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Domain-related problems of ferroelectric ceramics

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Abstract

Ferroelectric ceramics represent the widest application area of ferroelectric materials, for their electromechanical, dielectric and optical properties. In all cases domain-related aspects play a decisive role, whether positive or negative. Despite effective research efforts numerous essential problems remain unsolved. Here first an overview of them is shortly specified, related to static and dynamic aspects of domain systems in ceramic samples. Two issues are then addressed in more detail: the potential role of the “soft” energy in the poling process and the possibility to depole a ceramic sample in different ways, leading to domain symmetries of different macroscopic properties.

Keywords: C. Ferroelectric properties; C. Piezoelectric properties; D. PZT; D. $BaTiO_3$; Ceramics

1. Introduction

Although in the two recent decades thin films and single crystals have essentially increased their position in technical applications of ferroelectrics, ceramics plays still the most important role. Poling ceramic samples was in fact the first domain-related application. While here domains play a positive role, in some practical functions they result in negative aspects because of spatial distribution of tensorial characteristics. Compared to crystals or films domain properties are much more complicated in ceramics because of elaborate aspects such as distribution of permittivity and polarization axes, elastic and dielectric boundary conditions of grains and internal properties of grain boundaries. Therefore, despite of very essential and high level research many problems are still to a considerable extent open. Domain-related properties are discussed in many excellent available review papers on ceramics (see, e.g. [1–8]; however, sometimes measurable properties are addressed with more attention than the genuine domain aspects. Some of the latter we shortly specify in the following section. Then two items, role of the soft energy and depoling a ceramic sample are discussed in more detail.

2. Selected unsolved and interesting problems

Let us first consider the static case of a ceramic sample which can be ideally poled, partially poled or unpoled in three different ways (see below).

What are the macroscopic properties of averaged multidomain systems, including permittivity (ε), piezoelectricity (d) or elastic (s) characteristics? They are influenced by a number of domain-related aspects: orientation of crystallographic axes in individual grains; domain patterns in grains; boundary conditions of grains; response of domain walls; etc. Several theoretical approaches are possible for understanding macroscopic properties, such as: (a) averaging single crystal values assuming specific distribution of P_S axes and specific field-dependence of P_S distribution. Results of such theories [9] are still the mostly accepted ones. (b) Averaging single crystal values assuming specific forms of crystallites, e.g. spherical [10]. (c) Modelling approach to illustrate ε, d and s coefficients of both unpoled and poled samples, assuming a specific geometry of domain pattern in crystallites [11].

It is in fact the modelling approach which can specify the complicated situation of field distribution in ferroelastic domain systems and its consequence in macroscopic properties [12]. And it can be assumed that using the new modelling programs which are developing so fast the level of

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understanding properties of ceramic samples will highly increase.

There is another very interesting open issue: understanding macroscopic properties of specific domain patterns. Many are known, such as Forsbergh pattern [13] which appears both in crystals and grains and can be efficiently produced. Or Arlt patterns [14] specific for ceramics. Here even the symmetry aspects and tensorial properties are unknown and should be specified in the first place.

The problem of static domain patterns becomes even more complicated when phase coexistence within grains [15] would be taken into account.

Macroscopic properties related to domain dynamics are little understood. In single crystals, the basic ritual of the switching process (nucleation, domain growth, domain coalescence) is clear when non-ferroelastic 180° domains are considered. It is based on data obtained by applied pulse fields: the P_S reversal proceeds at $E =$ constant. This kind of switching studies is traditional even for crystals with more complicated domain patterns. For ceramics very few such data [16] are available although the condition $\bar{E} =$ const might lead to more involved discussions of dynamic domain phenomena.

