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Electromechanical properties of orthorhombic $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $0.43\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – 0.33PbTiO_3 single-domain crystal

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Abstract

Single-domain structure with orthorhombic symmetry has been achieved in morphotropic phase boundary composition $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $0.43\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – 0.33PbTiO_3 ternary single crystal by applying a large field along the pseudo-cubic direction $[011]_c$. Complete set of elastic, piezoelectric, and dielectric constants has been determined with self-consistency. This crystal shows very large thickness shear piezoelectric coefficient $d_{15}=4324$ pC/N and extremely high shear electromechanical coupling factor $k_{15}=96\%$. Three-dimensional orientation dependence of the longitudinal piezoelectric constant d_{33} was calculated and compared with experimental values, which revealed nearly 20% extrinsic contributions in domain engineered $[001]_c$ and $[111]_c$ poled conditions.

Keywords

Ferroelectrics; Piezoelectric materials; PIN-PMN-PT; Orthorhombic

1. Introduction

$[001]_c$ poled relaxor-PT single crystals with both rhombohedral and morphotropic phase boundary (MPB) compositions, show excellent longitudinal piezoelectric and electromechanical coupling properties, such as $d_{33}=2000$ pC/N and $k_{33}=92\%$ for $[001]_c$ poled PMN–0.30 PT (R phase), and $d_{33}=2820$ pC/N and $k_{33}=94\%$ for $[001]_c$ poled PMN–0.33 PT (MPB composition) single crystals [1,2]. While for $[011]_c$ poling, the macroscopic properties of rhombohedral composition with “2 R” domain structure are significantly different from those of MPB compositions with “1 O” domain structure [3–5]. Especially the longitudinal/transverse piezoelectric properties ($d_{33}=340$ pC/N, $d_{32}=260$ pC/N) of $[011]_c$

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poled MPB composition crystals were much lower than that of $[011]_c$ poled rhombohedral crystals ($d_{33}=1300$ pC/N, $d_{32}=-1680$ pC/N) [4].

Recently, the coexistence of M_A and M_C phases in as-grown PMN-0.32 PT single crystals were observed at room temperature by polarized optical microscopy [6]. From X-ray diffraction experiments, Singh et al. reported that the structure is tetragonal (T) phase for PMN- x PT with $x=0.35$, and R phase for PMN- x PT with $x=0.26$. In the MPB regions, monoclinic M_A is stable for $0.27 < x < 0.30$, while monoclinic M_C is stable for $0.31 < x < 0.34$ [7]. The monoclinic phase (M_C) and orthorhombic phase (O) were induced by electric field $E//[001]_c$ and $E//[011]_c$ for PMN-0.35 PT single crystal, respectively [8].

While after being poled along $[011]_c$, the MPB composition crystal approximately shows macroscopic orthorhombic $mm2$ point group symmetry since the monoclinic M_C phase is practically a slightly distorted orthorhombic O phase [5,9]. In this work, we report a complete set of elastic, piezoelectric, and dielectric constants of $[011]_c$ poled $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.43\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (0.24PIN-0.43PMN-0.33 PT) ternary single crystal. The poled 0.24PIN-0.43PMN-0.33 PT crystal shows macroscopically orthorhombic $mm2$ pseudo-single-domain properties. In addition, the three-dimensional orientation dependence of the longitudinal piezoelectric constant d_{33} has been calculated for 0.24PIN-0.43PMN-0.33 PT based on the measured full matrix single domain data, and compared with the measured d_{33} under $[001]_c$ and $[111]_c$ poling conditions.

2. Experimental

The 0.24PIN-0.43PMN-0.33 PT single crystals used in this work were grown by the modified Bridgman method [10,11]. The as-grown crystal was oriented by the Laue machine with an accuracy of $\pm 0.5^\circ$. Specimens used in the full matrix measurements were cut and

polished into parallelepiped with three pairs of parallel surfaces along $\begin{bmatrix} 0 & \bar{1} & 1 \end{bmatrix}_c$, $[100]_c$, and $[011]_c$. Moreover, the $[001]_c$, $[111]_c$, and $[011]_c$ oriented plates were prepared for the piezoelectric property measurements. The samples were sputtered with gold electrodes on the $[001]_c$, $[111]_c$, or $[011]_c$ pair surfaces, respectively, and poled at 15 kV/cm in silicone oil at room temperature. The piezoelectric constant d_{33} of $[001]_c$, $[111]_c$, and $[011]_c$ oriented plates were measured by using a ZJ-2 piezo d_{33} meter. The combined resonance and ultrasonic methods were used to get the complete set of constants with self-consistency.

3. Results and discussions

The measured and derived elastic, piezoelectric and dielectric constants of the 0.24PIN-0.43PMN-0.33 PT single crystal poled along $[011]_c$ direction have been determined and given in Table 1. Material constants marked with a star (*) were determined directly by resonance or ultrasonic measurements while others were derived values. It was found that the longitudinal/transverse piezoelectric constants $d_{33}=229$ pC/N, $d_{32}=291$ pC/N, and $d_{31}=110$ pC/N with “1 O” structure are much smaller compared to that of $[011]_c$ poled rhombohedral crystals with “2 R” structure, which possess large longitudinal/transverse properties with $d_{33}=1068$ pC/N, $d_{32}=1693$ and $d_{31}=675$ pC/N for $[011]_c$ poled

0.24PIN-0.46PMN-0.30 PT [12]. In addition, both shear piezoelectric constants d_{15} and d_{24} are very large with $d_{15}=4324$ pC/N and $d_{24}=1063$ pC/N for $[011]_c$ poled 0.24PIN-0.43PMN-0.33 PT single crystal, which is significantly different from $[011]_c$ poled 0.24PIN-0.46PMN-0.30 PT with large shear $d_{15}=3122$ pC/N but low $d_{24}=142$ pC/N [12]. This is because the polarization rotation is easier in the “1 O” domain structure under

electric field parallel to $\begin{bmatrix} 0 & \bar{1} & 1 \end{bmatrix}_c$ or $[100]_c$, since there is only one polarization orientation remains. Hence, both the shear piezoelectric constants d_{15} and d_{24} are large for the “1 O” single domain structure [4].

