STUDY OF PHASE TRANSITIONS AND PROPERTIES OF TETRAGONAL (Pb, La) (Zr, Ti)O3 CERAMICS—III TRANSITIONS INDUCED BY ELECTRIC FIELDS

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Abstract—The phase diagram of electrically poled, tetragonal PLZT materials has been investigated. In the higher La concentration range, a tetragonal, so-called β-phase occurs, which has no clear FE properties. The transition to the FE, phase has first order character and takes place only after a strong electric field has been applied to the material. The energetics of the β → FE, transition were investigated in several ways. The heat-effects associated with this transition have a small value of 6-20 cal/mol, dependent on composition. The transition β → FE, is accompanied by a relatively large activation energy ΔGf. The ΔGf(T) curve shows a minimum for materials, which do not show a spontaneous transition to the FE, phase. This minimum value of ΔGf (1-2.5 cal/mol) is large in comparison to the average thermal energy kT and prevents the spontaneous transition from the β phase to the FE, phase.

1. INTRODUCTION

Phase relations in PLZT 8/65/35 have been investigated extensively by several authors [1-5]. At high temperatures the material is paraelectric (PE) with a cubic symmetry. On lowering the temperature, a broadened anomaly in the permittivity curve is observed, however a crystallographic transition is absent and the material is (pseudo) cubic at low temperatures. A ferroelectric orthorhombic phase can be induced by the addition of electrical or mechanical energy. This latter transition is reversible at temperatures above a certain temperature Tg and non reversible at temperatures below Tg.

A similar behaviour has been reported for the more Ti rich, tetragonal PLZT materials. A study of the phase relations in thermally depoled x/30/70 materials has been reported in Part I of this paper. Contrary to PLZT 8/65/35, in these materials a spontaneous transition to a tetragonal phase occurs at all La concentrations. However at high La-concentrations, the tetragonal phase has no ferroelectric properties [6, 7] and this so called β, phase can be converted to the FE, phase by applying an electric field to the material [7]. The character of the (pseudo) cubic phase in PLZT x/65/35 materials and the β, phase in PLZT x/55/45 and PLZT x/30/70 materials is not yet clear, but the most current idea is the short range order model, discussed in Part II of this paper.

The transition β → FE, is accompanied by: (i) a jump in polarization, (ii) an anomalous change of physical properties such as ε, ε', light scattering, etc. (iii) an exothermic heat effect.

In the literature these facts have been put forward as criteria for the short range order → long range order transition. The aim of this paper is to report on phase relations in poled tetragonal PLZT materials. Experimental results and the phase diagram (T-x plot) for poled x/30/70 materials will be discussed in Sections 2 and 3.1 respectively.

A comparison with the phase diagram for thermally depoled material will show, that the FE, phase field grows at the expense of the β, phase field. Furthermore it will be shown, that the transition FE, → β, has first order character and takes place at a relative sharply defined temperature Tg.

The electrical induction of the FE, phase and the energetics of the transition β, → FE, will be discussed in Sections 2.2-3.4. The results are consistent with the short range order model. It will be made clear in these sections, that the fact, that the transition β, → FE, does not occur spontaneously for materials with a high La content, is the result of an activation energy, which is high in comparison with the average thermal energy kT. Finally in Section 3.6 a comparison with other PLZT materials will be made which leads to the conclusion, that the electrical induction of a FE phase is a general phenomenon for PLZT materials with a relative high La content.

2. EXPERIMENTAL METHODS AND RESULTS

The preparation of the PLZT materials and the experimental equipment for capacitance, X-ray and DSC measurements is described in [6].

2.1 Polarization measurements

By means of a modified Sawyer-Tower circuit, EP hysteresis loops were obtained at a frequency of 0.05 Hz. A typical sequence of EP hysteresis loops as a function of temperature is shown in Fig. 1. At low temperatures a square loop is observed, which changes into a double

In a private communication, Sternberg (Latvian State University, Riga, USSR) reported, that at low temperatures PLZT 8/65/35 shows a slight deviation from the cubic symmetry. This is in disagreement with the results of Keve et al. [2].

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loop at increasing temperature. At still higher temperatures a so-called slim loop is found, which gradually approaches linear dielectric behaviour.