It is known that for single crystals even when only 180° switching is possible, shapes of $P(E)$ hysteresis curves strongly differ; those of $BaTiO_3$ and TGS crystals are a good example. Defects may play here a very significant [17] role and the problem has not been yet fully addressed. Let us mention the $LiNbO_3$ case. For several decades a $P(E)$ hysteresis loop in crystals of this material could not be realized. Because of it some scientists even disagreed to call it a ferroelectric, although its species was known to be $m\bar{3}m$–Pd–$3m$ and often static domains were observed. Only much later [18] it was found that in stoichiometric crystals E_C is drastically decreased and $P(E)$ loops become authentic. This is one of the examples how big role the defects can play and it is of course expectable for ceramic samples as well.

The shapes of $P(E)$ loops of ceramics are very diverse although they are similar to those of crystals. This can be expected considering the complicated spatial distribution of the switching process and the role of coexistence of non-ferroelastic and ferroelastic switching. One of the interesting points is to compare the basic characteristic of the loop, coercive field. Considering the complicated situation of a ceramic sample due to the disorientation of grains and existence of grain boundaries one would expect that the value of E_C measured at normal T and ω conditions significantly exceeds that of single crystals.

For $BaTiO_3$ and TGS crystals the well known representative values are in the range $E_C = 100$–500 V/cm at T_{room} and for $f = 50$ Hz. For $BaTiO_3$ ceramics a number of data which are usually not exactly specified demonstrate E_C between 1 and 5 kV/cm at T_{room}. However, it depends on many aspects-additives, grain size, field amplitude, and in addition also the ageing effect. "Soft" $BaTiO_3$ ceramics can be prepared by specific additives [19] with a square loop and $E_C = 370$ V/cm, i.e. it is fully comparable with the crystal value.

For typical PZT ceramics close to the morphotropic phase boundary E_C lies between 4 and 6 kV/cm. It was for this material that the concept of "soft" and "hard" ceramics was introduced [20] when additives were specified which strongly influence the E_C value, typically from 4 to 15 kV/cm. Few theoretical discussions have been offered for understanding these properties. Let us just mention one interesting approach [21] in which the soft and hard aspects are explained by local electric fields arising from accumulation of impurity atoms or charged point defects.

One interesting aspect of ac switching is its frequency dependence. For TGS crystals, with f increasing from 50 to 10^5 Hz, E_C expands by a factor of 4. In fact for ceramic materials, usually the published E_C data are not specified by frequency; it is usually between 10 and 100 Hz. For PLZT 6.25/56/44 ceramics [22], with f increasing from 10^{-3} to 10^2 Hz, E_C grows from 10 to 13 kV/cm, i.e. by a factor of just 1.3. For a better comparison data for crystals and ceramics in the same frequency region would be needed.

Switching processes in ceramic are very complicated. And it is fair to mention that even for single crystals the E_C value has not been satisfactorily explained. The problem of unrealistically large nucleation energy offered by available theories is well known and has not been yet solved. In fact it was shown [23] that perfect explanation of hysteresis loops in crystals can be reached even without nucleation, when switching is assumed to start with residual domains. It appears probable that in ceramics nucleation plays no role. But in ceramics dynamic domain problems are difficult to solve theoretically-because of the complicating aspects such as spatial distribution of permittivity and polarization axes, elastic boundary conditions of individual grains or internal properties of grain boundaries. Yet some suggestive theoretical papers are available. It was shown [24] that for an individual grain coercive field is much smaller than the switching field. The factor contributing to this difference is that the grain gives rise to an internal field which assists the applied field in activating the switching in other grains.

Modelling approaches have become promising methods to understand the mentioned involved aspects in ceramics resulting in complexity of spatial distribution of the switching process. In fact modelling methods have been applied to dynamic domain properties more actively than to static properties; let's mention here just three papers as examples [25–27]. However, we suggest that modelling as well as calculations should be applied first for simplified domain geometries.

In addition to average polarization, hysteretic behaviour of many other macroscopic properties is represented by classical or double hysteresis loops. When the $P(E)$ curve is difficult to measure, $\varepsilon(E)$ is useful to specify the E_C values. No theory of ε as a function of the domain geometries seems to be available; the problem was addressed by modelling [11] and is still generally open.

