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Influence of cyclic phase transitions on some properties of the ferroelectric perovskites

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Abstract

The results of investigations of the influence of cyclic phase transitions on certain properties of the ferroelectric perovskites are presented. The materials were PZT-type ceramics obtained either by hot-pressing or by classical ceramic technology. It has been found that a close relationship exists between the concentration of linear defects and the stability of the resonant frequency as a function of temperature and time. The investigated samples can be divided into two groups: samples with high initial stability of resonance frequency and samples with low initial temperature stability. Our investigations show that in this two cases it is possible to distinguish three ranges of numbers of thermocycles, but the dependencies in the two cases differ one from the other. The change of concentration of defects and their distribution inside the crystallites lead to changes of temperature stability of resonant frequency. After 5–6 thermocycles the stability increases, but if the initial stability of the resonant frequency is high the changes are too small for practical applications. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The temperature stability of the resonant frequency is related to the domain structure and to the changes in the domain structure caused by external conditions. The mobility of domain walls is related to the presence of defects.[1–3] Such a conclusion is confirmed by the decrease of internal friction Q_m^{-1}[1] and the increase of coercive field E_c[2] with increasing number of vacancies in the O^{2-} node points of the perovskite ABO_3 cell. Such point defects make the movement of domain walls more difficult (i.e. stabilize the domain structure). However, the influence of linear defects on domain wall mobility is bigger.[3] Around dislocations there exist strong electric fields as a result of the inflow of charged point defects (Debye'–Huckel atmosphere) and admixture atoms (Cotrell atmosphere). The higher the density of dislocations and the stronger the local electric fields, the more effective is the limiting of domain wall mobility by dislocations. Consequently, there exists a close relationship between the concentration of linear defects and the temperature and time stability of the resonant frequency in materials used as piezoceramic electroacoustic transducers.[4]

The concentration of dislocations in ferroelectric ceramic samples can increase after heating to temperatures higher than the Curie temperature ($T_W > T_C$) and following cooling down to room temperature (T_r). During such a heating/cooling cycle, the sequence of two phase transitions: ferroelectric ($T < T_C$)↔ paraelectric ($T > T_C$) has taken place. During these phase transitions, the crystallites of the piezoceramic material undergo large mechanical tensions comparable with the tensions neede to exceed the elasticity limit of the material. These tensions favour change in the distribution of primary defects and the nucleation of new defects, especially dislocations.[5,6]

The aim of this work was to examine how repeated heating and cooling of the sample through the Curie point, i.e. so-called thermocycling can influence the temperature stability of the resonant frequency f_r, and the values of the basic dielectric and piezoelectric parameters.

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2. Experimental

The materials studied were piezoceramic samples of PZT type: $(x)PbTiO_3$–$(1–x–y)PbZrO_3$–$y[PbW_{2/3}Mn_{1/3}O_3$–$PbW_{1/2}Mg_{1/2}O_3]$ with $x=52.5$ mol% and $y=2.5$ mol%.

Ceramic powders of the PZT-type solid solution were prepared by the solid-phase synthesis methods of the simple oxides (PbO–TiO_2–ZrO_2–WO_3–MnO_2–MgO). The powder was pressed at pressure $p=2\times10^8$ Pa to form disk-shaped compacts of $d=10^{-2}$ m in diameter and $h=3$–5×10^{-3} m thick. Finally, the compacts were sintered by uniaxial hot pressing (HP) method. The customised USSK-1-type hot pressing unit was used to produced ceramic samples. Maximal pressure applied to the samples during sintering worked out at $p_s\approx30$ MPa. Maximal sintering temperature $T_s=1600$ K, and maximal heating rate was $v_T=400$ K/h. Pressure p_s was applied to the sample at room temperature (T_r) and released after sintering the sample at temperature T_s for a time t_s.

Samples have been divided into two groups:

1. samples with high initial temperature stability of the resonance frequency ($\Delta f_r/f_r$ from 0.20 to 0.23%);
2. samples with low initial temperature stability of the resonance frequency ($\Delta f_r/f_r$ from 0.36 to 0.40%).

