

Influence of niobium in the non lineal response of zirconium rich PZT ceramics

J. DE FRUTOS, F. J. JIMÉNEZ, A.M. GONZÁLEZ, M. C. DURO, E. MENÉNDEZ

Dpto Física Aplicada T.I. E.T.S.I.Telecomunicación-UPM.
Ciudad universitaria s/n. 28040 Madrid.

In this work a complete piezoelectric and electromechanical characterisation of zirconium rich Nb_2O_5 doped PZT ceramics obtained by means of new techniques is presented. The objective is to establish the correlation existing between the microscopic structure of these ceramic materials, the small variations in the cationic compositions and the differences in the response of the materials depending on their compositions.

Keywords: PZT, phase transition, FE-AFE, non-linearity, electroceramics..

Influencia del niobio en la respuesta no lineal de cerámicas de PZT ricas en circonio.

En este trabajo se presentan los resultados obtenidos tras realizar una caracterización piezoeléctrica y electromecánica completa haciendo uso de nuevas técnicas de caracterización, de muestras cerámicas de PZT ricas en circonio, y dopadas con Nb_2O_5 . El objetivo que perseguimos es establecer las correlaciones existentes entre la estructura microscópica de estos materiales cerámicos, las pequeñas variaciones de las composiciones catiónicas, y las diferencias en la respuesta de los materiales en función de las diferentes composiciones.

Palabras clave: PZT, transición de fase, FE-AFE, no linealidad, electrocerámicas

1. INTRODUCTION

PZT has been extensively studied, particularly in ceramics with a composition close to the morphotropic phase boundary where the electromechanical properties are more marked. When the composition of this solid solution shifts to the zirconium rich region, the tetragonal distortion is reduced almost to zero and becomes orthorhombic. Further Zirconium increase drives to a progressive change of the crystalline structure dipoles from an ordered, long-range configuration (Orthorhombic ferroelectric phase) to a short-range one (Antiferroelectric phase). At room temperature, this transition takes place for Zr/Ti fractions around 95/5. Within this region, the differences in free energy between the Rhombohedral Ferroelectric Phase at low temperature, FE_{RL} , the Rhombohedral Ferroelectric Phase at high temperature, FE_{RH} , and the Antiferroelectric phase, AFE, is very small (1). There are two forces coexisting in these compositions, one, long-range, and the other short-range, which bring about respectively the formation of ordered long-range and short-range structures, and which can be greatly influenced by the presence of external fields (2, 3) and small variations in the stoichiometric composition (4). For example, the application of an external electrical field that interacts with the dipoles in the PZT95, favours the presence of the FE phase with long-range order. Meanwhile the hydrostatical pressure decreases the distance between ions and favours to a large extent the appearance of short-range ordering thus leading to its transformation into AFE.

These PZT properties in the proximities of the FE-AFE transition gives rise to numerous and very interesting

applications, such as ceramic actuators (5-7) and high energy electric pulses power supply (8,9). Numerous papers have been published in the past few years on the properties of these materials and how to control this phase change. Most of these works concentrate on the effects of hydrostatic pressure and/or defects associated to the porosity (density) of the samples. In most of the cases, small quantities of Niobium are added to the composition since it is assumed that it facilitates the polarization / depolarization processes softening the ferroelectric response of the material, and stabilizes the ferroelectric phase for PZT95 (10,11). According to the bibliography, Nb^{5+} substitutes Zr^{4+} leading to a similar behaviour than Ti^{4+} . The ionic radius of both elements is similar, but Nb^{5+} is heavier than Ti^{4+} (92.9 for Niobium, 47.9 for Titanium). However, the most relevant difference is the electric charge which increases the mobility within the unit cell and consequently increases the ionic polarisation in the material.

In this work, we focus on the role played by Nb^{5+} in compositions close to 95/5, verifying whether it carries out a function similar to Ti^{4+} and modifies the ferro-piezoelectric properties of the material.

