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Domain wall displacements and piezoelectric activity of $KNbO_3$ single crystals

V Yu Topolov[1]

Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft, Institut für Materialforschung II,
Postfach 3640, D-76021 Karlsruhe, Germany

E-mail: topolov@phys.rsu.ru

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Abstract
The role of domain-orientation effects in forming the piezoelectric coefficient d_{33} of polydomain $KNbO_3$ single crystals in the $mm2$ phase is studied. Non-180° domain wall displacements in the electric field $\boldsymbol{E} \parallel [001]$ are analysed, and their contributions to d_{33} are evaluated. A link between these contributions and crystallographic characteristics of domain structures is revealed for the first time for different 60°, 90° and 120° domain structures.

The problem of the relationship between piezoelectric performances and domain structures of ferroelectric single crystals (SCs) has been the subject of various studies [1–6] in the last years. Perovskite-type SCs are of scientific significance due to the perspective of the search for specific domain patterns (or so-called *engineered domain structures*) [3, 7], heterophase structures [8, 9], optimal crystallographic orientations [9, 10] or poling treatment conditions [3, 4] that lead to improved piezoelectric properties and high electromechanical coupling factors. In recent experimental papers [3, 5] the potassium niobate ($KNbO_3$) SC received attention because of considerable dependences of its piezoelectric properties on the domain structures and related switching and rotation processes in the external electric field $\boldsymbol{E}$. In this connection it seems to be timely and interesting to consider the role of domain-orientation effects in forming the piezoelectric activity of the $KNbO_3$ SC. The objective of this paper is to analyse the influence of different non-180° domain wall (DW) displacements on the piezoelectric coefficient d_{33} characterizing the strain versus the electric field behaviour and actuator performance of this SC.

At room temperature $KNbO_3$ SCs belong to the point group $mm2$ and can be split into 180° and different non-180° domains being mechanical twins [11]. According to symmetry changes at structural phase transitions there are following non-180° domains in the ferroelectric $mm2$

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[1] Permanent address: Department of Physics, Rostov State University, 5 Zorge Street, 344090 Rostov-on-Don, Russia.

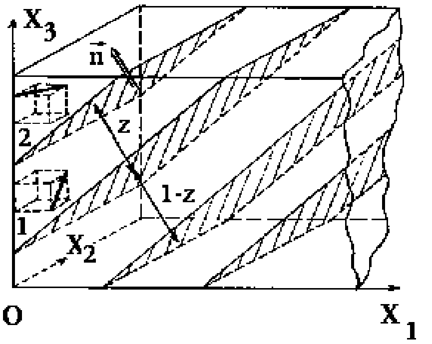

Figure 1. A fragment of the SC containing domains of the first and second types with volume concentrations z and $1 - z$, respectively. Rectangular coordinate axes $\mathrm{O}X_j$ are assumed to be parallel to the perovskite unit-cell vectors [100] ($j = 1$), [010] ($j = 2$) and [001] ($j = 3$). Orientations of the spontaneous polarization vectors $\boldsymbol{P}_s^{(i)}$ of the adjacent domains are shown for example only; different DWs are shown as dashed areas.

phase: the 90° ({100} DWs), 60° or 120° ({110} or S-type $\{11l\}$ DWs) domains [12, 13]. The DW orientations in brackets are written with respect to the perovskite unit-cell axes [11], and these DWs are regarded as zero-net-strain planes, i.e. planar boundaries that satisfy conditions for complete internal stress relief [14]. Now we consider an effect of the non-180° DW displacements on the piezoelectric activity of $\mathrm{KNbO_3}$ SCs.

