

STUDY OF PHASE TRANSITIONS AND PROPERTIES OF TETRAGONAL (Pb,La)(Zr,Ti)O₃ CERAMICS—I

PHASE DIAGRAM AND β -PHASE

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Abstract—The phase diagram ($T-x$ plot) of thermally deposed tetragonal PLZT materials has been investigated by means of X-ray diffraction, Capacitance and DSC measurements. Materials with a low La content show a classical $FE_r \rightleftharpoons PE_c$ transition. This transition has first or second order character, dependent on the Zr/Ti ratio.

Materials with a medium and high La content show a diffuse transition from the cubic high temperature phase to a tetragonal, so called β phase. This β phase has no clear FE properties and a spontaneous transition to the FE_r phase on lowering the temperature only takes place for materials with a medium La content. For materials with a high La content a spontaneous $\beta_r \rightarrow FE_r$ transition is not observed.

1. INTRODUCTION

Most investigations in the perovskite system (Pb, La) (Zr, Ti)O₃, usually called PLZT, have been concentrated on compositions $x/65/35$ (x being the La concentration in a material with a Zr/Ti ratio of 65/35). Both from a scientific and an application point of view, interesting properties were observed. Applications based on electrical controlled birefringence, deformation and light scattering are possible, because good electro-optic properties are combined with a high optical transparency and a low coercive field strength[1].

Applications of the more Ti rich, higher coercive, tetragonal materials are mainly based on the linear electro-optic effect. Besides research concerning applications, a number of studies were performed on phase relations in general and more particularly on electrical inducible phase transitions. In materials $x/65/35$ with a relative high La content ($x > 7$ at.% La) a broad maximum is observed in the permittivity curves at the apparent Curie temperature T'_c [3-5], but it is not yet clear whether this diffuse maximum is indicative for a phase transition and if so, what kind of transition takes place. It is a fact that the material does not show a transition from the cubic high temperature phase to a FE phase spontaneously and in a large temperature interval below T'_c , no macroscopic FE properties have been observed[2, 3, 5]. A transition to a polar phase together with true ferroelectric behaviour was observed below a temperature T_i (with $T_i \ll T'_c$), but only after having applied a strong electric field. The temperature region

around and below T'_c has been interpreted as a region where polar short range order develops[4], as a region where ordering of vacancies occurs[6], etc.

In both the Zr rich (Zr/Ti ratio $> 70/30$) and the Ti rich (Zr/Ti ratio $< 60/40$) part of the PLZT phase diagram[1], is a strongly broadened permittivity curve observed for materials with a relative high La content, but contrary to PLZT 8/65/35, a polar phase† develops spontaneously on cooling from the cubic high temperature phase at all La concentrations[1, 7, 8]. No X-ray studies as a function of temperature were reported for materials with a high Zr content but SHG measurements showed the existence of at least traces of a polar phase at temperatures far above the apparent Curie temperature T'_c [7].

On the other hand an extensive X-ray study in the Ti-rich part of the phase diagram has been performed by Wolters on PLZT $x/55/45$ materials[8]. In PLZT 11/55/45 a crystallographic tetragonal \rightarrow cubic transition characterised by a jump in the c/a ratio, occurs at a temperature T_x below the temperature T'_c , however a small remanent tetragonal distortion could be observed at $T > T_x$ in the X-ray and ESR spectra[8, 9].

In conclusion it can be stated, that it is not clear with regard to PLZT materials whether the observed broad maxima in the permittivity curves are related to a phase transition and the aim of this paper is to report on phase relations in thermally deposed tetragonal PLZT materials, with special attention to the crystallographic transition (Section 3.1). Tetragonal materials were used in this investigation, since the phase diagram is probably simpler than for rhombohedral materials. To eliminate the influence of the morphotropic rhombohedral/tetragonal boundary at a Zr/Ti ratio of about 55/45, compositions $x/30/70$ were chosen.

The criteria from which the phase boundaries have been constructed are necessarily discussed at some length in Section 3. It will be shown in Section 4.1 that a tetragonal β phase, which is not a classical FE phase, appears in materials with a relative high La content.

