

RELAXATIONAL POLARIZATION AND DIFFUSE PHASE TRANSITIONS
OF LA-SUBSTITUTED $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -CERAMICS

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ABSTRACT

Dielectric properties of $(\text{Pb},\text{La})\text{Zr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ ceramics have been investigated as functions of temperature and frequency. The dielectric constant as a function of temperature can be represented over a considerable temperature interval by a quadratic law of the type: $\epsilon^{-1} = \epsilon_{\text{max}}^{-1} + C(T - T_c')^2$. The permittivity versus temperature curves are strongly broadened around T_c' (where ϵ is at a maximum) and the dielectric behaviour is at least partly of a relaxational nature. Interpretation of the dielectric behaviour (broadening, frequency dependence, quadratic law) seems possible by assuming a distribution of local Curie temperatures; the standard deviation of which can be correlated with the La concentration.

Introduction

Lead-lanthanum zirconate-titanate ceramics (PLZT) are materials with interesting electrical and optical properties (1). In a certain composition range a strong broadening of the ϵ -T curve around the "Curie temperature" has been found, which is interesting from both 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 this work special attention has been given to the dependence of the dielectric constant on temperature and frequency around the 'ferroelectric-paraelectric' phase transition. There have been investigated $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ceramics with a Zr/Ti ratio of 55/45 and variable La contents (2-15 at.%). With this Zr/Ti ratio the phase diagram 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 with a comparable

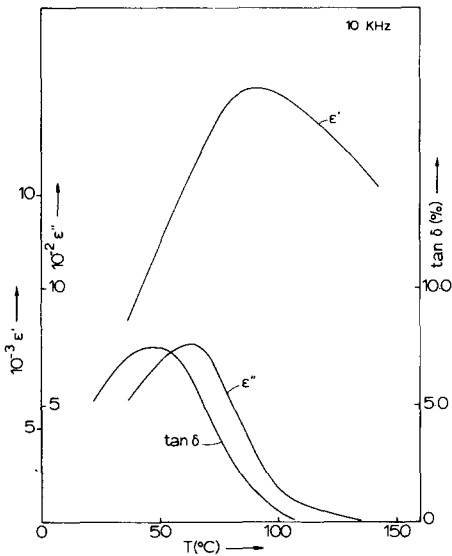


FIG. 1

Dielectric properties (ϵ' , ϵ'' , $\tan\delta$) as functions of temperature for PLZT 11.1/55/45.

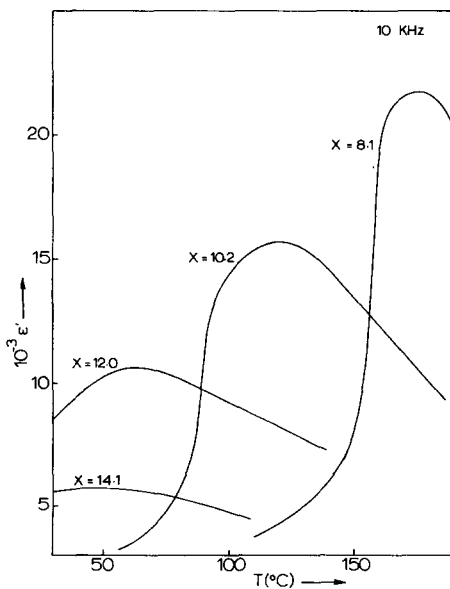


FIG. 2

Temperature dependence of the dielectric constant for PLZT x/55/45.

crystal structure and in which the same lattice position has been occupied by different ions.

Experimental Procedures

In (4) there has been given a general description of the used procedures. Only some remarks will be made here.

The following formulation is introduced for the description of the different compositions: PLZT x/55/45, in which x is the variable lanthanum concentration.

All PLZT ceramics used here have been sintered at 1250°C during 16 hours to achieve coarse-grained ceramics. The density of the sintered ceramics varied from 7.60-7.72 g/cm³, while the average grain size was larger than 5 μm.

The dielectric measurements have been made with a Wayne Kerr Universal Bridge B221 in the frequency range from 1-50 KHz and with a Wayne Kerr Radio Frequency Bridge B601 in the frequency range from 50-500 KHz.

At room temperature some hysteresis loops (P-E plot) have been measured with an experimental set-up as used by Carl and Geisen (2).

Results

Dielectric Measurements

The temperatures at which ϵ' and $\tan\delta$ are at a maximum are defined as respectively T_C' and T_t . It must be remarked that T_C' is the temperature where ϵ' is at a maximum and needs not to be the Curie temperature, at which the phase transition ferroelectric (FE) - paraelectric (PE) occurs in classical ferroelectrics as e.g. coarse-grained BaTiO₃.

