

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

DIFFUSE PHASE TRANSITIONS AND THERMODYNAMICS

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Abstract—The diffuse phase transition in tetragonal PLZT materials has been investigated. Strongly broadened permittivity curves were observed for materials with a relative high La content. Curie-Weiss behaviour in the permittivity curves is observed only at temperatures far above the apparent Curie temperature.

A latent heat effect is observed at the sharp FE_t → PE_c transition in PLZT *x*/30/70 materials with a low La content (*x* < 16 at% La). This heat effect decreases linearly with increasing La content. The diffuse tetragonal → cubic transition is attended with a very small heat-effect and a low value (~0.04 cal/mol°C) for the entropy difference between high and low temperature phase could be determined.

Consequently, polarisation fluctuations are possible in a certain temperature interval around the transition.

1. INTRODUCTION

Many phase transitions in macroscopic homogeneous materials are characterised by the fact that the transition temperature is not really sharply defined. In these so-called diffuse phase transitions (DPT), the transition is smeared out over a certain temperature interval, resulting in a gradual change of physical properties in this temperature region. This phenomenon is observed in several types of materials[1], but the most remarkable examples of DPT are found in ferroelectric materials. Characteristics for the DPT behaviour in this case are:

- broadened maxima in the permittivity curves,
- gradual decrease of spontaneous (remanent) polarisation with rising temperature,
- transition temperatures as obtained by different techniques do not coincide,
- relaxational character of the dielectric properties in the transition region,
- no Curie-Weiss behaviour in a certain temperature interval above the transition temperature.

The diffuseness of the phase transition is assumed to be due to the occurrence of fluctuations in a relatively large temperature interval around the transition. In this transition region a mixture of high and low temperature phases is present (hybrid crystal) and the physical properties related to the transition will gradually change, while on lowering the temperature the low-temperature phase will grow at the expense of the high-temperature phase. It should be noted that, though the notion "fluctuation" is generally accepted and fluctuations have been shown to exist (critical phenomena, spinodal decomposition, central mode), *direct* evidence for the occurrence of fluctuations in a large temperature interval around a transition is scarce in literature, especially for FE materials.

Usually two kinds of fluctuations are considered:

- compositional fluctuations
- polarization (structural) fluctuations.

A compositional fluctuation is an intrinsic phenomenon, occurring in solid solutions and compounds with an extended homogeneity range and ranges from short-range order and clustering to long-range order and spinodal decomposition waves. In most cases a compositional fluctuation can be regarded as a static frozen-in high-temperature situation. Fluctuations of this kind can result in distribution of transition temperatures over different micro-regions of the crystal and in this way will cause a DPT[4, 22]. As has been stated, *quantitative* experimental evidence for the occurrence of compositional fluctuations is scarce in literature. Recently Anderson *et al.*[2] showed the existence of quasistatic compositional fluctuations in ferroelectric layer compounds, e.g. Ba₂Bi₄Ti₅O₁₈. Possibly this can be coupled with the frequently observed broadening of the maxima of the permittivity curves in these types of materials. In non-ferroelectric aluminosilicates McConnell[3] observed low frequent compositional waves with a periodicity of 20–1000 Å dependent on composition and heat treatment. The most pronounced examples of DPT behaviour have been observed in FE solid solutions and although direct observation of compositional fluctuations in those materials is not reported in literature, it is clear that, from a thermodynamic point of view, compositional fluctuations will be present in solid solutions. It is not known however to what extent the phase broadening is caused by these fluctuations.

Polarization fluctuations are the result of small energy differences between high and low temperature phases around the transition. The small energy differences will result in a non-vanishing probability for the occurrence

of a small microvolume of the non-stable phase in a matrix of the stable phase. The fluctuation probability w , in zeroth order approximation, neglecting interaction of the fluctuation volume with the surrounding matrix is given by [4]:

$$w = \text{const.} \exp - \frac{v\Delta S(T - T_0)}{kT_0} \quad (1)$$

(v = volume of fluctuation, T_0 = transition temperature, ΔS = entropy difference per unit of volume).

A small entropy difference between the FE and PE phase will result in a large fluctuation probability. A classical example of polarization fluctuations around and FE \rightarrow PE transition has been given by Känzig[5]. He observed, by means of X-ray diffraction, that in a narrow temperature range around the transition, a single crystal of BaTiO₃ splits up into ferroelectric and paraelectric microregions. However the temperature range where the two phases coexist is only 1°C in this case.

