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## SEPARATE KINETICS OF THE POLAR AND ANTIFERRODISTORTIVE ORDER PARAMETERS IN THE ANTIFERROELECTRIC TRANSITION OF $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ AND THE INFLUENCE OF DEFECTS

### ODDZIELNE KINETYKI POLARNYCH I ANTYFERROELEKTRYCZNYCH DYSTORSJI PARAMETRÓW UPORZĄDKOWANIA W PRZEMIANIE ANTYFERROELEKTRYCZNEJ $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ORAZ WPŁYW DEFJEKTÓW

The transition from the rhombohedral-ferroelectric to the lower temperature orthorhombic-antiferroelectric phase in Zr-rich PZT involves two order parameters (OPs): 1) the polar OP for the displacements of the cations with respect to the O octahedra; 2) an antiferrodistortive OP responsible for tilting of the octahedra. It is shown that at Ti compositions near the morphotropic boundary with the FE phase ( $0.046 \leq x \leq 0.054$ ), the two OPs may be almost independent of each other at cooling rates of 0.5 K/min or faster, depending on the sample history. This fact gives rise to a great variety of shapes of the curves of the elastic compliance  $s(T)$ , but all of them can be fitted very well as superpositions of variously broadened steps for each of the modes involved in the transitions, including the tilt transition occurring in the untransformed FE fraction. The evolution of the  $s(T)$  curves includes enhancements up to a factor of four during aging for weeks in the region of the AFE/FE coexistence. Restiffening and reduction of the thermal hysteresis of the AFE/FE transition are recovered by heating up to 800-900 K. It is proposed that ageing is due to the clustering of relatively mobile defects, most likely O vacancies, at the domain walls in the coexisting AFE/FE phases. Such defect structures are probably at the origin of intense thermally activated relaxation processes observed above  $T_C$  in the dielectric and anelastic spectra, and can be annealed out above 800 K, allowing the AFE transition to recover a fast kinetics.

*Keywords:* antiferroelectric PZT, phase transitions, defects, elasticity

Przemiana fazy romboedrycznej-ferroelektrycznej do niskotemperaturowej fazy rombowej-antyferroelektrycznej bogatej w Zr ceramiki piezoelektrycznej PZT obejmuje dwa parametry uporządkowania (OP): 1) polarny OP z przemieszczeń kationów Zr/Ti w odniesieniu do oktaedrów tlenowych; 2) antyferroelektryczna dystorsja OP odpowiedzialna za przechylenie oktaedrów. Pokazano, że dla zawartości Ti w pobliżu morfotropowej granicy z fazą ferroelektryczną ( $0,046 \leq x \leq 0,054$ ), obydwa OP mogą być prawie niezależne od siebie podczas chłodzenia z szybkością 0,5 K/min lub mniejszą, w zależności od historii próbki. Ten fakt powoduje wielką różnorodność kształtów krzywych podatności sprężystej  $s(T)$ , ale wszystkie z nich mogą być bardzo dobrze przybliżone jako superpozycje różnie poszerzonych etapów dla każdego z trybów zaangażowanych w przemianę, w tym przemianę nachylenia występującą w nietransformowanej fazie ferroelektrycznej. Zmiana krzywych  $s(T)$  obejmuje czterokrotne poszerzenia krzywych po okresie starzenia przez kilka tygodni w regionie współistnienia faz antyferroelektrycznej (AFE) i ferroelektrycznej (FE). Zeszywnienie i zwężenie pętli histerezy termicznej przemiany AFE / FE są odzyskiwane przez podgrzanie do temperatury 800-900 K. Proponuje się, że starzenie się jest spowodowane grupowaniem się stosunkowo mobilnych defektów, najprawdopodobniej wakansów tlenowych, na ścianach domen w współistniejących fazach AFE / FE. Defekty te są zapewne przyczyną silnych, aktywowanych termicznie procesów relaksacyjnych obserwowanych powyżej temperatury krytycznej  $T_C$  w widmie strat dielektrycznych i mechanicznych, i mogą być wyżarzane powyżej 800 K, umożliwiając przejściu AFE odzyskanie szybkiej kinetyki przemiany.