Remanent polarization as a function of temperature was obtained from these EP hysteresis loops and is shown in Fig. 2 for several x/30/70 materials. All materials show a loss of overall polarization at a temperature \( T_r \). Although some polarization is retained above \( T_r \), the temperature \( T_r \) is sharply defined in nearly all cases. In Fig. 3, virgin EP curves are shown for several PLZT materials at different temperatures \( T < T_r \). In our opinion the kinks in the virgin EP curves for PLZT 17/30/70 and 20/30/70 at \( a \) and \( b \) are indicative for a phase transition. This phenomenon will be discussed extensively in Section 3.

### 2.2 Capacitance measurements

In the lower La concentration range (x/30/70 materials with \( x < 16 \) at % La) the \( e'(T) \) and \( e''(T) \) curves of poled and thermally depoled materials are equal. The temperature \( T_r \) is coincident with the temperature, where the dielectric constant is at maximum \( (T_r) \) and temperature where the dielectric loss is at maximum \( (T_b) \). Increasing the La content, however, leads to a completely different behaviour. The temperature dependence of the dielectric constant of 17/30/70 and 20/30/70 materials is shown in Fig. 4. Two different starting conditions, poled and thermally depoled, are shown in curves (a) and (b) respectively. At temperatures \( T < T_r \), the dielectric constant of the poled material is much lower than that of the thermally depoled material. The difference increases with increasing temperature.

However at temperature \( T_r \) the dielectric constant of the poled material shows a sudden increase, whereas in thermally depoled material such an increase is absent. Once depoled at the temperature \( T_r \) no further difference could be observed between poled and thermally depoled material on heating or cooling. The broadened maximum of the dielectric constant occurs at a higher temperature (called \( T_c \)) than \( T_r \) in all cases and the temperature difference between \( T_r \) and \( T_c \) increases rapidly with increasing La content (Table 1). Alternating

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A material is in its virgin state or thermally depoled state after heating to a temperature far above the Curie temperature, followed by slowly cooling. In this way the memory of the electrical history of the material is completely removed.

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Fig. 1. EP hysteresis loops for PLZT 17/30/70 material at different temperatures.

Fig. 2. Remanent polarization as function of temperature for several PLZT x/30/70 materials.

Fig. 3. Virgin EP curves for several PLZT materials at different temperatures (\( T < T_r \)). In our
Study of phase transitions

Fig. 3. Virgin EP curves for PLZT x/30/70 materials with x = 14 at % La (upper figures), x = 17 at % La (middle figures) and x = 20 at % La (bottom figures).

current depoled\textsuperscript{\dagger} material behaves in the same way as poled material.

2.3 DSC measurements

For x/30/70 materials with a low La content (x < 16 at % La) a latent heat effect is observed at a temperature \( T_p \), both for poled and thermally depoled material. The magnitude of this heat effect is more or less equal in both cases. Poled and a.c. depoled materials in the higher La concentration range (x > 16 at % La) show a latent heat at the temperature \( T_p \). The magnitude of this heat effect decreases linearly with increasing La content. For PLZT x/30/70 material with x > 20 at % La the heat effect vanishes, apparently because of its small value. It should be remarked, that the heat effects for materials with x > 16 at % La are very small and close to the sensitivity limit of our DSC equipment. Only the fact, that sharp DSC peaks were observed, made it possible to calculate values for the transition heat.

In Table 1 values of \( \Delta H \) and \( \Delta S \) for the transition \( \beta \rightarrow \beta \) are presented. \( \Delta S \) was calculated from the equation \( \Delta S = \Delta H / T_p \).

2.4 X-Ray measurements

X-Ray diffraction patterns were made at room temperature from poled and thermally depoled ceramic discs having a diameter of about 15 mm. Removable silver paste electrodes were used for the poling procedure. In all cases, poling resulted in a strongly increased intensity of hkI reflections with \( 1 > h + k \).

This result is expected because of the preferred orientation of the tetragonal axes in the poled material. However neither a change in symmetry nor a significant change in the c/a ratio could be observed in PLZT 17/30/70 and 11/55/45 materials due to poling (thermally depoled 17/30/70 is FE, thermally depoled 11/55/45 is a \( \beta \)-phase material at room temperature).

\textsuperscript{\dagger}A material can be a.c. depoled by continuously reducing the magnitude of the a.c. field strength which was initially equal to the maximum field used in hysteresis loop measurements.

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Finally it must be kept in mind that the crystallographic tetragonal → cubic transition takes place around or above the temperature where the dielectric constant is at maximum [6].

