Available online at www.sciencedirect.com

Journal of the European Ceramic Society 25 (2005) 963–967

www.elsevier.com/locate/jeurceramsoc

Dielectric, pyroelectric and ferroelectric behavior of PZTN 65/35/*x* ferroelectric ceramic system

A. Peláiz Barranco*, L. Y. Suárez Campos, A. Pentón

Facultad de Física-IMRE, Universidad de la Habana, San Lázaro y L, Vedado, La Habana 10400, Cuba

Received 1 September 2003; received in revised form 11 January 2004; accepted 18 January 2004
Available online 26 June 2004

Abstract

Niobium doping lead zirconate titanate [PZTN 65/35/x ($x = 1, 2, 4, 5$)] ferroelectric ceramics show perovskite structure and a rombohedral phase. The average grain size, the maximum dielectric permittivity, the transition temperature and the remanent polarization decrease when the niobium concentration increases, while the coercive field does not show any particular behavior and the porosity increases. The results are discussed taking into account the incorporation of the niobium to the lattice and the variation of the grain size. Preliminary results of the pyroelectric behavior are shown.

Keywords: Sintering; Dielectric properties; Ferroelectric properties; PZTN; Pb (Zr, Ti, Nb)O_3

1. Introduction

Since the discovery of the ferroelectric materials many attempts have been done describing their nature because their excellent properties, which them feasible for the development of electromechanical transducers, electric capacitors, etc.[1,2] Starting from the discovery and study of the barium titanate ($BaTiO_3$) has been developed an important number of studies on ferroelectric materials.[1] Lead titanate zirconate $PbZr_{1-x}Ti_xO_3$ (PZT) is one of the most widely studied ferroelectric materials due to its potential technological applications.[1–3] PZT has long been the subject of many experimental and theoretical research efforts to understand the physical origin of its striking ferroelectric properties. A perovskite structure (ABO_3) with excellent properties in the morphotropic boundary phase (Zr/Ti = 0.52–0.55)[1,2,4] and the presence of cationic vacancies are some of its fundamental characteristics.[1]

Many aliovalent compositional alterations to PZT have been studied either with higher valence substitutions (donors), either with lower valence ions (acceptors).[1,2,5] The niobium additive is one of the most used in order to evaluate the dielectric, piezoelectric, pyroelectric and electro-optic properties.[6–8] It can be considered as a donor dopant since it substitutes Zr^{4+}/Ti^{4+} ions, promoting the lead vacancies because of the charge compensation. Some papers have shown several improvements when the niobium doping on the PZT is produced as thin films.[9] In this work we present a study of the effects of the niobium on the PZT ceramics lead zirconate titanate (PZTN system), since their properties are very different on thin films. We will analyze the effects of the niobium on the dielectric, pyroelectric and ferroelectric properties in PZTN 65/35/x ($x = 1, 2, 4, 5$) ferroelectric ceramics.

2. Preparation of the samples

The ceramic samples were obtained by using the standard ceramic method with a nominal composition given by the expression: $Pb_{1-x/2}(Zr_{0.65}Ti_{0.35})_{1-x}Nb_xO_3$. This formula is simplified by the expression PZTN Zr/Ti/Nb representing the atomic percent of each one of the elements. Four different compositions were prepared, adding $x = 1, 2, 4, 5$ at.% of niobium whose representation will be PZTN 65/35/x.

High purity powders were blended and milled during 2 h, heated up to 800 °C for 1 h and again milled. The powders were pressed with 2000 kg/cm^2 in a hydraulic press and the

---

* Corresponding author. Fax: +537 8783471/335774.
E-mail addresses: pelaiz@ff.oc.uh.cu, pelaiz@yahoo.com (A.P. Barranco).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.01.028

sintering was made at 1200 °C for 1 h in air conditions. For the electric measurements, silver electrodes were deposited on the plane faces of the ferroelectric disks by a thermal treatment at 590 °C.

3. Experimental procedure

3.1. Structural analysis

X-ray diffraction analysis at room temperature was made by using a SIEMENS D5000 (35 kV, 30 mA) diffractometer and Cu Kα radiation. The microstructural studies (SEM) were carried out on the fractured samples by using a Cambridge-Leica Sterioscan 440 microscope.