†This polar phase is rhombohedral FE or orthorhombic AFE, dependent on the La content in the case of Zr-rich materials and tetragonal in the case of Ti-rich materials. In this latter case, the character of the unpoled tetragonal material is not yet quite clear. In both cases materials with a high La content only show ferroelectric behaviour after a strong electric field has been applied to the material[8, 10]. In this respect, the behaviour of these materials is similar to PLZT $x/65/35$ material.

Finally in Section 4.2 a comparison between $x/30/70$ and other tetragonal materials will be made. It will be shown, that the behaviour of the various PLZT materials is more or less similar. A further discussion on the topic of diffuse phase transitions in these materials together with the energetics of the transitions involved, will be given in Part II of this paper.

The electrical induction of phases in tetragonal PLZT materials will be the subject of Part III of this paper.

2. EXPERIMENTAL METHODS

All PLZT materials were prepared according to the general formula



by means of a mixed oxide method as described by Wolters[8], starting with a lead elimination factor $\alpha = 0.75$.

The final sintering was performed at 1250°C for 16 hr in a controlled O₂ and PbO atmosphere and resulted in ceramics having densities better than 96% of the theoretical density. Grain sizes were larger than 5 μm , except for materials with a very low La content. After sintering, lead elimination factors ranged from $\alpha = 1.1$ to $\alpha = 1.2$. No second phase has been observed with X-ray diffraction and scanning electron microscopy. Large scale compositional fluctuations will generally result in a broadening of the X-ray diffraction lines. However the half-widths of the (111) reflection lines ($\bar{D} \approx 0.19^\circ$) are comparable with the half-width of the unbroadened reflection lines of Si. This leads to the conclusion that large-scale compositional fluctuations are absent in the materials under investigation here. A more detailed description of the preparation of tetragonal PLZT materials has been given by Wolters[8]. Discs were made with a diameter of 6 mm and a thickness of 0.5 mm from the sintered specimens. To relieve strains, resulting from the mechanical processing, the discs were annealed at 800°C, followed by slowly cooling. For dielectric measurements, gold electrodes were evaporated on the discs.

X-ray powder diffraction patterns at room temperature and at elevated temperatures were determined by a Philips diffractometer using Cu-K α radiation. Unit cell parameters were calculated from several diffraction lines, using Si as an internal standard. The accuracy of the room temperature measurements was estimated at about 0.001 Å. Low temperature X-ray diffraction was performed by means of a low temperature Enraf-Nonius Guinier equipment. A Rohde and Schwartz bridge type VKB.BN3520 was used to measure the capacity and loss tangent of the samples at frequencies between 1 kHz and 300 kHz (applied voltage ≤ 40 V/cm). Heating and cooling rates were about 1 deg/min.

Long periods of aging resulted in phenomena as described by Schulze[7, 14]. To prevent such aging phenomena all samples were de-aged at 450°C during 15 min. Subsequently, the material was allowed to stand at the starting temperature of the measurement for about half an hour.

Transition heats were determined by Dupont type 990

Table 1. Characteristic temperatures in PLZT $x/30/70$ materials, obtained from X-ray, dielectric and thermal measurements[†]

x (at% La)	T _x [†] (°C)	T _c [†] (°C)	T _b [†] (°C)	T _s [†] (°C)	T _t [†] (°C)
5		340	337		337
8		277	277		279
10		233	231		237
12		191	191		193
14	132	130	130		130
15		104	102		98
16		85	77	72	72
17	65-90	53	40	37	37
18	35-50	33	17	6	3
19	-20-0	-4	-23		
20		-19	-40		
21		-32	-55		
23		-46	-77		
25		-62	-95		

DSC (differential scanning calorimetry) equipment, using ceramic discs.

The sensitivity limit for PLZT materials is estimated at 5 cal/mol.

A short summary of the experimental results is given in Table 1. The results will be discussed in the next sections.

3. EXPERIMENTAL RESULTS

3.1 X-Ray results

In Fig. 1 the unit cell parameters as a function of Lanthanum concentration for annealed powders (at $T = 20^\circ\text{C}$) are given for the series $x/30/70$. For $x \leq 18$ at.% La the material has tetragonal symmetry for $x \geq 19$ at.% La the material has cubic or pseudocubic symmetry.

