

THE ELECTRIC FIELD-INDUCED ANTIFERROELECTRIC TO FERROELECTRIC  
PHASE TRANSITION IN SOME  $(\text{Pb},\text{La})\text{Zr}_{0.55}\text{Ti}_{0.45}\text{O}_3$  CERAMICS

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ABSTRACT

Lanthanum substituted lead zirconate-titanate (PLZT) ceramics of composition 11.1/55/45 have been studied by measuring high electric field properties. Dc bias, dielectric and P-E hysteresis loop measurements have been employed to construct an E (electric field) versus T (temperature) phase diagram. At lower temperatures and small electric fields an antiferroelectric phase with tetragonal symmetry has been found. Applying high electric fields gives rise to a field-induced phase transition from the antiferroelectric to the ferroelectric state, however, without X-ray detectable change in crystal symmetry.

Introduction

In the perovskite system  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ , usually called PLZT, interesting electrical and electrooptical properties have been found. Especially PLZT with a Zr to Ti ratio of 65 to 35, abbreviated as PLZT x/65/35 (x=La content in at.%) offers possibilities for useful applications [1].

The phase relations and dielectric properties of PLZT x/65/35 have been investigated intensively [2,3,4]. For investigations of diffuse phase transitions in PLZT ceramics Wolters and Burggraaf [5,6] have chosen PLZT with a Zr to Ti ratio of 55 to 45 (PLZT x/55/45). These compositions have been chosen to avoid additional phase transitions like the rhombohedral to tetragonal phase transition (see the phase diagram for PLZT by Heartling [7]). This phase transition can disturb the ferroelectric (FE) to paraelectric (PE) transition, which is under study here. To know more about existing phases and phase transitions it looks useful to study high-field dielectric properties. It is already known that crystal structure and physical properties of PLZT

ceramics are strongly dependent on high electric fields [2,4,8,9]. Here, we especially want to know if high electric fields induce a FE phase or only align the (micro) domains in the already existing FE phase. The investigations reported here, have been restricted mainly to the composition PLZT 11.1/55/45. Properties of other PLZT  $x/55/45$  (with  $8.1 \leq x \leq 14.1$ ) ceramics at high electric fields have been studied too, but will not be reported extensively here.

### Experiments

For these experiments samples with a density better than 96% and a grain size larger than  $5 \mu\text{m}$  have been used. The preparation and characterisation have been described in ref. 5.

To study high field dielectric properties, two kinds of measurements have been performed. By means of a modified Sawyer-Tower circuit  $P$  (polarization) -  $E$  (electric field) hysteresis loops were obtained at a frequency of 0.05 Hz. Using a General Radio Impedance Bridge 1650A, with dc bias fields between 0 and 12 kV/cm, capacitance and dielectric losses were measured.

### Results

In the next sections the expressions "thermally depoled" and "ac depoled" will be frequently used. A material is thermally depoled by heating it to a sufficiently high temperature, followed

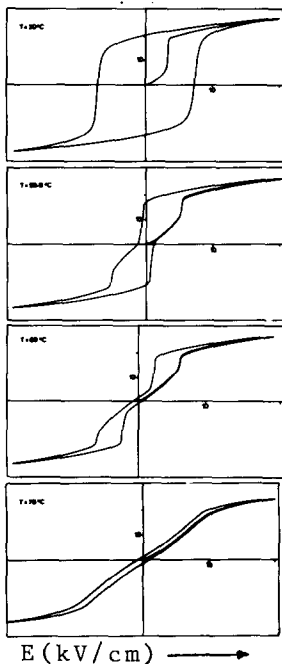


FIG. 1

P-E hysteresis loops for thermally depoled PLZT 11.1/55/45 ceramics at different temperatures.

by slow cooling in short-circuited condition. The material can be ac depoled by continuously reducing the ac field, which initially has been equal to the maximum field used in hysteresis loop measurements.

For PLZT 11.1/55/45 the P-E hysteresis loop changes with temperature as shown in fig. 1.a-d. At low temperatures a rather square loop is observed (fig. 1a) which changes in a "double loop" (fig. 1b,c) at increasing temperature. At still higher temperatures a so-called "slim-loop" is found (fig. 1d), which gradually approaches linear dielectric behaviour.

