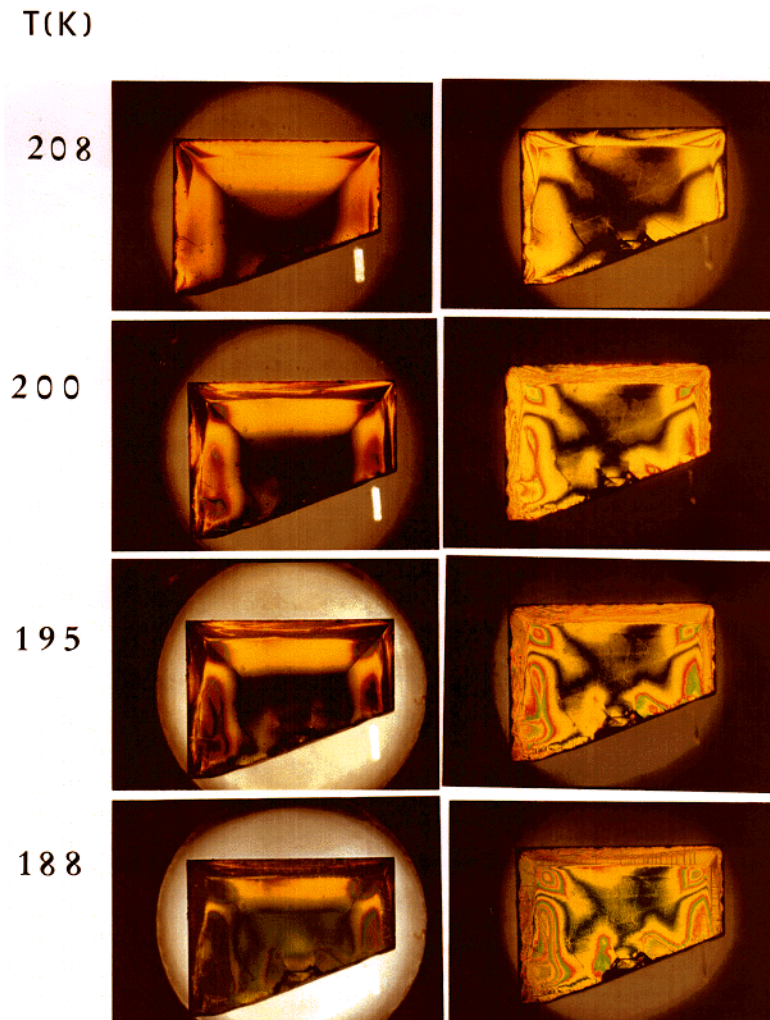


Figure 2. (Continued)

3. Results

3.1. Polarized light microscopy

The evolution of the birefringence pattern of $CRY(100)_1$ was followed with temperature under the microscope. Photographs at different temperatures, from 280 K to 188 K, are shown in figure 2. On the left, the crystal is observed under crossed polarizers parallel to $[110]_{cub}$. On the right, polarizers are parallel to $[100]_{cub}$.

At the beginning of the experiment, at room temperature, the crystal appears as a tiling of four well defined sectors. The dark central sector, which has its optical axis normal to the picture, is in extinction at any azimuth between crossed polarizers. The three lateral sectors, all having the principal sections of their tetragonal indicatrix in the plane of the picture, are extinct for crossed polarizers parallel to $[100]_{cub}$ and birefringent for crossed polarizers parallel to $[110]_{cub}$. The room temperature indicatrix of all sectors is uniaxial positive. From room

temperature down to about 270 K the birefringence of the bright sectors becomes smaller and smaller (see $T = 280$ K). At 275 K practically no more birefringence is measured.

At 270 K, the birefringence of lateral sectors begins to increase again. The re-growing birefringence is due to a uniaxial negative indicatrix, as verified by compensators.

On further lowering of temperature, sectors pass through a state in which they are observed as red and black regions ($T = 245$ K) and eventually reassume their original yellow colour at about 220 K. From 270 K to 220 K the birefringence is extinguished, under crossed polars parallel to $[100]_{cub}$, in most of the crystal. The uniaxial negative indicatrix (already present at 270 K) identifies therefore a new tetragonal phase, the lattice parameters of which are rapidly changing with temperature, producing an increasing spontaneous strain and thus an increasing birefringence.

