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Investigation of the Character of the Phase Transitions in Nb Doped Zr-rich PZT by Pyroelectric and Dielectric Measurements

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Abstract

We present a study of the character of the phase transitions of the solid solution $PbZr_{1-x}Ti_xO_3$. Using the spontaneous polarization curves we determined the mean-field parameters. These parameters show the first order character of the phase transitions for the richer Zr content and its evolution with composition. The F_{RL}–F_{RH} phase transition presents also first order character for high contents of Zr. The study of the thermal hysteresis, and the jump of the spontaneous polarization, allowed us to investigate this phase transition with composition. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: phase transitions, dielectric properties, ferroelectric properties, PZT.

1 Introduction

The solid solution $PbZr_{1-x}Ti_xO_3$, known as PZT, possesses numerous phases and lattice structure, depending on Zr/Ti ratio (x) and temperature.[1] For compositions lying in the Zr-rich region of the phase diagram, it exhibits three different phases. In the paraelectric-cubic phase (P_C), the material presents an ideal perovskite unit cell. This unit cell becomes rhombohedral, but remains pseudocubic, when the material is cooled down to the ferroelectric phase (below T_{FP}), dividing in two different regions: F_{RH} (ferroelectric-rhombohedral high-temperature), and F_{RL} (ferroelectric-rhombohedral low-temperature) phases.

The spontaneous polarization (P_S) is due to the cation displacements along the [111] crystallographic direction. The ferroelectric phase transition is of first order for most of the compositions investigated in this work ($0{\cdot}03 < x < 0{\cdot}23$). As the Ti content ($x$) is increased, the transition becomes second order and more diffuse.

In order to analyse the experimental data at the ferroelectric phase transition we used the effective field approach.[2] According to the theory, the spontaneous polarisation and temperature are related by the equation of state,

$$\frac{T}{T_C} = \frac{p_s\left(1 + gp_s^2 + hp_s^4 + ...\right)}{\tan h^{-1} p_s}, \qquad (1)$$

where T_C is the Curie temperature, $p_s = P_S N\mu$ is the normalised spontaneous polarization, and g and h are the quadrupolar and octupolar terms of the effective field expansion, respectively. Here, N is the number of elemental dipoles, and μ is the elemental dipole moment. We pay attention to the Curie temperature and the g parameter. The latter one gives the direct information about the character of the transition: if $g < 1/3$, the ferroelectric transition is of a second order, and a first order if $g > 1/3$.

In the F_{RL} phase (at $T < T_{LH}$), the oxygen octahedron is tilted along the [111] axis, which results in a bigger shift of the cationic displacements (bigger dipole moment per unit cell), and an additional spontaneous polarization.[3] According to the data from the structural analysis[4] the F_{RL}–F_{RH} phase transition is also of first order type for the composition $x = 0{\cdot}035$ ($X = 100x = 3{\cdot}5\%$ of Ti). This is observed considering the tilt angle of the oxygen octahedron like an order parameter.[5]

2 Experimental

For dielectric measurements we used a high-resolution capacitance bridge, Hewlett–Packard model

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4284A. For spontaneous polarisation characterisation we developed recently a special set-up[6,7] that allows to integrate the pyroelectric current released by the ferroelectric sample at low rate of heating ($20°C\,h^{-1}$, i.e. $\sim 0{\cdot}33°C$).

The samples were poled PZT ceramics, with compositions ranging from 3% of Ti content, up to 23%, and doped with 1% by weight of Nb_2O_5. The samples were prepared, at the Shanghai Institute of Ceramics (China), by the conventional mixed oxide ordinary methods.

3 Results and Discussion

As deduced from dielectric measurements, the F_{RH}–P_C phase transition is of the first-order type up to the composition[8] $X = 26\%$, independently of Nb content, if it is small.[9] The character of the phase transition is clearly visible from our polarisation-temperature curves, as shown in the figures.

Figure 1 shows the $P_S(T)$ curve for $X = 3{\cdot}5\%$ from low temperature (170 K) up to the paraelectric phase. In this plot it is possible to observe both, the F_{RL}–F_{RH} and F_{RH}–P_C phase transitions. In the first one, P_S falls abruptly at T_{LH}, denoting the first order character. Even more clearly, this character can be seen in the ferroelectric phase transition occurring at T_{FP}.

