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Ferroelectric behavior in 5/65/35 hot-pressed PLZT ceramics

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Abstract

Lanthanum lead zirconate titanate with 5 at.% of La (5/65/35 PLZT) hot-pressed ceramics have been studied in order to explore its dielectric properties below Burns temperature. Previous measurements of 6.5/65/35 hot-pressed PLZT ceramics revealed relaxor-ferroelectric behavior, i.e. coexisting ferroelectric and relaxor dielectric response. Similar relaxor behavior, though not so pronounced, was also expected at lower concentrations of La in 5/65/35 hot-pressed PLZT ceramics. We explored the possible duality of ferroelectric and glassy relaxor behavior in 5/65/35 hot-pressed PLZT ceramics with measurements of the complex linear dielectric susceptibility as a function of temperature and bias electric field. These experiments revealed no indications of prominent relaxor behavior. Results revealed solely a smeared relaxor to ferroelectric transition. Moreover, polarization hysteresis measurements below this transition confirmed existence of the ferroelectric phase in zero bias electric field in 5/65/35 hot-pressed PLZT ceramics without relaxor features like freezing process and frequency dependence.

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Keywords: Relaxor; Hot pressing; Dielectric properties; Ferroelectric properties; PLZT

1. Introduction

Investigations of ordinary (not hot-pressed) $x/65/35$ PLZT ceramics, one of the most widely used type of ceramics, have indicated that with La content varying between 4 and 12 at.% these PLZT ceramics belong to the relaxor-ferroelectric systems. [1] In the Lanthanum concentration range between 4 and 7 at.%, the macroscopic properties change from normal-ferroelectric to relaxor-ferroelectrics with increasing La content. For Lanthanum concentrations above 7 at.%, these materials shows only typical relaxor properties while ferroelectrical response completely vanishes in conditions of zero bias electric field. [2–6]

Scenarios on cooling PLZT ceramics are the same as for other relaxor-ferroelectric materials. Below Burns temperature, [7] where thermal fluctuation prevail over random field effects, PLZT ceramics behave superparaelectric-like or usually refereed to as ergodic relaxor-like. With further lowering temperature thermal fluctuations tend to diminish and random fields can take control. The result is that nanodomains which are pinned by local random fields start to grow towards micro sized domains. In contrast to PLZT ceramics with higher concentrations of La, ceramics with less La have less Pb vacancies which are responsible for breaking the long-range Coulomb interaction in the lattice. This consequently results in more pronounced effect of Coulomb coupling between ferroelectrical BO_6 octahedrons in ABO_3 perovskite PLZT structure, leading to the larger size of polar nanoregions and consequently to the higher dielectric response as the correlation length grows. [8]

Whether these polar regions will achieve a spontaneous ferroelectric phase on cooling or stay in ergodic relaxor phase and consequently, below freezing temperature, freeze into a non-ergodic relaxor phase depends upon La concentration. [1,3,4,9,10] Above critical (> 7 at.%) La content the decoupling is expected to be sufficiently strong to prevent spontaneous formation of a long-range ferroelectric state with micron-sized domains. Instead, on cooling, a locally polarized regions, which behave like spins feeling local electric random fields and interact via random bonds, [11,12] state is observed on a nanometer scale. Interesting behavior is therefore expected in the case of 5/65/35 hot-pressed PLZT ceramics. According to results of dielectric susceptibility measurements in 6.5/65/35 hot-pressed PLZT ceramics [13] where a coexistence of relaxor and ferroelectric state was seen, one would expect even more pronounced ferroelectric phase in the case of 5/65/35 hot-pressed PLZT ceramics as La content and thus also breaking of Couloumb interactions is smaller. [14] Until now no such detailed measurements were made in hot-

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pressed PLZT ceramics of 5 at.% La concentration. Additional question arises whether La content in 5/65/35 hot-pressed PLZT ceramics is small enough to prevent freezing process in coexisting relaxor phase or may be even to completely suppress the relaxor phase.

