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The nature and phase transition F_{RL}–F_{RH} in PZT doped with Nb

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Abstract

In the composition region of PZT rich in zirconium, ($0.05 < x < 0.35$) there are two phase transitions. The first takes place between the high and low temperature Rhombohedric phases F_{RL}–F_{RH} both of which are ferroelectric, and the second between the high-temperature ferroelectric Rhombohedric phase and the cubic phase which is paraelectric (F_{RH}–PE). The phase F_{RL}–F_{RH} transition of the PZT system has been studies using different methods. In all of the cases, the fundamental difficulty in establishing the transition characteristics has been the small alteration in the electrical parameters of this transition. In this work, we have verified, when the samples being studied are polarized, the changes are intensified significantly, undoubtedly allowing both the characterization of the transition temperature and its nature. In order to carry out our study, we have selected several PZT compositions doped with niobium, by moving the Zr/(Ti + Nb) > 90/10 region, in which we have determined the characteristics of the transition phase and the influence of niobium on it.

Keywords: PZT; Piezoelectric properties; Ferroelectric properties; Actuators; Functional applications

1. Introduction

The phase diagram of PZT rich in zirconium, underlines the coexistence of several phases, which together with the possible displacement induced by the effects of the polarizing field, and the influence and perturbations resulting from the presence of niobium in the composition, allows us to make the transition from the anti-ferroelectric phase, to that of the Rhombohedric ferroelectric, both at low and high temperatures. From the low temperature Rhombohedric ferroelectric a transition can be seen to that of high temperature, and finally, from this the transition to the paraelectric phase can take place.

The F_{RH}–PE transition phase has been studied in great depth, and its first and second order character has been determined in accordance with its composition.[1,2]

For its part, the F_{RL}–F_{RH} transition has been characterized using different experimental models. Barnett[3] was the first to report an anomaly in the dielectric losses, relaxation in the pyroelectric charge and an anomaly in thermal expansion at the transition point of PZT96/4 ceramics doped with 1% in weight of Nb_2O_5. Clarke and co-workers[4,5] observed a discontinuity in spontaneous polarisation, P_s, the tilt in the oxygen octahedron, and the deformation for PZT90/10 through the diffraction of neutrons with temperature. Considering the link between spontaneous polarisation and the tilt in the oxygen octahedron, Halemane et al.[5] developed a phenomenological model to describe this phase transition. However, the greatest amount of work has been carried out on compositions with the $Zr = Ti > 90 = 10$ relationship. In the case of compositions with the $Zr = Ti < 90 = 10$ relationship, no experimental anomalies have been observed in the dielectric, pyroelectric and thermal properties. It has only been possible to observe significant anomalies in the resonance frequency[6] and in the speed of longitudinal sound, in PZSnT[7] and PLZT $x = 65 = 35$[8] ceramics, which makes us assume that the characteristics of this transition phase are greatly modified in this state of polarization. This has encouraged us to study the transition in previously polarized samples, analysing a large number of possible parameters to quantify and study this phase transition.

2. Experimental

In order to achieve the objectives set out in the introduction, PNZT compositions have been prepared, similar to the composition of the triclinic point. The complete chemical formula

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Table 1
Studied compositions

Sample	M1	M2	M3	M4	M5	M6	M7	M8	M9
Ti fraction	3.0	3.0	3.5	3.5	3.5	3.5	4.0	4.0	4.0
%Nb	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0

of the compositions is expressed as $Pb_{1-y/2}(Zr_{1-x}Ti_x)_{1-y}Nb_yO_3$, where for three contents of titanium, three contents of niobium have been varied. Thus, nine compositions have come (Table 1).

The ceramic samples were prepared using a conventional method for mixing oxides, starting with oxides of a high purity. The mixtures were calcinated at 850 °C for 2 h, and then synthesized at 1290 °C for 1 h in a lead controlled atmosphere. The samples were shaped into discs of 15 mm in diameter, and 1 mm in thickness. Electrodes were fitted on a silver paste on parallel surfaces and which were later polarized in heat by applying field of 20 kV/cm for ten minutes at 120 °C, and allowed to cool down to room temperature with the field still applied.