3.2. Thermoelectric analysis

The dielectric analysis at 1 kHz was carried out in a wide temperature range by using a bridge RLC Philips.[10]

3.3. Ferroelectric hysteresis

A Sawyer–Tower circuit was used at 1 Hz and room temperature.[2]

3.4. Pyroelectricity

For pyroelectric measurements the samples were polarized at 1.33 kV/mm and 120 °C for 20 min. The temperature dependence of the pyroelectric current was obtained by using a multimeter Philips PM 2525 and the pyroelectric coefficient and the pyroelectric figure of merit were calculated at room temperature.[1,11]

4. Results and discussion

The crystallographic structure of the PZTN 65/35/*x* ceramics was examined considering the X-ray diffraction patterns shown in Fig. 1. The indexation is the same for all compositions. A perovskite structure and a pure rombohedral phase (hexagonal) were observed for all samples. All spectra show no evidence of pyrochlore phase formation. On the contrary, in the case of thin films, it has been reported[9] that niobium content acts to stabilize the transient pyrochlore phase after annealing temperature higher than 700 °C. The lattice parameters corresponding to the rombohedral (hexagonal) cell are shown in Table 1. The SEM studies (Fig. 2) showed that the niobium addition promotes the inhibition of the average grain size and increases the porosity.

The porosity is obviously more related to the sintering process and as well to the ceramic processing, but the incorporation of doping ions in the perovskite lattice could influence on it too. The niobium incorporation to the lattice (by the substitution of Zr^{4+}/Ti^{4+} ions) generates Pb-vacancies, which provides a desestabilization of the lattice. On the other hand, in the mixed-oxide route, lead titanate is the first reaction product to appear before the PZT solid solution is formed[1] because of the higher diffusion coefficients of Pb^{2+} and Ti^{4+} in comparison to Zr^{4+}. Therefore, PZT grains show a gradient of Zr/Ti concentration from the core to the shell. Then, is more probably the substitution of the Zr^{4+}/Ti^{4+} ions by Nb^{5+} ions in the center of the grains, and therefore, a higher desestabilization must be obtained there, which could be an origin of the formation of holes at the center of the grains during etching, increasing the porosity with the niobium concentration.

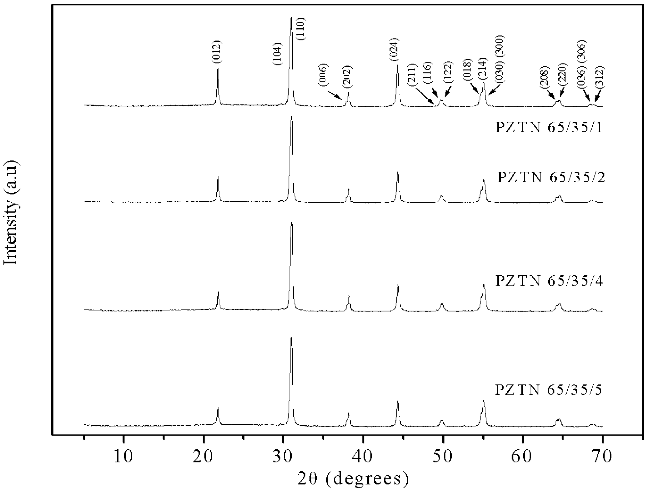

Fig. 1. X-ray diffraction patterns at room temperature for PZTN 65/35/*x* ferroelectric ceramics.

Table 1
Lattice parameters of the rombohedral (hexagonal) cell for PZTN 65/35/*x* ferroelectric ceramics

Compositions	*a* (Å)	*c* (Å)
PZTN 65/35/1	5.760	14.231
PZTN 65/35/2	5.763	14.225
PZTN 65/35/4	5.763	14.213
PZTN 65/35/5	5.763	14.212

The temperature dependence of the dielectric permittivity at 1 kHz is shown in Fig. 3. A decrement of its maximum (ε_{max}) is observed when the niobium concentration increases. All the compositions showed a Curie–Weiss behavior above the transition temperature (T_c).