This leads to the conclusion, that if the temperature \( T_p \) is indicative for a phase transition, this will be a tetragonal → tetragonal transition.

### 3. Discussion

#### 3.1 Phase diagram for poled material

The experiments, described above, strongly suggest that the depoling observed for materials with a high La content at temperature \( T_p \) is in fact a phase transition, but one which is not reversible on cooling. This necessarily implies, that thermally depoled materials with a

<p>| Table 1. Transition temperatures and thermodynamic quantities for the transitions in some tetragonal PLZT materials. Thermodynamic quantities were measured on poled samples† |
|---|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>material</th>
<th>( T_p ^\circ ) (°C)</th>
<th>( T_C ^\circ ) (°C)</th>
<th>( \Delta H_{\text{disc}} ) (cal/mol)</th>
<th>( \Delta S_{\text{disc}} ) (cal/molK)</th>
<th>( \Delta S_{\text{hyst}} ) (cal/molK)</th>
<th>transition at ( T_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/30/70</td>
<td>191</td>
<td>194</td>
<td>26</td>
<td>0.06</td>
<td>FE+PE</td>
<td></td>
</tr>
<tr>
<td>14/30/70</td>
<td>130</td>
<td>135</td>
<td>24</td>
<td>0.06</td>
<td>FE+PE</td>
<td></td>
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<tr>
<td>15/30/70</td>
<td>105</td>
<td>104</td>
<td>97</td>
<td>73</td>
<td>0.06</td>
<td>FE+PE</td>
</tr>
<tr>
<td>16/30/70</td>
<td>85</td>
<td>80</td>
<td>21</td>
<td>0.06</td>
<td>FE-PE</td>
<td></td>
</tr>
<tr>
<td>17/30/70</td>
<td>57</td>
<td>47</td>
<td>35</td>
<td>18</td>
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<td>16</td>
<td>0.06</td>
<td>FE-8</td>
<td></td>
</tr>
<tr>
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<td>-31</td>
<td>-43</td>
<td>13</td>
<td>0.05</td>
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<td>-80</td>
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<tr>
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<td>0.04</td>
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<tr>
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<td>50</td>
<td>33</td>
<td>12</td>
<td>0.05</td>
<td>FE-8</td>
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<td>11</td>
<td>33</td>
<td>12</td>
<td>0.05</td>
<td>FE-8</td>
</tr>
</tbody>
</table>

†\( T_p \): Temperature where the dielectric constant is at maximum.

\( T_p \): See text.

\( \Delta H_{\text{disc}} \): Transition enthalpy, as measured by means of a DSC equipment.

\( \Delta S_{\text{disc}} \): Transition entropy, calculated from \( \Delta S = \Delta H_{\text{disc}}/T_p \).

\( \Delta S_{\text{hyst}} \): Transition entropy, calculated from double EP hysteresis loops.
high La content undergo a non-reversible phase transition to a FE phase on poled at temperatures below \( T_p \).

We propose a phase diagram for poled PLZT 17/30/70 materials as shown in Fig. 5. In the lower La concentration range, the situation is relative simple and equals the situation for a thermally depoled material [6]. The first order transition \( \text{FE} \rightarrow \beta \) takes place at temperature \( T_1 = (T_a \text{ at maximum}) = T_b \) (disappearance of remanent polarization) = \( T_p \) (crystallographic transition). All these temperatures are coincident in this La concentration range. Increasing the La content finally leads to a difference in behaviour of thermally depoled and poled material. Compared with the phase diagram for thermally depoled material, the diagram for poled materials shows an extended FE phase field. The \( \beta \) phase field on the other hand decreases. The (sharp) \( \text{FE} \rightarrow \beta \) transition occurs at temperature \( T_1 \) (disappearance of remanent polarization, sharp increase of \( e' \) and \( e'' \), latent heat effect), whereas the diffuse transition \( \beta \rightarrow \text{FE} \) around the temperature \( T_2 \) (maximum \( e' \)) has been discussed in detail [6].

The transition \( \text{FE} \rightarrow \beta \), has first order character, which can be deduced from the following:

- a latent heat is observed at the transition
- double EP hysteresis loops are observed at temperatures \( T > T_p \). The FE character of the low temperature electrical induced phase becomes evident, in the first place from the observed square hysteresis loops and secondly from the fact that application of a bias field to the material results in an increase of temperature \( T_p \).

