

Exploring the electromechanical response and electric field-induced dielectric anomalies in PMN–PT electroceramics

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Electromechanical and dielectric properties of PMN–PT ferroelectric ceramics are investigated. In particular, dielectric response studies focus on the investigation of the influence of the DC applied electric field on the dielectric permittivity as a function of temperature and frequency. Results reveal an electric field driven dielectric anomaly in the dielectric permittivity curves, $\epsilon(E)$, which in turn prevails in the whole ferroelectric phase region and continuously vanishes for temperatures near the paraelectric-ferroelectric phase transition temperature. A schematic model for the domains dynamics of the studied material is proposed taking into account the simultaneous contribution of both 90° and 180° domains walls.

Keywords: Ferroelectrics; PMN–PT; domain-walls; dielectric response; electric field.

1. Introduction

The lead magnesium niobate-lead titanate system, $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$, (hereinafter referred to as PMN–PT), has been probably one of the most studied ferroelectric materials during the last two decades because of its excellent physical properties, which makes it a promissory material for practical applications.¹ The PMN–PT solid solution crystallizes in a complex perovskite structure, being a combination of the relaxor ferroelectric (PMN), with a pseudocubic rhombohedral symmetry, and a classical ferroelectric system (PT), with tetragonal symmetry.² Therefore, for compositions $x < 0.20$, the PMN–PT system displays a relaxor behavior with a diffuse paraelectric-ferroelectric phase transition, whereas the system shows more enhanced ferroelectric behavior for higher compositions (i.e., by increasing the PT content). As a result of the phases mixture within certain composition range in the phase diagram, the well-known morphotropic phase boundary (MPB) is formed, whose nature is still unclear upto today.^{2,3} It is believed that the MPB region is in the compositional range of $x = 0.30\text{--}0.35$ at room temperature. Since the structure and properties of the

PMN–PT solid solution are closely related to the composition, multifunctional materials with enhanced ferroelectric, pyroelectric and piezoelectric properties can be obtained by controlling the compositional stoichiometry.^{4–6} It is, in fact, in the MPB region where the highest piezoelectric performance is found, which has been ascribed to a polarization rotation mechanism along a specific direction, thus allowing to induce a relatively large strain by applying an external electric field.⁴

The structural, dielectric and piezoelectric properties of the PMN–PT system have been extensively investigated by many researchers, showing to be strongly dependent not only on the composition but also on the applied electric field. The observed behaviors have been mostly ascribed to their complex domain structures. Therefore, from the technological point of view, a better understanding of the system performance under external driving fields seems to be essential for the development of new solid-state devices operating under very high electric field level conditions. Although several theoretical models have been proposed in the literature,^{7,8} which try to explain the nature of the observed anomalies under high electric field levels, the real physical origin of the observed

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behavior is still not fully clarified up today, thus remaining a subject of extensive researches and discussions. In this context, the present work aims the investigation of the dielectric properties of the PMN–PT ferroelectric ceramic system with composition at MPB ($x = 0.35$) in a wide temperature and frequency range, by considering the influence of an external DC driving field. The effect of the DC electric field for temperatures below the paraelectric–ferroelectric phase transition temperature, which have not been extensively studied in the literature, is investigated.

2. Experimental Procedure

$0.65[\text{Pb}(\text{Mg}_{1/2}\text{Nb}_{2/3})]\text{O}_3-0.35\text{PbTiO}_3$ (PMN–35PT) ceramics were synthesized from the conventional solid-state reaction sintering method, as previously reported.⁹ Room temperature ferroelectric hysteresis loops (P – E curves) were performed at several frequencies, using a modified Sawyer–Tower circuit. The dielectric properties were investigated by considering an applied DC electric field with variable amplitude (E_{DC}), superimposed on the small signal AC electric field. A Keithley 237 high-voltage source-measure unit was used to obtain the dielectric permittivity (real and imaginary components) as a function of the electric field, measured in isothermal regime at 300, 370 and 400 K. In order to obtain the dielectric measurements for high electric fields levels, the experimental setup was protected by using a blocking circuit as previously reported.¹⁰

