

Investigation on switching behaviour of 90° ferroelectric domains in $(\text{Pb}_{0.85}\text{Sm}_{0.10})(\text{Ti}_{0.98}\text{Mn}_{0.02})\text{O}_3$ piezoelectric ceramics of ultra-high electromechanical anisotropy by the X-ray diffraction technique

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An investigation on Sm modified PbTiO_3 ceramics of typical ultra-high electromechanical anisotropy was carried out by means of X-ray diffraction (XRD) technique. By introduction of crystal plane orientation density $\rho(hkl)$, a good description of switching behaviour of 90° ferroelectric domains within the ceramic discs poled at different electric forces has been achieved. The results indicate that 90° domains show a strong spatial orientation preference so that most of the 90° walls are oriented with their normal vectors enclosing an angle 45° with the specimen surface. After poling treatment few changes occurred in the 90° wall distribution but noticeable domain wall shifts occurred. Another noteworthy result is that the thickness electromechanical coupling coefficient K_t develops with poling field almost at the same pace as the orientation density gain $\Delta\rho(002)$ of (002) crystal plane does. The implications of their mutual linkage are outlined.

1. Introduction

It is because of their unusually large anisotropy in electromechanical coupling factors and piezoelectric coefficients that modified PbTiO_3 ceramic materials are useful in many fields such as high frequency linear array transducers [1], SAW devices [2] and infrared sensors [3]. Now, at a laboratory scale, high qualified, modified PbTiO_3 piezoelectric ceramic discs can be produced, which have thickness to planar coupling ratio $K_t/K_p > 50$ in the neighbourhood of room temperature.

Up to now, however, the reasons why these ceramics have such novel properties have not been clarified, and no satisfactory explanation of the relationship between their chemical composition, domain configuration and macroproperties has been achieved. Takeuchi [4] and Yamashita [5] suggested that crystal lattice anisotropy and 90° domain rotation might be responsible for those abnormal properties. Damjanovic [6] speculated that according to their work the unusually large electromechanical anisotropy might arise from some extrinsic contributions to their conventional bulk properties. In addition, Mendiola *et al.* [7] thought that a possible presence of uncombined PbO on the grain boundaries of modified PbTiO_3 ceramics, presumably, promoted high preferential rotation of 90° domains during poling treatment and yielded an unusually large K_t/K_p value. Nonetheless, all these statements have not gone

beyond hypotheses. No evidence has yet, directly or indirectly, proved which one is true.

In the present work, X-ray diffractive characteristics of Sm modified PbTiO_3 ceramic discs with typical ultra-high electromechanical anisotropy is investigated in detail after they undergo poling treatment at various d.c. electric forces. An internal linkage between the X-ray diffractive characteristics and switching behaviour of 90° domains is discussed and a reasonable spacial orientation pattern of 90° domains has been derived, which is in good agreement with the experimental results, and therefore may be regarded as one of the dominant causes for the abnormal anisotropy in electromechanical properties.

2. Experimental procedure

The specimen discs used here are of chemical composition: $(\text{Pb}_{0.85}\text{Sm}_{0.10})(\text{Ti}_{0.98}\text{Mn}_{0.02})\text{O}_3$. The ceramics were prepared by conventional mixed-oxide process starting from analytical reagent (AR) grade oxides. After sufficiently blending, the raw mixture were calcined at 900°C for 1 h, and then the pressed discs (diameter: 10 mm and thickness: 1 mm) were sintered at 1100–1200°C for 2 h. Gold electrodes were sputtered on the major faces and poling treatment was carried out in silicon oil at 150°C for 15 min with the electric field taken as 2, 3, 4, 5 and 6 kV mm⁻¹, respectively.

X-ray diffraction measurement of the poled specimens were performed on a Rigaku D/max-rB X-ray diffractometer with working conditions: CuK_α radiation; graphite monochromator; tube voltage 40 kV; tube current 100 mA; and scanning speed 2°min^{-1} . The values of K_i for specimens were calculated from the ratio of overtone resonance frequency, f_2 to fundamental resonance frequency, f_1 of the thickness mode piezoelectric resonator, f_2/f_1 , by using Table II in Onoe *et al.* paper [8].