In both cases $\Delta f_r/f_r$ was defined for the temperature range from 213 to 353 K.

Samples belonging to the second group were obtained by using suboptimal conditions of technological process (usually the temperature of sintering 30–50 K lower than optimal temperature 1450 K). The average size of the grains of such samples did not exceed $r=2$–2.5 μm while for the first group $r=3.5$–5 μm. Previously, it has been stated that it had a close relationship between the average size of grains and the $\Delta f_r/f_r$ value.

The chemical composition of the ceramic samples was investigated by X-ray fluorescence (XRF) with accuracy of ±3% for the basic elements. The microstructure was investigated by scanning electron microscopy (SEM). The crystalline structure of the PZT-type ceramic samples was investigated by X-ray diffraction (XRD). The experiment was carried out on DRON 3.5 X-ray diffractometer (the radiation is CuK_α; nickel filter). The double lines of $K_{\alpha-1}$ and $K_{\alpha-2}$ were separated by the Rachinger method.[7]

For electrical measurements silver electrodes were deposited on the ceramic surfaces. Capacitance C and dielectric loss tangent (tgδ) was measured by a capacitance bridge (impedance analyser, Model 4.192A—Hewlett Packard) and the dielectric permittivity (ε) was calculated.

The Curie point (T_c) was determined on the basis of changes of the permittivity ε of the non-poled samples with the temperature T ($T=T_m=T_c$; T_m is the temperature at which $\varepsilon(T)$ reaches its maximum).

Poling treatment of the obtained ceramic samples was carried out in silicon oil 393 K by applying d.c. field of $E_{pol}=4\times10^6$ V/m for $t_{pol}=1$ h. The samples were then cooled to room temperature under the influence of the electric field in $t=30$ min. The high voltage amplifier of Matsusada Precision Inc. was used for poling.

The piezoelectric parameters were measured by the modified resonance–antiresonance method in the temperature range from 213 to 358 K.

3. Results and discussion

Samples were many times ($N_{T_c}=1$–40 cycles) heated up to $T_w=673$ K ($T_c=573$ K) and then cooled down to $T_r=293$ K. After thermocycling, measurements were made of the stability of resonance frequency ($\Delta f_r/f_r$), tangent of dielectric loss (tanδ), mechanical quality factor (Q_m), internal friction (Q_m^{-1}), half widths of X-ray reflections *00l* and *h00* ($\delta_{00l,\ h00}$). For comparison, it has been also measured the angle of disorientation of 90° structural twins in $PbTiO_3$ single crystals (i.e. 90° domains)-α_{tw} as a function of the number of cycles (N_{T_c}) of heating and cooling through the Curie point. The angle of disorientation in $PbTiO_3$ single crystals has been measured by using the optical polarizing microscope. In the case of ceramic samples the electrophysical and structural parameters (except $\Delta f_r/f_r$) have been measured at the room temperature. The half-width of the X-ray reflections ($\delta_{00l,\ h00}$) is a measure of the degree of structural perfection of the crystallites (structural twins).[4] The changes of the angle of twinning (α_{tw}) as a function of N_{T_c} can be connected to the linear disturbing of the translational symmetry. For the first group of samples, i.e. with high temperature stability of f_r, the dependencies of the quality of the crystalline structure has been estimated by measure the half width of X-ray maximum ($\delta_{00l,\ h00}$).

The dependencies of $\Delta f_r/f_r(N_{Tc})$ are presented in Fig. 1. For samples with high initial stability of resonant frequency, the obtained dependency can be described as follows:

- for $n=1$–5, $\Delta f_r/f_r$ decreases to a value of 0.18% (part A in Fig. 1);
- for $n=6$-20, $\Delta f_r/f_r$ significantly increases up to a value of 0.60%;
- for $n=20$–40, $\Delta f_r/f_r$ gradually decreases to values of 0, 4–0.5%.

