

Ferroelectricity of calcium modified lead titanate ceramics

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When a ceramic with grain boundaries rich in OPb is poled beyond 40 kV cm^{-1} at ferroelectric phase, the highest anisotropy of electromechanical coupling factor is obtained. An attempt to explain this behaviour is made in terms of domain switching and the strains and cracks generated during cooling down poling. Apart from composition, two more factors are revealed as contributing to the disappearance of radial coupling in Ca-modified lead titanate ceramics: microtexture and electric poling strategy.

1. Introduction

A low mechanical quality factor Qm and a large electromechanical anisotropy (ratio of electromechanical coupling factor for thickness vibration K_t to that of planar vibration K_p) are the most important factors to make high frequency ultrasonic ceramic transducers for use in echography. At present, PZT ceramics have been the most usual materials but these have technological disadvantages such as the use of back load and matching adapter films. In recent years the use of modified PbTiO_3 ceramics have been tried with success [1, 2], particularly that of calcium in Pb-positions.

Tetragonality [1], 90° domain rotation [3] as well as change of sign of the piezoelectric modulus d_{31} with temperature [4] have been suggested as possible reasons for the high anisotropy in electromechanical coupling factor, but knowledge of that mechanism is not conclusive. In this work we investigate electromechanical and ferroelectric behaviour with poling treatment in materials prepared by an alternative method based on enhanced reactivity in synthesis and sintering. Moreover, an explanation of how poling and microtexture affect the anisotropy of electromechanical coupling factors is proposed.

2. Experimental results

2.1. Preparation of samples

The material prepared for this work was basically that of chemical formula $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}\text{O}_3$ given by Yamashita *et al.* [2]. But the processing was quite different as is detailed by the authors elsewhere [5]. It is based on reactivity enhancement of both the chemical synthesis and ceramic sintering: during chemical synthesis the different cations are added in an adequate pH medium that results in what is basically a colloidal dispersion; this system is able to transform into a gel which exhibits high reactivity. On the other hand, the mineralizer F_2Ca is also added and ceramic sintering proceeds as a highly reactive process. By this method a very dense ceramic is obtained (higher than 96% with a mean grain size

of $2 \mu\text{m}$), with a homogeneous texture and is easily machinable without prior annealing.

The process has been controlled by powder X-ray diffraction and cell parameters $a = 0.3889 \text{ nm}$, $c = 0.4042 \text{ nm}$, $c/a = 1.039$ were obtained.

Sintered discs were cut into thin plates which were lapped and polished to a final thickness of less than 1 mm and 12 mm in diameter. Both faces were electroded with fired silver paint for electric and electromechanical measures.

In order to know the influences of poling on final dielectric and piezoelectric parameters, two methods of poling were used. The first consisted of warming the sample up to 140°C and letting the sample cool to room temperature with an applied electric field. Other samples were heated above the Curie temperature ($\sim 270^\circ\text{C}$) and then cooled to room temperature while applying a smaller electric field.

2.2. Measurement techniques

From the dimensions of the sample, relative permittivity is obtained by measuring the capacity at 1 kHz with an RCL-meter. Furthermore, from the temperature dependence, T_c was measured. Remanent polarizations P_r were obtained from P-T diagrams by recording the electric charge released as the temperature of sample is raised, using a charge integrating method; in order to avoid the involvement of the conducting charge, a fast heating of sample was successfully used.

Electromechanical coupling factors K_t and K_p were inferred from resonance and antiresonance frequencies, measured by the resonance method [6] with an Impedance Analyser. Piezoelectric constant d_{33} was directly measured by a Berlincourt Piezo d_{33} -meter at 100 Hz. The mechanical quality factor Qm and Poisson ratio were also calculated from the same resonance measurements.

Crystal structure characterization as well as integrated intensities of 002 and 200 reflections were measured by an automatic X-ray powder diffractometer. Variations of the ratio $R = I_{200}/I_{002}$ were

used to calculate the contribution N of 90° domain orientation after different poling treatments. Samples were previously annealed at 700°C and then, graphite electrodes were painted which are transparent to the CuK X-radiation used.

2.3. Results

Two sets of samples called TPC1 and TPC2 of the same composition which present a similar Curie temperature $T \sim 270^\circ\text{C}$ and tetragonality $c/a = 1.039$ were studied. The only difference was in sintering temperature, 1050 and 1000°C , respectively, which resulted in different density values.

