Sample Thickness Dependence of Electromechanical Properties of PZN-PT and PMN-PT Single Crystals

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ABSTRACT: We studied the electromechanical properties of PMN-PT and PZN-PT single crystal plates poled along [001] with thickness t ranging from 800 down to 70 μm. In the case of the tetragonal single domain state (1T), the properties of the thickness mode remain stable down to 250 μm. Below 250 μm, an instability of the polarization is shown. The plates exhibit regions where polarization lies in the plane of the plates. These emergence of these regions results in an additional shear mode at a frequency close to that of the thickness mode, an important increase of the dielectric constants ε^S_{33} and ε^T_{33} and a decrease of the coupling-factor k_t and longitudinal wave velocity v^D_{33t}. In the rhombohedral multidomain state (4R) a moderate variation of k_t can be observed while ε^S_{33} increases with decreasing thickness. The increase of the dielectric constant in the 4R state is also related to an additional shear mode. When t decreases, the volume ratios of each domain family are not equal, leading to a tilt of the average spontaneous polarization away from the poling electric field. Consequently the modification of the domain structure for thin plates leads to a change of the electromechanical properties.

Key words: piezoelectric, single crystal, domain, thickness, electromechanical, PZN-PT, PMN-PT

1. INTRODUCTION

The high electromechanical properties of relaxor based single crystals such as PZN-PT and PMN-PT suggest that these materials could contribute noticeably to increase the performances of piezoelectric transducers in acoustic imaging and sonars[1]. For these applications, it is well known that the thickness of the electro-active material is determined by the frequency of operation (i.e. 1–20 MHz for medical imaging) and usually ranges from 1 mm down to 100 μm[2]. The thickness depedance of the electromechanical properties of these new materials is therefore of great interest. We studied thin single crystal plates in the tetragonal phase (PZN-12PT) and in the rhombohedral phase (PZN-4.5PT, PZN-7PT, PMN-28PT and PMN-32PT). We have shown in a previous work that the tetragonal phase is in a single domain state (1T) at room temperature when it is poled in the direction (001), and the rhombohedral phase has an engineered domain structure (4R) when poled in the same direction[3]. The goal of this work is to show how these domain structures change when the thickness of the crystal is decreased.

2. EXPERIMENTAL PROCEDURE

We studied commercial materials PZN-7PT (Microfine Inc), PMN-28PT (Morgan Electroceramics Inc), PMN-32PT (TRS) and laboratory materials PZN-4.5PT and PZN-12PT processed by Thales using the flux method (PbO flux)[4]. The crystals were oriented using the Laue back scattering technique. They were then cut and polished along the [100]/[010]/[001] directions in order to obtain thin plates with parallel faces and aspect ratio higher than 15. Gold electrodes were sputtered on the (001) faces for dielectric and electromechanical measurements. Composition and homogeneity of the samples were controlled by T_c measurements and X-ray diffraction. Samples were poled using the field cooling method[3] with a DC field of 3 kV/cm, from the cubic phase ($>T_c$) down to room temperature. A tetragonal single domain state (1T) is obtained for PZN-12PT and a rhombohedral multidomain state (4R) is obtained for the other compositions. Electrical properties of the samples near their thickness resonance modes are measured on an Agilent 4395A impedance analyzer. Polarization measurements are made by integration of the DC current measured with a Keithley 617 when a bias field is applied.

3. FREQUENCY DEPENDENCE OF THICK PZN-PT CRYSTALS

We first made a study of the frequency behaviour of electromechanical properties of PZN-xPT thick single crystals (x = 4.5, 7 and 12%) at frequencies up to 100 MHz. Properties are deduced from the fit of the electrical input impedance, calculated with the KLM equivalent circuit model[5]. The calculation is made at each resonance, from the fundamental to the 21^{th} harmonic. Fig.1 shows clearly the stability of the electromechanical properties versus frequency when the measurement is made on a thick sample.

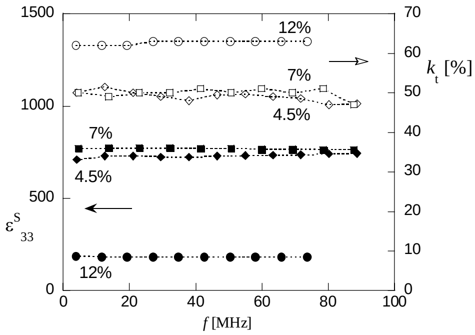

Fig.1: Evolution, with the harmonic order, of ε^S_{33} and k_t for PZN-PT (4.5, 7 and 12%).