The remanent polarization  $P_r$  and the coercive field  $E_c$  obtained from these loops as function of temperature are shown in fig. 2. At a certain temperature  $T_p$  we notice a sharp decrease in  $P_r$ . In a rather large temperature interval above  $T_p$  a finite remanent polarization  $P_r$  is still observed which decreases slowly with increasing temperature. Only in a temperature interval of a few degrees above  $T_p$  this decrease

of  $P_r$  with increasing temperature is fairly large. The characteristic temperature  $T_p$  can also be deduced from  $E_c$  versus temperature. At  $T_p$  the shape of the hysteresis loops changes from square to double loops.

In the same fig. 1 the initial P-E curves are also shown, starting from the thermally depoled state. A discontinuous change will be noticed at a certain electric field, called the critical field  $E_{cr}$ . Fig. 3 shows the variation of both  $E_c$  and  $E_{cr}$  as a function of temperature. It shows a decrease of  $E_c$  and an increase of  $E_{cr}$  with increasing temperature. Furthermore two parts of  $E_{cr}$  as a function of temperature can be distinguished with a breakpoint around  $T_p$ .

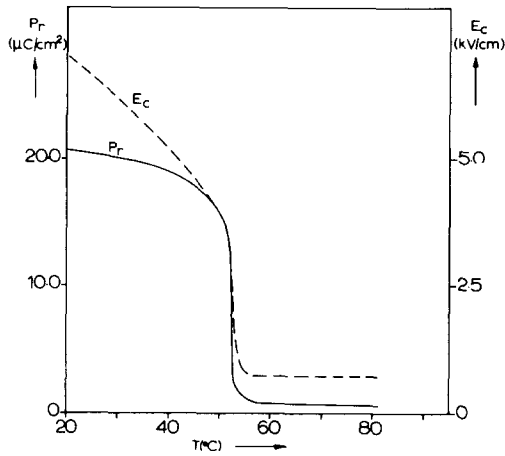


FIG. 2

Remanent polarization  $P_r$  and coercive field  $E_c$  as function of temperature for PLZT 11.1/55/45.

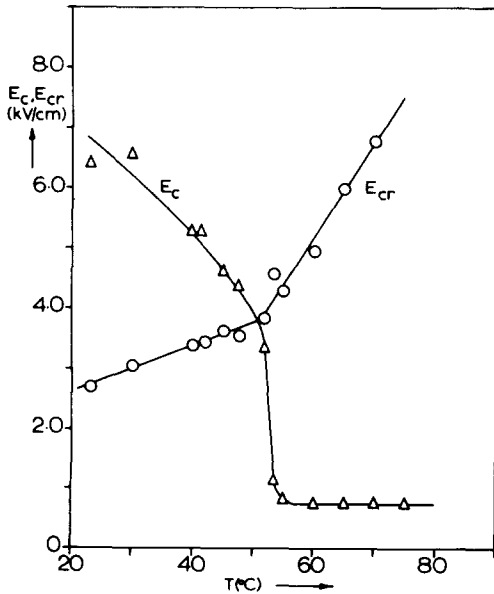


FIG. 3

Coercive field  $E_c$  and critical field  $E_{cr}$  versus temperature for PLZT 11.1/55/45.

Thermally depoled material below  $T_p$  gives P-E hysteresis loops of the type shown in fig. 4a. With electric fields smaller than  $E_{cr}$  only a small remanent polarization is found. However, with electric fields higher than  $E_{cr}$  normal square loops with high  $P_r$  are observed. So the hysteresis loop characteristics of thermally depoled material change suddenly at  $E_{cr}$ . Ac depoled material below  $T_p$  shows square loops both at electric fields smaller and