This is the theoretically expected result for a transition where a FE phase disappears [8].

3.2 EP hysteresis measurements

Virgin EP curves (Fig. 3) show a more or less normal domain orientation at all temperatures in the case of PLZT 14/30/70, which confirms the FE character of the thermally depoled material at \( T < T_p \). On the other hand, virgin EP curves of PLZT 20/30/70 clearly indicate the induction of the FE phase from the thermally depoled material at all temperatures where \( T < T_p \). At a certain critical field strength \( E_{\text{cr}} \) an FE phase is induced. This transition is accompanied by kinks at \( a \) and \( b \) in the virgin EP curve and by a sharp change in other properties (strong decrease of \( e' \) and \( e'' \) etc. see also [7]).

PLZT 17/30/70 and 18/30/70 materials show an intermediate behaviour. Both domain orientation and phase transition behaviour, dependent on temperature, can be seen in the virgin EP hysteresis loops. In a temperature region not too far below temperature \( T_p \), a phase transition behaviour is observed in the virgin EP curves, which is in accordance with the proposed phase diagrams for poled and thermally depoled material. At lower temperatures, thermally depoled material undergoes a spontaneous transition to an FE phase and in the virgin EP curves only domain orientation behaviour is observed. In the EP hysteresis loops, shown in Fig. 1, the critical fields \( E_{\text{cr}}^+ \) and \( E_{\text{cr}}^- \) are also defined.

The transition \( \beta \rightarrow \text{FE} \) occurs at the field \( E_{\text{cr}}^+ \), whereas at the field \( E_{\text{cr}}^- \), the opposite transition occurs. The temperature dependence of these critical fields for several materials is given in Fig. 6. It can be seen from this figure, that the transition \( \beta \rightarrow \text{FE} \) in PLZT 17/30/70 shows a rather large thermal hysteresis.

In the case of PLZT 20/30/70, hysteresis in a classical sense is absent. It can be seen from Fig. 6, that the critical field \( E_{\text{cr}}^+ \) exhibits a broad minimum. At low temperatures, the critical field \( E_{\text{cr}}^+ \) increases. This means that in zero or low field \( (E < 8 \text{kV/cm}) \), a spontaneous \( \beta \rightarrow \text{FE} \) transition does not occur. In high fields \( (E > 8 \text{kV/cm}) \) a more or less normal thermal hysteresis will be observed. This is illustrated in Fig. 6. At a field strength of \( 10 \text{kV/cm} \), the thermal hysteresis for the transition \( \beta \rightarrow \text{FE} \) will be \( T_a - T_b \).

From the double hysteresis loops an estimation of the free enthalpy difference between the FE and \( \beta \) phases can be obtained. This is illustrated in Fig. 7. Since hysteresis is observed in the EP curves, the real equilibrium curve for the field enforced transition is assumed to be represented by the line ABC in Fig. 7. The dashed line ABC in this figure was drawn in such a way, as to divide the area enclosed by the hysteresis loop into two equal parts. The area ABCE represents the transition.

\[ \text{Fig. 5. Phase diagram for poled PLZT 17/30/70 materials dotted line gives the transition FE} \rightarrow \beta \text{ in thermally depoled material.} \]
Fig. 6. Critical field $E_c$ and $E_t$ as function of temperature for PLZT 17/30/70 and PLZT 20/30/70. Open circles: $E_c$, closed circles: $E_t$, closed square: transition temperature as determined from zero field permittivity curve (see [6]).

Fig. 7 Determination of the transition free enthalpy $\Delta G_1$ and the activation energy $\Delta G_2$ from the double hysteresis loops.

Free enthalpy for the transition $\beta_r \rightarrow FE_r$. However a correction for the reversibly stored dielectric energy should be made. Therefore the more or less linear ferroelectric part of the hysteresis loop is extrapolated back to the $P$ axis (line DC). Now the dielectric energy is given by the area $\Delta E.C.E$, whereas the transition-free enthalpy $\Delta G_1$ for the transition $\beta_r \rightarrow FE_r$ is given by the crosshatched area $ABCD$. It should be kept in mind however, that the transition-free enthalpy from the $\beta_r$ phase to the poled $FE_r$ phase is determined in this way.

A correction for the energy involved in the domain orientation process has not been performed.

