Twente University of Technology, Department of Chemical Engineering,
Laboratory of Inorganic Chemistry and Materials Science, Enschede

Phase Relations and Dielectric Behaviour
of (Pb, La)Zr$_{0.55}$Ti$_{0.45}$O$_3$ Ceramics
with a Diffuse Phase Transition Region

By

M. Wolters and A. J. Burggraaf

Phase relations in (Pb, La)Zr$_{0.55}$Ti$_{0.45}$O$_3$ ceramics have been investigated by means of X-ray diffraction and dielectric measurements as functions of the La concentration and temperature. Between a tetragonal, ferroelectric phase (FE) and a cubic, paraelectric phase (PE), in the phase diagram a pseudo-cubic phase, a so-called quasi-ferroelectric phase (QFE) was found. The phase boundary FE–QFE found from dielectric and X-ray data approximately coincides, while the unit cell volume and unit cell dimensions show discontinuities at this boundary. The dielectric properties were investigated in the QFE and PE phase fields as functions of temperature and frequency. The dielectric constant ε as a function of temperature could be represented in both the phase fields by a quadratic law of the type $\varepsilon^{-1} = \varepsilon_{max}^{-1} + C(T - T_c')^2$, while T_c' as well as $\tan \delta_{max}$ were dependent on the frequency.

Die Phasenverhältnisse in den keramischen Werkstoffen (Pb, La)Zr$_{0.55}$Ti$_{0.45}$O$_3$ als Funktion der La-Konzentration und der Temperatur wurden mit Hilfe der Röntgenbeugung und dielektrischen Messungen untersucht. In dem Phasendiagramm befindet sich zwischen der tetragonalen, ferroelektrischen (FE) und der kubischen, paraelektrischen Phase (PE) auch eine pseudokubische, sogenannte quasiferroelektrische Phase (QFE). Die Phasengrenzen FE–QFE, die aus den dielektrischen und Röntgen-Daten bestimmt werden, fallen annähernd zusammen, während das Volumen und die Dimensionen der Einheitszelle an dieser Grenze Diskontinuitäten zeigen. Die dielektrischen Eigenschaften wurden in den QFE- und PE-Phasen als Funktion der Temperatur und der Frequenz bestimmt. Die dielektrische Konstante ε als Funktion der Temperatur kann in den beiden Phasen durch die quadratische Gleichung $\varepsilon^{-1} = \varepsilon_{max}^{-1} + C(T - T_c')^2$ dargestellt werden, während T_c' und $\tan \delta_{max}$ eine Frequenzabhängigkeit aufweisen.

1. Introduction

The quaternary lead–lanthanum zirconate–titanate system (PLZT) shows some unusual and interesting electrical and optical properties [1]. Especially the composition range, in which a strong broadening of the ε–T curve around the Curie temperature occurs, is interesting from scientific and application points of view. Recently, this composition range has been studied by Carl and Geisen [2] and Meitzler and O'Bryan [3] for PLZT compositions with a Zr/Ti ratio of 65/35. In a certain part of the phase diagram (T–x plot) the material is neither 'true' ferroelectric nor 'true' paraelectric, and has been called quasi-ferroelectric [2] or pen-ferroelectric [3].

In this work PLZT compositions with a Zr/Ti ratio of 55/45 and variable La contents (7 to 14 at%) have been investigated. With this Zr/Ti ratio the phase

diagram (T–x plot) is somewhat simpler and the only ferroelectric phase occurring has tetragonal symmetry. Study of the dielectric properties of PLZT ceramics has taken place in comparison with material systems in which so-called diffuse phase transitions occur (e.g. relaxator-type materials) as reported by Isupov [4, 5], Bokov and Mylnikova [6], Smolenski [7], and Kirillov and Isupov [8].

Special attention has been paid to the comparison between structural changes, as revealed by X-ray measurements and changes in the dielectric properties. So conclusions can be drawn with respect to the phase boundaries in a T–x plot of the phase diagram with a constant Zr/Ti ratio. An estimate of the stress sensitivity (grain size effects) can be achieved.