The analysis carried out until now has been based on the variation in the transition properties for different amounts of titanium, in our case the smallest component. On the other hand, the samples analysed here all have different degrees of niobium concentration (Nb) as a dopant. Given the relatively low titanium content, the existence of this dopant significantly alters the Curie temperature.[9] Nb^{5+} substitutes Zr^{4+} or Ti^{4+} which has similar ionic radii. This produces lead vacancies and an increase in resistance.[10,11] All of this redounds to an improvement in the specific PZT properties and a wider applicability of these materials.

In the F_{RL}–F_{RH} transition, the spontaneous polarization experiences a leap, ΔP_s, of approximately 2 μC/Cm^2 according to the composition.[12] The polarisation in the PZT in the F_{RL} and F_{RH} phases results from a tilt in the Pb^{2+} and $Zr^{4+}/Ti^{4+}/Nb^{5+}$ cations throughout the crystalline direction [1 1 1] (ferroelectric axis) in the Rhombohedric cell. On the other hand, the oxygens that are found on the faces of the perovskite cell in the shape of octahedrons, can experience torsion (a tilt of up to approximately 5°[13]) and distortion. The torsion around the ferroelectric axis is linked to the canonical movement, that is, with spontaneous polarization. When the oxygen octahedron rotate, the cations increase their movement, with is, increasing the spontaneous polarization.

The angle of tilt of the oxygen octahedron (θ_s) is taken as the order parameter associated with the transition, since it decreases slightly with the temperature in the F_{RLT} phase, but in the transition temperature of the phase F_{RH} (T_{LH}) falls dramatically to $\theta_s = 0$.

In order to carry out the study of the material, we are using combined techniques. The first characterization method used, known as complex piezoelectric characterization, which is well established, and is based on the determination of the piezoelectric and mechanical parameters taken from both radial and thickness resonance measurements.[14–16]

The resonance measurements have been carried out with small increases in temperature, 2–5 °C, and establishing the samples for 15 min before each measurement. The response in both the radial and thickness mode have been considered as variation parameters, both in accordance with the excitation field applied. The response of the different samples is very dependant on the excitation field. Fig. 1 detail the evolution of the admittance module for the M7 sample, in four excitation fields (10, 100, 200 and 1000 mV) which allows the strong dependency with this factor to be visualized, as well as the non-linearity in the response. The same thing can be seen in the rest of the samples, which is in agreement with the aforementioned description.[17] This non-linearity is associated with the composition and the type of parameter being analysed. Fig. 2a details the evolution of the anti-resonance frequency (fundamental radial mode) f_p according to the temperature. The study of the response of different samples shows a clear dependency on the oscillation field, and demands that some criteria be established for which the determination of the transition is not altered by it. The analysis for the study of the transition phase was carried out for oscillation tensions of 0.5 V.

The procedure followed for the characterization of the samples, was to work with polarized samples in resonant mode and to determine the associated parameters. From these stud-

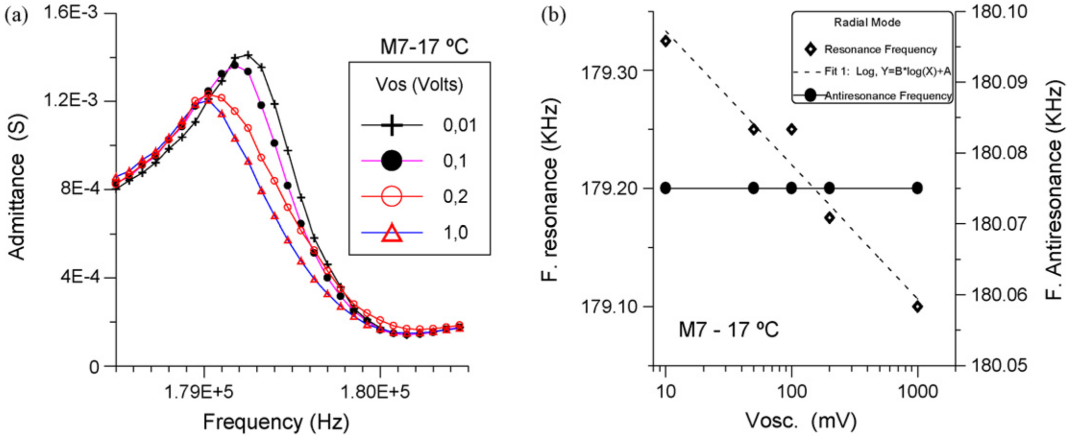

Fig. 1. (a) Admittance module vs. frequency for the M7 sample for different excitation fields. (b) Dependence of the Resonant and Anti-resonant Frequencies vs. excitation field.