Direct observation of polarization fluctuations in a large temperature interval around the transition is not reported in literature. Though, especially in the Russian literature[20–22] a lot of theoretical speculations were devoted to this subject, the hypothesis that a small entropy difference between FE and PE phases will result in a diffused phase transition is not well investigated experimentally. Combining available literature data, we find that in Ba_{0.33}Sr_{0.67}Nb₂O₆ single crystals a small entropy-difference (≈ 0.06 cal/mol K) between FE and PE phases is observed[6], together with a somewhat broadened permittivity curve and in (Ba,Sr)TiO₃ solid solutions, the increase of DPT behaviour with increasing Sr content is accompanied by a strong decrease of transition heat[7, 8]. Unfortunately in this latter case the magnitude of the effect is not reported.

In connection with polarization fluctuations, Fritsberg[7, 9] introduced the notion of ferroelectric stability, defined as:

$$\xi = \frac{1}{\epsilon_0} \cdot \frac{T_c}{C_w} \cdot P_{sc} \quad (2)$$

(T_c = curic temperature, C_w = curic constant, P_{sc} = jump of spontaneous polarization at the transition).

By making use of the well-known thermodynamic expression

$$Q = \frac{1}{2\epsilon_0} \cdot \frac{T_c}{C_w} \cdot P_{sc}^2 \quad (3)$$

(Q = latent heat) the equation for the ferroelectric stability can be rewritten in the form

$$\xi = \sqrt{\left(\frac{2}{\epsilon_0} \cdot \frac{T_c}{C_w} \cdot Q\right)}. \quad (4)$$

The ferroelectric stability has the meaning of a fictitious electric field, necessary to obtain a polarization equal to the spontaneous one. In Fritsberg's opinion, substances of less stability are expected to have a more

diffused transition. For both compositional and polarization fluctuations, model calculations, based on a Gaussian distribution of the fluctuation showed a rather good agreement with the experimental results[4, 10, 12]. Moreover these calculations resulted in a quadratic relation between permittivity and temperature for temperatures above the (average) transition temperature. This so-called quadratic law has been observed experimentally in several material systems and has the form

$$1/\epsilon' = 1/\epsilon'_{\max} + C(T - T_c)^\gamma \quad \text{with } \gamma = 2. \quad (5)$$

However in a number of cases, no quadratic relation is observed and exponents ranging from $\gamma = 1$ (normal Curie-Weiss behaviour) to $\gamma = 2$ are measured[10, 11]. Deviations from Curie-Weiss behaviour can be interpreted as an indication for the occurrence of fluctuations[10, 11].

It should be stressed, that the notion DPT is used here for material systems, which are homogeneous on a macroscale. The materials cannot be considered as classical two phasic systems. The fluctuations under consideration here, are dynamic (in equilibrium with temperature) or static and occurring in small domains (~ 100 Å).

The aim of this paper is to report investigations concerning the diffused tetragonal \rightarrow cubic transition in (Pb,La)(Zr,Ti)O₃ solid solutions. The experimental results together with a short review of results from Part I of this paper will be given in Section 2. Special attention will be paid to the energy differences between the high and low temperature phases in Sections 2.2 and 3.1. It will be shown, that for tetragonal materials with a relatively high La content, polarization fluctuations can occur in a certain temperature interval around the transition. In Section 3.2 a short comparison with other tetragonal PLZT materials will be made and finally the character of the β -phase, introduced in Part I of this paper, will be discussed in Section 3.3.

2. EXPERIMENTAL RESULTS

2.1 Dielectric properties

The experimental procedure, as well as the phase diagram for thermally depoled PLZT x/30/70, have been described in Part I of this paper. In the lower La concentration range ($x < 16$ at% La) classical sharp FE_t \rightarrow PE_c transitions were observed. Increasing the La content leads to materials which show a sequence of two transitions FE_t \rightarrow β_t \rightarrow PE_c and eventually to materials showing only the transition β_t \rightarrow PE_c.

The transition β_t \rightarrow PE_c shows DPT behaviour and an exact transition temperature is difficult to determine. X-Ray diffraction as a function of temperature showed a very gradual decrease of the c/a ratio by a rise in temperature and no exact temperature for the crystallographic transition could be determined. $\epsilon'(T)$ and $\epsilon''(T)$ curves show a broadened maximum around the temperatures T'_c and T_b respectively.

