ELSEVIER

Ceramics International 25 (1999) 239–244

CERAMICS
INTERNATIONAL

The effect of isostructural seeding on the microstructure and piezoelectric properties of PZT ceramics

Maria A. Zaghete[a,*], José A. Varela[a], Mario Cilense[a], Carlos O. Paiva-Santos[a], Wanda C. Las[a], Elson Longo[b]

[a]*Instituto de Química, Universidade Estadual Paulista - UNESP, CP 355 CEP 14800-900 Araraquara SP, Brazil*
[b]*Departamento de Química - Universidade Federal de Sao Carlos - UFSCar, CP 676 CEP 13565-905 Sao Carlos SP, Brazil*

Received 16 September 1997; accepted 11 February 1998

Abstract

Pechini's method was used to prepare lead titanate zirconate with Zr/Ti ratio equal to 53/47. X-ray diffraction data revealed the presence of a rhombohedral phase, rich in zirconium, due to difference in carbonate stabilities, in PZT ceramics calcined at 600°C. Infrared spectroscopy presented COO- bonds in the 1400 cm^{-1} region, which disappeared after calcining at 700°C. Seeds with rhombohedral (PZT 57/43) or tetragonal structure (PZT 45/55) were added to the precursor. The microstructure was differentially influenced by the nature of seed particles. Rhombohedral nuclei promoted preferential crystallization of lead zirconate. This heterogeneity directly reflected on values of k_p and d_{33}. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

In lead zirconate titanate (PZT) preparation, the control of some parameters is important to achieve the desired material properties. These parameters include the absence of intermediate crystalline phases, a defined and fixed stoichiometry, as well as a homogeneous lead distribution in the microstructure.

Methods such as sol–gel [1–3] and co-precipitation [1] have been used, although the former utilizes expensive precursors and a critical lengthy drying process; the latter is limited to cation solutions with similar solubility constants. Pechini's method [4] which employs complexing of cations in an organic medium, makes use of low cost precursors and results in a homogeneous ion distribution at molecular level. However, this process yields metastable precursor compounds which, when crystallized, go through polymorphic transformations before reaching a stable structure [5].

Recently, the control of microstructure and crystalline transformations have been studied by addition, to the metastable phase, of particles, called seeds, crystallographically similar to the desired final structure. Messing et al. [6,7] and Hennings [8] have proved the efficiency of such seeds in the production of α-alumina from boehmite nucleated with α-alumina or Fe_2O_3. The pioneer work of Turnbull and Vonnegut [9] shows that the larger the similarity between lattice parameters of seeds and the nucleating phase, the smaller the nucleation barrier energy.

It has been reported that the loss of stoichiometry by PbO evaporation during sintering, as well as the formation of lead-rich grain boundaries, generated by the introduction of a lead excess in the initial composition, decrease the planar coupling coefficient, k_p, and piezoelectric strain coefficient, d_{33}, values and affect their reproducibility [10]. Other factors such as defects [11], grain size [12], wall domain mobility [12] and density [10] are reported to affect the piezoelectric and dielectric properties.

2. Experimental

The procedure of PZT synthesis, based on Pechini's method [4], makes use of the capability that certain α-hydroxycarboxylic organic acids possess of forming polybasic acid chelates with several cations. When mixing with a polyhydroxylic alcohol and heating, the chelate

---

* Corresponding author.

PII: S0272-8842(98)00029-7

transforms into a polymer, maintaining the cations homogeneously distributed. The organic part is subsequently eliminated at temperatures as low as 300°C, forming reactive oxides with well-controlled stoichiometry. Pure PZT with composition $Pb(Zr_{0.53}Ti_{0.47})O_3$ was prepared from the metal-citrate complex polyesterified in ethylene glycol. Appropriate quantities of Zr, Ti and Pb solutions were mixed and homogenized by stirring at 90°C for 3 h. Next, the temperature was increased to 130–140°C, yielding a high viscous polyester resin.

Most of the organic matter was decomposed in a box furnace, by carefully heating the polyester inside a glass beaker from room temperature up to 300°C, next increasing to 400°C, soaking 2 h at each temperature. The resulting material was milled with zirconia balls in an isopropyl alcohol medium for 3 h. The powder was then calcined at 400°C for 1 h to eliminate the residual organic matter. Further calcining was conducted at 700°C for 3 h and the powder milled for 6 h.