2. Experimental Procedures

All compositions in the PLZT system have been prepared from oxides according to the general formula

$$Pb_{1-0.75x}La_x(Zr_{0.55}Ti_{0.45})O_{3+0.75x} \qquad (1)$$
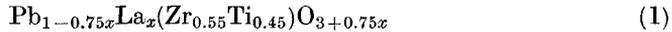
in which the La concentration (x) was varied from 7 to 14 at% of the total number of ions at the A position of the ABO_3 perovskite. The following formulation is introduced for the description of the different compositions: PLZT x/5 5/45, in which x is the variable lanthanum concentration.

Weight changes during sintering were considered as losses of PbO and have been converted into α-values (α lead elimination factor) which gave the following composition:

$$Pb_{1-\alpha x}La_x(Zr_{0.55}Ti_{0.45})O_{3+x(1.5-\alpha)} \qquad (2)$$
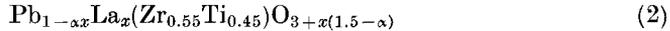
according to Härdtl and Hennings [9] (see Table 1).

Table 1

Density, grain size, and lead elimination
factor α after sintering for PLZT x/55/45
ceramics

x (at%)	density (g/cm³)	$\overline{G}$ (μm)	α
6.9	7.64	5.0	1.10
8.1	7.72	8.1	1.19
8.7	7.68	6.2	1.12
10.2	7.67	10.8	1.15
10.5	7.65	5.0	1.09
11.1	7.66	8.4	1.09
11.6	7.65	—	1.13
12.0	7.66	12.5	1.13
12.2	7.62	8.2	1.15
13.0	7.63	6.5	1.14
14.1	7.60	16.5	1.13

2.1 Material preparation

The specimens have been prepared from pure ($>$99.5%) oxides PbO, La_2O_3, TiO_2, and ZrO_2. These oxides have been ball-milled, after which pre-firing has taken place at 850 °C for 16 h. After dry ball-milling a powder was obtained

with an average grain size $\overline{G} < 3\,\mu m$. Sintering has taken place at 1250 °C for 16 h in a controlled O_2 and PbO atmosphere.

The bulk density after sintering was measured by the liquid (Hg) displacement technique. Grain sizes were determined from polished and etched (in HCl/HF mixtures) specimens by the linear-intercept method[1]) and by using the relation $\overline{G} = 1.56\overline{D}$ [10]. The chemical composition was analysed by means of X-ray fluorescence (Table 1). After sintering no second phase was observed by X-ray diffraction and (scanning electron) microscopy.

2.2 Physical and electrical measurements

All specimens were annealed at a temperature of 900 °C during 2 h and slowly cooled to room temperature.

X-ray diffraction patterns were determined with a spectrometer using $CuK\alpha$ radiation through an Ni filter. Measurements have been performed on sintered discs as well as powders of $\overline{G} \approx 3\,\mu m$ ($\overline{G}$ mean grain size). These powders were obtained by milling of the discs, followed by annealing. Unit cell measurements were determined from several diffraction lines with an accuracy estimated to be ± 0.002 Å for sintered discs and ± 0.001 Å for powders.

The dielectric measurements were made using capacitance bridges[2]) yielding the dielectric constant ε', the dielectric loss ε'', and the dielectric loss tangent $\tan\delta$, as functions of temperature at different frequencies (1 to 500 kHz). Measurements were made with 2V ac voltage applied to discs having evaporated gold electrodes. The heating rate was 2 deg/min.

3. Results

3.1 X-ray diffraction results

In Fig. 1 and 2 the unit cell dimensions as a function of lanthanum concentration for annealed powders of $\overline{G} \approx 3\,\mu m$ have been given (at $T = 20$ °C). For $x \leqq 11.0$ at% La the material shows tetragonal symmetry, for $x \geqq 11.5$ at% the material has cubic or pseudo-cubic symmetry. A notable change in unit cell dimensions as a function of La concentration takes place round $x = 11.5$ at% La. For the c/a ratio especially this is very clear.

