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Interrelationship between self-heating and ferroelectric properties in PZT ceramics during polarization reorientation

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Abstract. Ferroelectric ceramics when driven under high electric field have their ferroelectric properties modified due to the polarization reorientation, which induces the fatigue effect or domain depinning process. The self-heating process is another important characteristic that can be observed in this situation. In this work, we investigated the interrelationship among self-heating and both fatigue and depinning processes in PZT ceramics, calculated from the P – E hysteresis loop measurements. It was found that the fatigue and depinning processes are reflected mainly in the temperature trend of the sample during polarization reorientation at 60 Hz and they have the same profile in both cases. The heating process might be visualized as resulting from domain rotation in a viscous medium. For ‘hard’ PZT, the self-heating accelerated a depinning process. While the electric field cycles were accumulated the heat generated by the sample increased the complex defect mobility. In consequence, the domain could be depinned, increasing the amplitude rotation of the domains. For ‘soft’ PZT, the self-heating accelerated a fatigue process by space charge motion.

1. Introduction

Ferroelectric ceramics used to convert mechanical energy into electrical energy and vice versa are very important in the industrial applications such as igniters, transducers and actuators [1]. Since these ceramics have no net polarization due to the random orientation of the domains, domain alignment through poling process is necessary to use them in piezoelectric devices [1, 2]. Therefore, to improve the performance of these materials we need to understand the process of domain rotation under high electric field and its consequences.

In order to obtain the maximum polarization in bulk ceramics it has been observed that a high electric field must be applied for a long time [3, 4]. Transient current measurement [3, 5], x-ray diffraction [6] and acoustic emission [7] have shown that in ceramics with tetragonal symmetry switching polarization occurs mainly by 90° domain rotation rather than 180° domain reversal.

Ferroelectric fatigue can be induced when a ferroelectric ceramic is continuously driven by a bipolar electric field larger than the coercive field. A decrease of the polarization and an increase of the coercive field are attributed to a domain pinning [8]. This effect is observed in bulk ceramics as well as in thin films. Several mechanisms have been suggested to explain the fatigue effect. During switching polarization, space charges are trapped at domain boundaries and the switching polarization is suppressed by means of domain pinning [9, 10]. In this case, a thermal annealing above the ferroelectric–paraelectric phase-transition temperature (T_C) can

restore the ferroelectric properties [11, 12]. It was also proposed that polarization fatigue appears due dendritic grown of oxygen-deficient filaments that cause domain pinning or incomplete switching [13]. Again, the properties can be restored by thermal treatment above T_C . Another cause of ferroelectric fatigue comes from formation of microcracks [14, 15]. These microcracks could be formed due to both internal anomalies like voids or pores or high local stress concentration [14]. In this case, the properties cannot be restored by thermal treatment.

Ferroelectric properties can be strongly modified by impurity doping effects. It is well known that oxygen vacancies are introduced by valence compensation when ceramics are doped with acceptor atoms and these vacancies are trapped on the domain walls [16, 17]. Acceptor atoms and oxygen vacancies form electric dipoles called complex defects, which act as pinning points for the domain motion and the domain rotation is reduced [18]. Consequently, in the virgin state, $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics doped with acceptor atoms (e.g. Fe^{3+}) have their domains clamped by these complex defects ($\text{V}_O\text{-Fe}$) and their hysteresis loops are characterized by a constricted loop [16]. A bipolar electric field or dc poling, at high temperature, can induce the ferroelectric domain depinning process [19]. In this case removal of 90° domain pinning occurs and the sample shows a remarkable increase of the switching polarization. The constricted loop can be visualized in the initial loop as being composed of two sub-loops, which are shifted by internal bias ($\pm E_i$) with respect to the origin, one of the possible directions of the spontaneous polarization being favoured for each domain [16, 20]. Otherwise, when donor atoms (e.g. Nb^{5+}) are added we have the absence of complex defects and the domains become more mobile [16, 18].