Results on the structural properties (not shown here) obtained from X-ray diffraction (XRD) revealed a pyrochlore phase free perovskite structure with tetragonal $P4mm$ symmetry and without additional residual phases.⁹ A homogeneous grain-size distribution and morphology, with an average grain-size around $7.4 \mu\text{m}$, was revealed by scanning electronic microscopy (SEM) for the studied samples, as shown in a previous report.⁹

3. Results and Discussion

Figure 1 shows the electric field dependence of the polarization (typical hysteresis loops) for the studied PMN–35PT composition, obtained at room temperature and several frequencies. The ferroelectric properties revealed a square-like P – E loop, with a remnant polarization (P_R) ranging from $24.4 \mu\text{C}/\text{cm}^2$ to $21.2 \mu\text{C}/\text{cm}^2$, with the increase of the frequency from 200 mHz up to 2 Hz, respectively.

This slight variation in P_R could be associated to additional conduction mechanisms, which affect the macroscopic polarization.¹¹ The obtained values for the remnant polarization are in the order to those reported at room temperature for others investigated classical ferroelectrics with excellent piezoelectric properties (such as the PZT and PZT-PT families),^{12,13} and reveal to be higher than the obtained for other ferroelectric systems commonly used for practical applications.^{14,15} On the other hand, no relevant change was observed for the coercive field, with the increase of the frequency,

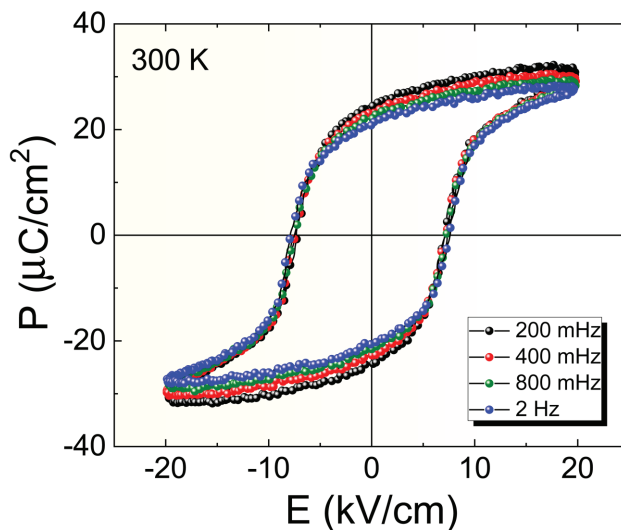


Fig. 1. Ferroelectric hysteresis loops of the studied PMN–35PT ceramic system, obtained at room temperature and several frequencies.

revealing an average value around 7.2 kV/cm. From the fundamental point of view, a better analysis of the intrinsic ferroelectric characteristics can be carried out by considering the electromechanical response, which might be performed by the characterization of the ferroelectric properties from the strain induced by the applied electric field and, in fact, offers a more quantitative information on the domains motions and switching.^{16,17} In this work, the electromechanical response has been then obtained by using a Solartron LVDT AX/0.5/S displacement transducer, coupled to the Sawyer–Tower circuit used for the ferroelectric measurements.

Figure 2 shows the electric field dependence of the strain (s) for the studied sample, at different frequencies, which

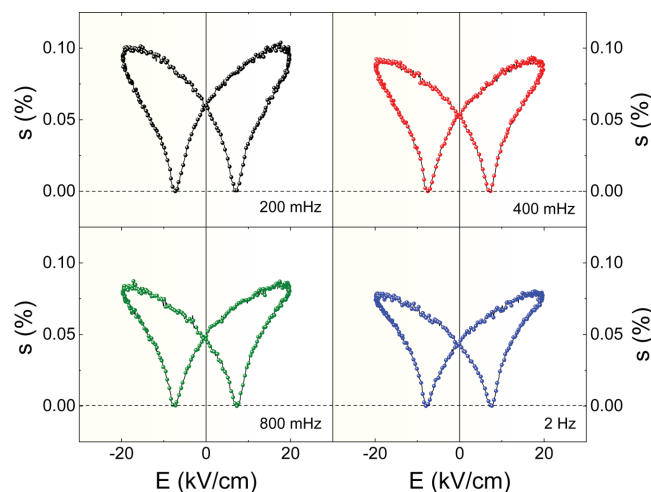


Fig. 2. Strain–electric field (s – E) hysteresis loop of the studied PMN–35PT ceramic system, at several frequencies.

indeed resembles a butterfly-like shaped hysteresis loop. This result can be explained by the normal converse piezoelectric effect, as well as the switching and/or motion of the ferroelectric domain walls, and reveals the excellent piezoelectric characteristics for the studied composition.