Very interesting hysteretic behaviour was observed in ceramic samples for some components of the piezoelectric coefficient. The $d(E)$ hysteresis loop has been often measured for both crystalline and ceramic samples. There are two interesting aspects. First, it is often assumed that for a ceramic sample $\bar{d} = 0$ when $\bar{P} = 0$. However, it can be shown (see also Section 4) that when hysteresis loop is passed, the field corresponding to $\bar{d} = 0$ is not the classical E_C field; or in other words that $\bar{d} \neq 0$ when $\bar{P} = 0$. Second, it was repeatedly observed that the $d_{31}(E)$ and $d_{33}(E)$ loops have sometimes a negative slope $\mathrm{d}d/\mathrm{d}E$ in the high field region. Only recently [28] the first interpretation was offered for single crystals. It is based on the fact that the permittivity of a polydomain crystal is the sum of two contributions: χ_{lat} of the crystal lattice and χ_{wall} due to displacements of domain walls. The average polarization P of a polydomain sample can be presented as the sum of spontaneous and lattice contributions

$$P = \bar{P}_{\mathrm{Sav}} + P_{\mathrm{lat}} \equiv P_{\mathrm{S}}(2\alpha - 1) + \chi_{\mathrm{lat}} E \tag{1}$$

where α is the volume fraction of the P_+-state in the domain pattern. These simple and fully acceptable assumptions lead to the following result for the piezoelectric coefficient

$$d = 2Q(P\chi_{\mathrm{lat}} + P_{\mathrm{lat}}\chi_{\mathrm{wall}}) = d_0 + \Delta d \tag{2}$$

The field dependences of d_0 and Δd contributions are significantly different and indeed their sum leads to the negative slope of the $d(E)$ loop at high fields. In addition, the theory explains the fact that the $d(E)$ curves for increasing and decreasing (e.g. positive) field cross each other.

An analysis of present understanding of domain phenomena in ceramics leads to a number of suggestions. Let us mention just one: could experiments be performed which would clarify the spatial distribution of the switching process in a ceramic sample?

3. Poling a ceramic sample: role of the soft energy

In ferroelectric materials, applied electric field of a general orientation leads to energetic preference of one of the domain states. In this selection the energy—(EP_{S}) is usually taken into account. In a single crystal, it prefers the domain states with the P_{S} vectors making the smallest angle with the homogeneous applied field, leading to classical ferroelectric switching. Traditionally, in ceramic samples maximum average polarization $\bar{P}$ is required, when due to poling all grains become single domain and their P_{S} vectors are as close as possible to the averaged applied field.

Since the symmetries of tensors representing spontaneous strain and dielectric permittivity ε_{ij} are the same, in any ferroelastic dielectric material domain states differ also in the permittivity tensor. Therefore, in applied electric field, ferroelastic domain states differ in the "soft" dielectric energy $\varepsilon_{ij}E_iE_j$. Thus, any ferroelastic material can exhibit such ferrobielectric [29] properties. From the practical point of view, the issue is interesting for ceramic materials. It was shown [30] that the soft energy can lead to qualitatively new aspects of poling and play an essential role in ferroelectric ceramics.

It is useful first to analyse the case of a ferroelectric and ferroelastic single crystal to which field of a general orientation is applied. In applied electric field, domain states differ in the "hard" ferroelectric energy—(EP_{S}) while ferroelastic domain states differ in the "soft" dielectric energy $\varepsilon_{ij}E_iE_j$. Thus, when no stress is applied, the following form of the free energy density of the domain state α is relevant:

$$F^{(\alpha)} = F_0 - \tfrac{1}{2}\varepsilon_{ij}^{(\alpha)} E_i E_j - E_i P_{\mathrm{S}i}^{(\alpha)} \tag{3}$$

Consequently, switching can be in principle induced also by the application of field even in a non-ferroelectric ferroelastic compound with $P_{\mathrm{S}i}^{(\alpha)} = 0$, due to soft energy and permittivity anisotropy.