2. EXPERIMENTAL PROCEDURE

In order to achieve the objectives described in the introduction, nine PNZT compositions close to the 95/5 composition were prepared. The complete chemical formula

of the compositions are expressed as $Pb (Zr_xTi_{1-x}) O_3 + z Nb_2O_5$ (z % in weight), with x 0.97; 0.965; and 0.96 and with z 1; 1,5 and 2 (Table I).

TABLE I. ANALYZED COMPOSITIONS, INDICATING ITS FRACTION OF TI, % OF Nb_2O_5 , IN WEIGHT, AND THE TI+NB FRACTION

Sample	Zr/Ti	% Nb_2O_5	Zr/(Ti+Nb)
M1	97/3	1.0	94.2/5.8
M2	97/3	1.5	92.9/7.1
M3	97/3	2.0	91.6/8.4
M4	96.5/3.5	1.0	93.7/6.3
M5	96.5/3.5	1.5	92.4/7.6
M6	96.5/3.5	2.0	91.1/8.9
M7	96/4	1.0	93.3/6.7
M8	96/4	1.5	91.9/8.1
M9	96/4	2.0	90.7/9.3

The percentage in composition expressed as $(Ti^{4+}+Nb^{5+})$ has been included as a complementary element given that in the bibliography, it is assumed that for compositions rich in Zr^{4+} , the ions Nb^{5+} substitute the Zr^{4+} and that they do not take interstitial positions, and consequently, the addition of small quantities of niobium has the same structural role as the addition of titanium.

Ceramic samples were prepared by means of a conventional method for mixing oxides. The mixtures were calcined at 850 °C for 2 hours, and sintered at 1290 °C for an hour in a lead controlled atmosphere. The samples were shaped into discs of 15 mm in diameter, and 1 mm in thickness. Discs were Ag electroded by means of a silver paste applied on the parallel surfaces and fired at 600°C. Samples were polarised by applying a field of 20 kV/cm for ten minutes at 120 °C, and cooling down to room temperature with the field still applied.

In order to determine the influence of Nb^{5+} , the non-linear behaviours were studied. For this purpose, two different and complementary characterisation methods have been used. In both cases, polarised materials were studied for different AC electrical potential and the influence of the Nb^{5+} was determined in the electromechanical response.

The first characterisation method used is known as complex piezoelectric characterisation, which is well established and based on the determination of the piezoelectric and mechanical parameters from the materials with measurements at the radial resonance and thickness resonance (12)

The second method used has been developed by the authors and it is known as the Laser Inspection System without contact for the characterisation of piezoelectric samples (SIL) (13,14).

3. RESULTS AND DISCUSSION

One of the objectives of the SIL technique is the dynamic determination of small variations and movements in the material. Figure 1 shows the response of the resonance frequency for two different electrical excitations ($V_{pp} = 20$ and 30 Volts), and out of the resonance for $V_{pp} = 30$ Volts. It is important to note that the resonance frequency moves towards lower frequencies as the excitation value increases, while the antiresonance frequency, remains practically constant. The validity of the experimental system is made clear, and we can

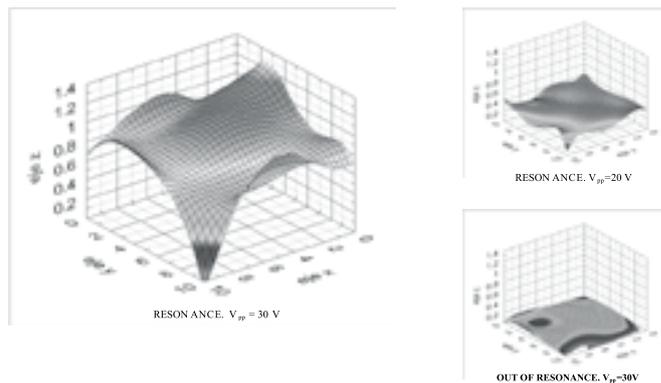


Fig. 1- Response of the M2 sample in the resonance frequency for two V_{pp} values (20 and 30 V), and outside the resonance for $V_{pp} = 30$.

find out the response of the material from different stimuli and working conditions.

