FIELD DEPENDENCES OF ELASTIC COEFFICIENTS OF FERROELECTRIC CERAMICS DURING POLARIZATION REVERSAL[1]

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In order to determine the variation of elastic coefficients of $Pb(Zr_x Ti_{1-x})O_3$ ceramics ($x = 0.55$ and 0.52) with an electric bias field during the polarization reversal, the resonance frequency f_r of bars excited to longitudinal vibrations and of disks excited to radial vibrations was measured. From the different shapes of the corresponding f_r vs. E plots it was concluded that, contrary to common assumtions, Poisson's ratio σ and the elastic compliance s_{12}^E increase considerably more during the polarization reversal than s_{11}^E. Even the influence of the composition on σ and s_{12}^E is more significant than on s_{11}^E.

I. INTRODUCTION

Piezoelectric PZT ceramics are the most commonly used transducer materials in ultrasonic today, at least from the technical point of view. One essential technological procedure of manufacturing piezoceramics is the poling process for providing polar properties. Many experiments have been performed for investigating the behaviour of PZT ceramics during the poling and the polarization reversal in order to study the mechanism of these processes. Different quantities like polarization and strain as well as coefficients characterizing permittivity, piezoelectricity, and elasticity have been measured in dependence of the electric field varying slowly in time.

The motive for our investigations was a discrepancy between the results on the field dependence of the elastic compliance s_{11} during the polarization reversal obtained in our laboratory and those published by other workers, e. g. by Uchida and Ikeda [1], Wersing [2], and Isupov and Stolypin [3]. All these investigations were done by the same method, i. e. by measuring resonance frequencies of ceramic resonators excited piezoelectrically to a natural mode of vibration.

1) Contribution presented at the 10th Conference of Ultrasonic Methods, ŽILINA, August 27
   —30. 1968.
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The field dependence of the resonance frequency of bars cut from modified PZT (NSM) ceramics (VEB Keramische Werke Hermsdorf) are shown in Figure 1 (Rosenkranz [4]). The components of all samples were the same, only the concentration ratio of Ti and Zr was different. All butterfly curves have qualitatively the same shape similar to that shown by Mason for BaTiO$_3$ ceramics [5]. They are all characterized by a minimum a little below the coercive field irrespective of the composition: In the polar phase the symmetry of NSM 48 and 57 is, resp., tetragonal and rhombohedral (the figures being the Zr concentration is mole %), whereas NSM 52.5 has a composition near the morphotropic phase boundary (MPB), where both phases coexist.
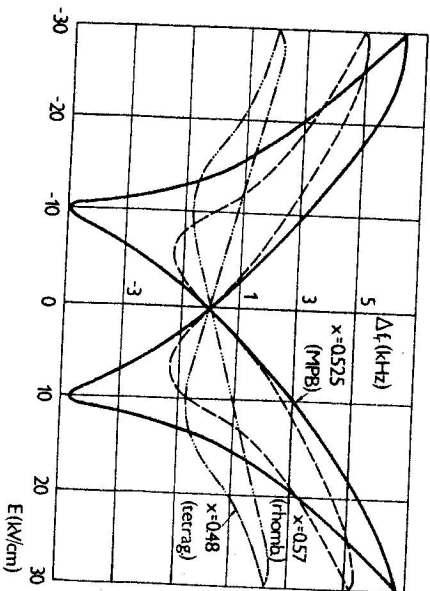

Fig. 1. Change of the resonance frequency Δf_r with the electric field strength E for bars of Pb$_0$((Ni$_{1/3}$Sb$_{2/3}$)$_{0.06}$Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with different Zr concentration x.