According to the converse piezoelectric effect, for a nearly constant piezoelectric coefficient the applied electric field produces a linear strain. When the electric field is parallel to the polarization directions, the strain increases with the increase of the electric field, reaching the maximum strain value at the maximum applied electric field. However, when a ferroelectric material is subjected to an electric field, the polarization switching leads to an electromechanical hysteresis loop (as shown in Fig. 2) because of the domain walls motion and switching. The loops clearly show a piezoelectric response as well as the polarization switching under a bipolar electric field. As observed, the sign of strain is strongly dependent on the relative directions of the polarization and the electric field. When the field and polarization are parallel, for instance, the lattice expands and a positive strain is

obtained, whereas a negative strain is observed for an anti-parallel direction between the polarization and electric field. As a consequence of the polarization switching, a sudden variation in the strain axis occurs, being the electromechanical response a reversible process. In practice, because of the contribution of a certain number of non-180° domains, the dynamics of the domain walls may involve a significant change in dimensions of the sample, in addition to the “pure” piezoelectric response of the material within each domain. So that, the obtained $s-E$ response could be, in most of the cases, slightly different to the expected theoretical one.¹⁶ The longitudinal piezoelectric coefficient (d_{33}) can be estimated from the slope of linear regions in the $s-E$ hysteresis loop, the values of which revealed to be in the range of 235–193 pC/N, as the frequency increases from 200 mHz up to 2 Hz, respectively. The obtained values for the d_{33} parameter are in the order of those reported in the literature for the same composition, obtained by direct piezoelectric measurements.¹⁸

Figure 3 shows the variation of the real (ϵ') and imaginary (ϵ'') dielectric permittivity under the applied DC bias electric