3. Results and discussions

3.1. Crystal lattice parameters versus poling field strength

To know whether poling field will influence the crystal symmetry and cell dimensions, the X-ray diffraction lines for every specimen are indexed, and then 15 lines in higher 2θ range are selected for calculation of lattice parameters by least-square method. The results indicate that the specimens keep their tetragonal symmetry at all various poling voltages and nearly no change has been observed in their cell dimensions, as shown in Table I.

3.2. The calculation of crystal plane orientation density $\rho(hkl)$ from XRD data

It is well known that ferroelectric ceramics of tetragonal symmetry are built of innumerable grains which contain many 90° and 180° domains. Poling treatment will make them partially switch toward the direction favourable to the total system energy, and then a macro piezoelectric properties will be afforded. But according to Friedel's law, the reversal of 180° domains during poling process could not be detected by X-ray diffraction. Therefore, it is true to suppose that all the changes in X-ray diffraction pattern of specimens poled at different poling voltages are brought about by the switching of 90° domains alone.

In order to make a quantitative description of switching behaviour of 90° domains, a crystal plane orientation density $\rho_{(hkl)}$ is introduced, which is defined as a volume fraction of the crystal grains with (hkl) plane parallel to specimen surface. Based on the general principle of X-ray diffraction, diffractive intensity $I_{(hkl)}$ for (hkl) plane can be usually expressed:

$$I_{(hkl)} = CAI_0 L |F_{(hkl)}|^2 N_{(hkl)} \rho_{(hkl)} \quad (1)$$

where I_0 stands for incident X-ray intensity; L , Lorentz angle factor; $F(hkl)$, structure factor for (hkl) plane; $N_{(hkl)}$, iterative factor; A , absorption factor; and C is known as measuring system constant. When the

measuring conditions and specimen are once given, C will be definite. Obviously, for a specimen without any preference in orientation, all its $\rho_{(hkl)}$ corresponding to the crystal planes (hkl) will be a constant and can be taken as 1 so as to simplify the mathematical process, so that

$$I_{(hkl)} = CrArI_0 L |F_{(hkl)}|^2 N_{(hkl)} \quad (2)$$

But it should be noted that when a definite preferential orientation is present within the specimen, the $\rho_{(hkl)}$ for those planes (hkl) with larger probability to orient parallel to specimen surface will increase, and the other will decrease. Making a division of Equation 1 by Equation 2, we have

$$I_{(hkl)}/I_{r(hkl)} = CA\rho_{(hkl)}/C_r A_r \quad (3)$$

Multiply two sides of Equation 3 by $I_{(hkl)}/\sum_i^n I_{(hkl)}$ as a weight factor and make a sum to n diffraction lines, the following equation can be obtained

$$\sum_i^n \frac{I_{(hkl)}^2}{I_{r(hkl)} \sum_i^n I_{(hkl)}} = \frac{CA}{CrAr} \sum_i^n \frac{I_{(hkl)} \rho_{(hkl)}}{\sum_i^n I_{(hkl)}} \quad (4)$$

It is not difficult to understand that when the number n is large enough, there will be Equation 5

$$\sum I_{(hkl)} \rho_{(hkl)} / \sum I_{(hkl)} = 1 \quad (5)$$

and then Equation 6

$$\frac{CA}{C_r A_r} = \sum_i^n \frac{I_{(hkl)}^2}{I_{r(hkl)} \sum_i^n I_{(hkl)}} \quad (6)$$

Substitute Equation 6 for $CA/C_r A_r$ in Equation 3, a general formula used to calculate plane orientation density $\rho_{(hkl)}$ for polycrystal specimens can be achieved as follows

$$\rho_{(hkl)} = \frac{I_{(hkl)} \sum_i^n I_{(hkl)}}{I_{r(hkl)} \sum_i^n I_{(hkl)}} \quad (7)$$

From the above derivation, it can be seen that the extent to which Equation 5 is correct is only the factor which influences the accuracy of $\rho_{(hkl)}$ if no regard is given to errors from XRD data. Our calculating practice proves that when 21 diffraction lines with 2θ from 20° to 100° are taken into consideration, Equation 5 can be satisfied with an error less than 10^{-6} .