Very different field dependences of the resonance frequency for specimens with different Zr:Ti composition were obtained, e.g., by Wersing [2] and Isupov and Stolypin [3]. For compositions near the morphotropic phase boundary (MPB) they found a maximum of the resonance frequency instead of a minimum for $E = E_c$. As already mentioned we all used the same resonance method and explained our results by the field dependence of the elastic compliance s_{11} of the ceramics during the polarization reversal. The only but obviously essential difference was the shape of the resonators. We used long and thin bars excited to longitudinal vibrations. The fundamental frequency is

$$f_r^\beta = 1/\{2l(\varrho s_{11}^E)^{1/2}\} \qquad (1)$$

where l and ϱ are the length and the density of the bart. The other workers used circular disks excited to radial vibrations. The fundamental frequency of this mode is after Mason [5]:

$$f_r = R_1/2\pi \cdot \{\varrho s_{11}^E(1-\sigma^2)\}^{-1/2} \qquad (2)$$

with R_1 being the first root of the equation

$$R_1 J_0(R_1) - (1-\sigma)J_1(R_1) = 0 \qquad (3)$$

(J_0 and J_1 are Bessel's functions of the 0th and the 1st order, r and σ are radius and Poisson's ratio of the disk). In all papers cited above Poisson's ratio was taken to be independent of the polarization state of the ceramics and to have the value 0.27 (yielding $R_1 = 2.03$) as suggested by Mason.

II. EXPERIMENTS AND RESULTS

The aim of our study was to find whether this assumption is justified or whether the above mentioned disagreement is caused just by the dependence of Poisson's ratio on the electric field. For this purpose we had to measure the field dependence of the resonance frequencies of both a bar and a circular disk cut from the same ceramic ingot. The frequency of the exciting voltage (ca 40 V/cm) was controlled by the resonance frequency of the ceramic resonators and plotted vs. the bias field which varied triangularly in time with typically 2 min per cycle. Our preliminary results obtained at a temperature of 120°C for PZT 55 ($x = 0.55$, rhombohedral) and PZT 52 (near MPB) are shown in Figures 2 and 3.

We obtained the same $f_r(E)$ dependence for both bars as that found earlier by Rosenkranz. The small irregularities seen in Figure 3b near the coercive fields are caused by the zero transitions of the voltage controlling the frequency of the hf generator. For the disks, however, we find the minimum of the resonance frequency at lower absolute values of the bias field followed by a steep increase. This increase leads to a huge maximum at E_c in the field dependence of f_r^p of the PZT 52 disk. This different behaviour of bars and disks has obviously to be attributed to the field dependence of Possion's ratio. This can be evaluated from equations (1) and (2)

by means of a plot of $R_1 \cdot (1-\sigma^2)^{-1/2}$ vs. σ, provided f_r^p and f_r^β belong to the same polarization state. As this assignment cannot be carried out very accurately from Figures 2 and 3, the field dependence of σ as plotted in Figure 4 may show only the characteristic behaviour rather than describing the exact details during the polarization reversal.
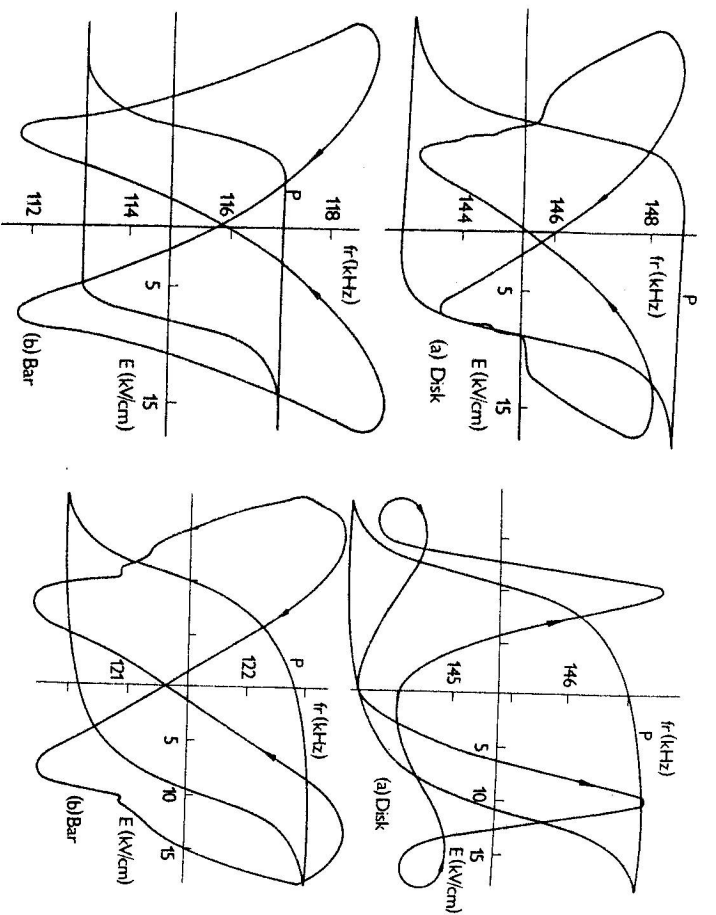
$$\pi r/l \cdot f_r^p/f_r^\beta = R_1 \cdot (1-\sigma^2)^{-1/2} \qquad (4)$$