X-Ray diffraction experiments as a function of temperature were performed on several compositions. A high accuracy could not be achieved because the X-ray diffractometer equipment was not optimally designed for this type of measurement.

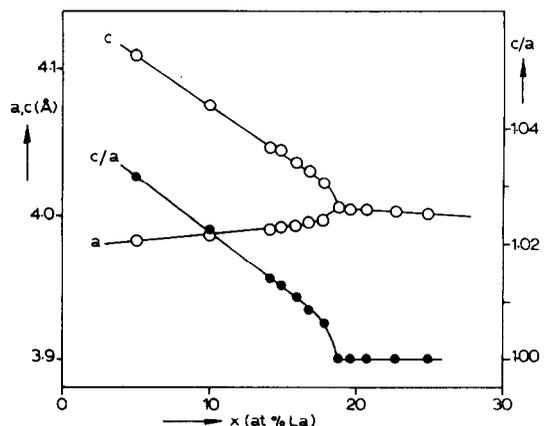


Fig. 1. Unit cell parameters as a function of x for PLZT $x/30/70$ materials at 20°C .

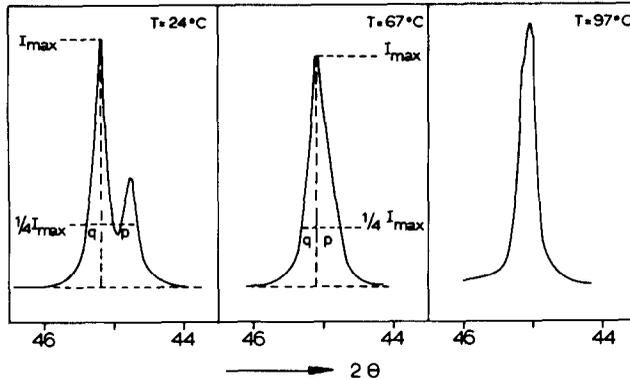


Fig. 2. Tetragonal splitting of the 200 reflection at several temperatures, as measured on powdered PLZT 17/30/70.

The tetragonal splitting of the (200) reflection was measured at different temperatures. A typical example is given in Fig. 2. At low temperatures a clear tetragonal splitting is seen. On increasing the temperature, this splitting becomes smaller and eventually only a shoulder at the low-angle side of the (200) reflection remains. At still higher temperatures a cubic symmetry is observed.

Because of the small magnitude of the tetragonal splitting, it was not possible to calculate accurate c/a ratios in the phase transition region. In Fig. 3 the ratio p/q (p and q are defined in Fig. 2) is given as a function of temperature for two different compositions. Because of the fact, that the $\text{CuK}\alpha_2$ radiation gives an asymmetric deformation of the (200) reflection at the high-angle side, we expect $p/q < 1$ for purely cubic materials. On the other hand, a tetragonal splitting, as observed in PLZT $x/30/70$ materials, will produce a deformation at the low-angle side, so that $p/q > 1$. It can be seen in Fig. 3, that PLZT 14/30/70 shows a more or less sharp tetragonal \rightarrow cubic transition at 132°C. In contrast to this PLZT 17/30/70 shows a diffused tetragonal \rightarrow cubic transition in the temperature region 65–90°C. In this region no tetragonal splitting is observed, but the material is not yet completely cubic.

PLZT $x/30/70$ materials with $x > 17$ at.% La and PLZT 11/55/45 showed the same behaviour. The results for some PLZT $x/30/70$ materials are given in Table 1,

whereas for PLZT 11/55/45 a transition region at 75–90°C is observed.

In conclusion it can be stated, that PLZT materials with a relative high La content ($x/30/70$ with $x > 16$ at.% La and 11/55/45) show a gradual tetragonal \rightarrow cubic transition.

In a certain temperature region the tetragonal splitting is not present in X-ray diffraction patterns, but deviations from the cubic symmetry are observed. An exact determination of a crystallographic transition temperature is impossible for these materials.

3.2 Dielectric results

From a dielectric point of view, three different La-concentration ranges can be distinguished in PLZT $x/30/70$.