An obvious source of energy loss and consequently heat generation in ferroelectric materials lies in their characteristic hysteresis loops. This effect, termed the macrohysteresis effect, is manifested in the familiar (P , E) hysteresis loops and begin when the applied field is sufficient to make a boundary switching from one position to another [21]. Several parameters such as sample size, electric field strengths and frequency can influence the energy loss [22]. The sample heating rate can be also greatly modified by adulteration of the cation site with ions of different valence [23]. When ions with greater valence than the normal valence are added (donors) the rate of temperature rise is faster than when ions with lower valence are added (acceptors) [23].

In summary, several researchers have observed that when a bipolar electric field, larger than the coercive field, continuously drives a ferroelectric ceramic three effects can be observed: domain depinning [19], ferroelectric fatigue [24, 25, 26] or self-heating of the sample [22, 23]. However, these works have not reported a direct relationship between both ferroelectric properties and self-heating trend under high bipolar electric field. Thus, an important question regarding to the existence of a correlation between these properties remain open.

In this work, we investigated the interrelationship among self-heating and both fatigue and depinning process in PZT ceramics calculated from the P - E hysteresis loops. In order to investigate the influence of the doping and frequency effect on these proprieties, PZT ceramics were doped with Nb_2O_5 (donors) or Fe_2O_3 (acceptors) and the measurements were made at 60 Hz and 100 mHz. The results are discussed in terms of the doping and frequency effect on the domain rotation and its consequence on the heat generation.

2. Experiment

$\text{Pb}(\text{Zr}_x, \text{Ti}_{1-x})\text{O}_3$ ceramics with $\text{Zr}/\text{Ti} = 53/47$ doped with 1 wt% Nb_2O_5 (PZTN) or Fe_2O_3 (PZTF) were prepared by a conventional oxide mixing process. The precursor oxides mixed in a ball mill and dried were calcined at 850°C for 3.5 hours. After pressing, disc shaped samples were sintered at 1250°C in a saturated PbO atmosphere. The sintered samples 17 mm

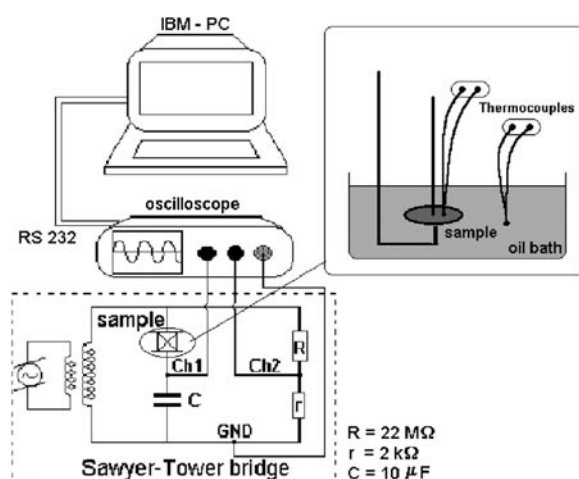


Figure 1. Schematic Sawyer-Tower circuit for hysteresis loop measurement.

in diameter were polished to a thickness of 0.35 mm. After that, they were heat-treated at 600 °C for 30 minutes to release stress introduced during polishing. Silver electrodes were painted on both sides of the discs and fired in an oven at 100 °C for 10 minutes. Scanning electron micrographs showed that the average grain size of the ceramic lies between 3.0 and 3.5 μm .

A Sawyer-Tower-like system bridge was used for ferroelectric hysteresis characterization. High amplitude sinusoidal bipolar electric field (60 Hz or 100 mHz) was used in the ceramic samples to induce switching polarization. The experimental set-up for conducting the measurements is shown in figure 1. The samples were introduced into the silicon oil bath on a controlled temperature system. The heat generation experiment was measured by monitoring the sample temperature during continuous electric field driving. A chromel-alumel thermocouple was attached on the sample surface to monitor the temperature. Silver adhesive was used as a thermal connective material.

For all measurements, the oil bath temperature was monitored and it remained constant at the room temperature.

3. Results

Figure 2 shows the ferroelectric hysteresis loops for the PZTN measured at 60 Hz for several fatigue cycles. It can be seen that during the fatigue cycles both the saturation (P_S) and remanent (P_R) polarizations gradually decreased whereas the coercive field (E_C) increased. Consequently, the hysteresis loop becomes rounded. Figure 3(a) shows P_S , P_R and E_C versus the number of cycles for the PZTN obtained from the hysteresis loop measurements at 60 Hz (figure 2). In the initial cycles P_S and P_R decrease quickly while E_C increases accordingly. When the coercive field levels out the polarization tends to equilibrium.