Table 1
Relative difference between maximum and minimum values of elastic coefficients during polarization reversal of PZT ceramics (120°C)

	elastic compliance s_{11}^E	Poisson's ratio	elastic compliance s_{12}^E
Pb(Zr$_{0.55}$Ti$_{0.45}$)O$_3$	13%	33%	58%
Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$	4.5%	15%	19%

Table 2
Relative difference between elastic coefficients of Pb(Zr$_{0.55}$Ti$_{0.45}$)O$_3$, an Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (120°C)

	elastic compliance s_{11}^E	Poisson's ratio	elastic compliance s_{12}^E
minimum values	17%	40%	71%
remanence	14%	35%	53%
maximum values	9%	20%	29%

The preliminary results of our study can be summarized as follows:
1. Possion's ratio $\sigma = -s_{12}/s_{11}$ is by no means constant during the polarization reversal. On the contrary, it changes considerably more with the field strength than s_{11} (cf Figure 4 and Table 1).
2. Even the influence of the composition on the elastic coefficients is more pronounced for σ than for s_{11} (cf Table 2).

Fig. 2. Variation of the resonance frequency f_r with the electric field for (a) a disk (diameter 15 mm, thickness 0.55 mm) and (b) a bar (length 14.9 mm, width 1.55 mm, thickness 0.55 mm) of PZT 55 (120°C)
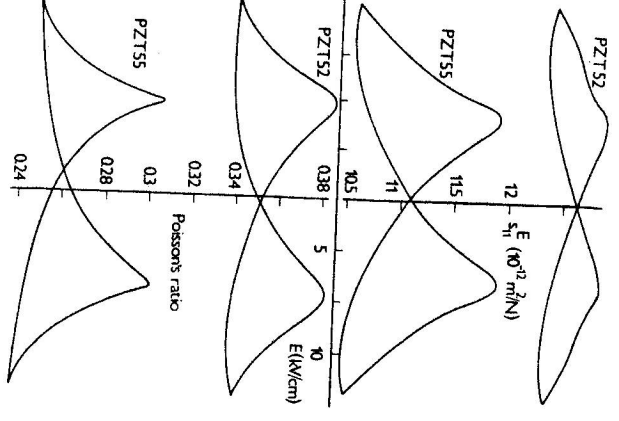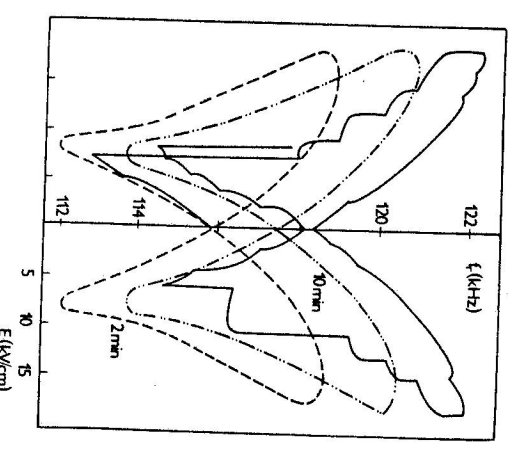
Fig. 3. Electric field dependence of f_r for (a) a disk (15 × 0.55 mm) and (b) a bar (13.5 × 0.52 × 0.55 mm) of PZT 52 (120°C)

