

The disordered structure of the complex perovskite $\text{Pb}(\text{Fe}_{0.5}\text{Ta}_{0.5})\text{O}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 8201

(<http://iopscience.iop.org/0953-8984/9/39/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 10:37

Please note that [terms and conditions apply](#).

The disordered structure of the complex perovskite $\text{Pb}(\text{Fe}_{0.5}\text{Ta}_{0.5})\text{O}_3$

Alessandra Geddo Lehmann[†], Frank Kubel[‡] and Hans Schmid[‡]

[†] Dipartimento di Scienze Fisiche, Università di Cagliari, Via Ospedale 72, 09124 Cagliari, Italy

[‡] Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, 30 Quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

Received 19 February 1997, in final form 1 July 1997

Abstract. The structure of the complex perovskite $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PFT), which belongs, according to the literature, to the ferroic species $m\bar{3}mF3m$, has been refined by single-crystal and powder x-ray diffraction at room temperature, i.e. within the range of stability of the cubic phase. Attention has been paid to the possible presence of tetragonal spontaneous strain, suggested by the anomalous uniaxial birefringence of each $(100)_{\text{cub}}$ pyramidal growth sector. A crystal cut from a single growth sector was measured and compared with an as-grown one. Several models, both cubic ($Pm\bar{3}m$) and tetragonal ($P4/mmm$), these latter used in refining the single growth sector, are compared. The main feature of all the refined structures is the positional disorder at the Pb site, the importance of which in connection with the ferroic transitions is briefly discussed.

1. Introduction

The complex perovskite $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PFT), first prepared as a ceramic by Smolenskii *et al* [1] in 1959, presents some unsolved crystallographic problems. This compound belongs to the wide family of lead-based oxides with general formula $\text{PbB}'_{0.5}\text{B}''_{0.5}\text{O}_3$, in which two cationic species, in a 1:1 ratio, occupy the B-site lattice of the perovskite structure ABO_3 . These materials have been and still are extensively studied for their interesting ferroic behaviour. They generally undergo a sequence of temperature-induced phase transitions, which can either be purely structural (ferroelastic) or lead to ferro/antiferroelectric, ferro/antiferromagnetic final states. Phase transitions in perovskite-type compounds consist in small modifications of a high-symmetry, ideally undistorted structure—the one stable at the highest temperatures—which is called the *parent phase* or *prototype*. 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. A rather complete compilation of the known structural data at room temperature and below the ferroic phase transitions are found in [2] and [3]. Clear insights about symmetry aspects of ferroic transitions are contained in [4].

The sequence of phases in PFT one can find in Landolt–Börnstein [2], i.e. the one determined for ceramic samples, is 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^{5+} statistically distributed over B sites. A transition, slightly smeared, around 243 K leads to a derived equitranslational ferroelectric phase, the most likely symmetry of which was indicated as rhombohedral $R\bar{3}m$ [5, 6]. Even if none of the previous structural modifications has been fully characterized from

a diffractometric point of view, there is apparently general agreement on their symmetries, so that PFT would be assigned to the ferroic species $m\bar{3}mF3m$, in the Aizu notation [7].

However, the previous picture has become more complicated since single crystals were synthesized [8]. Observations by polarized light microscopy of thin crystal sections of PFT identified two main unsolved and interconnected problems, as described in the following.

The most intriguing problem concerns the *cubic* room-temperature phase: it was found that crystals of PFT grown from PbO flux, which display the {100} cubic form, are actually composed of six pyramidal growth sectors uniaxial from the point of view of optical symmetry (figure 1(a)). The value of the birefringence, due to a positive tetragonal indicatrix, is of the order of 10^{-4} . Sectors are disposed in such a way to give individual crystals with octahedral point symmetry (figure 1(b)).

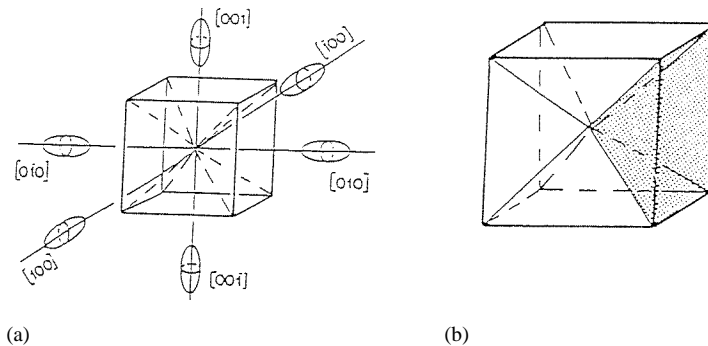


Figure 1. (a) Orientational states of the uniaxial indicatrix with respect to (100) growth sectors. (b) Optically tetragonal sectors disposed to give individuals with overall octahedral symmetry.