Figure 2 shows a set of data of the spontaneous polarisation curves for the compositions $X = 3$, 3·5, 4, 5, 8, 14 and 23%. The F_{RH}–P_C phase transition can be analysed by means of eqn (1), as described in our previous work.[10] From these plots we observe the dependence of $P_S(T)$ with composition. In order to observe both, the 'jump' in the spontaneous polarisation and the thermal hysteresis in the F_{RL}–F_{RH} phase transition, we measured $P_S(T)$ in the following way: first heating up to $T > T_{LH}$, decreasing again the temperature below T_{LH} and then heating up to the paraelectric phase ($T > T_{FP}$).

The final analysis from the $P_S(T)$ data for all the seven compositions are represented in Figs 3 and 5.

Figure 3 plots the Curie temperature, T_C, and the g parameter resulting from the fitting of eqn (1) to the experimental $P_S(T)$ curves at ferroelectric phase transition, in the neighbourhood of T_{FP}. As can be seen, T_C increases linearly with the Ti content. The g parameter, with stronger dependence of composition, determines the phase transition character, being *discontinuous* for compositions $X \leq 14\%$ and *continuous* for the composition $X = 23\%$.

From the above results, one could say that the tricritical composition is placed between 14 and 23% of Ti content. However, using exclusively dielectric measurements,[8] we found the tricritical composition to be $X_{TCP} \cong 26\%$. The main difference is the preparation of the material. In the present case, it is in the poled ceramic samples, which implies the change of some behaviour with temperature. Poled electroceramic implies internal stresses, and a high internal electric field. All these factors reflect in a change in the Curie's temperatures, and the shape of $P_S(T)$ curves.

Figure 4 plots the dielectric constant for the compositions $X = 3$, 3·5, 4, 14 and 23%. For the

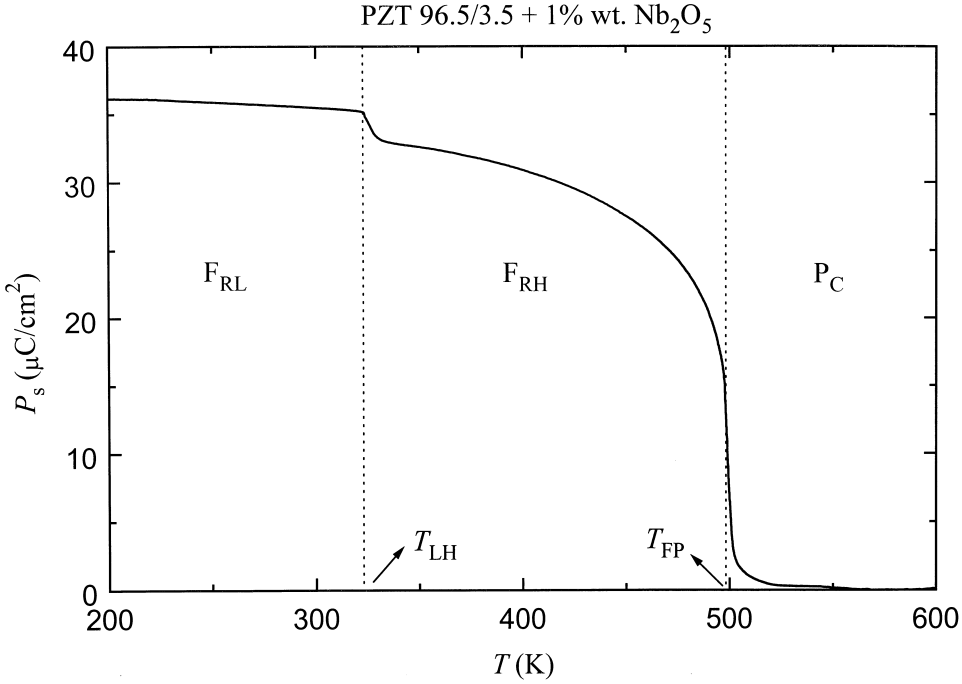

Fig. 1. Spontaneous polarisation curve for the composition $X = 3{\cdot}5$. The corresponding phases are denoted in each interval of temperatures.

