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The defect-induced ferroelectric phase in thin $PbZrO_3$ single crystals

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Abstract. In the $PbZrO_3$ crystals a transient phase does not exist spontaneously below T_c, although normal ferroelectric loops can be observed near T_c on both heating and cooling. A strong electric field causes the crystal to be permanently defected. Defects produced in this way are the reason for the appearance of a transient ferroelectric phase. In the virgin crystal, separation of point defects in an external DC electric field induces ferroelectric behaviour below T_c in the internal field of the crystal. It was found that for $PbZrO_3$, T_c depends on sample thickness.

1. Introduction

At present, there is a great deal of information available on lead zirconate ($PbZrO_4$) considered as a model antiferroelectric. Detailed x-ray and neutron diffraction investigations established the space and point group of the antiferroelectric order with orthorhombic symmetry as P*ba*m and mmm, respectively (Tanaka *et al* 1982, Fujishita and Hoshino 1984). However, many papers on this material deal with transient phase existence and properties in the vicinity of T_c. Most researchers confirm the presence of a transient phase of ferroelectric type, in both ceramics and single crystals, although the temperature range in which its existence was detected differs. The ferroelectric nature of this phase was determined from a study of the hysteresis loop, the domain structure and the pyroelectric effect. Recent investigation of Raman scattering with simultaneous observation of the $\varepsilon(T)$ function also showed the existence of a transient phase (Roleder *et al* 1987). Structural tests (Tennery 1965, Hańderek *et al* 1985) revealed that a ferroelectric phase of rhombohedral symmetry coexists with neighbouring antiferroelectric or para-electric phases. It was found that an external DC field broadened and stabilised the transient ferroelectricity but that hydrostatic pressure rapidly removed it (Hańderek *et al* 1981). It is noteworthy that in certain Japanese papers (see, e.g., Sawaguchi *et al* 1951, Fujishita and Hoshino 1984) the transient phase was described as antiferroelectric.

Relatively few papers have studied the properties of $PbZrO_3$ single crystals. In general, the properties described were similar although there were differences in the $\varepsilon(T)$ curves especially near T_c. The main phase transition was normally observed at 230–235 °C. The temperature range of the transient phase in $PbZrO_3$ crystals depends on the purity of ingredients or solvent used (Whatmore and Glazer 1979) and also on growth temperature. Scott and Burns (1972) reported that, the higher the temperature of the growing process, the wider the temperature range of the transient phase. In their opinion

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this is associated with non-stoichiometry in the Pb sublattice. The influence of defects in both the Pb and the O sublattices, produced by heating the samples in a vacuum, on the properties and existence of the transient phase in $PbZrO_3$ ceramics has been described in many later papers, a survey of which can be found in a paper by Ujma (1984). Observing the varying range of the transient phase in samples of different Pb and O defect concentrations, a cluster mechanism for the appearance of the ferroelectric state in $PbZrO_3$ has been proposed (Benguigui 1968, 1971, Ujma and Hańderek 1981, Roleder *et al* 1987).

The brief review given above refers to investigation of $PbZrO_3$ ceramics and crystals with dimensions, in general, greater than 1 mm × 1 mm × 1 mm. In this paper are presented dielectric, pyroelectric and thermo-optic investigations on thin-plate $PbZrO_3$ single crystals not exhibiting a transient phase below T_c.

2. Sample preparation

Single crystals were grown from 82.8 mol.% PbO–14.7 mol.% B_2O_3–2.5 mol.% $PbZrO_3$. A mixture of ZrO_2, PbO and B_2O_3 was placed in a Pt crucible and maintained at 1040 °C for 4 h. Then the melt was cooled at a rate of 6 K h^{-1} to 900 °C and the solvent was poured off. Transparent light-grey crystals in the form of thin plates were obtained.

3. Optical, dielectric and pyroelectric investigations

Prior to the dielectric measurements a sample of dimensions 3 mm × 1 mm × 0.024 mm was placed in a polarising microscope in order to observe the phase front movement with a constant temperature gradient of 10 K mm^{-1}. One sharp phase front corresponding to the transition between para-electric and antiferroelectric phases is shown in figure 1(*a*). In the antiferroelectric phase the crystal had an *a* domain nature with the *c* axis parallel to the surface of the plate. The shape and orientation of the phase front were stable and independent of both heating and cooling. X-ray tests of powders from the technological process described above also showed the existence of one phase transition only (Dec and Kwapuliński 1988).