As can be seen from Fig. 1, the broadening of the maximum in the permittivity curves increases with increasing La content. Frequency affects the temperature

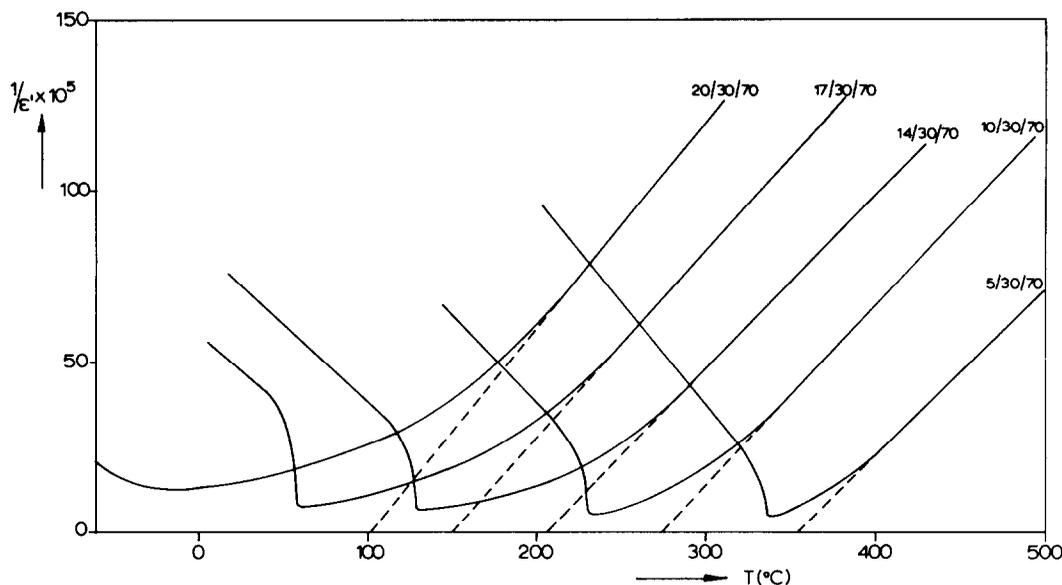


Fig. 1. Temperature dependence of the reciprocal dielectric constant (10 kHz) for PLZT $x/30/70$ materials.

dependence of the dielectric constant and the dielectric loss. For the compositions $x/30/70$ this frequency dependence is qualitatively similar to the frequency dependence in $x/55/45$ materials [4]. It shows that T'_c and T_b increase with increasing frequency just as ϵ''_{max} does. The value of ϵ''_{max} decreases with increasing frequency.

For all the materials under investigation here in a certain temperature interval $T'_c < T < T_{cw}$ (definition in Table 1), the temperature-dependence of the dielectric constant can neither be described by a normal Curie-Weiss law, nor by a quadratic law, as given in eqn (5). Exponents varied in a rather irregular way, from $\gamma = 1.2$ to $\gamma = 1.6$ for different materials.

However in all cases, at high temperatures ($T \geq T_{cw}$) a normal Curie-Weiss behaviour is found. This is illustrated in Fig. 1 and Table 1. Two striking facts are worthwhile mentioning:

—Contrary to classical ferroelectric materials, the extrapolated Curie temperature (T'_0) is *higher* than

the temperature where the dielectric constant is at maximum (T'_c).

—The temperature region where deviations from a normal Curie-Weiss behaviour appear, increases for increasing La content and increasing broadening of the maximum in the permittivity curve.

2.2 Thermal properties

In DSC measurements for materials $x/30/70$ with $x < 16$ at% La, a latent heat-effect is observed at the transition $FE_t \rightarrow PE_c$. This transition enthalpy decreases linearly with increasing La content (Fig. 2). Entropy differences between FE and PE phases, as calculated from these measurements, only show a slight decrease with increasing La content. Thermally depoled materials with $16 \leq x \leq 18$ at% La do show a small latent heat-effect, which is associated with the transition $FE_t \rightarrow \beta_t$.

However DSC measurements on PLZT materials $x/30/70$ with $x > 16$ at% La did not show a notable heat-effect around the $\beta_t \rightarrow PE_c$ transition.