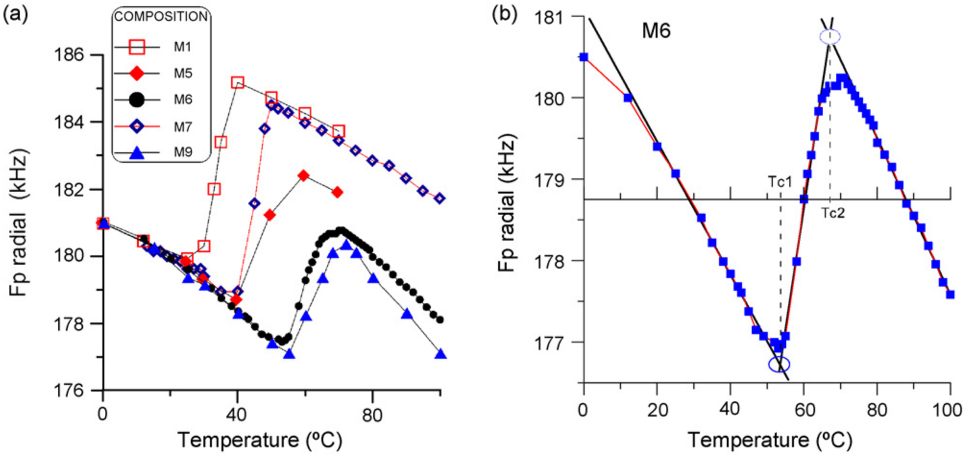

Fig. 2. Anti-resonance frequency (fundamental radial mode) f_p according to the temperature. (a) Data for different samples and (b) calculus of the T_{C1} and T_{C2}.

ies, we have both dielectric and piezoelectric parameters, and in radial and thickness mode, that which means a wide range of possibilities for the analysis.

The analysis carried out came up with some very interesting results. On the one hand, the parameters determined from the vibration radial mode presented a more uniform behaviour than those associated with the resonant mode in thickness and allowed a better study of the transformation experienced by the material. In all of the cases, it was clear that the Niobium content partially affected the samples, being a determinant in both shape and type of associated transition. Samples M1 and M7 correspond to the two extremes of composition with titanium, both having the same Nb content. If we concentrate on the curves referred to the same origin, we can see that both samples present a very similar behaviour, superimposing the response in both simples both before and alter their respective transition, and the jump reduced for the increases in temperature and with very similar slopes. When the niobium content increases, the behaviour moves away a little from that seen in this case, but the response is also very similar, enough to see that the M6 and M9 samples, both with the same Nb content, and with different Ti values.

Of all the parameters and coefficients analysed, we have considered the value of the anti-resonance frequency determined for the fundamental radial vibration mode (Fig. 2b), as the most suitable for determining the transition temperature and the type of associate transition, since the presence of a very suitable behaviour for the study as well as the field being practically independent of the excitation field used for its characterization.

In order to determine the transition temperature for each of the samples, it is verified that both for the resonance and the anti-resonance, the intersection of the straight-line adjustments before and after the transition, take place at the same temperature. From these data, we have determined the possible transition temperatures associated to each sample (Fig. 2b), and the increase between transitions that are observed. These values are set out in Fig. 3.

In order to determine the type of transition associated with each composition, we shall have to make use of the transition profiles, and more specifically the increase in temperature between the two transition temperatures considered and the increases in magnitude analysed for these temperatures. The increase in temperature between the two transition temperatures considered is represented, and the relative increase experienced between both temperatures and the magnitude analysed. As the Nb + Ti fraction increases, the value of the increase in temperature also increases, and the relative increase between the transition points decreases. This clearly shows an increase in the order of the transition as the Zr content decreases, since the transition reduces the magnitude with the increase in the Nb + Ti fraction, and requires a greater increase in temperatures to take place. We can affirm that the transition analysed is a diffuse transition that is more approximate to a first order for very high Zr values and tends toward a second-order transition since the content of Ti + Nb is increased.

