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Evaluation of Nontrivial Behaviour of Electromechanical Coupling Factors in $PbTiO_3$-type Ferroelectric Ceramics

Vitali Yu. Topolov, Anatoly V. Turik* and Andrey I. Chernobabov

Department of Physics, Rostov State University, Zorge str. 5, 344090 Rostov-on-Don, Russia

Abstract

Results of evaluations of electromechanical coupling factors k^*_{31}, k^*_{33} *and* k^*_{15} *in* $PbTiO_3$*-based ferroelectric ceramics are reported. A sensibility of these parameters to changes in electromechanical constants, temperature, 90° domain structure of grains, and composition of ceramics is discussed. © 1999 Elsevier Science Limited. All rights reserved*

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Electromechanical properties of ferroelectrics and related materials are various and very important for many applications. Needless to say, information is of value on an anisotropy of these properties and on ways of creating high-anisotropic materials. In particular, an interest in the problem of the large piezoelectric anisotropy in ferroelectrics and related materials is associated with investigations of physical mechanisms responsible for this effect[1–5] and with various applications of these materials. In a case of perovskite-type $PbTiO_3$-based polarized ferroelectric ceramics (FC) it has been shown in our previous papers[2–4,6,7] that the small anisotropy of dielectric permittivities of stress-free single-domain crystals forming FC grains as well as the 90° domain structure of the grains lead to considerable increasing of the anistropy of piezoelectric moduli $d^*_{33}/|d^*_{31}|$ or electromechanical coupling factors $k^*_{33}/|k^*_{31}|$. The majority of experimental papers (see, e.g. Refs. 1,8 and 9) contain incomplete information on a behaviour of the k^*_{ij} factors of FC mentioned above if to take into account possible effects of the domain structure, temperature, electric and mechanical fields, modifying ions, etc. Among theoretical works devoted to an interpretation of effects connected with the large piezoelectric anisotropy one can single out a paper[10] where some electromechanical coupling factors were evaluated for $PbTiO_3$-based ceramic compositions by taking into account the role of unit-cell spontaneous strains and an orientation of spontaneous polarization vectors in grains. The present paper is aimed at calculations of the k^*_{ij} factors as functions of the 90° domain volume concentration, temperature or the molar concentration of modifying ions. Objects chosen for our study are FC of $PbTiO_3$ (PT) and $(Pb_{1-x}Ca_x)$ $[(Co_{0.5}W_{0.5})_{0.04}Ti_{0.96}]O_3$ (PCT). A preference for such the choice consists in the presence of experimental data on stress-free single-domain PT crystals[2] and of corresponding data evaluated for PCT compositions by using our approach.[4] Some differences in the k^*_{ij} functions of these two FC will also be discussed in the paper.

Our consideration is realized in terms of a model of the spherical grain whose electromechanical interaction with the surrounding FC medium is described by Marutake self-consistent method.[11,12] The grain is assumed to be split into 90° domains of two types having the volume concentrations m and $1 - m$, respectively. It may be assumed that the m value corresponds to the domain type whose spontaneous polarization vector P_s is oriented closely to a direction of an external electric field E used for poling the FC sample. We do not take into consideration 180° domains disappearing under the field E exceeding the coercive field of 180° reorientations. We assume that 90° domain walls are motionless or very slightly movable in the grains, as follows from experimental results[13] concerning the behaviour of chemically pure PT FC in external electric or mechanical fields. The transition from piezoelectric, dielectric and elastic constants

