Journal of the European Ceramic Society 21 (2001) 1353–1356
www.elsevier.com/locate/jeurceramsoc

Effect of Nb doping on the microstructural and electrical properties of the PZT ceramics

M. Pereira *, A.G. Peixoto, M.J.M. Gomes

Department of Physics, IMAT, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Received 4 September 2000; received in revised form 5 December 2000; accepted 10 December 2000

Abstract

The aim of this study is the determination of the effect of the aliovalent Nb^{5+} doping in PZT (65/35) based bulk materials in their microstructural evolution and their electrical properties. The Nb content was chosen in the range 0–10 mol%. These materials were prepared using the conventional way. The calcined mixture was found to be monophasic perovskite powder. The characteristics of the as-formed powder were described and related to the microstructural ones in the sintered material, namely the grain size evolution and the porosity elimination. Nb addition was found to alter significantly the parameters of the crystal cell, and so, the dielectric and ferroelectric properties. The electrical properties were compared with those of common PZT and PLZT materials; As in the case of PLZT (x/65/35), several Nb containing compositions show diffuse phase transition (DPT) characteristics. The Nb content is also leading to softening of the PZT. However, the ferroelectric and dielectric behaviour kept strongly dependent on the microstructural characteristics. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Ferroelectric properties; Perovskites; PZT; Sintering

1. Introduction

Since the discovery of ferroelectric ceramics in the 1940s, lead-based perovskites have emerged as one of the most widely studied and technologically important classes of ferroelectric oxides. Among these, one of the more investigated compounds, the lead zirconate titanate, (PZT) crystallises in the perovskite structure, i.e. $A^{II}B^{IV}O_3$ unit cell structure.[1,2]. Many aliovalent compositional alterations to PZT have been studied either with higher valence substitutions (donors), either with lower valence ions (acceptors). La^{3+} is a common substitution on Pb^{2+} site, leading to the well-known high performance PLZT materials. Therefore, some of the critical properties of PZT were optimized by the addition of donor dopant ions. Several modified PZT materials have found applications such as piezoelectric and electrostrictive devices in the bulk form, and multi-layer capacitors, electro-optic shutters and pyroelectric sensors in the thin film form.[3]

Also, Nb^{5+} can be considered as a donor dopant for PZT materials, since it substitutes Ti^{4+}/Zr^{4+} ions. Because of the charge compensation, vacancies in A and/or B sites are created in the perovskite structure, at least for PLZT.[4] Barlingay et al.[5] assume that in bulk PZT ceramics, lead vacancies, V''_{Pb}, are the compensating defects, whereas, in Nb doped films produced by sol-gel, the compensation is due to V''''_{Ti}.

In the case of niobium doping, i.e. PZTN materials, some recent works deal with several improvements when produced as thin film: an increase in the electrical resistivity and an enhancement of hysteresis squareness and fatigue behaviour.[6,7] Few publications deal with PZTN bulk materials and the relationship microstructure-properties. In the present paper, we intend to present a detailed study of the effects of the niobium doping on the perovskite formation and its stability, since these properties are very different on films.

2. Experimental

The materials were prepared by conventional powder processing technique, i.e. starting from high purity raw

---

* Corresponding author. Tel.: +351-25360-4320; fax: +351-25367-8981.

E-mail address: mpereira@fisica.uminho.pt (M. Pereira).

0955-2219/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(01)00017-6

materials, TiO_2 (Merck, 99%), ZrO_2 (Aldrich, 99%), Nb_2O_5 (Aldrich, 99.9%) and $PbCO_3$ (Merck, 99%). Stoichiometric amount of the oxides and carbonate were weighed according to the general formula of PZTN (65/35/x) assuming lead vacancies formation:

$$Pb_{1-x/2}(V''Pb)_{x/2}(Zr_{0.65}Ti_{0.35})_{1-x}Nb_xO_3$$

where x, the Nb content, is adjusted in the range 0–10% mol.

After 2 h ball milling with ZrO_2 balls, the mixed powder was calcined in air, 2 h, at 875°C.