To determine the small heat-effects around the $\beta_t \rightarrow PE_c$ transition, the specific heat as function of tem-

Table 1. Curie-Weiss parameters and ferroelectric stability for PLZT $x/30/70$ materials†

x (at% La)	T'_c (°C)	T'_0 (°C)	T_{cw} (°C)	$C_w \times 10^{-5}$ (°C)	ξ (kV/cm)
5	340	354	400	2.07	570
8	277	310	365	1.90	510
10	233	275	350	1.88	450
12	191	242	310	1.78	420
14	130	205	290	1.97	330
17	50	152	250	1.77	
20	-19	106	230	1.62	190

† T'_c , Temperature where the dielectric constant is at maximum. T'_0 , Extrapolated Curie-temperature. T_{cw} , At $T > T_{cw}$ a Curie-Weiss law is observed, whereas at $T < T_{cw}$, deviations from a normal Curie-Weiss law occur. C_w , Curie constant. ξ , Ferroelectric stability. For $x = 20$ at% La the ferroelectric stability has been calculated from the heat effect associated with the $\beta_t \rightarrow PE_c$ transition.

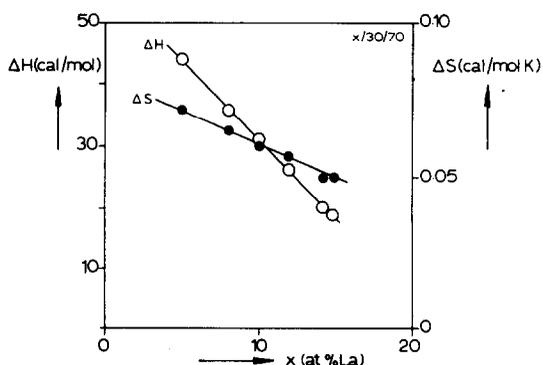


Fig. 2. Transition enthalpy and entropy, as a function of the La content, for the transition $FE_t \rightarrow PE_c$ in PLZT $x/30/70$ materials.

perature has been measured for powdered, thermally deoiled PLZT 20/30/70, by means of a sensitive adiabatic calorimeter. The experimental set up is described in [19]. The results are given in Fig. 3. In this figure a very small deviation from the (extrapolated) baseline can be seen in the temperature interval -55 to -20°C . In our opinion this heat-effect is associated with the $\beta_i \rightarrow \text{PE}_c$ transition. Integrating the area under the anomalous part of the curve, we obtained a transition enthalpy $\Delta H \approx 10$ cal/mol and a transition entropy $\Delta S \approx 0.04$ cal/mol $^\circ\text{C}$.

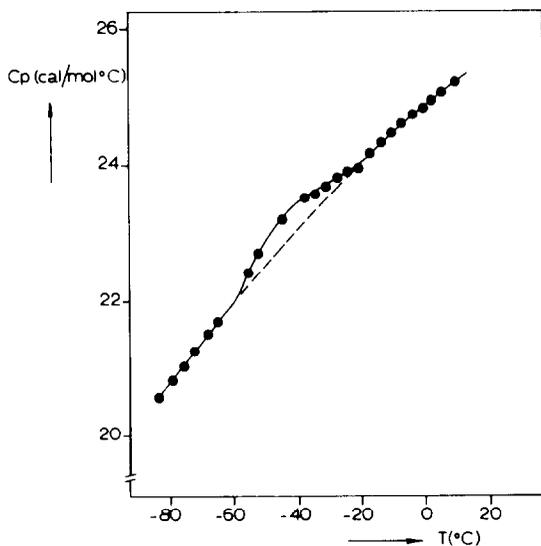


Fig. 3. Specific heat as a function of temperature for PLZT 20/30/70.

3. DISCUSSION

3.1 The diffuse $\beta_i \rightleftharpoons \text{PE}_c$ transition in $x/30/70$

By a comparison of the literature concerning DPT, the striking fact emerges, that in ferroelectric solid solutions two types of diffuse phase transitions are observed. In the first type DPTs occur in solid solutions without an immiscibility region if one of the end members is a material with only weak or without FE properties. This is the case in systems like $(\text{Ba}, \text{Sr})\text{TiO}_3$, $\text{Ba}(\text{Ti}, \text{Sn})\text{O}_3$, $(\text{Pb}, \text{Ba})\text{ZrO}_3$ and $\text{Ba}(\text{Hf}, \text{Ti})\text{O}_3$.

