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Crystallogometry of phase transitions in PbZrO_3 single crystals

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Abstract. Two groups of PbZrO_3 crystals were studied. One exhibited an intermediate rhombohedral ferroelectric phase; in the second this phase did not occur. Flat and crystallographically prominent phase boundaries were observed only in the crystals which exhibited a direct transition from the cubic to the orthorhombic phase. The observed relationships were interpreted in terms of the Roitburd theory. Additional lines were found to occur in the diffraction diagram of the crystals with the intermediate ferroelectric phase.

1. Introduction

Investigation of the phase boundaries in ferroelectrics and antiferroelectrics are of both practical and theoretical importance. The orientation and structure of the phase boundaries determine to a large extent the configuration of the domain structure which forms during phase transition. Hence the problems encountered in obtaining single-domain crystals or crystals with a predetermined domain structure cannot be fully resolved without an exhaustive study of the rules determining the formation of the phase boundaries (Shuvalov *et al* 1985). On the contrary, such studies also permit a fuller understanding of the process of evolution of the system undergoing the phase transition (Dec 1989).

PbZrO_3 is a well known antiferroelectric substance. The room-temperature antiferroelectric phase of PbZrO_3 has the point group mmm (Tanaka *et al* 1982). These crystals undergo a para-electric-to-antiferroelectric phase transition in the vicinity of 230–236 °C to the cubic phase with the point group $m3m$. Some researchers (see, e.g., Tanaka *et al* 1982, Ujma and Hańderek 1975, Fujishita and Hoshino 1984) reported the presence of the intermediate phase between the antiferroelectric room-temperature phase and the para-electric high-temperature phase. These results differ from each other, however.

The domain structure formation at a para-electric-to-antiferroelectric phase transition in PbZrO_3 crystals has not been experimentally studied until now. Nevertheless the problem of orientation of phase boundaries in PbZrO_3 has been examined from the theoretical viewpoint by Mendelson (1981). On the basis of the temperature dependence of the lattice constants reported by Sawaguchi *et al* (1951), Mendelson calculated that the phase boundary should make an angle of $17^\circ 57'$ with the (100) plane and that the orthorhombic phase should be subject to twinning.

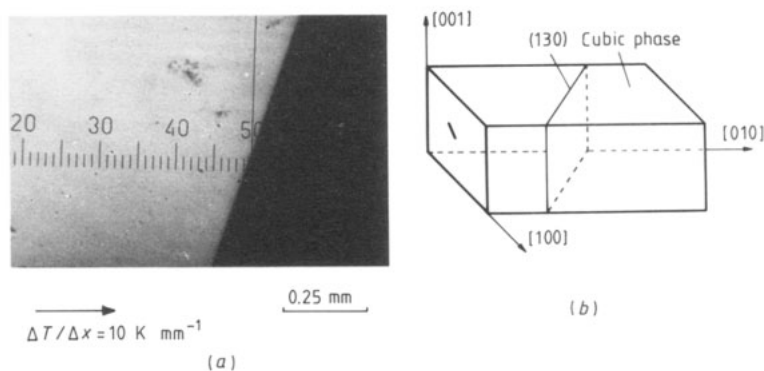


Figure 1. Sharp phase boundary. The Curie point was determined from the x-ray examinations: $T_c = 240^\circ\text{C}$.

The main object of the studies reported here was to find experimental justification for these conclusions.

2. Experimental details

Two groups of PbZrO_3 single crystals were obtained by the flux method. Crystals from the first group were obtained using the procedure described by Smotrakov and Fesenko (1975). The prepared charge of composition $\text{PbO}:\text{B}_2\text{O}_3:\text{PbZrO}_3$ in the proportions 82.8 mol%:14.7 mol%:2.5 mol% was placed in a platinum crucible and heated at a temperature of 1040°C for 4 h and then cooled at a rate of 6 K h^{-1} . A constant temperature gradient along the axis of the crucible of about 10 K cm^{-1} was maintained throughout. At a temperature of about 900°C the solution was poured out and, after the solution had been cooled to room temperature, the crystals obtained were washed in an aqueous solution of acetic acid. A small number of light-grey single crystals were obtained, eminently suitable for thermo-optical tests.