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*To whom correspondence should be addressed. Fax: + 7-8632-244311; e-mail: turik@phys.rnd.runnet.ru of the single-domain crystal (grain) to the similar constants of the grain with the regular laminated 90° domain structure proceeds by using formulae[14] generalized for any values of $0 \leq m \leq 1$. These formulae belong to a ($X^0Y^0Z^0$) rectangular coordinate system for a laminated structure with $2m$ symmetry where the axis 2 is parallel to the (OZ^0) axis and the mirror plane is perpendicular to both the (OX^0) and (OY^0) axes. Hereafter spontaneous polarization vectors of two types of the 90° domains are (P, P, 0) and (−P, P, 0). Some piezoelectric moduli d^0_{ij} of these domains are determined in the ($X^0Y^0Z^0$) system as follows:[14]

$$d^0_{31} = (d_{31} + d_{33} - d_{15})/(2\sqrt{2}),$$
$$d^0_{32} = d_{31}/\sqrt{2},\, d^0_{33} = (d_{31} + d_{33} + d_{15})/(2\sqrt{2}), \text{ and}$$
$$d^0_{24} = [2s_{66}/(s^E_{44} + s_{66})]d_{15}/\sqrt{2},$$

where d_{ij} and s^E_{ij} are the piezoelectric moduli and elastic compliances of the single-domain crystal with $4mm$ symmetry. A next step supposes averaging d^0_{ij}, elastic and dielectric constants written for the ($X^0Y^0Z^0$) coordinate system by taking into account boundary conditions for electric and mechanical fields at the 90° domain walls and volume concentrations of the 90° domains. The procedure of further averaging the derived constants of the polydomain crystal can be realized on the basis of results[11,12] and enables to obtain a series of evaluated constants of the FC sample, e.g. dielectric permittivities $\varepsilon^{*\sigma}_{ij}$ for the stress-free state, piezoelectric moduli d^*_{ij} and elastic compliances s^{*E}_{ij} at $E=\text{const}$.

As is known, the electromechanical coupling factors are used for a quantitative description of a conversion of electric and mechanical energy contributions. These factors contain all three basic types of electromechanical constants of FC and are described by formulae[15]

$$k^*_{31} = d^*_{31}(s^{*E}_{11}\varepsilon^{*\sigma}_{33})^{-1/2},$$
$$k^*_{33} = d^*_{33}(s^{*E}_{33}\varepsilon^{*\sigma}_{33})^{-1/2} \quad \text{and}$$
$$k^*_{15} = d^*_{15}(s^{*E}_{44}\varepsilon^{*\sigma}_{11})^{-1/2}$$

Results of our evaluations are shown in Fig. 1 and Table 1. For example, the k^*_{ij} factors demonstrate distinct dependences on the 90° domain volume concentration m and temperature T (Fig. 1). Changing the k^*_{31} sign by a variation of m and/or T is associated with a possibility of $d^*_{31}(m, T) \rightarrow 0$. It provides the very large anisotropy of PT FC, including $d^*_{33}/|d^*_{31}| \rightarrow \infty$. Our evaluations testify also to the small anisotropy of elastic compliances