In all cases a linear relationship between $\Delta G_1$ and $T$ is observed (Fig. 8). Extrapolating the $\Delta G_1(T)$ curve back to the $T$ axis, yields the temperature $T_0$, where the transition should take place.

However, as will be made clear, a large activation energy will prevent the spontaneous occurrence of the transition $\beta_r \rightarrow FE_r$ in materials with a high La content. The slope $\alpha = (\partial \Delta G_1/\partial T)$ of the curve equals the tran-

Fig. 8. Transition free enthalpy $\Delta G_1$ as function of temperature for PLZT 20/30/70 and PLZT 21/30/70.
sition entropy for the transition $\beta_1 \rightarrow \text{FE}_1$. In Table 1 the transition temperatures as obtained from different measurements, together with the results of the thermal measurements, are presented. From this table two striking facts should be observed:

(a) A large difference between the theoretical transition temperature $T_0$ and the experimental transition temperature $T_e$ is observed. This difference increases with increasing La content.

(b) The values for the entropy differences between the $\text{Fe}_1$ and $\beta_1$ phases as obtained by different techniques, are almost equal.

In the calculations of $\Delta S$ from the double hysteresis loops, errors will result from the facts that the curve ABC in Fig. 7 is only an approximation of the true equilibrium curve, that the ferroelectric part of the hysteresis loop is not really linear and that we have used ceramic samples in which a complete saturation of the dielectric polarization is not obtained. However the results prove the reliability of the calculations of $\Delta G_2$ from EP curves.

An estimation of the activation energy $\Delta G_2$ for the transition $\beta_1 \rightarrow \text{FE}_1$ can be obtained from the virgin hysteresis loops. This is illustrated in Figs. 7 and 10, where the shaded region corresponds to the activation energy $\Delta G_2$, being the maximum amount of energy stored in the material (corrected for the dielectrically stored energy). A plot of $\Delta G_2$ as a function of temperature is constructed in Fig. 9 for two different materials. For PUT 17/30/70 it can be seen, that on lowering the temperature the activation energy decreases and eventually $\Delta G_2$ becomes so small, that the transition $\beta_1 \rightarrow \text{FE}_1$ occurs spontaneously.

PLZT 20/30/70 shows a different behaviour. On lowering the temperature, the activation energy decreases, but around the temperature $T_p$ no further decrease is observed and a constant value of about 1.5 cal/mol is obtained. A further lowering of the temperature eventually leads to an increase of the activation energy to rather high values. For microrregions with linear dimensions of 100 Å (volume $v = 10^6 \, \text{Å}^3 = 2.5 \times 10^{-22} \, \text{mol}$) the values of $V, \Delta G_2$ are large in comparison with the average thermal energy $kT$ and in our opinion this activation energy will prevent the spontaneous occurrence of the $\beta \rightarrow \text{FE}$ transition and will be the reason for the temperature difference between the real (calculated) transition temperature $T_0$ and the observed transition temperature $T_p$ for the transition $\text{FE}_1 \rightarrow \beta_1$. The origin of the large activation energy in these materials is not yet clear.

3.3 Heat effects during the electrically induced $\beta_1 \rightarrow \text{FE}_1$ conversion

In this section it will be shown that the field-induced $\beta_1 \rightarrow \text{FE}_1$ transition is accompanied by an exothermic heat-effect, which supports the ideas, developed in the previous sections.

If the material is $\text{FE}_1$, the heat liberated during poling is very small, but if the material is in the $\beta_1$ state, a notable heat-effect is observed during poling. This heat-effect appears to be in good agreement with the endothermic heat-effect, observed during the depoling of the material at temperature $T_p$.

Our DSC equipment is essentially the same as the one Keve and Annis used for their experiments [3]. Ceramic discs with evaporated gold electrodes were used. Fine platinum leads connected the sample in the DSC cell to an external power supply. Measurements were made on several materials at temperatures $T < T_p$. Since the heat effect involved in the $\text{FE}_1 \rightarrow \beta_1$ transition at $T_p$ is endothermic (Section 2), we expected the opposite, field induced, transition to be exothermic. Applying an electric field $+ V$ to thermally depoled material indeed resulted in the expected exothermic heat-effect $Q_t$. This heat-effect must be corrected for the electrical heat dissipation and for the reversibly stored dielectric energy $(Q_2)$. Furthermore a calibration of the DSC peaks should be made.

