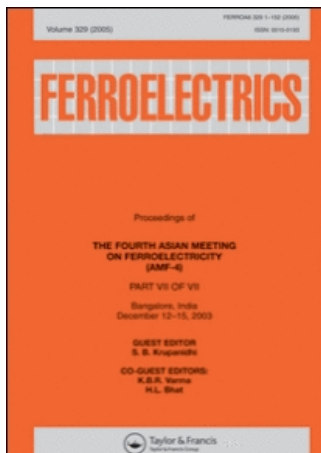


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Study of the Spontaneous Relaxor to Normal Ferroelectric Phase Transition in La-Doped Lead Titanate

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Highly lanthanum doped lead titanate ceramics exhibit relaxor properties and undergo on cooling a subsequent spontaneous macroscopic phase transition. The dielectric response is strongly affected by chemical (copper) doping and is found to become independent of the applied ac field for temperatures lower than the phase transition one.

Keywords: Relaxor ferroelectrics; dielectric properties; phase transition

INTRODUCTION

Relaxor ferroelectrics, like PMN ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$), display a large dielectric permittivity in the vicinity of T_{max} and dispersion for $T \leq T_{\text{max}}$. This broad dielectric maximum in the $\epsilon_1(T)$ curve does not correspond to a phase transition and can be seen as a dynamic effect due to relaxational processes. In the mixed B - site cation family, $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$, the relaxor behaviour is believed to arise due to a

compositional heterogeneity, resulting in partially ordered materials. Meanwhile, a real phase transition can be induced at a temperature called T_{R-nFE} ($< T_{max}$) either by an external stress (pressure^[1] or dc electric field^[2]) or by changing the ordered domain size (thermal treatments^[3] or chemical doping^[4]).

The case where two different cations occupy the A crystallographic position of a perovskite (ABO_3) is less understood. The most studied systems, due to their technological applications, are $(Pb,La)(Ti,Zr)O_3$ (PLZT) together with PLT, i.e. $(Pb_{1-\alpha}La_{\alpha})TiO_3$ (with $\alpha \approx 1.5$ ^[5]). The purpose of the present study is to investigate the dielectric response of samples containing 30 at. % La.

SAMPLES

Ceramics have been prepared by a conventional mixed oxide method, eventually with introducing copper on the B site. This substitution of reverse sign valency La^{3+}/Pb^{2+} and Cu^{2+}/Ti^{4+} induces a decrease of lead vacancies content according to the chemical formula^[6] $(Pb_{1-x-3y/2}La_y□_{y/2-x})(Ti_{1-x}Cu_x)O_3$. It is worthwhile to note that lanthanum favours copper doping (up to $y/2$); in the same time, copper increases also the maximum amount of La which can be incorporated in lead titanate from about 35 at. % ($x = 0$) to 42 % ($x = 0.2$). In the following, we will be mainly concerned by samples containing 30 % of lanthanum and $x = 0, 0.025$ or 0.10 .

In PLT, the disruption of the translational periodicity of the lattice induced by aliovalent La modification is known to lead to dramatic changes in the phase transformational characteristics of $PbTiO_3$. Not only the phase transition is monotonously shifted to lower temperatures as the amount of lanthanum increases but also its nature changes from a first order to a diffuse transition. These results can be confirmed by calorimetric measurements (figure 1) which show that

the enthalpy of transition is gradually reduced : finally, for $y > 0.25$, no phase transition can be detected by DSC as the dielectric response (figure 2) closely resembles that of relaxors, like PMN. In PLT ($y = 0.30$), some local dipolar nanodomains, randomly oriented, are known to appear at a temperature much higher than $T_{\text{max}}^{[7]}$, which no more coincides with a symmetry change (cubic to tetragonal like in the pure sample) : no macroscopic phase transition can be detected in the vicinity of T_{max} by means of X-ray diffraction.

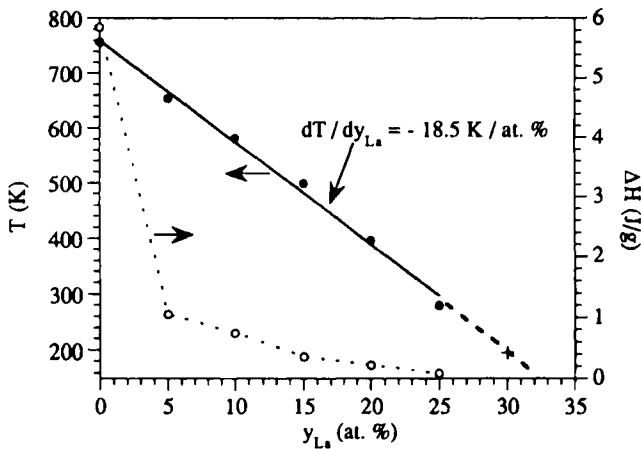


FIGURE 1 Transition temperatures and enthalpies of PLT ceramics deduced from DSC curves measured on heating (+ 10 K/min). The cross indicates the hypothetical temperature of the ferroelectric phase transition in a sample containing 30 at. % La.

