OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 6, No. 5-6, May - June 2012, p. 573 - 576

Dc-tunability properties of substituted PZT ceramics investigated with multipolar models

L. P. CURECHERIU[*], N. HORCHIDAN, S. POPESCU[a], V. CIUPINA[a]
Department of Physics, Al. I. Cuza Univ., 11 Bv. Carol I, 700506 Iasi, Romania
[a]*Department of Physics, Ovidius Univ., Bv. Mamaia no.124, 900527, Constanta, Romania*

The electric field dependence of the dielectric constant (dc-tunability) for PZT based- ceramics with excess and deficit of lead was investigated. Dense and homogeneous substituted PZT samples with moderate dielectric constant and low dielectric losses were prepared by solid state reaction. Their dc-tunability characteristics were investigated and the experimental data were discussed in terms of the Johnson model completed with a Langevin term that describes “extrinsic” contribution to the nonlinear $\varepsilon(E)$ dependences.

(Received September 8, 2011; accepted June 6, 2012)

Keywords: PZT based- ceramics, Dc-tunability, Nonlinear $\varepsilon(E)$ dependences

1. Introduction

In the last years, properties related to hysteresis behavior of ferroelectrics have been intensively studied [1-3]. However, the dielectric properties as a function of the applied electric field have been less studied, mainly due to the difficulty of performing dielectric measurements under a wide electric field range, especially at high electric fields. The electric-field dependence of the dielectric response i.e. the *tunability* can provide very useful information for understanding the dielectric/ferroelectric behavior in polar dielectrics. In addition, a new type of electronic device making use of the variation of the dielectric constant of polar dielectrics under dc-electric fields has been recently developed for wireless communication (next generation radar and microwave communication) systems [4-7]. Therefore, a study of the dielectric nonlinear behavior under electric fields is also technologically important. For such applications, relatively high tunability in combination with non-hysteretic behavior, moderate dielectric permittivity and low losses even at high frequency are necessary [8].

PZT ceramics were less studied from the point of view of tunability, due to their high dielectric constant and hysteretic behavior, which make this category of ferroelectrics inappropriate for tunability applications. However, the study of tunability is very important also from fundamental point of view. By using appropriate models for fitting the tunability data, it is possible to extract information about the polar contributions to the dielectric constant [9].

In the present paper, the role of different lead compositions in substituted PZT based-ceramics on the dc-tunability properties was reported. The non-linear dielectric properties were described by multi-polar mechanism of polarisation with composition-dependent parameters.