### 1. Introduction

The transition from the rhombohedral ferroelectric (R-FE,  $R3m$ ) to the lower temperature orthorhombic antiferroelectric (O-AFE,  $Pbam$ ) phase in Zr-rich PZT involves two order parameters (OPs): 1) the polar OP responsible for the change from a prevalent FE  $\langle 111 \rangle$  displacement of the Ti cations to the prevalent AFE  $\langle 110 \rangle$  displacement of Pb; 2) an antiferrodistortive OP responsible for tilting of the  $\text{ZrO}_6$  octahedra [1]. It

has been recognized that this transition may have extremely large thermal hysteresis and slow kinetics, partially attributed to the stabilization of the FE phase by charged defects [2], but a recent combined anelastic, dielectric and X-ray diffraction study on PZT with  $x(\text{Ti}) = 0.05$  revealed additional unexpected features [3], further studied in connection with the effect of aging and high temperature annealing [4].

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## 2. Experimental

Samples of PZT have been prepared with  $x(\text{Ti}) = 0.046, 0.050, 0.054$  with the solid state reaction method, as described elsewhere [3]. The anelastic spectra were measured on bars  $40 \times 5 \times 0.6 \text{ mm}^3$  electroded with Ag paint, suspended on thin thermocouple wires and electrostatically excited on their odd flexural modes, whose frequencies are in the ratio 1:5.4:13. The compliance was computed as  $s'(T)/s_0 = f_0^2/f(T)^2$  and in Figs. 2,3 it was  $f_0 = 1.5 \text{ kHz}$  for the fundamental mode (the only one shown). The dielectric susceptibility was measured on discs 12 mm in diameter and 0.7 mm thick with a HP 4284A LCR meter at 0.2-200 kHz.

## 3. Results and discussion

Figure 1 presents the region of interest of the phase diagram of PZT. The compositions were chosen within the range of the AFE phase, but close to the border with the FE phase. The anelastic spectra at higher Ti content showed that, with respect to the traditional phase diagram, there is an additional instability line  $T_{IT}$ , identified with the onset of disordered octahedral tilting not yet observed in diffraction experiments [5]. Adapting Glazer's notation for octahedral tilting, we refer to this disordered tilting as  $a^*a^*a^*$  and assume therefore that in the  $R3m$  R-FE phase the octahedra are locally tilted. Further cooling below  $T_T$  causes the long range ordering of the tilts with the same angle about all the three axes and in antiphase along each axis ( $a^-a^-a^-$ ), equivalent to tilting about the polar axis [111]. Below  $\sim 6\%$  Ti the low- $T$  phase is O-AFE, with a tilt pattern  $a^-a^-c^0$  where the rotation about the pseudocubic  $c$  axis is absent. The anelastic spectra show that the  $T_T$  line continues into the region of coexistence of the R-FE and O-AFE phases [3,4].

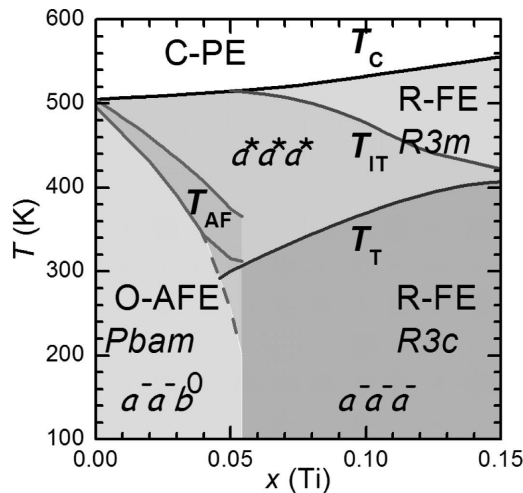


Fig. 1. Phase diagram of PZT, with the symmetry groups and tilt patterns of the various phases. The boundary to the O-AFE phase on cooling may be shifted to lower  $T$ , depending on the state of the sample

The crossing of all these phase borders can be revealed as more or less broadened steps in the elastic compliance  $s'(T)$ , and generally also in the  $Q^{-1} = s''/s'$ , but we will consider the losses only when dealing with the relaxations at high  $T$ . The evolution of such curves is shown in Fig. 2 for a sample with

4.6% Ti. After some weeks in the as prepared state, the sample was largely in the O-AFE phase, as indicated by the narrow steps at 388 K due to the AFE/FE and OT/RT components of the transition to the R-FE phase (curve 1). The PE/FE transition occurs always at  $T_C = 512 \text{ K}$ , with little thermal hysteresis. During the subsequent cooling at  $\sim 1 \text{ K/min}$ , the transition to the AFE phase is retarded below the tilt instability at  $T_T = 294 \text{ K}$  within the R-FE phase (curve 2), and occurs gradually and separately for the OT and AF modes. With aging at room temperature, the compliance progressively softens, as shown by curve 3. After 25 days  $s'$  was about four times softer than initially (not shown, well out of scale in Fig. 2), but partially restiffened to curve 3 after heating up to 630 K. The losses and softenings above 600 K reveal the presence of thermally activated relaxation processes, evidently due to various types of relatively mobile defects. Curves 3-5 demonstrate a fact observed also in other samples: after prolonged aging at room temperature two peaks P1 and P3 are prominent, and convert into the intermediate P2 after the first heating above 800 K; P2 remains stable during the following runs. Additional relaxations with maxima above 900 K are always visible. The P1+P3 to P2 conversion is associated with a general restiffening and with the recovery of a fast kinetics for the transition to the AFE state. Curves 4 and 5 show that after high temperature annealing the AFE/FE transition is sharp and with a reduced thermal hysteresis.