Fig. 4. Variation of the elastic compliance s_{11}^E and of Poisson's ratio with the electric field E for PZT 52 and PZT 55 (120°C)

Fig. 5. Variation of the resonance frequency f_r of a PZT 55 bar with the electric field E at 120°C for different regimes (cf text)

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3. If we compare the variations of s_{11} with that of $s_{12} = -\sigma_{11}$ the differences are still greater (Table 1 and 2).

4. Up to now we have presented only results for a continuously varying field. Whenever the variation of the electric field is stopped, after-effects are observed with a different sign depending on the switching state of the specimen. This is shown in Figure 5 for a PZT 55 bar where the bias field was held constant for 2 min. after each step. At lower temperatures it takes much more time before nearly equilibrium values are attained. Therefore our measurements were conducted at 120°C.

III. CONCLUSIONS

In order to estimate material coefficients of ferroelectric ceramics, usually the first step is to take the average of the coefficients of single-domain crystals taking account of the distribution of orientations of the grains. Because of the lack of PZT single crystals no such data exist and calculations of this kind are not feasible. Therefore only qualitative estimations have been made taking account of the results concerning crystals and ceramics of barium titanate.

The polarization reversal in perovskite-type ferroelectrics is usually explained by 180° and 90° reorientations of domains in the tetragonal phase, and by 180°, 109°, and 71° reorientations in the rhombohedral phase. The latter, however, will be assumed to be equivalent to the 90° reorientations in the tetragonal phase. Usually the change of the elastic compliance s_{11}^E during polarization reversal is explained mainly by 90° reorientations of anisotropic domains, whereas the 180° processes should influence additionally the dielectric constant by means of domain clamping. Poisson's ratio was assumed to be constant. Only Uchida and Ikeda [1] considered that even other coefficients may change during the polarization reversal. Iusupov and Stolypin [3] suggested the anomalous behaviour of the resonance frequency of ceramic disks with compositions near the MPB to be caused by contributions of oscillations of boundaries between coexisting tetragonal and rhombohedral phases to s_{11}^E. It seems to be not unlikely that such elastic deformations due to field and stress induced phase changes may scarely be involved by changes of volume thus yielding large values of Poisson's ratio.

In order to improve the knowledge on the polarization-reversal mechanism further investigations combined with measuring the field dependence of other quantities and coefficients even in other compositions and systems are in progress.

References

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ЗАВИСИМОСТЬ УПРУГИХ ПОСТОЯННЫХ ПЬЕЗОЭЛЕКТРИЧЕСКОЙ КЕРАМИКИ ОТ ПОЛЯ В ПРОЦЕССЕ ИЗМЕНЕНИЯ ПОЛЯРИЗАЦИИ

Для определения изменения упругих постоянных керамики $Pb(Zr_xTi_{1-x})O_3$ ($x = 0.55$ и 0.52) в процессе изменения поляризации направленного электрического поля измерялась резонансная частота f_r стержней, возбуждаемых продольными вибрациями, и дисков, подвергающихся радиальным вибрациям. На основе различных форм графиков соответствующих частот f_r как функций E сделано заключение, что, в противоположность общим представлениям, отношение Пуассона σ и упругая податливость S_{12}^E возрастает более заметно в процессе изменения поляризации, чем величина S_{11}^E. Кроме того, влияние состава на σ и S_{12}^E более значительно, чем на S_{11}^E.