(a) $0 < x < 16$ at.% La. The maxima in the $\epsilon'(T)$ and $\epsilon''(T)$ curves are sharp. The temperature where ϵ' is at a maximum (T'_c) and the temperature where ϵ'' is at a maximum (T_b) coincide. These temperatures are frequency independent and only a small thermal hysteresis is observed (Fig. 4a).

(b) $16 \leq x \leq 18$ at.% La. The maxima in the $\epsilon'(T)$ and $\epsilon''(T)$ curves are somewhat broadened. The temperature T'_c does not coincide with the temperature T_b any longer and is frequency dependent. In the permittivity curve a second characteristic temperature is apparent. In a small

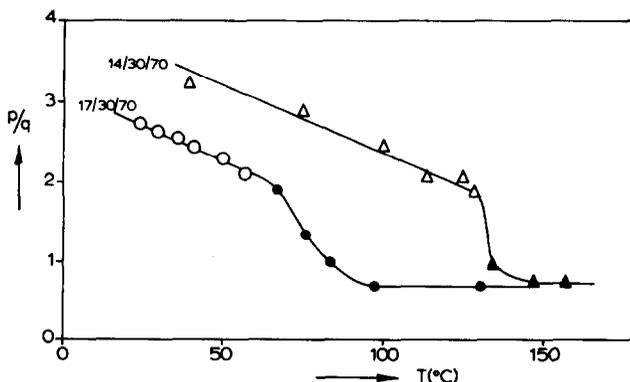


Fig. 3. The p/q ratio as function of temperature for PLZT 14/30/70 and 17/30/70. Open circles and triangles: clear tetragonal splitting. Closed circles and triangles: no clear tetragonal splitting.

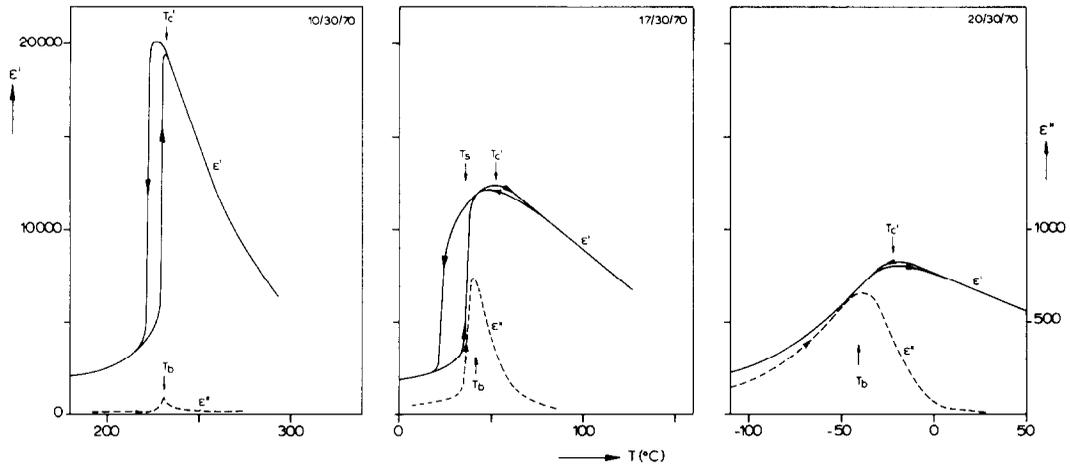


Fig. 4. Permittivity and dielectric loss as function of temperature for PLZT 10/30/70 (left), 17/30/70 (centre) and 20/30/70 (right). The meaning of the temperatures T'_c , T_s and T_b is explained in the text.

temperature interval (ca. 4°C) around the temperature T_s , the dielectric constant of the material rises to about three times the low temperature value. In PLZT 17/30/70 for example, the temperature T_s equals 37°C . At 35°C the dielectric constant of the materials is about 4000 and subsequent heating leads to a dielectric constant of about 11,000 at 38°C . In a normal ferroelectric material with a first order FE \rightarrow PE transition the temperature T_s and the temperature where the dielectric constant is at maximum more or less coincide. In this case however a significant difference exists between the temperatures T_s and T'_c . It will be shown in Section 3.3 that at temperature T_s a latent heat-effect occurs. The crystallographic tetragonal \rightarrow cubic transition, however, takes place at a significantly higher temperature. A second notable feature of the temperature T_s , is the complete frequency independence. Thermal hysteresis in the permittivity curve is limited (largely) to temperatures $T \leq T_s$ (Fig. 4b).