DTA analyses of resins precalcined at 300°C for 2 h in a box furnace, were carried out in atmosphere of synthetic air (WHITE MARTINS) at a heating rate of 10°C/min and TG analyses of resins prepared at 140°C were carried out in atmosphere of synthetic air at a heating rate of 5°C/min.

Rhombohedral single phase PZT (57/43) and tetragonal single phase PZT (45/55) prepared by Pechini's method were respectively used as rhombohedral (RS) and tetragonal (TS) seeds. The powder was calcined at 800°C for 2 h and ball milled for 2 h in ethylene glycol medium. The suspension was centrifuged at 3000 rpm for 30 min to separate the large particles. The floating material was standardized by gravimetry and stored. A sedimentation test showed that 80% of the seed particles had sizes between 0.3 and 0.1 μm and 20% were smaller than 0.1 μm. Seeded PZT was prepared by adding seeds to the PZT precursor resin and homogenizing as described above. The high organic solution viscosity allows a homogeneous seed distribution and prevents separation. Seeds were added in the proportion of 1, 3 and 5 wt %, relative to the final product mass.

Powders were analysed by X-ray diffraction (XRD) for phase determination and by infrared (IR) and Raman spectroscopies for the presence of organic radicals. The powders were isostatically pressed (230 MPa) into pellets, using 2 wt% solution of polyvinyl alcohol (PVA) in water as a binder. The pellets were sintered inside a box furnace at 1100°C for 2 h in a closed system containing 15 wt% of ($PbZrO_3 + 5$ wt% ZrO_2), relative to the pellets' mass, to generate a lead atmosphere. The density of fired pieces was determined by the water displacement method. A scanning electron microscope (SEM) was used to analyse the microstructure, shape and size of grain. Energy dispersive X-ray microanalysis spectroscopy (EDS) was used for compositional determination.

The samples were coated on the parallel surfaces with silver paste to provide electrodes and poled by applying a dc electric field of 30 kV/cm at 100°C for 30 min in a silicone oil bath. The resonance and anti-resonance frequencies, f_r and f_a, were measured in the HP Spectrum Analyzer, model 3585A, and k_p was determined according to the procedure described by Haertling [13]. The d_{33} was determined using an American Piezo Ceramics apparatus calibrated with piezoelectric standards.

3. Results and discussion

There are controversies about the width of the morphotropic region when chemical processes are used to prepare PZT [14–17]. On one hand, there is agreement that the PZT tetragonal phase is the first one to crystallize in conventionally prepared PZT, since titanium is more reactive to form the lead titanate. However, XRD data [18] obtained for samples prepared by Pechini's method show an opposite behaviour, since the rhombohedral phase is the first one to be formed during calcination, independently of sample stoichiometry. Fig. 1 shows the XRD data for one composition (52/48) where, up to 700°C, peaks appear at 2° equal to 21°, 44°, 50° and 54°, characteristic of the rhombohedral phase. At 800°C, these peaks split into the characteristic peaks of the tetragonal phase. IR spectroscopy carried out on PZT samples showed two vibrational peaks, one in the 800–400 cm^{-1} region and the other at $\sim$1407 cm^{-1} (Fig. 2). The former is due to metal-oxide binding; the latter refers to carbon-oxygen vibrations in carbonates. Raman spectroscopy shows a small peak in 1057 cm^{-1}, characteristic of carbonates, in agreement with IR. This is also in agreement with Kumar et al. [19], where the presence of carbonates was observed in $BaTiO_3$ prepared by the Pechini process. The peak at 1400 cm^{-1} is very small after calcining at 600°C. Considering that PZT is formed by solid solution of lead zirconate (PZ) and lead titanate (PT), these phases were separately