The calcined powders were then cold pressed into cylindrical pellets 20 mm in diameter, and about 2 mm thick. The compacts were sintered at 1200°C for 40 min with the double crucible arrangement, with $PbZrO_3$ atmosphere powder.

The phase content of the samples was monitored by X-ray diffraction (XRD) (Philips PW 1710) using Ni filtered CuK_α radiation. Morphology studies and grain size measurements (line-intercept method) were performed by scanning electron microscopy (SEM) using a microscope Leica S-360 equipped for energy dispersive spectroscopy (EDS). The density of the sintered compacts was measured by the Archimedes' method using water.

The dielectric properties of the ceramics were investigated using an inductance–capacitance–resistance (LCR) meter (Model QuadTec 7600 Precision), in the frequency range 100 Hz to 1 MHz. The P–E hysteresis loop was determined with a modified Sawyer-Tower circuit by applying a maximum field of 3 kV/mm at 50 Hz.

3. Results and discussion

3.1. Evolution of the cell parameter

Taking into account the different coordination numbers [12] and [6] of the different cations A and B, respectively, in the perovskite structure, Herbert[1] reported that cations would fit exactly into the idealized structure if they have ionic radii of 1.38 Å for A cations, and 0.57 Å for B sites, assuming 1.38 Å for the radius of O^{2-}.

In the present case, PZT, the ionic radii reported elsewhere[8] give Pb^{2+} [12] = 1.63 Å, Zr^{4+} [6] = 0.86 Å, Ti^{4+} [6] = 0.745 Å, the structure with these larger ionic radii accommodate these different ions. The introduction of Nb^{5+}, which ionic radius [6] is about 0.78 Å, i.e. an intermediary value, should also give a perovskite phase.

The XRD spectra of some PZTN (65/35/x) ceramics after sintering are presented in Fig. 1. It shows mainly a set of peaks with regular distribution, which corresponds to a rhombohedral phase. It is worthy to note that, up to 7% mol Nb, all spectra show no evidence of pyrochlore phase formation. On the contrary, in the case of thin films, Klissurska et al.[6] reported that Nb content acts to stabilize the transient pyrochlore phase after annealing temperature higher than 700°C. At 8%, some additional peaks appear that could be indexed as the reflections of a fluorite type structure.[9] The intensity of these additional peaks increased with the niobium content. The solubility limit of Nb^{5+} ions in the perovskite structure seems to be reached close to 7% mol. Above this amount, the niobium contributes to the formation of a secondary phase, as indicated by XRD spectra (Fig. 1).