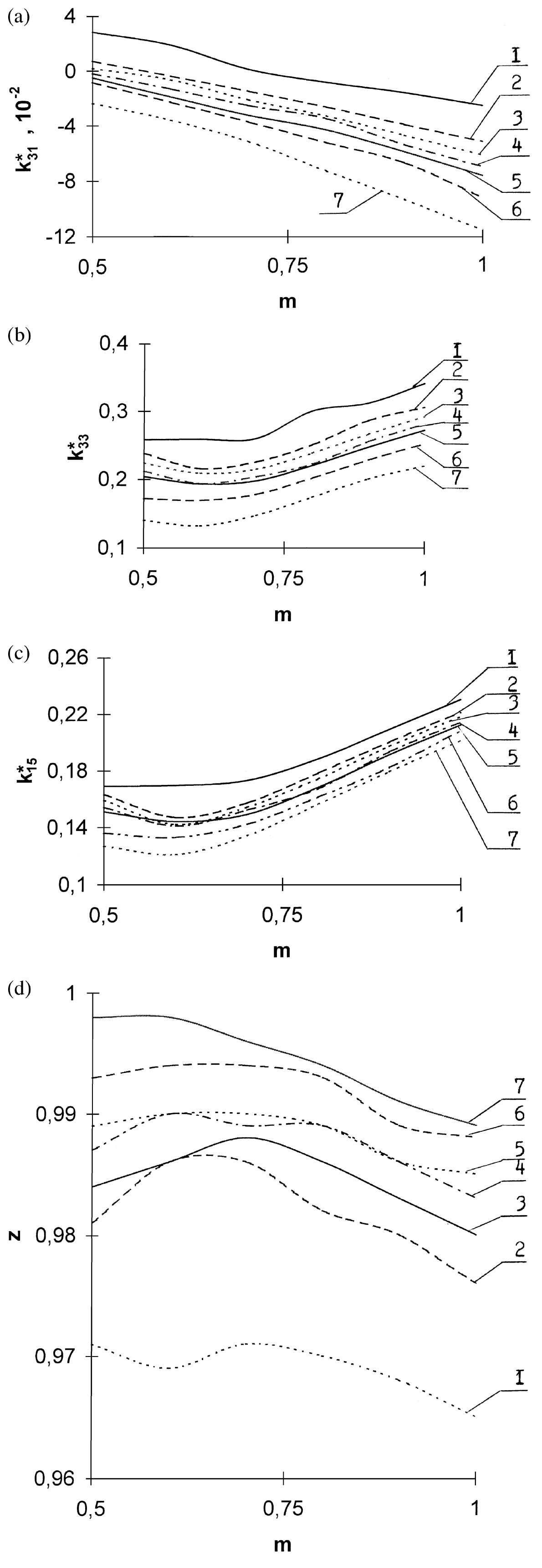

Fig. 1. Electromechanical coupling factors k^*_{ij} (a, b and c) and dielectric anisotropy z (d) as functions of the 90° domain volume concentration m and temperature T in $PbTiO_3$ ferroelectric ceramics. (a) $ij=31$, (b) $ij=33$ and (c) $ij=15$. In all plots curves 1, 2, 3, 4, 5, 6 and 7 correspond to temperatures $T = -150$, -50, 0, 25, 50, 100, and 200°C, respectively. Calculations were performed by using experimental data[16,17] on stress-free single-domain crystals.

Table 1. Electromechanical coupling factors k^*_{ij} and dielectric anisotropy z of $(Pb_{1-x}Ca_x)[(Co_{0\cdot5}W_{0\cdot5})_{0\cdot04}Ti_{0\cdot96}]O_3 + 0\cdot01\ MnCO_3$ ferroelectric ceramics for different 90° domain volume concentrations m and Ca molar concentrations x[a]