Here as a representative example we consider the species $m\bar{3}m$–$4mm$ which represents many classical ceramic materials like $\mathrm{BaTiO_3}$ or PZT compounds on the $\mathrm{PbTiO_3}$ side. Six states $\alpha = 1, \ldots, 6$ can appear in this species, with orientation of P_{S} along the crystal axes. When electric field is applied to a sample, in each grain spontaneous polarization arises along one of the crystallographic axes. The choice of the axis and the sign of P_{S} correspond to the demand that the energy (Eq. (3)) is minimum. It turns out [30] that when the soft energy is taken into account, the choice of the axis along which P_{S} should arise depends not only on the angle ϑ between the E and P_{S} vectors but also on the field magnitude. All angles ϑ resulting in P_{S} along a given axis are represented by one or even more intervals. A detailed discussion shows that the character of these intervals substantially differs for "weak", "average" or "strong" fields, related to the field E^* depending on permittivity anisotropy and defined by $E^* = 2P_{\mathrm{S}}/\Delta\varepsilon$ where $\Delta\varepsilon \equiv \varepsilon_{\perp} - \varepsilon_{\parallel}$. We assume $\Delta\varepsilon > 0$ which is the case of tetragonal ferroelectric perovskites.

In the following text the results obtained for a crystal are applied to ceramics [30]. The average value of polarization in a ceramic sample is given by

$$P_{\mathrm{av}} = \langle P_{\mathrm{S}} \cos\theta \rangle = \left(\frac{4P_{\mathrm{S}}}{\pi}\right) \sum_i \int_{\theta_i}^{\theta_i + \Delta\theta_i} \cos\theta \,\mathrm{d}\theta \tag{4}$$

where $0 < \theta < \pi$.

Here ϑ specifies the angle between the applied field E and the z-axis along which the resulting polarization is expected; the interval $(\vartheta_i, \vartheta_i + \Delta\vartheta_i)$ $(i = 1, 2, 3)$ represents the interval of angles for which the state of P_{S} along the positive direction of z-axis is realized.

For weak fields fulfilling the condition $E < E^*/\sqrt{2}$ the result is $P_{\mathrm{av}} = (4/\pi\sqrt{2})P_{\mathrm{S}}$. Thus, the conclusion is the same as if the soft energy term in Eq. (3) were not taken into account and the P_{av} value does not depend on the field magnitude. P_{S} points along the axis which makes the

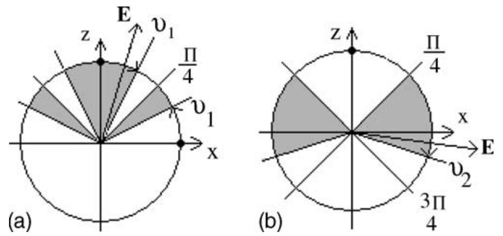

Fig. 1. Regions of field directions (represented by dark areas) for which P_S occurs along the z-axis of a single crystal. (a) “Intermediate field” $E^*/2 < E < E^*$. (b) “Strong field” $E > E^*$.

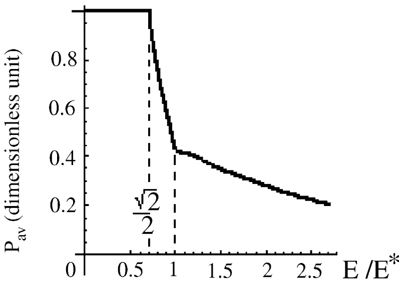

Fig. 2. The case of ceramics. Average value P_{av} of polarization along the direction of applied field depending on the field magnitude. P_{av} is represented by the dimensionless quantity $P_{av}/\pi 2\sqrt{2} P_S$. For $E > E^*/\sqrt{2}$, P_{av} decreases with increasing field.

smallest angle with the field direction; the angle is in the (0, $\pi/4$) interval. This is the generally assumed situation.