During the switching polarization, the temperature of the PZTN sample was continuously monitored. The temperature dependence on the number of cycles is shown in figure 3(b). It can be seen that the temperature increases suddenly immediately after the electric field cycling begins. Then, it passes through a maximum (near 90 °C) and decreases continuously until reaches its stabilization at 60 °C, after about 7.5×10^5 cycles. It can be observed that both P_S and P_R change in a similar manner as the temperature and they stabilize as the sample temperature tends to equilibrium (figure 3).

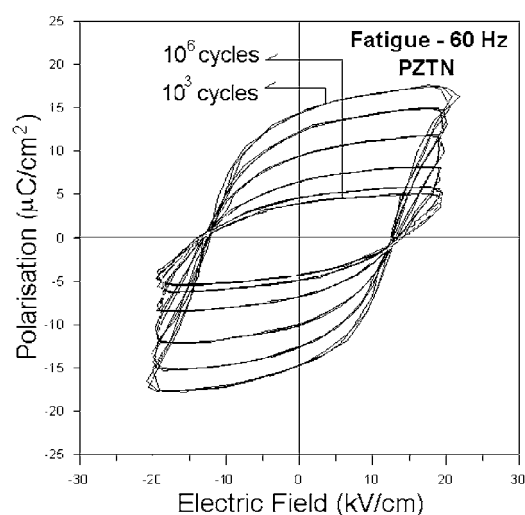


Figure 2. Hysteresis loops for the PZTN for several fatigue cycles.

After the sample temperature has reached the equilibrium, the oil bath temperature was quickly increased up to 90 °C as shown in detail in figure 3(b). This temperature corresponds to the maximum temperature reached by the PZTN sample during the initial cycles of polarization reorientation. Consequently a small increase of P_S and P_R and a decrease of E_C occurred, but these variations were not large enough to reach the initial values. Then, the oil bath was cooled until the room temperature. The PZTN kept the same polarization trend, as presented before the oil heating (figure 3(b)).

In order to verify any influence of the frequency of the electric field in the fatigue process and self-heating, the PZTN was measured at 100 mHz after the sample to be annealed above T_c . Under these conditions, no changes were detected in the sample temperature. Figure 4(a) shows the ferroelectric hysteresis loops for the PZTN measured at 100 mHz in the virgin state and after 4.4×10^3 cycles. Figure 4(b) shows the polarizations and coercive field dependence on the numbers of cycles. As observed earlier for the 60 Hz case, during the cycles of the electric field both P_S and P_R polarizations gradually decrease whereas the coercive field (E_C) increases. This means that the fatigue process occurs independently of the frequency of the electric field or self-heating. After the thermal annealing above T_c , the sample recovered again its virgin state without fatigue memory. As with the 60 Hz characterization, space charges caused the fatigue process. The difference is that the stabilization of E_C , P_S and P_R occurred earlier (smaller number of cycles) for measurements at 60 Hz than at 100 mHz (figures 3 and 4). These results suggest that the self-heating increases the fatigue process.

Figure 5 shows the ferroelectric hysteresis loops for the PZTF measured at 60 Hz for several fatigue cycles. In the virgin state, the PZTF was characterized by a constricted hysteresis loop, but after a continuous electric field switching a normal ferroelectric loop was observed (figure 5). Figure 6(a) shows a remarkable continuous increase of the polarizations (P_S and P_R) and coercive field for the PZTF with the number of cycles. Similar behaviour has been observed in PZT films [19]. During the switching polarization, the PZTF sample temperature was also monitored. The temperature dependence on the number of cycles (at 60 Hz) is shown in figure 6(b). It can be seen that the temperature increased continuously during all electric field cycling. The results obtained for the PZTF clearly differ from those obtained for the PZTN as will be discussed further.