Secondly DPT behaviour is observed in solid solutions if one of the end members is a non FE material with a different structure. This is the case in materials like $\text{Ba}_{1-x}\text{Sr}_x\text{Nb}_2\text{O}_6$ (BSN), $\text{K}_{1-x}\text{Sr}_{1/2x}\text{NbO}_3$ (KSN) and PLZT, etc. An immiscibility region or a two-phase region exists and increasing the content of the non FE material

eventually leads to a macroscopic segregation of the second phase. The first step in this segregation process, on approaching the immiscibility region or the two phase region, will be a macroscopically non-observable spinodal decomposition or respectively clustering. Though the materials are homogeneous on a macroscale, the compositional fluctuations on a microscale will disturb the long range FE order. It is not known however, to what extent those effects play an important role in the observed DPT behaviour.

In both cases, the incorporation of the non-ferroelectric material results in strongly weakened FE properties and both the transition temperature and the energy needed to destroy the polarisation at the transition temperature (latent heat at the Curie point) will decrease, which is observed experimentally in $(\text{Ba}, \text{Sr})\text{TiO}_3$ and BSN. Our measurements on PLZT $x/30/70$ materials ($x < 16$ at% La) show the same trend, as can be seen from Fig. 2. Calculating the ferroelectric stability from these measurements, leads to the values as given in Table 1. It can be seen that for the classical first order $\text{FE} \rightarrow \text{PE}$ transitions in PLZT $x/30/70$, an increase of La content leads to a decrease of ferroelectric stability. This result supports the statement of Fritsberg[7], that a decreasing ferroelectric stability may lead to DPT behaviour.

In Section 2.2 we have seen that the heat-effects associated with the transition $\beta_i \rightarrow \text{PE}_c$ are very small.

For PLZT 20/30/70 a transition entropy $\Delta S \approx 0.04$ cal/mol $^\circ\text{C}$ was observed. Using eqn (1), it can be concluded, that in a temperature interval of at least 20° around the transition temperature (about -20°C), fluctuations with a linear dimension of 50 \AA will have a non-vanishing probability.

However to explain the observed very broadened permittivity curves fluctuations should occur in a much larger temperature interval. In PLZT 20/30/70 for example deviations from the normal Curie-Weiss behaviour are observed more than 200°C above the transition temperature (see Table 1). At this temperature the fluctuation probability as given in eqn (1) is negligibly small. It can be concluded therefore that the broadening of the permittivity curves in such a large temperature interval, if caused by dynamic polarisation fluctuations cannot be completely explained by a simplified model as given in eqn (1).

The role of compositional fluctuations in the DPT is not well understood. The occurrence of compositional fluctuations is beyond any doubt in solid solutions like PLZT, but in our opinion a direct relation between the normal statistical compositional fluctuations† and the DPT is absent in those materials. This can be concluded from the following:

—PLZT 12/55/45 shows a very pronounced DPT behaviour while in PLZT 12/30/70 a sharp $\text{FE}_t \rightarrow \text{PE}_c$ transition is observed. If enthalpy effects are neglected (see footnote) the same fluctuations occur in the Pb, La and vacancy distribution. It can be concluded therefore, that the DPT in PLZT materials is not primarily caused by normal compositional fluctuations in the Pb, La and vacancy distribution.

†Compositional fluctuations are characterised by a Gaussian distribution with a mean deviation

$$\Delta x^2 = \left[\frac{n}{x(1-x)} - \frac{2Z \cdot \Delta H}{kT} \right]^{-1}$$

in which x is the overall concentration of one of the components, n is the number of unit cells in a microregion which has a compositional difference Δx from the average composition, Z is the coordination number and ΔH is the interaction enthalpy. Under normal statistical fluctuations we understand the case that $\Delta H = 0$. See for a complete treatment for example [4].

Keeping the Zr/Tr ratio constant and changing the La content, the same conclusion can be drawn with respect to the Zr/Ti distribution. For example PLZT 12/30/70 shows a sharp transition and PLZT 20/30/70 shows a strongly broadened permittivity curve. In these materials the Zr/Ti ratio is equal and therefore the same fluctuations occur in the Zr/Ti ratio. It should be stressed that these considerations are valid only in the case that enthalpy effects are absent.

—Wolters proved for PLZT $x/55/45$ [4], that the DPT in these materials can only be explained by assuming unusually large compositional fluctuations.