In Fig. 4, we show the values of the T_{C2}, T_{C1} transition temperature and the average value of both together with the experimental values referred to in the bibliography for both PZT and PNZT in this region. Considering any of these temperatures

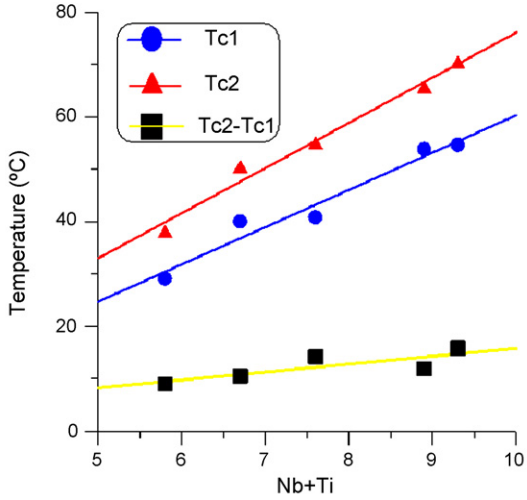

Fig. 3. Values of the possible transition temperatures associated to each sample, and the increase between transitions.

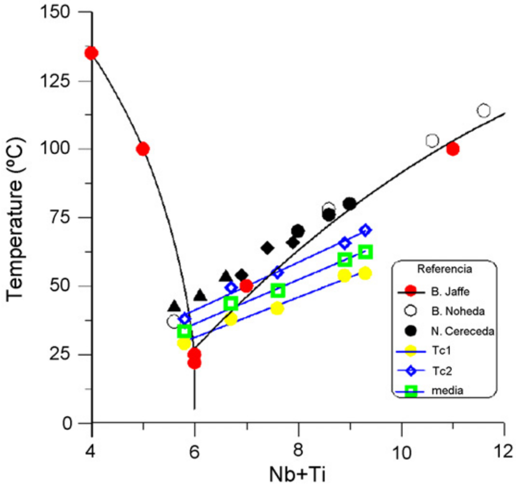

Fig. 4. Values of the T_{C2}, T_{C1} transition temperature and the average value of both together with the experimental values referred to in the bibliography for both PZT and PNZT in this region.

as the transition temperature, there is a displacement of them with respect to the value referred to in the bibliography. Bearing in mind the way in which this temperature has traditionally been determined[18], the value of the most accurate temperature would correspond to the average temperature. Making use of this temperature, we can consider that samples with a lower level of niobium have a very similar behaviour to that envisaged assuming that the Nb substituted the Ti and Zr in the composition. However, as the Nb content is increased, the displacement with respect to that set out in the bibliography makes it more obvious. In order that the transition values correspond to that described by Jaffe, the molar fraction that the samples should have should be reduced by approximately 0.5 for the Nb contents of 1.5% and 1.2 when the content is 2%. This deviation can be justified bearing in mind that for the Ti and Nb content of our composition, the Nb content is even greater than that of Ti. The niobium and lead are combined in an oxide forming $PbNb_2O_6$, a non-perovsquita structure with a paraelectric phase which is not cubic but tetragonal. Therefore a greater presence of Nb^{+5} ions in the network will contribute to a greater deformation of the cell. This could also justify some of the anomalous results described in previous sections associated to deviations in the behaviour of the samples when Nb is included.

3. Conclusions

In conclusion, from the study of the response of these materials with temperature, a marked transition depending on the Ti and Nb content in the material becomes clear. The determined transition temperature is even greater as the relative content of Ti and Nb becomes greater. This transition temperature fits in fairly well with the values determined by Jaffe,[18] Noheda[19] and Cereceda[20] as long as the Nb content is less than 1.5% in weight. Since the Nb content is increased, the transition temperatures deviate by the value determined by Jaffe, at a proportion equivalent to 0.5 mols for contents of 1.5% in weight, and of the order of 1.2 mols for contents of 2% in weight of Nb. This result is justified by the possibility of the formation of the Pb and Nb oxide, $PbNb_2O_6$ with a structure equivalent to Bronze-Tungsten. This compound has a high transition temperature, which justifies the greater distance from the values referred to in the bibliography for those composition with a high Nb content.

The transition analysed is a diffuse transition that with a high Zr content is close to a first-order transition, and has a tendency towards a second-order transition as it reduces the Zr content. This result is coherent with that established for a ferroelectric–paraelectric transition within this range of compositions.

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