For the theoretical description of this effect we propose a model of the (001) platelike SC containing one of the types[2] of non-180° DW that are displaced in the uniform electric field $\boldsymbol{E} \parallel \mathrm{O}X_3 \parallel [001]$ (figure 1). The DW normal vector $\boldsymbol{n}(\cos\alpha_1, \cos\alpha_2, \cos\alpha_3)$ is expressed in terms of angles $\alpha_j = (\mathrm{O}X_j, \hat{}\,\boldsymbol{n})$. The bulk energy density associated with the elastic DW displacement and the electrostatic interaction, 'spontaneous polarization vectors $\boldsymbol{P}_s^{(i)}$ of the adjacent domains ($i = 1; 2$)—field $\boldsymbol{E}$', is expressed as the sum of two competing contributions, f_{elas} and f_{el}, respectively. An infinitesimal change $\mathrm{d}\xi_j^\Delta$ in the strain of the SC along the $\mathrm{O}X_j$ axis is associated with a change in the volume concentration of the first domain type by $\mathrm{d}z$ and with a differential

$$\mathrm{d}f_{elas} = \sum_j [\sigma_j^{(1),\Delta}\,\mathrm{d}\xi_j^\Delta z + \sigma_j^{(2),\Delta}\,\mathrm{d}\xi_j^\Delta (1-z)]. \tag{1}$$

In equation (1) mechanical stresses caused by the DW displacements are defined as $\sigma_j^{(i),\Delta} = \Sigma_k c_{jk}^{(i),E}\xi_k^\Delta$, where elastic moduli $c_{jk}^{(i),E}$ of the ith domain type (E = constant) are chosen by taking into account the $\boldsymbol{P}_s^{(i)}$ orientation with respect to the coordinate axes $\mathrm{O}X_j$. The strain $\xi_k^\Delta = z\delta_k \cos\alpha_k$ is written in terms of [10], where $\delta_k = (p_k^{(1)}/p_k^{(2)}) - 1$ depends on unit-cell parameters $p_k^{(i)}$ of the adjacent domains along the $\mathrm{O}X_k$ direction. After integration of $\mathrm{d}f_{elas}$ from equation (1) over the volume concentrations $0 \leqslant z \leqslant z_\Delta < 1$ the bulk energy density for the elastic interaction is written in a general form as

$$f_{elas} = C_I(z_\Delta^3/3) + C_{II}(z_\Delta^2/2) \tag{2}$$

where C_I and C_{II} depend on the elastic moduli $c_{jk}^{(i),E}$ and parameters δ_k of the domains as well as on angles α_k of the orientation of the DW normal vector.

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[2] Perovskite-type SCs having vast regions with one of the types of non-180° DW were experimentally observed and described in papers [13] ($\mathrm{KNbO_3}$), [14] ($\mathrm{PbZrO_3}$) and monographs [15] ($\mathrm{BaTiO_3}$ and $\mathrm{PbTiO_3}$) and [16] ($\mathrm{BaTiO_3}$).

The bulk energy density associated with the above-mentioned electrostatic interaction is given by an expression

$$f_{el} = -[\boldsymbol{P}_s^{(1)} z_\Delta + \boldsymbol{P}_s^{(2)}(1 - z_\Delta)]\boldsymbol{E} = -P_s E[z_\Delta \cos\theta_1 + (1 - z_\Delta)\cos\theta_2] \quad (3)$$

where $\theta_i = (\boldsymbol{P}_s^{(i)}, \hat{}\ \boldsymbol{E})$ and $P_s = |\boldsymbol{P}_s^{(i)}|$. By minimizing the energy densities (2) and (3) we take into account conditions $\mathrm{d}(f_{elas} + f_{el})/\mathrm{d}z_\Delta = 0$ and $\mathrm{d}^2(f_{elas} + f_{el})/\mathrm{d}z_\Delta^2 > 0$. The corresponding volume concentration of the first domain type is determined from a formula

$$z_\Delta = \{-C_{II} + [(C_{II})^2 - 4C_I P_s E(\cos\theta_2 - \cos\theta_1)]^{1/2}\}/(2C_I). \quad (4)$$