Crystals in the second group were grown in a similar manner but the heating temperature was 1050°C and the heating time was prolonged to 20 h. Yield from the crystallisation process conducted in these conditions was considerably higher and the plate crystals obtained had a light-red colour and also exhibited no macroscopic imperfections. The crystals had a thickness of about 20–200 μm with a surface area up to 9 mm^2 .

Phase transitions in both groups of crystals were examined using a polarisation microscope (Dec 1986) and a Dron 1.5 x-ray diffractometer. Samples in the form of powdered single crystals were prepared for the x-ray tests.

3. Results and interpretation

Thermo-optical examination of phase transitions in PbZrO_3 crystals from the first group carried out using a polarisation microscope showed the existence of only one phase transition (figure 1). This result was corroborated in x-ray studies and also in tests on permittivity and pyroelectric effects (Roleder and Dec 1989). Thus in these crystals may be observed a direct transition from the para-electric cubic phase to the antiferroelectric orthorhombic phase. Additionally, as may be seen in figure 1, the interface exhibits a

prominent crystallographic orientation relative to the coordinate system associated with the cubic phase ($\alpha = 71 \pm 1^\circ$, $\beta = 19 \pm 1^\circ$ and $\gamma = 90 \pm 1^\circ$). This phase boundary corresponds to planes of type $\{310\}$. At the same time, no twinning is observed in the orthorhombic phase, and this fact can be utilised to obtain single-domain samples (without twins). Hence the experimental results found in these studies differ appreciably from the predictions of Mendelson (1981).

In accordance with the Roitburd (1974) theory, a crystallographically prominent phase boundary can be observed during phase transitions in which the specific strain ϵ_0 of transition is a flat invariant plane strain satisfying the equation

$$\epsilon_0 = \frac{1}{2}(\mathbf{r} \cdot \mathbf{n} + \mathbf{n} \cdot \mathbf{r}) \quad (1)$$

where \mathbf{r} is the displacement vector, \mathbf{n} is the normal to the phase boundary and

$$\mathbf{r} \cdot \mathbf{n} = r_i n_k \quad i, k = 1, 2, 3.$$

In such a case during the phase transition the twinning process does not occur.

Studies on the temperature dependence of lattice parameters carried out by Sawaguchi *et al* (1951) and also our own measurements show that the specific strain tensor ϵ_0 for the considered transition from the cubic to the orthorhombic phase has the following form:

$$\epsilon_0 = \begin{bmatrix} 0 & 0 & m \\ 0 & \epsilon & 0 \\ m & 0 & 0 \end{bmatrix} \quad (2)$$

where

$$\epsilon = b/a_0 - 1 \quad m = \tan[(\varphi - 90^\circ)/2].$$

φ is the inter-axial angle of the monoclinic pseudo-cubic subcell, b is the parameter of the monoclinic pseudo-cubic subcell. The other parameters are $a = c = a_0$ at the transition point, where a_0 is the parameter of the cubic cell.

This specific strain is not a flat strain and thus equation (1) cannot be solved. Nevertheless, experiment shows that the crystallographically prominent phase boundary really exists (figure 1). Such behaviour can be explained by an assumption that in the vicinity of the interface both contacting lattices undergo an additional strain ϵ_1 , which accommodates the structures of two neighbouring phases and, as a result, the total strain $\epsilon_t = \epsilon_0 + \epsilon_1$ becomes an invariant plane strain. For this purpose the strain ϵ_1 should be given by

$$\epsilon_1 = \begin{bmatrix} 0 & m & -m \\ m & 0 & 0 \\ -m & 0 & 0 \end{bmatrix}. \quad (3)$$