(c) $x > 18$ at.% La. The maxima in the $\epsilon'(T)$ and $\epsilon''(T)$ curves are strongly broadened. The temperatures T'_c and T_b do not coincide and a strong frequency dependence is observed. Thermal hysteresis as well as a temperature T_s are absent in the $\epsilon'(T)$ and $\epsilon''(T)$ curves.

Characteristic temperatures as obtained from the dielectric measurements are presented in Table 1. It should be noted that the crystallographic tetragonal \rightarrow cubic transition occurs in a temperature region close to temperature T'_c and in our opinion the poorly defined broadened maximum in the $\epsilon'(T)$ curves is directly related to the diffused tetragonal \rightarrow cubic transition. The fact that at temperatures $T > T'_c$ deviations from the cubic symmetry were observed, points to the occurrence of fluctuations, as will be pointed out in Part II of this paper.

3.3 Results of thermal measurements

Making the same distinction in three La concentration regions as has been done for the dielectric measurements (Chapter 3.2), the results for PLZT $x/30/70$ materials are:

(a) $0 < x < 16$ at.% La. A latent heat effect is observed

at a temperature T_l . This temperature appears to be coincident with the (dielectric) temperatures T'_c and T_b . The observed latent heat decreases strongly and linearly with increasing La content (Part II of this paper).

(b) $16 \leq x \leq 18$ at.% La. A small latent heat-effect is observed again. The temperature T_l appears to coincide with the temperature T_s . At the temperatures where the dielectric constant (T'_c) or the dielectric loss (T_b) are at maximum no heat-effect could be observed by means of DSC-measurements.

(c) $x > 18$ at.% La. All (latent) heat-effect is absent in these materials. Although the sensitivity of our DSC measurements is not better than 5 cal/mol, it will be clear that in these materials a tetragonal \rightarrow cubic transition occurs without a notable heat-effect. This can be concluded from the fact that these materials possess a tetragonal symmetry at low temperatures ($T \ll 20^\circ\text{C}$, see also Table 1).

4. DISCUSSION

4.1 Phase relations in thermally depoled PLZT $x/30/70$

For thermally depoled material, we propose a phase diagram as shown in Fig. 5. In this figure three parts can be distinguished:

(a) $x < 16$ at.% La. In the lower La-concentration range the situation is not very complicated, because a more or less classical, sharp phase transition occurs. Characteristic temperatures as T'_c , T_b , T_l and T_x are more or less coincident and have been used as criteria for the transition $\text{FE}_t \rightarrow \text{PE}_c$. The observed thermal hysteresis and latent heat points, in our opinion, to a first order character of this transition.

(b) $16 \leq x \leq 18$ at.% La. Starting from the low temperature FE_t phase, a transition $\text{FE}_t \rightarrow \beta_t$ takes place on heating at a temperature characterised by T_l and T_s . However the material is still tetragonal after this transition and the high-temperature PE_c phase develops on further heating at a poorly defined temperature.

In the phase diagram the temperature where ϵ'

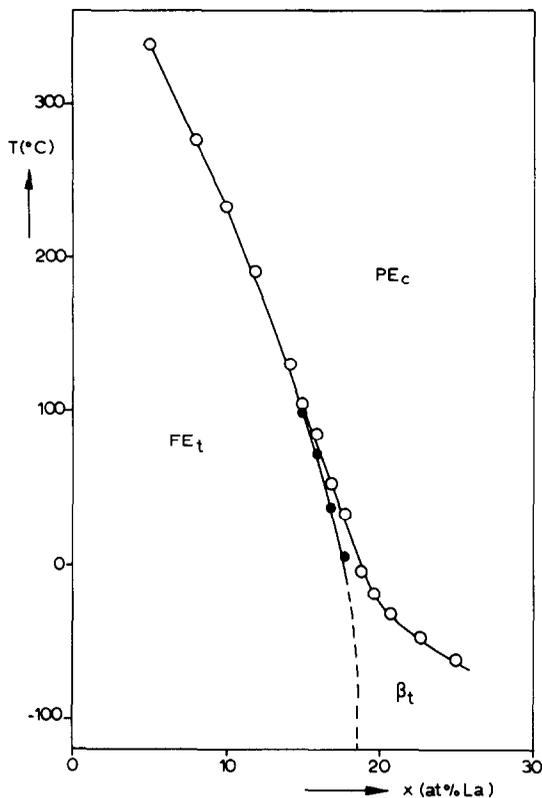


Fig. 5. Phase diagram for thermally depoled PLZT $x/30/70$ materials. The transition temperatures were determined from heating cycles.