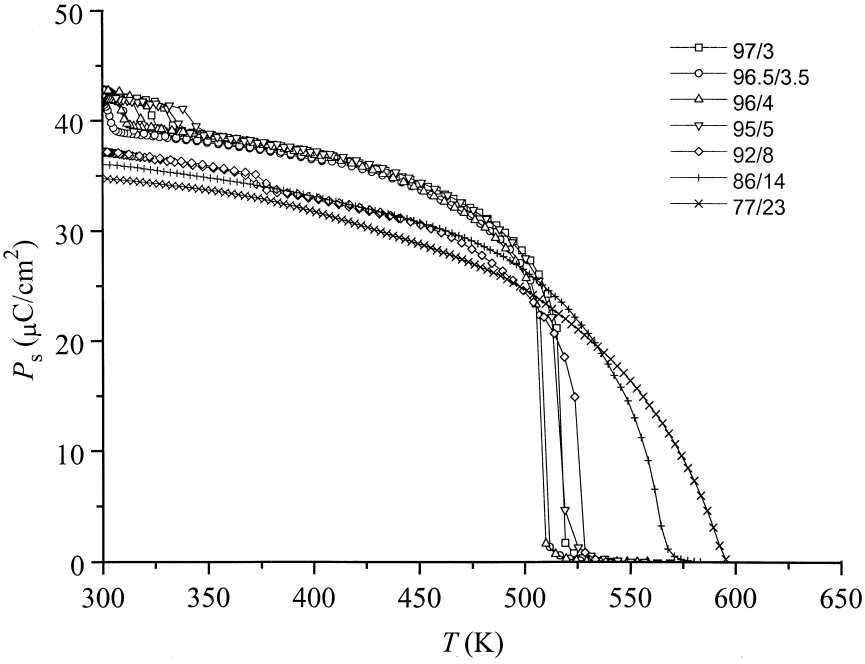

Fig. 2. Spontaneous polarisation curves for the compositions used in this work. Legend indicates the Zr/Ti ratio.

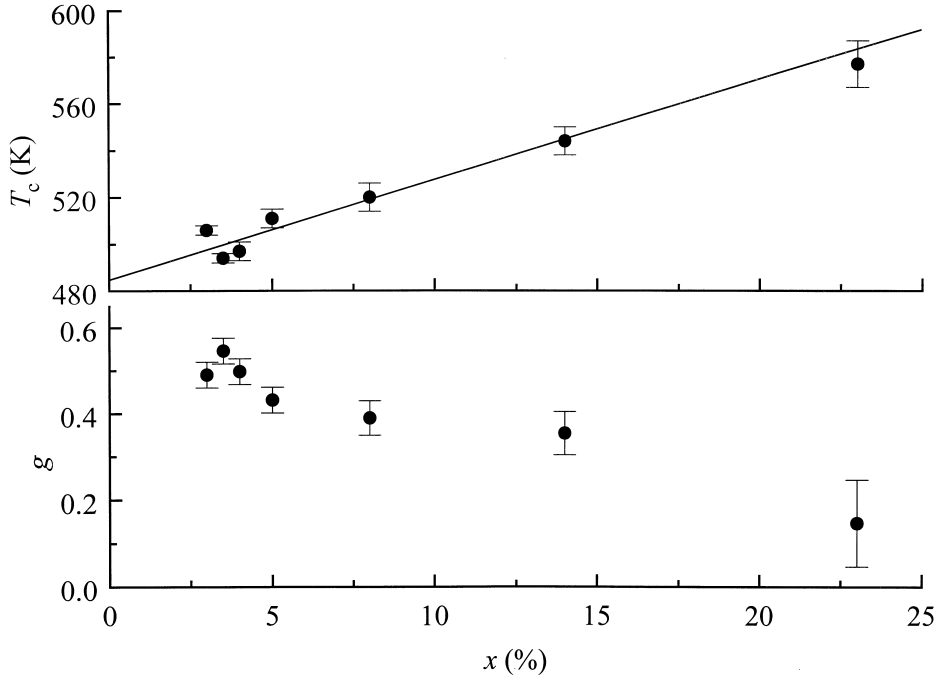

Fig. 3. Composition dependence of the Curie temperature (T_C), and quadrupolar parameter (g) of effective field expansion.