Meanwhile, the temperature of the dielectric maximum (T_{max}) is still standing on the straight line $T_{\text{transition}}$ versus y deduced from DSC measurements performed on samples containing less than 25 at. % of La (the cross in figure 1). The crossover between relaxor and normal ferroelectric states in this system is between a La content of 23 and 24

$\%^{[8]}$, critical compositions which exhibit a relaxor to normal transformation. For $y = 0.30$, the disorder is supposed to hinder the onset of long – range ferroelectric order ; in such a picture, the polar nanodomains, which increase in size with decreasing temperature, condense at low temperatures into a glasslike state with no macroscopic symmetry change.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of both ϵ_1 and j , the current density, recorded mainly during cooling (-1 K/min) using a HP 4284A LCR meter or a Keithley 236 respectively.

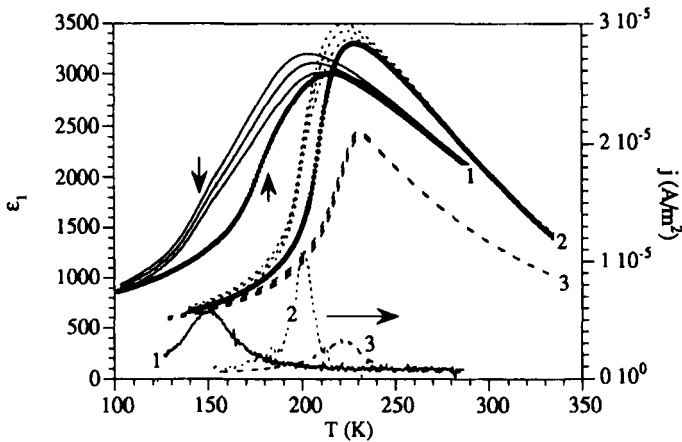


FIGURE 2 Real part of the dielectric constant (weak ac field : 0.01 kV/cm) measured either on heating (circles, $f = 10$ kHz) or on cooling (0.1 ; 1 and 10 kHz, from the top to the bottom) for the three studied samples ($y = 0.30$) with $x = 0$ (1), $x = 0.025$ (2) and $x = 0.10$ (3). Right scale : current density detected upon a dc field cooling under 2 kV/cm.

Several remarks can be made :

- the copper effect upon the T_{max} value is quite negligible (shift of about 30 K) ; in the same time the relaxor properties gradually vanish : for $x = 0.10$, T_{max} is nearly independent on the measuring frequency and the dispersion disappears.
- the thermal hysteresis for $T < T_{\text{max}}$ becomes increasingly less marked as x increases.
- in the same time, the small hysteretic and frequency independent shoulder (arrows in figure 2 for $x = 0$) shifts near T_{max} .

This shoulder in the $\epsilon_1(T)$ curves can be ascribed to a spontaneous relaxor to normal ferroelectric phase transition occuyring on cooling at $T_{\text{R-nFE}} \approx 140$ ($x = 0$), 205 ($x = 0.025$) and 220 K ($x = 0.10$). This anomaly (or the associated peak of a poling current, figure 2) may be shifted to higher value ($T_{\text{transition}} \rightarrow T_{\text{max}}$) when a dc bias field is applied. This field sensitivity is less and less important as the Cu content increases. The more convincing experiment that proves the existence of a ferroelectric phase transition is X-ray diffraction experiments performed on the same samples during a field free heating (figure 3). The splitting of some diffraction lines (in particular the (200) reflection), revealing a long – range tetragonal distorsion of the crystalline cell, disappears at a temperature $T_{\text{nFE-R}} > T_{\text{R-nFE}}$ (180 K for $x = 0$ or 220 K for $x = 0.025$) which increases with x and which can be compared with the values deduced from the depoling current or dielectric measurements.