In a previous work [9] we discussed the hypothesis that the *optical anomaly* might have structural origin and might arise from spontaneous tetragonal strain hidden to a diffractometric analysis performed with conventional resolution on powder. To gain indications about the correctness of this hypothesis, we tried first of all to evidentiate ferroelastic properties in the optically tetragonal phase, which would have proved its derived character from a crystal system of higher symmetry. Attempts at ferroelastic switching of domains were performed by the application of concentrate load perpendicular to optically c-type growth sectors, i.e. sectors cut normally to their optical axis, thus appearing always dark when observed between crossed polarizers. Results of such experiments are recalled for the sake of clarity: irreversible birefringent regions were created around the point of indentation, shaped as rosettes with four or eight bright petals (figure 2). In analogy with the interpretation adopted for the identical experimental result in tetragonal barium titanate [10], such petals were suggested to be a-type ferroelastic domains rotated through 90° with respect to the original one. The phase transition toward a cubic paraelastic phase above room temperature was then looked for. With this aim, we followed under the optical microscope changes of the birefringence Δn of a-type sectors, i.e. sectors cut parallel to the principal section of the uniaxial indicatrix. As known, the value of Δn should tend to zero approaching the transition to the undistorted phase. However, we were unable to reveal any transformation up to at least 750°C [9]. Above this temperature, even our thinnest sections ($20\ \mu\text{m}$) appeared completely dark because of strong absorption due to Fe^{3+} . No thermal signal was detected in DTA up to 950°C .

In the absence of a phase transition toward the ideally undistorted phase, the recognized optical symmetry of growth sectors has to be taken as the prototype symmetry of PFT.

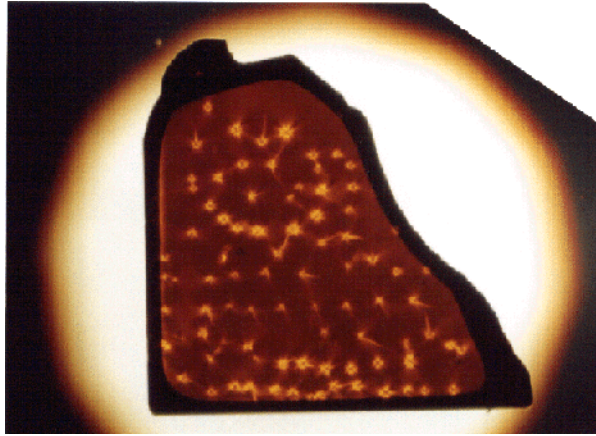


Figure 2. Birefringent rosettes, obtained by indentation of a c-type growth sector, seen under a polarized light microscope. The crystal is a $(100)_{cub}$ section ($60 \mu\text{m}$ thick) cut very near to the natural (100) face of an as-grown cube. In the absence of indentation rosettes, it would appear always extinguished at any azimuth: in fact such a section contains, in practice, only the growth sector having its optical axis perpendicular to the surface. Rosettes are observed between crossed Nicols with their transmission directions parallel to $[110]_{cub}$.

The birefringent rosettes then receive an alternative explanation. Instead of being switched ferroelastic domains, they might arise from stress field around dislocations mechanically created in the tetragonally strained matrix. This last picture is corroborated by the result shown in figure 3, in which the rosettes produced by indentation were obtained in three adjacent growth sectors, both c-type (central, dark) and a-type (top and left lateral, bright): as can be seen, the symmetry of the rosettes reflects the orientation of the tetragonal lattice with respect to each sector (cf figure 1).

The problem of the correct symmetry of the prototype reflects itself in the possible symmetry of the ferroelectric phase: in fact with a tetragonal prototype the rhombohedral symmetry assessed until now below the phase transition is unlikely because of the lack of group-subgroup relations.

In our opinion the revision of the phase sequence of PFT in terms of crystal systems is necessary. As a first step in that direction we report in this paper the refinement, which was hitherto lacking, of the PFT structure at room temperature by single-crystal x-ray diffraction. With the aim of reconciling optical and diffractometric symmetries, results from intensities of single growth sectors displaying uniaxial optical symmetry will be discussed. Cubic and tetragonal structural models will be compared.

2. Experimental details

2.1. Crystal morphology and optics

Single crystals of $PbFe_{0.5}Ta_{0.5}O_3$ were grown in sealed Pt crucibles by slow cooling of a high-temperature solution by the flux method as described in [8]. Crystals always display the $\{100\}$ cubic form. Growth sectors are present, such that the obtained cube shaped crystals are sectorized into six $(100)_{cub}$ growth pyramids. As we have already remarked [9], the optical symmetry of each growth sector is uniaxial, with tetragonal positive indicatrix oriented as in figure 1(a).

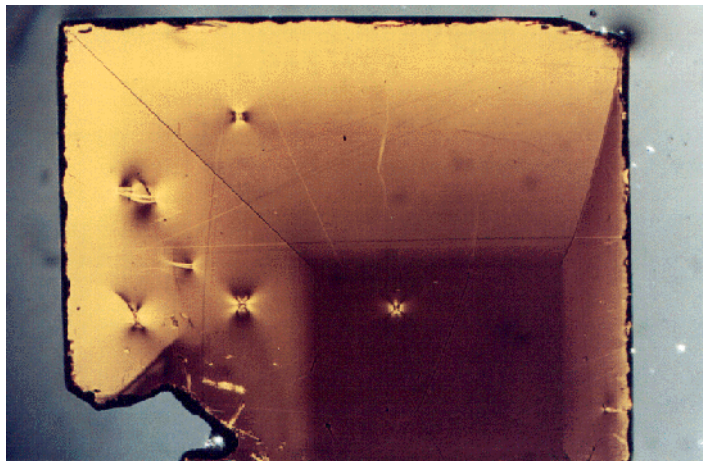


Figure 3. The effect of indentation on three adjacent (100) sectors. Central, c-type; symmetry of the rosette, fourfold. Top and left lateral, a-type; symmetry of the rosette, twofold. The crystal is a $(100)_{\text{cub}}$ section ($60 \mu\text{m}$ thick) cut at a suitable depth within an as-grown cube so to contain the three orientational states of the optically tetragonal axis (cf figure 1). Rosettes are visible between crossed Nicols parallel to $[110]_{\text{cub}}$.