With our experimental system, we are characterising piezoelectric electroceramic materials in conditions of resonance and antiresonance. The frequencies used in the study correspond to the fundamental radial mode, and with the geometry of the samples studied, these frequencies correspond to values of between 150 kHz and 200 kHz. For the determination of the piezoelectric coefficients, we will measure the deformation of the ceramic under working conditions. In the resonance/antiresonance conditions the sample is vibrating, as a result of which it expands and contracts at each axis. The equation that allows both increments to be related is:

$$dV = 0 = \pi 2rdrh + \pi r^2 dh \Rightarrow dr = -\frac{rdh}{2h} \tag{1}$$

The experimental system is optimised to measure the deformation in the thickness direction (Δh), therefore in the radial mode it is necessary to make use of the previous equation to estimate the deformation on the radial plane (Δr), and it corresponds to a direct method of characterisation (12-14). The direct measurements of the piezoelectric constants are used to quantify both the direct and inverse effects of the piezoelectric samples. The method used consists of applying an AC electric field to the sample registering its deformation to determine the relationship between the applied electric field, the deformation and the mechanical pressure developed, that is, the inverse piezoelectric effect based on the basic equations on piezoelectricity (Ec 2 and Ec 3). The direct measurements allow functional models for the devices to be obtained as well as an efficient integration of these devices in applications.

$$S_{ij} = s_{ijkl}^E T_{kl} + d_{ijk} E_k \tag{2}$$

$$D_i = \epsilon_{ij}^T E_j + d_{ijk} T_{jk} \tag{3}$$

Effectively, movement measurements in piezoelectric actuators are carried out to determine the magnitude and sign of the relationship between the electric field applied and the deformation experienced by the device. For a thin PZT

disc if there are no external forces acting on the deformation model; as in our case, it is a function only of the product of the coefficient d_{ij} and the applied electric field E .

$$S_j = d_{ij} E_i \quad [4]$$

We will make use of this equation to determine the values of d_{ij} associated to our measurements.

Thus, from the data presented in figure I, the data set out in Table II are obtained for the M2 sample, where a great dependence of the sample response with the electrical excitation is made clear.

In order to compare the response of the different

compositions, previously polarised samples are characterised in their state of vibration. Figure 2 shows some of the more representative signals obtained and figure 3 shows the results once they have been processed in accordance with the aforementioned description.

The first result that stands out from the previous data is the great dependency in this region of the response of the material with the electrical excitation. For all cases, this dependence implies an increase in the response with the field, but the increase varies from 8 % for the M8 sample to 90 % for the M2 sample. From this data, it is pointed out that there are numerous factors intervening, and this is what we will try to clarify by using the additional information provided by the electromechanical characterisation by making use of the

TABLE II. EXPERIMENTAL PIEZOELECTRIC AND MECHANICAL PARAMETERS OBTAINED BY MEANS OF SIL

	Δh (10^{-6} m)	Δr (10^{-6} m)	d_{33} (10^{-12} C/N)	d_{31} (10^{-12} C/N)
Resonance ($V_{pp}=30$ V)	1,280	3,850	60,434	181,300
Resonance ($V_{pp}=20$ V)	0,445	1,340	31,466	94,399
Outside resonance (30 V)				

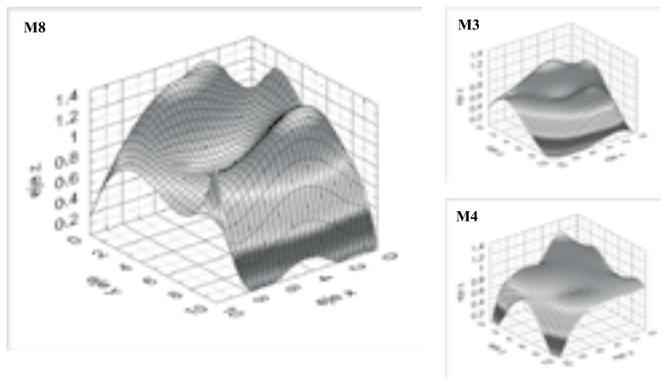


Fig. 2- Some of the more representative signals obtained by means of SIL.