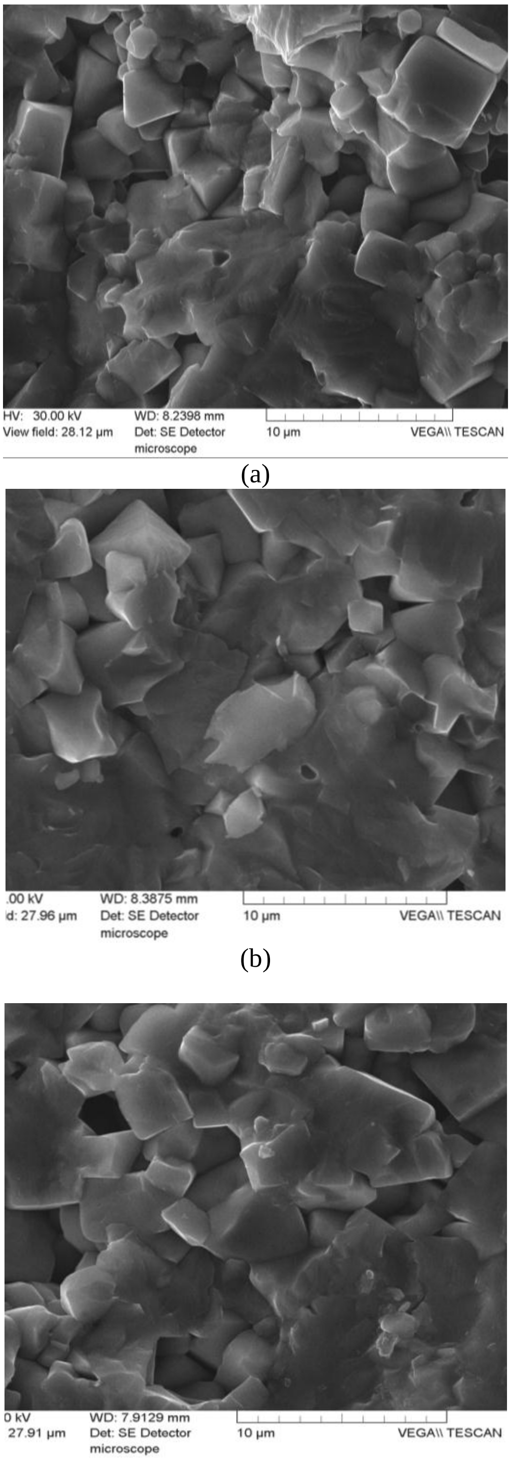
2. Experimental details

The PZT based-ceramics doped with Sr, Sb and Mn, with lead deficient (-3% and -4% of PbO) and excess (+3% and+4% PbO) were prepared by solid state reaction as described elsewhere [10]. After sintering at 1300^0C for 4 hours, the samples exhibit pure phase and good densification. The microstructures and the local chemical composition of the ceramics were investigated with a VEGA TESCAN scanning electron microscope coupled with EDX. For measuring the high voltage dc-tunability, the electroded ceramic pellets were placed in a cell containing transformer oil. For obtaining accurate tunability data, a circuit was designed and realized, as described in detail in the Ref. [11], in which the high voltage up to 30 kV was obtained by using a function generator coupled with a TREK 30/20A-H-CE amplifier.

3. Results and discussion

The SEM analyses were performed on the surface of the pellets sintered at 1300 ^{o}C and are shown in Fig. 1. All the ceramic have a homogeneous microstructure with cubic large grains. Adding in excess PbO an increasing of grain size was obtain together with a better densification. A dramatic microstructural change occurs in case of PbO deficit samples. A bi-modal grain size distribution is obtained with large grains around 7 μm and small around 1 μm and also a reduction of densification.

The dc-tunability for PZT based-ceramics with deficient and excess of lead were determined at room temperature at increasing/decreasing dc-field and they are shown in the Fig. 2. A strong nonlinearity is observed for all the compositions, without saturation even for very high fields (~ up to 5 × 10^6 V/m). After the first increasing/decreasing cycles of the dc-field, the non-linear field-dependence $\varepsilon(E)$ tends to stabilize and the tunability data are reproducible. For a given value of the applied field (E=4,5 × 10^6 V/m) the higher tunability, $n=\varepsilon(E)/\varepsilon(0)$, was obtained for the sample with 4% excess of PbO n=1.85 , while the sample with 3% deficit has the lower value, n=1.16. As remark, the tunability increased with PbO excess, and decrease for in case of the sample with PbO deficit.



(a)

(b)

(c)

Fig. 1. SEM image of PZT-based ceramics: (a) stoichiometric sample; (b) excess 3% of PbO; (c) deficit 3% of PbO.

The hysteretic nature of the $\varepsilon(E)$ curve remains almost constant for sample with lead excess but is significant reduce in sample with lead deficit.

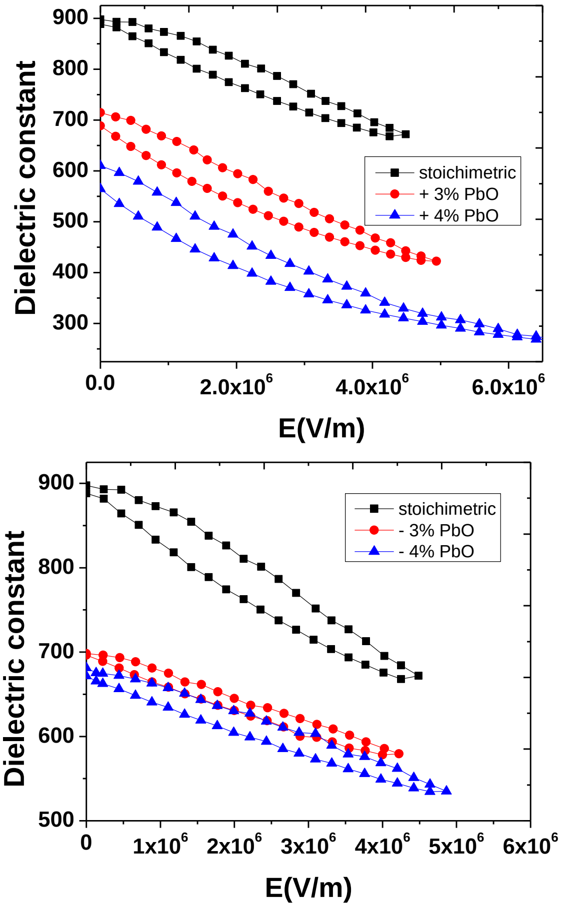


Fig. 2. Dc-tunability data for PZT-based ceramics: (a) excess of PbO (b) deficit of PbO.