2.2. Choice of samples for x-ray measurements

Results for the following two crystals, representative of many measured ones, will be compared.

(1) CRYPOLY: an as-grown small crystal chosen for its favourable shape (for absorption correction). It showed, like all other natural crystals, a complex birefringence pattern when observed at high magnification in immersion oils. Dimension: $V = 0.288 \times 10^{-2} \text{ mm}^3$.

(2) CRYMONO: a crystal cut from a single growth sector to assure the presence of only one orientation on the optical indicatrix. Parallel faces for optical observations were mechanically polished. Photographs of CRYMONO between crossed polarizers are shown in figure 4(a) and (b), in which the optically tetragonal axis $[001]$ is in the plane of the photos. Dimensions: $(0.22 \times 0.24 \times 0.05) \text{ mm}^3$.

2.3. Collection of x-ray intensities

Intensity measurements were performed at room temperature on a STOE four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) in θ - 2θ scan mode (measuring time 7 s/step). Cell constants were determined by using 25 reflections and refined to the values $a = 4.0073(2) \text{ \AA}$ (CRYPOLY) and $a = 4.0076(2) \text{ \AA}$ (CRYMONO). Experimental conditions for single-crystal data collections are summarized in table 1. Measured unique reflections were reduced by Lorentz polarization and absorption corrections, this latter performed analytically by considering the shape of the crystals. Observed unique reflections were refined using the program XTAL [11], by minimizing the function $\sum w_i (F_i^r - F_i^c/k_i)^2$. Extinction correction was applied. The weighting scheme $w_i = 1/\sigma_i^2(F^r)_i$, based on counting statistics alone, was adopted. This weighting scheme is usually applied to those perovskites in which weak difference reflections are not present, as undistorted cubic aristotypes or ettotypes without octahedral tilting. For instance, the weight $1/\sigma_i^2(F^r)_i$

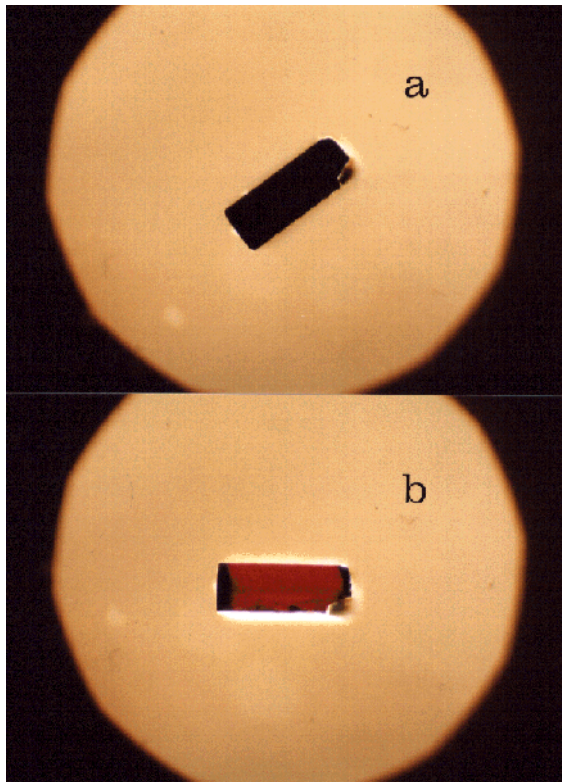


Figure 4. Crystal CRYMONO cut and polished from a single sector viewed between crossed polarizers. The tetragonal c axis lies in the plane of the figure. (a) Crystal in extinction, (b) polarizers parallel to $[110]_{cub}$.

Table 1. Experimental details for x-ray data collection. Diffractometer: STOE, Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$, ω - 2θ scan.

Sample	CRYPOLY	CRYMONO
Crystal volume (mm^3)	0.288×10^{-2}	3×10^{-2}
a (\AA)	4.0073(2)	4.0076(2)
$\frac{\sin \theta_{min}}{\lambda}$ (\AA^{-1})	0.125	0.125
$\frac{\sin \theta_{max}}{\lambda}$ (\AA^{-1})	0.958	1.143
θ range ($^\circ$)	5.1–42.9	5.1–54.3
Range of hkl	hkl from -7 to 7	hkl from -9 to 9
Absorption correction	analytical	analytical
μ (calculated) (mm^{-1})	89.1	88.9
Refined in symmetry	$Pm\bar{3}m$	$P4/mmm$
Measured unique reflections	1896	2947
Observed unique reflections ($>3\sigma$)	74	282

has been applied in refinements of the prototype in the case of $PbFe_{0.5}Nb_{0.5}O_3$ [12] and $PbMg_{0.33}Nb_{0.67}O_3$ [13]. Different weighting schemes are suitable when important structural information is thought to be contained in very weak reflections. For example, in a recent detailed reinvestigation of the orthorhombic structure of $PbZrO_3$ [14] from x-ray data, a Tukey–Prince weighting scheme with three parameters was adopted for the purpose of

examining the crystal pseudo-symmetry, by carefully checking weak l -odd reflections, which would have been obviously weighted down by the usually applied statistic weight $w_i = 1/\sigma_i^2(F^r)_i$ [14].