Consequently the total strain ϵ_t has the following form:

$$\epsilon_t = \begin{bmatrix} 0 & m & 0 \\ m & \epsilon & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4)$$

and equation (1) has solutions for the directional cosines of the normal \mathbf{n} :

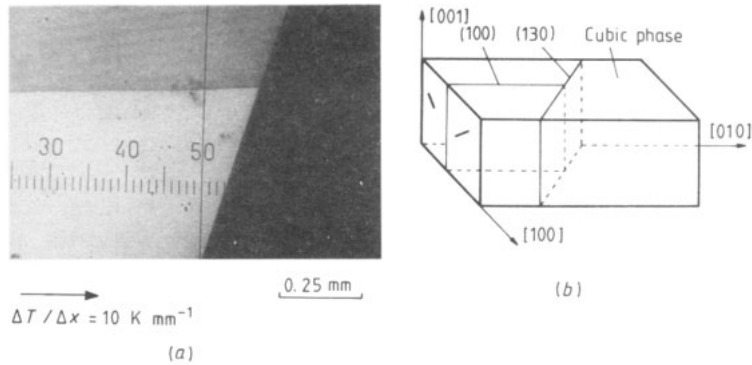


Figure 2. Formation of domains behind a flat phase boundary.

$$\begin{aligned}
 h_1 &= \sqrt{4m^2/(4m^2 + \varepsilon^2)} & h_2 &= 0 \\
 k_1 &= \sqrt{\varepsilon^2/(4m^2 + \varepsilon^2)} & k_2 &= 1 \\
 l_1 &= 0 & l_2 &= 0.
 \end{aligned} \tag{5}$$

We obtained two families of solutions from which it may be concluded that the phase boundary which is an invariant plane can take either an orientation as determined by the cell parameters or, independent of cell parameters, a certain orientation corresponding to crystallographic planes of type $\{100\}$.

The components of the specific strain tensor ε_0 determined on x-ray examination have the following values: $\varepsilon = -0.005797$ and $m = 0.00105$. For these values of the components of the tensor ε_0 , the normal to the phase boundary should form with the axes of the coordinate system associated with the cubic phase at the following angles: $\alpha = 70^\circ 10'$, $\beta = 19^\circ 50'$ and $\gamma = 90^\circ$. These values of angles are in a good agreement with those observed experimentally.

Experimental observations, however, did not show phase boundaries corresponding to planes of type $\{100\}$ but only those corresponding to $\{310\}$ planes. This is most probably due to presence in the crystal of planar defects, as described by Prisedskii *et al* (1979), in the form of the so-called crystallographic shear planes. The existence of such defects in PbZrO_3 single crystals was confirmed experimentally by Dobrikov and Presnyakova (1981). It is interesting to note that defects of this kind have the orientation of $\{310\}$ -type planes. Hence the agreement between the orientation of planar defects and phase boundaries results in a situation where there is very little probability of the occurrence of boundaries of $\{100\}$ orientation. To observe such boundaries would most probably require crystals of very high quality. The existence of such defects may also be interpreted by the fact that in PbZrO_3 crystals it is very difficult to change the orientation of a phase boundary by changing the orientation of the sample relative to the temperature gradient. This is evidenced by the fact that a system of planar defects once formed constitutes a fairly permanent structure in the crystal.