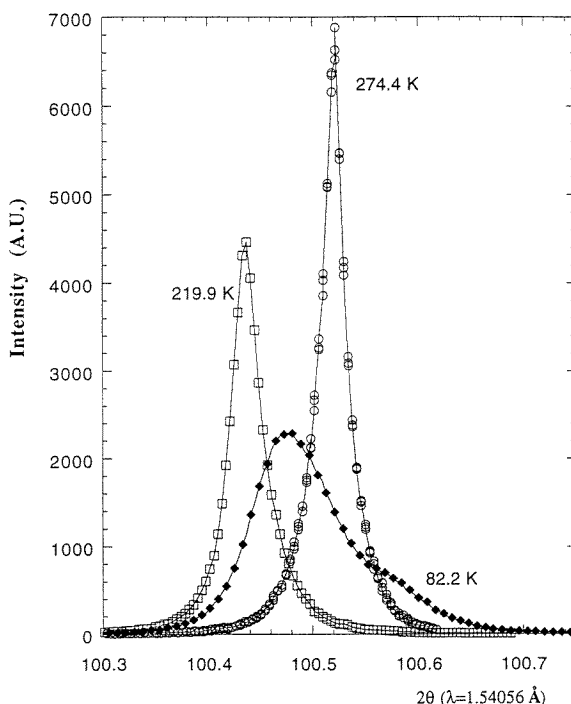


Figure 3. The 400 cubic reflection at different temperatures (measured crystal $CRY(100)_2$).

At 220 K new regions are visible: they are shaped as red petals symmetric with respect to the $[110]_{cub}$ directions joining growth sectors. These petals, which are not extinguished at 45° , rapidly grow in dimensions from 220 K to 208 K. At 200 K new domains are clearly visible. They suddenly appear near the petals and rapidly propagate in the crystal, mainly near the edge of the cube. The section of the optical indicatrix of these domains is oriented with principal axes roughly parallel to $[110]_{cub}$. The new domains in great number are well visible at 195 K and 188 K.

3.2. X-ray diffraction

In order to determine the symmetry of the prototypic and derived phases, the behaviour of selected Bragg reflections was followed in temperature from 80 K to 300 K. The reflections

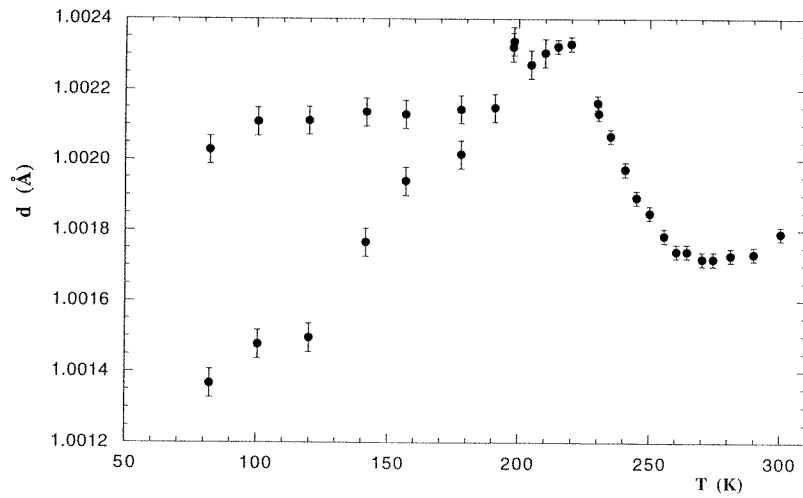


Figure 4. Interplanar distances d , calculated from the position of the 400 reflection, against temperature (measured crystal CRY(100)₂).

