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Uniaxial Stress Dependence of the Permittivity of Electroceramics

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Abstract

The dependence of the permittivity on uniaxial pressure of ceramics in the paraelectric, ferroelectric and relaxor phases has been investigated for $BaTiO_3$, $Pb(ZrTi)O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$. In the paraelectric phase, upon the application of stress, a reversible decrease in the permittivity is observed. In the ferroelectric phase, the observed behaviors can be divided in two classes depending on the type of ionic defects present in the ceramics. Both behaviors are characterized by an instantaneous increase in the permittivity at both stress application and release ($\Delta\sigma$) but they differ in the following relaxation which can be a decrease (type A) or an increase (type B) in the permittivity. In relaxor materials the behaviors observed are similar to the paraelectric and ferroelectric phases as the temperature is lowered. The mechanisms of the different observed behaviors are discussed.

Keywords: dielectric properties, electrostriction, sensors.

1 Introduction

The hydrostatic pressure dependence of the Curie temperature (T_c) of ferroelectric and high permittivity (ε') materials has been widely studied.[1,2] However, little attention has been devoted to the particular case where the permittivity varies as a function of pressure at constant temperature. Furthermore the pressure dependence of the permittivity in relaxors has not been thoroughly studied.

The achievable $\Delta\varepsilon'/\Delta\sigma$-ratios in these systems can be of great interest in sensor applications. However, for use in applications, the temperature and the time dependence of the permittivity must be as small as possible.

The analysis of the dielectric behavior of high permittivity materials in different phases as a function of uniaxial pressure at constant temperature has been undertaken to identify the mechanisms standing behind the origin of the observed phenomena. The results for $BaTiO_3$ (BT), hard and soft $Pb(ZrTi)O_3$ (PZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) will be reported.

2 Experimental Method

Ceramic samples of cylindrical or cubic shape were prepared by the mixed oxide method. Platinum electrodes were deposited by sputtering. The permittivity was measured at constant temperature as a function of pressure and time using an HP 4284A precision bridge at frequencies ranging from 1 to 100 kHz.

To guarantee the application of highly stable compressive stresses, a mechanical lever press was used. The unpoled ceramic samples were pressed between two metallic cylinders acting as electrodes. An hemispherical piece of zirconia was used to compensate for misaligned or inhomogeneous forces on the sample surfaces. The uniaxial load was varied from 20 (prestress) to 2000 N. The DC stress was applied (or released) and maintained for a certain time while the dielectric permittivity was measured in the same direction as the applied stress.

3 Experimental Results and Discussion

3.1 Paraelectric phase

Materials in the paraelectric phase show an instantaneous and reversible decrease in their permittivity upon stress application (Fig. 1). The instantaneous change with stress is linear (Fig. 2) and its magnitude strongly depends on the value of

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the permittivity before loading. When measured at high temperatures ($T > 100°\mathrm{C}$), a short term relaxation is observed, which is probably of mechanical origin (Fig. 1). The converse electrostrictive effect is the intrinsic mechanism responsible for this behavior. The same effect has been used in low-ε materials to measure their electrostrictive coefficients.[3] It is derived from the free energy of a crystal, by considering the case of no spontaneous polarization, i.e paraelectric phase. For a uniaxial compressive stress ($\sigma < 0$), the permittivity is expressed as $\chi_3{}^{-1} = \alpha - 2Q_{11}\sigma$ (α is the dielectric stiffness) or $\partial\chi_3/\partial\sigma = 2Q_{11}\chi^2{}_3$ (true for small stresses). The values of Q_{11} for perovskite ceramics are positive, hence a compressive stress results in a decrease in the permittivity. The value of Q_{11} calculated for BT in this study is in agreement with the values reported in the literature.

3.2 Ferroelectric phase

Materials in the ferroelectric phase show a very different behavior compared to the intrinsic one as observed in the paraelectric phase. Among the ferroelectric materials studied (BT, PZT), one can distinguish two types of behavior that will be denoted as type A and B. Details are given below.