Table 2 shows the ε_{max} and T_c values. The increment of the niobium concentration promotes a decrement of ε_{max}

Table 2
Dielectric parameters for PZTN 65/35/*x* ferroelectric ceramics

Compositions	ε_{max}	T_c (°C)
PZTN 65/35/1	45,509	265
PZTN 65/35/2	26,832	260
PZTN 65/35/4	10,588	245
PZTN 65/35/5	6,089	235

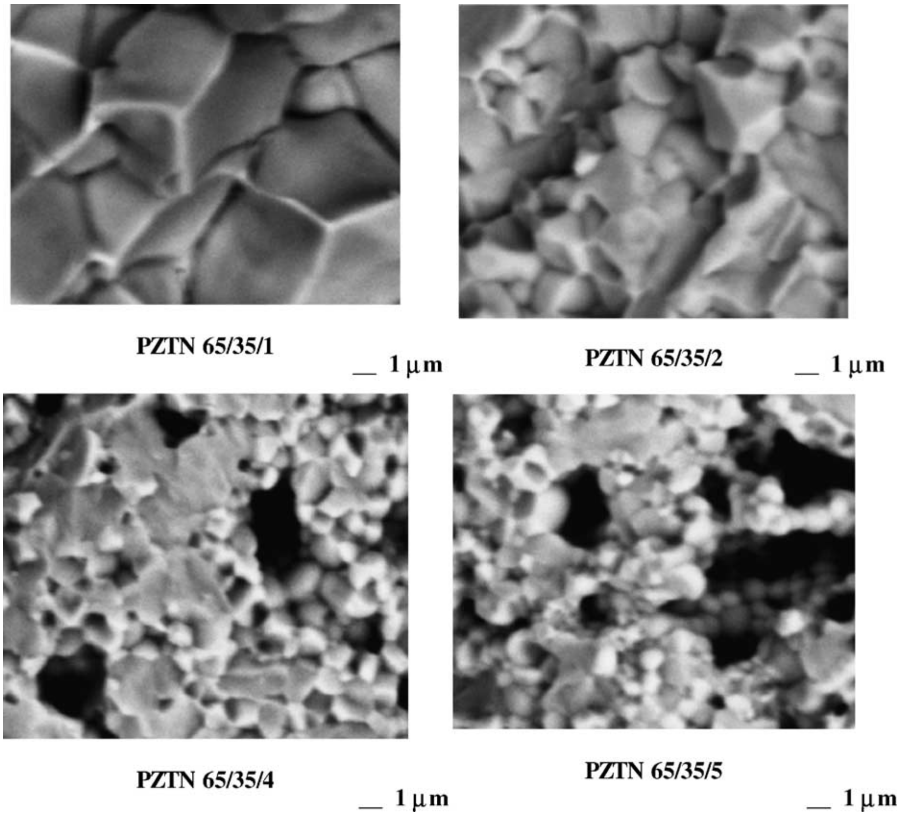

Fig. 2. SEM results at room temperature PZTN 65/35/*x* ferroelectric ceramics.

and T_c. The incorporation of the niobium in the B-site substitution creates vacancies in the A-site of the perovskite structure. It is believed to break the long-range interaction between ferroelectrically active oxygens in octahedra containing B-sites cations, which affects the ferroelectric properties of the system.[1] Then, for a higher niobium concentration a lower thermal energy will be necessary to provide a ferroelectric–paraelectric transition, decreasing T_c. On the other hand, the niobium incorporation also affects the total dipolar moment of the system and then the polarization, which is reflected in the variation of the dielectric permittivity with the doping.

Fig. 4 shows the hysteresis results at room temperature for a maximum applied field of 1.1 kV/mm and Table 3 picks up the values of the remanent polarization (P_r), the max-