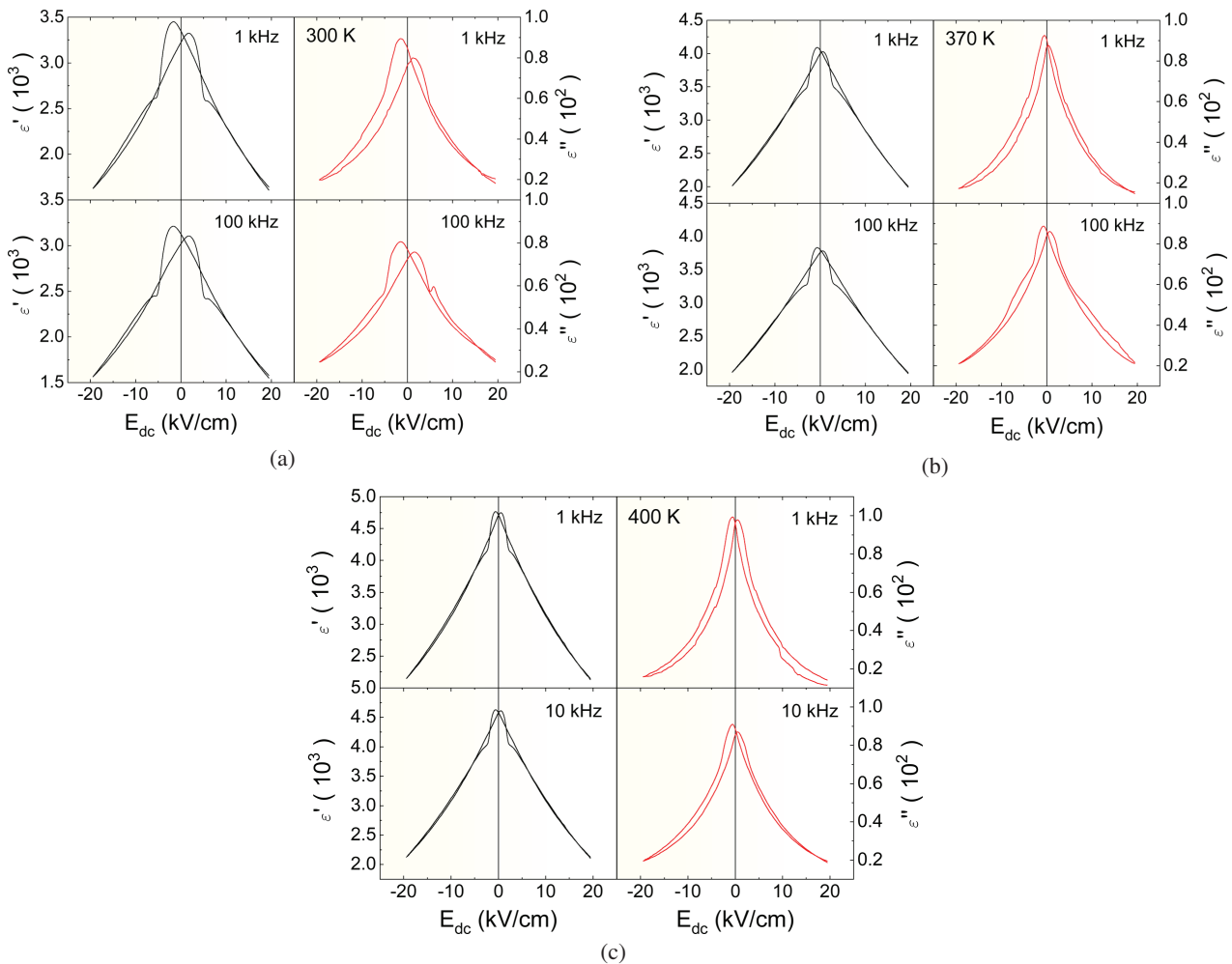


Fig. 3. Electric field (DC bias) dependence of the real (left) and imaginary (right) dielectric permittivity ($\epsilon-E$ curves) for the PMN-35PT ceramic system, at three different temperatures, in the ferroelectric region: (a) 300 K, (b) 370 K and (c) 400 K.

fields (ϵ - E curves), for three different temperatures below the paraelectric-ferroelectric phase transition temperature ($T_m \sim 447$ K, at 1 kHz).¹⁰ It is important to point out that, the investigation of the influence of the external electric field on the dielectric properties have been scarcely reported in the literature for PMN-PT ceramics, for compositions close to the MPB. Indeed, most of the reported works in the literature have been focused mainly for single crystals and/or thin films^{19,20} and for ceramics relaxor compositions ($x \leq 0.32$).²¹ So that, the obtained results in the present work for the PMN-35PT composition were not reported before. As can be observed in Fig. 3, the field dependence of ϵ' and ϵ'' evidences two dielectric permittivity maxima, showing “butterfly-like” hysteresis loops, which in turn vanishes as the temperature increases close to T_m (~ 447 K). This behavior is typical of ferroelectric materials owing to the domain-wall motion during the switching of polarization. Each peak was dependent of the electric field path way and evidenced the electric dipoles switching (electric field dipole orientation and reversing). In turn, the dielectric permittivity maxima correspond to the points where the dipoles have a higher mobility to contribute for the measured macroscopic dielectric permittivity. The maximum in the DC electric field dependence of the dielectric permittivity appears in the vicinity of the coercive field (E_C), for the P - E hysteresis curves, when most of the domains switch and the material appears to be dielectrically very “soft”.