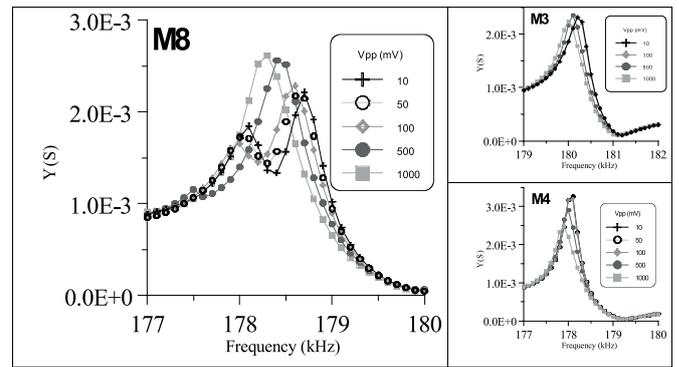


Fig. 4- Admittance Module in the proximities of the resonance for different electrical excitations and for the three groups of samples.

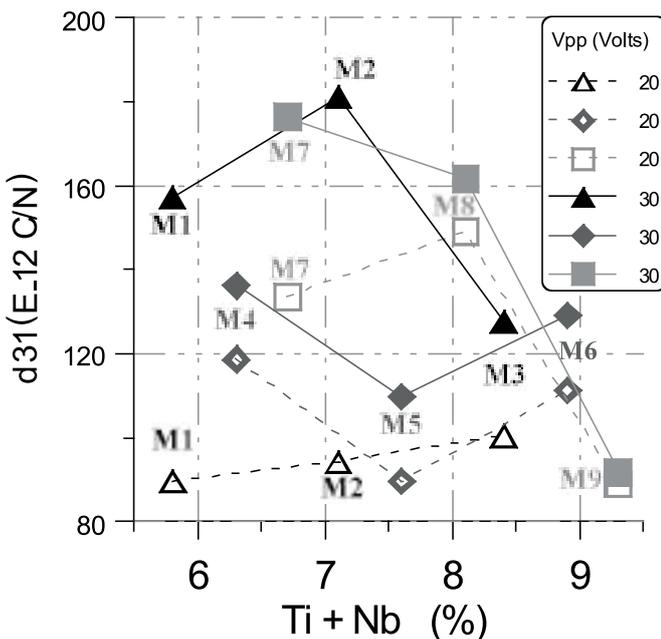


Fig. 3- d_{31} values obtained by means of SIL in the resonance frequency for two electrical V_{pp} values (20 and 30 V)

Automatic Measurement in Resonant Mode.

In order to carry out this objective, these compositions were studied assuming a non-linear response so that the characterisation was carried out by sweeping the electrical excitation in the range allowed by the measurement system. That is from 10 mV to 1 V, and as the thickness of the simple is 1 mm, the effective field applied is very small, and in any case, less than 10 V/cm, very far from the electrical polarisation which was 20 kV/cm at 120 °C.

The results obtained were diverse, with some of them being especially significant. For representative samples, Figure 4 details the admittance module for different electrical excitation in the proximities of the resonance.

From the first analysis of these results we can distinguish three different behaviours. On the one hand there are the M4, M7 and M9 samples, and even the M6 sample with a very similar behaviour to that previously described in other works. As the excitation field increases, the loss coefficients also increase, or similarly with a damped oscillator, the damped coefficient increases, going further away from the ideal resonance if there are no losses. This should coincide with the antiresonance frequency and diminishing the amplitude of the maximum in the resonance. Another group of samples is made up of M1, M5 and M8. These samples clearly show

an anomalous behaviour con with respect to the previous ones. The most significant is the separation that can be seen when the field exceeds a certain threshold. In spite of it being a similar behaviour, there are sufficiently differential aspects in the samples to merit a more detailed explanation. The third group could be included in the previous one, or halfway between the two previous ones, and is made up of samples M2 and M3.

From the piezoelectric characterisation of these samples, and seeing its evolution with the excitation field, complementary results on the response of the different samples were obtained. We have set out the evolution of the coefficient k_p according to the electrical oscillation for the different compositions in figure 5.