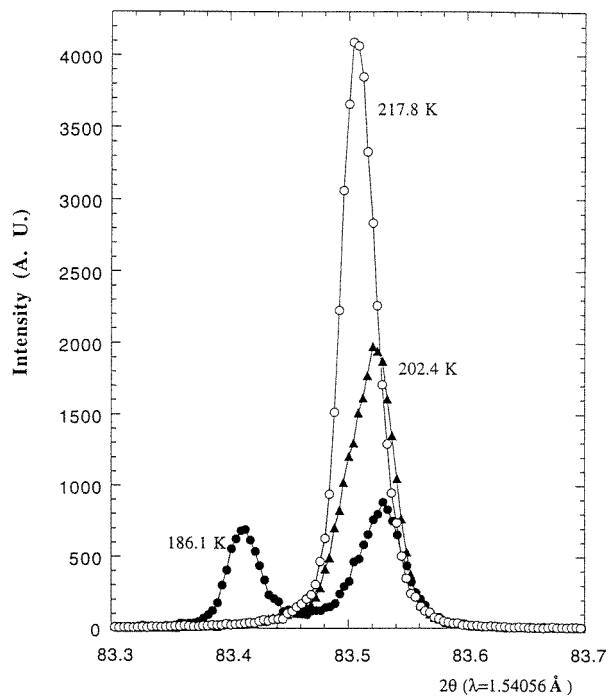


Figure 5. The 222 cubic reflection at different temperatures (measured crystal CRY(111)).

were chosen on the basis of considerations about the possible ferroelastic domain structure of PFT below each phase transition, when the measured samples are in a multidomain state.

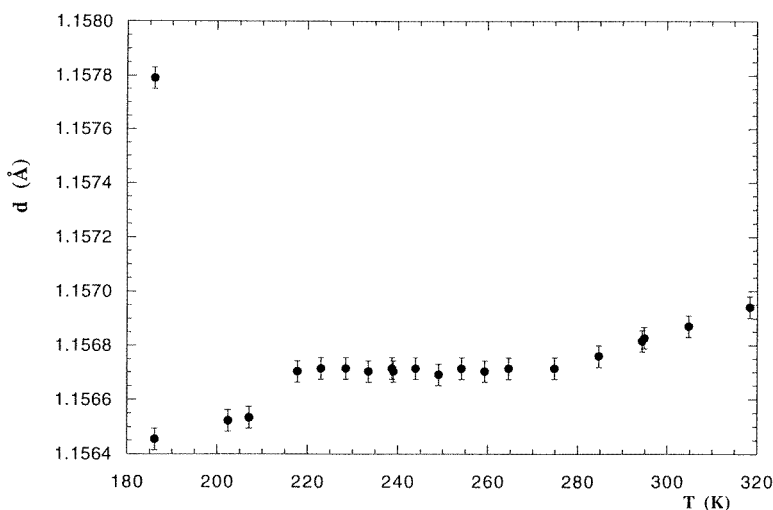


Figure 6. Interplanar distance d , calculated from the position of the 222 reflection, against temperature (measured crystal CRY(111)).

With a cubic prototype, split $h00$ -type reflections characterize a tetragonal distortion, while split hhh -type reflections indicate a rhombohedral distortion. The cubic reflections 400 and 222 were therefore followed with temperature.

The evolution of the 400 cubic reflection was followed on CRY(100)₂. As shown in figure 3, at $T = 82.2$ K a split reflection was clearly observed. In contrast, no split was observed above 219 K. The variation of interplanar distances d , defined by the peak angular position, is reported against temperature in figure 4. Three regions are distinguished: a decrease of the lattice dimension is observed from room temperature down to 270 K: this region identifies the field of stability of the cubic prototype. In the intermediate region $270 > T > 220$ K, in contrast, a rapid increase of the measured lattice dimension is observed on cooling. Finally, for $T < 200$ K, the increasing splitting of the reflections indicates an increasing lattice distortion.

Figure 5 shows the behaviour of the 222 cubic reflection measured on CRY(111). Two split reflections were present below 200 K and a single one above 219 K. The lattice dimension d , defined by the position of the 222 peak, is reported in figure 6. As can be seen, the position of the 222 reflection is independent of temperature for $220 \text{ K} < T < 270 \text{ K}$, which is worth noting for the following discussion.