In the following, the same properties are studied as a function of plate thickness and they are extracted from the fundamental resonance only. It is then possible to compare the properties of a plate with thickness t and fundamental resonance frequency f to those extracted from the $(2n + 1)^{th}$ harmonic of a plate having a thickness $(2n + 1)\,t$.

4. THICKNESS DEPENDENCE

4.1 Tetragonal Single Domain State 1T: PZN-12%PT

The electromechanical resonance frequencies of the thickness mode increased from ~2.5 to 25 MHz when the crystal thickness was decreased from 750 to 75 µm. Fig.2 shows that the free and clamped dielectric constants both increase strongly when the thickness of the crystal is decreased below 300 µm. At 75 µm, the values of ε^S_{33} and ε^T_{33} are 3 or 4 times higher than that of the thick crystals.

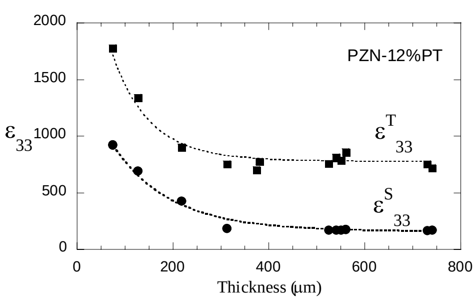

Fig.2: Evolution of ε^S_{33} and ε^T_{33} with crystal thickness for tetragonal PZN-12%PT (1T).

The impedance as a function of frequency obtained for the thin plates shows an additional resonance mode below the expected thickness resonance mode (Fig.3). This mode vanishes when a bias field of 7.14 kV/cm is applied during the impedance measurement. Considering the mode wave velocities measured on thick crystals, this additional mode was assigned to a shear mode with polarization parallel to the plate surfaces. Extracting the electromechanical parameters from these two resonances showed that the thickness coupling coefficient k_t decreases from 60% to 40% when the thickness becomes lower than 300 µm.

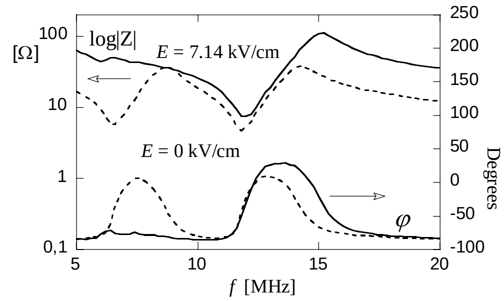

Fig.3: Electric impedance modulus and phase of a thin (140 µm) PZN-12PT crystal around its fundamental thickness mode. The shear mode at lower frequency vanishes under bias field.

Below 200 µm, it was possible to extract the shear coupling factor k_{15}, which remains apparently constant around a value of 62% (Fig.4).

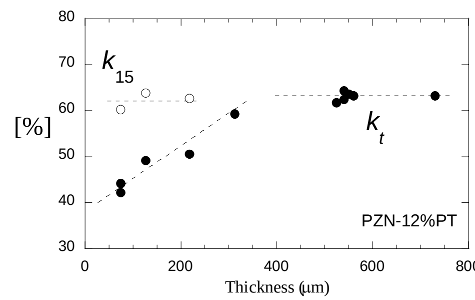

Fig.4: Evolution of the thickness coupling factor k_t and the shear coupling factor k_{15} with crystal thickness for tetragonal PZN-PT (1T).

From the same resonance modes, we extracted the values of the sound waves velocities of the longitudinal mode v^D_{33t} and of the shear mode v^D_{15} (Fig.5). The velocity seems nearly constant with decreasing thickness, around 4100 m/s, though an accident on the curve seems to happen with the apparition of the shear mode at 2500 m/s. The shift of the longitudinal velocity, below 300 µm thick, may be due to a coupling between these two modes.

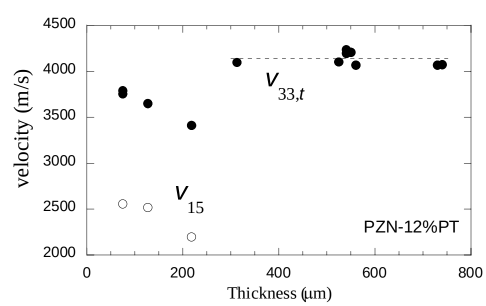

Fig.5: Evolution of sound wave velocities (longitudinal v^D_{33t} and shear v^D_{15} modes) with crystal thickness for tetragonal PZN-12%PT (1T).

