

The Influence of the Microstructure on the Properties of Ferroelectric Ceramics

G. ARLT

Institut Für Werkstoffe der Elektrotechnik
Aachen University of Technology, D-52056 Aachen, F.R.G.

Conventional ferroelectric perovskite type ceramics have dielectric, piezoelectric and elastic properties which depend on grain size and on domain configuration. Very fine grained ceramic is not splitted in domains. This causes strong elastic stress fields in the grains which counteract ferroelectricity. Tetragonal fine grained ceramic has a simple laminar domain structure and high elastic stress fields inside the grain and at the grain boundaries. These stress fields cause very high permittivity. In coarse grained ceramics the stress fields inside the grain are eliminated by a three-dimensional network of domains. In fine and in coarse grained ceramics the domain walls contribute considerably to the dielectric, piezoelectric and elastic constants at frequencies below a relaxation frequency which is between 200 and 1000 MHz. At low temperatures, however, the domain wall contributions freeze in. Acceptor doping lowers the domain wall contributions and shifts the relaxation frequency to higher values.

The properties of the conventional ceramics will be compared with properties of thin films and with properties of relaxor ceramics.

Key words: Ferroelectrics, relaxors, ceramics

Influencia de la microestructura sobre las propiedades de cerámicos ferroeléctricos

Las cerámicas ferroelectricas tipo perovskita poseen propiedades dieléctricas, piezoeléctricas y elásticas que dependen del tamaño de grano y de la configuración de dominios. Hay cerámicas de granos muy pequeños que no presentan dominios. Esto origina campos de tensión elástica fuerte que contrarrestan la ferroelectricidad. Los cerámicos tetragonales de grano pequeño presentan una estructura laminar simple y altos campos de tensión elástica dentro de los granos y en los bordes de grano. Estos campos de tensiones son la causa de una muy alta permitividad. En los cerámicos de granos grandes el campo de tensiones dentro de los granos se elimina por una red de dominios tridimensional. En los cerámicos de grano pequeño y en los de grano grande las paredes de dominio contribuyen considerablemente a las constantes dieléctricas, piezoeléctricas y elásticas a frecuencias por debajo de la frecuencia de relajación la cual se encuentra entre 200 y 1000 MHz. Sin embargo, a bajas temperaturas, modifica la contribución de las paredes de dominio queda congelada. El dopado con aceptores disminuye la contribución de las paredes de dominio y eleva la frecuencia de relajación. Se comparan las propiedades de cerámicos convencionales con las propiedades de láminas delgadas y cerámicos relaxores.

Palabras clave: Ferroeléctricos, relaxores, cerámicos.

1. INTRODUCTION

The microstructure of ferroelectric ceramics is mentioned in about every fifth publication on these ceramics. The field on which the title of this report is centered is extremely wide and it is not possible to cover all aspects of the microstructure in one lecture or publication. Therefore I restrict myself to those microstructural effects on which we have worked in the past. Almost all of these effects are related to the domain formation in ferroelectric ceramics.

When the ceramic comes to existence during sintering each crystalline grain is circumvented by other grains. The grains grow such that they fill the space without holes and without elastic stress inside and outside the grains. If the thermal expansion is isotropic this stress free state remains when the ceramic is cooled down to the Curie temperature. At the temperature of the phase transition from par-to-ferroelectric, each grain would deform spontaneously like a single crystal if it were not hindered by the neighbouring grains.

Indeed the grain is clamped by its environment and the spontaneous deformation is compensated by high internal stress. Homogeneous compressive stress then appears in the direction in which the grain tries to expand and homogeneous tensile stress appears in those directions in which the grain tries to shrink.