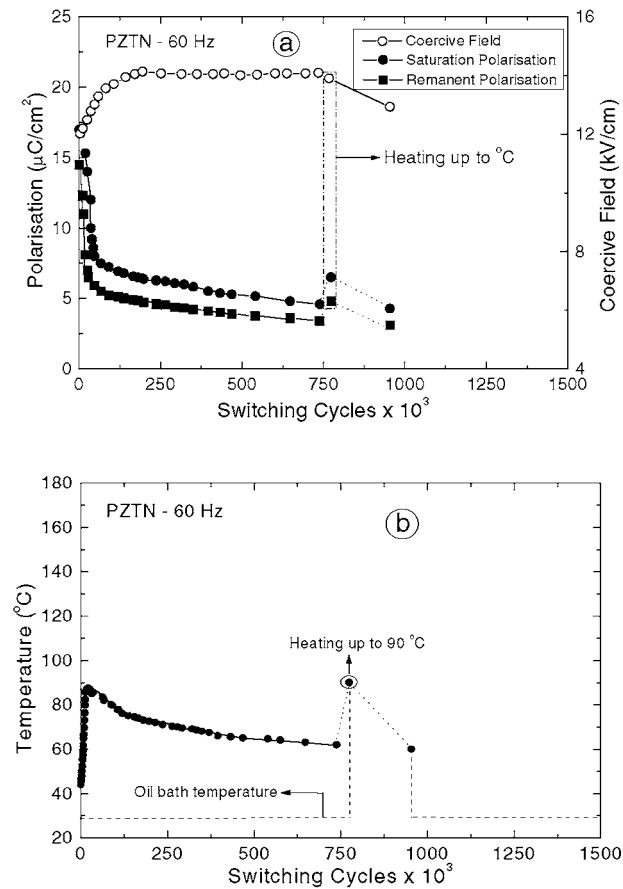


Figure 3. Dependence on the number of cycles for the PZTN measured at 60 Hz for: (a) saturation and remanent polarizations and coercive field; (b) sample temperature.

In a new measurement, the polarization was switched until the PZTF sample reached 70°C and, consequently, its polarization increased considerably (figure 7). When the electric field was turned off the sample temperature returned to room temperature (oil bath temperature). In order to examine the recovery of the constricted hysteresis loop, new measurements were made after three annealed conditions: a few minutes after the electric field was turned off, after 12 hours annealing at room temperature and finally after 6 days annealing at 100°C . Figure 7 shows the results obtained for each case. After annealing at room temperature (few minutes or 12 h) the PZTF sample quickly reached the former values of the temperature, polarizations and coercive field. In both cases the PZTF behaved similarly to the PZTN, that means, the temperature increases quickly as the polarization starts to be switched easily. Otherwise, after 6 days at 100°C the hysteresis loop practically recovered its virgin state, which is characterized by a constricted hysteresis loop and low heating rate.

4. Discussion

It is well known that PZT doped with donor elements (Nb) promotes the formation of Pb vacancies, which releases the local stress, favouring an increase of the domain mobility [18].

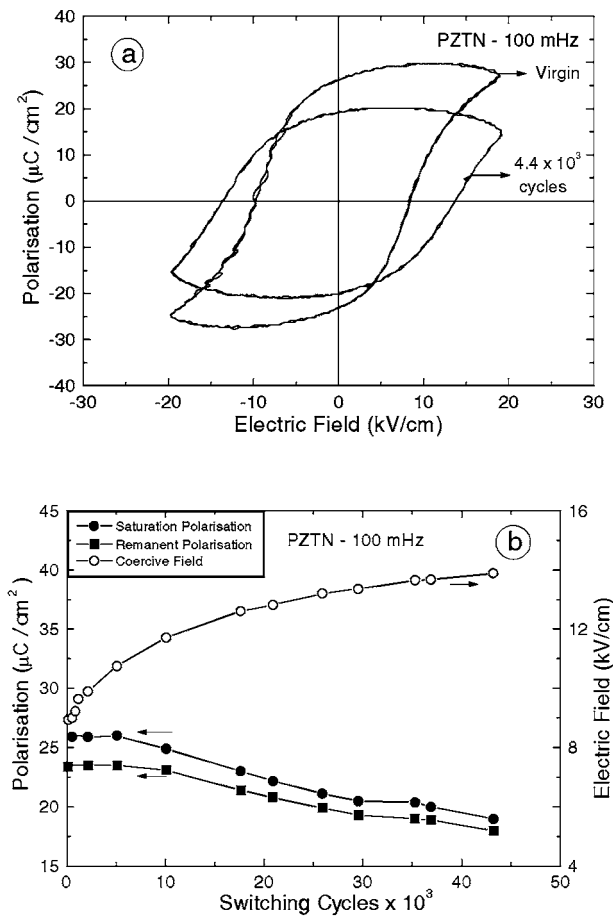


Figure 4. (a) PZTN hysteresis loop curves recorded during fatigue tests measured at 100 MHz; (b) saturation and remanent polarizations and coercive field dependence on fatigue cycles for the PZTN.

