

EFFECTS OF MICROSTRUCTURE ON THE DIELECTRIC PROPERTIES OF
LANTHANA SUBSTITUTED PbTiO_3 AND $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -CERAMICS

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ABSTRACT

The effect of grain size on unit-cell dimensions and dielectric properties has been studied in ceramic lanthana-substituted leadtitanate and leadtitanate-zirconate mixed crystals of the general composition $\text{Pb}_{1-\alpha}\text{La}_\alpha\text{Zr}_y\text{Ti}_{1-y}\text{O}_{3+x(1.5-\alpha)}$. The influence of grain size has been investigated in the range from $0.6\mu\text{m}$ - $10\mu\text{m}$ and can be distinguished from other microstructural influences by its effect on dielectric properties. A decrease of the grain size leads to a decrease of the maximum of the dielectric constant ϵ' at the "Curie" temperature T_C' , while the value of T_C' shifts to a lower temperature and the ϵ' -T curve (phase transition) becomes broadened. The results can be discussed in terms of a distribution of internal compression stresses spreading around an average value which increases with decreasing grain size.

Introduction

In a large number of ferroelectric ceramics the paraelectric-ferroelectric phase transition has been found to be broadened and to deviate from the Curie-Weiss behaviour (exhibited e.g. by pure BaTiO_3 single crystals). The magnitude of the real (ϵ') and imaginary (ϵ'') part of the dielectric constant and the temperature T_C' at which the maximum value of ϵ' occurs, vary considerably with microstructure and preparation procedure. The magnitude of the changes in properties is composition dependent while sometimes frequency-dependency occurs.

The possible causes of the above mentioned effects can be divided in three main groups and may be listed as follows:

- a) macroscopic large scale inhomogeneities of composition and stress (scale large with respect to domain size)
- b) stress and stress distribution induced by grain size (scale comparable with domain size)
- c) microscopic inhomogeneities within one phase (scale 50 - 1000\AA)

The inhomogeneities in this category are in thermodynamic equi-

librium at high temperature and may be frozen in at lower temperatures. They include ordering and clustering, compositional fluctuations and (thermal) polarisation fluctuations.

The inhomogeneities mentioned in group a) originate in most cases from non-complete reactions during preparation of polycrystalline materials, growth striae and inclusions during growing of single crystals and strains related with these inhomogeneities or with pressing operations during preparation. In most cases these inhomogeneities have to be eliminated. In some cases however they can be used fruitfully e.g. in manipulating the temperature coefficient of the dielectric constant (1).

The effects of grain size and stress (group b) on dielectric properties has been investigated thoroughly in BaTiO_3 (2-4), and substituted lead titanate (5) and are interpreted mainly in terms of induced stress distribution due to domain clamping. In other systems little is known of the grain size effect on dielectric properties.

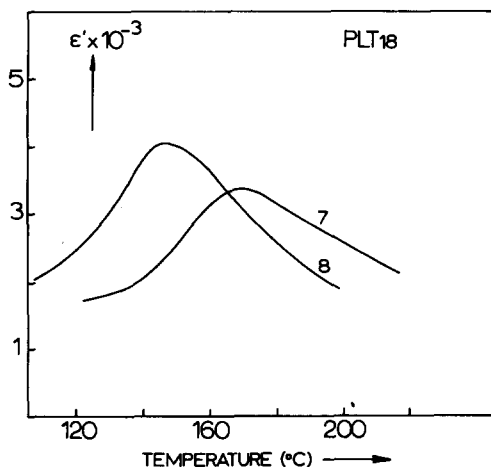
Inhomogeneities mentioned in group c) may lead to a strong broadening of the phase transition region, deviation from Curie-Weiss behaviour and frequency dependence of ϵ' (7,8).

From both a scientific and technological point of view it is important to distinguish and to separate the several effects mentioned above and to relate each of them to chemical composition.