In order to better understand the different mechanisms that contribute to the non-linear dielectric properties, it has to be taken into account that permittivity in perovskite ferroelectrics is the result of multiple polarization mechanisms whose behavior under electric field sequence is rather difficult to be disclosed. There is not a direct relationship between high spontaneous polarization, high permittivity and high tunability [8]. Although the domain walls in the ferroelectric phase give an extrinsic contribution to the permittivity, their role in tunability is not essential, since high tunability in the paraelectric state or in relaxors was commonly reported. According to the early model proposed by Diamond [12], a system with a mixture of ferroelectric and paraelectric regions gives rise to a high tunability, due to the fact that a field-induced transformation of paraelectric into ferroelectric state is realized. This model explains the larger tunability in substituted materials or in solid solutions rather than in pure perovskites.

The dc-tunability data of a ferroelectric system with a single polarization mechanism is commonly explained within the Landau-Ginzburg-Devonshire theory and its approximations (*e.g* semi-empiric Johnson equation [13]). The experimental data of stoichimetric sample of PZT based-ceramics are well fitted with Johnson's equation [13], with a correlation coefficient of 0.9996 (Fig. 3).

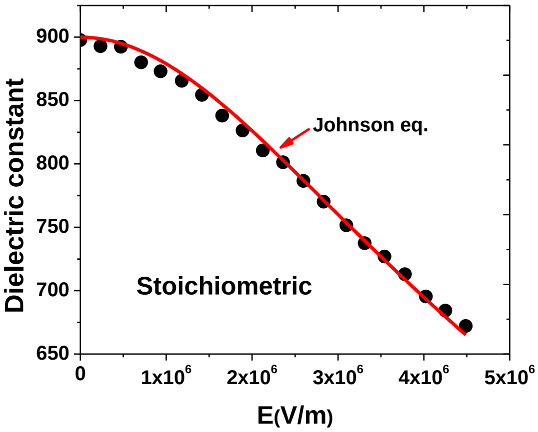


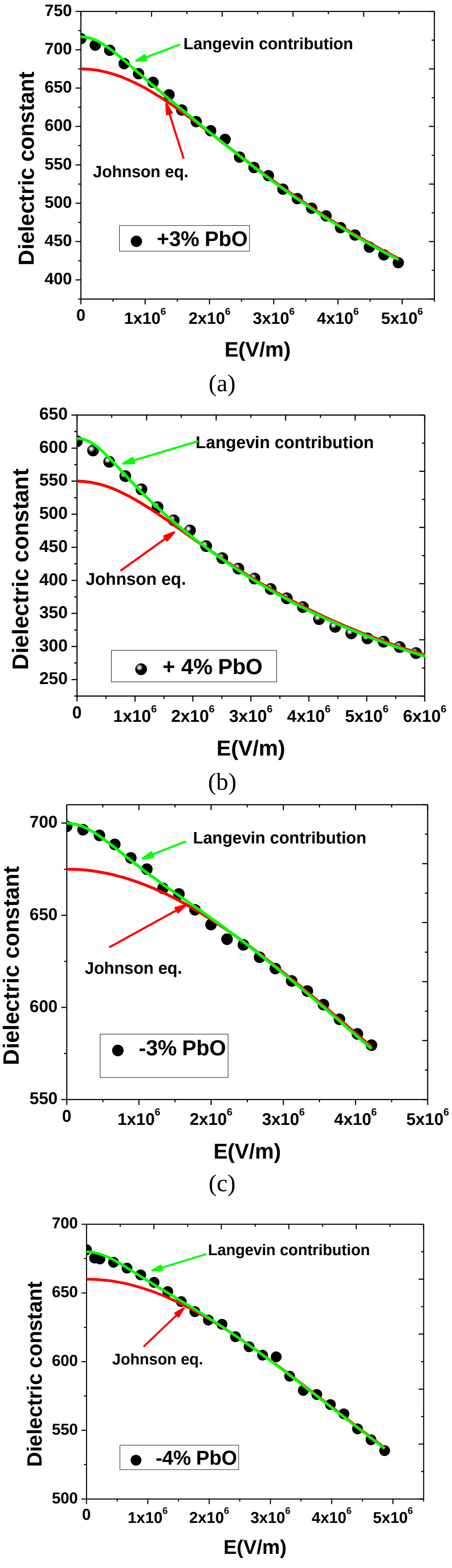
Fig. 3. Experimental tunability data and fits with Johnson eq. for PZT stoichiometric sample.