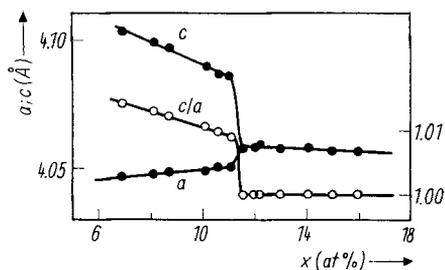Fig. 1. Unit cell dimensions a, c, and c/a as functions of the La concentration (x) in PLZT $x/55/45$ at $T = 20$ °C for annealed powders

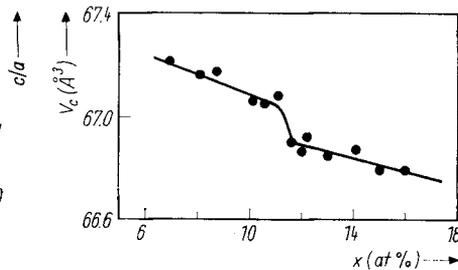Fig. 2. Unit cell volume V_c as a function of the La concentration (x) in PLZT $x/55/45$ at $T = 20$ °C for annealed powders

---

[1]) Scanning electron microscopy.

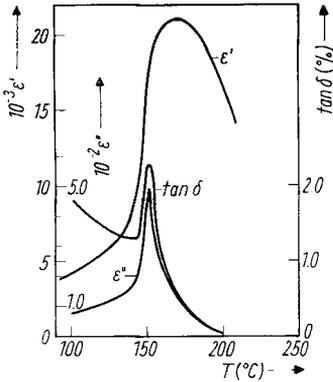[2]) Wayne Kerr Universal Bridge B 221 (1 to 50 kHz); Wayne Kerr Radio Frequency Bridge B 601 (50 to 500 kHz).

Fig. 3. The dielectric constant ε', dielectric loss ε'', and dielectric loss tangent tan δ as functions of temperature for PLZT 8.1/55/45 at 10 kHz
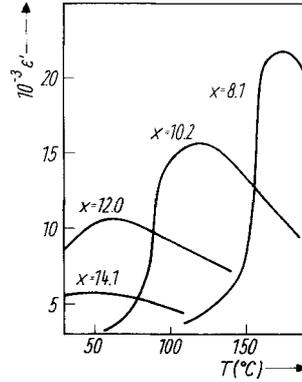
Fig. 4. The dielectric constant ε' as a function of temperature for PLZT x/55/45 with $x = 8.1$; 10.2; 12.0; 14.1; 10 kHz

For the unit cell dimensions as a function of La concentration for annealed discs an analogous behaviour as for powders has been found (at $T = 20\ °C$). But the marked change in unit cell dimensions as a function of La concentration occurs at different La concentrations for powders and sintered discs, respectively. For powders this change appears round $x = 11.5\ \mathrm{at\%}$ La and for discs round $x = 11.0\ \mathrm{at\%}$ La. The unit cell volume for powders is larger than that for discs of the same composition, which may be an indication of existing stress in the ceramic samples.

3.2 Dielectric results

Fig. 3 shows the dielectric constant ε', dielectric loss ε'', and dielectric loss tangent tan δ, as functions of temperature for one La concentration, measured at a frequency of 10 kHz. The temperatures where ε', ε'', and tan δ are at a maximum are defined as T_c'[3]), T_b, and T_t, respectively.

Table 2

Dielectric data for PLZT x/55/45 measured at a frequency of 10 kHz

x (at%)	T_c' (°C)	ε'_{max}	T_b (°C)	ε''_{max}	T_t (°C)	tan δ_{max} (%)	$\varepsilon'_{20\ °C}$ *)	tan $\delta_{20\ °C}$ (%)*)
6.9	201.5	27800	187.5	400	186	1.8	2400	1.7
8.1	171.5	21100	152	490	152	2.3	2200	2.1
8.7	148.5	19200	126	550	126	3.6	2300	1.8
10.2	117.5	15900	91.5	750	91.5	5.6	2800	2.6
11.1	89	13100	62	880	50	7.5	6000	5.7
12.0	63.5	10900	37	620	≤ 22	≥ 7.7	8200	7.7
12.2	60	9600	37	600	≤ 22	≥ 7.8	7000	7.8
14.1	45	6000	≤ 22	≥ 225	≤ 22	≥ 4.0	5700	4.0

* tan $\delta_{20\ °C}$ and $\varepsilon'_{20\ °C}$ are values measured at 20 °C.

---

[3]) T_c' is the temperature where ε' is at a maximum and need not be the Curie temperature, at which the phase transition FE–PE occurs in normal ferroelectrics as e.g. $BaTiO_3$.