This elastic stress and its energy can be reduced by domain splitting inside the grain as shown in Fig. 1a and b. In the case of Figs. 1a a grain which was a cube in the paraelectric state forms a stack of laminar 90° domains. The cross section of the grain by this domain splitting becomes a square again, however, with some surface ripple on the right and left sides. The angle α (in rad) in tetragonal ferroelectrics is given by the spontaneous deformation $S_0 = c/a - 1 = \alpha$. In the third direction (perpendicular to the paper) the grain still has the extension as before the domain splitting. Thus the domain splitting as shown in Fig. 1a allows the grain partly to deform spontaneously by adjusting its shape to the space which is allowed by its environment. Without domain splitting the origi-

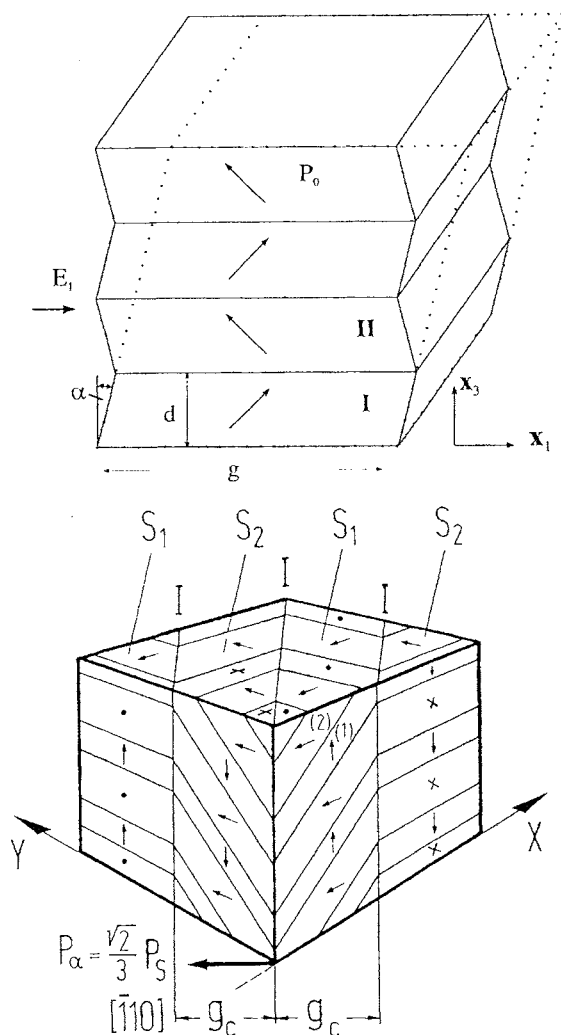


Fig. 1 a) Laminar domain configuration of a fine grain of tetragonally distorted perovskite type ceramic, b) banded domain structure in a coarse grained ceramic.

nally cubic grain, if not clamped, would deform spontaneously as indicated by dotted lines. By splitting the homogeneous stress inside the grain is reduced at the expense of domain wall energy. In equilibrium the width of the domains is determined by the minimization of the sum of stress and domain wall energy. The calculation (1) of the equilibrium domain width d gives with $d = \text{const} \cdot \sqrt{g}$ proportionality to the root of the grain size g . If the grain is so small that $d \approx g$ domains can no longer form. This can be understood by looking at the stress energy and domain wall energy is proportional to the volume of the grain $\propto g^3$ and the domain wall energy is proportional to the area of the cross section $\propto g^2$. Above the intersection of both curves (Fig. 2a) there is enough energy to create one or more twins, below this critical grain size g_{crit1} domain splitting is not possible. By extrapolation one finds this critical grain size in barium titanate to be about $g_{\text{crit1}} \approx 0.04 \text{ m}$. In grains as fine as this, however, other effects can prevail.

Another critical grain size g_{crit2} exists at much larger grain size as shown in Fig. 2b. Here a new kind of mixed domain wall (designated with I in Fig. 1b) is formed which enables the grain to have a cubic shape, i.e. to have the shape as in the paraelectric phase. Fig. 1b shows the domain configuration in this case. The surface ripple which is similar to the two rippled sides in Fig. 1a is not shown in Fig. 1b. In BT the critical grain size g_{crit2} is about $10 \text{ }\mu\text{m}$.

By these different domain splitting effects we can expect a ferro-

electric ceramic to subsist in three different domain modifications with different grain sizes and different properties:

1. Coarse grained ceramic has negligible internal stress (the stress energy w in Fig. 2b is almost zero) and has a three-dimensional domain network (2).