The variety of  $s'(T)$  curves that are found in the various samples during repeated cycling can always be fitted surprisingly well with steplike softenings for the T and AF modes and stiffening for the OT mode [3,4], and Fig. 3 presents two examples fitted with the steps, each of the form  $A \tanh[(T - T_0)/w]$ , with the same amplitude  $A$  in the consecutive heating/cooling runs. The assumption of steplike anomalies is justified by the fact that the elastic softening is produced by the coupling of strain  $\varepsilon$  with the OP,  $Q$ , which is of the form  $\varepsilon Q^2$  both for the polarization (AF mode) and the rotation angle of the octahedra. According to the Landau theory of phase transformations a steplike softening occurs in the elastic constants coupled in the linear-quadratic manner to the OP [6]. The fact that a stiffening is observed at the OT transition may be justified by the fact, explained at the beginning of this Section, that, in passing from the R-FE phase with disordered rotations about all axes to the O-AFE phase, tilting about the  $c$  pseudocubic axis is lost, and therefore the lattice becomes stiffer.

The sequence of measurements in Fig. 2 shows a remarkable general softening during aging for few weeks at room temperature, within the range of coexistence of the AFE and FE phases. Such a softening may be as large as a factor of four at room temperature, which is extraordinary for a ceramic material. Even more surprising is the fact that complete recovery of the stiffer state and a drastic reduction of the hysteresis phenomena at the AFE/FE transition is obtained by quickly (faster than 4 K/min) heating up to 800-900 K. During such temperature runs it is difficult to imagine consistent migration of the cations, and it is more likely that aging is associated with the clustering of O vacancies at the walls separating the AFE and FE domains, or some types of twin walls within the AFE phase. Also broken bonds due the large misfit between the volumes of the AFE and FE cells may play a role [7]. Such linear or planar defect structures would be responsible

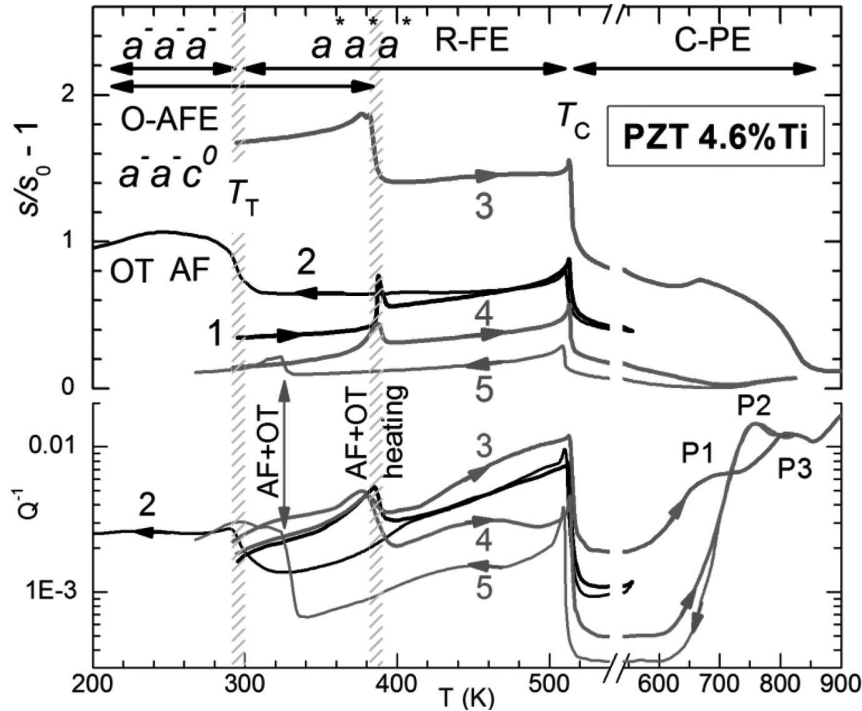


Fig. 2. Elastic energy loss coefficient  $Q^{-1}$  and compliance  $s'$  of PZT 95.4/4.6 during various heating/cooling cycles over 1 month. The  $T$  scans are numbered and many intermediate cycles are not shown for clarity. In the upper part the ranges of existence of the various phases and the tilt patterns are indicated