Taking nontextured powder modified PbTiO_3 as a standard specimen and applying Equation 7 to the calculation of $\rho_{(hkl)}$ for poled specimens, we get $\rho_{(hkl)}$, as listed in Table I, and $\Delta\rho_{(hkl)}$ shown in Fig. 1 (here $\Delta\rho_{(hkl)} = \rho_{(hkl)} - 1$). It is easy to see that for different (hkl) planes, the corresponding $\rho_{(hkl)}$ apparently does not vary with poling field in the same way. But there are some conspicuous regularities among their poling field dependences. As the angle θ begins to rise from 0° , the orientation density gain $\Delta\rho_{(hkl)}$ increases with poling field at a decreasing rate, and when θ is about 49° , such a growth pattern disappears. With a continual augmentation of θ , however, there occurs a minus poling field dependence for those (hkl) planes like (312) , (201) , etc. The larger the angle θ , at the

TABLE I Crystal lattice parameters versus poling electric field, E_3

E_3 (kV mm $^{-1}$)	0	2	3	4	5	6
a (Å)	3.909	3.907	3.910	3.909	3.907	3.908
c/a	1.042	1.042	1.042	1.041	1.042	1.042

TABLE II The calculated results of $\rho_{(hkl)}$ for (hkl) planes; θ is the angle between the normal vectors of (002) and (hkl) planes

θ (hkl)	0.00 (002)	27.53 (102)	36.39 (112)	46.19 (202)	49.30 (212)	58.76 (312)	64.38 (201)	72.27 (301)	90.00 (200)
E_3 (kV mm ⁻¹)									
2	1.257	1.132	1.114	1.100	1.042	0.985	0.873	0.797	0.771
3	1.516	1.315	1.254	1.160	1.072	0.905	0.775	0.672	0.590
4	1.732	1.567	1.394	1.185	1.049	0.795	0.583	0.504	0.409
5	1.977	1.804	1.560	1.340	0.979	0.645	0.357	0.348	0.200
6	2.067	1.874	1.690	1.460	0.981	0.560	0.300	0.280	0.146

larger rate the orientation density gain $\Delta\rho_{(hkl)}$ decreases. And finally, the $\Delta\rho_{(200)}$ for (200) plane shows a minus maximum.

3.3. Analysis of switching behaviour of 90° domains

In general, switching process of 90° domains, incited by poling field, is a complex one. It involves physical and chemical changes. Fewer systematical studies engaged in this field have been reported. In the present investigation, we find that careful analysis of the poling field dependence of orientation density gains for different (hkl) planes will help understand this process and more important, information about reasons for the unusually large anisotropic electromechanical properties can be drawn out.

Now let us set up a model, in which switching process of 90° domains is viewed as displacement of the walls. For any pair of 90° domains in ferroelectric grains, as shown in Fig. 2, an internal coordinate system $oxyz$ is fixed on its wall, with the z and x axes parallel and antiparallel to spontaneous polarization vectors in domain (2) and domain (1), respectively; and the y axis parallel to the specimen surface. In such a coordinate system, accordingly, there are

$$(Pi')_1 = P_o \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}; \quad (Pi')_2 = P_o \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (8)$$

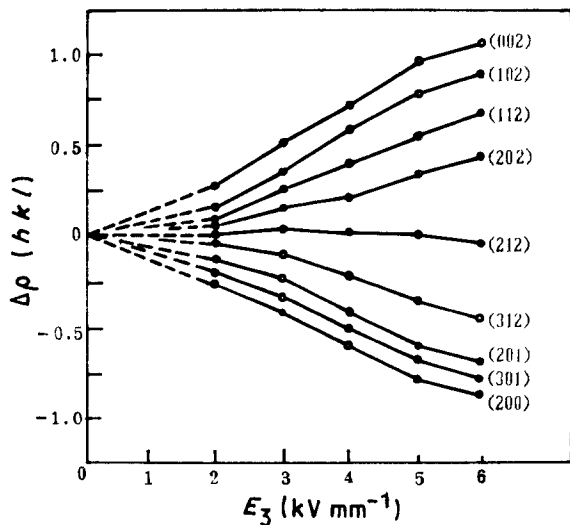


Figure 1 The poling field dependence of orientation density gain $\Delta\rho_{(hkl)}$.