Before describing and discussing the results of the two types, it is essential to determine if the intrinsic converse electrostrictive effect changes when the material undergoes a ferroelectric phase transition. Calculations have been carried out as in the case of the paraelectric phase, but with $P_s \neq 0$. (Steiner, O. in preparation). The variation of the permittivity with stress was calculated in the direction of the applied stress. Since a ceramic has randomly oriented grains, the following two limiting cases have been considered for simplicity:

1. stress applied parallel to P_s
2. stress applied perpendicular to P_s.

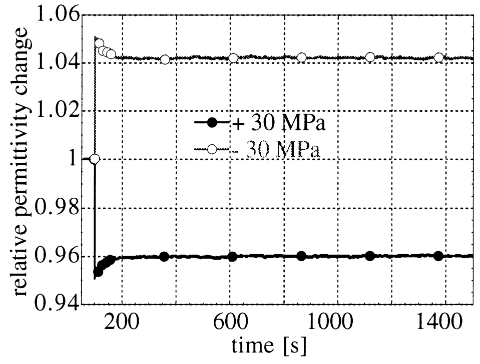

Fig. 1. Relative permittivity change at stress application and release for BT at 185°C (over T_c).

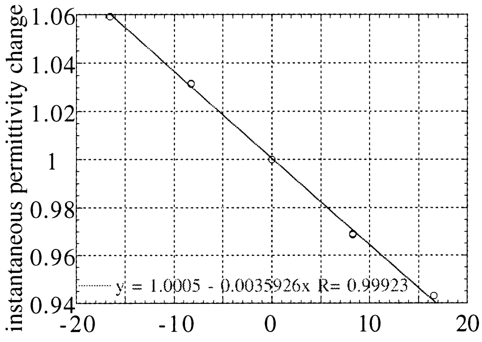

Fig. 2. Instantaneous permittivity change for BT at different stresses at 150°C (over T_c).

It was found that the results are qualitatively the same for both second and first order phase transitions. In the parallel case, the permittivity increases with the applied stress while in the perpendicular case, the permittivity decreases with the applied stress. However, both the absolute value of the permittivity and the amplitude of its change are substantially greater in the perpendicular case. The overall effect for ceramics is dominated by the contribution of the perpendicular case, thus the intrinsic effect in the ferroelectric phase results in a decrease in the permittivity under compressive stress as in the case for the paraelectric phase.

3.2.1 *Type A ferroelectrics*

This is the behavior observed in tetragonal BT with coarse grains ($d \approx 20$–$30\,\mu$m) and in soft doped (Nb) tetragonal, rhombohedral and morphotropic PZT. We shall describe the behavior of BT in this section. The slightly different behavior of soft PZT will not be discussed here.

The behavior of BT is characterized by a significant instantaneous increase in the permittivity at both stress application and stress release, followed by a substantial short term negative relaxation (Fig. 3) and a long term logarithmic-like decrease. The instantaneous increase in the permittivity is higher after stress release than after stress application. However, as compared to the instantaneous increase, the short term relaxation is more important after stress application. When the temperature increases, the main effect consists of a

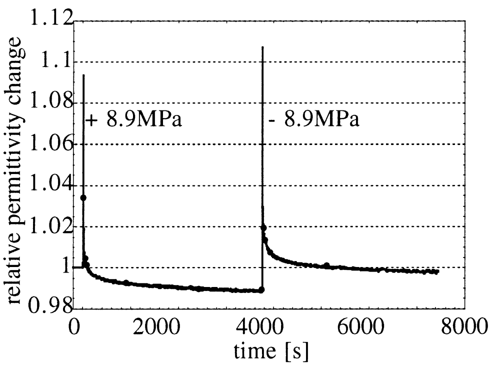

Fig. 3. Relative permittivity change at stress application and release for BT at 25°C (under T_c).

faster short term relaxation (Fig. 4). The time needed to reach the permittivity prior to the stress application decreases drastically from about 60 s at 25°C to less than 0·2 s at 100°C for the level of loading. This time is also dependent on the applied stress (shorter when $\Delta\sigma$ increases) and on the history of the sample: the first cycle of stress application/release is different from the following ones.