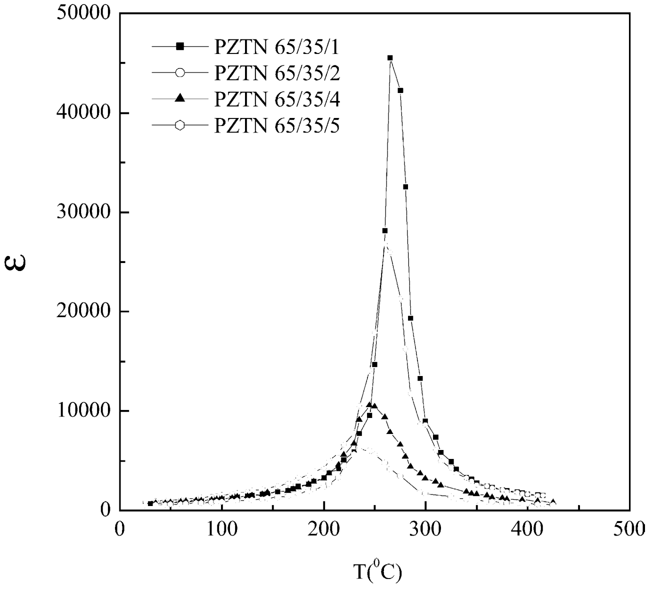

Fig. 3. Temperature dependence of the dielectric permittivity at 1 kHz for PZTN 65/35/*x* ferroelectric ceramics.

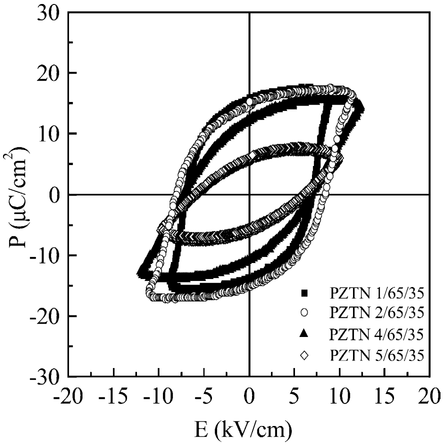

Fig. 4. Ferroelectric hysteresis results at room temperature and 1 Hz for PZTN 65/35/*x* ferroelectric ceramics.

Table 3
Parameters of the ferroelectric hysteresis for PZTN 65/35/x ceramics

Compositions	P_r (μC/cm^2)	P_{max} (μC/cm^2)	P_r/P_{max}	E_c (kV/cm)
PZTN 65/35/1	15	17	0.88	7.04
PZTN 65/35/2	15	18	0.83	8.44
PZTN 65/35/4	12	15	0.80	6.92
PZTN 65/35/5	6	7	0.71	6.13

imum polarization (P_{max}) and the coercive field (E_c). The remanent polarization shows a decrease with the increment of the dopant, which is associated to the variation of the total dipolar moment due to the niobium incorporation to the structure. The fraction P_r/P_{max} show high values, which could offer information concerning a near saturation sate, but note that the highest concentration shows conductive behavior rather than saturation.

The coercive field does not show any particular behavior. Its increase is associated to the decrease of the grain size and its decrease for PZTN 65/35/4 and 65/35/5, in spite of the decrease of the grain size, it can be attributed to an increment of the electrical conductivity of the material providing the domains orientation with a smaller electric field.[12] It is well known that PZT-based ceramics possess p-type conductivity because of the PbO vapor evaporation during the sintering process.[1] The niobium acts as donor[1] substituting to the (Zr, Ti), which increases the Pb-position vacancy concentration and leads to the decrease of the charge carrier concentration. As a result, the electrical conductivity of PZTN is decreased. However, with a further increase in the concentration of the Nb ion could promote the increase of the electrical conductivity of PZTN ceramics, as shown in Fig. 4 for the highest concentration where the curve shows conductive behavior rather than saturation.

With decreasing grain size, the coercive field must become larger, which could be associated to the presence of internal elastic stresses from grain boundary and surrounding grains. The stresses hinder the motion of the domain walls, which controls the polarization switching in ferroelectric ceramics.[13] The internal stresses are in fact residual stresses related with the development of the domain structure below the transition temperature.[14] These stresses should be higher in the fine-grained ceramics, mainly because the domain structure cannot compensate completely the change of the shape of individual grains during phase transformation.[13,14]

Finally, Table 4 shows the pyroelectric results at room temperature. The pyroelectric coefficient (p) decreases with the niobium addition corresponding with the decrease of the polarization of the ceramic system with the increment of the niobium concentration. The results of both parameters show suitable ceramics for pyroelectric sensors.[11,15,16]

Table 4
Pyroelectric coefficient (p) and pyroelectric figure of merit (R_v) at room temperature for PZTN 65/35/x ferroelectric ceramics

Compositions	p (μC/m^2 °C)	R_v (μC/m^2 °C)
PZTN 65/35/1	503	0.73
PZTN 65/35/2	471	0.53
PZTN 65/35/4	443	0.59
PZTN 65/35/5	413	0.80

5. Conclusions

PZTN 65/35/x ($x = 1, 2, 4, 5$) ferroelectric ceramics showed perovskite structure and a pure rombohedral phase. The average grain size, the maximum dielectric permittivity, the transition temperature and the pyroelectric coefficient decreased with the niobium addition while the porosity increased. On the other hand, the coercive field did not show any particular behavior. The results were discussed taking into account the niobium incorporation to the structure and the variation of the grain size. The pyroelectric parameters show suitable ceramics to be used in practical applications.