Electroded ceramics were poled by the first method. The resulting behaviour of the piezoelectric and electromechanical coupling factors are shown in Figs 1 and 2 for sample TPC1. Note how the piezoelectric modulus d_{33} , increases with poling field as polarization does in that kind of system. The behaviour of the electromechanical coupling factors are very different since the change of K_p is small and K_t increases a large amount.

A sample of TPC2 was poled at different and increasing electric fields at 300°C (paraelectric phase) by using the above mentioned method. Figs 3 and 4 show variations of piezoelectric modulus d_{33} , electromechanical coupling factors K_p and K_t and remanent polarization P . Another similar sample of TPC2 heat poled now at the ferroelectric phase (starting at 140°C) displays the behaviour shown in Figs 5 and 6 for similar parameters. It can be observed that d_{33} changes as before; radial electromechanical coupling factor K_p increases up to 20 kV cm^{-1} , then decreases and disappears beyond 40 kV cm^{-1} (as reported by Yamashita *et al.* [2]). The mechanical quantity of Q_m also decreases starting at 20 kV cm^{-1} .

A previously poled TPC2 sample from the paraelectric phase that exhibited $K_p \neq 0$, as described before, was again "poled" in the ferroelectric phase with 50 kV cm^{-1} . Then, the radial mode was measured, resulting in $K_p \simeq 6$, similar to that of the previous situation. Nevertheless, if the same sample is thermally depoled by short circuiting and poled again with 50 kV cm^{-1} , below the Curie temperature, the radial mode is not present at all, being $K_p = 0$. Generally, if the sign of the electric field is alternatively changed, Q_m decreases.

Integrated intensities of the 002 and 200 reflection profiles were measured for the two kinds of sample.

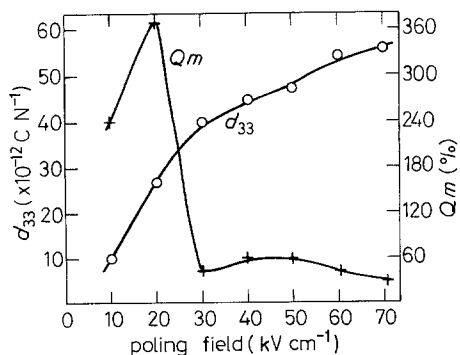


Figure 1 TPC1. Poling field dependence of piezoelectric constant d_{33} and mechanical factor Q_m . Poling at ferroelectric phase.

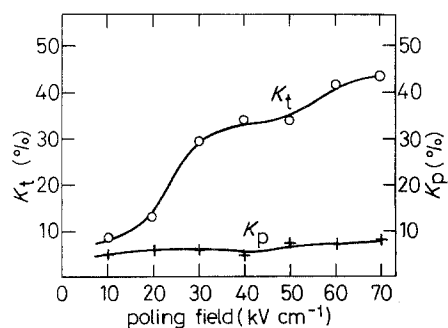


Figure 2 TPC1. Poling field dependence of electromechanical coupling factors (K_t : thickness mode, K_p : radial mode). Poling at ferroelectric phase.

Values of R' after poling in both ferroelectric and paraelectric phases were close to 1.50. Since the R value for the unpoled state is about 2.0, the amount N of 90° domains that contribute to remanent polarization was calculated with the equation $N = R/(1 + R)(1 + R')$; N is in all cases similar and lower than 8%.

3. Discussion

From these experimental results we conclude that the disappearance of the radial coupling K_p is dependent on composition, poling process and also on microtexture. This last dependence is inferred from the density variation with sintering temperature, due to the existence of the volatile phase PbO . Therefore, TPC1 material should contain more free PbO than TPC2. According to the results obtained by Auger spectroscopy [7] in a similar system fractured through grain boundaries, lead oxide must remain at boundaries. Thus, it is thought that the difference in piezoelectric behaviour of these materials is related to the structure of grain boundaries.

Ceramic TPC1 behaves as is usual for a ferro-piezoceramic. The behaviour of TPC2 is different. During the cooling down from the sintering temperature, the grain boundaries of TPC2 act as sinks for the intrinsic strains that arise on the cubic-tetragonal phase transition. Therefore, the grains in general remain less stressed than for the TPC1 material.

