INFLUENCE OF COMPLEX DEFECTS ON THE DOMAIN SWITCHING DYNAMICS IN FERROELECTRIC CERAMICS

M. H. Lente, A. Picinin, J. P. Rino and J. A. Eiras
Universidade Federal de São Carlos, Departamento de Física, Grupo de Cerâmicas Ferroelétricas, São Carlos – SP – Brazil

ABSTRACT
In this work, the influence of the complex defects on the domain switching dynamics in doped $Pb(Zr_{0.53},Ti_{0.47})O_3$ bulk ceramics (PZT) was investigated. It was verified that the complex defects, present in the hard PZT, initially reduce the coercive field and increase the percentage of backswitching. Nevertheless, during the continuous polarization switching these defects tend to reorient perpendicularly to the spontaneous polarization of domains, thus, increasing the coercive field and reducing the backswitching. Additionally, the frequency dependence of the coercive field was strongly influenced by the configuration of complex defects into the ferroelectric matrix.

RESUMEN
En este trabajo fue investigada la influencia de defectos complejos sobre la dinámica de reorientación de dominios en cerámicas de $Pb(Zr_{0.53},Ti_{0.47})O_3$ modificadas (PZT). Fue verificado que los defectos complejos, presentes en el sistema PZT duro, reduce el campo coercitivo y aumenta el porcentaje de retorno de la polarización. Por otro lado, durante una continua reorientación de la polarización, estos defectos tienden a reorientarse perpendicularmente a la dirección de la polarización espontánea, aumentando así el campo coercitivo y reduciendo el retorno de la polarización. Además, la dependencia del campo coercitivo con la frecuencia fue influenciada por la configuración de los defectos complejos dentro de la matriz ferroeléctrica.

INTRODUCTION

Ferroelectric materials have been widely employed in the technological industry as electromechanical as well as nonvolatile memory devices [1]. The rich physical phenomena associated with the domain reorientation process have attracted the attention of many physicists over the last 50 years. For single crystals, the polarization switching has been interpreted as being constituted by nucleation of antiparallel domains followed by their growth by domain wall motion [2,3]. However, recently, some experimental works revealed that the polarization switching process in ferroelectric bulk ceramics is much more complex than that observed for the single crystals [4,5]. These works showed that the polarization reversal is composed of two ferroelectric mechanisms: 90^{o} domain rotation immediately followed by 90° domain walls rearrangement [4,6]. It was also reported that the type of impurity and the electric field strength have a strong influence on the reorientation behavior of domains [5,7]. Although some interesting papers on the domain reorientation in defect-free systems have been reported, few attentions have been paid on systems containing dipolar defects.

In this paper, the influence of the dipolar defects on the domain switching dynamics in $Pb(Zr_{0.53},Ti_{0.47})O_3$ bulk ceramics (PZT) was investigated through hysteresis loops measurements as a function of the frequency of the electric field. In order to obtain the influence of the defects distribution into the domain structure on the polarization switching the measurements were done in the virgin and in the depinned state. The results are analyzed and discussed in terms of the configuration of complex defects into the ferroelectric matrix and the influence of the frequency of the electric field on the domain reorientation.

EXPERIMENTAL PROCEDURE

$Pb(Zr,Ti)O_3$ ceramics with molar ratio Zr/Ti = 53/47 were prepared by conventional oxide mixing process [1] and doped with 1 wt.% of Fe_2O_3 (hardener), hereafter labeled as PZTF. The precursor oxides were mixed in ball mill, dried and calcined at 850 ^{o}C for 3.5 hours. Discs shaped samples were sintered at 1250 ^{o}C in a saturated PbO atmosphere. Scanning electron micrographs showed that the average grain size lies between 3.0-3.5 μm . Discs shaped samples with 17 mm in diameter were polished to a thickness of 0.5 mm . After that, they were heat-treated at 600 °C for 30 minutes to release stress. Hysteresis loops were measured, at room temperature, in a Sawyer-Tower set up applying a triangular electric field of amplitude of 25 kV/cm on the samples. This frequency is low enough to avoid the self-heating [6], which can change drastically the ferroelectric response. The frequency dependence of the ferroelectric hysteresis loops was characterized for the sample in its virgin state and after a depinning process induced by a continuous polarization switching [6].