(10 kHz) is at maximum is used as a criterion† for this latter transition.

(c) $x > 18$ at.% La. Only one transition occurs in these materials. This $\beta_t \rightleftharpoons PE_c$ transition is a very diffused one so that the transition temperature is poorly defined.†

†The apparent Curie temperature is not a very good criterion for the tetragonal \rightarrow cubic transition. In a commonly used model the broadening of the maxima in the permittivity-curves is ascribed to a distribution of transition temperatures and the superposition of permittivity curves having sharp maxima at different temperatures leads to the observed broadening. An unambiguous indication for the value of the average transition temperature can be obtained from the permittivity curves only in cases, where the starting curves are more or less symmetrical. See for example Wolters[8].

‡A material is in a virgin condition after being heated to a temperature far above T_c , if it is allowed to cool slowly. In this way the memory of the electrical history of the material is completely removed.

In Fig. 5 the $FE_t \rightarrow \beta_t$ transition for $x > 18$ at.% is indicated by a vertical dashed line. The reason is, that for PLZT 18/30/70 a transition $FE_t \rightleftharpoons \beta_t$ was observed, but for PLZT 19/30/70 no characteristics indicative for such a transition, as discussed in Section 2, were observed. This indicates that PLZT $x/30/70$ materials, with $x \geq 19$ at.% La do not show a *spontaneous* transition to a FE_t phase on lowering the temperature. For the phase diagram this means that the β -phase field extends down to very low temperatures in this case. However in the T - x plot of Fig. 5, the exact position of the $FE_t \rightarrow \beta_t$ transition line is not known for $18 < x < 19$ at.% La.

The distinction between FE_t and β_t phase deserves some explanation, since the two phases both have a tetragonal symmetry. A discussion in full detail of the transition $\beta_t \rightarrow FE_t$ will be given in Part III of this paper, where it will be shown, that after having applied a strong electric field to the β_t phase, a transition to the FE_t phase takes place. The difference between the β_t and FE_t phase is expressed by the two following facts:

1. As can be seen from Table 2, poling of the β phase results in a very strong decrease of the dielectric constant. If the material is already FE before poling such an anomalous decrease is absent.
2. Polarisation as function of the electrical field curves of β -phase material clearly show a phase transition, whereas FE phase material shows an EP curve more indicative for domain orientation.

This behaviour can be seen from Fig. 6, where virgin‡ EP curves of PLZT 17/30/70 are shown at two different temperatures. At 43°C the material is in the β state and at the critical field E_c a transition to the FE state takes place.

Similar effects were observed by Wolters[8], who extensively investigated tetragonal PLZT $x/55/45$ materials.

It should be noticed, that the situation in tetragonal PLZT materials is comparable with PLZT 8/65/35. In PLZT 8/65/35 however it is doubtful if the material at temperatures $T \gg T'_c$ is different from materials at temperatures $T \ll T'_c$, because in both cases a cubic symmetry is observed[2, 3]. Therefore in this case a clear distinction exists between the electrically induced FE (orthorhombic) phase and the cubic β phase. In the case of tetragonal PLZT materials, the situation is just the opposite. Because of the different symmetries a distinction can be made between the tetragonal β phase and the cubic PE phase, but a distinction between the FE and β phase is less clear. The character of the β phase will be discussed in Part II of this paper.