2. Fine grained ceramic has large internal stress and a laminar domain configuration.

3. Extra fine grained ceramic has extremely large internal stress and no domain splitting.

The properties which are dependent on the domain configuration and on the domain size are described in the following.

2. THE DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF CERAMICS

Since the polarizations on both sides of a 90° domain wall (abbreviated DW) are different, any displacement of the DW will cause a change of the net polarization P . The DW contributes to the permittivity with $\Delta\epsilon = \Delta P / \epsilon_0 E$ if the displacement of the wall is caused by the force which is exerted onto the wall by an electric field E . This contributions has to be added to the intrinsic permittivity of the ceramic which has to be ascribed to electronic and ionic polarizabilities of the ferroelectric lattice. The displacement of the DW also causes contributions to the piezoelectric and to the elastic properties of the ceramic. All three contributions, therefore, are correlated (3-4).

In coarse and in fine grained ceramics the DW contribution to the dielectric constant at room temperature (R.T.) mostly is of the same order of magnitude as the intrinsic effects. There is a strong temperature dependence of this contribution. At very low temperatures, e.g. at 4K the DWs are clamped by the periodic lattice potential. In some kind of relaxation processes (which are not understood in detail) with widely distributed relaxation times the DWs are set free from the lattice potentials when the temperature is enhanced up to a temperature at which the release is complete. In this quasi-free state the displacement of the DWs is opposed by elastic and electric constraints (5) of the grain. Fig. 3 gives an example of the measured dielectric constant of Lead Zirconate Titanate (PZT). The dielectric losses, characterized by the imaginary part of the permittivity $\Delta\epsilon''$ has a maximum below this temperature and is small above this temperature.

The contribution of the DWs to the dielectric constant in the temperature region in which they are quasi-free has been calculated (5-7). In BT $\Delta\epsilon$ is about 500 to 1000 and in PZT it is somewhat smaller in agreement with measurements. One important result of this calculation is the following: one can anticipate that fine grained ceramics which have a very dense network of DWs contribute more to the permittivity than coarse grained ceramics (8). This assumption however turned out to be wrong. The density of the domain walls has no effect on the DW contribution $\Delta\epsilon$. A grain with one wall gives the same contribution as a grain with many walls.

The contribution of the DWs to the piezoelectric coefficients is even larger than the intrinsic contribution (3,9) Thus the piezoelectric coupling factors of ceramics are also considerable larger than those for single domain crystals.

The frequency range in which the DWs contribute to the permittivity has an upper limit. The displacement of the DWs causes a shift of matter parallel to the wall on both sides of the DW. The vibrating DWs, therefore, emit acoustic shear waves which are scattered and absorbed in the ceramic. When half a wavelength of these waves is about equal to the domain width the emis-