The calibration of the DSC peaks is carried out by measuring the heat-effects during a complete EP hys-
Fig. 10. Calculation of the activation energy $\Delta G_2$, the reversibly stored dielectric energy $Q_2$ and the energy $Q_3$ from a square hysteresis loop.

A quite different behaviour is seen for PLZT 17/30/70. At low temperatures, the material is already ferroelectric and only a small heat-effect is observed during poling. Increasing the temperature eventually leads to a transition $\beta_1 \rightarrow FE_1$ at the temperature $T_s$ (see Part I of this paper).

Applying an electric field to the material at temperatures $T_s < T < T_p$ results in a non-reversible transition $\beta_1 \rightarrow FE_1$, and the value of $Q$ increases rapidly. The small heat-effect observed at low temperatures may be due to a non-complete spontaneous conversion $\beta_1$-FE in the thermally depoled material. Further it can be stated, that the observed exothermic heat-effect during poling again points to a field induced transition. It should be

![Diagram of hysteresis loop](image)
Study of phase transitions

3.4 Frequency dependence of the $\beta$ phase

To estimate whether the observed decrease in dielectric constant after poling is related to normal domain processes, we have measured the frequency dependence of the dielectric constant and dielectric loss of PLZT 20/30/70 at $-90^\circ\text{C}$. It can be seen from Fig. 12, that at low frequencies there is an extra contribution to the dielectric constant and dielectric loss, which can be removed by poling. As the measuring frequency increases the extra contribution to the dielectric constant becomes smaller. If it is allowed to extrapolate the curves to high frequencies it can be concluded, that somewhere in the GHz range the dielectric constants of poled and unpoled material become equal. This suggests, that the extra contribution to the dielectric constant in unpoled material could be due to a domain wall relaxation. However the dielectric loss for unpoled material does not show the expected maximum as frequency increases.\footnote{It should be remarked, that at high ($>300\ \text{kHz}$) and low ($<200\ \text{Hz}$) frequencies the accuracy of the $\varepsilon'$ measurements is not better than 15%. It is possible that a very broad maximum can be observed in this frequency range if more accurate measurements are carried out. Moreover the frequency range in our measurements is rather limited.}

In conclusion it can be stated that the fact that we have observed a strongly dispersive dielectric constant together with a non dispersive dielectric loss in a frequency range 100 Hz-1 MHz does not point to normal domain processes.

3.5 Thermal hysteresis

In our opinion, the effects observed in PLZT materials with a high La content are related to thermal hysteresis. In a previous section it was made clear, that in PLZT 17/30/70 a more or less normal, though large, thermal hysteresis for the transition $\beta_{\text{ls}} \rightarrow \text{FE}$, is observed. In zero field the transition $\beta_{\text{ls}} \rightarrow \text{FE}$ occurs on cooling at temperature $T_a$, whereas the opposite transition takes place on heating at temperature $T_b$. This thermal hysteresis is caused by a rather large activation energy, as can be seen from Fig. 9. In PLZT 20/30/70 the situation is not essentially different. In this case however the activation energy exhibits a minimum as a function of temperature.

At low temperatures this activation energy is so large, that a spontaneous $\beta_{\text{ls}} \rightarrow \text{FE}$ transition does not occur. One can say that the thermal hysteresis has become infinite in this case. Measurements on PLTZ 19/30/70 and 21/30/70 materials showed that the $\Delta G(T)$ curves are qualitatively similar to the one that is shown in Fig. 9. However the minimum value of $\Delta G$ increases rapidly with increasing La content. The minimum values are 1 and 2.5 cal/mol for 19/30/70 and 21/30/70 respectively.

In conclusion it can be stated, that in PLZT materials, the $\beta_{\text{ls}} \rightarrow \text{FE}$, transition is accompanied by an unusual thermal hysteresis. This unusual character is phenomenologically expressed by the fact that the thermal hysteresis becomes infinite for materials with a high La content. This so called "infinite" thermal hysteresis for unpoled materials is strongly dispersive and $\varepsilon'_{\text{unpoled}} > \varepsilon'_{\text{poled}}$. In this case a maximum in the dielectric loss as function of frequency is observed at about $10^4\ \text{Hz}$. The phenomena in KSN are explained by a model, which assumes the existence of micro-domains seperated by thick (50 Å) domainwalls. In our opinion this model is closely related to the short range order model discussed in Part II of this paper.
teresis" is probably not caused by nucleation problems. To understand this it should be kept in mind that both the $\beta$-phase and the FE phase are tetragonal. In the short range order model (see Part II of this paper) the $\beta$-phase is considered as a phase with FE microdomains and therefore it is illogical to suppose that a nucleation problem prevents the spontaneous transition $\beta_r \rightarrow FE_r$.