With the increase of the electric field, the dipoles begin to be aligned with the electric field direction and then the mobility is decreased, resulting in the decrease of the measured macroscopic dielectric permittivity. However, by examining in detail in Figs. 3(a)–3(c), it can be noticed the presence of an intermediate secondary dielectric peak (shown as a discrete symmetrical peak), which appears around ± 6 kV/cm. Indeed, as observed, at room temperature the higher dielectric permittivity peaks showed to be asymmetric in the DC electric field pattern. These behaviors, which in turn decrease with the increase of the temperature, were not ever reported like in this work for the PMN-PT system. It is interesting to point out that, different to the results obtained for ferroelectric thin films,^{22–24} similar behaviors have been previously observed in ferroelectric materials,^{25–27} which indeed revealed two different peaks in the ϵ - E curves. This behavior has been explained by different coercive fields related to 180° and non- 180° domains,²² so that the absence of a second peak in ϵ - E curves in most of thin films could thus be an indication of limited switching of non- 180° domain-walls. It is timely pointing out that, because of the contribution of conductive processes, which directly reflect in the dielectric losses, the expected shoulders related to the domain-wall dynamics, seem to be not evident in the imaginary dielectric permittivity.

In order to explain the observed anomalies in polycrystals, several theoretical models, based on the domain reversal contribution in perovskite-type structure ferroelectrics (such as PZT and BaTiO₃), were proposed earlier in the

literature.^{25,26,28} In this way, the effect of the “domain clamping” on ceramics in the tetragonal and/or orthorhombic state, which follows from the piezoelectric deformations of the domains, has been considered. However, the identification of the nature of the observed anomalies has not been fully clarified nowadays, although similar results found in some other ferroelectric systems. Nevertheless, in order to clearly understand the observed features in the PMN-35PT ceramics a tentative model of polarization, which takes into account the reversal of 180° domains and rotation of 90° domains,²⁸ can be used. This model considers the contribution of 180° reversal and 90° rotation separately. When the material (i.e., the studied PMN-35PT system) is in the “virgin state”, that to say in a non-poled configuration, all the polarization directions are equivalent and the macroscopic polarization is zero. Nevertheless, by applying a relatively strong electric field this configuration has been modified and the ceramics are now in the poled state. In this way, most of the ferroelectric crystallites are closely oriented parallel to the applied electric field direction. In fact, this new configuration is directly related to the ferroelectric state of the studied material.^{29,30}

On the other hand, it is well known that there exist several types of domains in perovskite-type ferroelectrics: 180° and 90° ferroelectric domains in the tetragonal phase, and 180° , 109° and 71° domains in the rhombohedral one.^{27,30,31} In this way, regarding the obtained results in Fig. 3 for the studied PMN-35PT ceramic system, the reversal of 180° domain and the rotation of 90° domain could play their respective role in changing the physical parameters under the DC electric field. For instance, the parallel orientations produced by 180° reversals remove the clamping effects, and 90° reorientations enhance the contributions of anisotropic effects to the parameters of the ceramic samples. In order to better understand the DC electric field dependence, the results will be analyzed in terms of the domains reorientation promoted by the DC electric field. The schematic representation of Fig. 4 (with alphabetic symbols), which describes the dielectric permittivity of the PMN-35PT sample obtained at room temperature, has been used as an example of the observed behavior.

With the increase of the electric field from A to E, the corresponding peaks at the B and D points are observed. At the same time, with the further decrease of the electric field from E to A two additional peaks are also observed at F and H points. A comparison of Fig. 4 with Figs. 3(b)–3(c) reveals that, with the increase of the temperature from room temperature up to 400 K, the anomaly peaks seem to be more symmetric. An interpretation of the observed features in the dielectric response for the studied PMN-35PT ferroelectric ceramic system can be conducted according to the phenomenological model reported by Bar-Chaim *et al.*,³¹ which is described in terms of the applied electric field direction with respect to the polarization axis, and discussed as follows:

For the 180° domains configuration, according to the Bar-Chaim’s model,³¹ the domains reversal is observed for the