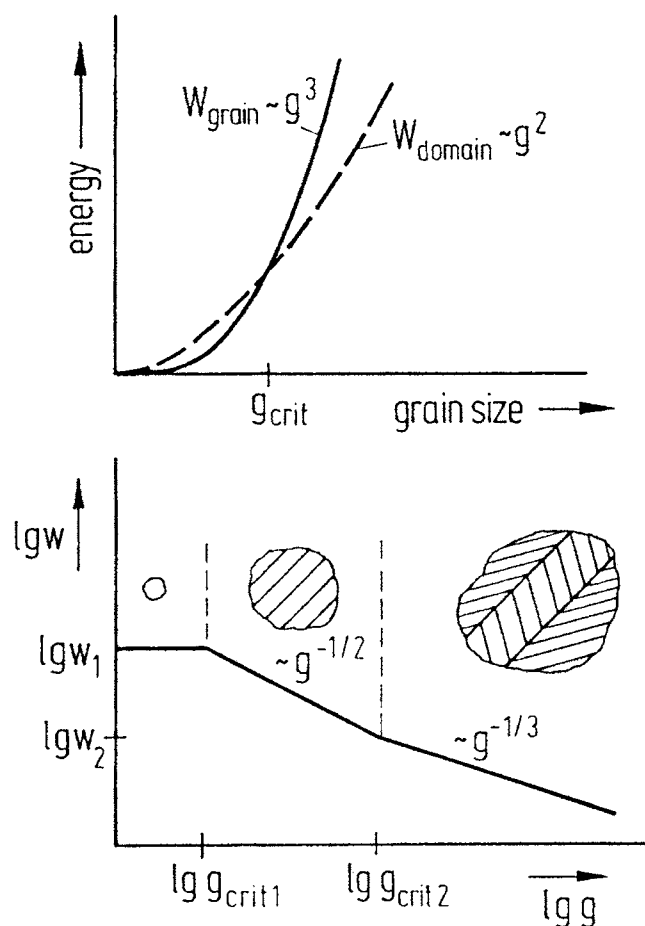


Fig. 2 a) The dependence of elastic stress energy and domain wall energy on grain size (schematic), b) the decrease of the stress energy in the ceramic with increasing grain size.

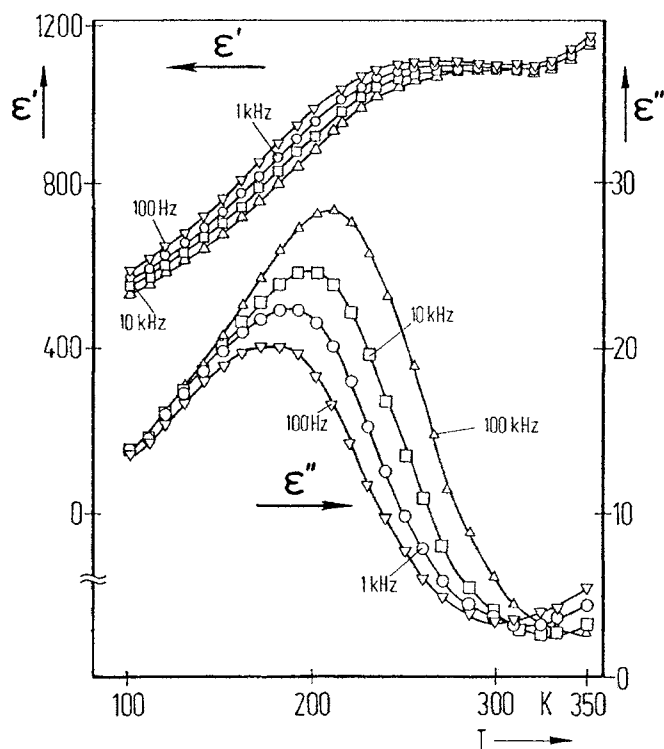


Fig. 3 Temperature dependence of the complex dielectric constant of tetragonally distorted ferroelectric PZT ceramic, $\text{Pb}_{0.92}\text{Ca}_{0.08}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$.

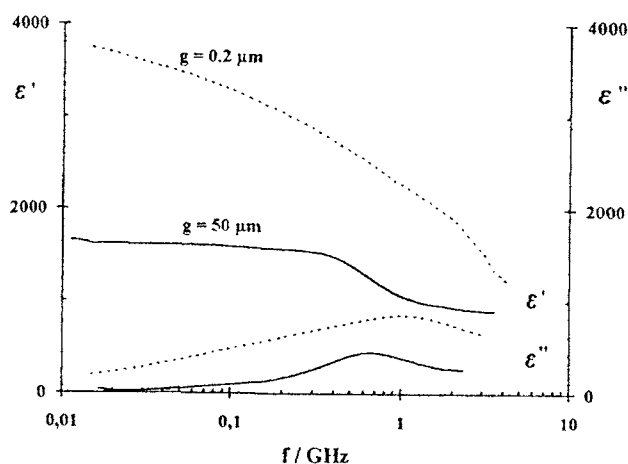
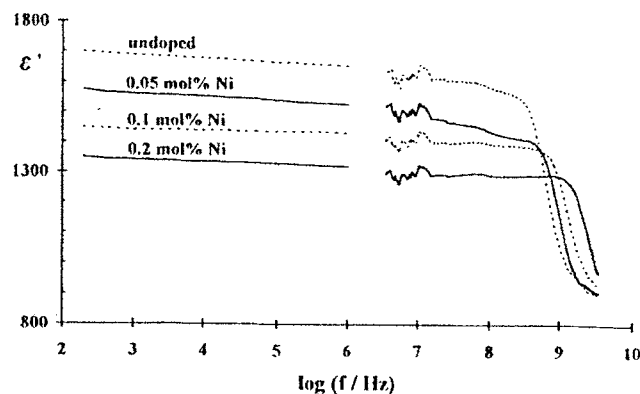