Therefore, in this article a P-E hysteresis and complex linear dielectric susceptibility measurements in 5/65/35 hot-pressed PLZT ceramics are presented in order to compare the effects of La concentration on relaxor-ferroelectric PLZT ceramics material behavior.

2. Experimental procedures

Measurements were made on three PLZT 5/65/35 hot-pressed ceramic samples with thickness around 0.530 mm. Samples were prepared by a mixed oxide method starting from high purity oxides (> 99.9%). After being hot-pressed at 1150 °C for 2 h in PbO excess environment, gold electrodes were sputtered onto the sample by the evaporation technique. Complex dielectric susceptibility was measured using a Hewlett-Packard 4282A Precision LCR meter. The amplitude of the ac excitation voltage was 1 V. The measurement voltages were small enough to neglect the influence of the ac field on dielectric susceptibility values. Measurements were performed on heating and cooling the sample in between 350 and 490 K in several dc bias electric fields from 0 to 5 kV/cm. The temperature heating and cooling rate was typically ±30 K/h and the frequency range was between 20 Hz and 1 MHz.

The dc field dependance of the polarization was determined by cooling an annealed sample down to room temperature of 295 K. Then dc bias electric field was applied and the corresponding polarization charge was measured by the Keithley 617 programmable electrometer.[15]

Since it is well known that history-dependent effects play an important role in relaxor systems, the samples were annealed at 450 K for 1 h before each measurement, in order to ensure identical conditions for all measurements and to eliminate the effects of previous treatments.[4,16]

3. Results and analysis

According to predictions presented in introduction measurement of dielectric polarization (Fig. 1) indeed reveal a pure ferroelectric hysteresis, indicating a ferroelectric state at room temperature. Observed spontaneous polarization of 0.34 As/m^2 is quite high, but again expected in comparison to the values obtained in higher La concentrated PLZT ceramics.[4,9,17] Rather high coercitive field $E_c \approx 4$ kV/cm is merely an indication of pinned ferroelectric domains and not a sign of a critical field for an induced ferroelectricity within non-polar ergodic relaxor phase. Thus, 5/65/35 hot-pressed PLZT ceramics behave as a spontaneous ferroelectric material at room temperature.

Measurements of a real part of complex linear dielectric susceptibility on heating (Fig. 2) revealed a frequency independent step at 465 K beside otherwise rather smooth temperature dependence. We believe, on the basis of analogy with dielectric measurements in 6.5/65/35 hot-pressed PLZT ceramics, that

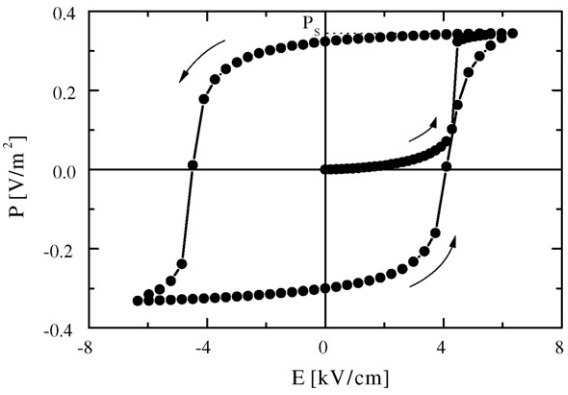

Fig. 1. P-E hysteresis loop at room temperature (295 K). Indicated spontaneous polarization P_s has value of 0.34 As/m^2.

this step anomaly is an indication of ferroelectric to ergodic (superparaelectric-like) relaxor phase transition of the first order.[18] The absence of the pronounced frequency dispersion, well known from higher La concentrated PLZT ceramics,[13,17] confirms that the majority of the material is indeed in the ferroelectric phase, while ergodic relaxor phase is present in only small areas or is probably even completely replaced by a ferroelectric phase at lower temperatures.