Next, electrodes of 0.4 mm diameter were deposited on a small part of the sample using Ag paste. Temperature dependence of the electric permittivity ε was measured at a field strength of 0.4 kV cm^{-1} and a frequency of 1 kHz (figure 1(*b*)). The thermocouple was in contact with the sample. At T_c, on both heating and cooling, a sharp increase in ε takes place, with no additional anomalies of ε below T_c being observed for samples exhibiting the transient phase. In the para-electric phase the Curie–Weiss law is obeyed. For AC electric fields, electric hysteresis loops were observed in the range of a few degrees Celsius below T_c for both heating and cooling. Remnant polarisation at 40 Hz and 13 kV cm^{-1} was about 20 $\mu C\ cm^{-2}$ and the induced transient phase existed over 3 °C. After removal of the electrodes from the crystal surface (HNO_3 etching) the shape and orientation of the phase front were similar to those before the $\varepsilon(T)$ and electric loop observations (figure 1(*a*)).

After the crystal had been heated at 320 °C for 0.5 h, T_c decreased by about 10 °C and the phase front became irregular (figure 2). After this phase front the crystal had, in principle, a *c* domain nature with the *c* axis perpendicular to the crystal surface. The form of $\varepsilon(T)$ was similar to that in figure 1(*b*). In an electric field of low frequency

(0.07 Hz) and low strength (20 kV cm^{-1}), above T_c, double-hysteresis loops associated with the first-order phase transition, normal ferroelectric loops and then double antiferroelectric loops were observed (figure 3). The maximum value of remnant polarisation, calculated from the ferroelectric loops existing under the measurement conditions used, at about 1 °C, was evaluated as 50 μC cm^{-2}. For a higher frequency of the AC field of the order of 40 Hz, hysteresis loops were also observed.

After detection of the hysteresis loops in the high electric field of low frequency the dependence $\varepsilon(T)$ was measured again (figure 4). In comparison with figure 1(*b*), distinct changes in the para-electric phase, an increase in the thermal hysteresis of the phase transition and a diffusion of $\varepsilon(T)$ below T_c are clearly visible. For this crystal state, using the quasi-static method, the pyroelectric effect was found without prior poling. Weak current signals of both signs were found and thus are presumably connected with the appearance and disappearance of polarisation (figure 5). The shape of the pyroelectric