Fig. 4 Decline of the domain wall contribution to the permittivity at high frequencies due to inertia and to internal bias fields a) in coarse grained ceramics of barium titanate plain and doped, b) in fine and in coarse grained ceramics of barium titanate.

sion is strongest. At his frequency the dielectric loss has a maximum. Fig.4a shows some measured curves of BT. At frequencies above the limit the inertia of the mass of the domain impedes any further domain wall displacement (10). Doping can increase the critical frequency at which the DW contribution declines as will be discussed below. When the domain walls have a diameter larger then the acoustic wavelength the emitted beam of shear waves is very narrow. In this case the emitted waves frequency dependence of the permittivity. The result is a relaxational behaviour of the Debye type where the decline of the DW contribution occurs in a small frequency interval. This is different in fine grained ceramics when the wavelength of the shear wave is larger than the diameter of the DW as e.g. in fine grained BT at a grain size of $1 \mu\text{m}$ and smaller. The decrease of the DW contribution to the permittivity then is distributed over a very wide frequency interval as shown in Fig.4b.

Another effect discussed at the end of the next chapter is the internal bias field and the aging of the dielectric (and piezoelectric) properties. When ferroelectric ceramics like BT or PZT are doped with acceptor ions these occupy the cations, e.g. the Ti sites. In this case oxygen vacancies are formed during sintering and are attracted by the acceptor ions via electrostatic forces. The pair acceptor-oxygen vacancy is a strong electric dipole. This dipole, thus, can orient parallel to the ferroelectric polarization, which is the orientation in which they have the lowest energy. The oriented dipoles establish an electric field which is called the internal bias field (4).

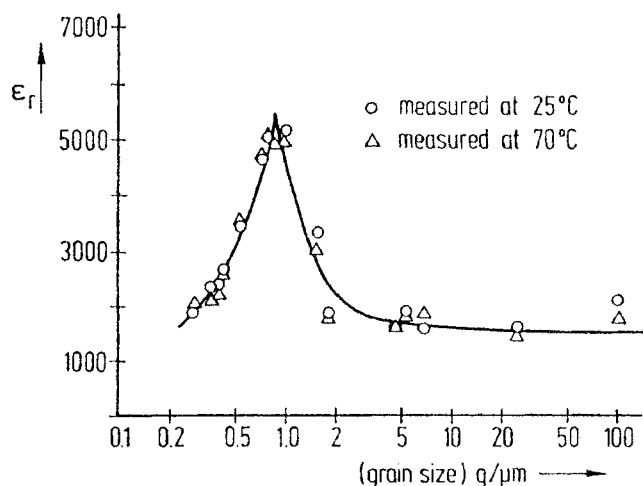


Fig. 5 The dependence of the permittivity of Barium Titanate on grain size.

This bias field has a dramatic effect on the domain wall displacements. It exerts a pressure on the walls from both sides such that the force constant for the domain wall displacement is increased. Since the internal bias field develops slowly in time, the domain wall contribution is slowly reduced in time. This effect, called aging, is a disadvantage for many applications of the ceramic. The increase of the force constant for the DW displacement in addition leads to a strongly increased critical frequency at which the DW contribution to the dielectric constant ceases and to a decrease of the dielectric contribution (see Fig. 4a). The disadvantage thus becomes an advantage when ceramics are required which have a high permittivity at a frequency which is above the normal critical frequency of the DW contribution.

In fine grained ceramics there is another important enhancement of the permittivity as shown in Fig. 5. In BT this amounts to about $\epsilon \approx 6000$. As stated above there is considerable stress in the grain, the smaller the grain the higher the stress. In addition, the boundaries of the grain if it were free are rippled as shown in Fig. 1a. In the clamped condition the ripple is smoothed by elastic deformation (1) which causes inhomogeneous stress in and near the surface of the grain. Both kinds of stresses, the homogeneous ones and the inhomogeneous ones have a direction which counteracts the spontaneous deformation. This kind of stress is known to decrease the Curie temperature and to increase the intrinsic dielectric constant (11-13). The stress near the boundary is higher than that inside the grain. Therefore, there is very high permittivity and low spontaneous polarization, near the boundaries and somewhat less increased permittivity and spontaneous polarization in the center of the grain. The inhomogeneity of the permittivity and of the polarization is confirmed by the strongly slanted hysteresis loop of these ceramics.