Such compositions are known as ‘soft’ PZT [16, 18]. Otherwise, by doping with acceptor elements (Fe) oxygen vacancies are formed, creating complex defects, which increase the local stress and act as pinning points for the ferroelectric domains, characterising the ‘hard’ PZT [16].

4.1. Influences on the self-heating

The remarkable observation reported in this work is that for all measurements made at 60 Hz the sample temperature change, due to the polarization reorientation, presented the same profile as the polarization. However, different behaviours depending of the kind of doping (donor or acceptor) were observed. While for the PZTN the polarizations (P_R and P_S) and temperature reached a maximum value before stabilizing at smaller values, for the PZTF they increased continuously.

We assume that the self-heating is caused by the rotation of the ferroelectric domains, in a viscous medium, due to the switching of the external electric field. This relationship might be imagined as the domain moving through a viscous medium producing heat. The importance

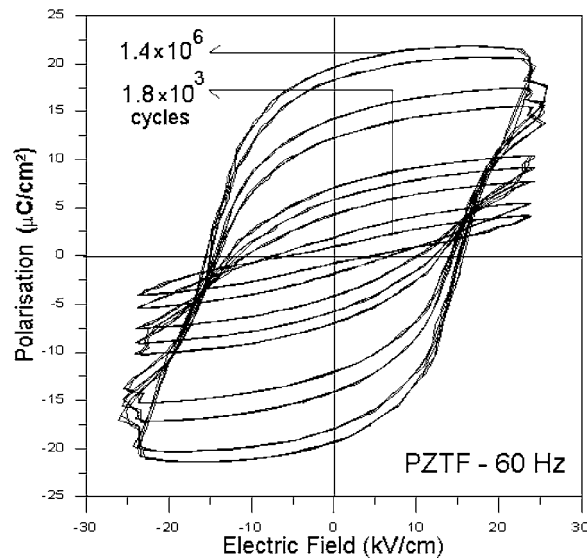


Figure 5. Hysteresis loops for the PZTF after several numbers of cycles.

of viscosity has been already considered to explain the switching properties of ferroelectrics [27, 28]. Aiming to explain the experimental results, the influence of doping and frequency of the electric field on the sample self-heating is discussed just below.

4.1.1. Influence of the doping. Nb_2O_5 addition increases remarkably the domain mobility and the domains can be reoriented easily in the field direction. Consequently, due to the high and fast domain amplitude rotation the sample temperature quickly increases. As the number of cycles increases the fatigue process, caused by domain pinning by space charges, reduces the domain degree reorientation, consequently decreasing the polarization. Then, as the fatigue process stabilizes the sample temperature tends to a constant value. In this situation the heat produced and dissipated are equal (figure 3). A similar initial trend between polarization and temperature for the PZTN could not be seen probably because high electric field in soft ceramics accelerates the domain mobility process and quickly the saturation polarization is obtained [25].

The PZTF in the virgin state presents a constricted hysteresis loop due to the pinning of the ferroelectric domains by the $\text{V}_O\text{-Fe}$ complex defects [16]. When the external electric field is switched ferroelectric domains tend to rotate and the depinning process starts. This increase of the polarization, by a continuous increase of the degree of domain reorientation, induced a continuous heating of the sample. In our experiment, a constant polarization value could not be reached during the cycling time investigated probably because a saturation of the depinning process was not reached.

Thus, the viscosity of the medium may be modified by different kinds of additive increasing or decreasing the loss. Fe_2O_3 addition decreased the domain mobility and increased its loss. Consequently, the PZTF reached higher temperature than the PZTN but with smaller heating rate. Another point that indicates the influence of the doping on the self-heating comes from the direct comparison between the polarization value and the respective sample temperature. For the same polarization, the temperature for the PZTF is always higher than PZTN. This explanation corroborates that different doping produces modifications in a viscous medium.