two last ones it shows an increase in the transition temperature and in the peak-height. This behaviour is expected while taking into account the tendency towards second order instead of first order as Ti content increases. Dielectric response was in all cases measured at 1 KHz frequency in an unpoled ceramics. The $\varepsilon(T)$ curve for $X=23\%$ presents a mixture of first and second order behaviour, demonstrating that the phase transformation is an intermediate case, which looks second order for poled samples.

The F_{RL}–F_{RH} phase transition takes place between two similar ferroelectric phases. Only small differences exist between F_{RL} and F_{RH} phases, which involves the change of space group from R3c (F_{RL}) to R3m (F_{RH}). In the high temperature phase (F_{RH}), cation displacements are responsible for the spontaneous polarisation. Below the temperature, T_{LH}, a tilt of the oxygen octahedron appears.[3] This effect makes the material to have a stronger displacement of the cations along the ferroelectric axis, and then an extra polarisation is obtained (see Fig. 1).

In Fig. 2 shows the spontaneous polarisation versus temperature, including the 'jump' occurring in this phase transition for all the used compositions.

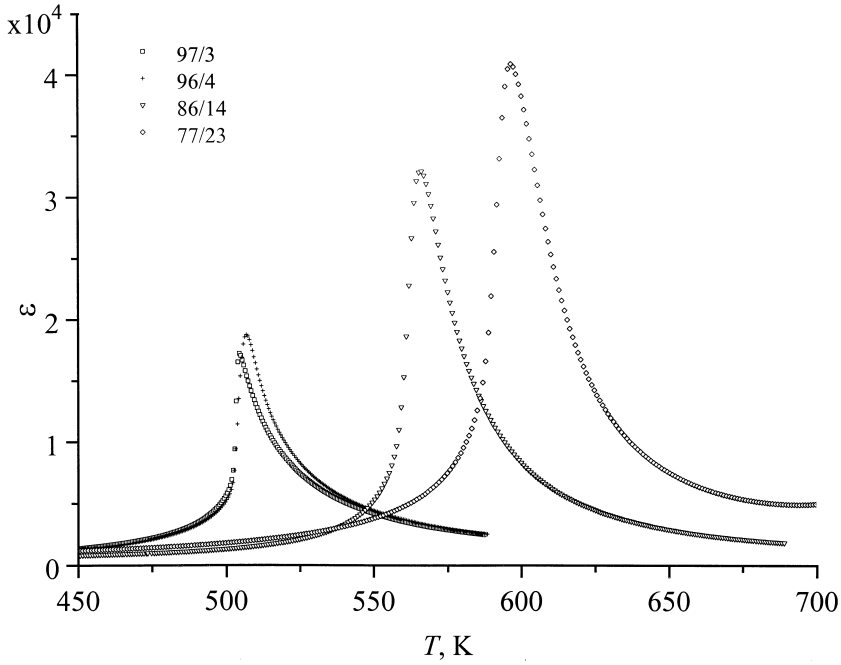

Fig. 4. Dielectric response for the compositions $X = 3$, 4, 14 and 23%.

As demonstrated before, it is of the first order kind.[5] If the phase change is produced in a discontinuous phase transformation, we should expect the occurrence of a thermal hysteresis between the heating and cooling processes. Figure 5 shows the variation of the thermal hysteresis ΔT_{LH} of the transition temperature (T_{LH}) with composition and the jump of the spontaneous polarisation $\Delta P_S(T_{LH})$, deduced from the curves plotted in Fig. 2. The thermal hysteresis and the 'jump' decreases with Ti content. This result suggests the change from discontinuous to continuous phase transition, but also reveals the difficulty to observe it, because no distinction can be made in the spontaneous polarisation.