In extra fine grained ceramics with no domain walls the spontaneous deformation and polarization are almost no longer present. Crystallographic X-ray investigations show weak reflexions which can not be attributed to the tetragonal or orthorhombic or rhombohedral phase.

3. HYSTERESIS LOOP

Hysteresis loops can indicate whether nonferroelectric layers or inclusions are present in the ferroelectric matrix. This only holds for layers or inclusions which are thin or small enough not to be

screened by free charge carriers. The effect is similar to that of a hard magnetic circuit: if an air gap is introduced the effective hysteresis curve is sheared. Besides the shearing of the hysteresis curve the layers or inclusions modify the effective permittivity and the effective coercive field (14). The electric field inside the ferroelectric E_2 (in contrast to the electric field in the film or in the inclusions) has been calculated to be

$$E_2 = \left(1 - \frac{c(\epsilon_2 - \epsilon_1)}{B}\right) E_0 + \frac{-cP_2}{\epsilon_0 B} \quad [1]$$

Here E_0 is the field applied from outside, P_2 is the polarization of the ferroelectric (subscript 2), ϵ_2 and ϵ_1 are the permittivities of the ferroelectric (subscript 2) and of the layer or inclusion (subscript 1), and c is volume concentration of the layer or inclusion phase. For a thin film we have to use $B = B_{\text{film}} = \epsilon_1 + c(\epsilon_2 - \epsilon_1)$ and if the second phase consists of spherical inclusions we have to use instead $B = B_{\text{sph.incl.}} = 2\epsilon_2 + \epsilon_1 + c(\epsilon_2 - \epsilon_1)$. With the help of eq. [1] we can construct the hysteresis curve which would be measured in this ferroelectric containing a nonferroelectric second phase: the hysteresis loop of the pure ferroelectric is $P_2(E_2)$ (Fig. 6a). The scale of the field axis in this case is E_2 , that one we are seeking to construct is E_0 . The additional field term in the ferroelectric (second term in eq. [1]) $-cP_2/(\epsilon_0 B)$ has to be added to the hysteresis curve as shown in Fig. 6b. It has to be compensated by an external field with opposite sign. The result is a sheared hysteresis curve. Finally the scale of the field axis, which was E_2 and which should become E_0 has to be compressed or expanded by dividing through the term in front of E_0 in eq. [1]. This transformation modifies the apparent coercive field.

The effective dielectric constant varies for low concentrations c of the second phase with the following equation

$$\epsilon_{\text{mix}} = \epsilon_2 \left(1 - \frac{c(\epsilon_2 - \epsilon_1)a}{B}\right) \quad [2]$$

again with using B as given above for the film and spherical inclusion respectively and $a = 1$ if the second phase is a film and $a = 3$ if the second phase consists of spherical inclusions.

Another effect is the shift of the hysteresis curve along the E -axis which is called internal bias field. If the thin film or the inclusions are polar and nonferroelectric with no preferential orientation of their dipole moments there appears only shearing of the hysteresis curve as described above. If, however, the dipoles are oriented parallel to the polarization of the ferroelectric they create an additional electric field $\approx c_p P_1/(\epsilon_0 B)$ which is the internal bias field and which appears as a shifted hysteresis curve. c_p then is the volume concentration of those dipoles which are oriented in the direction of P_2 and which are not compensated by dipoles oriented in the opposite direction. P_1 is the polarization of the nonferroelectric material.

The hysteresis loop in fine grained ceramic very often has been found to be sheared. It has not yet been worked out, whether this shearing originates from second phase contributions as discussed above or whether it is an inherent property which is correlated to the grain size.