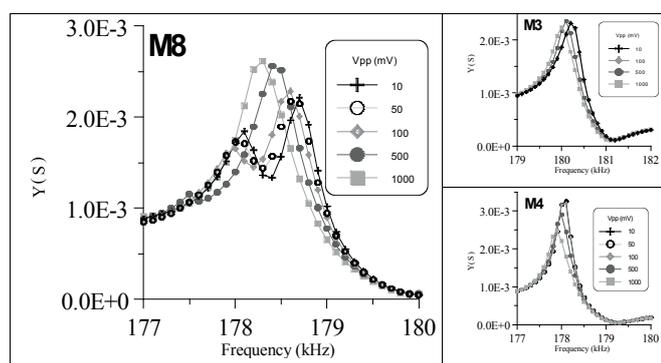


Fig. 5- Evolution of the coefficient k_p according to the electrical oscillation.

Coherent with the aforementioned observations, the different behaviour of the sample groups becomes clear. From k_p a group of behaviours stand out from M4, M7, M9 and even M6. Samples M2 and M3 have a very similar behaviour to the first group, but with a deviation of approximately 10 %. Samples M1, M8 and to a lesser extent sample M5 show a behaviour very strongly dependent on the excitation field. If

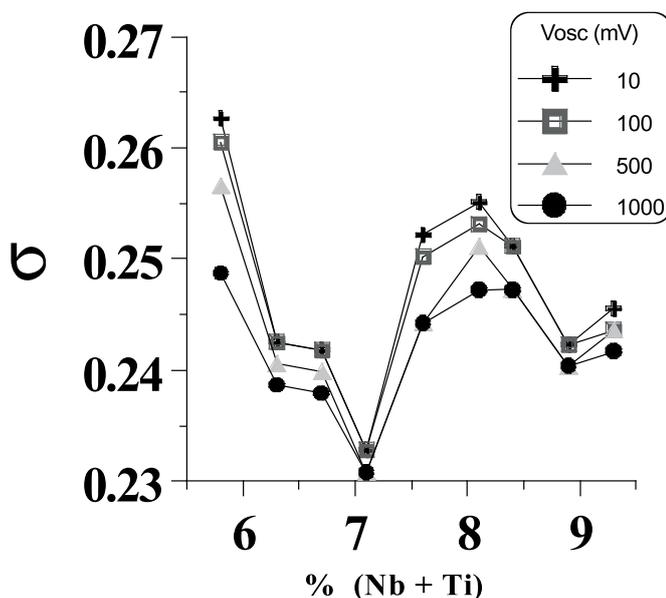


Fig. 6- Evolution according to the Nb+Ti fraction and for different excitation fields of the Poisson coefficient, σ .

we analyse the results for the other parameters represented similar results are obtained.

The behaviour of some samples is strongly non-linear, as can be seen in figures 4 and 5, and they do not seem to follow the pattern of a coherent variation. As we have previously said in the bibliography, it is assumed that Nb^{5+} carries out a role very similar to that of Ti^{4+} , which is why in order to study in this region the total fraction is considered as a combination of the fractions of Ti^{4+} and Nb^{5+} combined. In order to clarify this, figure 6 details the evolution according to the Nb+Ti fraction and for different excitation fields of the poisson coefficient, σ . The same study was carried out on the piezoelectric parameters d_{31} and K_p , and with the value of ϵ_{33}^T . In all of the cases, at least three regions with differentiated response are clear. The first for Nb+Ti fractions of less than 6,8 %, the second corresponds to fractions of between 6,8% and 8,2%, and the third for fractions between 8,2% and 9,5%. The non-linearity is clear especially in the second region and more specifically in the parameters associated to the radial response which in response to the thickness, where it is practically negligible in the value of ϵ_{33}^T .

4. CONCLUSIONS

At the analysis temperature, 25 °C, sample M1, even assuming Nb^{5+} playing the same role as Ti^{4+} , is placed in the antiferroelectric region of the phase diagram. This would mean a greater dependence on the short-range interactions for which a strong dependency with the excitation field and the non-linearity of the response is expected. Sample M4 would be located in the FE_{RH} region, the rest of the compositions would be in the FE_{RL} region. By analysing the piezoelectric responses of the different compositions, and determined by both techniques, it is clear that the addition of Nb^{5+} provides a maximum in the response for contents of 1,5 % in weight. As the excitation field increases, the response of the samples with a higher Nb^{5+} content improves.