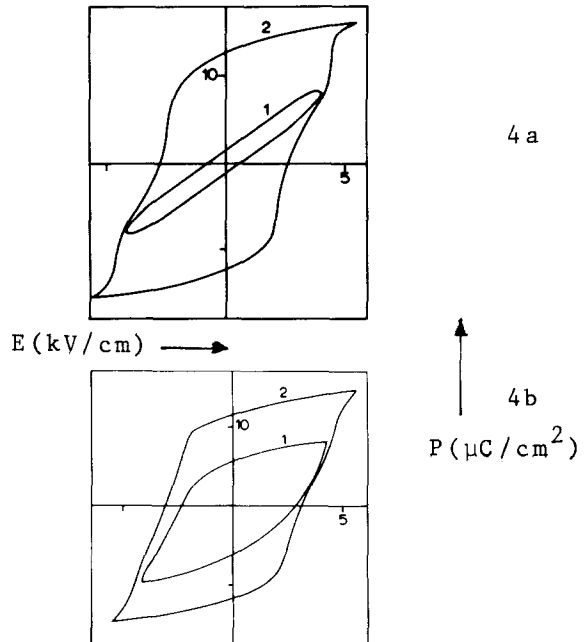


FIG. 4

P-E hysteresis loops for thermally depoled (4a) and ac depoled (4b) PLZT 11.1/55/45 at 40°C. (1:  $E_{max} < E_{cr}$ ; 2:  $E_{max} > E_{cr}$ ).

higher than  $E_{cr}$  (fig. 4b). At temperatures above  $T_p$  no differences in the P-E hysteresis loops between thermally and ac depoled materials have been found.

In fig. 5 the results of dielectric measurements on ac depoled samples are shown. The temperature at which  $\epsilon'$  is maximum will be called  $T'_c$ , while  $T_b$  is the temperature corresponding to the maximum value of  $\epsilon''$ . The application of a bias field causes a shift of  $T_b$  to higher temperature, whereas  $T'_c$  is only weakly influenced (compare Table I). For thermally depoled material a small decrease in  $T_b$  (and  $T'_c$ ) has been found for increasing dc bias electric fields smaller than  $E_{cr}$  (Table I), while  $T_b$  increases for increasing fields larger than  $E_{cr}$  (Table I, poled materials). At temperatures below  $T_b$ ,  $\epsilon'$  and  $\epsilon''$  for ac depoled materials and for poled materials are considerably smaller than those for thermally depoled materials. For temperatures above  $T_b$  there is a little difference between thermally and ac depoled materials. Once again it must be remarked that there are no or only little differences in dielectric behavior between the poled and the ac depoled condition, whereas thermally depoled material shows a rather different dielectric behaviour.

X-ray experiments show no detectable differences in crystal symmetry or unit cell dimensions of the ac depoled and thermally depoled materials. Nor have there been found any superstructure reflections. The crystal structure has been indexed as tetragonal with a rather small deviation from the cubic symmetry [5]. For PLZT 11.1/55/45 there has been found a c/a ratio of 1.005 ( $\pm 0.001$ ).

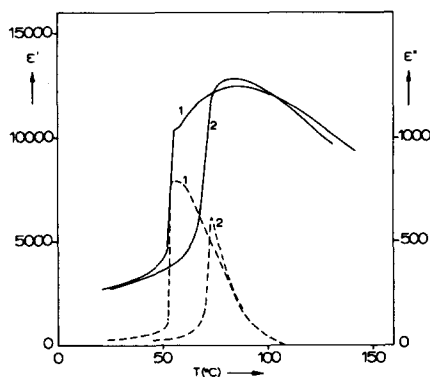


FIG. 5

Dielectric permittivity  $\epsilon'$  and loss  $\epsilon''$  (10 kHz) versus temperature for ac depoled PLZT 11.1/55/45.