Actually, the relevant R factors in Pb-based perovskites without complex cell doublings seem to be rather related to a not completely satisfactory absorption correction [15]. Owing to the large absorption coefficient of PFT (μ calculated $\approx 90 \text{ mm}^{-1}$), small crystals should be measured, but this reduces the accuracy on crystal shape. Moreover, in the case of CRYMONO, which was cut by hand from within a single growth sector of a crystal containing six such sectors and then shaped as a parallelepiped by polishing, it was not possible to reduce the dimensions below $V = 3 \times 10^{-2} \text{ mm}^3$ (R_{int} before and after absorption correction 12.2 and 5.9).

Powder diffractograms were collected at room temperature for ground crystals on a Philips diffractometer (Bragg–Brentano geometry) with Cu $K\alpha$ radiation (step scan 0.005° , measuring time 7 s). Structure refinement was performed by the Rietveld method, with a PC version of the program DBWS [16].

3. Structure refinement

The ideal cubic perovskite structure was taken as a starting model for cubic refinement of CRYPOLY. Refinements in tetragonal symmetry were performed for CRYMONO, i.e. the crystal containing just one orientational state of the optical indicatrix.

3.1. Background: Pb disorder in the prototype of $\text{PbB}'_{0.5}\text{B}''_{0.5}\text{O}_3$ compounds

The cubic prototype of Pb-based 1:1 complex perovskites has some peculiar structural features which will be described in the following. The ideal structure is shown in figure 5 for statistical disorder on site B; the ideal structure has symmetry $Pm\bar{3}m$ and a lattice parameter of about 4 Å; Pb is at the origin of the cell, B and B' share the central octahedral site and oxygen atoms are located at the centres of the faces of the cube. Depending upon ionic radii and charges, 1:1 long-range ordering of octahedral cations may occur with formation of a centred cell with the $(\text{NH}_4)_3\text{FeF}_6$ structure, of symmetry $Fm\bar{3}m$ and double cell parameter. Compounds with ordered prototype are sometime called in the literature 'double perovskites' and are indicated with double stoichiometry. For example, Pb_2CoWO_6 , thermally annealed $\text{Pb}_2\text{ScTaO}_6$, Pb_2MgWO_6 , $\text{Pb}_2\text{MgTeO}_6$ and $\text{Pb}_2\text{YbNbO}_6$ have the double $Fm\bar{3}m$ prototype. In contrast $\text{PbYb}_{0.5}\text{Ta}_{0.5}\text{O}_3$, $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ and $\text{PbCo}_{0.33}\text{Nb}_{0.67}\text{O}_3$ are disordered, with prototypic symmetry $Pm\bar{3}m$. Much work, both theoretical and experimental, has been devoted to the study of the effect of different degrees of B-site substitutional disorder on the character (normal or relaxor-type) of the ferroelectric transition [17–24].

In spite of its apparent simplicity, the ideal structure seems to be never realized in real samples. The most recent diffractometric studies revealed, on the contrary, a high degree of cationic *positional disorder*, to which, in view of its fundamental interest in perovskites, great attention must be paid.

Structure refinements, performed either on powders or on single crystals when available, have been published for the prototype of seven compounds, i.e. Pb_2CoWO_6 ($Fm\bar{3}m$) [15], $\text{Pb}_2\text{MgTeO}_6$ ($Fm\bar{3}m$) [25], Pb_2MgWO_6 ($Fm\bar{3}m$) [26], $\text{PbSc}_{0.5}(\text{Ti}_{0.25}\text{Te}_{0.25})\text{O}_3$ ($Fm\bar{3}m$) [27], ordered $\text{Pb}_2\text{ScTaO}_6$ [24] and $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ [12] and the relaxor-type compound $\text{PbMg}_{0.33}\text{Nb}_{0.67}\text{O}_3$ ($Pm\bar{3}m$) [13, 24], which belongs to the strictly related family with 1:2 cationic ratio. In all these phases, neither Pb nor B' and B'' were found at their ideal special Wyckoff positions, being instead statistically split over several sites around them.

Split positions were also proposed for oxygen. B-type positional disorder was found to be superimposed on the substitutional one in the case of $PbMg_{0.33}Nb_{0.67}O_3$. The split sites can be chosen among the sets of Wyckoff positions listed for the $Pm\bar{3}m$ or $Fm\bar{3}m$ space group. Taking into consideration only the disorder at Pb site, which is the most evident in x-ray measurements, we can represent the different disordered models of symmetry $Pm\bar{3}m$, which is appropriate for random occupation of B sites as in PFT, as in figure 5. In this figure, the simple form polyhedra for the cubic holohedry $4/m\bar{3}2/m$, corresponding to the different sets of Wyckoff positions, are drawn around the origin of the cell. In the disordered structures, n equal fractions of Pb must be imagined to occupy the centre of the n faces of the polyhedra.

3.2. Refinement of CRYPOLY in $Pm\bar{3}m$ symmetry: A-site disorder

Atoms were at first fixed at special positions: one Pb in 1 a , (0.5Fe + 0.5 Ta) in 1 b , three O in 3 c . With Pb at the origin of the cell, the residual did not attain R values lower than 18%, even with anisotropic atomic displacements refined. The final atomic displacements for Pb were abnormally large. In order to retain the cubic symmetry, split positions were adopted for Pb. In contrast, iron, tantalum and oxygen were left at their special sites, after verification that their displacements did not improve the refinement.