The results, as partly represented in Figs. 1 and 2, show that in the composition range 8-14 at.% La a relatively strong broadening of the ϵ' -T and ϵ'' -T curves occur compared with the curves for coarse-grained BaTiO₃. This broadening increases with increasing La concentration, while at the same time the maximum value of ϵ' (ϵ'_{max}) decreases. The values of T_t and T_C' decrease with increasing La concentration, while the difference

between T_t and T_c' increases with increasing La concentration (4).

The dielectric constant round T_c' is frequency-dependent as can be seen in Fig. 3 for PLZT 12.0/55/45. In most cases T_c' , T_t and $\tan\delta_{\max}$ increase with increasing frequency, while ϵ'_{\max} decreases. At temperatures far from T_c' , in the FE and PE phases, frequency dependence almost vanishes.

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:

$$\epsilon^{-1} = \epsilon_{\max}^{-1} + C_2 (T - T_c')^2 \quad (\text{eq.1})$$

both above and below T_c' , however with different values of C_2 . In Fig. 4 this has been shown for two compositions and with $T > T_c'$. The temperature interval above T_c' in which the dielectric behaviour can be described by the above mentioned quadratic law increased with increasing La concentration and reaches 50 degrees or more.

Below T_c' the dielectric constant can be described by this quadratic law in a relatively small temperature region, which almost coincides with the temperature region between T_c' and T_t (4).

X-ray diffraction measurements

In a former publication (4) there have been given the unit cell dimensions as function of the lanthanum concentration for annealed powders ($\bar{G} \approx 3 \mu\text{m}$) at 20°C. For $x < 11.0$ at.% La the material clearly shows tetragonal symmetry (at 20°C). A notable change in unit cell dimensions as function of La concentration takes place round $x = 11.5$ at.% La. For the c/a ratio especially this is very clear. For $x > 12.0$ at.% La the material still has a tetragonal symmetry with a very small distortion ($c/a \approx 1.00$). The c/a ratio in this case cannot be measured adequately from the X-ray reflection lines, but the asymmetric form of some reflection lines indicates that the material still has a tetragonal structure (for $x = 12.0$ at.% La the ratio c/a has been estimated as $\approx 1.003 \pm 0.002$, from the 002/200 reflection line, in which a small shoulder has been found,

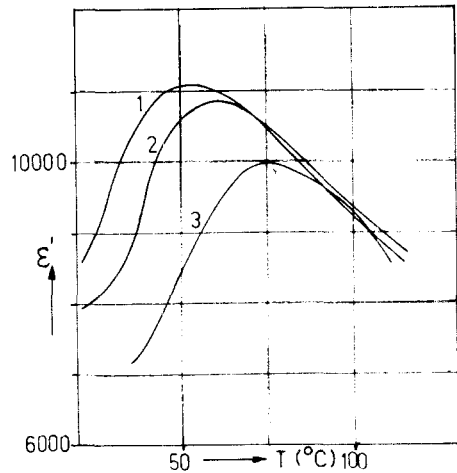


FIG. 3

Permittivity as a function of temperature for PLZT 12,0/55/45 at three frequencies (1=1KHz; 2=10KHz; 3=500KHz).

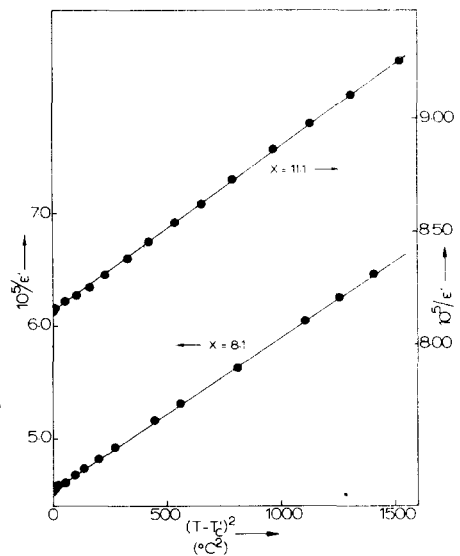


FIG. 4

Dependence of $1/\epsilon'$ on $(T - T_c')^2$ for PLZT 8.1/55/45 and PLZT 11.1/55/45 at 10KHz ($T > T_c'$).