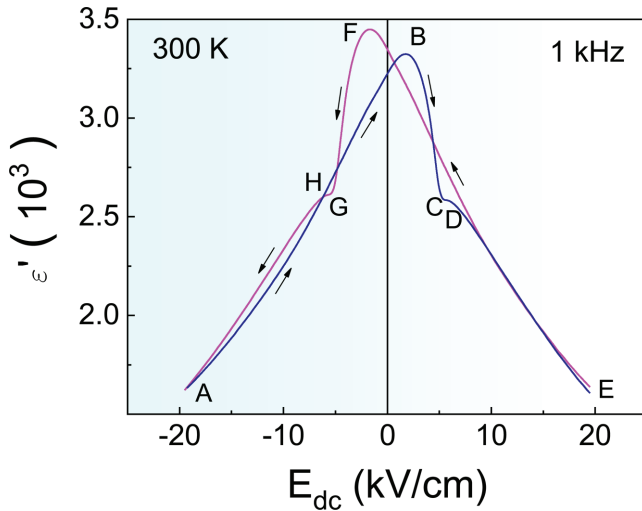


Fig. 4. ϵ' - E curves for the PMN-35PT ceramic, at room temperature and 1 kHz, showing the electric field path ways by arrows and alphabetic symbols.

electric field oriented in the polarization direction, and the 180° domains tend to be aligned in the electric field direction. In this case, the change in the polarization direction gives rise a transition between both domains' orientation states. When the applied DC electric field (E_{DC}) is higher than the coercive electric field, the saturation state is reached, in which condition most of the domains remain aligned in the E_{DC} direction. With a further decrease in the electric field, most of the domains remains aligned in the previous direction. However, interestingly, even being the electric field positive, some domains can be reversed, thus leading to the well-known "back-switching" behavior. As a result, a butterfly-like hysteresis loop can be observed in the DC electric field dependence of the dielectric permittivity, due to the contribution of the 180° ferroelectric domains. Therefore, the dielectric response manifests itself by the presence of a single-peak in both positive and negative electric field regions.

For the 90° domains configuration instead, in the absence of the external electric field, the initial state (not shown in Fig. 5) presents a random profile in the domains' orientation. This is equivalent to the state shown in Fig. 5(a), which corresponds to the A point, as observed in Fig. 5(h), when the material evolves from D to E. Under the maximum electric field (E_m) condition, the domains align parallel to the electric field direction after the 90° reorientation. Following the Bar-Chaim's model, by changing the field direction between both maxima field values (E_m and $-E_m$) two 90° rotations are observed, the first of which leads to the original domain state. The other domain rotation promotes the antiparallel orientation of the domains with respect to the initial polarization direction. In fact, the rotation of the 90° domains promotes significantly high mechanical stress, which allows the domains remain in their 90° profile. Therefore, because of the

contribution of the 90° domains two peaks are observed in the DC electric field dependence of the dielectric permittivity, as depicted in Fig. 5(h). Both the first and second observed peaks are related to the 90° reorientation due to the positive and negative electric field's directions, respectively. The two other observed peaks result from the hysteretic behavior. Therefore, in a ferroelectric system, when the dynamics of the domain-wall motion is governed by both 180° and 90° domains, the contributions of the two domain types have to be taken into account. Thus, the observed dielectric anomalies in the electric field dependence of the dielectric permittivity can be directly related to the influence of both 180° and 90° domains. Therefore, the DC bias mediated dielectric response obtained for the studied PMN-35PT ceramic system, clearly reflects the contribution of the ferroelectric domains to the total dielectric permittivity.

3.1. Domains' dynamics model

A schematic model for the domains dynamics as a function of the DC electric field has been proposed, as shown in Fig. 5. For a better observation, the domains orientations, which are