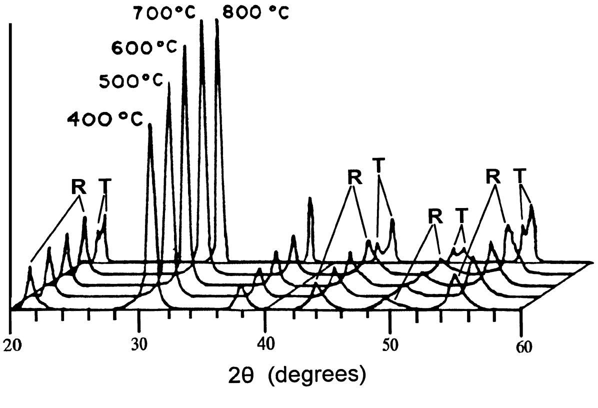

Fig. 1. XRD data for PZT 52/48 powder calcined for 3 h at the temperatures indicated.

prepared and analysed by IR spectroscopy. Semi-quantitative determination of formed carbonates was performed with samples prepared by weighing equimolar amounts of zirconium and titanium ions and diluting each of them in the same KBr quantity. Analyzing the 1400 cm^{-1} band intensities for both materials, it was observed that they are due to lead titanium carbonate in the PT sample (Fig. 3) and to lead zirconium carbonate in the PZ sample (Fig. 4), and that the former is larger than the latter. During the polymer decomposition in this synthesis method, mixed lead and zirconium (Pb/Zr) carbonate as well as mixed lead and titanium (Pb/Ti) carbonates are formed with different stabilities, depending on the bonded ion (titanium or zirconium). The titanate anion is more reactive and favours the formation of Pb/Ti carbonate. TGA analysis was carried out for PT, PZ and PZT resins, showing that PT decomposition is slower than PZ decomposition (Fig. 5). Above 465°C there is no weight loss for PZ but there is still a small weight loss ($\approx 2\%$) for PT around 727°C. Thus, after calcining PZT for 3 h at 600°C, there is less Pb/Zr carbonate left than Pb/Ti carbonate. This leads to the formation of a zirconium rich PZT phase, since more zirconium ions are available than titanium, from

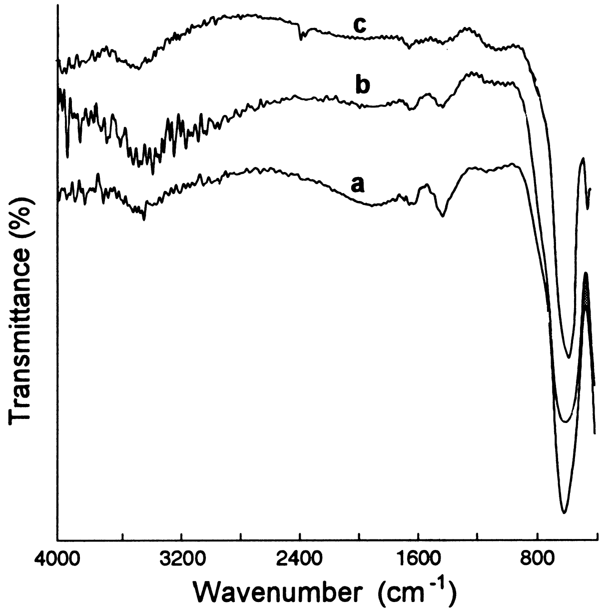

Fig. 2. IR bands for PZT 53/47 powder calcined at (a) 400°C, (b) 500°C and (c) 600°C for 3 h.

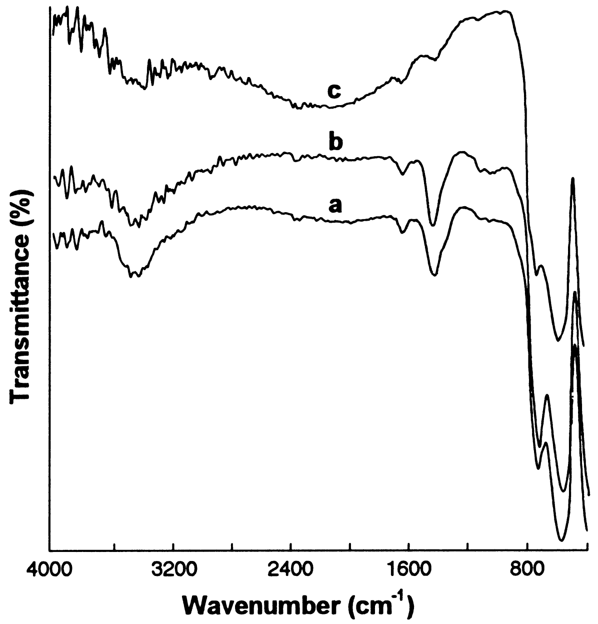

Fig. 3. IR bands for PbTiO$_3$ powder calcined at (a) 400°C, (b) 600°C and (c) 700°C for 3 h.