m	*0·5*	*0·6*	*0·7*	*0·8*	*0·9*	*1·0*
$x=0\cdot1500$						
k^*_{31}, 10^{-2}	–2·25	–2·52	–3·25	–4·52	–6·07	–7·74
k^*_{33}	0·288	0·288	0·290	0·295	0·306	0·312
k^*_{15}	0·203	0·208	0·220	0·236	0·255	0·272
z	0·977	0·978	0·980	0·984	0·985	0·986
$x=0\cdot2000$						
k^*_{31}, 10^{-2}	–1·56	–1·81	–2·58	–3·84	–5·46	–7·42
k^*_{33}	0·287	0·288	0·291	0·299	0·311	0·319
k^*_{15}	0·200	0·205	0·217	0·234	0·252	0·259
z	0·976	0·976	0·979	0·982	0·982	0·983
$x=0\cdot2300$						
k^*_{31}, 10^{-2}	–0·958	–1·19	–1·90	–3·10	–4·62	–6·23
k^*_{33}	0·285	0·287	0·291	0·300	0·313	0·330
k^*_{15}	0·195	0·200	0·212	0·228	0·247	0·265
z	0·975	0·975	0·977	0·978	0·980	0·980
$x=0\cdot2400$						
k^*_{31}, 10^{-2}	–0·737	–0·977	–1·72	–2·94	–4·48	–6·14
k^*_{33}	0·289	0·290	0·295	0·305	0·319	0·336
k^*_{15}	0·197	0·202	0·214	0·230	0·249	0·267
z	0·974	0·974	0·976	0·978	0·978	0·978
$x=0\cdot2450$						
k^*_{31}, 10^{-2}	–0·568	–0·795	–1·50	–2·67	–4·17	–5·76
k^*_{33}	0·293	0·295	0·300	0·311	0·325	0·343
k^*_{15}	0·199	0·203	0·215	0·232	0·250	0·269
z	0·972	0·972	0·974	0·975	0·977	0·977
$x = 0\cdot2475$						
k^*_{31}, 10^{-2}	−0·494	0·725	−1·50	−2·66	−4·01	−5·58
k^*_{33}	0·295	0·295	0·300	0·314	0·329	0·347
k^*_{15}	0·199	0·203	0·215	0·233	0·252	0·270
z	0·971	0·972	0·973	0·975	0·975	0·975
$x=0\cdot2500$[b]						
k^*_{31}, 10^{-2}	–0·419	–0·628	–1·29	–2·40	–3·83	–5·39
k^*_{33}	0·298	0·300	0·306	0·317	0·332	0·351
k^*_{15}	0·201	0·205	0·217	0·234	0·253	0·271
z	0·970	0·9671	0·972	0·973	0·974	0·974
$x=0\cdot2525$						
k^*_{31}, 10^{-2}	–0·432	–0·642	–1·30	–2·42	–3·86	–5·41
k^*_{33}	0·299	0·301	0·307	0·318	0·333	0·352
k^*_{15}	0·201	0·206	0·218	0·235	0·254	0·272
z	0·970	0·971	0·972	0·974	0·974	0·974
$x=0\cdot2550$						
k^*_{31}, 10^{-2}	–0·442	–0·655	–1·33	–2·47	–3·88	–5·43
k^*_{33}	0·300	0·302	0·308	0·319	0·334	0·353
k^*_{15}	0·202	0·207	0·218	0·236	0·254	0·273
z	0·970	0·970	0·972	0·974	0·974	0·974
$x=0\cdot2575$						
k^*_{31}, 10^{-2}	–0·458	–0·668	–1·34	–2·50	–3·91	–5·46
k^*_{33}	0·300	0·302	0·308	0·320	0·335	0·354
k^*_{15}	0·202	0·207	0·219	0·236	0·255	0·274
z	0·970	0·970	0·971	0·973	0·974	0·974
$x=0\cdot2600$						
k^*_{31}, 10^{-2}	–0·468	–0·677	–1·34	–2·55	–3·92	–5·48
k^*_{33}	0·300	0·303	0·310	0·321	0·336	0·355
k^*_{15}	0·203	0·208	0·220	0·237	0·256	0·275
z	0·970	0·971	0·972	0·973	0·974	0·974
$x=0\cdot2650$						
k^*_{31}, 10^{-2}	–0·648	–0·871	–1·56	–2·72	–4·22	–5·81
k^*_{33}	0·299	0·302	0·308	0·319	0·335	0·353
k^*_{15}	0·204	0·208	0·221	0·238	0·257	0·276
z	0·970	0·971	0·972	0·974	0·975	0·975
$x=0\cdot2800$						
k^*_{31}, 10^{-2}	–1·16	–1·40	–2·17	–3·43	–5·01	–6·70
k^*_{33}	0·299	0·301	0·307	0·317	0·332	0·350
k^*_{15}	0·206	0·211	0·224	0·241	0·260	0·279
z	0·972	0·973	0·975	0·976	0·978	0·978
$x=0\cdot3000$						
k^*_{31}, 10^{-2}	–1·67	–1·94	–2·78	–4·14	–5·84	–7·62
k^*_{33}	0·288	0·290	0·295	0·304	0·318	0·336
k^*_{15}	0·203	0·207	0·220	0·237	0·257	0·276
z	0·976	0·976	0·978	0·981	0·982	0·982

[a] Experimental data on stress-free single domain crystals were taken from Ref. 4. All the evaluated data correspond to $T = 25°C$.
[b] The highest density of x values was chosen in the extrema region for $k^*_{ij}(m, x)$ functions.