Finally the difference in character between the $\beta_s$=FE transition and the FE$\rightarrow$FE transition is remarkable. The transition $\beta_s$=FE is very diffused, without any thermal hysteresis, whereas the transition $\beta_s$=FE is a much "sharper" transition with an unusual thermal hysteresis. Only in PLZT 21/30/70 is some diffuseness of the FE$\rightarrow$FE transition observed.

3.6 Comparison with other PLZT materials

Tetragonal PLZT x/55/45 materials were investigated extensively by Wolters et al. [7]. In these materials the phenomenon of inducing a FE phase by means of an electric field was also observed. In this case a distinction between $\beta_s$ and FE, phases can also be made [6,7] and the transition $\beta_r \rightarrow FE_r$ has the same characteristics (exothermic heat-effect during poling, anomalous decrease of $\epsilon$ during poling, etc.) as in the case of PLZT x/30/70 materials. As has been illustrated by our results on 11/55/45, shown in Table 1, the transition $\beta_r \rightarrow FE_r$ in PLZT x/55/45 materials is of first order and a large temperature difference is observed between the real transition temperature $T_0$ and the actual transition temperature $T_e$. Just as in the case of PLZT x/30/70 materials with $x > 18$ at % La, the transition $\beta_r \rightarrow FE_r$ does not occur spontaneously in PLZT 11/55/45 and a determination of the activation energy $\Delta G_2$ (see Section 3.2) as a function of temperature results in a $\Delta G(T)$ curve, which is qualitatively similar to the one observed for PLZT x/30/70 materials.

The broad minimum in the $\Delta G(T)$ curve is observed in the temperature region 0-50°C and the minimum value is about 1 cal/mol. This large activation energy (with respect to the average thermal energy) will prevent the spontaneous occurrence of the $\beta_r \rightarrow FE_r$ transition. By comparison with the x/30/70 series, one can see, that an increase of the Ti content leads to an increase of the La concentration range where a classical FE$\rightarrow$PE transition is observed and an increase of the La content is necessary for observing a field induced $\beta_r \rightarrow$ FE transition. In PLZT 11/55/45 for example, the FE phase only forms after poling, but in PLZT 11/30/70 no such behaviour is observed. Field induced transitions are observed in PLZT x/30/70 materials for $x > 16$ at % La.

Increasing the Ti content still more, eventually leads to a situation observed in PLT. In these materials a more or less classical FE$\rightarrow$PE transition occurs up to very high La concentrations [9]. A notable broadening of the minimum in the $\epsilon(T)$ curve is observed for $x \approx 30$ at %La, but an induction of the FE phase is not observed.

Also in non-tetragonal PLZT materials, the induction of a FE phase by means of an electric field is possible. The situation in PLZT x/65/35 materials is reviewed shortly in the introduction and a field induced cubic$\rightarrow$orthorhombic transition is observed in PLZT x/65/35 materials for $x > 7$ at % La. Finally in PLZT x/85/15 materials a non-reversible field induced AFE$\rightarrow$FE transition is observed [10]. In conclusion it can be stated, that the electrical induction of a FE phase is a universal phenomenon in PLZT materials. However the La concentration at which this phenomenon is observed and the characteristics of the field induced transition are different for different parts of the phase diagram.

Unfortunately, little is known about the value of the transition heat for the field induced transition in other PLZT materials. Keve and Annis [3] determined a transition heat of 8 cal/mol for PLZT 86/65/35. This value is in the same order of magnitude as the values that have been observed for tetragonal PLZT materials (12 cal/mol for PLZT 11/55/45 and 6-20 cal/mol for PLZT x/30/70 materials dependent on x). A comparison with some other polar$\rightarrow$non-polar transitions has been made in Table 2. It can be seen that the heat effects involved in the field induced transitions PLZT materials are small.