To understand the observed behavior we have to know how the applied stress compares with an equivalent electric field. It is possible to compare the mechanical and the electrical energies brought to the system, which are given as $2\sigma U_s \sim 2P_s E_f$ where σ, U_s, P_s, E_f stand for the applied stress, the spontaneous deformation of the lattice ($\sim$ 1% for BT at 25°C), the spontaneous polarization (15 μC cm^{-2} for BT at 25°C) and the effective electric field, respectively. The estimated effective electric field equivalent to an applied stress of 20 MPa is then 13 kV cm^{-1} for BT at 25°C. This value is more than 6 times higher than the coercitive field of BT (2 kV cm^{-1}). This means than the applied stress can not only move but also annihilate the 90° domain walls.

We can now distinguish several contributions to the instantaneous change of the permittivity upon stress application and release:

1. the reversible intrinsic converse electrostrictive effect (decrease at stress application and increase at stress release),
2. domain walls movement and depinning (similar increase at both stress application and release),
3. domain wall suppression due to the stress application (decrease at stress application, no effect at stress release).

The third point is thought to be responsible for the hysteretic behavior observed in BT (Fig. 3) where it was found that the permittivity after the stress cycle is smaller than before stress application.

The main contributions to the long term relaxation come from the pinning of the domain walls with random potential defects. When the stress is applied or released, the domain walls are partially unpinned. Some time is needed for the restoration of new pinning configurations (diffusion of the pinning centers) and for the domain walls to find new equilibrium positions. The faster long term relaxation rates observed at higher temperatures can be related to the faster diffusion of defects.

3.2.2 *Type B ferroelectrics*

This is the behavior observed in morphotropic hard doped PZT. It is characterized at 25°C by an instantaneous increase of the permittivity at stress application followed by a small short term decrease and by a long term increase of the permittivity (Fig. 5). At stress release, a very small instantaneous increase is followed by a significant short term decrease and a negative relaxation. The long term increase of the permittivity is strongly stress dependent, i.e. the application of 10 MPa instead of 20 MPa results in almost no long term increase (Fig. 5). This stress dependent behavior was reproducible. As the temperature is increased, the short term decrease after stress application disappears and the instantaneous increase at stress release becomes much more pronounced.

Compared to soft PZT, the domain walls are strongly pinned by oriented dipoles (random field defects). However, the observed behavior is not the same as in the paraelectric phase. To explain the overall increase of the permittivity after stress application, we need to invoke another mechanism in addition to those discussed for the type A ferroelectrics. For random field defects, the energy of a domain wall can be expressed as an 'absolute value' function instead of the classic parabolic one.[4] When a stress is applied, a domain wall, initially in position A (Fig. 6), will move to position B. It will be able to move more easily in this position than in position A because all the oriented dipoles around it will be oriented in the same direction and will not impede its movements. This will result in an increase in the permittivity. With this type of defects, no restoration occurs with time.

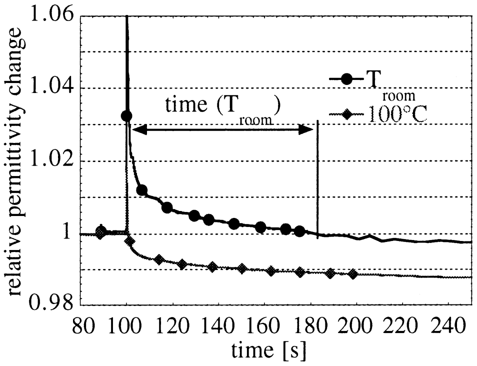

Fig. 4. Relative permittivity change at stress application for BT at 25 and 100°C (under T_c).

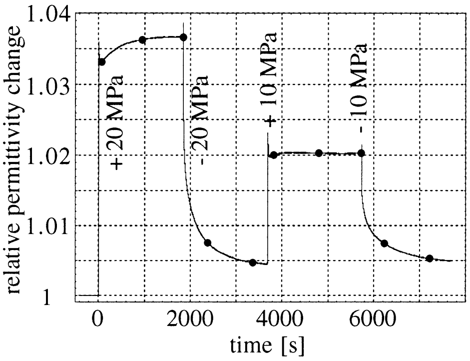

Fig. 5. Relative permittivity change at stress application and release for hard PZT at 30°C.