The F_{RL}–F_{RH} phase transition can be observed by means of the dielectric constant near T_{LH}. Figure 6 shows the plot of $\varepsilon(T)$ for the compositions 3, 3·5 and 4% of Ti content. The arrows indicate the transition temperatures, because the transitions are easily detectable in these cases. The situation turns out to be more complicated for richer contents in Ti, as presented in Fig. 7. This figure shows the plots of the inverse of the dielectric constant versus temperature for the compositions $X = 14\%$ and $X = 23\%$. This representation is more useful than

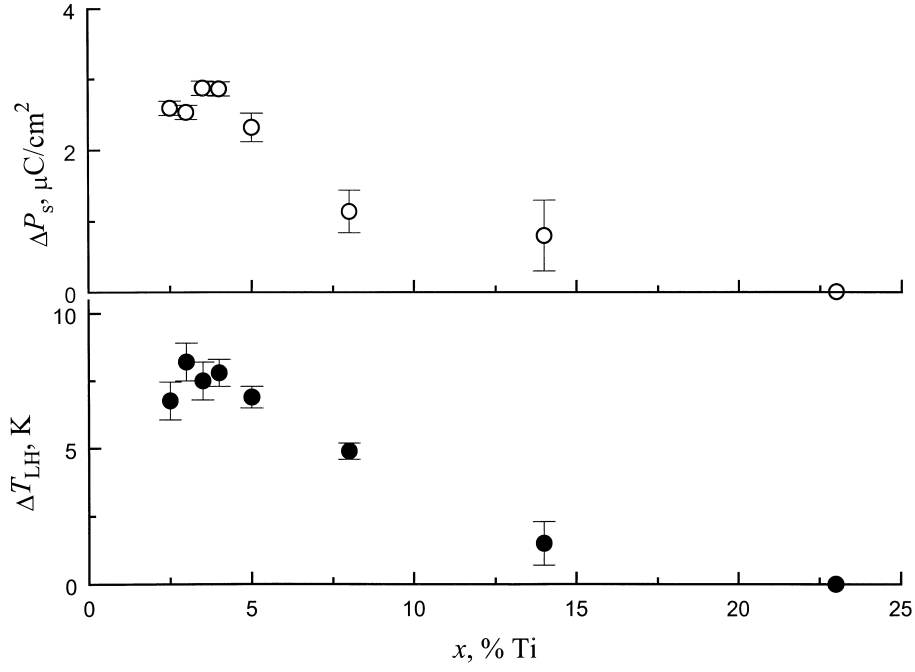

Fig. 5. Change of the spontaneous polarisation and thermal hysteresis in the F_{RL}–F_{RH} phase transition.

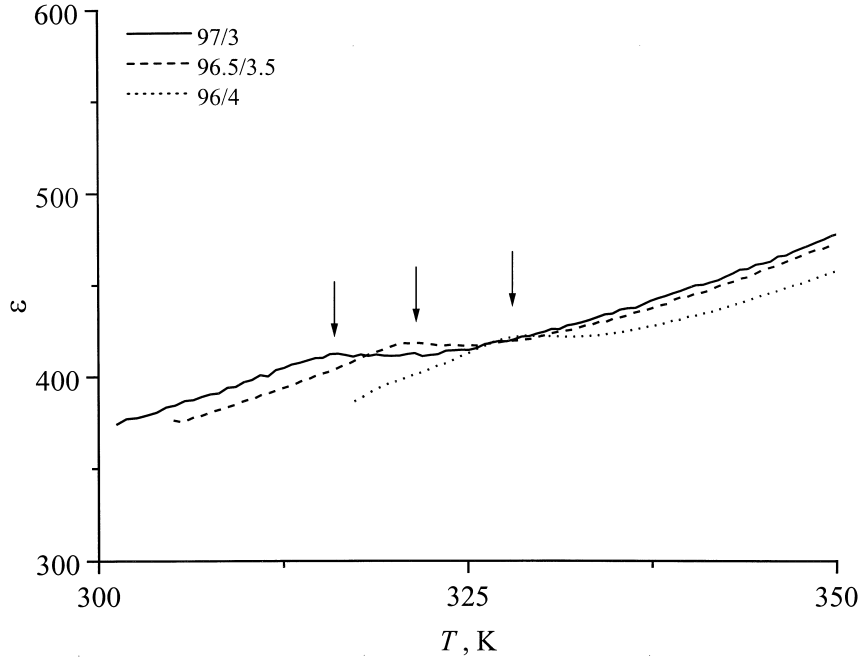

Fig. 6. Dielectric response in the neighbourhood of F_{RL}–F_{RH} phase transitions for the compositions 3, 3·5 and 4%.