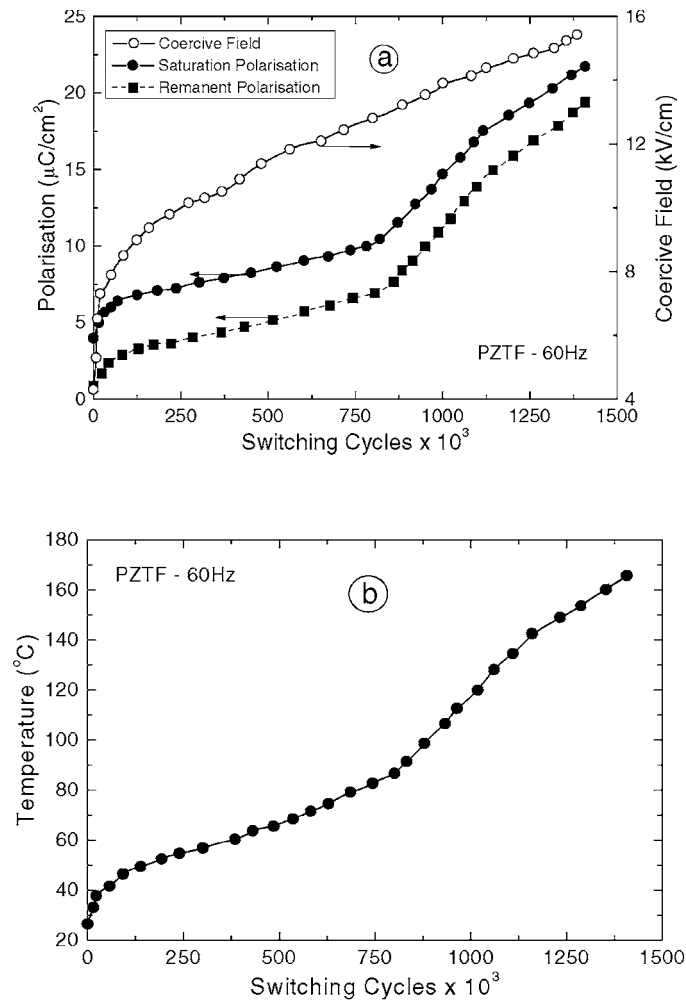


Figure 6. Dependence on the number of cycles for the PZTF measured at 60 Hz for: (a) saturation and remanent polarizations and coercive field; (b) sample temperature.

4.1.2. Influence of the degree of domain orientation. It is well known that the hysteresis area and the remanent polarization can represent the ferroelectric loss per driving cycle [22] and the degree of domain orientation [29], respectively. Thus, the results from the PZTN and PZTF samples show us that there is a narrow relationship between the degree of the domain rotation and the self-heating. When the domains have plenty of mobility the heating rate is large as observed for the PZTN and rejuvenated PZTF. However, when the domains are pinned, as for the virgin PZTF sample, the rotation degree is lower and consequently the heating rate is smaller. Therefore, our results indicate that a continuous increase or decrease of the degree of domain rotation induces a higher or smaller loss, respectively. The continuous increase of the temperature of the PZTF sample during the ferroelectric hysteresis loops may be explained as resulting from the continuous increase of domain motion by the depinning process. This is reflected in a relaxation of the constricted hysteresis loop and consequent increasing of the polarization (figures 5 and 6). In contrast, for the PZTN the temperature decreased due to