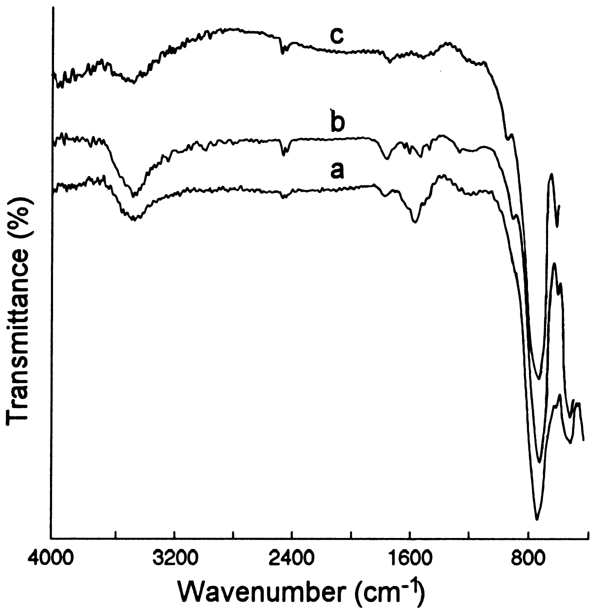

Fig. 4. IR bands for PbZrO$_3$ powder calcined at (a) 400°C, (b) 600°C and (c) 700°C for 3 h.

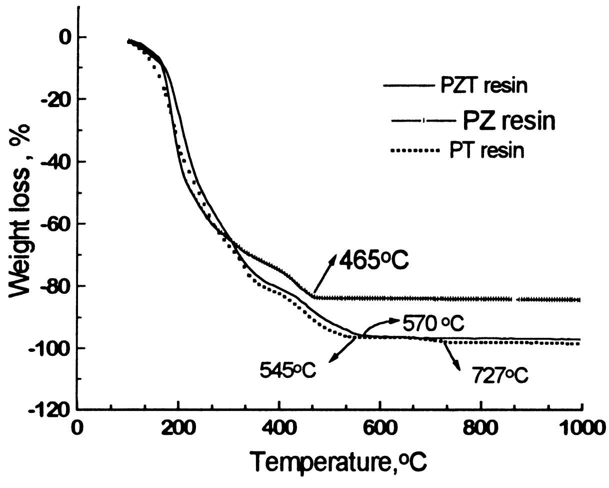

Fig. 5. TG curves for PT, PZ and PZT resins, obtained at synthetic air atmosphere and heating rate of 5°C·min^{-1}.

the carbonate decomposition. During increase of the calcining temperature, the Pb/Ti carbonate continues to dissociate up to 727°C. At this temperature, the IR band due to carbonates is very small. During this process, the remaining Ti ions diffuse into the zirconium rich PZT phase, forming the stoichiometric PZT.

Pechini's method, therefore, differs from the conventional method, in two aspects. One refers to the PZT synthesis temperature, which is lower in the present procedure. In the conventional method, the PZT phase is obtained above 800°C, while in the present method, this phase begins to form at 400°C, without the presence of intermediate phases. The other aspect refers to the different carbonate stabilities, which favor the rhombohedral phase, rich in zirconium, instead of the tetragonal phase. The rhombohedral phase becomes dominant when calcining below 700°C. This result is corroborated by a quantitative analysis of XRD data [18]. Recently Leite et al. [20] also observed the preferential formation of the rhombohedral phase for unseeded PZT 53/47 prepared by partial oxalate precipitation and calcined at low temperature (500°C).