Another $OXYZ$ coordinate system is built on the specimen, in which the plane determined by OXY is parallel to the surface and the Z axis lies along the same direction as the normal vector of specimen surface. In the general case, both $oxyz$ and $OXYZ$ systems are linked through Euler's angles θ and ψ in terms following transformation matrix

$$(A_{im}) = \begin{pmatrix} \cos \theta \cos \psi & -\sin \psi & \cos \psi \sin \theta \\ \sin \psi \cos \theta & \cos \psi & \sin \psi \sin \theta \\ -\sin \theta & 0 & \cos \theta \end{pmatrix} \quad (9)$$

In the $OXYZ$ system, therefore, the spontaneous polarizations can be expressed

$$(Pi)_1 = P_o \begin{pmatrix} -\cos \psi \cos \theta \\ -\sin \psi \cos \theta \\ \sin \theta \end{pmatrix};$$

$$(Pi)_2 = P_o \begin{pmatrix} \cos \psi \sin \theta \\ \sin \psi \sin \theta \\ \cos \theta \end{pmatrix} \quad (10)$$

Under the action of poling field, a polarization change ΔP due to unit displacement of 90° wall may take place

$$(\Delta P) = (Pi)_2 - (Pi)_1$$

$$= P_o \begin{pmatrix} \cos \psi \sin \theta + \cos \psi \sin \theta \\ \sin \psi \sin \theta + \sin \psi \cos \theta \\ \cos \theta - \sin \theta \end{pmatrix} \quad (11)$$

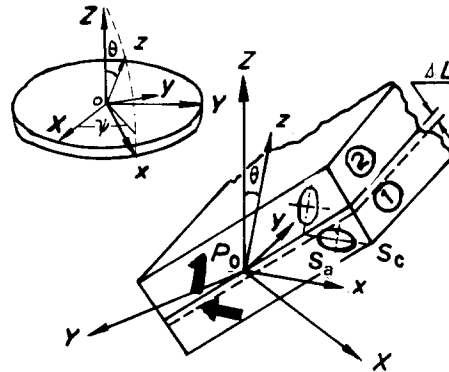


Figure 2 Schematic diagram of 90° domain wall displacement model.

Because the ellipsoid elastic dipoles in two domains are oriented just in the directions orthogonal to each other, as illustrated in Fig. 2, any displacement of the wall will necessarily yield elastic stress in neighbouring region of the wall, which acts as an impediment to wall shift. Consequently, when this stress develops up to such a magnitude as to counterbalance the electric force exerted on the wall, motion of the wall will stop, and then an equilibrium relation can be established

$$F = (\Delta P)E/2 = kS_0\Delta L \quad (12)$$

where ΔL is wall displacement amplitude; $S_0 = S_c - S_a$ difference between long and short axes of ellipsoid elastic dipole; and k a proportional constant.

From Equation 12, we can get for displacement amplitude ΔL when the external field $E_1 = E_2 = 0$ but $E_3 \neq 0$

$$\Delta L = P_0E_3(\cos \theta - \sin \theta)/2kS_0 \quad (13)$$

And at the same time, a change in domain volume can be obtained when wall interfacial area A is considered.

$$\Delta V = P_0E_3A(\cos \theta - \sin \theta)/2kS_0 \quad (14)$$

Obviously, Equation 14 tells us that the change in domain volume is dependent not only upon poling field strength but also the angle θ , between its spontaneous polarization vector and the direction of poling field. From the definition of crystal plane orientation density $\rho_{(hkl)}$, it easily follows that the plane orientation density gain $\Delta\rho_{(hkl)}$ should be proportional to $\Delta V(\theta)$ because poling field E_3 takes the same direction as the normal vector of specimen surface, and the diffractive intensity of (hkl) planes parallel to specimen surface are proportional to corresponding $\Delta V(\theta)$ whenever Bragg diffraction requirements are satisfied. Namely

$$\Delta\rho_{(hkl)} = K\Delta V(\theta) \quad (15)$$

Therefore, we can see that as angle θ grows, plane orientation density gain $\Delta\rho_{(hkl)}$ increases with poling voltage with a decreasing amplitude; and when the θ is equal to 45° , $\Delta V = 0$. With further growth of θ , moreover, $\Delta\rho_{(hkl)}$ decreases with poling voltage and shows such a completely symmetrical pattern as in the case where angle θ is less than 45° . Doubtlessly, this deduction from Equation 15 is in good agreement with the results shown in Fig. 1. Moreover, deeper discussions can be made.