A final remark must be made with respect to the $\beta_r$ phase. Wolters [7] regarded the $\beta_r$ phase in PLZT x/55/45 materials as AFE, but the evidence for antiferroelectricity was rather poor and in PLZT x/30/70 materials no AFE properties were observed. In our opinion the short range order model is the more likely model. In this model, described in more detail in [4] and [6], a ferroelectric phase with short range order develops spontaneously from the paraelectric phase in the temperature region, where the permittivity curve exhibits a broad-

Table 2. Transition enthalpies ($\Delta H$) and entropies ($\Delta S$) of some ferroelectric and antiferroelectric compounds

<table>
<thead>
<tr>
<th>material</th>
<th>transition temp (K)</th>
<th>$\Delta H$ (cal/mol)</th>
<th>$\Delta S$ (cal/molK)</th>
<th>transition</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO$_3$</td>
<td>763</td>
<td>1150</td>
<td>1.51</td>
<td>FE$\rightarrow$PE</td>
<td>11</td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>708</td>
<td>190</td>
<td>0.28</td>
<td>FE$\rightarrow$PE</td>
<td>11</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>393</td>
<td>47</td>
<td>0.12</td>
<td>FE$\rightarrow$PE</td>
<td>11</td>
</tr>
<tr>
<td>PbZrO$_2$</td>
<td>503</td>
<td>440</td>
<td>0.88</td>
<td>AFE$\rightarrow$PE</td>
<td>13</td>
</tr>
<tr>
<td>Pb$<em>{0.5}$Sr$</em>{0.5}$TiO$_3$</td>
<td>666</td>
<td>57</td>
<td>0.06</td>
<td>FE$\rightarrow$PE</td>
<td>12</td>
</tr>
<tr>
<td>PLZT 18</td>
<td>428</td>
<td>24</td>
<td>0.06</td>
<td>FE$\rightarrow$PE</td>
<td>this paper</td>
</tr>
<tr>
<td>PLZT 17/30/70</td>
<td>320</td>
<td>18</td>
<td>0.06</td>
<td>FE$\rightarrow$E</td>
<td>this paper</td>
</tr>
<tr>
<td>PLZT 20/30/70</td>
<td>212</td>
<td>10</td>
<td>0.05</td>
<td>FE$\rightarrow$E</td>
<td>this paper</td>
</tr>
<tr>
<td>PLZT 11/55/45</td>
<td>321</td>
<td>12</td>
<td>0.04</td>
<td>FE$\rightarrow$E</td>
<td>this paper</td>
</tr>
<tr>
<td>PLZT 8/65/35</td>
<td>328</td>
<td>8</td>
<td>0.02</td>
<td>FE$\rightarrow$E(?)</td>
<td>3</td>
</tr>
</tbody>
</table>
maximum. A transition to a FE phase with long range order, occurs only after having applied a strong electric field to the material. It is not clear in this model, whether the field induced transition should be regarded as a real transition or more as a conversion from one ferroelectric state to another.

As has been stated in [6], if the material exhibits a more or less complete FE short-range order, a considerable proportion of the material exists in the domain walls between the ordered ferroelectric microdomains. These domain walls resemble a PE phase and poling will result in a transition of these PE walls to a FE phase. This process, together with an alignment of the FE microdomains, results in a FE long-range order.

4. CONCLUSIONS

1. The phase diagram for poled tetragonal PLZT materials was determined. In comparison with the phase diagram for thermally depoled materials, the FE phase field has grown at the expense of the BE phase field.

2. The transition $\beta \rightarrow$FE has a first order character and shows an unusual thermal hysteresis behaviour. This thermal hysteresis is caused by an activation energy, which is high in comparison with the average thermal energy $kT$. For materials with a high La content ($x/30/70$ materials with $x > 18$ at % La) a minimum in the activation energy was observed as a function of temperature. The minimum value of the activation energy increases with increasing La content and is larger than 1 cal/mol in all cases.

3. Transition enthalpies and entropies for the transition $\beta \rightarrow$FE were determined. Results obtained with different methods agree rather well. The transition enthalpy decreases with increasing La content and has a low value (6–20 cal/mol for $x/30/70$ materials). The transition entropy is more or less independent of the La content in $x/30/70$ materials ($\Delta S = 0$, 04-06 cal/mol K) and has comparable or lower values for known materials with a higher Zr content.

4. The electrical induction of a FE phase is a general phenomenon for the whole PLZT system.

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REFERENCES