In this paper grain size effects for compositions with the general formula $\text{Pb}_{1-\alpha}\text{La}_x\text{Zr}_y\text{Ti}_{1-y}\text{O}_{3+x(1.5-\alpha)}$ are presented.

Experiments

The general composition of the samples in $\text{Pb}_{1-\alpha}\text{La}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_{3+(1.5-\alpha)}$ compositions with $y=0$ will be abbreviated as PLT, others as PLZT. The α value for PLT and PLZT composition is $\alpha = 1.20 \pm 0.05$ and $\alpha = 0.95$ respectively. Sample preparation and measurements have been described by Keizer and Burggraaf (5). To avoid stresses which are not introduced by grain size effects the



sintered discs have been annealed at 900°C during 2 hrs and cooled down slowly. In the case of hot-pressed samples annealing at a temperature slightly (40°C) above the hot pressing temperature during 30 minutes appeared to be necessary. No changes in composition, determined by X-ray fluorescence analysis, have been found after annealing.

The grain sizes, the X-ray parameters and the dielectric constant have been measured using a scanning electron microscope type Jeol, a Philips X-ray diffractometer and a high temperature Guinier camera and a Wayne Kerr admittance bridge respectively.

Effect of annealing procedure on dielectric constant ϵ' for PLT18 (sample no. see Table 1)

Results

Macroscopic inhomogeneities and microstructure

The preparation procedure has a considerable influence on dielectric properties. This has been shown for compositional inhomogeneities in $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and $\text{Pb}_{1-\alpha}\text{La}_\alpha\text{TiO}_{3+x(1.5-\alpha)}$ by Keizer et al (9) where a single sintering step at a relative low temperature leads e.g. to an increased value of the apparent Curie temperature T_C' (\equiv temperature at which the maximum value of ϵ' occurs) and to a broadening of the phase transition.

The same effect occurs as large stress fluctuations originating from hot-pressing operations are not removed adequately by an appropriate annealing procedure. This is demonstrated in Fig. 1 for samples with the same composition and grain size but different thermal history.

In all samples used for investigating grain size effects macroscopic compositional and stress fluctuations have been eliminated. It appears that these can be distinguished dielectrically from grain size effects by their opposite effect on T_C' as will be shown further. The density of all samples is better than 96% and in most cases better than 98% of theoretical density.

Effect of grain size

The effect of grain size has been investigated by varying the average grain size from values smaller than $1\mu\text{m}$ ($0.6\text{-}0.8\mu\text{m}$) to larger than $10\mu\text{m}$. For PLT compositions the effect of grain size on the dielectric and crystallographic properties has been discussed by Keizer et al (5). For compositions with $x = 0.07$ (PLT7) the effect of grain size on dielectric constant ϵ' in the phase transition region is demonstrated in Fig. 2, while the effects on other characteristic dielectric parameters have been collected in Table 1 for both PLT7 and PLT18.

It is obvious that decreasing grain size causes a broadening of the ϵ' - T -curve (phase transition region), a decrease of ϵ'_{max} and ϵ''_{max} and a decrease of T_C' .

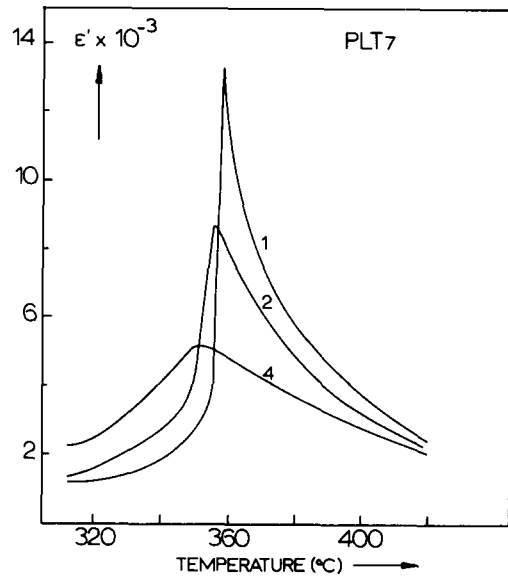


FIG. 2

Effect of grain size on dielectric constant ϵ' around T_C' for PLT7 (sample no. see Table 1)