1. Fig. 1 shows that only when θ reaches about 49° , $\Delta\rho_{(hkl)} = 0$. As to why this phenomenon could happen, three reasons can be found. First, the material of tetragonal symmetry has axis ratio $c/a = 1.042$, and so the angle θ should be 46.2° when $\Delta\rho_{(hkl)} = 0$. Next, during the previous derivation, no consideration on self-rotation of domain around its spontaneous polarization axis was made. In fact, a tiny disturbance of self-rotation angle ϕ can still satisfy Bragg diffraction conditions due to steady existence of a small divergence angle for incident X-ray. And finally, the intensity data of diffraction lines always contain small but definite errors.

2. In order to describe switching behaviour of 90° domains in whole ceramic discs, taking a spatial

orientation distribution function $R(\theta\psi\phi)$ and an average bulk density of 90° domain walls, q , into consideration is necessary. In view of the fact, that the size in radius is much larger than the thickness for the ceramic discs, it is reasonable to consider that spatial orientation of 90° domain wall is symmetrical with respect to the Z axis. And the orientation distribution along self-rotation angle ϕ is put aside for the time being. With these assumptions, the total change in 90° domain volume incited by poling field can be written as follows

$$\Delta V(\theta) = AqP_0E_3(\cos \theta - \sin \theta)R(\theta)\sin \theta\Delta\theta/2kS_0 \quad (16)$$

It can be seen from Equations 15 and 16 that if orientation distribution of 90° walls along angle θ were isotropic, then $\Delta V = 0$ when θ took the value 0. Evidently, this is contradictory to the experimental results, which indicates that (002) plane has a maximal orientation density gain $\Delta\rho_{(002)}$. Consequently, it follows that 90° domain walls lie along angle θ not in an isotropic pattern.

Try to take $R(\theta) = |\cos 2\theta|/(2\sin \theta)$ and substitute it into Equation 16, thus

$$\Delta V(\theta) = AqP_0E_3(\cos \theta - \sin \theta)|\cos 2\theta|\Delta\theta/4kS_0 \quad (17)$$

By comparing Equation 17 with those results reprinted in Fig. 1, we can find that Equation 17 is a rather fitting analytical expression for the curves in Fig. 1. Hence, we reach a conclusion that 90° domains in Sm modified PbTiO_3 ceramics show a strong spatial orientation preference. One of the most possible distribution pattern is given in Fig. 3, in terms of $R(\theta) = |\cos 2\theta|/(2\sin \theta)$. In such case, the most probable orientation is characterized by the normal vectors of 90° walls enclosing 45° with the specimen surface.

3. A scrupulous examination of Fig. 1 will reveal that the poling field dependence of $\Delta\rho_{(hkl)}$ does not exactly follow a linear mode as given in Equation 17. As to this phenomenon, a precise explanation will be made in another paper. We think that it is principally caused by a slight change in 90° wall orientation distribution during poling treatment.

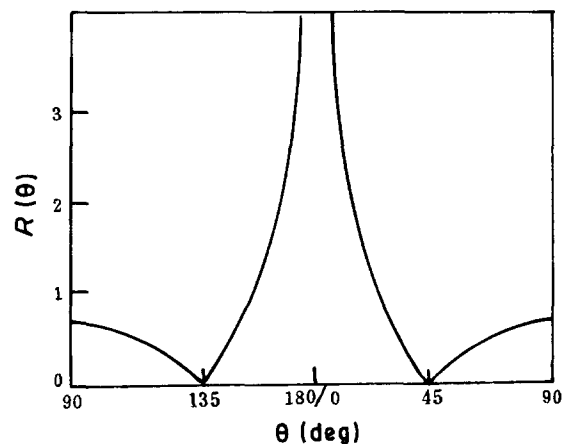


Figure 3 The orientation distribution function $R(\theta)$ of 90° domain walls.