For this PLZT composition (PLZT 8.1/55/45) an $\varepsilon'-T$ curve around T'_c is observed, which is relatively broad compared with that for the $\varepsilon'-T$ behaviour round T'_c in coarse-grained $BaTiO_3$ [11] and other normal ferroelectric materials. For other PLZT compositions investigated the same behaviour was found.

From Table 2 it can be seen that for $7 \leqq x \leqq 10$, $T_b = T_t < T'_c$, and for $x \geqq 11$ that $T_b \neq T_t < T'_c$.

The $\varepsilon'-T$ curves for variable La contents have been given in Fig. 4. It is seen that the maximum value of ε' decreases with increasing La concentration (see Table 2) while the 'diffuseness' of the $\varepsilon'-T$ curve around T'_c increases. At high La concentrations (e.g. $x = 14$) ε' changes only a little in a large temperature region round T'_c, in other words the $\varepsilon'-T$ curve has been considerably broadened. Thus broadening increases with increasing La concentration.

The results of the dielectric measurements have been collected in Table 2. It can be seen that T'_c, T_b, and T_t decrease with an increasing La concentration, while the difference between T'_c and T_t rises more clearly than $T'_c - T_b$ (which is about 23 °C from 8 to 12 at% La). Maximum values of ε'' and $\tan \delta$ as functions of the temperature are highest around 11 to 12 at% La; in this concentration range the values of ε' and $\tan \delta$, at room temperature, also show a marked increase.

Frequency affected the temperature dependence of the dielectric constant ε', dielectric loss ε'', and dielectric loss tangent $\tan \delta$. For one composition, PLZT 10.2/55/45, the frequency dependence has been illustrated in Table 3. It shows that T'_c, T_b, and T_t increase with increasing frequency, just as ε''_{max} and $\tan \delta_{max}$.

Table 3

Dielectric data for PLZT 10.2/55/45 as a function of frequency

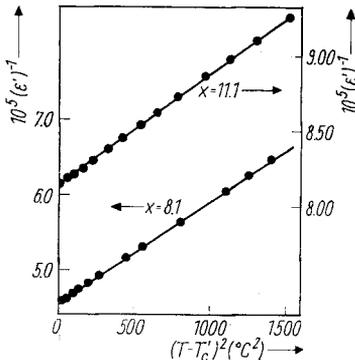| freq. (kHz)	T'_c (°C)	ε'_{max}	T_b (°C)	ε''_{max}	T_t (°C)	$\tan \delta_{max}$ (%)
1	113	15900	85	710	79.5	5.2
10	117.5	15900	91	750	91.5	5.6
500	121	15300	103	870	94	6.9

Fig. 5. Dependency of $1/\varepsilon'$ on $(T - T'_c)^2$ for PLZT 8.1/55/45 and PLZT 11.1/55/45 at 10 kHz $(T > T'_c)$
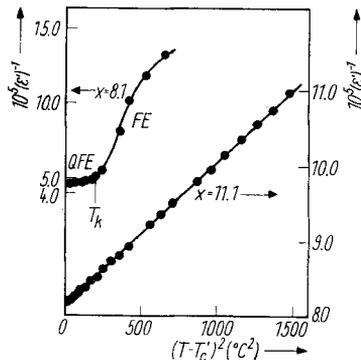
Fig. 6. Dependency of $1/\varepsilon'$ on $(T - T'_c)^2$ for PLZT 8.1/55/45 and PLZT 11.1/55/45 at 10 kHz $(T < T'_c)$

With increasing frequency the maximum value of ε', ε'_{max}, only decreases a little. For $T \gg T'_c$ (e.g. $T > T'_c + 40$ deg) the values of ε' are independent of frequency.

This frequency dependence of the dielectric behaviour was the same for all PLZT compositions investigated, but the change of e.g. T'_c with the frequency is smaller with decreasing La concentration. ($T'_c = k \ln$ (frequency), with k increasing with increasing La concentration.)