As this additional shear mode disappears when we apply a bias field parallel and in the same direction as the initial poling field (Fig.3), we investigated the influence of this field on the dielectric constant ε^T_{33} (Fig.6). It was clear that the dielectric constant of the thick crystal was retrieved when an increasing bias field up to 8 kV/cm was applied on a thin crystal. When the field was decreased again down to zero, the initial value of ε^T_{33} was not immediately restored, showing that this process is due to a slow and unstable phenomenon.

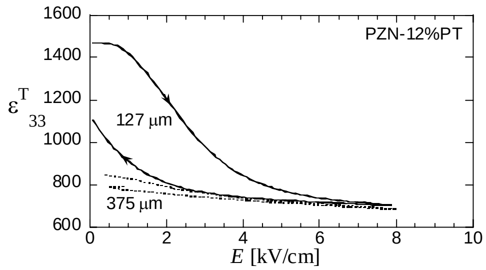

Fig.6: Free dielectric constant as a function of quasistatic increasing and decreasing bias field for tetragonal PZN-12%PT (1T) for two different thicknesses.

To show the relation between the high dielectric constant of the thin crystals and the polarization, we measured the change in polarization under bias field, starting from a poled 1T state and applying a field in the same direction as the poling field (Fig.7). We observe that for the thinnest crystal (127 µm), the saturation polarization increase reaches 30% of the spontaneous polarization P_S (~0.27 C/m^2) obtained on thick sample. The polarization decreases again when the field is removed, but does not recover immediately its initial value. This non-remanent polarisation is related to the decrease in ε^T_{33} observed in Fig.6 as we shall explain in the discussion.

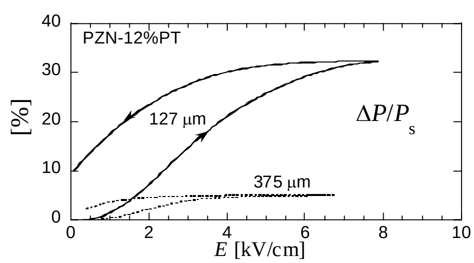

Fig.7: Change in polarization when a bias field is applied parallel to the initial poling field on tetragonal PZN-12PT (1T) with different thickness.

4.2 Rhombohedral 4R Multidomain State

We carried out the same experiments on domain-engineered crystals having the 4R rhombohedral domain structure: PZN-xPT (x = 4.5, 7) and PMN-xPT (x = 28, 32). We observed sometimes the apparition of an additional shear mode below the thickness mode on thin plates (see for example the case of PMN-32PT in Fig.8). Like in single domain 1T tetragonal crystals, ε^S_{33} increases when the crystal thickness decreases (Fig.9(a)), but to a less extend than for single domain crystals (less than a factor of 2). When the additional shear mode is absent or very weak (this is the case for PMN-28PT and PZN-4.5PT), the increase of the dielectric constant is even weaker. The thickness coupling factor decreases too like in single domain 1T crystals, but in a less extent (Fig.9(b)).

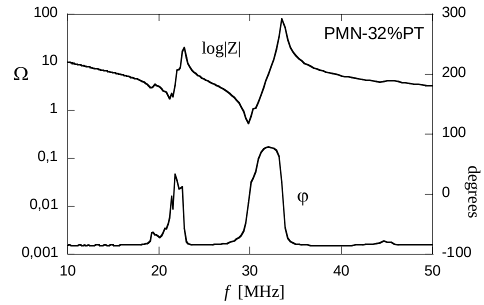

Fig.8: Impedance modulus and phase of a thin (70 µm) rhombohedral PMN-32PT multidomain (4R) crystal around its fundamental thickness resonance.

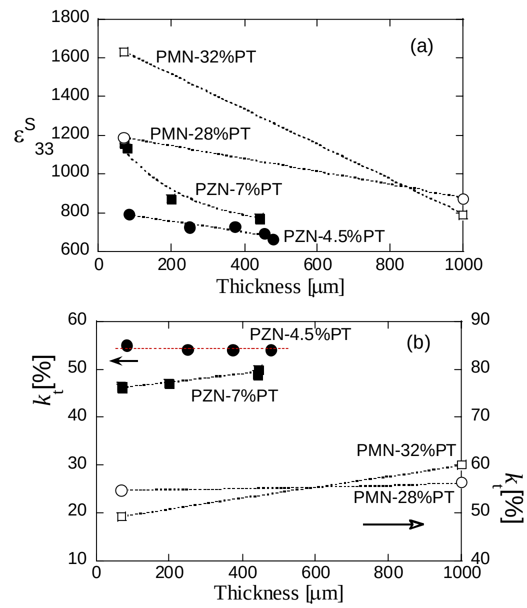

Fig.9: Evolution of (a) ε^S_{33} and (b) thickness coupling factor k_t with crystal thickness for rhombohedral multidomain compositions (4R)**.**