Table 2. Comparison among Pb-disordered cubic models for PFT. R and R_w from F; space group $Pm\bar{3}m$; origin at (0, 0, 0).

Model	{x00}	{xxx}	{xx0}	{xxz}
R	0.029	0.032	0.030	0.034
R_w	0.033	0.031	0.031	0.031
x_{Pb} (Å)	0.249(3)	0.139(3)	0.187(3)	0.092(3)
y_{Pb} (Å)	0	0.139(3)	0.187(3)	0.092(3)
z_{Pb} (Å)	0	0.139(3)	0	0.268(4)
$d_{(Pb-origin)}$ (Å)	0.249(3)	0.241(5)	0.264(4)	0.298(5)

Table 3. Structure refinement of PFT single-crystal data in the {x00} disordered cubic model (CRYPOLY). Space group $Pm\bar{3}m$ (No 221). $a = 4.0073(2)$ Å. Atomic positions, isotropic displacements, site occupation parameters (Pop), anisotropic atomic displacements ($U_{12} = U_{13} = U_{23} = 0$ for given symmetry). U_{is} of Fe and Ta are constrained. $R = 0.029$; $R_w = 0.033$; $S(\text{goF}) = 2.723(5)$; observed unique reflections = 74.

Atom	x/a	y/a	z/a	U_{is}	Pop	U_{11}	U_{22}	U_{33}
Pb	0.0621(7)	0	0	0.0221(4)	0.1667	0.0144(6)	0.0260(7)	U_{22}
Fe	1/2	1/2	1/2	0.0065(2)	0.5	0.0065(3)	U_{11}	U_{11}
Ta	1/2	1/2	1/2	0.0065(2)	0.5	0.0065(3)	U_{11}	U_{11}
O	1/2	1/2	0	0.0144(8)	1	0.0172(1)	U_{11}	0.009(2)

The structure was very well refined as cubic disordered, with disorder confined only at the Pb site. Most models represented in figure 5 gave comparable results, as can be seen from table 2, in which some of them are briefly compared. To choose a particular set of Wyckoff positions for Pb is, at least at this level, to a great extent a matter of personal