(1: no bias field; 2: with dc bias field of 9.43 kV/cm; —:  $\epsilon'$ ; ---:  $\epsilon''$ )

TABLE I

Variation of characteristic dielectric parameters (at 10 kHz) by applying dc bias fields to thermally depoled, ac depoled and poled PLZT 11.1/55/45 ceramics.

dc bias (kV/cm)	$T_b$ ( $^{\circ}$ C)	$\epsilon''_{max}$	$T'_c$ ( $^{\circ}$ C)	$\epsilon'_{max}$
<u>Thermally depoled</u>				
0	57	750	87	12500
1.32	56	850	84	12900
<u>A.c. depoled</u>				
0	56	810	84	12800
1.32	56	860	84	12900
3.77	62	1130	82	13800
9.43	73	620	84	12800
<u>Poled</u>				
0	55	850	85	12600
1.32	58	850	88	13150
9.43	74	575	87	13000

### Discussion

In this section a restriction has been made to phenomena occurring mainly in the temperature region below  $T_p$ , in which temperature region square P-E hysteresis loops have been found.

The characteristic temperature  $T_b$  is almost equal to  $T_p$  (at  $E = 0$ ) and is probably a transition temperature. At this temperature a strong decrease in ferroelectric properties ( $P_r$ ,  $E_c$ ) as well as a maximum in dielectric losses occur. At this temperature preliminary work has shown a rather sudden decrease in unit cell dimensions too. The temperature of the maximum in the dielectric constant  $T'$ , however, occurs at a much higher temperature.

The discontinuous change in the first run of P-E hysteresis loops (fig. 1) indicates an electric field-induced transition. Another indication for this transition is the change in the shape of the hysteresis loop for thermally depoled material by passing through  $E_{cr}$  (fig. 4a). At room temperature we have also noticed a marked decrease of  $\epsilon'$  and  $\epsilon''$  by passing through  $E_{cr}$  in dielectric measurements performed under increasing dc bias fields (to be published).

This discontinuous change in the initial P-E curve does not represent the alignment of domains as normally found in ferroelectrics. For  $E_{cr}$  (characterising the discontinuous change) increases at increasing temperature (fig. 3), whereas domain alignment will occur at decreasing critical fields with increasing temperatures. This phenomenon of easier domain orientation is reflected in the temperature dependence of  $E_c$ .

In thermally depoled materials little indications for ferroelectricity have been found (a very low  $P_r$ , illustrated in fig. 4a). A ferroelectric domain structure has not been found too. On the other hand there are indications that thermally depoled material has antiferroelectric (AFE) features. In AFE materials the transition temperature to the PE state, here probably  $T_b$ , should decrease at increasing dc bias field, as the latter has a higher dielectric constant. This corresponds with our results for PLZT 11.1/55/45 (table I and fig. 3).

Ac depoled materials and poled materials clearly show FE features like square hysteresis loops (fig. 4b) and an increase in the transition temperature to PE with increasing dc bias fields  $|8|$ , which is illustrated in fig. 5, table I and fig. 3.

So in thermally depoled material (at temperatures below  $T_p$ ) electric fields higher than  $E_{cr}$  will induce a phase transition from AFE to FE. The reverse transition will occur only by heating the material above  $T_b$  and slow cooling below  $T_b$ . So at temperatures below  $T_b$  and at fields lower than  $E_{cr}$  a metastable FE phase can exist.

The preceding considerations make it possible to construct from fig. 3 an E-T phase diagram for (thermally depoled) PLZT 11.1/55/45, which is presented in fig. 6. The phase transition AFE to PE is given by the transition temperature  $T_b$  versus dc bias field (table I), which gives a rather weak decrease of  $T_b$  with increasing field. The transition FE to PE is indicated by the high temperature part of  $E_{cr}$  versus T above the breakpoint in fig. 3. This FE to PE phase transition can also be indicated by the change of  $T_b$  at higher dc bias fields (table I, poled materials), which shows a comparable temperature dependence, although the absolute values are different. At last the AFE to FE transition is defined by the lower temperature part of  $E_{cr}$  versus temperature in fig. 3.