In relaxor type materials the freezing temperature can be deduced from the analysis of the frequency and temperature dependent dielectric peaks which behave according to the Vogel-Fulcher law. The Vogel-Fulcher temperature actually corresponds to the temperature for ergodic relaxor to non-ergodic relaxor phase transition.[4,13] All signatures of relaxor freezing process are suppressed in 5/65/35 hot-pressed PLZT ceramics, as it seems that long-range correlations prevail over the whole material. The only similarity to the relaxor behavior are a smeared frequency dependent dielectric susceptibility maximum peaks above ferroelectric to ergodic relaxor phase transition temperature. Instead of Curie-Weiss like behavior, typical for ferroelectric to paraelectric phase transition, only a smeared dielectric susceptibility peaks are seen. The susceptibility frequency dependence is therefore rather weak in contrast to the relaxor behavior at higher La concentrations and is more reminiscent of smeared ferroelectric phase transition.

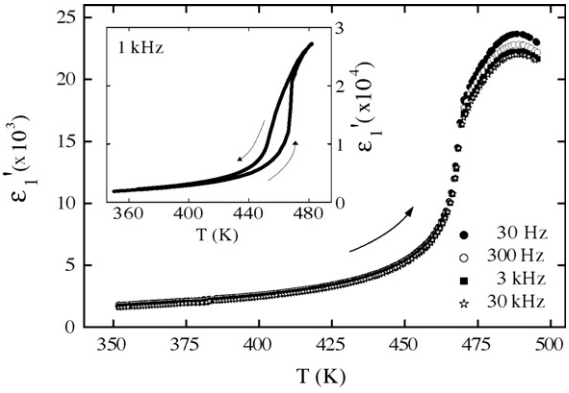

Fig. 2. The real part of dielectric susceptibility as a function of temperature for several measurement frequencies taken on heating. Inset shows hysteresis effect between cooling and heating run.

The reason why at higher temperatures, above ferroelectric to ergodic relaxor phase transition temperature, peaks are frequency dependent is due to a dynamic consequence of measurements. With lower temperature polar nanoregions tend to surpass thermal fluctuations and start to form microscale polar regions. It appears that bigger regions have slower relaxation than smaller regions and as such they do not contribute to a high frequency ac susceptibility.[3] Consequently, susceptibility value becomes suppressed and also frequency dependent. Effectively when experimental time scale becomes shorter than relaxation frequencies the susceptibility contribution from these relaxations is not detected and thus maximum in dielectric response becomes lower and also changes with frequency (Fig. 2).

Inset in Fig. 2 shows a hysteresis effect between heating and cooling run. The accompanying hysteresis effect is proportional to a degree of transformational strain in polar nanodomain state.[8,19] Effect appears due to space charge field from redistribution of defects in the PLZT material. Normally this field is stabilized with spontaneous polarization, though some field still develops due to the dielectric aging. When sample is heated these space charges disappear, thus leading to the appearance of hysteresis effect.[8] Additional increase in dielectric loss at even higher temperatures beside diffuse dielectric maximum occurs due to enhanced electrical conductivity resulting from higher concentrations of deppined point defects in the material.[19]

Similar frequency independent step-like behavior as seen in Fig. 2 in real part of the complex dielectric susceptibility is also seen on $\tan\delta$ on heating run (Fig. 3a) at 465 K. In addition, above the ferroelectric to relaxor phase transition temperature substantial differences between various frequencies in $\tan\delta$ are consequence of the dynamic effect in the relaxor material as well as increased thermal energy fluctuations due to increased temperatures. Interestingly, on cooling at 452 K again frequency independent small peak is seen (Fig. 3b), though at lower temperature as on heating and also not so step-like. This feature, not seen in 6.5/65/35 hot-pressed PLZT ceramics,[13] indicates a transition from an ergodic relaxor to a ferroelectric phase. Again no signs of a freezing process is seen. Due to the hysteresis effect this transition is not so pronounced as on the heating run.