$s_{11}^{*E}/s_{33}^{*E} \to 1$ that cannot considerably change the approximate proportion $k_{33}^*/|k_{31}^*| \approx d_{33}^*/|d_{31}^*|$ within the m and T ranges chosen in Fig. 1. It should be noted that the wide temperature range of $-150°C \leq T \leq 200°C$ is favourable for reaching the large piezoelectric anisotropy (i.e. $k_{33}^*/|k_{31}^*| \gg 1$ or $d_{33}^*/|d_{31}^*| \gg 1$) because of the small dielectric anisotropy $z = \varepsilon_{11}^{*\sigma}/\varepsilon_{33}^{*\sigma} < 1$, as it was analysed earlier.[2–4] It is remarkable that the characteristic values of this anisotropy $z = 0{\cdot}989...0{\cdot}998$ correspond to temperatures which are lower by ca 300°C than the Curie point of PT crystals.[16,17]

Another interesting example of $k_{ij}^*(m, x)$ functions is shown in Table 1. First for all the increasing $|k_{ij}^*(m, x)|$ functions for any $x = \text{const}$ and the fact that the highest anisotropy in this case is realized for polydomain grains ($m = 0{\cdot}5$) without passing k_{31}^* through the zero value should be pointed out. Various types of the monotonic $k_{ij}^*(m, x)$ functions of PCT FC are realized for any $m = \text{const}$. In particular, for the equal domain volume concentrations, these functions contain extreme points within the range of $0{\cdot}23 \leq x \leq 0{\cdot}28$, e.g. diffuse minima and maxima in $k_{33}^*(0{\cdot}5, x)$ and $k_{15}^*(0{\cdot}5, x)$ as well as a maximum in $k_{31}^*(0{\cdot}5, x)$. The concentration range is characterized by a diffuse peak[3,4] of a function of the electrostrictive constant $Q_{12}(x)$ of PCT in the vicinity of $x_0 = 0{\cdot}25$), and this circumstance influences results of calculating all the FC electromechanical constants, especially the piezoelectric moduli d_{ij}^* (e.g. $d_{33}^*/|d_{31}^*|$ has a maximum at $x = x_0$) and electromechanical coupling factors k_{ij}^*. Therefore, one can speak on the concentration range of $0{\cdot}23 \leq x \leq 0{\cdot}28$ surrounding the x_0 point where the mentioned extrema are present. The important feature of this range is a fulfilment of an inequality $k_{33}^*(0{\cdot}5, x)/|k_{31}^*(0{\cdot}5, x)| \gg 1$. Increasing the domain volume concentration $m \to 1$ leads to a violation of this inequality that may be interpreted as the negative effect of trends in the monodomenization on the FC piezoelectric anisotropy. As in the case of PT FC, the dielectric anisotropy $z \to 1$ does not undergo considerable changes within the wide m range for $x = \text{const}$, but it has weak minima in dependences on x for fixed m value (Table 1) that favours the large piezoelectric anisotropy in PCT FC.

The study of the $k_{ij}^*(m, T)$ and $k_{ij}^*(m, x)$ dependences in PT and PCT FC, respectively, allows to establish some quantitative conditions for the realization of the large piezoelectric anisotropy. Of particular interest are the extrema of the $k_{ij}^*(m, x)$ functions within the region of $0{\cdot}23 \leq x \leq 0{\cdot}28$. The comparison of the evaluated k_{ij}^* with the experimental data on the electromechanical coupling factors $k_{ij\,\text{exper}}^*(x)$ of PCT FC[8] shows some quantitative agreement for $ij = 31$, however, the presence of extreme for $ij = 33$; 15 and $m = \text{const}$ within the concentration x range needs a further experimental proof. It should be also taken into account that revealing these extrema can be prevented because of possible negative influence of 90° domain-well displacements, microstructural and technological factors on the $k_{ij}^*(m, x)$ dependences in PCT FC.

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