A more complicated case occurs for the “average” fields region which is limited from both sides, fulfilling the condition $E^*/\sqrt{2} < E < E^*$. Now polarization results along the axis which makes the angle with the applied field within the interval (0, ϑ_1) or interval ($\pi/4$, $\pi/2-\vartheta_1$) (Fig. 1a). Here ϑ_1 is inside the (0, $\pi/4$) interval and is defined by the relation $\sin(\vartheta_1 + \pi/4) = 2E^*/E$ (Fig. 1a). In this region

$$P_{av} = \left(\frac{4}{\pi\sqrt{2}}\right) P_S \left(\frac{\sqrt{2}E^*}{E} - 1\right) \tag{5}$$

An interesting situation occurs also for higher fields $E > E^*/\sqrt{2}$ when to polarization pointed along a certain crystallographic axis contribute even fields of directions whose components along spontaneous polarization are negative. Now the interval of angles ϑ, which result in spontaneous polarization along the crystal z-axis is ($\pi/4$, ϑ_3), where ϑ_3 is within the ($\pi/4$, $3\pi/4$) interval (Fig. 1b) and satisfies the condition sin ($\vartheta_3 + \pi/4$) = $2E^*/E$. We obtain

$$P_{av} = \left(\frac{4}{\pi\sqrt{2}}\right) P_S \left[\frac{1}{\sqrt{2}}\frac{E^*}{E_{xy}} + \sqrt{1 - \frac{1}{2}\left(\frac{E^*}{E}\right)^2} - 1\right] \tag{6}$$

so that now polarization decreases with increasing field. This fact is the specific consequence of taking into account the soft energy.

The three field regions resulting in different $P_{av}(E)$ dependences are shown in Fig. 2. It is an interesting result that applying a field which exceeds a certain value is non-effective since the resulting polarization decreases and would approach zero for $E \to \infty$. New experiments should be realized to verify these conclusions. Dielectric anisotropy of the investigated materials should be known.

To show the principles of the discussed problem, here we have demonstrated the simplified case of a two-dimensional sample; P_S can direct along the axis z or x. In is shown in [30] how the 3D case can be solved.

Let us mention two additional aspects. First, because of the soft energy role, cooling in applied ac field could also result in redistribution of the P_S distribution. Second, if the material is non-ferroelectric, only the soft energy plays the role and the number of ferrobielectric domain states equals the number of ferroelastic states. Thus, the soft energy role could be checked experimentally in many ceramic materials, e.g. in $SrTiO_3$.

4. Depoling a ceramic sample: potential macroscopic properties

For applications, the poling process of ceramic samples was the first domain-related application aspect and is still widely used. It was observed already in the first period of ceramic applications that often the poled samples degrade their piezoelectric properties with time; this is traditionally elucidated by the spontaneous depoling effect, usually referred to as the ageing process. One of its main sources is the decrease of elastic energy due to proper domain reorientation. By “depoling” is designed the decrease of the average polarization. In principle, the ageing effect approaches the $\bar{P} = 0$ state. But in fact the process how $\bar{P} = 0$ is reached

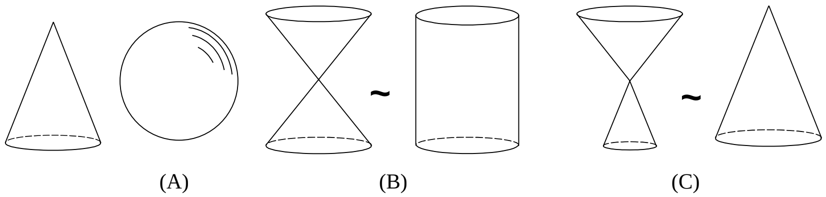

Fig. 3. Three ways of depoling a ceramic sample. (A) Thermal depoling: classical method by heating above T_{TR}. (B) Depoling by reduced switching: the amplitude of applied field is decreased to zero at constant temperature in the ferroelectric phase. (C) Depoling by stopped switching: the switching process in applied low frequency ac field is discontinued when $\bar{P} = 0$.