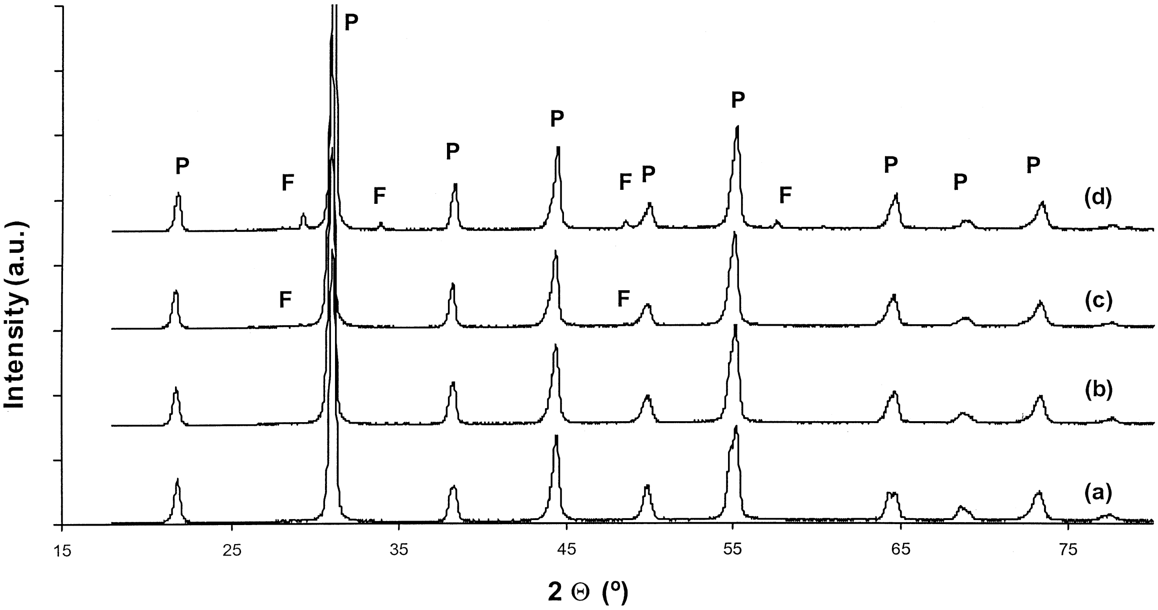

Fig. 1. XRD patterns for PZTN compositions (65/35/x) with various Nb content: (a) 2% mol; (b) 5% mol; (c) 8% mol; (d) 10% mol; (F, fluorite phase; P, perovskite phase).

Moreover, EDS analyses (Table 1) show that a minor phase (fluorite) with high Nb and low Zr content is present in the PZTN (65/35/10). The main phase (perovskite) was found to have a composition near the theoretical one but with lower Pb and higher Zr content.

Based on the rhombohedral structure, the calculation of the cell parameter and distortion angle has been done by least-squares method (Table 2). The lattice parameters error is 0.05%. The theoretical density of monophasic samples has then been calculated in order to evaluate sintered materials.

As the Nb content increases, the rhombohedral cell of the PZT tends to spread in the (111) plane. Niobium addition produces a strain of the cell because of the increase of the electrostatic interaction in the NbO_6 octahedra. Also, the density of the PZTN phase decreases linearly with the increase of the Nb doping. In fact, Nb enters in the perovskite up to 7%; but above 8% part of the niobium reacts mainly with Pb and Ti to form a secondary phase, allowing the formation of a Zr rich perovskite phase of PZTN. The later explains the expansion of the lattice of the perovskite phase, in Table 2.

3.2. Influence of niobium content on the sintering and on grain growth

The influence of the niobium content on the grain size and density is presented in Fig. 2. In comparison to previously published work on bulk PZTN,[10] for comparable heat treatment temperature (1200°C) and equivalent density (7.7 g/cm^3), the sintering holding time in our work is very short (up to 1000 min vs. 40 min). This is mainly due to the reactive powders used as raw materials, and to the reactive ones produced after calcination (carbonate decomposition). The mean particle size of the calcined-ball milled powder is about 0.2–0.5 μm.

Table 1
EDS analyses (% mol) of the phases present in PZNT (65/35/10)

Phase	Pb	Zr	Ti	Nb
65/35/10 (Theor.)	49	30	16	5
Perovskite	44	36	16	3
Fluorite	51	13	11	25

Table 2
Structural data for Nb-doped PZT (65/35/x) compounds

x% Nb	a (Å)	α (°)	Cell volume (Å^3)	Theor. density (g/cm^3)
0	4.0863	89.85	68.23	8.062
1	4.0748	89.82	67.66	8.083
2	4.0811	89.81	67.97	7.999
3	4.0803	89.76	67.93	7.958
4	4.0913	89.89	68.48	7.848
5	4.0818	89.97	68.01	7.856
6	4.0879	89.96	68.31	7.775
7	4.0930	90.03	68.57	7.699
8	4.0950	90.03	68.67	–
9	4.0912	89.93	68.48	–
10	4.1030	90.05	69.07	–

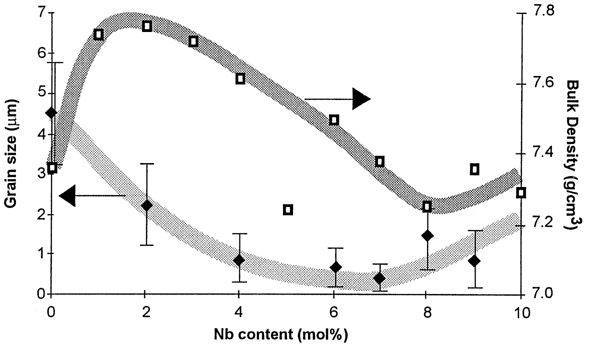

Fig. 2. Density and grain size for some PZTN compositions vs. Nb content, after firing (1200°C, 40 min).