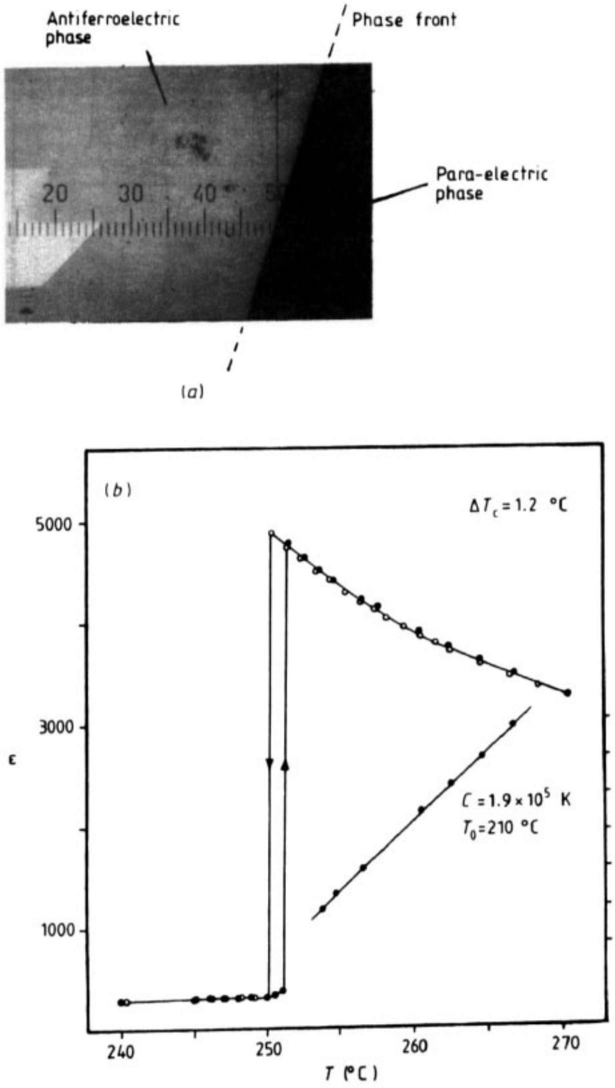

Figure 1. (*a*) The phase front in a temperature gradient of 10 K mm^{-1}; (*b*) plot of electric permittivity (1 kHz) against temperature for a thin $PbZrO_3$ plate. 1 division = 10 μm.

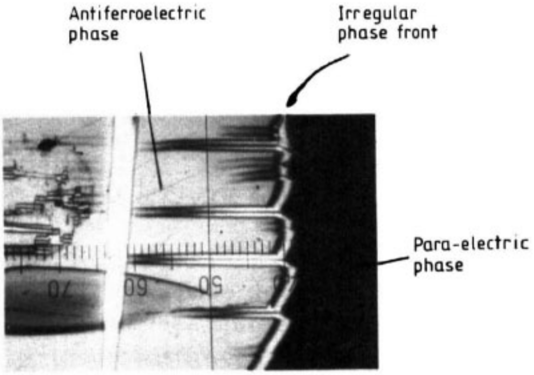

Figure 2. The phase front observed in the same conditions as in figure 1(a) but after the sample had been heated at 320 °C. Its irregular character is clearly visible. 1 division = 10 μm.

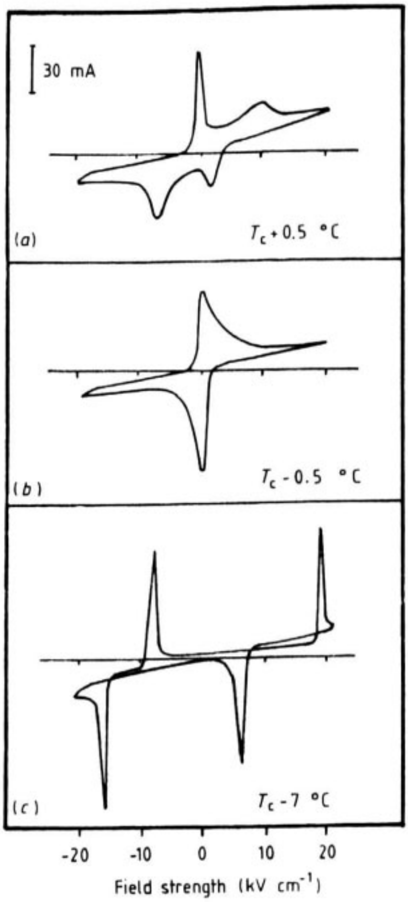

Figure 3. Low-frequency (0.07 Hz) current hysteresis loops for $PbZrO_3$ in the vicinity of the phase transition: (a) induced double loops just above T_c; (b) induced ferroelectric loop below T_c; (c) double loops in the antiferroelectric phase.

signals detected on cooling corresponds to only two phase transitions, i.e. between the para-electric and ferroelectric and between the ferroelectric and antiferroelectric states. The temperature range of the ferroelectric phase depended on the cooling rate up to a rate of 0.07 K s^{-1}; the faster the cooling, the wider the temperature range in which the pyroelectric effect was detected. At a rate greater than 0.07 K s^{-1} the range of polar phase appeared to stabilise.

In these investigations, it was surprising that the T_c point detected was considerably higher than those reported in the literature. Hence, for $PbZrO_3$ single crystals obtained from the same technological process the dependence of T_c on crystal thickness was checked (figure 6). In all cases the crystals were aged at 320 °C for 0.5 h and cooled at a constant rate. For a defined crystal thickness, the values of T_c were independent within the measurement field range 0.4–2 kV cm^{-1}. Figure 6 shows that, with increasing sample thickness, the temperature T_c decreases towards the value reported by most workers. It should be mentioned that for thick crystals an intermediate phase was clearly visible.