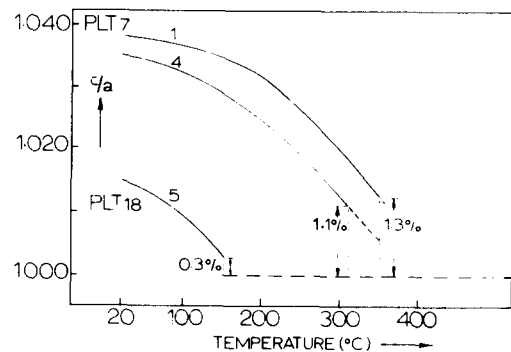


FIG. 3

The c/a ratio as a function of temperature for PLT7 and PLT18 (sample no. see Table 1)

TABLE 1

The Maximum Values of the Dielectric Constant ϵ'_{\max} and the Dielectric Losses ϵ''_{\max} of PLT7 and PLT18 and the Corresponding Temperatures at the Phase Transition.

sample no.	system	grain size (μm)	$\epsilon'_{\max} \times 10^{-3}$	$T'_{\epsilon} (\text{°C})$	ϵ''_{\max}	$T''_{\epsilon} (\text{°C})$	$T'_{\epsilon} - T''_{\epsilon} (\text{°C})$
1	PLT7	3.1	13.3	357	110	356	1
2	PLT7	1.1	8.6	355	40	353	2
3)	PLT7	0.6	4.7	358	20	354	4
4) 1)	PLT7	0.6	5.2	351	15	347	4
5) 2)	PLT18	10.9	16.9	157	100	155	2
6)	PLT18	3.1	8.7	152	75	150	2
7) 1)	PLT18	0.8	3.7	168	35	155	13
8) 2)	PLT18	0.8	4.1	147	45	134	13

- 1) Hot-pressed samples
- 2) Samples annealed at 40°C above the hot-pressing temperature.

TABLE 2

The Differences in Physical Properties between the Largest and Smallest Grain Size of PLT7, PLT18 and BaTiO₃

property differences		BaTiO ₃	PLT7	PLT18
$\Delta\epsilon'_{\max}$	1)	-2000	-8000	-13000
$\Delta\epsilon'_{20}$	1)	1600	80	30
$\Delta\epsilon'_{T_C-100}$	1)	1600	450	130
$\Delta(c/a-1)_{T_C}$	2)	-	0.007	-
$\Delta(c/a-1)_{20}$	2)	0.0015	0.003	0.005
$(c/a)_{T_C}^I$	3)	0.005	0.013	0.003
$\Delta T_C (\text{°C})$	4)	2	6	10

- 1) $\Delta\epsilon'$ = difference in the dielectric constant at T_C' , 20°C and (T_C-100) °C resp.
- 2) $\Delta(c/a-1)$ = difference in the $(c/a-1)$ -parameter at T_C and 20°C resp.
- 3) $(c/a-1)_{T_C}$ = jump in the lattice constants at T_C for the largest grain size
- 4) ΔT_C = difference in T_C' .

The same holds approximately for the magnitude of the lowering of the dielectric constant ϵ' at T_C' and for both the change in tetragonality $(c/a-1)$ (absolute and relative to the value for coarse grained, unstressed, material) and the change in unit cell volume at room temperature. This suggests a correlation between the magnitude of the changes in crystallographic parameters and that in some dielectric properties.

The effect of grain size on crystallographic parameters can be deduced from Fig. 3 and Table 2. It is clear that decreasing grain size causes a decrease of the tetragonality factor $(c/a-1)$.

Furthermore it can be concluded from Table 2 that grain size effects on dielectric properties in PLT are most pronounced around the Curie temperature and for $x=0.18$. The changes in tetragonal distortion $(c/a-1)$ at room temperature are considerable (0.005 for PLT18 and 0.003 for PLT7) but are not accompanied by strong changes in the value of the dielectric constant at this temperature.