4. Discussion

X-ray results and optical observations agree with the existence of two phase transitions, with critical temperatures of about $T_{c1} = 270$ K and $T_{c2} = 220$ K. The field of stability of the cubic phase ($T > 270$ K) is identified by the region in which the normal lattice contraction on cooling is observed. Concerning the symmetry changes, the analysis of the line splitting observed below each transition allows us to make the following considerations:

(i) In the intermediate phase no splitting is observed. This could be consistent with a cubic symmetry. However, the contemporary constancy of the cube diagonal (cf figure 6) and the rapid change of one lattice dimension (cf figure 4) indicates that the symmetry of the intermediate phase is tetragonal (or lower). Given its strong dependence on temperature, the

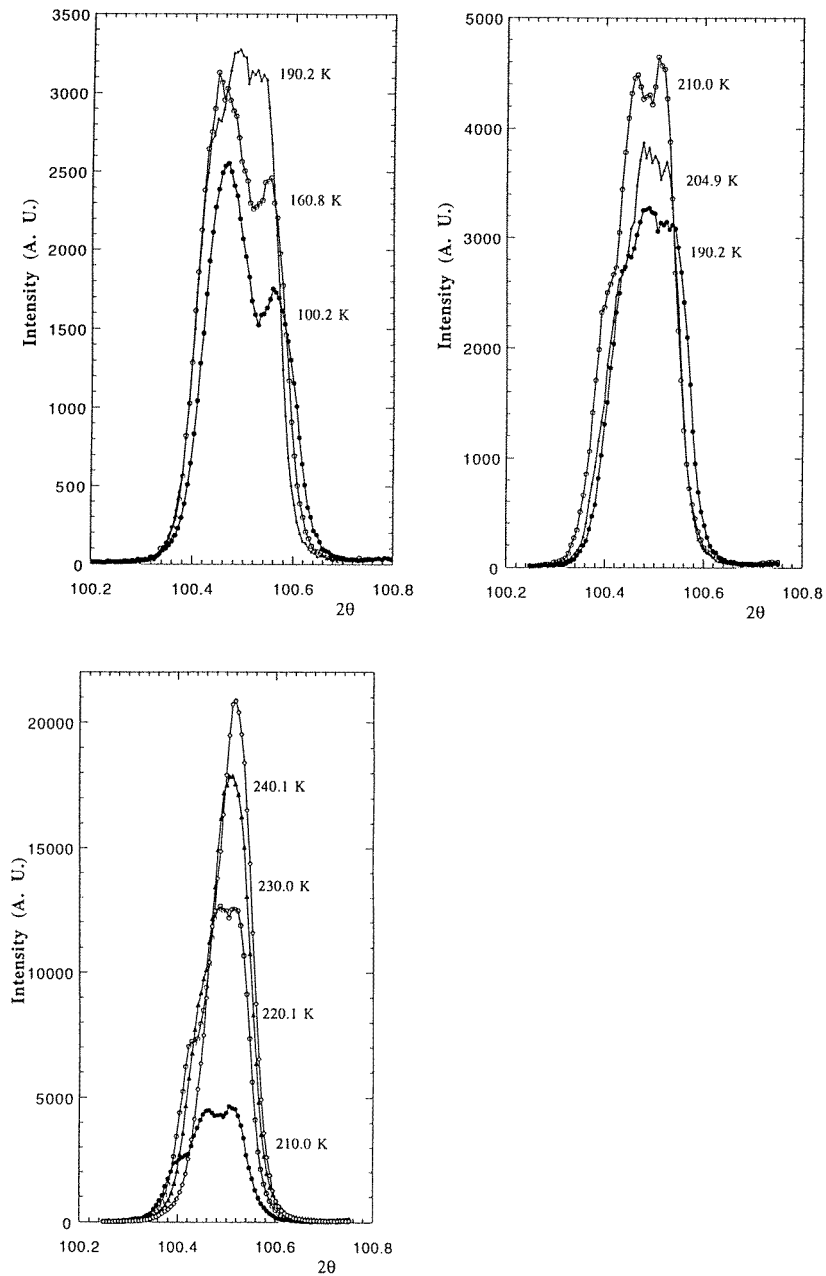


Figure 7. The 400 cubic reflection at different temperatures (measured crystal $CRY(100)_1$).