RESULTS AND DISCUSSIONS

Figure 1 (a) shows the representative hysteresis loops data for the PZTF in its virgin state and during a continuous polarization switching at 1 Hz. Figure 1 (b) shows the respective normalized curves. It is verified that the PZTF in the virgin state presents a constricted hysteresis loop, as also reported by Takahashi [9]. This fact may be related to the presence of acceptor atoms (Fe^{3+}) and oxygen vacancies (V_O^{2-}) that form electric dipoles, also called complex defects, which in the virgin state are aligned parallel with the polar direction of the domains [9,10]. Consequently, they act as pinning agents for the domain motion [5,9]. However, the data in Figure 1 reveal that the continuous electric field switching induces a gradual depinning process of the switchable domains due to a realignment of these defects perpendicularly to the polar direction of domains. Therefore, as the number of electric field cycles increases, the polarization values are increased due to a major alignment between the domains with the electric field [6]. The remarkable interaction between the complex defects and domains may be identified systematically through the backswitching evolution. Initially, in the virgin state, when all complex defects are aligned parallel along to the direction of the spontaneous polarization of each domain the strong interaction between the pair domain-complex defect is responsible for the small realignment between domains and domain walls with the applied electric field. This high interaction results in very low polarization values and high backswitching (Figure 1) [7]. Nevertheless, the continuous realignment of these defects perpendicularly to the polar direction of domains reduces sensitively the interaction domain-complex defect allowing higher polarization values as well as a smaller backswitching. An extreme situation is when all complex defects tend to be oriented perpendicularly to the polar direction of domains and, consequently, the interaction domain-complex defect becomes zero. In this case, the backswitching is considerably reduced being very similar to that observed for the defect-free system [6]. On the other hand, focusing on the coercive field behavior, it is possible to suppose that when the complex defects are aligned parallel to the polar direction of domains the interaction between domains-complex defects reduces the barrier energy of the system, thus, reducing the coercive field as a whole, as predicted theoretically [1]. Nevertheless, when the alignment between the switchable domains with the complex defects passes from parallel to perpendicular the interaction between them tend to be null and the values of the coercive field return to the defect-free case [11,12].

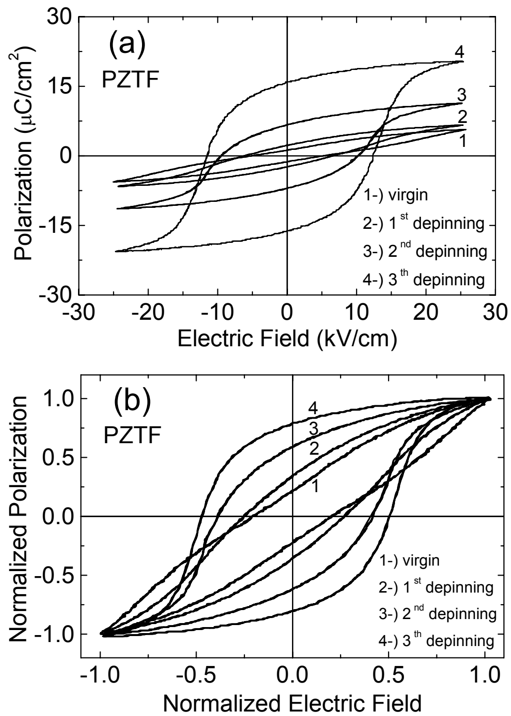

Figure 1. (a) representative hysteresis loops data for the (PZTF in its virgin state and during a continuous polarization switching at 1 Hz; (b) respective normalized curves.

In order to investigate the dynamics of the domain motion and the influence of the defects on this dynamics the frequency dependence of the hysteresis loops were characterized in the virgin state and for different degrees of depinning. From these results, the relative coercive field [E_C/E_{Max}] was calculated for each frequency from the respective normalized hysteresis loops (Figure 1(b)). The results are shown in Figure 2. The frequency dependence of the coercive field showed to be strongly influenced by the depinning process. Remarkably, for the virgin PZTF sample, its coercive field was practically frequency independent in all range of frequency investigated. However, after the depinning process, it showed to be slight frequency dependent at lower frequencies tending to level out at higher ones with higher values. It is possible to explain the PZTF results for the coercive field assuming that initially, when the complex defects are aligned parallel to polar direction of the domains, there is a strong interaction between them that reduces sensitively the threshold field necessary to reorient the 90° domains [11,13]. Nevertheless, when these defects pass to realign perpendicularly to the polar direction of domains the threshold field increases thus increasing the coercive field values. It is possible supposed that during the polarization switching both a restoring (F_R)

and a viscous forces (F_V) act on the domains during their reorientation. The importance of viscosity has been already considered for explaining the switching properties of the ferroelectrics [14,15]. Therefore, the coercive field may be interpreted as an effective field necessary to overcome these resistance forces ($F_V + F_R$) during the polarization switching. Thus, at lower frequencies, when the velocity of the domains is low, the viscous force might be neglected and, consequently, the coercive field is reduced. Nevertheless, at higher frequencies the viscous force increases accordingly, increasing the “apparent” coercive field. Finally, the range of frequencies where the coercive field is frequency independent might be interpreted as being a range where the resulting force that acts on the domains vanishes.