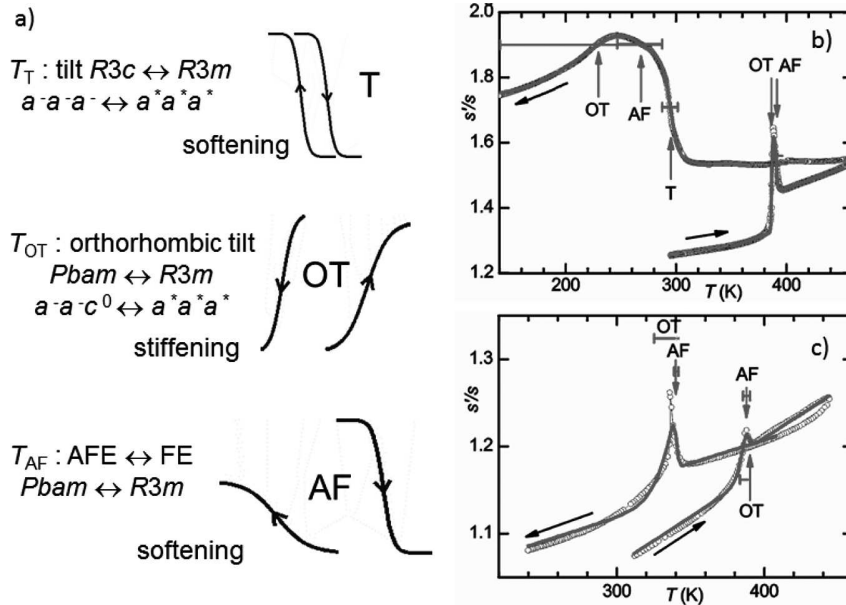


Fig. 3. a) Shapes of the anomalies of  $s'(T)$  associated with the transitions within the AFE and FE states of PZT. b,c) Curves of  $s'(T)$  measured in a sample with 4.6%Ti and fitted sharing the amplitudes of the steps in subsequent heating/cooling cycles: (b) large thermal hysteresis in the as prepared state (curves 1 and 2 of Fig. 2); (c) sharper transitions with smaller hysteresis after annealing up to 900 K

for the progressive softening with aging and for the hindering of the transformation to the AFE state during cooling, but would be annealed out above 800 K.

It is also likely that the relaxation peaks P1-P3, also observed in the dielectric susceptibility, are connected with the clustering/dissolution of these extended defect structures and the O vacancies themselves. In fact, while the dielectric spectra at high temperature, which do not coincide with the anelastic ones, may in principle be explained in terms of the

free charges from the ionization of the defects, the anelastic relaxation must be associated with the defects themselves. Attempts to fit these peaks measured at different frequencies during the same run demonstrate that they are far from pure Debye relaxations. They are very broad and the relaxation frequencies have extremely high effective activation energies and attempt frequencies, in agreement with the hypothesis of strongly interacting defects or defect structures.

#### 4. Summary

In PZT, near the morphotropic boundary with the FE phase ( $0.046 \leq x(\text{Ti}) \leq 0.054$ ), the polar modes (Pb and Zr/Ti displacements) and the rotations of the O octahedra producing the AFE phase act together in quasistatic experiments or during heating. Instead, when cooling at rates of 0.5 K/min or faster they may be greatly hindered and develop almost independently of each other, depending on the sample history. This fact gives rise to a great variety of curves of the elastic compliance  $s(T)$ , but all of them can be fitted very well as superpositions of differently broadened steps for each of the following partial transformations: 1) AFE/FE cation displacements (softening when cooling), 2) octahedral tilting from the nominally untilted, but actually locally tilted, rhombohedral FE phase to the orthorhombic AFE phase (stiffening); 3) tilting within the non-transformed rhombohedral FE phase (softening), the latter always sharp and with small thermal hysteresis.

The evolution of the shapes of the  $s(T)$  curves includes a general softening during aging at room temperature, within the region of coexistence of the AFE and FE phases, that may be as large as a factor of four after few weeks. The pristine stiffer state and prompt transformations to the AFE state can be fully recovered by heating up to 900 K, with a concomitant change of the high temperature spectrum, containing intense thermally activated anelastic and dielectric relaxation peaks.

It is postulated that the slow transformation kinetics, the softening during aging and the high temperature relaxations

are associated with the formation of extended defects, that are annealed above 800 K.

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