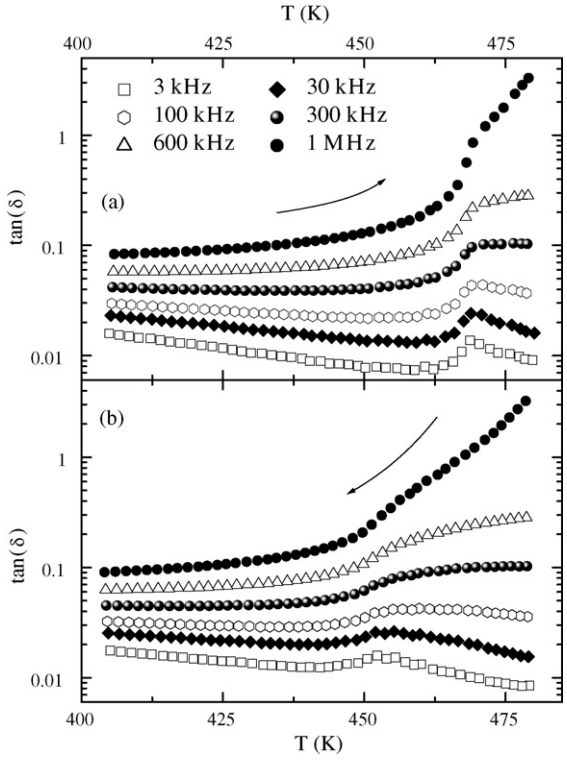

Fig. 3. The dielectric loss factor $\tan\delta$ as a function temperature for several measurement frequencies taken on (a) cooling and (b) heating runs in zero bias electric field.

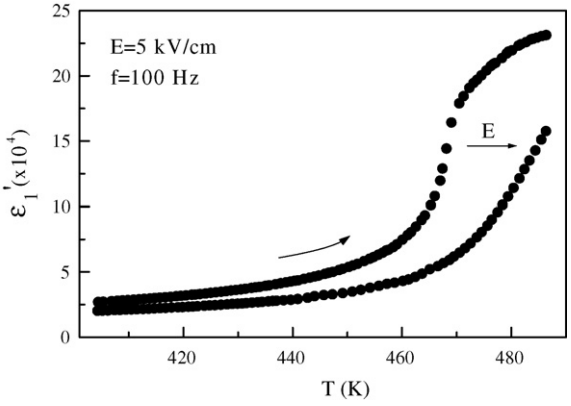

Fig. 4. The real part of dielectric susceptibility on heating run as a function of temperature measured at 100 Hz in zero bias electric field and in $E = 5$ kV/cm.

The dc bias field impact on the transition temperature between the ferroelectric and ergodic relaxor phase is shown in Fig. 4. Direct current electric field affects the random fields in the material, as it contributes to the changes of positions of the interphase regions. This external field forces the polar regions to reorient in a direction parallel to the electric field, to merge with other neighboring domains and thus diminishing the total area of boundaries. An external electrical field can thus overcome the random local fields in such a way that a normal ferroelectric phase may be induced at higher temperatures than normally as energy fluctuations can be overcomed. The positions of dielectric maximums shift towards higher temperatures as thermal fluctuations needs to increase in order to move bigger dipole moments.[2,20]

4. Conclusions

Well known fact that La content places disorder in PLZT ceramics was confirmed for 5/65/35 hot-pressed PLZT ceramics. However, this effect was found to be much smaller than in 6.5/65/35 hot-pressed PLZT ceramics and thus no freezing process towards non-ergodic relaxor state was seen. Only a transition between an ergodic relaxor and a ferroelectric phase was detected in cooling and heating runs. It appears that the PLZT hot-pressed ceramic with 6 at.% of La content may be viewed as the limiting case between the systems showing glassy relaxor-ferroelectric duality ($x > 6\%$) and pure ferroelectric systems ($x < 6\%$).

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