It is a fact however, that the broadening of the phase transition becomes very pronounced if the two-phase region is approached at higher La concentrations (see modified phase diagram of Land *et al.*[14] in [13]). Perhaps enthalpy effects (non ideality of the solid solutions) in the higher La concentration range result in large compositional fluctuations which will be sensitive to heat treatments. However Wolters[4] did not observe a change in the DPT behaviour after annealing.

In our opinion the influence of the vacancies on the dielectric properties is limited, for as far as the DPT is concerned. This conclusion can be drawn from the fact that related materials like $(\text{Pb,Ba})(\text{Zr,Ti})\text{O}_3$ and $(\text{Pb,Sr})(\text{Zr,Ti})\text{O}_3$ without large (extrinsic) vacancy concentrations also show broadened permittivity curves[15]. Moreover varying the lead-elimination factor α between 1.0 and 1.4 did not result in a significant change of the dielectric properties.

At high temperatures ($T \gg T_c$), the temperature dependence of the permittivity can be described by a Curie–Weiss law and in our opinion, this points to a normal PE behaviour at high temperatures. Experimental values for the Curie constants are normal for FE perovskite materials with a displacive type FE \rightarrow PE transition. The fact that the extrapolated Curie temperature is much higher than the temperature where the dielectric constant is at maximum, has not been explained so far. In a certain temperature region above the transition temperature, deviations from the normal Curie–Weiss law were observed, pointing to anomalous PE behaviour and probably to fluctuations.

3.2 Comparison with other tetragonal PLZT materials

The behaviour of PLZT materials with a very high Ti content is not very interesting with respect to DPT behaviour. Though PLT materials show a strong decrease of transition entropy for the transition $\text{FE}_t \rightarrow \text{PE}_c$ with increasing La content, a rather high value of ΔS is observed up to high La contents ($\Delta S = 0.06 \text{ cal/mol K}$ for PLT 23). A notable broadening of the $\epsilon'(T)$ curve is observed only for PLT 30[16].

Tetragonal PLZT materials with a high Zr content ($x/55/45$ materials) on the other hand show a very

pronounced DPT behaviour[4]. At a very low La concentration the $\text{Fe}_t \rightarrow \text{PE}_c$ transition is probably of second order and very smooth DSC anomalies together with sharp $\text{FE}_t \rightarrow \text{PE}_c$ transitions were observed (Part I of this paper).

At increasing La content a small latent-heat effect (8–11 cal/mol) is observed at the transition $\text{FE}_t \rightarrow \beta_t$, but the diffuse $\beta_t \rightarrow \text{PE}_c$ transition takes place without a notable heat effect (DSC measurements). Although it is impossible to give an exact value for the transition entropy, this value will in our opinion be small just as in the case of $x/30/70$ materials with $x > 16$ at% La. Consequently polarization fluctuation are possible in a certain temperature interval around the transition temperature in $x/55/45$ materials with a relatively high La content.

Finally a remarkable effect in tetragonal PLZT materials is noticed, with respect to the exponent γ in eqn (5). For $x/55/45$ materials an exponent $\gamma = 2$ is observed[4] at all La concentrations,[†] whereas in PLT materials a gradual increase from $\gamma = 1$ to $\gamma = 1.7$ is seen on increasing the La content[11]. In PLZT $x/30/70$, the exponents γ range from $\gamma = 1.2$ to $\gamma = 1.7$ in a rather irregular way. The reason for this irregular behaviour in tetragonal PLZT materials is not known, but it proves, that the quadratic law is not a general characteristic for diffuse phase transitions. However the observed deviations from the normal Curie–Weiss behaviour in PLZT materials can be regarded as indications for the occurrence of fluctuations and hybrid crystals.

3.3 The character of the β phase

Anti-ferroelectricity has been assumed in PLZT materials with a high Zr content ($\text{Zr/Ti} > 70/30$) and therefore it must be determined whether the β phase in $x/30/70$ materials has AFE properties. In AFE materials the transition temperature for the transition $\text{AFE} \rightarrow \text{PE}$ should decrease with increasing d.c. bias field[17]. High field measurements on materials 17/30/70 and 20/30/70 however did not reveal AFE properties. As can be seen from Fig. 4, the temperature T_s , where the transition $\text{FE} \rightarrow \beta$ takes place, is clearly field dependent and shifts

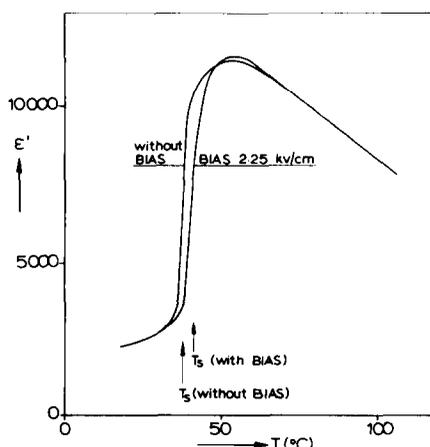


Fig. 4. Influence of a small bias field on the permittivity curve of PLZT 17/30/70 material (10 kHz, heating curves).