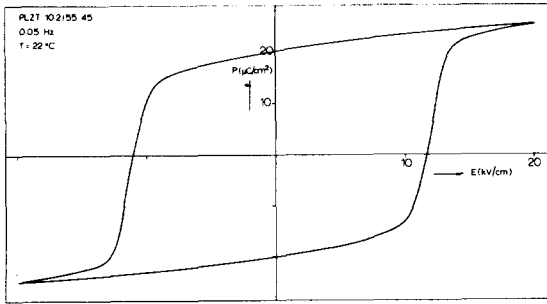


FIG. 5a

Hysteresis loop for PLZT
10.2/55/45 at 20°C

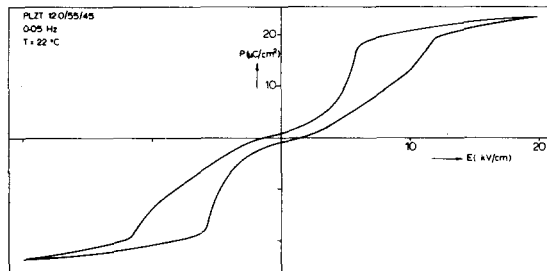


FIG. 5b

Hysteresis loop for PLZT
12.0/55/45 at 20°C

which has not been caused by the CuK α radiation.

Measurements of hysteresis loops

In Fig. 5b there have been given hysteresis loops (at 20°C) for PLZT 10.2/55/45 and PLZT 12.0/55/45. For low La concentrations ($x < 11.1$ at.% La) there have been found so-called square loops and for $x > 12.0$ at.% La so-called 'slim' loops, the latter occurring at temperatures larger than T_t .

Discussion

Phase relations for PLZT x/55/45

In classical ferroelectrics as e.g. BaTiO₃, one finds a phase transition between the ferroelectric (FE) and paraelectric (PE) phases at a distinct temperature. At this Curie temperature different properties show some remarkable features, as for example the permittivity is at a maximum, crystal symmetry becomes cubic, changes in crystallographic parameters occur and hysteresis loop vanishes. However, in PLZT ceramics a region between the FE and PE phase has been found which has not a true FE nor a true PE nature.

In literature this region has been called quasi-ferroelectric (QFE) (2) or penferroelectric (3). This QFE region has been described as a 'phase' which has no or only weak measurable ferroelectricity without applying an electric field. But on applying an electric field the material becomes real ferroelectric. This raises the question if the ferroelectric behaviour exists already at zero field or is induced by the field. As a consequence the hysteresis loops in the QFE region show a so-called 'slim-loop' behaviour, as can be seen in Fig. 5b. Moreover in this work it has been seen that there are some indications that the material is not entirely cubic in this QFE region, but still has a very little distortion which may be used as an indication for the occurrence of micro-regions.

It must be remarked that the 'phase-transition' FE-QFE has been characterised (2,3,4,5) by many phenomena which also occur at the FE-PE phase transition in classical ferroelectrics (a change in crystallographic parameters, hysteresis loop changes in shape, dielectric losses are at a maximum). However the maximum value of the permittivity does not occur at the 'phase transition FE-QFE, but at a different temperature, called the apparent Curie temperature T_c' .

Dielectric behaviour of PLZT x/55/45

A further discussion of the results shall have to treat at least the strong broadening of the ϵ' -T curve and the frequency dependence of the dielectric properties.

A broadening of the ϵ' -T curve can be caused by four different groups of causes:

- a) macroscopic inhomogeneities originating from the preparation procedure.
- b) internal stress effects caused by grain size (scale comparable with domain size).
- c) submicroscopic inhomogeneities (scale 50-1000Å).
- d) relaxational polarization.

As has been discussed in (4) macroscopic inhomogeneities and grain size don't play a major role with respect to the phenomena under discussion and in the materials which are reported here (mean grain size > 5 μm). Microscopic inhomogeneities (50-1000Å) within one phase remain as a possible cause of broadening. These inhomogeneities are in thermodynamic equilibrium at high temperature and may be frozen in at lower temperatures. They include e.g. compositional fluctuations (9-11). Thermal polarization fluctuations (6-8) may be another form of submicroscopic inhomogeneities causing broadening of the ϵ' -T curves.

The frequency dependence of some properties round T_C' points to the occurrence of a relaxational polarization mechanism. If this mechanism plays an important role the very large value of ϵ'_{max} can be explained by assuming a contribution of very large dipoles probably of a ferroelectric nature and connected with the microregions mentioned before.

So we can distinguish two contributions to the total polarization and ϵ' :

- a) relaxational polarization.

This is caused by a reorientation of the electric moments of polar micro regions with respect to the weak, electric (alternating) field.

- b) induced (electron-ion) polarization.

It includes the contribution of a ferroelectric phase transition. This transition may be sharp (one single T_C) or diffuse (distribution of T_C).

Both contributions may play a role. At high frequencies only the contribution under b remains, which will be called ϵ'_{∞} .