In samples with low initial stability of resonant frequency the character of the obtained dependency is similar but the magnitude of the changes is smaller (see Fig. 1). The character of the changes in Q_m^{-1} (N_{T_c}), and

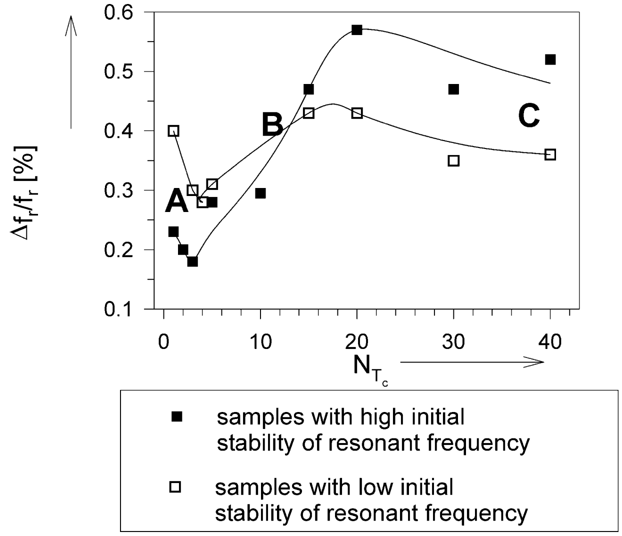

Fig. 1. The dependence of $\Delta f_{\mathrm{r}}/f_{\mathrm{r}}$ on $N_{T_{\mathrm{c}}}$ for two groups of investigated samples.

tan$\delta(N_{T_{\mathrm{c}}})$ (see Fig. 2) is similar, i.e. it is possible to identify three regions.

The experimental data can be explained in the following way. For $N_{T_{\mathrm{c}}}=1$–5 the destruction of the originally existing distribution of defects takes place inside the crystallites. Such supposition has been confirmed by experiments on PbTiO$_3$ single crystals with single plane phase boundary between tetragonal and cubic phases. The dependencies of half widths $\delta_{002}(N_{T_{\mathrm{c}}})$, $\delta_{200}(N_{T_{\mathrm{c}}})$ and $Q^{-1}(N_{T_{\mathrm{c}}})$ (in details presented in Ref. 8) in general are similar to the dependency $Q^{-1}(N_{T_{\mathrm{c}}})$ for ceramic samples presented in Fig. 2 (i.e. can be also divided into similar parts). In the case of PbTiO$_3$ single crystals after 2–3 thermocycles the repeatable and stable domain structure was formed. Such domain structure having the form of laminar plates with 1/3 relative widths destroys earlier existing structure of defects and forms new defects structure (which is necessary to form semicoherent boundaries between domain/twins). Such a process takes place up to 6–7 cycles. In the case of ceramic samples this process means the migration of defects towards the surfaces of the crystallites (since the domain dimensions are comparable with the dimensions of the crystallites) and, as a consequence, the concentration of defects inside the crystallites decreases. The stabilization of the borders of the structural domains by defects considerably decreases their mobility, which in turn decreases $\Delta f_{\mathrm{r}}/f_{\mathrm{r}}$, i.e. increases the temperature stability of f_{r}. This picture is supported by the simultaneous decrease of Q_{m}^{-1} and tanδ as a function of $N_{T_{\mathrm{c}}}$ (see regions A in Fig. 2) because these parameters characterize losses of mechanical and electric energy.

Further cycles of phase transformations ($N_{T_{\mathrm{c}}}=6$–20) leads to opposite changes: increase of Q_{m}^{-1} and tanδ (see in regions B Fig. 2). Comparison with PbTiO$_3$ single crystals leads to the conclusion that the concentration of defects inside the crystallites increases which leads to phenomena conditioned by the interaction of defects in the volume with those on the borders of the crystallites. The increase in $\Delta f_r/f_r$ for $N_{T_{\mathrm{c}}}=6$–20 (decrease of stability of f_{r}) may be a consequence of the general instability of the disordered arrangement of defects, which influences the worsening of the structural characteristics and electrophysical parameters of the piezoceramics.