After atmosphere sintering, the final density is high (> 92%). As the Nb content is increased, the densification seems to be more effective in relation to the undoped PZT. The relative density increased up to 96% and the grain size keeps small. For Nb > 7%, the new biphasic structure, fluorite and perovskite phases, seems to enhance the grain growth.

Atkin et al.[10] reported that sintering kinetics of the undoped PZT can be described by lattice diffusion of vacancies from pores to grain boundaries (Coble's model), and that Nb doping reduces the diffusion coefficient: the vacancies as created by this doping are supposed to be bound to the impurity ion (Nb), so that they inhibit the mass transport.

Considering the grain growth, doping with Nb keeps the grain size small, i.e. Nb is an effective grain growth inhibitor. In several materials[11] it was reported that pores, second phase inclusions, or solid solution impurities inhibited the grain growth; also here, the doping ions can concentrate near the grain boundaries and reduce their mobility. Moreover, with a reduced grain size, i.e. remaining reactive, these powders based on PZTN are more effective in accelerating sintering.

3.3. Dielectric and polarization investigations

The dielectric constant was measured as a function of temperature for various PZTN compositions. Plots of dielectric constant measured at 1 kHz are shown in Fig. 3. The permittivity and the Curie point decrease with the niobium content. Also, the dielectric constant as a function of temperature does not show a sharp transition but exhibits diffuse behaviour. The observed broadening of the transition region in PZTN ceramics can be a result of compositional fluctuations. Large differences in the valence of the various B ions result in a strong tendency for the material to order through electrostatic

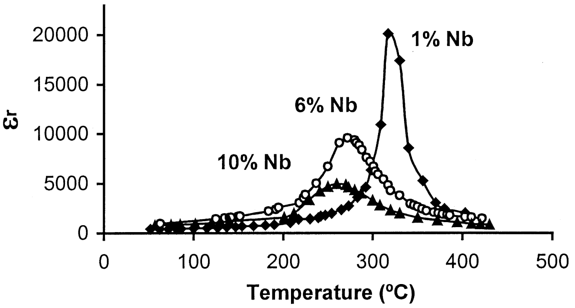

Fig. 3. Dielectric behaviour for various PZTN compositions with Nb content between 1 and 10% mol.

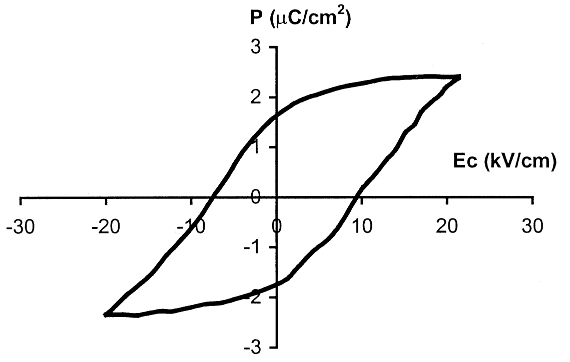

Fig. 4. Polarization vs. electric field hysteresis loop of PZTN (65/35/5).

forces,[12] hence here the low difference in the valences (25%) gives an ordering less than perfect and chemical inhomogeneity remains.

Ferroelectric properties were obtained from P–E hysteresis loops, on PZTN (65/35/5). As shown in Fig. 4, this composition possesses a ferroelectric memory loop with remnant polarization 2 μC/cm^2. The loop presents squarer shape than PZT (65/35) or PLZT (6/65/35). As comparison, in the case of PZT (65/35), Dai et al.[13] reported a dielectric constant and remnant polarization of 500 and ≈0 μC/cm^2 (double loop characteristics), respectively, at room temperature, while in the case of PLZT (6/65/35), the dielectric constant and the remnant polarization are about 1800 and 33 μC/cm^2, respectively.[3] The lower polarization in this PZTN material could be due to the residual porosity (measured around 7.9%),[14] the low grain size (~1 μm)[14] and the composition of the perovskite.[1–3] Also, it is interesting to note that the coercive field in PZT is over 15 kV/cm, whereas with Nb doping the field needed is about 9kV/cm, which is higher than the one of PLZT (6 kV/cm), i.e. La enhances the polarization switching better than Nb.