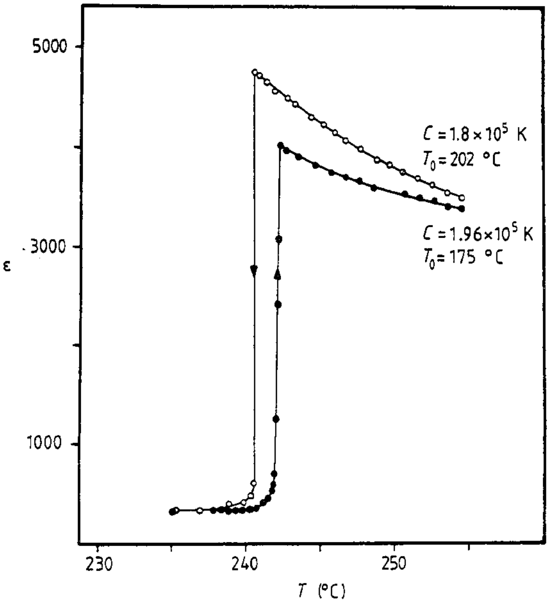

Figure 4. Temperature dependence of the electric permittivity (1 kHz) after strong electric field action. $\Delta T_c = 1.7$ °C.

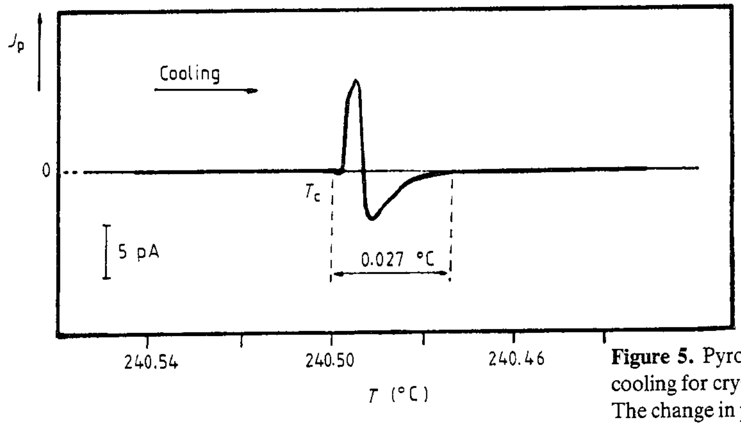

Figure 5. Pyroelectric effect detected on cooling for crystal with $\varepsilon(T)$ as in figure 4. The change in polarisation (upper peak) is of the order of 0.004 $\mu C\ cm^{-2}$.

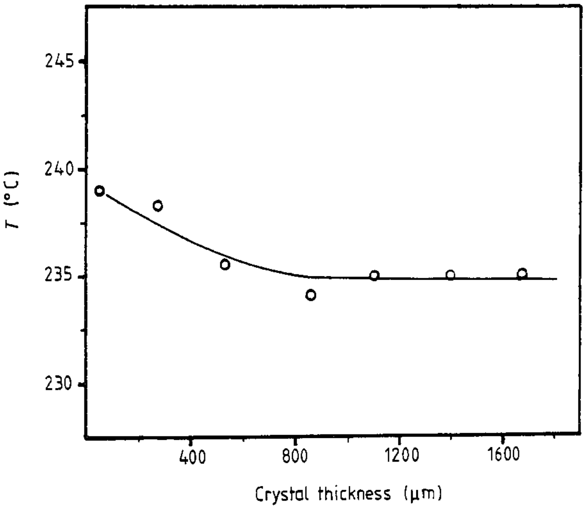

Figure 6. Dependence of T_c on crystal thickness for $PbZrO_3$ grown in the same technological process (Roleder *et al* 1987).

Moreover, for a defined crystal thickness, the values of T_c and permittivity ε were sensitive to the aging time and aging temperature but for thin crystals the deviations observed were considerably greater. Therefore it may be assumed that the concentration and state of the defects, their mode of diffusion and their mutual interactions are, in principle, responsible for the effects observed.