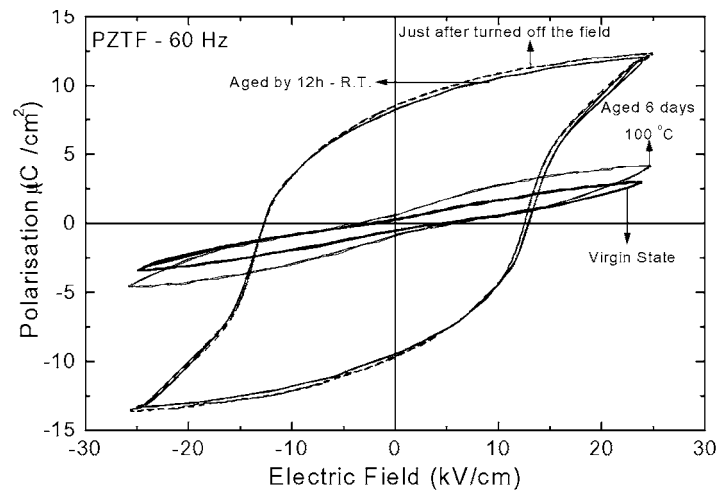


Figure 7. Hysteresis loop evolution for the PZTF for several ageing conditions.

the fatigue processes, caused by pinning of the domains by space charges. When the pinning process stabilizes the sample temperature also reaches a constant value.

4.1.3. Influence of the frequency. The frequency of the electric field cycling is another important parameter that showed influence on the heating. Although the PZTN domain mobility is high, the measurement realized at 100 mHz did not produce any heating. As cited earlier, this behaviour may be explained assuming the domains move through a viscous medium. Considering the PZTN domains have high mobility, their low frequency of rotation produces less heating. Consequently, the dissipation of the heat to the oil bath does not permit sample heating. On the other hand, the measurement realized at 60 Hz produces heat at a higher rate, which cannot be totally dissipated in the oil bath, increasing the sample temperature.

4.2. The fatigue and depinning process

The observed fatigue process is also influenced by self-heating for the PZTN. Due to the high domain mobility and absence of a constricted hysteresis loop high temperature was quickly reached. Then, the fatigue process was quickly initialized, for the PZTN measured at 60 Hz, because of the high mobility of the space charges at high temperatures [30]. When the motion of the space charges finished the polarization stabilized. As mentioned previously, after the polarization reaches equilibrium the PZTN sample was heated to 90 °C (figure 3). The results showed that only a small increase of the polarizations occurred but they remained smaller than the initial value. The fact that the polarization is only partially recovered indicates that the pinning forces are strong enough to significantly reduce the effect of the temperature increase. Therefore, the mobility of domains could not be restored by an increase of temperature. As consequence of this, after the oil bath was cooled both the sample temperature and polarization trends remained unaltered and returned to their previous values as can be seen in figure 3.

An important fact observed was that after the thermal annealing above T_c the PZTN sample recovered its initial state without fatigue memory. Two kinds of mechanism can induce ferroelectric fatigue in bulk ceramics: space charges and microcracks [26]. It has been reported that in a sintered sample, the fatigue process is mainly due to domain pinning by space