PZT seed particles rich in zirconium or titanium were added to the precursor resin of PZT with stoichiometry 53/47. Fig. 6 shows differential thermal analysis (DTA) results for unseeded and seeded precursors, where a displacement to low temperatures (Te) of the crystalline phase formation is seen. For the unseeded PZT, $T_e = 435$°C, whereas for PZT with 3 and 5% of seeds this temperature decreases respectively to 375 and 360°C. The decrease in T_e is a consequence of the lower apparent activation energy for crystallization needed to nucleate the crystalline phase.

Considering the predominance of the rhombohedral phase of PZT 53/47 obtained by calcining at temperatures below 700°C and the presence of mixed carbonates of Pb/Ti and Pb/Zr, a model for the action of seeds is proposed. During precursor decomposition between 400 and 600°C, there is liberation of Zr ions because its carbonate is less stable. When the seeds are present, they absorb that Zr ions liberated, growing as PZT grains rich in Zr. At that temperature, the Zr-rich PZT seeds (RS) are in the paraelectric phase with cubic unit cell higher than that of Ti-rich PZT [21,22], and can favor the epitaxial grain grow around the seeds during the PZT phase formation and, consequently, a matrix slightly less-rich in zirconium results. The PZT grains grown from these seeds are indicated in Figs. 7a and b as dark grains distributed in the matrix. The higher the seed concentration in the amorphous phase the higher the dark grain frequency observed in the sintered material. Quantitative analysis of these dark grains and of matrix (pure) were made by EDS and are shown in Table 1. The analysis indicates that these grains are rich in zirconium and its concentration is variable.

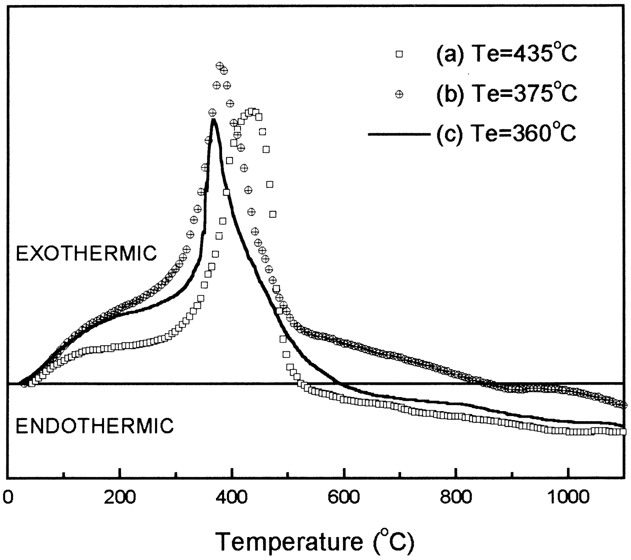

Fig. 6. DTA curves for resins pre-decomposed at 200°C. (a) Unseeded PZT; PZT seeded with: (b) 3 wt% and (c) 5 wt%.

Otherwise tetragonal seeds, rich in titanium, when in a matrix rich in zirconium ions do not favor epitaxial growth but decrease the energy for nucleation of the PZT crystalline phase as shown in Fig. 5. For samples with tetragonal seeds sintered at 1100°C for 2 h, no dark grains are observed (Figs. 7e and f). Therefore, the resulting microstructure is more uniform, with smaller and regular grains, and more homogeneous than for unseeded (Figs. 7c and d) and rhombohedral seeded PZT (Figs. 7a and b).

The composition heterogeneity caused by the addition of rhombohedral seeds affects the piezoelectric properties as observed in Fig. 8. The general compositional change, shown in Table 1, is responsible for relatively small k_p and d_{33} values. On the other hand, the tetragonal seeds do not promote this change, since there is no preferential growth, and, as a consequence, these parameters are higher.

Although there are regions with heterogeneous composition, caused by the difference in carbonate stability, there is also a positive action, from both types of seeds, in the microstructure characteristics. Seeded material present a more uniform microstructure than unseeded material. Although the microstructure is uniform, the phase rich in zirconium causes the decrease in k_p and d_{33} values. These constants are higher for the tetragonal seeded samples, since polarization is maintained due to the difficulty in dipole reorientation in a homogeneous and uniform microstructure.