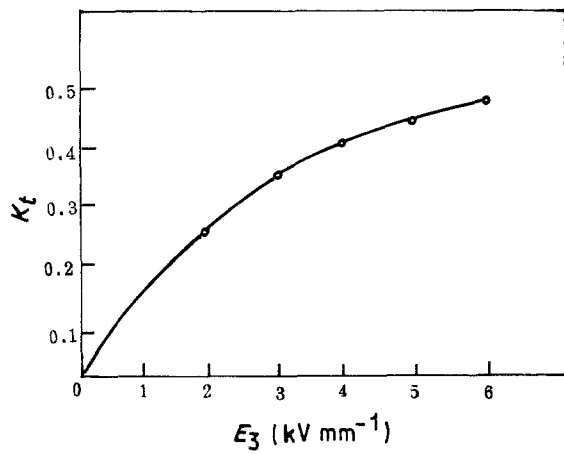


Figure 4 The thickness coupling factor K_t versus poling field.

However, what should be emphasized here is that the orientation distribution of 90° domains as a whole only has a tiny change, not enough to destroy the basic agreement between Equation 17 and Fig. 1. Therefore, we may conclude that displacement of 90° domain walls forced by poling field is a dominant mechanism to yield a non-zero macropolarization. And the strong orientation preference of 90° walls is principally determined by the material itself, as well as its manufacturing conditions but not granted by poling treatment.

3.4. The measurement of electromechanical behaviour

With the purpose of connecting the switching behaviour of 90° domains with electromechanical properties, the thickness electromechanical coupling coefficient K_t of specimens poled at various electric forces has been measured at room temperature and the result data are schematically given in Fig. 4. As can be seen from Fig. 4, with the poling field E_3 increasing, K_t grows rapidly and strongly depends on E_3 . By comparison of K_t - E_3 curve in Fig. 4 with $\Delta\rho_{(002)}$ - E_3 curve in Fig. 1, it can be found that there is a great resemblance between the two curves. K_t and $\Delta\rho_{(002)}$ seem to develop with the poling field E_3 almost at the same pace. In the high field region, moreover, they both show a slight but clear saturation of growth. Doubtlessly, such a resemblance cannot be thought of as a casual concordance. We think, to a large extent, the poling field dependence of K_t is closely associated with that of $\Delta\rho_{(002)}$, and it is the strong orientation preference of 90° domain walls that determines a maximal growing rate at which (002) plane orientation density gain increases with poling field, and there-

fore make K_t develop so large as shown in Fig. 4, with a great contribution to an unusually large ratio of K_t/K_p .

4. Conclusions

1. The crystal plane orientation density $\rho_{(hkl)}$ calculated by the present method can provide a good description of the switching behaviour of 90° domains in Sm modified PbTiO_3 ceramic discs poled at different electric forces.

2. The (hkl) plane orientation density gain $\Delta\rho_{(hkl)}$ is not only determined by poling field, but also influenced by the angle θ between spontaneous polarization axis and the normal vector of (hkl) plane. An equation, derived from 90° wall shift mode, can offer a particular connection between $\Delta\rho_{(hkl)}$, E_3 and θ

$$\Delta\rho_{(hkl)} = KAqP_0E_3(\cos\theta - \sin\theta)|\cos 2\theta|/\Delta\theta/4kS_0$$

3. 90° ferroelectric domains in Sm modified PbTiO_3 ceramic discs show a strong orientation preference, and it is essentially determined by the material itself, as well as its manufacturing conditions but not by the poling process. When the distribution function $R(\theta)$ takes the form $|\cos 2\theta|/(2\sin\theta)$, a basic agreement with experimental results can be reached. This distribution pattern implies that most of the 90° domain walls are so located that their normal vectors make a most probable angle, 45° , with the surface of specimen.

4. A strong orientation preference of 90° domain walls gives a maximal growing rate for (002) plane orientation density $\rho_{(002)}$, and then endows this ceramic material with rather high K_t .

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