A further singular feature of the phase transition observed in PbZrO_3 is that the multiple-domain state (figure 2) can be formed behind a flat phase front despite the fact that the strain ε is an invariant plane strain. In an earlier paper (Dec and Kwapuliński 1989) the conclusion was formulated that, if the strain of transition is a so-called invariant plane strain, then behind the flat phase front a single-domain state occurs. For PbZrO_3 crystals, an a-domain (figure 1) is formed behind the flat phase front of orientation (130). Nevertheless, because of the form of the deformation strain (2), in which two diagonal

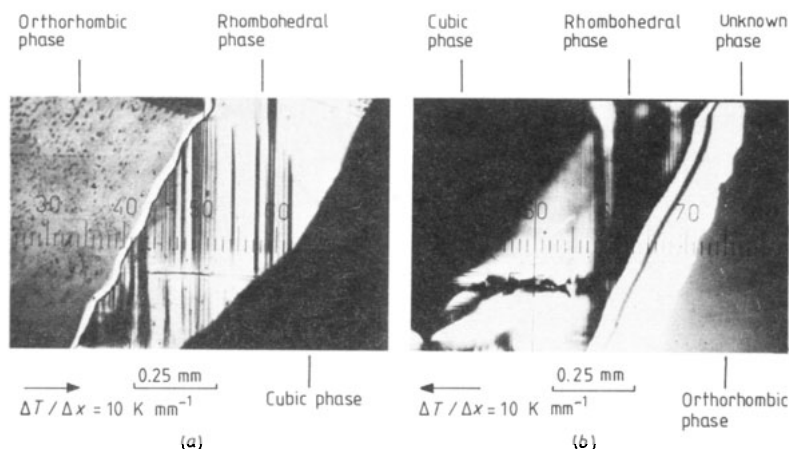


Figure 3. Complex phase boundaries in crystals from the second group.

components are equal to zero, there are two possible orientation states of this domain, differing by 90° . If accidentally the nucleus of a domain of the other orientation should occur in a certain part of the crystal, then it is able to grow freely and a multiple-domain state arises in the crystal. Therefore in order to obtain a single-domain crystal it is simply necessary to heat this crystal above the transition point and to repeat the process of controlled phase transition. Although the twinning process can occur at this phase transition, it cannot be treated as an inseparable process.

The crystals in the second group behaved quite differently from those in the first group as described. In these crystals we observed an intermediate rhombohedral ferroelectric phase (figure 3(a)). The occurrence of such an intermediate phase has been previously reported by many researchers (Tennery 1966, Ujma and Hańderek 1975). As may be seen from figure 3, in passing both from the orthorhombic phase to the rhombohedral phase and also from the rhombohedral to the cubic phase, interfaces do not have a determined crystallographic orientation or a regular structure. Apart from this, certain crystals in this group exhibited a further additional phase transition occurring between the orthorhombic and the rhombohedral phases (figure 3(b)), the nature of which is not yet known.

The photographs in figure 3 were taken during the heating process when the sample was placed in a temperature gradient $\Delta T/\Delta x$ of 10 K mm^{-1} directed along the direction [010]. During the cooling process the distance between phase boundaries is considerably greater and it is impossible to photograph them simultaneously. This is in agreement with the earlier observed large temperature hysteresis of the tested phase transitions in PbZrO_3 (Ujma and Hańderek 1975).

The x-ray examinations of powdered crystals carried out at room temperature showed that, while the diffraction diagram for the samples in the first group is typical of an orthorhombic system with a monoclinic pseudo-perovskite cell (figures 4(a) and 4(b)), the corresponding profiles for samples from the second group were complex (figures 4(c) and 4(d)). Analysis of these profiles indicated that a complex diffraction profile of this type may be interpreted as the superposition of two different orthorhombic systems with monoclinic pseudo-perovskite cells. Parameters of the pseudo-perovskite cells and also the homogeneous deformation parameter δ (Kupryanov 1968, Fesenko 1972) at room temperature are given in table 1. On increase in temperature, in single crystals of the first group a sharp transition to the cubic system took place (without the