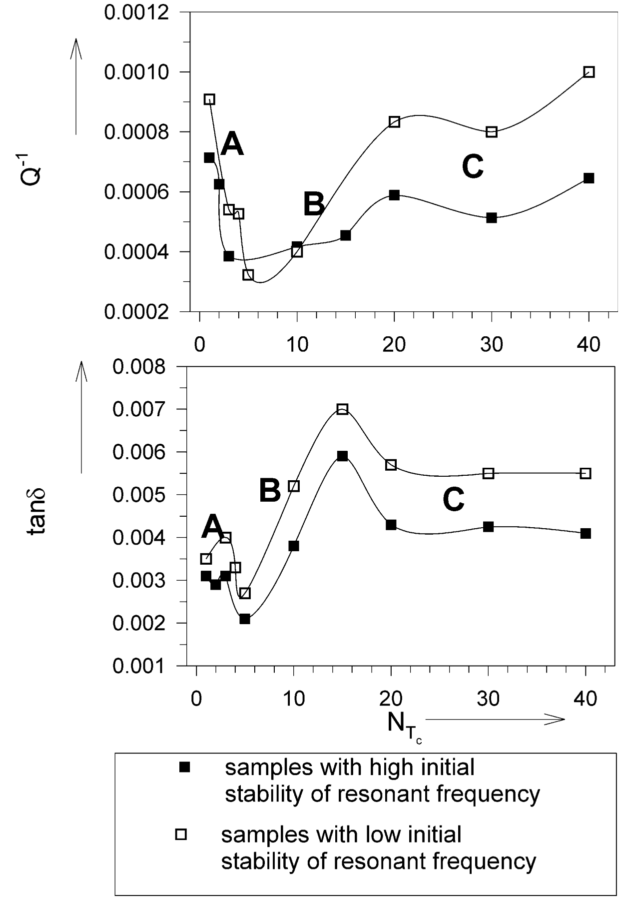

Fig. 2. The dependencies of 1/Q and tanδ on $N_{T_{\mathrm{c}}}$ for two groups of investigated samples.

In the case of $N_{T_{\mathrm{c}}}>15$–20 (see regions in C Fig. 2) a stable system of defects probably forms inside the volume of the crystallites which stabilizes the properties of the piezoceramics. Such conclusions are supported by the structural investigations. The half width of the X-ray reflections (δ_{00l} and δ_{h00}) can be chosen as a measure of the structural perfection of the crystallites.^{5} The change of these parameters as a function of the number of thermocycles is presented in Fig. 3.

With further cycles of the phase transitions ($N_{T_{\mathrm{c}}}>40$), further saturation of the inside parts of the crystallites by defects takes place. This leads to the appearance of clusters of defects (so-called "ultradislocations") and, as a consequence, to damage of the sample. This is the so-called "fatigue of the ferroelectric" caused by the sequence of phase transitions.

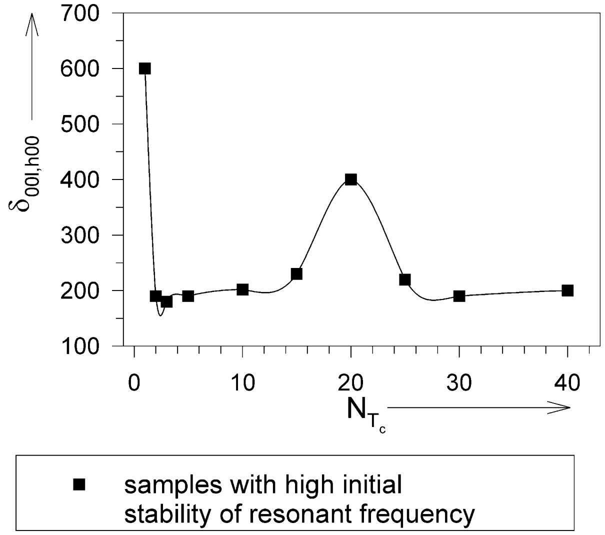

Fig. 3. Half width of X-ray reflexes δ_{001} and δ_{002}) as a function of number of thermocycles.

4. Conclusions

Changes in the concentration of defects and their distribution inside the crystallites result in changes of the temperature stability of the resonant frequency. The stability increases for $N_{T_c} = 5$–6. However, if the initial stability of the resonant frequency is high, the changes are too small for practical applications.

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