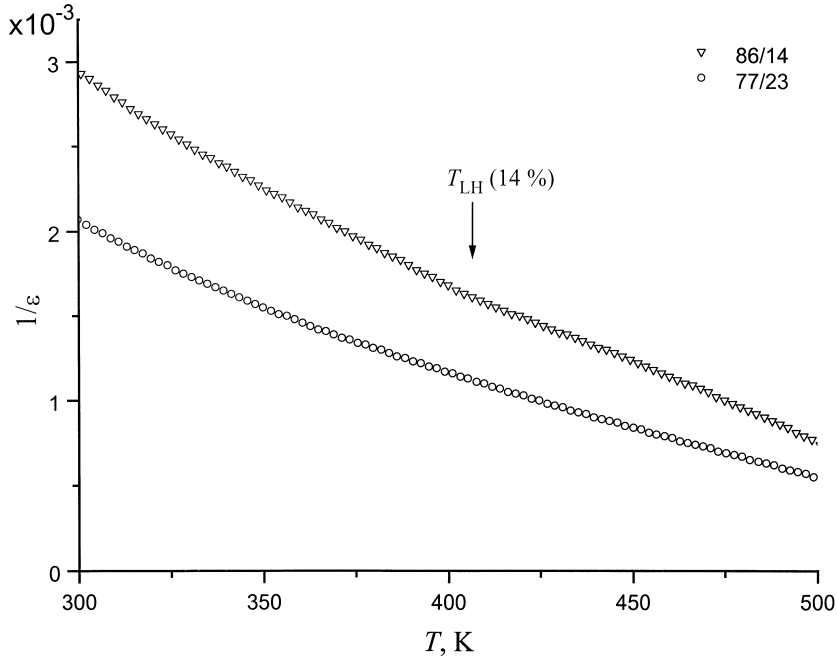

Fig. 7. Inverse of the dielectric response for the compositions 14 and 23% of Ti content near the F_{RL}–F_{RH} phase transition. Arrow indicates the transition temperature for $X = 14\%$.

the $\varepsilon(T)$, because it is easier to visualise the changes produced during the transition.

As Ti content increases, the F_{RL}–F_{RH} becomes more diffuse, in such a way that can not be observed by any electric measurement. From $1/\varepsilon(T)$ it is still possible to estimate the transition temperature in the 14% composition, but not for the 23% one.

If we make a comparison between the F_{RL}–F_{RH} and F_{RH}–P_C phase transitions and its evolution with composition, observing Figs 3 and 5, there exists a similarity between them. The *g*-parameter, which represents the order of the transition, and ΔT_{LH}, as well as $\Delta P_S(T_{LH})$, shows basically the same behaviour with composition. It would be interesting to check more precisely this effect, which may reveal the relation between the transition investigated here.

Last results reported by Corker *et al.*[11] about the F_{RL}–F_{RH} phase transition thus become now important. They pointed out the disappearance of the tilt of the oxygen octahedron for a composition lying around 38% of Ti content. In the low-temperature ferroelectric phase (F_{RL}) they found that

the Zr shifts (connected with the elemental dipole moment) are approximately the same as the Ti shifts. However, at a composition close to 30% of Ti, both shifts diverge. This effect results in a growing differentiation of the unit cells containing Zr or Ti cations. This may be also connected with the processes involved in the F_{RH}–P_C phase transition.

More recently, data reported by B. Noheda, J. A. Gonzalo and M. Hagen (pers. comm.) showed that octahedral strain-octahedral distortion coupling disappears at $X > 30\%$ for PZT$(100-X)/X+1\%$ wt Nb_2O_5. All these results place the compositions in the range 20–38% of Ti to have a especial importance in these materials.

Acknowledgements

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