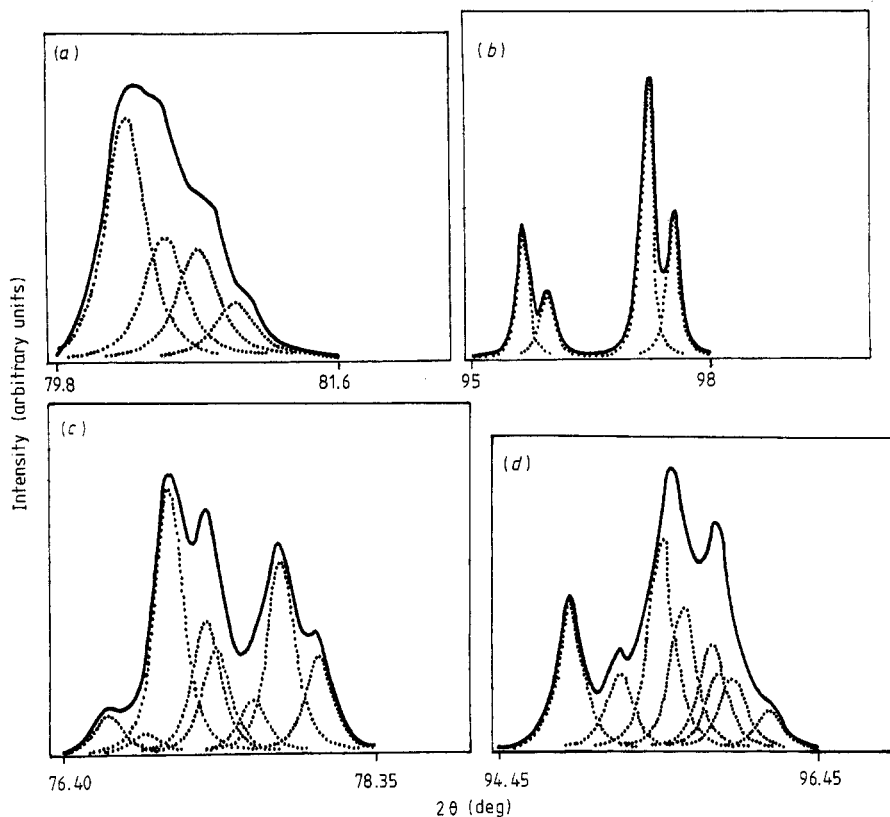


Figure 4. Profiles of diffraction lines {222} and {400} for samples (a), (b) from the first group and (c), (d) from the second group; —, experimental data; ····, component profiles obtained numerically. All the profiles are taken at room temperature.

Table 1. Parameters of pseudo-perovskite cells in an orthorhombic system at room temperature. $\bar{a} = V^{1/3}$; $\delta = a(1 - \cos \varphi)^{1/2}/\bar{a} - 1$; V is the volume of the cell.

Parameter (units)	Single crystals of first group	Single crystals of second group	
		System I	System II
$a = c$ (Å)	4.159	4.183	4.159
b (Å)	4.109	4.163	4.152
φ	90°24'	90°21'	90°22'
\bar{a} (Å)	4.143	4.176	4.157
δ	0.008	0.005	0.004

intermediate rhombohedral phase). However, in crystals of the second group, lines from the rhombohedral phase and next from the cubic system were observed. Additional reflections were observed, however, after transition to the cubic phase (figure 5) and these were found to appear right up to a temperature of 550 °C. Analysis of these complex reflections showed that they may be interpreted as coming from two cubic systems of minimally differing lattice constants. Parameters of the perovskite cells at temperatures of 460 and 550 °C for both groups of crystals are given in table 2. A similar effect was