4. RELAXOR CERAMICS

In relaxor ceramics the microstructure is completely different from that discussed above; they contain no domains of the conventional type (15). The ferroelectric micro regions in the paraelectric

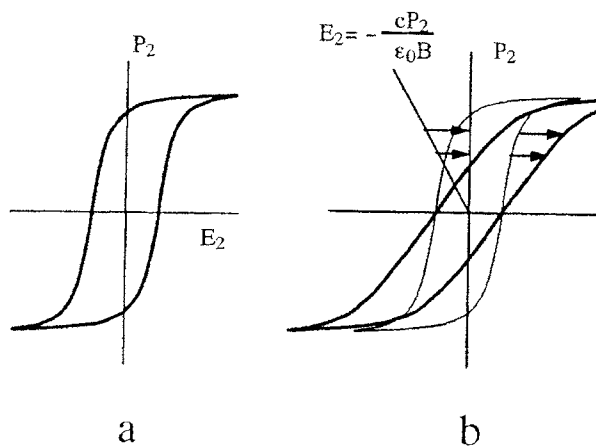


Fig. 6 a) Hysteresis loop of a pure ferroelectric, b) hysteresis loop of a ferroelectric containing nonferroelectric layers on inclusions. The axis of the electric field has to be scaled by the relation $E_0 = E_2/K$, where K is the factor in front of E_0 in eq.(1).

matrix sometimes are called microdomains. The above ideas about the microstructures can not be applied to relaxors. The strong dielectric dispersion caused by the polarized micro regions is not caused by the emission of acoustic waves because the effect is present at frequencies below the resonance frequencies of the sample.

When this material at low temperature is fully in the ferroelectric state it has a normal hysteresis curve. This curve gets sheared and the coercive field and the remanent polarization are reduced by increasing the temperature. This can be interpreted similar as above: the ferroelectric micro regions are embedded in the paraelectric material which corresponds to the second phase described above. The role is somewhat inverted: the ferroelectric inclusions now are very small and their concentration decreases with higher temperature and the second (nonferroelectric) phase is the matrix. The shearing effect, therefore, is coupled with a strong decrease of polarization.

5. THIN FILM CERAMICS

Some properties of thin film ceramics deviate clearly from conventional ceramics as discussed above. Some of these differences to conventional ceramics are caused by the gross structure: 1) the grains at least on one side of the film are intimately bound to the substrate, the 90° switching as observed in normal ceramics (16,17) therefore at least in this bound layer can not occur, 2) the orientation of the grains which are bound to the substrate in addition can have preferential directions e.g. (111) or (110) i.e. we find a texture in the thin film. 3) the grains can be as thick as the film, e.g. as columnar grains which constitute a mono grain layer. Accordingly the domain configuration can be different, the DW contribution to the permittivity and piezoelectricity can be different and the switching process can be different to the conventional ceramics.

In very thin films of BT no domains were found (18) and the permittivity was between 500 and 800 when the grain size is below 0.1μm. This is in agreement with normal ceramics as described above. With different preparation techniques the grain size of thin films of PZT can be controlled from coarse (near 0.5-1μm) to very fine (near 0.07-0.25μm). The large grains have a kind of banded domain structure and the smaller grains have a more laminar structure as is observed in coarse and in fine grained ceramics. Permittivities up to 1500 have been observed (18) in thin films of

PZT which indicates, that the DWs contribute substantially to the dielectric properties.

The coercive field in thin films has been observed to be 3 to 20 times larger than in bulk ceramics. The broad scattering in these factors implies that different effects may contribute to it and that the quality of the films also has some scatter. Let us examine first the role of a nonferroelectric thin layer between one electrode and the ferroelectric. Since the ferroelectric films are generally very thin a nonferroelectric film of a thickness of only one lattice constant can have a strong influence on the coercive field. If the ferroelectric and nonferroelectric have permittivities of $\epsilon_2 = 1000$ and $\epsilon_1 = 10$ and thicknesses 200Å and 4Å respectively we can derive from eq. [1] that the factor in front of E_0 is 1/3. The effective coercive field, therefore, by this layer appears to be three times larger than it would be without nonferroelectric layer. If the same concentration of the second phase would exist as spherical inclusions in the film instead of a layer the increase of the coercive field would be only one percent as can be deduced also from eq.[1]. Due to the bonding of a mono grain layer with the substrate as mentioned above, however, a higher coercive field can be expected.