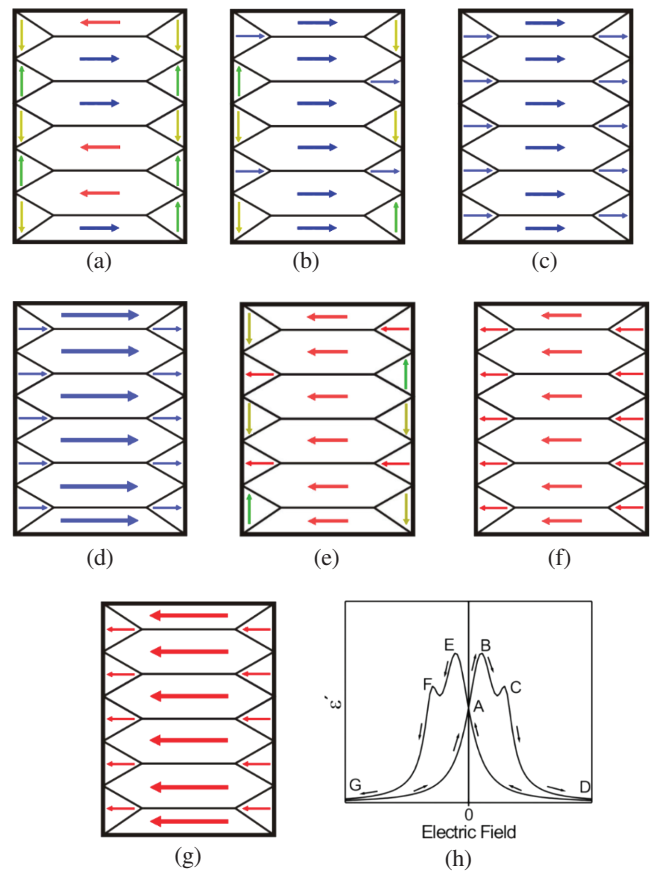


Fig. 5. Schematic representation of the proposed model for the domain dynamics during the application of the DC electric field.

represented by arrows, have been identified by different colors in Figs. 5(a)–5(g). The external rectangles represent the configuration of the ferroelectric domains. The 90° domains are represented by triangles and the inside arrow shows the dipoles direction. In the central part of the rectangle are represented the 180° domains, showing the internal arrows the direction for the dipoles' orientation. The diagram shown at the bottom and right side of the figure describes the behavior of the dielectric permittivity as a function of the DC electric field, indicating by capital letters the different orientation configurations for the dipoles, from the “virgin state” of the material point A-(a) up to G-(g).

When the DC electric field is increased, the dielectric permittivity increases, thus reaching its maximum value at the B point. Such increase in the dielectric permittivity is related to the rotation of the 180° domains and the contribution of the first rotation of several 90° domains, as shown in Fig. 5(b). The coincidence of these two processes finishes at the peak of the B point. A continuous increase in the DC electric field in the positive direction promotes the rotation of the other 90° domains, resulting in the second peak of the dielectric permittivity at the C point. Figure 5(c) illustrates that all domains are oriented parallel to the applied DC electric field direction. After the C point, an increase in the DC electric field causes a decrease in the dielectric permittivity because all the electric dipoles are oriented in the direction of the polarization axis. So, the increase of the electric field induces an increase in the electric dipole moment, Fig. 5(d), causing an “anchorage” of such dipoles and significantly reducing the dielectric permittivity.

On the other hand, with the reduction of the external DC electric field, many domains remain oriented in the previous direction of the electric field, so that the curve of the dielectric permittivity does not return along the same path way, exhibiting a hysteresis effect. The reversal in the electric field direction produces a symmetrical curve along with the positive orientation, so that a similar behavior to that described for the application of the DC electric field in the positive direction, can be obtained for the domains' configuration in the negative direction of the electric field. Such behaviors are illustrated in the Figs. 5(e), 5(f) and 5(g).

In order to better clarify this issue, it is important to point out that detailed investigations taking into account the non-linear dielectric properties, including measurements related to the influence of the AC (of variable amplitude) and DC electric fields on the dielectric response, not only in “normal” but also for relaxor compositions of PMN–PT ferroelectric ceramics, should also be studied.

4. Conclusions

A phenomenological model for the dynamics of the ferroelectric domains has been proposed in order to describe the dielectric response in $0.65[\text{Pb}(\text{Mg}_{1/2}\text{Nb}_{2/3})\text{O}_3-0.35\text{PbTiO}_3$ ceramics. The electric field dependence of the dielectric

response was investigated in a wide temperature interval, at different frequencies. The $\epsilon-E$ properties revealed symmetrical peaks and shoulders for three different temperatures below T_m . The obtained results for the PMN–35PT ceramic revealed to be a clear evidence of the simultaneous contribution on switching of 90° and 180° domains walls.

Acknowledgments

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