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$_x$O$_3$. 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 FRL–FRH 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

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1 Introduction
The solid solution PbZr$_{1-x}$Ti$_x$O$_3$, known as PZT, possesses numerous phases and lattice structure, depending on Zr/Ti ratio (x) and temperature. 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 (0.03 < x < 0.23). 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. According to the theory, the spontaneous polarisation and temperature are related by the equation of state,

$$\frac{T}{T_C} = p_s \left(1 + gp_s^2 + hp_s^4 + \ldots\right) \tan^{-1} p_s,$$  (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 $\mu$ 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. According to the data from the structural analysis the F$_{RL}$–F$_{RH}$ phase transition is also of first order type for the composition $x = 0.035$ ($X = 100x = 3.5\%$ of Ti). This is observed considering the tilt angle of the oxygen octahedron like an order parameter.

2 Experimental
For dielectric measurements we used a high-resolution capacitance bridge, Hewlett–Packard model...
4284A. For spontaneous polarisation characterisation we developed recently a special set-up\textsuperscript{6,7} that allows to integrate the pyroelectric current released by the ferroelectric sample at low rate of heating (20°C h\textsuperscript{-1}, i.e. \(\sim 0.33°C\)).

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\textsubscript{2}O\textsubscript{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 FRH–PC phase transition is of the first-order type up to the composition\textsuperscript{8} \(X = 26\%\), independently of Nb content, if it is small.\textsuperscript{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 \(X = 3.5\%\) from low temperature (170 K) up to the paraelectric phase. In this plot it is possible to observe both, the FRL–FRH and FRH–PC 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 FRH–PC phase transition can be analysed by means of eqn (1), as described in our previous work.\textsuperscript{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 FRL–FRH 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,\textsuperscript{8} we found the tricritical composition to be \(X_{TCP} \geq 26\%\). 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 of 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
two last ones it shows an increase in the transition
temperature and in the peak-height. This beha-
viour 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 \( T \) curve for \( X = 23\% \)
presents a mixture of first and second order beha-
viour, demonstrating that the phase transform-
tion 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 \( F_{RH} \) pha-
ses, 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 tem-
perature, \( T_{LH} \), a tilt of the oxygen octahedron
appears.\(^3\) This effect makes the material to have a
stronger displacement of the cations along the fer-
roelectric axis, and then an extra polarisation is
obtained (see Fig. 1).

In Fig. 2 shows the spontaneous polarisation ver-
sus temperature, including the ‘jump’ occurring in
this phase transition for all the used compositions.

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**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.
As demonstrated before, it is of the first order kind. 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 $\Delta T_{LH}$ 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

![Figure 4](image1.png)

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

![Figure 5](image2.png)

**Fig. 5.** Change of the spontaneous polarisation and thermal hysteresis in the $F_{RL}$–$F_{RH}$ phase transition.
As Ti content increases, the FRL–FRH becomes more diffuse, in such a way that cannot 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 FRL–FRH and FRH–PC 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 \( \Delta T_{LH} \), 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 FRL–FRH 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 (FRL) they found that the \( \varepsilon(T) \), because it is easier to visualise the changes produced during the transition.

Fig. 6. Dielectric response in the neighbourhood of FRL–FRH 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 FRL–FRH phase transition. Arrow indicates the transition temperature for \( \chi = 14\% \).
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\textsubscript{RH}–P\textsubscript{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$_2$O$_5$. All these results place the compositions in the range 20–38% of Ti to have a special importance in these materials.

Acknowledgements

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References

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