An interesting feature is that the dielectric constant as a function of temperature for all compositions and all measured frequencies can be described by a *quadratic law* of the type

$$\varepsilon^{-1} = C_1 + C_2 (T - T'_c)^2 \qquad (3)$$

both above and below T'_c, however with different values of C_2. This is shown in Fig. 5 (for $T > T'_c$) and in Fig. 6 (for $T < T'_c$, in a certain temperature region) for two compositions and will be discussed further in Section 4.2.
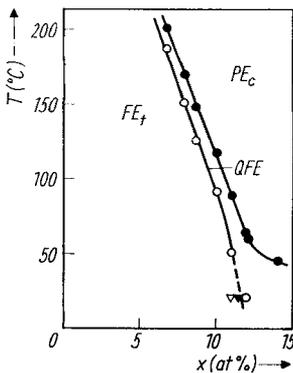
4. Discussion

4.1 Phase relations for PLZT x/55/45

In the literature [2, 3, 12] for PLZT compositions with a Zr/Ti ratio of 65/35 a few criteria are mentioned describing the transitions ferroelectric (FE)–quasi-ferroelectric (QFE) and paraelectric (PE)–quasi-ferroelectric. A property of the quasi-ferroelectric [2] or pen-ferroelectric [3] region is that, without applied electric fields there is no or only weak measurable ferroelectricity. But on applying an electric field, the material becomes clearly ferroelectric as appears from double hysteresis loops at ac voltages above a certain value, as has been found by Carl and Geisen [2] and in our preliminary experiments, too.

In general a criterion taken for the phase transition between PE and QFE is the temperature, T'_c, where ε' is at a maximum [2, 3, 12]. For the phase transition FE–QFE some more criteria have been given in literature [2, 3, 12].

By using some of the criteria for the phase transitions FE–QFE and QFE–PE a T–x plot of the phase diagram has been constructed for PLZT x/65/35 by Meitzler and O'Bryan [3]. In this work some of the given criteria have also been used to construct the T–x plot of the phase diagram for PLZT x/55/45, as is shown in Fig. 7. T_t, the temperature where $\tan \delta$ is at a maximum, has been used as a criterion for the phase transition FE–QFE, and T'_c, the temperature where ε' is at a maximum, for the phase transition PE–QFE. An uncertainty arises from the fact that in our experiments the phase boundaries are dependent on the frequency (Table 3). The same holds for T'_c and T_t for PLZT x/65/35 by Carl and Geisen [2], while T'_c and T_t given by Meitzler and O'Bryan are independent of the frequency.

Fig. 7. Phase relations in 55/45 PLZT as a function of temperature and La content (c cubic; t tetragonal; FE ferroelectric; PE paraelectric; QFE quasi-ferroelectric). ● max. in $\varepsilon'(T'_c)$; ○ max. in $\tan \delta(T'_c)$; ▽ X-ray ceramics; ▼ X-ray powders

In our work a crystallographic criterion has been added for the phase transition FE–QFE derived from the X-ray investigations (Fig. 1 and 2). The La concentration at which the structure changes from tetragonal to (pseudo-) cubic has been given in the phase diagram at 20 °C for powders as well as for ceramic discs. The phase boundary FE–QFE, at 20 °C, constructed in this way almost coincides with the phase boundary FE–QFE obtained by dielectric measurements (at 10 kHz). If the crystal structure exists with unit cells where c/a is almost 1.000, there will be no or only weak ferroelectric properties and will thus be called 'quasi-ferroelectric'. Meitzler and O'Bryan [3] suppose a pseudo-cubic structure of the material in the QFE–phase field and a polar (non-cubic) phase with very little distortion and small dimensions (no visible domains). Direct proofs for the existence of these micro-domains have not so far been found in the literature. In this work for PLZT 12.0/55/45 a tetragonal structure with very little distortion has been found (at $T = 20$ °C; in the QFE phase region).

If we assume that stresses occur in the ceramic samples due to clamping of the ferroelectric domains (as a result of grain size effects), a certain shift of the phase boundary in the $T–x$ plot must be expected. The difference in unit cell volume between powders and dense ceramics, and the different La concentrations at which a marked change in unit cell dimensions occurs for powders and sintered discs, indicate some influence of stress. Therefore it is probable that the ceramic grain size also has some influence on the dielectric behaviour as has been reported by Okazaki and Nagata [13] for PLZT 8/65/35. The influence of grain size on dielectric behaviour, at constant homogeneity, is under investigation now.

4.2 Dielectric behaviour of PLZT x/55/45

The temperature dependence of the dielectric constant of the materials under investigation cannot be represented by a normal Curie-Weiss law (at $T > T'_c$) but follows a quadratic law of the type (3). This is true for all compositions investigated and all frequencies used (1 to 100 kHz, sometimes 500 kHz).