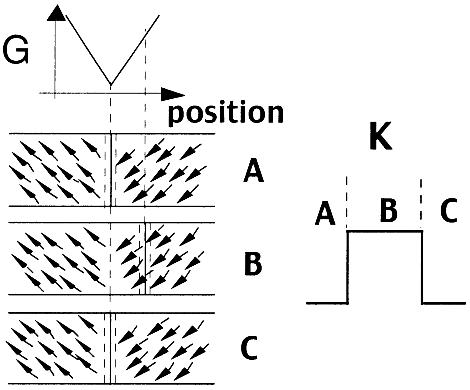

Fig. 6. Dipole oriented mechanism in hard doped morphotropic PZT.

3.3 Relaxor material

At temperatures higher than −20°C, PMN shows a linear behavior (Fig. 7) similar to materials in the paraelectric phase (zone 1, Fig. 8). When the permittivity is measured parallel to the stress application, a decrease of the permittivity is observed. However, when it is measured perpendicular to the stress, the instantaneous effect is reversed. This is due to the different signs of the Q_{11} and Q_{12} coefficients. When the temperature is lowered (zone 2, Fig. 8), some relaxation is observed after the instantaneous changes at both stress application and release. At even lower temperatures ($T < -70$°C; zone 3, Fig. 8) the behavior becomes similar to materials of type A in the ferroelectric phase. The boundary between zone 1 and 2 is close to −20°C at an applied stress of 20 MPa. For PMN, such a stress is equivalent to an electric field of about 10 kV cm^{-1}. Some studies[5,6] have shown that a ferroelectric phase can be field-induced at low temperatures in PMN. The upper temperature limit of stability of this induced phase depends on the applied electric field. At 10 kV cm^{-1}, this temperature is close to −13°C. This could be considered as an indication that a ferroelectric phase can be stress-induced in PMN. Furthermore, the observed relaxation at temperatures lower than −20°C can be attributed to the existence of this ferroelectric phase.

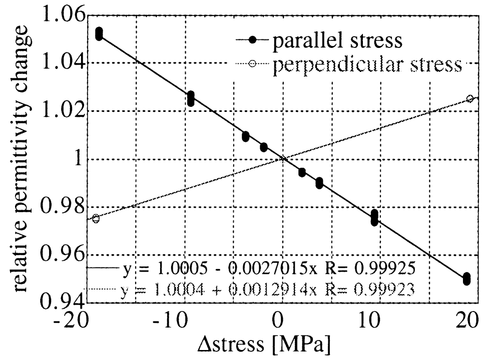

Fig. 7. Instantaneous permittivity change for PMN under parallel and perpendicular stress at 50°C (over T_m).

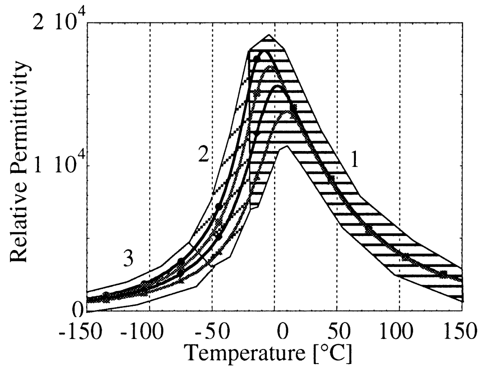

Fig. 8. Zones of different behaviors under stress for PMN (see text for details).

4 Conclusion

The dependence of the permittivity on uniaxial pressure of materials in the paraelectric, ferroelectric and relaxor phases has been investigated for BT, soft and hard PZT and PMN.

In the paraelectric phase, the effect is linear and is a manifestation of the intrinsic converse electrostrictive effect.

In the ferroelectric phase, two types of behavior could be distinguished, related to the interaction of the domain walls with random potential and random field defects. The intrinsic converse electrostrictive effect was calculated for the ferroelectric phase. Its magnitude and sign was found to depend on the order of the phase transition and on the orientation of P_s with respect to σ.

PMN shows three different types of behavior: paraelectric-like at $T > -20$°C, paraelectric-like with relaxation between −50 and −20°C and ferroelectric-like (type A) at $T < -70$°C. At temperatures lower than −20°C, there is an indication that a ferroelectric phase could be stress-induced.

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