4. Conclusions

The difference in stability of mixed carbonates, formed during decomposition of organic matter in the Pechini's synthesis, promotes heterogeneity in the PZT

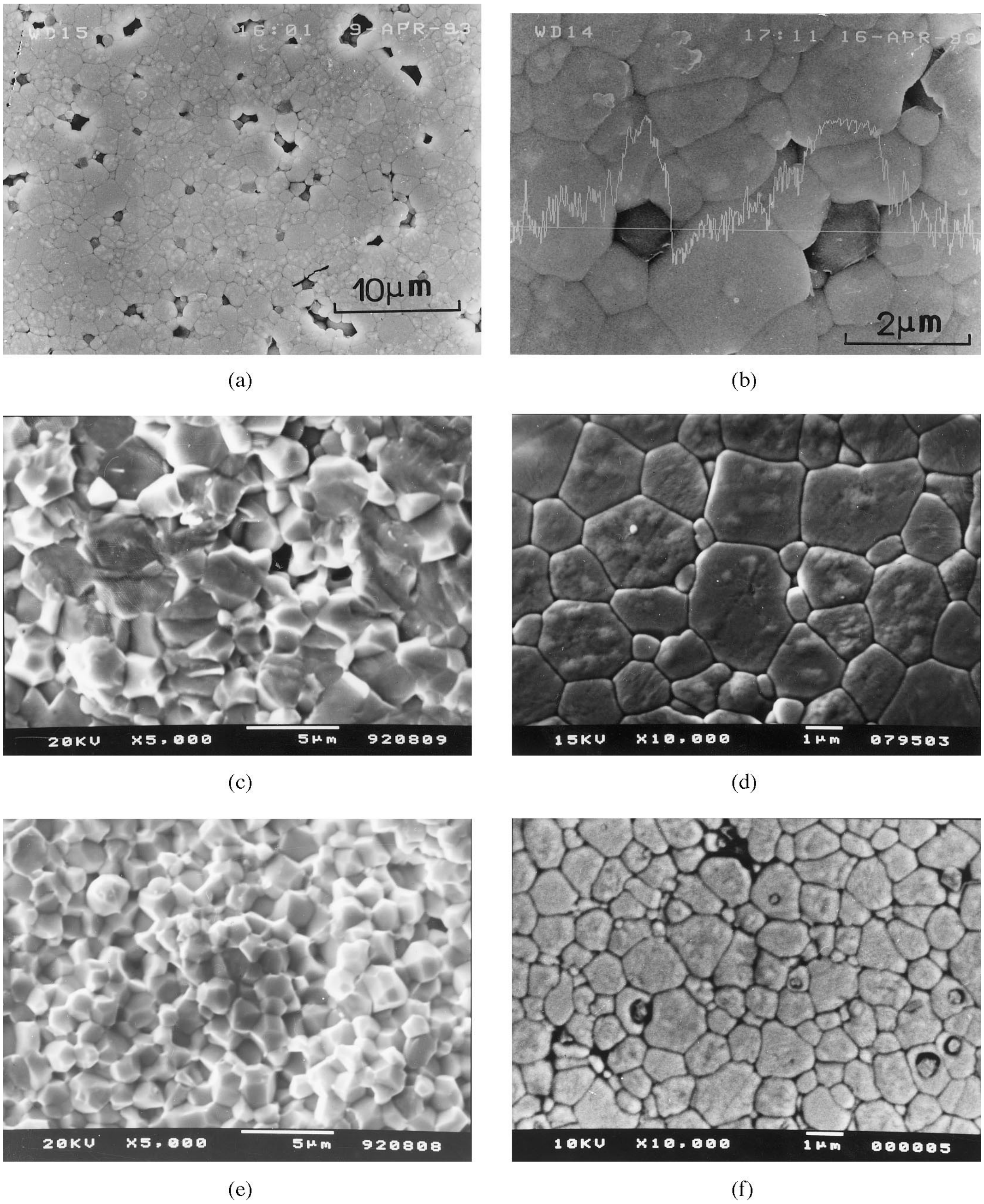

Fig. 7. Microstructures of PZT 53/47 sintered at 1100°C for 2 h: (a) with 5 wt% of rhombohedral seeds showing grains rich in PZ; (b) the same with zirconium quantification; (c) fractured and (d) polished surface of unseeded PZT; (e) fractured and (f) polished surface of PZT with 5 wt% of tetragonal seeds.