Equation (3) even holds good in the QFE region ($T < T'_c$) down to a temperature T_k (near T'_b and T_t) below which it is no longer applicable.

Table 4

Various parameters describing the dielectric behaviour of PLZT x/55/45 with a quadratic law (at 10 kHz)

x (at%)	T_t (°C)	T_k (°C)	$10^{-3}\varepsilon'_{max}$	$T > T'_c$		$T < T'_c$	
				C_2 (10^8 °C^{-2})	δ (°C)	C_2 (10^8 °C^{-2})	δ (°C)
6.9	187.5	188.5	28	1.71	33	2.4	27
8.1	156.5	158	21	1.36	42	2.0	34
8.7	126	128.5	19	1.24	46	1.4	43
10.2	91.5	92.5	16	1.07	54	1.56	45
11.1	50	—	13.1	0.84	69	1.90	46
12.0	≦22	≦22	10.9	0.86	74	2.03	48
12.2	≦22	≦22	9.6	1.09	69	3.08	41
14.1	≦22	≦22	6.0	1.17	84	1.84	68

Examples of this behaviour are given for two compositions in Fig. 5 and 6, while characteristic parameters for all compositions have been collected in Table 4. As can be seen from this table $T_k \approx T_t$, therefore the quadratic law holds good over almost the complete QFE region.

Further analysis and interpretation can be given following a model proposed by Isupov [4, 5], Kirillov and Isupov [8], and Smolenski [7] for interpreting diffuse phase transitions, mainly in niobates.

Essentially, they assumed the existence of a mixture of polar and non-polar micro-regions (having volumes of $\approx 10^4$ cells). It was also presumed that the polar micro-regions had different local Curie temperatures. For the distribution of numbers of micro-regions, $n(T_c)$, a Gauss distribution was assumed around the mean Curie temperature T'_c with a standard deviation δ.

Isupov believes that the occurrence of a distribution of local Curie temperatures is caused by compositional fluctuations in the solid solution. This hypothesis will not be discussed now, but only references to other possible causes will be made, e.g. stress fluctuations.

Furthermore Isupov and Smolenski assume two contributions of the polar micro-regions to the total polarization and thus to ε':

a) Relaxation polarization. This is caused by a reorientation of the electric moments of the polar regions with respect to the weak, electric (alternating) field and with a relaxation time τ.

b) Induced (electron–ion) polarization. In this case the contribution of the polar and non-polar regions can be calculated from the same distribution of local Curie temperatures as used under a).

Both contributions may play a role. The contribution a) gives rise to a frequency dependence of ε'_{max} (and ε''_{max}). At high frequencies ($\omega > \tau$) only the contribution b) remains, which will be called ε'_∞.

Under the above-mentioned assumptions Kirillov and Isupov [8] derived an expression for ε' in the form

$$\frac{1}{\varepsilon' - \varepsilon'_\infty} = \frac{1}{\varepsilon'_{max}} + \frac{(T - T'_c)^2}{2\varepsilon'_{max}\delta^2} + \text{higher terms} . \tag{4}$$

If ε'_∞ and higher terms, involving $(T - T'_c)^4$ can be ignored, this equation (4) is the same expression as (3) with

$$C_1 = (\varepsilon'_{max})^{-1} , \tag{5}$$

$$C_2 = (2\varepsilon'_{max}\delta^2)^{-1} . \tag{6}$$

In Table 4 the values of C_2, ε'_{max}, and δ from (4) to (6) for all compositions have been collected. From Table 4 it can be concluded that C_2 passes through a minimum value as a function of the La concentration, while ε'_{max} decreases and δ increases continuously with increasing La concentration. Within the model this implies that the fluctuations of local T_c-values become more intense the larger the La concentration and the wider (broader) the QFE region are. According to Isupov [4], using the model of compositional fluctuations, δ should rise in solid solutions as the ratio of the concentrations of different types of ions in the same sub-lattice approaches unity. In the case in question the ratio [La]/[Pb] indeed increases together with δ.