The effect of grain size in PLZT8 ($y=0.55$, $x=0.08$, $\alpha=0.95$) is qualitatively the same as for PLT as is shown for the dielectric constant in Fig. 4 and for some crystallographic parameters in Table 3. Again considerable changes in dielectric properties in the phase transition region occur (shift of T_C' of -40°C for the finest grain size) while at room temperature the changes in dielectric properties are small despite considerable effects on the tetragonality factor $(c/a-1)$.

The magnitude of the shift in T_C' (or $\Delta T_C/T_C'$) for several materials as a function of grain size follows the sequence PLZT8 > PLT18 > PLT7 > BaTiO₃.

Grain size effects in terms of internal stresses

One of the most probable causes of internal stress and stress fluctuations in homogeneous fine grained ferroelectric ceramics is the clamping of domains at the phase transition and this is most effective if grains and domains are approximately of the same size (e.g. $\sim 0.6 \mu\text{m}$ for PLT7).

The experimental results can be interpreted if it can be assumed that smaller grain size results in an increasing average value of the internal compression stresses in the samples.

Support of this assumption can be achieved in two ways. Firstly from the decrease of the c/a ratio with decreasing grain size. This decrease is caused mainly by a decrease of the length of the c -axis (the a -axis is nearly constant). Furthermore from a slight decrease in the unit-cell volume as measured in ceramic discs with respect to that measured in fine powders; this difference increases with decreasing grain size. An example for PLZT8 has been given in Table 3.

Secondly we can compare our results with some results in the literature on hydrostatic pressure effects. It has been shown by Keizer et al. (5) that the effect of externally applied hydrostatic pressure on ϵ'_{max} , T_c , Curieconstant and T_0 of ceramic materials is analogous to that of decreasing grain size.

So we may assume that decreasing grain size leads to a higher level of compression stresses in the bulk of the material and to an increase of the stored mechanical energy in the system. An estimate of the stress sensitivity of some dielectric properties of a given

TABLE 3

The Lattice Parameters of PLZT8 of Ceramic Discs as a Function of the Grain Size

grain size (μm)	preparation method	$a(\text{\AA})^3$	$c(\text{\AA})^3$	c/a	$v_c(\text{\AA}^3)$
8.1	SSR ¹⁾	4.045	4.092	1.011	67.00
4.1	SSR	4.061	4.077	1.004	67.23
4.1 (powder)	SSR ₂₎	4.056	4.099	1.011	67.43
1.4	WCP ²⁾	4.046	4.065	1.005	66.53

- 1) SSR = solid state reaction of mixed oxides
- 2) WCP = wet chemical powder preparation
- 3) standard deviation: 0.002 for 8.1 and 4.1 (powder) samples. 0.005 for 4.1 and 1.4 samples.

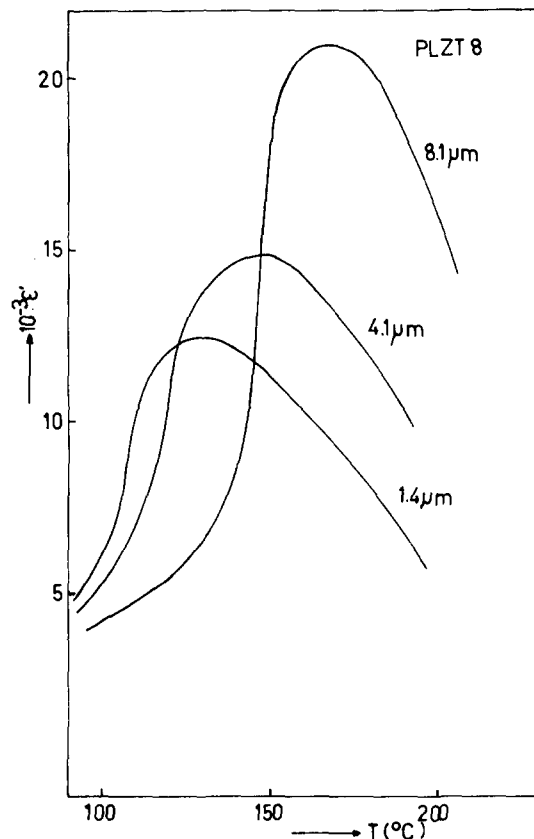


FIG. 4

Effect of grain size on dielectric constant ϵ' for PLZT8.