A thermodynamical description of phase transitions in AFE materials has already been given by Okada  $|10|$ . For

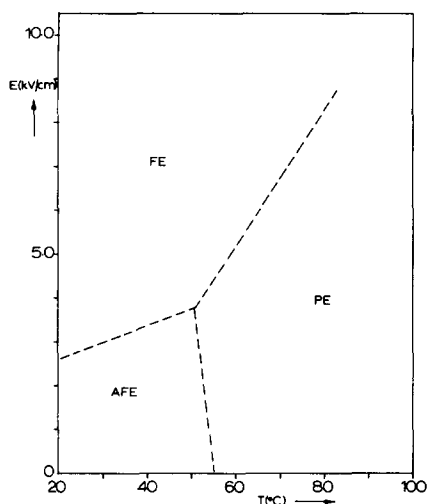


FIG. 6

The electric field (E) - temperature (T) phase diagram for PLZT 11.1/55/45.

a first order transition from the AFE to the FE state he stated that  $E_{cr}$  is decreasing slowly when the temperature is raised. Whereas for the induced first order phase transition from PE to FE Okada predicted a strong increase of  $E_{cr}$  with increasing temperature. This predicted behavior for  $E_{cr}$  is observed in our experiments for the PE to FE transition (fig. 3). However, we did not find a small decrease of  $E_{cr}$  (below  $T_b$ ), but just the opposite viz. a small increase of  $E_{cr}$  with increasing temperature.

It must be remarked that theoretically all phase transitions, e.g. AFE to PE, FE to PE and AFE to FE can be broadened. Indeed there are indications that for instance the FE to PE transition is a diffused one. For above  $T_b$  (the phase transition temperature) the remanent polarization has still a finite value, which slowly decreases with increasing temperatures to zero.

For PLZT 10.5/55/45 the same kind of properties as for PLZT 11.1/55/45 have been found. For thermally depoled materials with La concentrations  $< 10.2$  at.% and at temperatures below  $T_b$  we did not observe an electrically induced phase transition. For these compositions we have only observed domain orientation in the already FE material at increasing dc electric fields. In thermally depoled PLZT 12.0/55/45 and PLZT 12.2/55/45 and at temperatures below  $T_b$  indications for the existence of an AFE phase have been found too. Applying high electric fields to this material also results in a phase transition to the FE phase; removal of this field however gives the reversible transition from the FE phase to the AFE state without heating and cooling procedure as for PLZT 11.1/55/45. Still higher La concentrations, as e.g. PLZT 13/55/45, already show at room temperature linear behaviour between polarization and electric field and are considered as PE.

For PLZT ceramics with a Zr to Ti ratio near 55 to 45 an induced AFE to FE phase transition has not been reported in literature. Though for PLZT ceramics with a high Zr content (e.g. PLZT 10/80/20) this transition has already been observed [9]. Suggestions were made for the existence of an AFE phase in some PLZT x/65/35 ceramics [3,11,12], though no clear indications for such an AFE phase were given. Carl and Geisen [3] rejected the AFE concept in the case of PLZT x/65/35 because the losses were considered too high. Indeed AFE materials having few (and rather large) domains should possess low losses. But for the PLZT compositions under consideration here the energy differences between the FE AFE and PE phases are probably small (diffuse phase transitions). So in the AFE phase a certain amount of FE phase can exist (metastable, fluctuations). This will raise the dielectric losses, in accordance with our experiments.

Keve et al. [4] clearly found field-induced phase transitions in PLZT x/65/35 ceramics. The similarity between our observed

field-induced phase transitions and those of Keve et al. is the occurrence of a non-reversible phase transition and the occurrence of ferroelectric features for poled and ac depoled materials. The difference is that no detectable crystal structure change has been observed at our field-induced phase transitions where both phases have tetragonal symmetry, whereas, Keve et al. found a cubic (non ferroelectric) structure for thermally depoled material, which changed over to a tetragonal or orthorhombic structure at the field-induced transition.

It is concluded that thermally depoled ceramic PLZT 11.1/55/45 possesses dominating AFE features at temperatures below the transition to the PE state. Applying electric fields gives a field-induced phase transition to a FE state. "Coexistence" of one stable with one or two metastable phases in a certain temperature-electric field region seems possible on the basis of quasi-static fluctuations (heterophase fluctuations). This will give rise to broadening of the phase transition. An explanation along this line has been given by Cook |13| for phase transitions in some metal systems. For ferroelectric materials this concept of heterophase fluctuations has already been used by Fritsberg |14|.

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