The fact that (4) can be used in the PE as well as QFE phase fields implies that there is no sharp distinction between the two regions. Equation (4) has now been derived under the assumption of micro-regions with physical properties which are independent of each other (without any one of very weak interaction). Although this is reasonable at high temperature in the PE phase, it is certainly not justified in the FE phase but may be true to a certain extent in the QFE phase. Going from the PE to the QFE phase it seems reasonable to assume that a small but increasing interaction due to increasing electrical interaction and deformation (stress interaction) of the micro-regions takes place. Such a weak interaction can only be present in the case of values of c/a near to unity. Near T_k this ratio starts to increase, polarization and stress interaction increase, and (3) and (4) do not apply, while stable macroscopic ferroelectric domains are formed (at $T < T_t \approx T_k$).

The frequency dependence of the measurements at constant concentration can be qualitatively explained by the above-mentioned relaxation model (with increasing frequency resulting in increasing T'_c, T_t, T_b, ε''_{max}, and tan δ_{max} and a decreasing ε'_{max}). Carl and Geisen [2] found an analogous frequency dependency for the composition PLZT 8/65/35, as Salaneck [14], however Meitzler and O'Bryan [3] did not find any frequency dependence. The frequency range used by Meitzler and O'Bryan however was limited to 100 Hz to 10 kHz, which may be rather low. None of the above-mentioned authors further analysed the dielectric results.

As a final remark it must be stated that the broadening of ε'-T curves in absence of frequency dependence can be explained by assuming only a distribution of local Curie temperatures without referring to the relaxational contribution or compositional fluctuations. Calculations of this type have been performed by Diamond [15] for (Ba, Sr) TiO$_3$ and Kirillov and Isupov [8]. Mechanical stress fields (grain size effects) can be incorporated in these calculations and their possible influence is now under investigation.

5. Conclusions

1. For the "phase transition" FE–QFE a crystallographic criterion, derived from X-ray investigations, was found (at $T = 20$ °C). At this phase boundary unit cell dimensions and volume show a sharp change, while crystal symmetry changes from tetragonal to (pseudo-)cubic.

2. At room temperature the phase boundary FE–QFE, derived from X-ray experiments, is observed at a lower La concentration for discs than for powders.

3. The phase transition FE–QFE, obtained with dielectric measurements, almost coincides with this phase transition derived from X-ray investigations (at $T = 20$ °C).

4. The dielectric constant ε as a function of temperature can be described by a quadratic law $\varepsilon^{-1} = C_1 + C_2 (T - T'_c)^2$, both above (in the PE phase region) and below T'_c (in the QFE phase region), however, with different values of C_2 above and below T'_c (T'_c is the temperature at which ε is at a maximum).

5. Frequency affected the temperature dependence of the dielectric constant ε' and dielectric loss ε'' (relaxator behaviour).

6. Interpretation of the dielectric behaviour seems possible by assuming a distribution of local Curie temperatures; the standard deviation of which could be correlated with the La concentration.

References

[1] G. H. Haertling and C. E. Land, J. Amer. Ceram. Soc. 54, 1 (1971).
[2] K. Carl and K. Geisen, Proc. IEEE 61, 967 (1973).
[3] A. H. Meitzler and H. M. O'Bryan, Jr., Proc. IEEE 61, 959 (1973).
[4] V. A. Isupov, Soviet Phys. — J. tech. Phys. 1, 1846 (1956).
[5] V. A. Isupov, Soviet Phys. — Solid State 5, 136 (1963).
[6] V. A. Bokov and I. E. Mylnikova, Soviet Phys. — Solid State 3, 613 (1961).
[7] G. A. Smolenski, J. Phys. Soc. Japan, Suppl. 28, 26 (1970).
[8] V. V. Kirillov and V. A. Isupov, Ferroelectrics 5, 3 (1973).
[9] K. H. Härdtl and D. Hennings, J. Amer. Ceram. Soc. 55, 230 (1972).
[10] M. I. Mendelson, J. Amer. Ceram. Soc. 52, 443 (1969).
[11] B. Jaffe, W. R. Cook, and H. Jaffe, Piezoelectric Ceramics, Academic Press, Inc., London/New York 1971 (p. 71).
[12] E. T. Keve and A. D. Annis, Ferroelectrics 5, 77 (1973).
[13] K. Okazaki and K. Nagata, J. Amer. Ceram. Soc. 56, 82 (1973).
[14] W. R. Salaneck, J. appl. Phys. 43, 4468 (1972).
[15] H. Diamond, J. appl. Phys. 32, 909 (1961).