material can be made for first order transitions by means of the Clausius-Clapeyron equation,

$$\frac{dT_c}{dp} = T_c \frac{\Delta V}{L} = \frac{\Delta V}{\Delta S} \quad (1)$$

where ΔV and ΔS are the discontinuous changes in volume and entropy at the transition and L is the latent heat.

Introduction of the literature values of ΔV and L for BaTiO_3 and PbTiO_3 gives values for dT_c/dp of -6.0°C/kbar and -8°C/kbar respectively, in agreement with experimental values.

For PLT7 values of ΔV and L measured by the authors are $\Delta V = (0.2-0.3)\text{\AA}^3$ and $L = (34+6)\text{cal mol}^{-1}$ which leads to a calculated value of $dT_c/dp \approx -(50-100)^\circ\text{C/kbar}$. This value indicates a rather large sensitivity of T_c' for stress and so for stress fluctuations for PLT7.

It must be expected that the influence of grain size on dielectric properties will increase the larger the ratio of stored mechanical energy is, with respect to the enthalpy (ΔH) of the ferroelectric transition.

Now it is postulated that in a first approximation this ratio will be larger if the spontaneous deformation (here tetragonal deformation c/a) of the undisturbed coarse grained material decreases. This postulate explains qualitatively the sensitivity sequence mentioned before but needs further justification.

A model for calculating the ϵ' -T curve

The ϵ' -T curve can be calculated quantitatively under a number of assumptions of the same type as those of Diamond (6). The calculation procedure makes it possible to characterise a broadened ϵ' -T curve by only two parameters and so facilitates the classification and study of a large amount of experimental curves.

The assumptions used are:

- 1) The material consists of a mixture of small areas with varying Curie temperatures. The distribution of Curie temperature is approximated by a Gaussian distribution function around a value T_R and with a variance α .
- 2) Each group of areas with local Curie temperature T_c exhibits a first order phase transition. At $T > T_c$ the dielectric constant follows a Curie-Weiss law, at $T < T_c$ the dielectric constant is approximately constant with an average value ϵ_{av} .
- 3) The material is considered as an electrical circuit of capacities in series. This means that the dielectric constants of the local areas are added reciprocally. It can be shown that this will give better results than adding arithmetically.
- 4) There is no contribution of orientational polarisation.

The average value for dielectric constant in the phase transition region can be represented by the following equation

$$\langle \epsilon^{-1} \rangle (T) = \frac{\int_0^\infty \epsilon^{-1}(T, T_c) \exp[-(T_c - T_R)^2 / \alpha^2] dT_c}{\int_0^\infty \exp[-(T_c - T_R)^2 / \alpha^2] dT_c} \quad (2)$$

with

$$\epsilon(T, T_c) = \begin{cases} \epsilon_{av} & \text{for } T < T_c \\ C(T - T_0)^{-1} = C(T - T_c + \Delta T)^{-1} & \text{for } T > T_c \end{cases} \quad (3)$$

$T_0 = \text{temperature for which } \epsilon \rightarrow \infty$

The ϵ' - T curve for PLT7 has been calculated now with the help of eq. (2) and (3).

The values of C , ϵ_{av} and T have been extracted from the experimental ϵ' - T curves for the material with the largest grain size (stress free values) and are considered independent of stress. They have been used for all other grain sizes.