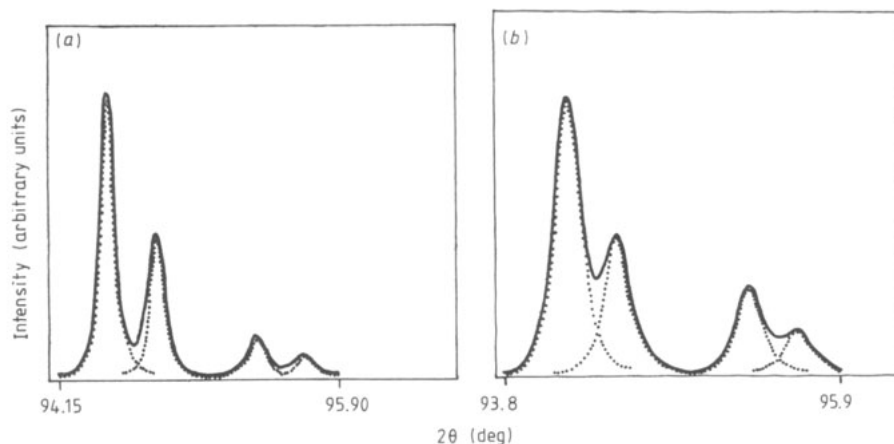


Figure 5. Profiles of diffraction lines {400} for cubic system samples from the second group at (a) 460 °C and (b) 550 °C.

Table 2. Parameters of perovskite cells in the cubic system.

Temperature (°C)	Single crystals of first group (Å)	Single crystals of second group	
		System I (Å)	System II (Å)
460	4.165	4.197	4.165
550	4.168	4.206	4.168

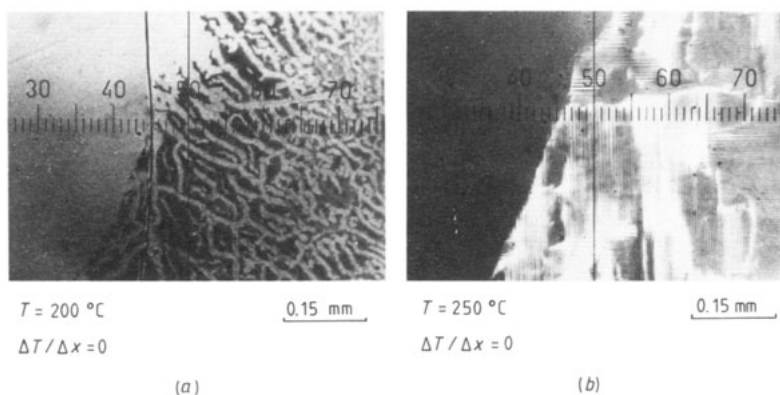


Figure 6. Coexistence of phases.

observed by Tennery (1966) who interpreted such additional reflections as superstructure reflections.

Another individual feature of phase transitions in crystals from the second group was that they did not take place jumpwise but, in the vicinity of phase transition points, coexistence of phases was observed. This coexistence phase effect has previously been observed for ceramic samples (Hańderek *et al* 1985). This effect may also be easily observed using a polarisation microscope (figure 6). Traces of the old phase are visible in the form of patches distributed in the area of the new phase. In figure 6(a) may be

seen patches of the old phase in the area of the orthorhombic phase, while in figure 6(b) the remains of the rhombohedral phase are visible in the cubic phase. This observed coexistence of phases, however, occurred only in certain crystals of the second group, while in the given crystal this was only found in certain places.

X-ray examination thus showed that crystals of the first group are structurally more perfect than those of the second group which exhibit structural non-homogeneity. A similar conclusion may be drawn from the results of light absorption studies (Wójcik 1989), in which it was ascertained that in crystals of the first group the absorption edge is sharply marked.

From the results of investigations reported in this paper, it may be concluded that the properties of PbZrO_3 crystals depend not only on the purity of the reagents used for their synthesis (Whatmore and Glazer 1979) but, within the limits of the given class of reagents, also on the technological conditions.

4. Conclusions

Regular and crystallographically prominent phase boundaries were found to occur only in those PbZrO_3 crystals which were structurally homogeneous. The observed crystallographic dependences may be satisfactorily explained in terms of the Roitburd theory. The observed regularities in the course of the phase transitions can serve as a basis for obtaining single-domain antiferroelectric PbZrO_3 samples.

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