Table 1
Chemical analysis by EDS of PZT sintered at 1100°C for 2 h

Ratio Zr/Ti	Cation	Cation molar percentage		
		Pure PZT	RS-PZT	
			Black grains	Gray grains
53/47	Zr	29.48	68.70	53.39
	Ti	26.27	9.40	14.69
	Pb	44.25	21.90	31.92

composition, favouring the formation of a zirconium rich grains in rhombohedral seeded ceramics. The heterogeneous composition promoted by rhombohedral seeds, has deleterious effect on the piezoelectric constant and the planar coupling factor. The tetragonal and rhombohedral seeds accelerate the PZT phase formation and promote uniform microstructure, although only tetragonal seeds are able to improve the k_p and d_{33} constants.

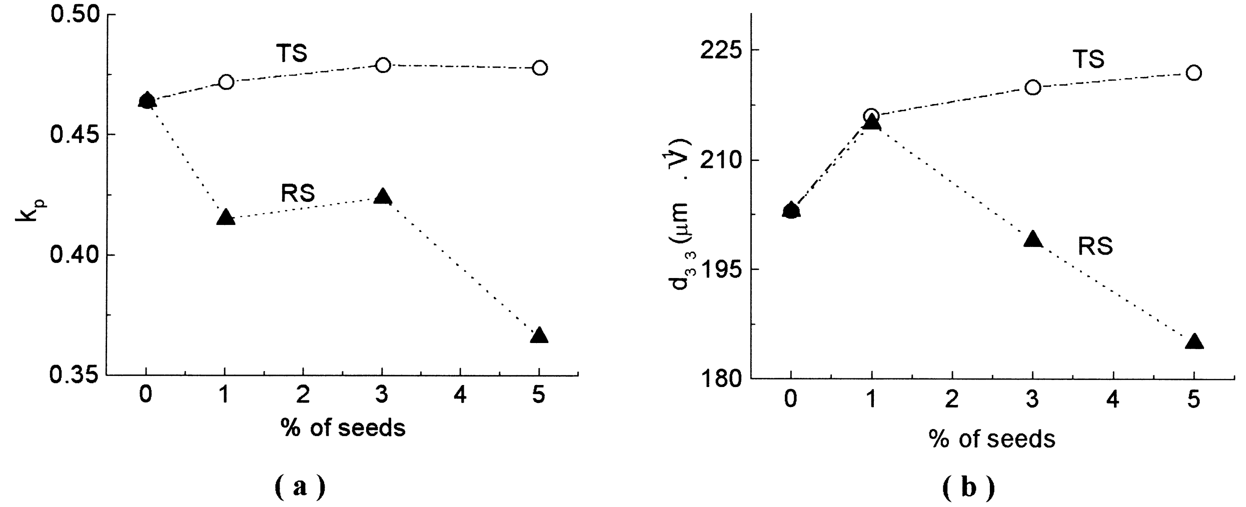

Fig. 8. Planar coupling factor (a) and piezoelectric constant (b), for PZT 53/47 seeded with (TS) tetragonal seeds; (RS) rhombohedral seeds.

Acknowledgements

The authors acknowledge FAPESP, FINEP/PADCT and CNPq for granting this research. They are also indebted to Dr. P. S. Pizzani, from the Universidade Federal de Sao Carlos, Brazil, for the Raman spectroscopy analysis.