Even the best thin films which were investigated have amorphous inclusions and other heterogeneities. This makes a comparison of thin film properties with the properties of normal ceramics difficult. ♦

REFERENCES

1. G. Arlt, « Twinning in ferroelectric and ferroelastic ceramics: stress relief ». J. Mat. Sci. **25**, 2655-2666 (1990).
2. G. Arlt, P. Sasko, « Domain configuration and equilibrium size of domains in BaTiO₃ ceramics. J. Appl. Phys. **51**, 4956-4960 (1980).
3. G. Arlt, H. Dederichs, R. Herbiel, « 90° Domain Wall Relaxation in Tetragonally Distorted Ferroelectric Ceramics ». Ferroelectrics, **74**, 37-53 (1987).
4. U. Robels, G. Arlt, « Domain wall clamping in ferroelectrics by orientation of defects », J. Appl. Phys. **73**, 3454-3460 (1993).
5. G. Arlt, N.A. Pertsev, « Force constant and effective mass of 90° domain walls in ferroelectric ceramics ». J. Appl. Phys. **70**, 2283-2289 (1991).
6. N.A. Pertsev, G. Arlt, « Internal stresses and elastic energy in ferroelectric and ferroelastic ceramics: calculation by the dislocation method ». Ferroelectrics **123**, 27-44 (1991).
7. N.A. Pertsev, G. Arlt, « Theory of the banded domain structure in coarse grained ferroelectric ceramics ». Ferroelectrics **132**, 27-40 (1992).
8. G. Arlt, D. Hennings, G. De With, « Dielectric properties of fine grained Barium Titanate ceramics ». J. Appl. Phys. **58**, 1619-1625 (1985).
9. Q.M. Zhang, H. Wang, N. Kim, L.E. Cross, « Direct evaluation of domain wall and intrinsic contributions to the dielectric and piezoelectric response and their temperature-dependence on Lead-Zirconate-Titanate ceramics ». J. Appl. Phys. **75**, 454-459 (1994).
10. G. Arlt, U. Böttger, S. Witte, « Dielectric dispersion of ferroelectric ceramics and single crystals at microwave frequencies ». Ann. Phys. **3**, 578-588 (1994).
11. W.R. Buessem, L.E. Cross, A.K. Goswami, « Phenomenological theory of high permittivity in fine grained Barium Titanate ». J. Am. Ceram. Soc. **49**, 33-36 (1966).
12. G.A. Samara, « Pressure and temperature dependences of the dielectric properties ». Phys. Rev. **151**, 378-386 (1966).
13. G.A. Rosetti, K.R. Udayakumar, M.J. Haun, E.L. Cross, « Thermodynamic theory of single crystal Lead titanate with consideration of elastic boundary condition ». J. Am. Ceram. Soc. **73**, 3334-3338 (1990).
14. U. Robels, J.H. Calderwood, G. Arlt, « Shift and deformation of the hysteresis curve of ferroelectrics by defects: an electrostatic model ». J. Appl. Phys. **77**, 4002-4008 (1995).
15. L.E. Cross, « Relaxor Ferroelectrics ». Ferroelectrics **76**, 241-267 (1987).
16. Sp. Li, A.S. Bhalla, R.E. Newnham, L.E. Cross, Cy. Huang, « 90-degree domain reversal in Pb(Zr_xTi_{1-x})O₃ ceramics ». J. of Mat. Sciences **29**, 1290-1294 (1994).
17. U. Robels, A. Mellage, G. Arlt, « Aging after polarization reversal in acceptor doped ferroelectrics », Proceedings of Electroceramics IV, 4th Intern. Conf. on Electronic Ceramics and Applications, Aachen 5.9-7.9.94, Vol. I, 373-376 (1994).
18. M. Klee, A. de Veirman, P. van de Weijer, U. Mackens, H. van Hal, « Analytical study of the growth of polycrystalline Titanate thin films ». Philips J. of Res. **47**, 263-285 (1993).