Table 2. Dielectric constant (low field measurement, frequency 10 kHz) before and after poling for several PLZT $x/30/70$ materials

x (at.% La)	T (°C)	ϵ' unpoled	ϵ' poled	phase in unpoled condition
16	50	2500	2200	FE
17	20	2300	2000	FE
	45	12100	3500	β
20	-90	3050	1400	β
	-60	6000	2500	β

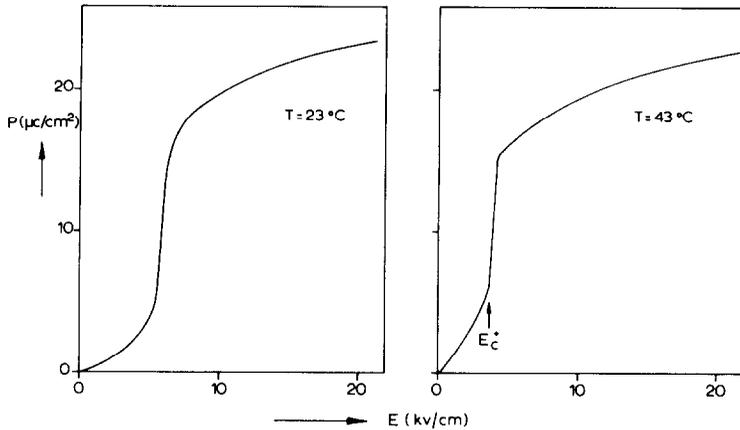


Fig. 6. Virgin EP curves for PLZT 17/30/70 at 25°C and 43°C (frequency 0.05 Hz).

4.2 Comparison with other tetragonal materials

The situation in the high Ti-part of the PLZT phase diagram is relatively simple. Extensive studies have been performed on PLT[11] and the sharp first order $FE_t \rightarrow PE_c$ transition resembles the same transition in PLZT $x/30/70$ materials in the lower La-concentration range. Only in materials with a very high La content ($x = 30$ at.% La) is some broadening of the permittivity curves observed[11].

More complicated is the situation for materials with a Zr/Ti ratio larger than 30/70. Wolters[8] studied the phase relations in PLZT $x/55/45$ and a careful examination of his results together with some additional measurements, revealed a great similarity between the systems $x/30/70$ and $x/55/45$. For PLZT $x/55/45$ the three La-concentration regions are:

1. $x < 4$ at.% La. Classical sharp $FE_t \rightarrow PE_c$ transitions.
2. $4 < x < 10.5$ at.% La. Sequence of two transitions $FE_t \rightarrow \beta_t \rightarrow PE_c$ at respective temperatures T_s and T_c' .
3. $x > 10.5$ at.% La. Only one (diffuse) transition $\beta_t \rightarrow PE_c$ is observed at temperature T_c' .

With respect to the tetragonal \rightarrow cubic transition in the medium and higher La-concentration ranges, some remarks should be made.

Wolters considered the temperature, where the dielectric loss is at maximum, characteristic for the transition tetragonal \rightarrow cubic. Furthermore he observed a jump in the c/a ratio at this temperature, however without a complete disappearance of the tetragonal distortion. More recent investigations showed that the temperature where the dielectric constant is at maximum† (10 kHz) is more indicative for this transition. Just as in the case of $x/30/70$ materials, the disappearance of the tetragonal distortion is a gradual process without notable discontinuities and indications for a tetragonal distortion have been observed at temperatures slightly above the temperature T_c' .

In conclusion it can be said that the phase diagrams ($T-x$ plot) for thermally depoled tetragonal PLZT

materials are qualitatively similar to the one we have proposed for PLZT $x/30/70$ materials. However the La concentration where a deviation from the classical behaviour occurs, is different for materials with a different Zr/Ti ratio.

Although the shape of the phase diagram is similar for all tetragonal PLZT materials, the character of the transitions in PLZT $x/55/45$ materials is different from that of $x/30/70$ materials. In the first place the transition $FE_t \rightarrow PE_c$ is probably second order for PLZT $x/55/45$ materials with a low La content. This can be deduced from the following:

- For PLZT 0/55/45 and 2/55/45 a more or less symmetrical anomaly in the $\epsilon'(T)$ curve is observed without a notable thermal hysteresis.
- A latent heat effect is absent in those materials. Only smeared-out dips around the transition temperatures were observed in the experimental DSC baselines.