4. Thermo-optical investigations

After experiments with a strong electric field, the electrodes were removed from the crystal surface and thermo-optical investigations were performed. The crystal was placed in a controlled temperature gradient of 10 K mm^{-1}. In figure 7 the three phases of the crystal are shown: figure 7(*a*) shows the para-electric phase, figure 7(*b*) the phase transition and figure 7(*c*) the antiferroelectric phase. In each case a permanent trace in the place where the electrodes had been attached was visible. In particular, evident changes in the crystal which had been in a strong electric field are visible in the para-electric phase as bright spots (figure 7(*a*); long exposure time). The observations were not sufficient to enable the nature and structure of the bright spots to be determined. During the phase transition, at the place where the electrodes had been removed, a complex domain structure appears (figure 7(*b*)). The shape of the phase front is irregular. The characteristic trace is still present deep in the antiferroelectric phase (figure 7(*c*)). Heating the crystal at 450 °C slightly simplifies the domain structure created within this trace. The number of bright spots increased with increasing strength and time of

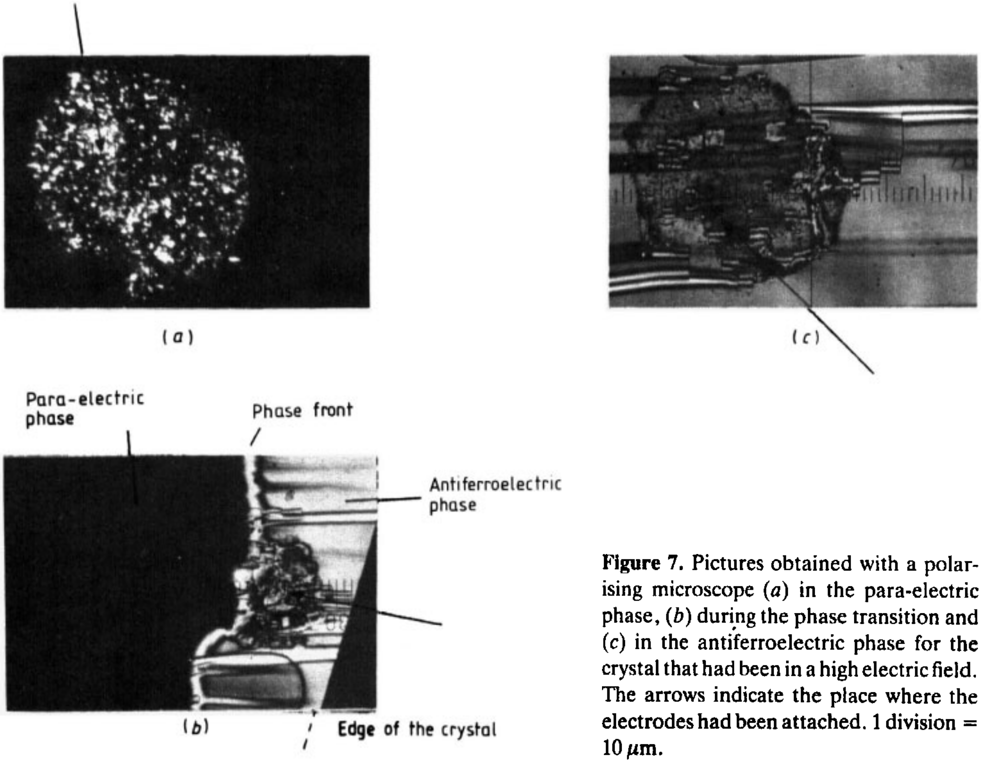

Figure 7. Pictures obtained with a polarising microscope (*a*) in the para-electric phase, (*b*) during the phase transition and (*c*) in the antiferroelectric phase for the crystal that had been in a high electric field. The arrows indicate the place where the electrodes had been attached. 1 division = 10 μm.

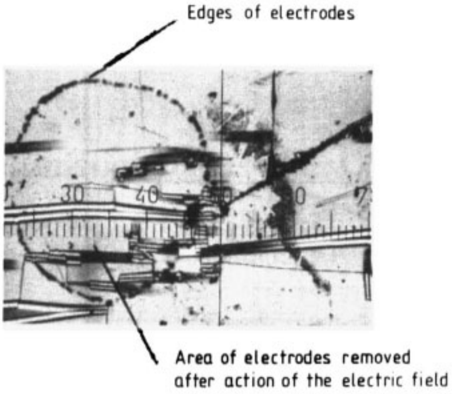

Figure 8. Small changes in the crystal observed at the edges of electrodes after the action of an electric field of 8 kV cm^{-1} and 0.07 Hz (the antiferroelectric phase).

application of the external electric field. A field of 8 kV cm^{-1} and 0.07 Hz applied for a short time introduces only small changes which are visible at the edges of the electrodes used (figure 8).