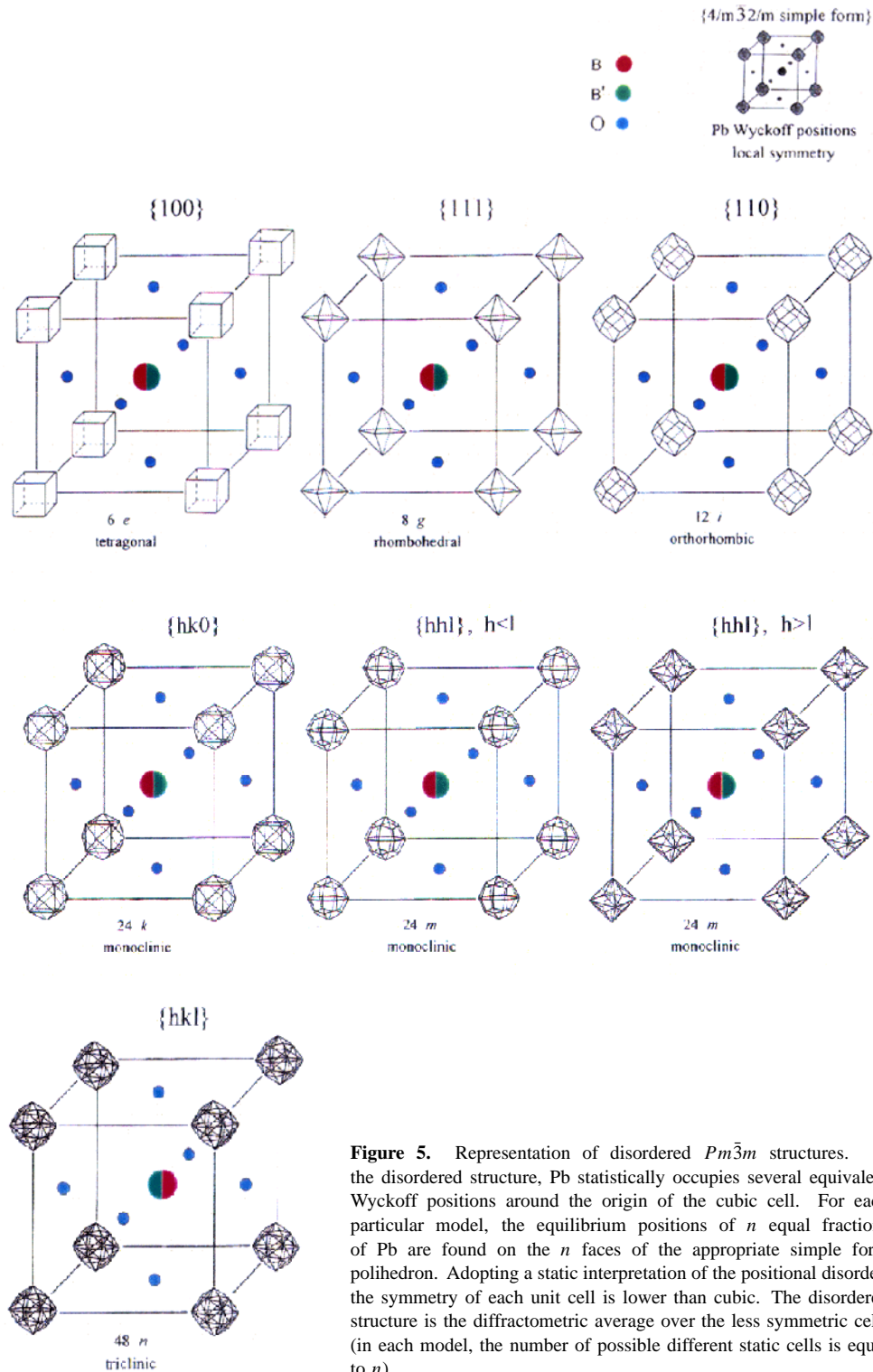


Figure 5. Representation of disordered $Pm\bar{3}m$ structures. In the disordered structure, Pb statistically occupies several equivalent Wyckoff positions around the origin of the cubic cell. For each particular model, the equilibrium positions of n equal fractions of Pb are found on the n faces of the appropriate simple form polyhedron. Adopting a static interpretation of the positional disorder, the symmetry of each unit cell is lower than cubic. The disordered structure is the diffractometric average over the less symmetric cells (in each model, the number of possible different static cells is equal to n).

taste. We propose herein to adopt the $\{x00\}$ model. This choice can be eurystically justified with a static interpretation of the positional disorder: in fact in this approach the cubic disordered structure reflects the overall symmetry averaged over a large number of cells, each one of tetragonal symmetry if Pb is on $(x00)$ positions (cf figure 5). Correlations among such unit cells could explain the observed birefringence. However, we must say that precession photographs collected with copper and molybdenum radiation did not reveal diffuse scattering beside the thermal one, in spite of long exposure time.

The refined atomic positions and atomic displacements for the $\{x00\}$ -disordered cubic structure are reported in table 3.

3.3. Some considerations about the A-site disorder: the hypothesis of mimetic twinning and x-ray refinement on powder

In contrast to the refined disordered structure, attention has been paid to the possible existence of a less symmetric but ordered model. In particular we posed ourselves the question of whether the analysed crystals could be twinned, because it is known that twinning can simulate a disordered structure [28].

In the case of PFT, an interesting point is the formal coincidence between $(100)_{cub}$ growth sectors and transformation twins (domains) for the cubic-to-tetragonal transition defined by the ferroic species $m\bar{3}mF4/mmm$ (or $m\bar{3}mF4mm$) [4, 7]. In fact the orientational states of the optical indicatrix identified by the sectors are three in number (see figure 1(b)) and the $(110)_{cub}$ crystallographic planes, joining adjacent sectors, are the correct domain walls [29]. The disordered cubic structure could then arise from twinning of ordered tetragonal domains, the structure of which would have Pb displaced just toward one of the three equivalent $[100]$ cubic directions. The main objection to the hypothesis of twinning is that crystals cut from a single sector, which would be single domain, would have had clearly revealed this more ordered structure, which did not happen. However, we thought there could be a problem of microtwinning within each growth sector. Given the fact that twinning does not affect powders, ground crystals were analysed by powder x-ray diffraction. The main results of the analysis were the following: the pattern geometry was cubic, without any sign of tetragonal splitting or line broadening. As far as conventional resolution is employed, the metric of PFT appears cubic beyond any doubt. As concerns the crystal structure, we again found it necessary to introduce a split position for Pb to lower the residual below $R_{wp} = 15\%$. Results in the $Pm\bar{3}m - \{x00\}$ model were $R_p = 2.6\%$, $R_{wp} = 4.0\%$, $R_{exp} = 1.2\%$, $S = 3.3$ and $R_{Bragg} = 3.9\%$ with $x_{Pb} = 0.077(2)$, in reasonable agreement with single-crystal results. It can then be assessed that the disorder of Pb atoms is a characteristic feature of the structure of PFT and that it must be retained in the choice of a model, no matter whether cubic or tetragonal.

3.4. Refinement of CRYMONO in tetragonal symmetry

Taking into account the uniaxial character of CRYMONO, refinements in tetragonal symmetry were attempted. We tested several models of symmetry $P4/mmm$, because the room-temperature phase of PFT is known to be paraelectric.

In all cases it was necessary to split Pb over several sites to attain a reasonable refinement. We retained an $\{x00\}$ disordered configuration of Pb, with reference to a calculation performed on $PbTiO_3$ [30], in which Pb was found to be dynamically split over six sites along the $[100]$ cubic directions. In the first tested model the tetragonal strain was ascribed to different population of the six $(x00)$ sites (actually 2 g $(00z)$ and 4j $(x00)$),

with reference to the *six-site model* [31]. However, there was no gain compared to the statistical distribution and the refinement became unstable. Further approaches made clear that any attempts at altering the Pb configuration failed in leading to a good refinement. For example, a model with axial disorder of Pb, i.e. based on a centrosymmetric analogue of tetragonal barium titanate (with half Pb in $+z$ and half in $-z$), completely failed. The same was true for models containing a so to speak 'strong' degree of axial anisotropy, like the axial disorder of Fe/Ta.