It must be kept in mind, that PLZT $x/55/45$ compositions with a low La content are situated close to the morphotropic rhombohedral/tetragonal boundary (see phase diagram of Land *et al.*[1]), and that rhombohedral $PbZr_yTi_{1-y}O_3$ solid solutions show a second order $FE \rightarrow PE$ transition for $y > 0.06$ [12]. In the opinion of Ari-Gur *et al.*[13] an area of mixed tetragonal/rhombohedral phases exists in $PbZr_xTi_{1-x}O_3$ solid solutions ranging from $x = 0.49$ to $x = 0.64$. However we did not observe a rhombohedral structure in PLZT 0/55/45 and 2/55/45 solid solutions by means of X-ray diffraction. The materials under investigation here are monophasic tetragonal and probably the composition range in PZT and PLZT materials, where classical second order $FE \rightarrow PE$ transitions occur, extends into the tetragonal phase field. Increasing the Ti content leads to a change over to a first order $FE \rightarrow PE$ transition as has been observed in $PbTiO_3$ and PLZT $x/30/70$ materials with a low La content.

Finally it should be noted that in PLZT $x/55/45$ materials a strict boundary line between materials with a low La content ($x < 4\%$) and materials with a medium La content ($4 < x < 10.5\%$) cannot be drawn. A more or less gradual change from the low La concentration to the higher La concentration range is observed.

†It should be kept in mind that $T_b < T_c$ for materials $x/55/45$ with $x > 4$ at.% La.

This is in contrast with the observations in $x/30/70$ materials.

CONCLUSIONS

1. The phase diagram ($T-x$ plot) was determined for thermally depoled PLZT $x/30/70$. Characteristic dielectric, thermal and crystallographic temperatures were used for the construction. In materials with a high La content ($x \geq 16$ at.% La) a tetragonal β phase, which is macroscopically non FE, has been observed.

2. Comparison with earlier work on tetragonal PLZT materials leads to the conclusion, that similar phase diagrams can be constructed for other tetragonal materials.

The β phase in materials with a higher Ti content occurs at a higher La concentration than in materials with a lower Ti content.

3. Tetragonal materials with a composition close to the morphotropic rhombohedral/tetragonal boundary and a low La content ($x/55/45$ with $x < 4$ at.% La) probably show a second order $FE_t \rightarrow PE_c$ transition, with a classical dielectric behaviour. Increasing the Ti content leads to a change to a first order transition, as observed in PLZT $x/30/70$ materials with $x < 16$ at.% La.

4. The maxima in the permittivity curves of tetragonal PLZT materials with a high La content are correlated

with a tetragonal \rightarrow cubic transition, having a diffused character as measured by X-rays.

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REFERENCES

1. Land C. E., Thacher P. D. and Haertling G. H., *Appl. Solid State Sci.* **4**, 137 (1974).
2. Keve E. T. and Bye K. L., *J. Appl. Phys.* **46**, 810 (1975).
3. Keve E. T. and Annis A. D., *Ferroelectrics* **5**, 77 (1973).
4. Carl K. and Geisen K., *Proc. IEEE* **61**, 967 (1973).
5. Meitzler A. H. and O'Bryan H. M., *Proc. IEEE* **61**, 959 (1973).
6. Meitzler A. H., *Ferroelectrics* **11**, 503 (1975).
7. Schulze W., Ph.D. Thesis, Pennsylvania State University, University Park, Pennsylvania, U.S.A. (1973).
8. Wolters M., Ph.D. thesis (1976), Twente University of Technology, Enschede, The Netherlands (1976).
9. Heilborn M., Ph.D. Thesis (1977), Twente University of Technology, Enschede, The Netherlands (1977).
10. Thouy G. and Paletto J., *Bull. Soc. Fr. Cer.* **113**, 71 (1976).
11. Keizer K. and Burggraaf A. J., *Ferroelectrics* **14**, 671 (1976).
11. Keizer K. and Burggraaf A. J., *Ferroelectrics* **14**, 671 (1976).
12. Clarke R. and Glazer A. M., *Ferroelectrics* **14**, 695 (1976).
13. Ari-Gur P. and Benguigui L., *J. Phys. D: Appl. Phys.* **8**, 1856 (1975).
14. Schulze W. A. and Biggers J. V., *Ferroelectrics* **9**, 203 (1975).