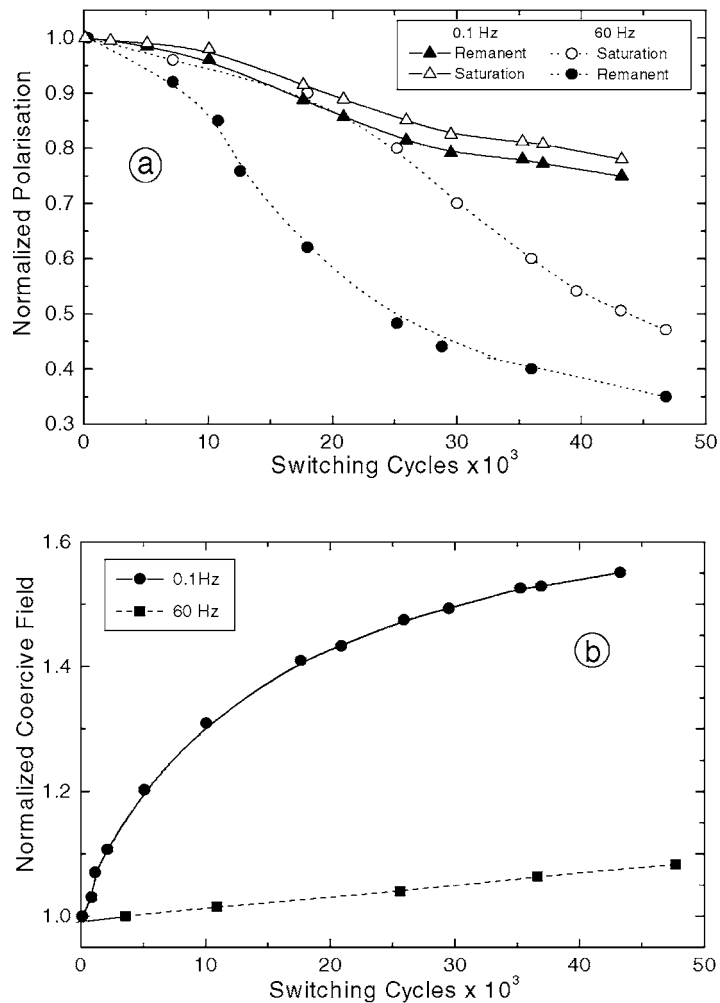


Figure 8. The normalized results for the PZTN obtained at 60 and 100 mHz measurements for: (a) polarizations; (b) coercive field.

charges [26]. Thus, this supports the view that the fatigue process occurring in PZTN for both frequencies can be attributed to the space charges, since that fatigue state due microcracking could not be recovered by thermal treatment [26].

Initially, the virgin PZTF sample showed a constricted loop, which gradually became a normal loop. When a virgin sample modified with acceptor atoms is left for a certain time at a temperature above T_c and after that it is cooled to a temperature below T_c its polarization is considered to be randomly orientated. In this case, immediately after the cooling, the hysteresis loop observed is normal [30]. However, when the sample is left for a long time at a temperature below T_c the hysteresis loop gradually changes into a constricted loop [30]. Just after the sample is rejuvenated, each domain points in the same direction. Consequently, the complex defects orient themselves parallel to the spontaneous polarization of each domain stabilizing it [16, 30]. Then, the change observed in the loop (figure 6) during the field application is caused by the internal bias field relaxation [16].

The comparative results between the polarizations and coercive field for PZTN measured at 60 Hz and 100 mHz are shown in figures 8(a) and (b), respectively. The results obtained from hysteresis loop measurements for both frequencies shown the same behaviour: P_S and P_R decreased while E_C increased with the number of cycles. However, the polarization fatigue is larger at 60 Hz than at 100 mHz. We can see that while for 60 Hz the polarizations decrease by about 50% and stabilize, for 100 mHz they decrease by only 20% after the same number of cycles. Another important characteristic is that for the measurement carried out at 100 mHz no self-heating was detected whereas at 60 Hz the sample reached 90 °C. These measurements can be considered to be isothermal and non-isothermal, respectively. We believe that the fatigue effect was higher for 60 Hz measurement because the high temperature reached by the sample increased the space charge mobility, which could move quickly and pinned the domain. On the other hand, for the isothermal measurement the space charge did not have much mobility and consequently a smaller polarization fatigue effect was observed. The heating can justify the coercive field change observed for the 60 and 100 mHz measurements. The lower variation obtained by 60 Hz measurement is explained if we assumed that during the fatigue process the increase of the coercive field, by pinning of the domains, was almost compensated by increase of the temperature, which normally decreases the coercive field [31]. It is important also to notice that for both frequencies the virgin state was recovered after thermal annealing, that means fatigue by space charges occurs independently of the frequency of the field.

5. Conclusion

In this work, the interrelationship among the self-heating process and both ferroelectric polarization fatigue and the domain depinning process in PZT ceramics was investigated. It should be stressed that saturation and remanent polarization had the same behaviour shown by sample temperature during ferroelectric switching, implying a correlation between them. We found that the domain depinning process was related to relaxation of the complex defects which increased the sample temperature by self-heating. On the other hand, the fatigue process induced a decrease of the sample temperature. For the PZTN domain the depinning process occurred firstly, followed immediately by the fatigue process due to domain pinning by spatial charges. For the PZTF, the domain depinning process occurred during the whole fatigue cycle causing a continuous increase of the amplitude of the domain rotation and consequent increase of the self-heating. The self-heating origin is probably interaction between the domain and defects. The heating rate can be visualized as the heat generated by friction of the domains moving in a viscous medium. If the frequency is low enough the heat generated can be dissipated in the oil bath and no thermal influences will occur in the fatigue or depinning processes.

Acknowledgments

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