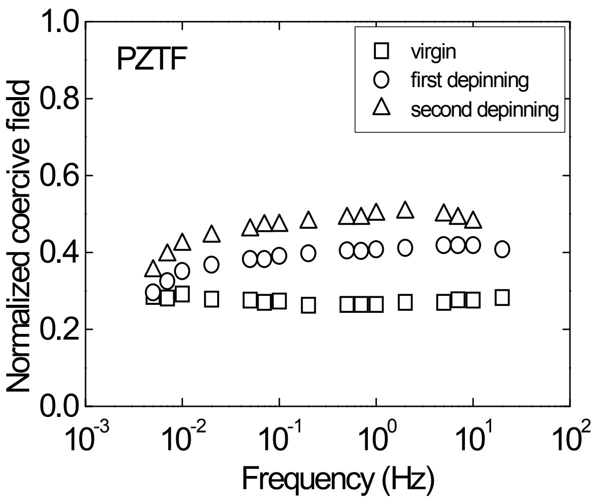

Figure 2. Relative coercive field for the PZTF in the virgin state and for each depinned state.

Doubtless, one very interesting result presented in this work is the fact that the coercive field can reach a saturation value in the relative short frequency range investigated, being extremely dependent on the configuration of defects in the ferroelectric matrix. It seems to exist an upper frequency limit of the coercive field being activated when domains are strongly hindered. On the other hand, we could not find if exist a lower switching threshold because at extremely low frequencies the electronic current becomes higher than that related to domain contribution thus limiting the resolution of our measurements. Further works will be conducted in order to investigate the existence of a possible lower limit to the coercive field in polycrystalline materials.

CONCLUSIONS

The dynamics of ferroelectric domains switching was investigated in hard $Pb(Zr_{0.53},Ti_{0.47})O_3$ (PZTF) ceramics through analysis of hysteresis loops obtained at different frequencies in the virgin and depinned states. It was verified that the complex defects in PZTF tend to reorient perpendicularly to the domain polarization during switching increasing the polarization and the coercive field. The frequency dependence of the coercive field seems to be determined by viscous force acting during the domain switching mainly at higher frequencies. Due to limitations in the experimental setup, it was not possible to obtain conclusive results to assure if there is or not a lower threshold field for domain reorientation.

ACKNOWLEDGMENTS

The authors thank to FAPESP and CNPq for financial support.

REFERENCES

1. UCHINO, K. (2000): “Ferroelectric Devices” (Marcel Dekker, Inc. 2000).

2. MERZ, W. J. (1954): **Phys. Rev**. 95, 690.

3. FATUZZO, E. and W. J. MERZ (1967): “Ferroelectricity” (John Wiley & Sons, New York).

4. MOREIRA, E.N.; M. H. LENTE, J. M. POVOA and J. A. EIRAS (1998): **J. Korean. Phys. Soc**. 32, 742.

5. LENTE, M.H. and J. A. EIRAS (2001): **J. Appl. Phys**. 89, 5093.

6. ___________________________ (2000): **J. Phys. Cond. Matter** 12, 5939.

7. ___________________________ (2001): **Ferroelectrics** 257, 227 (2001).

8. JAFFE, B.; W. R. COOK and D H. JAFFE (1971): **Piezoelectric Ceramics** (Academic, New York).

9. TAKAHASHI, S. (1982): **Ferroelectrics** 41, 143.

10. WARREN, W.L.; D. DIMOS, G. E. PIKE and R. RAMESH (1995): **Appl. Phys. Lett.** 67, 1689.

11. AHLUWALIA, R. and W. CAO (2001): **Phys. Rev**. B 63, 2103.

12. LENTE, M.H.; A. PICININ, J. P. RINO and J.A. EIRAS: **J. Appl. Phys**. – Submitted.

13. WU, Y.; D. YAO and Z. LI (2002): **Solid. State Commun**. 122, 395.

14. OMURA, M.; H. ADACHI and Y. ISHIBASHI (1991): **Jpn. J. Appl. Phys**. 30, 2384.

15. MITOSERIU, L.; D. RICINSCHI; C. HARNAGEA; M. OKUYAMA and V. TURA (1996): **Jpn. J. Appl. Phys**. 35, 5210.

16.