A good tetragonal model appeared to be the one shown in figure 6. The weak uniaxial anisotropy rises from planar disorder of Fe/Ta atoms, which are split on $4k$ positions in the plane perpendicular to the unique c axis. In a first step we fixed both O(1) and O(2) in ideal positions. Pb(1) and Pb(2) distances from ideal positions were constrained to the same value. When this constraint was not imposed, refined x Pb(1) and z Pb(2) spontaneously converged to the same value within the estimated standard deviation. As we noted that oxygen atomic displacements attained rather large values, in a successive stage we introduced disorder at oxygen site O(1), the one above and below the Fe/Ta species in the unit cell, to have for anions the same kind of planar disorder as adopted for the small cationic species. The refinement with such an additional planar splitting of O(1) on $4j$ positions is reported in table 4. The quality of agreement coefficients for the two models—with or without O(1) disorder—is, however, almost the same, as can be read in caption of table 4. The model of figure 6, with its weak planar anisotropy, was considered with interest because we noted, while grinding crystals for powder preparation, a tendency to form lamellae parallel to the (100) plane. This was evident in Bragg–Brentano x-ray diffraction, which posed us serious problems of preferred orientation, with very strong enhancement of $h00$ reflections.

It can be interesting to compare the results of table 4 with a refinement performed in the same tetragonal symmetry but without Fe/Ta planar disorder, i.e. with B-type cations fixed in $1/2, 1/2, 1/2$. This limit case of the $P4/mmm$ model corresponds in all respects to the cubic structure adopted for CRYPOLY. With such a model the fitting coefficients were $R = 0.061$, $R_w = 0.042$, $S = 3.21(12)$, significantly worse, in spite of the greater number of free parameters, than in the cubic models.

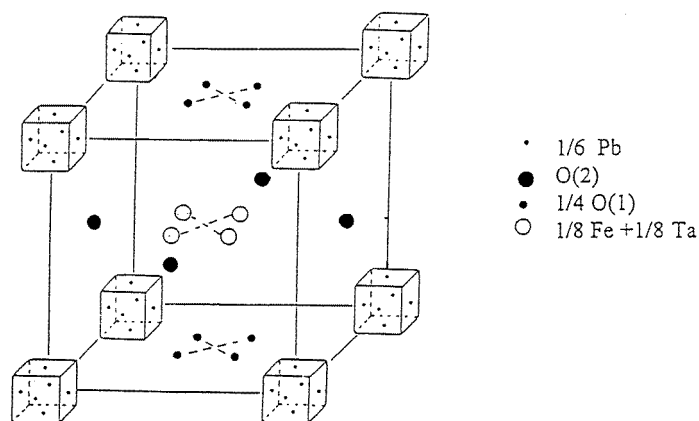


Figure 6. Tetragonal model herewith proposed for $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (cf table 4).

Table 4. Structure refinement of PFT from single-crystal data in tetragonal symmetry (CRYMONO). Space group $P4/mmm$ (No 123) $a = c = 4.0076(2)$ Å. Atomic positions, isotropic displacements, site occupation parameters (Pop), anisotropic atomic displacements ($U_{12} = U_{13} = U_{23} = 0$ for given symmetry). $R = 0.046$; $R_w = 0.027$; $S(\text{goF}) = 2.06(5)$; observed unique reflections = 282; (NB without O(1) disorder $R = 0.040$, $R_w = 0.030$, $S = 1.96(9)$).

Atom	x/a	y/b	z/c	U_{is}	Pop	U_{11}	U_{22}	U_{33}
Pb(1)	0.0617(2)	0	0	0.0214(2)	0.1667	0.0135(3)	0.0273(4)	0.0244(3)
Pb(2)	0	0	0.0617(2)	0.0215(3)	0.1667	0.0263(4)	U_{11}	0.0114(3)
Fe	0.5093(3)	0.5093(3)	1/2	0.0061(1)	0.1250	0.0061(1)		
Ta	0.5093(3)	0.5093(3)	1/2	0.0061(1)	0.1250	0.0061(1)		
O(1)	0.5257(10)	0.5257(10)	0	0.0063(5)	0.25	0.0063(5)		
O(2)	0	1/2	1/2	0.0147(6)	1	0.0071(8)	0.020(1)	0.017(1)

4. Discussion: the disorder of Pb in connection with the ferroic transitions

The disordered configuration of Pb has been shown to be the most interesting feature of the refined structure of PFT, whether tetragonal or cubic.

This compound then increments the list of Pb-based complex perovskites with A-site positional disorder. Beside the general interest in disordered crystalline structures, the particular importance of this kind of disorder—whether at site A or B—in perovskite-type ferroics resides in the fact that its presence seems to imply an order–disorder component even in those which were traditionally considered the most typical examples of displacive phase transitions. Positional disorder at site B has been discussed in the framework of the so-called *eight-site model* [32], according to which the sequence of distortive ferroelectric transitions in perovskites would be better regarded as a sequence of order–disorder processes taking place at the octahedral sites. The model, proposed for barium titanate and potassium niobate, suggests that starting from the isotropic (i.e. cubic) situation in which the cation B has access to eight equivalent sites disposed symmetrically along $[111]_{cub}$ directions around the $(1/2, 1/2, 1/2)$ Wyckoff position, the low-temperature phases, i.e. the tetragonal, then the orthorhombic and finally the rhombohedral ones, are obtained by constraining the B cation to occupy just four, then two and finally one of the eight previous sites.

The hypothesis can be formulated that an analogous model is valid for site A in all compounds which have Pb^{2+} as large cationic species. Stereochemical considerations suggest, in fact, that the ion Pb^{2+} , with its lone pair of electrons, would never be found at the origin of the cubic perovskite cell, as has been stressed for example in [33]. One way to retain the cubic symmetry would be the adoption of a split configuration. At least if the disorder of Pb is thermally activated, transitions towards more ordered, less symmetric phases can occur when the temperature is lowered. Such transitions, which do not concern directly the B-oxygen octahedra, may be not connected to *ferroelectricity*, but it can be argued that they would be important in the case of *antiferroelectricity*, in which antiparallel displacements of Pb in adjacent unit cells are directly involved.