All of this shows that the role of Niobium in Zirconium rich PZT compositions is far from that of Ti^{4+} . Therefore it is not right to assume that they carry out a similar role in this kind of materials.

5. ACKNOWLEDGEMENTS

This work has been supported by the MEC under the CICYT MAT2004-04843-C02-02 project, and to whom the authors would like to show their gratitude.

REFERENCES

1. B. Jaffe, W. R. Cook, H. Jaffe, Piezoelectric Ceramics, edit by J. P. Roberts and P. Popper (Academic Press, London, 1971).
2. P. Yang, D.A. Payne, "The Effect of External Field Symmetry on the Antiferroelectric-Ferroelectric Phase Transformation," J. Appl. Phys., 80, 4001-4005, (1996).
3. G. A. Samara, P. S. Peercy, "The Study of Soft-Mode Transitions at High Pressure," Solid State Physics: Advances in Research and Applications, edit by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1981), Vol. 36, p. 1.
4. K. Uchino and S. Nomura, "Electrostriction in PZT Family Antiferroelectrics," Ferroelectrics, 50, 191-194 (1983).
5. W. Y. Pan, Q. M. Zhang, A. Balla, L. E. Cross, "Field-Forced Antiferroelectric-to-Ferroelectric Switching in Modified Lead Zirconate Titanate Stannate Ceramics," J. Am. Ceram. Soc., 72, 571-578 (1989).

6. P. Yang, D. A. Payne, "Thermal Stability of Field-Forced and Field-Assisted Antiferroelectric-Ferroelectric Phase Transformation in $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$," *J. Appl. Phys.*, 71 (3) 1361-1367, (1992).
7. D. Zeuch, S. T. Montgomery, D. J. Holcomb, "The Effects of Nonhydrostatic Compression and Applied Electric Field on the Electromechanical Behavior of Poled Lead Zirconate Titanate 95/5-2Nb Ceramic During the Ferroelectric to Antiferroelectric Polymorphic Transformation," *J. Mater. Res.*, 14, 1814-1827 (1999).
8. B. A. Tuttle, P. Yang, J. H. Gieske, J. A. Voigt, T. W. Scofield, D. H. Zeuch, W. R. Olson, "Pressure-Induced Phase Transformation of Controlled-Porosity $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ Ceramics," *J. Am. Ceram. Soc.*, 84, 1260-1265, (2001).
9. S. J. Lockwood, E. D. Rodman, S. M. Deninno, J. A. Voigt, D. L. Moore, "Chem- Prep PZT 95/5 for Neutron Generator Applications: Production Scale-Up Early History," SAND report 2003-0943, Sandia National Laboratories, (2003).
10. S. J. Lockwood, E. D. Rodman, J. A. Voigt, D. L. Moore, "Chem-Prep PZT 95/5 for Neutron Generator Applications: Powder Preparation Characterization Utilizing Design of Experiments," SAND Report 2003-2332, Sandia National Laboratories, (2003).
11. J. de Frutos, A. M. González M.C. Duro, J.F. Fernandez "No linealidad en muestras cerámicas de PZT muy delgadas". *Bol. Soc. Esp. Cerám.* V. 38, 5, 507-510 (1999)
12. M. González y C. Alemany: "Determination of the frequency dependence of characteristic constants in lossy piezoelectric materials", *J. Phys. D: Appl. Phys.*, 29, 2476-2482 (1996)
13. F.J. Jiménez, J. de Frutos "Noncontact inspection laser system for characterization of piezoelectric samples", *Rev. Sci. Instrum.*, 75, (11), 4497-4504 (2004)
14. F. J. Jiménez, J. de Frutos, "Virtual instrument for measurement, processing data and visualization of vibration patterns of piezoelectric devices", *Computer Standards & Interfaces*, 27, (6) , 653-663 (2005)

Recibido: 15.07.05

Aceptado: 09.02.06