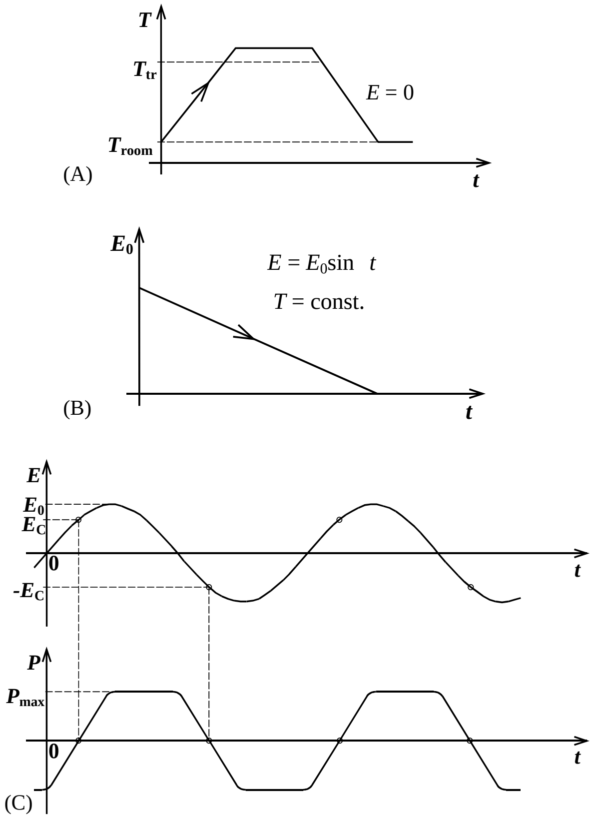

Fig. 4. Representation of symmetries of a poled ceramic sample (P) and of samples depoled in the three ways (A–C). In cases B and C on the left side the geometry of P_S distributions is represented, on the right side the classical representation of the achieved symmetry is shown.

can be realized in three ways [31], depending on the time dependence of the applied electric field, if any. These procedures result in domain states of different symmetries and tensorial macroscopic properties.

The classical way is thermal depoling achieved by heating into the paraelectric phase and subsequent cooling. It results in the $\infty\infty m$ symmetry with zero piezoelectricity (A in Figs. 3 and 4). A different symmetry can be expected when depoling by reduced switching is realized. A low frequency ac field is applied whose amplitude is reduced with time (B in Fig. 3). Then the arrangement of P_S directions results in zero value of $\bar{P}$ but does not return to a homogeneous distribution of spherical symmetry; we can expect the vector distribution corresponding to a double-cone of symmetry ∞/mm (B in Fig. 4). Tensorial properties of a sample depoled in this way do not seem to have been investigated. Let us note that tensorial properties in the samples depolarized by the two mentioned ways would differ [32], by symmetry; e.g. in tensors of symmetries V^2 (thermoelectrical coeffients), $[V^2]$ (permittivity), $\varepsilon V[V^2]$ (electrogyration), $V[V^3]$ (higher order permittivity) and $[[V^2]^2]$ (elastic coefficient).

In the third way depoling by stopped switching at $\bar{P} = 0$ can be realized. The $P(E)$ hysteresis loop is slowly passed (C in Fig. 3). It can be expected that at the $\bar{P} = 0$ state the domain geometry will significantly differ from those reached by the above mentioned methods. Evidently, now the P_S distribution around the original poling direction can be narrower than that around the opposite direction (C in Fig. 4). Thus, the ∞mm symmetry would still be kept although in the arrived state $\bar{P} = 0$ and the sample could still exhibit piezoelectric properties. A detailed discussion of this situation was offered by Luchaninov and Shil'nikov [33].

Investigations of ceramic samples depoled in the three mentioned ways may offer interesting information on poling processes and new application aspects.

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