The values for T_r and α are adjusted in such a way that the experimental curve is fitted in the best way. A physical interpretation of T_r and α will be discussed at the end of this section. The value for T_r has been chosen in such a way that the calculated temperature (T_c') at which the maximum of ϵ' occurs coincides with the experimental value.

The value for α has been chosen so that the calculated and experimental values for ϵ'_{max} coincide.

The results have been collected in Fig. 5 and Table 4. It can be seen that a good agreement is achieved between calculated and experimental curves. At temperatures considerably lower than T_c' deviations occur; this is due to the fact that ϵ_{av} is in this case not strictly constant.

From Table 4 it can be concluded that with decreasing grain size the value of T_r decreases considerably (-29°C for the smallest grain size) while at the same time the value of α increases.

From computer simulation and Table 4 it can be shown that the value of T_r does not influence the width (sharpness) of the ϵ' - T curve but only displaces T_c' to a value lower than T_c of the stress free (coarse grained) material. Increasing value of α shifts the value of T_c' to a higher value with respect to T_r but the value of T_c' is in all cases lower than T_c of the coarse grained material.

A physical reason of the distribution of Curie temperatures (α) in this case seems to be a distribution of stress, the value of T_r being a measure for the average stress level.

As was described by Keizer and Burggraaf (5) this average stress level has the character of hydrostatic pressure. However if the variance of the stress distribution is relatively large compared with the stress level, in some microregions there exist stress with tensile character. The Curie temperature of these microregions increases with respect to the stress-free value. This

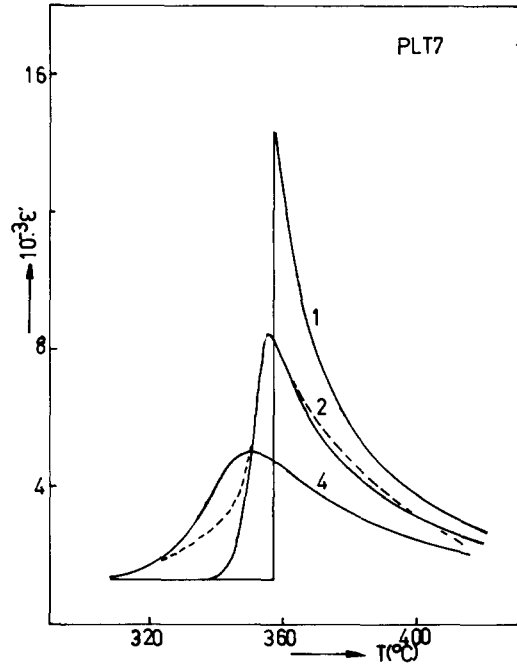


FIG. 5

The calculated and measured (dashed line) dielectric constant ϵ' for PLT7 (sample no. see Table 1)

TABLE 4

The Calculated Values of T_r and α for PLT7.

sample nr.	T_r	α
1	357	0
2	346	6
4	328	18

is one of the reasons that the dielectric constant of coarse-grained and fine-grained material are also different above the Curie temperature of the coarse-grained ceramic. A second reason for this difference is that at a grain size of $0.6\mu\text{m}$ the hydrostatic pressure introduced by surface tension is about 70 bar if the surface energy is 1N/m . This effect is independent of the ferroelectric phase transition and causes a shift in the value of T_0 in the Curie-Weiss law and so a lowering of the value of ϵ' . This stress value is about 20% of the total value of 300-600 bar calculated for the smallest grain size with the value of $dT_C/dp \approx -(50-100)^\circ\text{C/kbar}$ for PLT7.

This last stress value can occur in ceramics without deterioration of the material. Otherwise it means that in materials which are rather stress sensitive (large dT_C/dp) large shifts of T_C' (low T_r) are physically possible.

The higher the stress sensitivity the more small deviations in the material will cause deviations from the average stress value and will lead to an increase of α . It must be expected that in this case an increasing variance in the grain size distribution will lead to an increasing value for α and so to an increasing broadening of the ϵ' -T curve.

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