References

[1] A. Kato, Study on powder preparation in Japan, Am. Ceram. Soc. Bull. 66 (4) (1987) 647–650.
[2] L.M. Sheppard, International trends in powder technology, Am. Ceram. Soc. Bull. 68 (5) (1989) 979–985.
[3] G. Tomandl, A. Stiegelschmitt, R. Bohner, Lowering the sintering temperature of PZT ceramic by sol-gel processing; in: L.L. Hench, D.R. Ulrich (Eds.), Science of Ceramics Chemical Processing, John Wiley & Sons, New York, 1986, pp. 3–173.
[4] M.P. Pechini, Method for preparing lead and alkaline-earth titanates and niobates and coating method using the same to form a capacitor U. S. Patent n° 3 330 697, 1967.
[5] C.N. Rao, J. Rao, Phase transformations in solids, Prog. Solid State Chem. 4 (1967) 67.
[6] G.L. Messing, M. Kumagai, R.A. Shelleman, J.L. McArdle, Seeded transformation for microstructural control in ceramics, in: L.L. Hench, D.D. Ulrich (Eds.), Science of Ceramic Chemical Processing, John Wiley & Sons, New York, 1985, pp. 259–271.
[7] J.L. McArdle, G.L. Messing, Seeding with γ-alumina for transformation and microstructure control in boehmite-derived α-alumina, J. Am. Ceram. Soc. 69 (5) (1986) C98.
[8] D. Hennings, Control of microstructure with seed grains, Ceramics Intern. 17 (1991) 283–286.
[9] D. Turnbull, B. Vonnegut, Nucleation catalysis, Ind. Eng. Chem. 44 (6) (1952) 1292–1298.
[10] S.C. Chiang, M. Nishioka, F.M. Fulrath, J.A. Pask, Effect of processing on microstructure and properties of PZT ceramic, Ceramic Bull. 60 (4) (1981) 484–489.
[11] L. Wu, C.-C. Wei, T.-S. Wu, C.-C. Teng, Dielectric properties of modified PZT ceramics, J. Phys. C : Solid State Phys. 16 (1983) 2803–2812.
[12] T. Yamamoto, Optimum preparation methods for piezoelectric ceramics and their evaluation, Ceramic Bull. 71 (6) (1992) 978–985.
[13] G. H. Haertling, Piezoelectric and electrooptic ceramics, in: R. C. Buchanan (Ed.), Ceramic Materials for Electronics, Marcel Dekker, New York, 1986, c.3, p. 3.
[14] P. Ari-gur, L. Benguigui, X-ray study of the PZT solid solutions near the morphotropic phase transitions, Solid State Commun. 15 (6) (1974) 1077–1079.
[15] S.A. Mabud, The morphotropic phase boundary in PZT solid solutions, J. Appl. Cryst. 13 (1980) 211–216.
[16] A. Barbulescu, E. Barbulescu, D. Barb, Phase transitions in PZT solid solutions, Ferroelectrics 47 (1983) 221–230.
[17] J.F. Fernandes Lozano, C. Moure, Sinterizacion a Baja Temperatura y Desarrolo Micro-Estrutural de Materiales PZT Obtenidos a Partir de Diferentes Precursores, Bol. Soc. Esp. Ceram. Vidr. 27 (1) (1988) 17–23.
[18] M.A. Zaghete, C.O. Paiva Santos, J.A. Varela, E. Longo, Y.P. Mascarenhas, Phases characterization in PZT obtained from organic solutions of citrates, J. Am. Ceram. Soc. 75 (8) (1992) 2088–2093.
[19] S. Kumar, G.L. Messing, W.B. White, Metal organic resin derived barium titanate: I. Formation of barium titanium oxycarbonate intermediate, J. Am. Ceram. Soc. 76 (3) (1993) 617–624.
[20] E.R. Leite, M. Cerqueira, L.A. Perazoli, R.S. Nasar, E. Longo, J.A. Varela, Mechanism for $Pb(Zr_xTi_{1-x})O_3$ phase formation synthesized by partial oxalate method, J. Am. Ceram. Soc. 79 (6) (1996) 1563–1568.
[21] K. Kakegawa, K. Watanabe, Yamamura Jun-ichi Mohri, Shin-ichiShiraki H., Fluctuation of composition of $Pb(Zr_xTi_{1-x})O_3$, Nippon Kagaku Kaishi 3 (1975) 413–416.
[22] V.V. Eremkin, V.G. Smotrakov, E.G. Fesenko, Structural phase transitions in $PbZr_{1-x}Ti_xO_3$ crystals, Ferroelectrics 110 (1990) 137–144.