Acknowledgements

The authors wish to thank to the Third World Academy of Sciences for financial support (RG/PHYS/LA No. 99-050) and to the ICTP, Trieste-Italy, for financial support of Latin-American Network of Ferroelectric Materials (NET-43).

References

1. Xu, Y., *Ferroelectric Materials and Their Applications*. Elsevier Science Publishers B.V., The Netherlands, 1991.
2. Jaffe, B., Cook, W. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, New York, 1971.
3. Fernández, J.F., Durán, P. and Moure, C., Materiales cerámicos ferroeléctricos y sus aplicaciones. *Bol. Soc. Esp. Cer. Vidr.* 1993, **32**(1), 5–15.
4. Noheda, B., Cox, D. E., Shirane, G., Gonzalo, J. A., Cross, L. E. and Park, S. E., A monoclinic ferroelectric phase in the $Pb(Zr_{1-x}Ti_x)O_3$ solid solution. *Appl. Phys. Lett.* 1999, **74**(14), 2059–2061.
5. Haertling, G. H., Ferroelectric ceramics: history and technology. *J. Am. Ceram. Soc.* 1999, **82**, 797–818.
6. Dai, X. and Wang, Y., Multistage heat-electric energy conversion working on $F_{R(LT)}$–$F_{R(HT)}$ phase transition in Nb-doped PZT 97/3 ceramics. *Ferroelectrics* 1990, **109**, 253.
7. Duan, N., Cereceda, N., Noheda, B. and Gonzalo, J. A., Dielectric characterization of the phase transitions in $Pb_{1-y/2}(Zr_{1-x}Ti_x)_{1-y}Nb_yO_3$ ($0.03 \leq x \leq 0.04$, $0.02 \leq y \leq 0.05$). *J. Appl. Phys.* 1996, **82**(2), 779.
8. Ujma, Z., Handerek, J. and Kugel, G. E., Phase transitions in Nb-doped $Pb(Zr_{0.95}Ti_{0.05})O_3$ ceramics investigated by dielectric, pyroelectric and Raman scattering measurements. *Ferroelectrics* 1997, **198**, 77.
9. Klissurska, R. D., Brooks, K. G., Reaney, I. M., Pawlazcyk, C., Kosec, M. and Setter, N., Effect of Nb doping on the microstructure of sol–gel derived PZT thin films. *J. Am. Ceram. Soc.* 1995, **78**(6), 1513–1520 [and references therein].
10. Peláiz Barranco, A., *Sistemas Ternarios Basados en $PbTiO_3$–$PbZrO_3$ (PZT)*. Grade thesis, Havana University, Cuba, 1995.
11. Peláiz Barranco, A., *Propiedades Ferroeléctricas y Mecanismos de Conductividad en el Sistema PZT Modificado*. Ph.D. thesis, Havana University, Cuba, 2001.

12. Okazaki, K. and Nagata, K., Effects of grain size and porosity on electrical and optical properties of PLZT ceramics. *J. Am. Ceram. Soc.* 1972, **56**(2), 82–86.
13. Randall, C. A., Kim, N., Krucera, J. P., Cao, W. and Shrout, T. R., Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics. *J. Am. Ceram. Soc.* 1998, **81**, 677–688.
14. Arlt, G., *Ferroelectrics* 1990, **104**, 271.
15. Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology, Vol 29*. Springer-Verlag, Berlin, 1993, pp. 339–351.
16. Lozinski, A. H., Two-stage processing of electrooptic PLZT ceramics. In *Proceeding of Photovoltaic and Optoelectric Processes*. Bucharest, Romania, July 4–7, 1998, pp. 69–71.