[†]Recent investigations by the authors showed that at high temperatures ($T \gg T_c$), the permittivity curves of $x/55/45$ materials show a normal Curie–Weiss behaviour. For example 11/55/45 with $T_c = 80^\circ\text{C}$, $T_0 = 190^\circ\text{C}$ and $C_w = 1.90 \times 10^5$.

to higher values on applying a small electric bias field to the material. However this is a normal feature for a transition, where an FE phase disappears.

The other parts of the permittivity curves were scarcely affected by a small bias field, whereas in PLZT 20/30/70 the whole permittivity curve is field independent in small bias fields ($E < 4$ kV/cm). In this latter case increasing the bias field probably resulted in a partial poling of the material. So in both cases, no clear AFE properties could be observed.

On the other hand, Wolters regarded the β phase in tetragonal PLZT $x/55/45$ materials as AFE[4]. He concluded this mainly from the fact, that an increasing bias field resulted in a small decrease of the transition temperature (in his opinion T_b) for the transition $\beta \rightarrow$ PE. However the observed effect is very small and moreover it is doubtful whether the temperature T_b is indicative for the transition $\beta \rightarrow$ PE. Those effects, together with the fact, that $x/30/70$ materials do not show AFE properties lead, in our opinion, to the conclusion that the β phase in tetragonal PLZT materials is probably not an AFE phase.

A second model, partly proposed by Carl and Geissen[18], is based on the concept of polar short-range order. In this model the broadened maximum in the permittivity curve is indicative for a gradual change-over from a PE phase to a phase with an FE short-range order.

At decreasing temperature, the number of microregions with polar short-range order increases continuously and a hybrid crystal is formed. At low temperatures the conversion to the FE short-range order is more or less complete, however a transition to a polar long-range order takes place only on applying a strong electric field to the material.

The temperature region, where the dielectric constant has a maximum, is a region, where hybrid crystals exist: a (fluctuating) mixture of PE and FE microdomains is present. In our opinion, even in the case of a more or less complete FE short-range order a considerable proportion of the material exists in the region between the ordered *microdomains* (therefore in the domain walls). These regions have a net polarisation zero and a decreasing ordering degree, thus they resemble a paraelectric phase and consequently the β phase has a strongly hybrid character.

It should be stressed that the short-range order model is descriptive and that we do not have any knowledge about the size and the shape of the domains or the domain walls.

According to the literature concerning DPT's the domains should have a rather irregular shape with linear dimensions of about 100–1000 Å[22]. The walls are expected to have a rather large, strongly temperature dependent average thickness[12, 22].

4. CONCLUSIONS

(1) The enthalpy and entropy difference between FE,

and PE_c phases decreases linearly with increasing La content for PLZT $x/30/70$ materials (Fig. 1).

(2) The enthalpy and entropy difference between β_i and PE_c phases is very small (DSC measurements, specific heat measurements). For PLZT 20/30/70 a transition entropy $\Delta S = 0.04$ cal/mol°C has been determined. Consequently polarization fluctuations are possible in a certain temperature interval around the transition temperature.

(3) Normal statistical compositional fluctuations can hardly explain the very pronounced observed DPT behaviour in tetragonal PLZT materials.

(4) For all materials investigated here, a normal Curie-Weiss behaviour is observed for $T \gg T'_c$, pointing to a normal PE behaviour at high temperatures. In a temperature region $\Delta T = 50$ to 250°C, dependent on composition, a pseudo Curie-Weiss behaviour, with exponents γ deviating from 1, is found. In this temperature-interval fluctuations probably occur and a hybrid crystal exists.

(5) The character of the β phase is not completely clear yet. No distinct AFE properties were observed for tetragonal PLZT materials. A descriptive model for the β phase has been presented in Section 3.3.

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