Copper, which favours La incorporation in PbTiO_3 and reduces nanometric heterogeneity (as evidenced from high resolution electron microscopy images, not shown here), reduces the relaxorlike behaviour. But, in all the cases (i.e. even without copper doping), a macroscopic phase transition takes place at a temperature which can be

several tens of degrees lower than T_{\max} . This finding is very similar to what has been observed in $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ^[9].

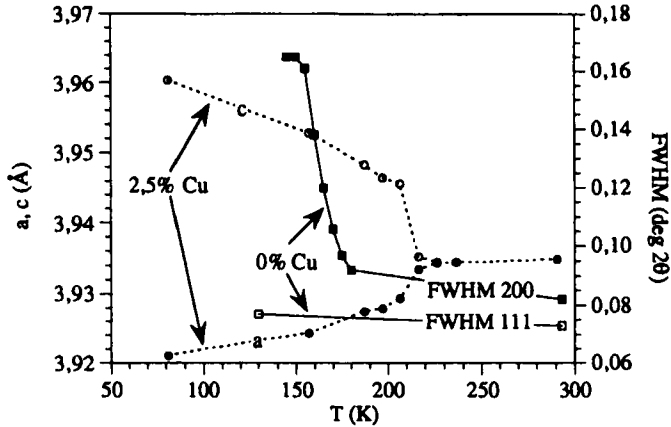


FIGURE 3 Temperature dependence of the FWHM of the 111 and 200 reflections ($x = 0$) and of the lattice parameters ($x = 0.025$) measured from X-ray diffraction on heating.

Figure 4 shows the change in the dielectric permittivity with increasing the amplitude of the ac measurement field from 0.03 kV/cm (small signal of the order of what is normally used for measuring ϵ_i) to 0.67 kV/cm (curves 1 to 4). The most essential features of the non-linear effect (increasing E_{ac} acts on ϵ_i like decreasing the frequency: T_{\max} shifts to lower values since ϵ_{\max} increases) are analogous to what has been reported for PMN^[10] and ascribed to the contribution of slow relaxators ($\tau > \omega^{-1}$) to the dielectric response. However, the ac non-linear component, $\Delta\epsilon_{ac}$, tends towards zero exactly at T_{R-nFE} (205 K for $x = 0.025$, figure 4).

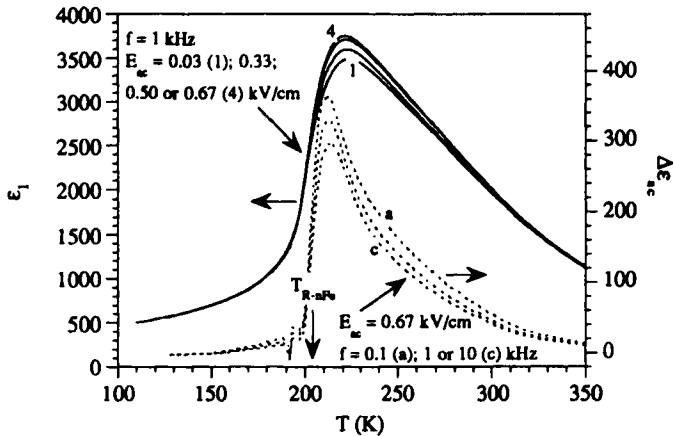


FIGURE 4 Dielectric permittivity (recorded on cooling) of a PLT ceramic ($y = 0.30$ and $x = 0.025$) at various amplitudes of the ac measurement field ($f = 1$ kHz); deduced non – linear part $\Delta\epsilon_{ac} = \epsilon(0.67 \text{ kV/cm}) - \epsilon(0.03 \text{ kV/cm})$ at several frequencies.

At such a temperature, the polar nanoregions reach a sufficient size to percolate and induce micropolar domains revealed by X-ray diffraction. Whatever the physical explanation of the relaxor properties (polar clusters or dissipative motion of domain walls), the number of entities which can respond to the external field decreases at the phase transition temperature: the drastic change in the relaxation time spectrum at T_{R-nFE} strongly affects the ac non – linear properties which is found to be both hysteretic and copper dependent.

CONCLUSION

Even for a lanthanum content as high as 30 at. %, PbTiO_3 : La ceramics undergo a macroscopic phase transition about sixty degrees below T_{max} . Copper doping, by changing the chemical composition and

nanostructure, destroys the relaxorlike properties of the material so that the transition occurs closer and closer to T_{\max} . As the polar nanodomains turn into microdomains, the dielectric response no more depends on the ac field amplitude.

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