5. Transient phase induced in the internal fields of defects

The experiments described above showed that in thin $PbZrO_3$ crystals without the transient phase the appearance of permanent defects caused by a strong electric field induces this phase. It is difficult to say which mechanism is responsible for defects created in this way. We may guess that it is connected with damage to the chemical bonds caused by electron and ionic defect migration towards the surface. In the opinion of Hańderek (1988), these defects can be produced by electrons and ions created during the discharge in the uncompensated electric field of the spontaneous polarisation reoriented in the neighbouring domains. This could also explain the permanent change in the crystal (figure 7). The mechanism of discharge in a high P_s field, observed at the surface of several ferroelectrics, has been described in the paper on $BaTiO_3$ (Samchenko and Florova 1975). Except for the effects described above, the migration of defects will follow even in weak external fields. The separation of defects (Pb and O vacancies in $PbZrO_3$) arising in this way is a source of local stresses and an uncompensated electric field which can lead to polarisation of the surroundings. To verify this hypothesis, the electrodes were deposited on a virgin part of the crystal under investigation. We first checked that the pyroelectric effect did not exist in the vicinity of T_c. Next a DC electric field of 3 kV cm^{-1} was switched on in the para-electric phase (T_c + 1 °C). Under this field the sample was cooled to the antiferroelectric phase (T_c − 3 °C). After the field had been switched off, the pyroelectric effect was measured on heating (figure 9). Observed variations in the pyroelectric current indicate the appearance and disappearance of polarisation in the internal field of the crystal. Current pulses give evidence of a non-homogeneous distribution of polarisation. To observe this pyroelectric effect repeated polarisation was again necessary. A change in polarisation direction reverses the sign of the pyroelectric current flow. Hence, we may speak of induced ferroelectric behaviour between the antiferroelectric and para-electric states. The shape of pyroelectric signals, the number of pulses and also the temperature range of their existence changed in successive polarisation processes. This could explain the appearance of ferroelectric behaviour below T_c in internal fields of separated defects (cluster mechanism).

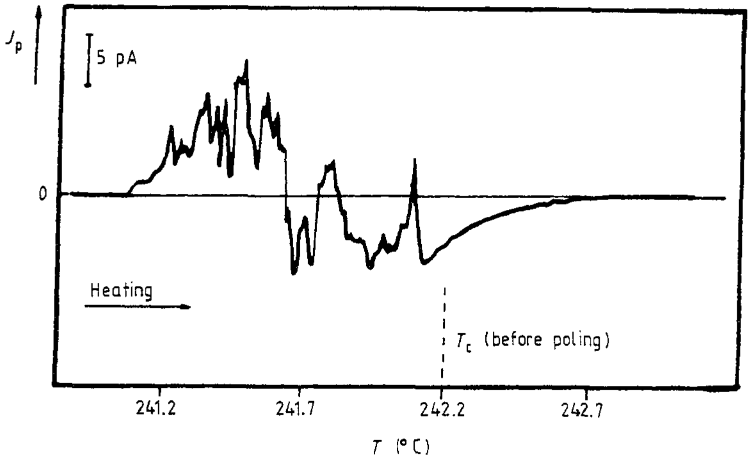

Figure 9. Pyroelectric effect below T_c induced by defect separation. For details, see text. The evaluated change in polarisation (upper part of signals) is of the order of 0.02 μC cm^{-2}.

6. Summary

(1) In the thin $PbZrO_3$ crystals investigated, the transient phase does not appear spontaneously below T_c.

(2) The action of strong external electric fields produces irreversible changes in the crystal. The presence of defects produced in this way is the reason for the appearance of the transient ferroelectric phase.

(3) The transient phase in $PbZrO_3$ can also be induced in the internal fields of the crystal owing to prior defect separation made in the DC electric field.

(4) For $PbZrO_3$ samples thinner than 500 μm, the temperature T_c depends on the sample thickness.

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