lattice parameter measured in $CRY(100)_2$ is identified with the polar axis c of a ferroelectric tetragonal phase. The absence of splitting of the 400 reflection indicates that in $CRY(100)_2$ only one among the three possible tetragonal ferroelastic domains is present. This non-statistical domain structure is in agreement with the optical observations. In fact the domain structure of PFT appears to be strongly influenced by the physical constraints imposed by the growth sectors (cf figure 2). Since the (100) natural face of $CRY(100)_2$ belongs to a single growth

sector, with its optical axis normal to the face, a single tetragonal domain with the c axis normal to the analysed face is likely to have formed during the cubic-to-tetragonal transition under x-rays.

(ii) The actual low-temperature symmetry of PFT is lower than rhombohedral. In fact, even if the observed splitting of the 222 reflection for $T < 200$ K (cf figure 5) were consistent with trigonal symmetry, the split of the 400 reflections (cf figure 3) is not. The low-temperature symmetry appears therefore to be monoclinic.

We identify petals and lamellar domains visible at 220 K (cf figure 2) with the monoclinic phase. The nucleation of this phase is likely to be favoured by local deformations at walls joining growth sectors.

No lamellar domains are visible at the transition from the high-temperature phase toward the intermediate one. One reason for this can be suggested in the fact that the crystal has actually undergone, from the optical point of view, a tetragonal-to-tetragonal transition, which is not ferroelastic. In this context it is interesting to note, as we have already remarked [8], the formal coincidence between growth sectors and tetragonal ferroelastic domains in the room-temperature optically anomalous prototype of PFT. In fact the number of differently oriented sectors (i.e. three) coincides with the number of ferroelastic domains expected for a cubic-to-tetragonal transition [9]; and the crystallographic planes joining sectors, i.e. the cubic (110) ones, would be the correct domain walls for such a transition [12]. Therefore in 'cubic' PFT crystals a sort of *morphological tetragonal domain structure* is present that could be at the origin of the observed anomalous birefringence. We propose to call the birefringence of the cubic phase 'precursor', and to consider it as a sign of the incipient phase transition towards the truly tetragonal intermediate phase. Such precursor birefringence reflects anomalies in plastic coefficients, owing to the proximity of the phase transition.

With the aim of obtaining information on the tetragonal parameter a of the intermediate phase, $\text{CRY}(100)_1$ was analysed by x-rays. The 400 reflection was followed against temperature. Results are displayed in figure 7. Between 270 K and 240 K only one reflection was observed, which seems to correspond to parameter a . Below 240 K this reflection disappeared, while the one corresponding to parameter c appeared, which indicates a change of the domain structure. As already found in the other crystals, at low temperature two well split reflections were present, while the splitting disappeared above 220 K. Between 200 K and 220 K more than two peaks were observed, which is probably due to the coexistence of the tetragonal and monoclinic phases (first order transition). However, it was not possible to separate the different reflections and to follow their evolution with temperature.

5. Concluding remarks

By comparing x-ray diffraction and polarized light microscopy, we can definitely assess that two transitions take place in PFT at $T_{c1} = 270$ K and $T_{c2} = 220$ K. The existence of the intermediate phase in the perovskite PFT is then confirmed. The symmetry of this phase appears to be tetragonal. The tetragonal intermediate phase is the only one present at least between 270 K and 220 K.

In contrast to what was assessed in the literature, the low-temperature symmetry of PFT is monoclinic. The monoclinic phase coexists with the tetragonal one between 220 K and 200 K.

Concerning the high-temperature phase, even if a weak asymmetry of the 400 reflection (measured on $\text{CRY}(100)_1$) was observed for $T > 270$ K, its evaluation was at the limit of the experimental resolution herewith adopted. In spite of the evident optical anomaly, therefore, the diffractometric prototypic symmetry of PFT appears to be cubic.

As a final remark, it is interesting to note that the sequence of crystal systems herewith

proposed for PFT is in all respects similar to the one encountered in the perovskite $PbFe_{0.5}Nb_{0.5}O_3$ (PFN), as recently reported [13], apart from an overall shift towards lower temperatures.

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