5. Concluding remarks

Single-crystal and powder x-ray diffraction data have been refined for the room-temperature phase of $PbFe_{0.5}Ta_{0.5}O_3$. In spite of the evident optical anomaly, according to which so-called ‘cubic’ crystals are actually uniaxial, the diffractometric lattice symmetry of PFT appears to be cubic, at least at the level of experimental resolution adopted in this work.

However, the structure of crystals cut from a single uniaxial growth sector can be refined in tetragonal symmetry (cf table 4), with a weak gain with respect to cubic models. Even if the obtained gain is at the limit of the potentiality of the experimental method, adopted herein, nevertheless it appears to be significant when considered together with the optical analyses.

The tetragonal character of the refined structure is in any case weak. The etiology of the evident optical anisotropy of PFT, whether it is connected with structural properties or related to extrinsic factors, need further investigations. The presence of dislocations at the boundaries between growth sectors is likely to play a role. We hope to contribute to the solution of this problem by high-resolution x-ray structural investigations, the results of which, still under analysis, will be communicated in our next paper.

References

- [1] Smolenskii G A, Agranovskaia A I and Ysupov V A 1959 *Fiz. Tverd. Tela* **1** 990 (Engl. Transl. *Sov. Phys.—Solid State* **1** 907)
- [2] *Landolt–Börnstein New Series* 1990 Group III, vol 28 (Berlin: Springer)
- [3] Galasso F 1969 *Structure, Properties and Preparation of Perovskite-type Compounds* (New York: Pergamon)
- [4] Salje E K H 1990 *Phase Transitions in Ferroelastic and Co-elastic Crystals (Cambridge Topics in Mineral Physics and Chemistry)* student edn (Cambridge: Cambridge University Press)
- [5] Nomura S, Takabayashi H and Nakagawa T 1968 *Japan. J. Appl. Phys.* **7** 600
- [6] Nomura S, Kaneta K and Abe M 1978 *Japan. J. Appl. Phys.* **18** 681
- [7] Aizu K 1969 *J. Phys. Soc. Japan* **27** 387
- [8] Brixel W, Boutellier R and Schmid H 1987 *J. Cryst. Growth* **82** 396
- [9] Geddo Lehmann A, Kubel F, Ye Z-G and Schmid H 1995 *Ferroelectrics* **172** 277
- [10] Grekov A A, Kramarov S O and Borodina V V 1996 *Ferroelectrics* at press
- [11] Hall S R and Stewart J M 1987 *XTAL3.0 User's Manual* (University of Western Australia and Maryland)
- [12] Kolesova R and Kupriyanov M 1993 *Phase Transitions* **45** 271
- [13] Verbaere A, Piffard Y, Ye Z-G and Husson E 1992 *Mater. Res. Bull.* **27** 1927
- [14] Corker D L, Glazer A M, Dec J, Roleder K and Whatmore R W 1997 *Acta Crystallogr. B* **53** 135
- [15] Baldinozzi G, Sciau Ph and Lapasset J 1992 *Phys. Status Solidi a* **133** 17
- [16] DBWS, Sakthivel A and Young R A School of Physics, Institute of Technology, Atlanta, GA 30332
- [17] Stenger C G F and Burgraaf A J 1980 *Phys. Status Solidi a* **61** 275
- [18] Stenger C G F and Burgraaf A J 1980 *Phys. Status Solidi a* **61** 653
- [19] Setter N A and Cross L E 1980a *J. Mater. Sci.* **15** 2478
- [20] Setter N A and Cross L E 1980b *J. Appl. Phys.* **51** 4356
- [21] Smolenskii G A 1970 *Proc. 2nd Meeting on Ferroelectricity (Kyoto, 1969) J. Phys. Soc. Japan* **28** (Supplement) 26
- [22] Cross L E 1987 *Ferroelectrics* **76** 241
- [23] Randall C A and Bhalla A S 1990 *Japan. J. Appl. Phys.* **29** 327
- [24] Zhukov S G, Chernyshev V V and Aslanov L A 1995 *J. Appl. Crystallogr.* **28** 385
- [25] Baldinozzi G, Sciau Ph and Buffat P A 1993 *Solid State Commun.* **86** 541
- [26] Baldinozzi G, Sciau Ph, Pinot M and Grebille D 1995 *Acta Crystallogr. B* **51** 668
- [27] Alonso J A and Rasines I 1988 *J. Phys. Chem. Solids* **49** 385
- [28] Flack H D 1987 *Acta Crystallogr. A* **43** 564
- [29] Sapriel J 1975 *Phys. Rev. B* **12** 5128
- [30] Nelmes R J, Piltz R O, Kuhs W F, Tun Z and Restori R 1990 *Ferroelectrics* **108** 165
- [31] Godefroy L, Derouiche A and Benzagouta A 1984 *Ferroelectrics* **54** 13
- [32] Comes R, Lambert M and Guinier A 1970 *Acta Crystallogr. A* **26** 244
- [33] de Nathan N, Husson E, Calvarin G, Gavarrri J R, Hewatt A W and Morewell A 1991 *J. Phys.: Condens. Matter* **3** 8159