Thus the contribution from the non-180° DW displacements influences the total strain ξ_3 of the polydomain SC in the electric field $\boldsymbol{E} \parallel \mathrm{O}X_3$ because of the presence of the item with $z_\Delta \neq 0$ (see equation (4)): $\xi_3(E) = \xi_{3,piezo} + \xi_3^\Delta = d_{33}^0 E + z_\Delta \delta_3 \cos\alpha_3$, where the piezoelectric coefficient d_{33}^0 is assumed to be measured at $E \to 0$. Finally, the piezoelectric coefficient of the SC is evaluated as $d_{33} = d_{33}^0 + \Delta d_{33}$ where the contribution Δd_{33} from the non-180° DW displacements follows from a derivative

$$\Delta d_{33} = \mathrm{d}\xi_3^\Delta/\mathrm{d}E = \mathrm{d}(z_\Delta \delta_3 \cos\alpha_3)/\mathrm{d}E. \quad (5)$$

Our evaluations of the contribution $\Delta d_{33} = \Delta d_{33}(E)$ from equation (5) are carried out by using experimental data on the unit-cell parameters [11], elastic moduli c_{jk}^E and spontaneous polarization P_s [17] of single-domain KNbO$_3$ SC samples at room temperature. Results of calculations made for different non-180° DW displacements are listed in table 1. Variants shown in table 1 are divided into two groups. Calculations in the first group concern the field strength $E \leqslant 5 \times 10^5$ V m^{-1} whereas the second group of calculations is associated with the field strength $E > 5 \times 10^5$ V m^{-1}. The analogous division of experimental curves was made in [5] where considerable changes in both the strain $\xi_3(E)$ and derivative $\mathrm{d}\xi_3(E)/\mathrm{d}E$ were observed at $E = (5–6) \times 10^5$ V m^{-1}. These changes can occur due to microcracking [5] on increasing the electric field strength E, that, in our opinion, leads to a decrease of the parameters δ_k (mainly δ_3). For comparison, our calculations from variants 2 and 4 (see table 1) correspond to the parameter δ_3 being half the same parameter in variants 1 and 3. On the whole, the $\xi_3^\Delta(E)$ dependences from variants 1–4 are in good agreement with experimental data [5] on the difference $\xi_3(E) - \xi_{3,piezo}(E)$. It is remarkable that this agreement takes place even despite features peculiar to the 60° domain structure [13, 14] in real SC samples. Moreover, the practically linear field dependence of the above-mentioned difference at $E \leqslant 5 \times 10^5$ V m^{-1} [5] is also pronounced in the calculated $\xi_3^\Delta(E)$ dependence that stems from an inequality $|C_I| \ll C_{II}$ (see table 1). There is a reasonable chance that the results of our calculations of $\xi_3^\Delta$and Δd_{33} from variants 1–4 can be regarded as suitable for KNbO$_3$ SCs with various 60° DWs.

Further increasing the Δd_{33} value is realized in cases of 120° and 90° DW displacements (variants 5 and 6). In contrast to the known engineered 90° domain structure with $\boldsymbol{P}_{s,eng}^{(1)}(P_s/\sqrt{2}, 0, P_s/\sqrt{2})$, $\boldsymbol{P}_{s,eng}^{(2)}(-P_s/\sqrt{2}, 0, P_s/\sqrt{2})$ and $\Delta d_{33} = 0$ [5] the 90° domains from variant 6 have $\boldsymbol{P}_s^{(2)} = -\boldsymbol{P}_{s,eng}^{(2)}$. Due to this arrangement feature the DWs become charged as, for example, was shown [5] for the 60° DWs. It is felt that fairly weak fields $E < 5 \times 10^5$ V m^{-1} would not reorientate the second domain type (i.e. a rotation $\boldsymbol{P}_s^{(2)} \to -\boldsymbol{P}_{s,eng}^{(2)}$ is not yet realized) and can favour the DW displacement along the $\boldsymbol{E}$ direction. The corresponding DW contribution Δd_{33} becomes larger than in variants 1, 3 and 5; however, $d_{33}^0 \to 0$ because of an equality $P_{s3}^{(1)} + P_{s3}^{(2)} = 0$ (see variant 6 in table 1). In accordance with data from [5] and variant 5, $d_{33}^0 \approx 90$ pC N^{-1} in the limiting case of the single-domain SC with the spontaneous polarization $\boldsymbol{P}_s^{(1)}$, and therefore the total piezoelectric coefficient d_{33} does not exceed 205 pC N^{-1}. It is beyond doubt that variants 5 and 6 provide the highest piezoelectric activity of the polydomain KNbO$_3$ SCs along the OX_3 axis in weak electric fields.