5. DISCUSSION AND CONCLUSION

We observe the same qualitative behaviour on single domain 1T crystals and multidomain 4R crystals when the thickness is decreased:

- increase of the dielectric constant
- decrease of the thickness coupling factor
- emergence of a resonant shear mode

However, the interpretation in both cases is quite different. In the single domain state 1T, the remanent polarization is parallel to the thickness of the plate when it is thick enough (t > 300 µm). This leads to a relatively low dielectric constant since it is well known that in single domain ferroelectric perovskites ε_{33} is much lower[6] than ε_{33}. When the thickness is decreased below 300 µm, as demonstrated recently by Jeong *et al*[7], optical transmission observations using polarized light show that part of the crystal contains domains with polarization parallel to the plate surfaces (Fig.10). This explains the much larger dielectric constant since this part of the crystal contributes by ε_{11} instead of ε_{33}. For the same reason, the thickness coupling coefficient decreases (Fig.4) because these domains do not contribute to k_t. But these "shear domains" are responsible for an additional shear resonance mode. When a bias field is applied, the shear domains disappear, the shear mode vanishes and the value of the polarization parallel to the field increases because of this 90° domain switching (Fig.7). The 1T domain structure is therefore not completely stable below 300 µm and an additional bias field is necessary to keep high thickness properties at high frequency.

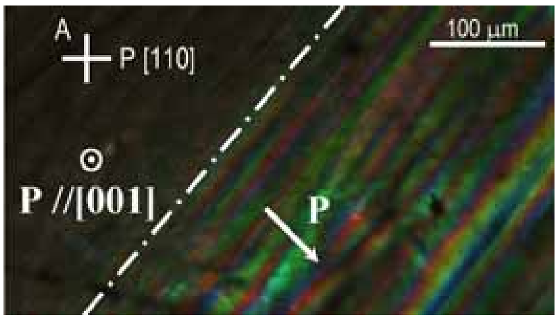

Fig.10: Transmission polarized light optical microscopy image of (001) poled PZN-12PT (127 µm). The region on the right has a polarization that is not normal to the face.

The results obtained on thin plates are therefore not comparable with the high frequency measurements of the thickness modes on thick crystals using the harmonic method. In this case, the crystal has a stable domain structure 1T and the higher resonance modes reflect the local properties inside an ideal crystal. These are constant with frequency. For thin crystals the single domain state is not stable and polarization should be more stable when it is parallel to the large faces. It is clear that boundary conditions could have some effects due to the small size of the crystal as regard to the domain size. These boundary (surface) effects can be due to stresses coming from the electrodes, trapped charges at the surface, residual stress from polishing …

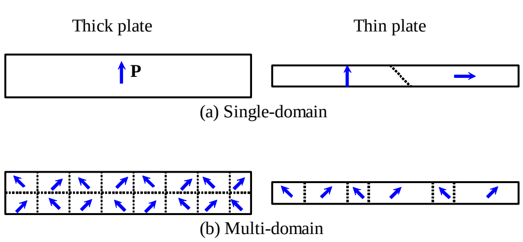

Fig.11: Schemas of domain structures of thick and thin plates for single domain and multidomain states.

On multidomain 4R structures, it is surprising to observe the same kind of effects, since the local polarization is already tilted by ~54° from the poling direction in each of the 4 families of domains. We propose a different explanation: in a large crystal, the statistical number of each kind of domain is the same and the resultant polarization parallel to the plate vanishes. In each domain family, the shear mode is clamped by the adjacent domains and no resulting shear mode can happen. In thin crystals (thickness compared to the average domain size), this statistical equilibrium may not be reached resulting in a non zero macroscopic polarization component parallel to the plate surfaces. The predominance of one or two of the four families of domains can explain the presence of a shear resonance mode which cannot be completely clamped by the other domains.

The explanation of the increase of the dielectric constant in Fig.9(a) involves the assumption that this shear mode is related to domain wall mobility leading to an extrinsic effect. In a perfectly domain engineered structure where all the domains compensate and are clamped, the dielectric constant increase due to this extrinsic effect is much lower.

Further works are planned to better understand the relation and stability of the domain structures under electric field by optical observations with polarized light.

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