When the TPC2 ceramic is poled starting at the paraelectric phase, the lining up along $[001]$ is enhanced by the applied electric field during the transition. Apart from a switching of 180° domains, a small contribution of the 90° domain takes place, that will

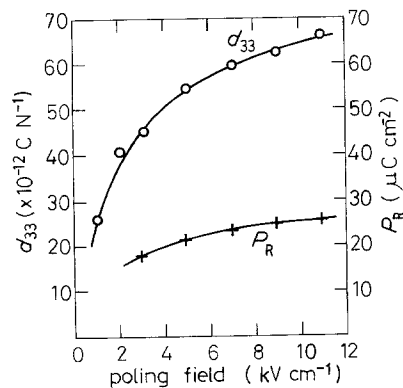


Figure 3 TPC2. Poling field dependence of piezoelectric constant d_{33} and remanent polarization P_R . Poling starts at paraelectric phase.

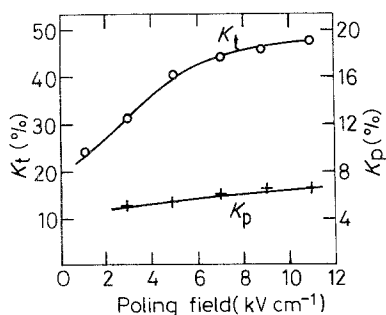


Figure 4 TPC2. Poling field dependence of electromechanical coupling factors (K_t : thickness mode, K_p : radial mode). Poling starts at paraelectric phase.

produce a deformation if compared with the unpoled former situation at room temperature. This poling state is obtained with relatively small electric fields. If a strong electric field is further applied to that poled system at ferroelectric phase, neither change of P nor electromechanical behaviour are observed, as is expected from a system previously poled at saturation.

If the TPC2 ceramic is poled by first starting at a temperature lower than T_c (ferroelectric phase) the remanent polarization and deformation obtained are similar to the situation described before, although by a different way: now, switching of 180° domains is smaller and therefore, the contribution of 90° domains larger than in the paraelectric case. As the poling electric field increases, values of P , d_{33} , K_t and K_p also increase up to 20 kV cm^{-1} ; beyond this value a micro-cracking effect could start as reported before [2, 8], causing an acoustic uncoupling and a decreasing of Q_m . Moreover, according to Yamamoto *et al.* [9], such a poled system becomes mechanically weak through the grain boundaries and this could contribute to more feasible cracking when the electric poling field is increased. Therefore it seems reasonable to ascribe the diminishing of K_p or d_{31} [10] to variation of elasticity of a system with free lead oxide into the grain boundaries when strong electric fields are applied.

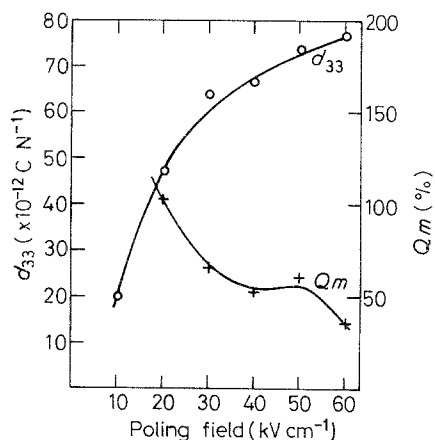


Figure 5 TPC2. Poling field dependence of piezoelectric modulus d_{33} and mechanical factor Q_m . Poling at ferroelectric phase.

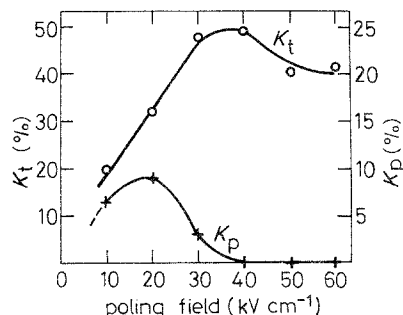


Figure 6 TPC2. Poling field dependence of electromechanical coupling factors. (K_t : thickness mode, K_p : radial mode).

4. Conclusions

Three conditions must all be fulfilled for a ceramic of Ca-modified PbTiO_3 not to exhibit radial mode vibrations:

- Composition close to the ratio $\text{Pb}/\text{Ca} = 76/24$ which presents the highest tetragonality compatible with the ability to be poled and mechanically support the para-ferroelectric phase transition.
- A processing method of preparing the ceramic which results in a microtexture with free lead oxide at the grain boundaries.
- The ceramic must be electrically poled at a temperature as close as possible and below the Curie temperature, compatible with conductivity.

At present, more information about grain boundaries and mechanical properties are necessary to reinforce our hypothesis.

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Received 4 February
and accepted 28 April 1987