4. Conclusions

The solubility limit of niobium in PZT materials (perovskite structure) is about 7% mol. Above this concentration, a secondary fluorite phase is formed, containing also Pb and Ti. Niobium oxide is a good sintering aid for PZT based materials (high density, low grain size). The addition of Nb decreases the dielectric constant maximum and the Curie point. At low concentration (5% mol), Nb doping in PZT (65/35) leads to an enhanced ease of the polarization switching under ac-field, i.e. "soft PZT" behaviour, and shows the nonlinear loop from a memory ferroelectric.

Acknowledgements

This work was supported by the Science and Technology Portuguese Council (FCT), under the project PRAXIS/C/CTM/12140/1998.

References

1. Herbert, J. M., *Ferroelectric Transducers and Sensors*. Gordon and Breach Science Publishers, London, 1985 pp. 299–300.
2. Moulson, A. J. and Herbert J. M., *Electroceramics — Materials-Properties-Applications*. Chapman et Hall, London, (pp. 79 and 247–248).
3. Dausch, D. E. and Haertling, G. H., The domain switching and structural characteristics of PLZT bulk ceramics and thin films chemically prepared from the same acetate precursor solutions. *J. Mater. Sci.*, 1996, **31**, 3409–3417.
4. Härdtl, K. H. and Hennings, D., Distribution of A-site and B-site vacancies in (Pb,La)(Ti,Zr)O_3 ceramics. *J. Am. Ceram. Soc.*, 1972, **55**(5), 230–231.
5. Barlingay, C. K. and Dey, S. K., Dopant compensation mechanism and leakage current in $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films. *Thin Solid Films*, 1996, **272**, 112–115.
6. Klissurska, R. D., Brooks, K. G., Reaney, I. M., Pawlaczyk, 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.
7. Griswold, E. M., Sawyer, M., Amm, D. T. and Calder, I. D., The influence of Nb doping on lead zirconate titanate ferroelectric thin films. *Can. J. Phys.*, 1991, **69**, 260–264.
8. Muller, O. and Roy, R., *The Major Ternary Structural Families*. Springer-Verlag, Berlin, 1975 pp. 5–7.
9. Wilkinson, A. P., Speck, J. S., Cheetham, A. K., Natarajan, S. and Thomas, J. M., In-situ X-ray diffraction study of crystallization kinetics in $PbZr_{1-x}Ti_xO_3$ (PZT, $x=0.0$, 0,55, 1.0). *Chem. Mater.*, 1994, **6**, 750–754.
10. Atkin, R. B. and Fulrath, R. M., Point defects and sintering of Lead Zirconate-Titanate. *J. Am. Ceram. Soc.*, 1971, **54**(5), 265–270.
11. Rahaman, M. N., *Ceramic Processing and Sintering*. Marcel Dekker, New York, 1995 pp.476–482..
12. Ganesh, R. and Goo, E., Dielectric and ordering behaviour in $Pb_xCa_{1-x}TiO_3$. *J. Am. Ceram. Soc.*, 1997, **80**(3), 653–662.
13. Dai, X., Xu, Z. and Viehland, D., Effect of oxygen octahedron rotations on the phase stability, transformation characteristics and polarization behaviour in the Lead Zirconate Titanate crystalline solution series. *J. Am. Ceram. Soc.*, 1995, **78**(10), 2815–2827.
14. Okazaki, K. and Nagata, K., Effect of grain size and porosity on electrical and optical properties of PLZT ceramics. *J. Am. Ceram. Soc.*, 1973, **56**(2), 82–86.