By broken the stoichiometry of the sample, the response of permittivity on the applied electric field has more than one contribution. In this case the dc-tunability data will be explained considering a complete model that takes into account the intrinsic ferroelectric polarization contribution, as well as extrinsic mechanisms that occur from cluster polarization, normally active at moderate fields [14]. This additional contribution to the polarization is due to the polar (but non-ferroelectric) nanodomains which are re-orientable by the applied field. The presence of such polarizable regions is commonly described by completing the Johnson's equation [13] with a Langevin term, which is dependent on the nanodomains' volume and polarization and on the temperature, according to the relation:

$$\varepsilon_r = \frac{\varepsilon_r(0)}{\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3 E^2\}^{1/3}} + \frac{P_0 x}{\varepsilon_0}[\cosh(Ex)]^{-2},$$

$$x = P_0 V / k_B T \qquad (1)$$

where: P_0 is the polarization of a nanodomain, V is its volume, k_B the Boltzmann constant and T is the temperature [14]. Using Eq. (1), the dc-tunability data of the present PZT-based ceramics in excess and deficit of PbO were well fitted (with a statistical correlation of 0.998), as shown in the Fig. 4 (a, b, c, d).



(a)

(b)

(c)

(d)

Fig. 4. Tunability data for PZT ceramics with various compositions and fits with multipolar mechanism model (Eq. 1).

The different contributions to the dc-tunability were estimated as following: at low fields (up to ~ 2×10^6 V/m), the extrinsic contribution is important and it may be correlated with the orientation degree of the polar nanoregions, while at moderate and high fields the dielectric nonlinearity can be described again with the Johnson model and is mainly related to the field-induced ferroelectric polarization response. The highest contribution to the dielectric constant given by extrinsic mechanisms (of about ~10%) was obtained for the samples with 4% excess of PbO. For deficit amounts of PbO the contribution is almost constant around 3%. The samples with 4% excess of PbO seem to present an optimum of composition (that gives extrinsic contribution) that induces a strong nonlinearity. In any case, the reduced dielectric constant ($\varepsilon \sim 650$), low losses at zero field ($\tan \delta < 6\%$) and tunability around 1.5 make from PZT-based ceramics promising candidate for tunable applications.

4. Conclusion

Different composition of PZT based-ceramics prepared by solid state reaction were investigated by measurements of the dc-tunability at room temperature. The non-linear properties and tunability of the ceramic samples were reported for the first time. The dc-nonlinear behavior was analyzed using a multipolar mechanism model able to explain the higher tunability values in terms of other additional polarization mechanisms, as described by considering Langevin contribution to the $\varepsilon(E)$ dependence.

Acknowledgements

L.C. acknowledges financial support from POSDRU 89/1.5/S/49944 and the POSDRU/88/1.5/S/56668 Project.

References

[1] M. E. Lines, A. M. Glass, Oxford University Press, London, 1977.
[2] J. C. Burfoot, G. W. Taylor, Macmillan Press Ltd., London, 1979.
[3] J. A. Gonzalo, World Scientific, Singapore, 1991.
[4] O. G. Vendik, E. Kollberg, S. S. Gevorgian, A. B. Kozyrev, O. I. Soldatenkov, Electron. Lett. **31**, 654 (1995).
[5] A. B. Kozyrev, T. B. Samoilova, A. A. Golovkov, E. K. Hollmann, D. A. Kalinikos, V. E. Loginov, A. M. Prudan, O. I. Soldatenkov, D. Galt, C. H. Mueller, T. V. Rivkin, G. A. Koepf, J. Appl. Phys. **84**, 3326 (1998).
[6] C. Ang, A. S. Bhalla, R. Guo, L. E. Cross, Appl. Phys. Lett. **76**, 1929 (2000).
[7] Z. Yu, C. Ang, R. Guo, A. S. Bhalla, Appl. Phys. Lett. **81**, 1285 (2002).
[8] A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, N. Setter, J. Electroceram. **11**, 5 (2003).
[9] L. P. Curecheriu, A. Ianculescu, N. Horchidan, S. Stoleriu, F. Tudorache, S. Tascu, L. Mitoseriu, J. Appl. Phys. **109**, 084103 (2011).
[10] S. Popescu, et al (send to).
[11] F. M. Tufescu, L. Curecheriu, A. Ianculescu, C. E. Ciomaga, L. Mitoseriu, J. Optoelectron. Adv. Mater. **10**, 1894 (2008).
[12] H. Diamond, J. Appl. Phys. **32**, 909 (1961).
[13] K. M. Johnson, J. Appl. Phys. **33**, 2826 (1962).
[14] C. Ang, Z. Yu, Phys. Rev. B **69**, 174109 (2004).

---

[*] Corresponding author: lavinia_curecheriu@stoner.phys.uaic.ro