Table 1. Crystallographic characteristics and calculated contributions from non-180° DW displacements to strain $\xi_3^{\Delta}(E)$ and piezoelectric coefficient Δd_{33} of polydomain KNbO$_3$ SCs.

Variants	$\boldsymbol{P}_s^{(i)}$ and domain types	DW orientations	C_I (10^6 Pa)	C_{II} (10^6 Pa)	E (10^5 V m^{-1})	$10^3\xi_3^{\Delta}$ (%)	Δd_{33} (pC N^{-1})	$\omega = (\boldsymbol{P}_s^{(1)}, \hat{} \boldsymbol{P}_s^{(2)}) + \alpha_3 + \lvert\theta_1 - \theta_2\rvert$ (deg)
1	$\boldsymbol{P}_s^{(1)}(0, P_s/\sqrt{2}, P_s/\sqrt{2})$, $\boldsymbol{P}_s^{(2)}(P_s/\sqrt{2}, P_s/\sqrt{2}, 0)$ (60° domains)	$\alpha_1 = \alpha_3 = 46.6°$, $\alpha_2 = 76.2°$ (S-type [18])	−4.96	30.2	1	0.981	52.9	152
					2	1.96		
					3	2.94		
					4	3.93		
					5	4.91		
2	S. variant 1	S. variant 1	−1.24	7.55	5.3	15.2	288	—
					6	17.2		
					7	201		
3	S. variant 1	$\alpha_1 = -135°$, $\alpha_2 = 90°$, $\alpha_3 = 45°$ (s. figure 1)	−3.15	72.3	1	0.421	42.1	150
					2	0.842		
					3	1.26		
					4	1.68		
					5	2.11		
4	S. variant 1	S. variant 3	−0.788	18.1	5.3	8.71	164	—
					6	9.86		
					7	11.5		
5	$\boldsymbol{P}_s^{(1)}(-P_s/\sqrt{2}, 0, P_s/\sqrt{2})$, $\boldsymbol{P}_s^{(2)}(P_s/\sqrt{2}, P_s/\sqrt{2}, 0)$ (120° domains)	$\alpha_1 = 90°$, $\alpha_2 = \alpha_3 = 45°$	0	26.7	1	1.14	114	210
					2	2.28		
					3	3.42		
					4	4.56		
					5	5.70		
6	$\boldsymbol{P}_s^{(1)}(P_s/\sqrt{2}, 0, P_s/\sqrt{2})$, $\boldsymbol{P}_s^{(2)}(P_s/\sqrt{2}, 0, -P_s/\sqrt{2})$ (90° head-to-head domains)	$\alpha_1 = \alpha_2 = 90°$, $\alpha_3 = 0°$	0	39.1	1	2.20	220	270
					2	4.41		
					3	6.61		
					4	8.81		
					5	11.0		

It should be noted that there is a correlation between contributions Δd_{33}, calculated in variants 1, 3, 5 and 6, and the angle ω (table 1) characterizing the mutual domain and DW orientations with respect to the $\boldsymbol{E}$ direction. The largest Δd_{33} value corresponds to the largest angle ω, and this trend points the way to forming the new engineered non-180° domain structures that provide considerable DW displacements and related piezoelectric performances in different ferroelectric SCs.

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