For the moment further analysis and interpretation will be given following a model proposed by Isupov et al. (9,10,11) for interpreting diffuse phase transitions 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 presumed that the polar micro-regions had different local Curie temperatures. For the distribution of numbers of micro-regions, $n(T_C)$, a Gaussian distribution was assumed around a mean Curie temperature, e.g. T_C' , with a standard deviation δ .

Under the above mentioned assumptions Kirillov and Isupov (11) derived an expression for ϵ' in the form:

$$\frac{1}{\epsilon' - \epsilon'_{\infty}} = \frac{1}{\epsilon'_{\text{max}}} + \frac{(T - T_C')^2}{2\epsilon'_{\text{max}}\delta^2} + \text{higher terms} \quad (\text{eq. 2})$$

TABLE 1

Quadratic Law Parameters for
PLZT x/55/45. (10KHz)

x (at.%)	$10^{-3} \epsilon'_{\max}$	$C_2 (10^8 \text{ } ^\circ\text{C}^{-2})$	$\delta (^\circ\text{C})$
2.0	19.2	5.4	23
4.2	23.8	4.0	22
6.3	21.7	2.3	32
6.9	28	1.71	33
8.1	21	1.36	42
8.7	19	1.24	46
10.2	16	1.07	54
11.1	13.1	0.84	69
12.0	10.9	0.86	74
12.2	9.6	1.09	69
14.1	6.0	1.17	84

If ϵ'_∞ and higher terms, involving $(T-T_C')$, can be ignored (polarization is mainly relaxational) eq. 2 is the same expression as eq. 1 with:

$$C_2 = (2\epsilon'_{\max} \delta^2)^{-1} \quad (\text{eq.3})$$

In this work it has been shown (Fig. 4) that the dielectric behaviour of (Pb,La)(Zr,Ti)O₃ ceramics over a considerable temperature interval can be described by a quadratic law. In Table 1 the values of C_2 , ϵ'_{\max} and δ have been collected for all measured compositions above T_C' .

From Table 1 it can be concluded that C_2 passes through a minimum value as a function of

the La concentration, while δ increases continuously with increasing La concentration. Within the used 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.

The occurrence of a distribution of local Curie temperatures may be caused by compositional fluctuations in the solid solution. Then it can be derived from statistical considerations that in a (pseudo) binary system and for a linear relationship between composition and T_C δ reaches a maximum value as the ratio of the cation concentrations (here concentrations of different types of ions in the same sublattice) reaches the value one. Indeed δ increases together with the ratio $([\text{La}] + [\text{Pb-vacancies}]) / [\text{Pb}]$.

The value of δ is frequency dependent; for PLZT 12.0/55/45 the standard deviation δ of the T_C distribution function is 78^oC at 1 KHz, 74^oC at 10 KHz and 70^oC at 500 KHz. So with increasing frequency δ decreases. This follows from the model too (contribution- and fraction of dipoles taking part in the relaxational polarization process decreases with increasing frequency). At very high frequency the shape of the ϵ' -T curve should reflect the contribution of the induced polarization only and the remaining value of " δ " would then be a measure for the diffuseness of the "true" phase transition.

In preliminary results there has been found a strong effect of the grain size (1-8 μm) of PLZT 8/55/45 on the broadening of the ϵ' -T curves round T_C' (12). However, grain size did not or only weakly influence the 'fluctuation parameter' δ . For a mean grain size of 8 μm there has been found a δ of $42 \pm 2.5^\circ\text{C}$ and for 1.4 μm material δ is $47 \pm 2.5^\circ\text{C}$.

Dielectric behaviour of some other materialsystems

The validity of eq. 1 in a number of other systems has been tested with the help of literature values.

With $\delta > 20$ degrees and within a temperature interval of at least 30 degrees, eq. 1 was obeyed by:

a) a limited number of (A₁,A₂)BO₃ perovskites. In most cases a

normal Curie-Weiss behaviour is followed.

- b) a rather large number A(B₁, B₂)O₃ perovskites, e.g. Ba(Ti_xSn_{1-x})O₃ (13).
- c) a number of (A₁, A₂)(B₁, B₂)O₃ perovskites in which a very strong effect occurs e.g. (Pb, Ba)(Ti, Zr)O₃ (14).
- d) a number of niobates with wolfram-bronze and other structures e.g. Ba_xSr_{1-x}Nb₂O₆ (15).

Because in most cases the dependence on frequency was not investigated, the meaning of δ in these cases is merely that of a distribution of Curie temperatures and does not imply a relaxator behaviour. The lack of X-ray and grain size data causes that at the moment nothing can be said on the physical background of the broadening in these cases.

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