The three-dimensional orientation of d_{33} by the coordinate transformation using the “1 O” full matrix data is shown in Fig. 1, which revealed large spatial anisotropy. The theoretical

value of $d_{33}^{[001]}$ was calculated in the $\begin{bmatrix} 0 & \bar{1} & 1 \end{bmatrix}_c - [001]_c$ plane to be 1649 pC/N by Eq. (1), which accounts for 81% of the measured $d_{33}=2038$ pC/N for $[001]_c$ poled 0.24PIN-0.43PMN-0.33 PT multi-domain crystal. It shows that the orientation effect plays an important role in the material properties of domain engineered relaxor-PT ferroelectric crystals but the extrinsic contribution for this system is also significant. We can also conclude that the origin of this large piezoelectric coefficient $d_{33}^{[001]}$ is mainly from the large shear property d_{15} of the single-domain crystal.

$$d_{33}^{[001]} = \frac{1}{2\sqrt{2}} (d_{15}^O + d_{31}^O + d_{33}^O) \quad (1)$$

Similarly, the theoretical value of $d_{33}^{[111]}$ was calculated in the $[100]_c - [011]_c$ plane to be 334 pC/N by using Eq. (2), which contributed 83% of the measured $d_{33}=400$ pC/N for $[111]_c$ poled 0.24PIN-0.43PMN-0.33 PT domain engineered crystal. It is important to note that this is consistent with the fact that higher piezoelectric strain is obtained under an electric field along $[001]_c$ than a field along $[111]_c$ [11]. Based on Eq. (2), the origin of piezoelectric properties $d_{33}^{[111]}$ is mainly from the shear piezoelectric constant d_{24} , since the d_{24} is much higher than d_{32} and d_{33} in the orthorhombic single-domain crystal.

$$d_{33}^{[111]} = \frac{\sqrt{2}}{3\sqrt{3}} (d_{24}^O + d_{32}^O) + \frac{2\sqrt{2}}{3\sqrt{3}} d_{33}^O \quad (2)$$

On the other hand, for domain engineered 0.24PIN-0.43PMN-0.33 PT single crystal, the extrinsic (domain structure) contribution is about ~20%, much higher than that in domain engineered rhombohedral crystal with only ~5% extrinsic contribution [13]. In the case of relaxor-PT single crystal, ferroelectric domain structures miniaturize down to nanometer scales when the composition approaches the MPB, which implies that domain structures play a greater role near the MPB since high density of domain walls are present in the crystals [14].

4. Summary and conclusions

A complete set of elastic, piezoelectric, and dielectric constants of $[011]_c$ poled $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $0.43\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – 0.33PbTiO_3 ternary single crystal with orthorhombic symmetry has been measured. The $[011]_c$ poled single crystal shows macroscopic orthorhombic single-domain properties with ultra-large thickness shear mode piezoelectric coefficient $d_{15}=4324$ pC/N and very high shear electromechanical coupling factor $k_{15}=96\%$. Both polarization rotation effect and domain wall motions play important roles in the enhanced macroscopic properties for the domain engineered $[001]_c$ poled 0.24PIN – 0.43PMN – 0.33 PT single crystals.

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Fig. 1. Calculated three-dimensional orientation dependence of d_{33} by the co-ordinate transformation using the “1O” full matrix data of 0.24PIN-0.43PMN-0.33 PT single crystal.

Table 1

Measured and derived material constants of $[011]_c$ poled 0.24P1N-0.43PMN-0.33 PT single crystal. [Directly measured constants are marked by a star (*)].

Elastic stiffness constants: C_{ij}^E and C_{ij}^D (10^{10} N/m ²)											
C_{11}^E	C_{12}^E	C_{13}^E	C_{22}^E	C_{23}^E	C_{33}^E	C_{44}^E	C_{55}^E	C_{66}^E			
20.35	10.93	6.67	13.25	9.13	15.31	4.92	0.32	7.42			
C_{11}^D	C_{12}^D	C_{13}^D	C_{22}^D	C_{23}^D	C_{33}^D	C_{44}^D	C_{55}^D	C_{66}^D			
21.00	10.30	8.44	13.87	7.41	20.11	7.62	4.33	7.42			
Elastic compliance constants: S_{ij}^E and S_{ij}^D (10^{-12} m ² /N)											
S_{11}^E	S_{12}^E	S_{13}^E	S_{22}^E	S_{23}^E	S_{33}^E	S_{44}^E	S_{55}^E	S_{66}^E			
8.89	-7.92	0.85	19.86	-8.40	11.17	20.33	312.50	13.48			
S_{11}^D	S_{12}^D	S_{13}^D	S_{22}^D	S_{23}^D	S_{33}^D	S_{44}^D	S_{55}^D	S_{66}^D			
7.80	-5.03	-1.42	12.23	-2.39	6.45	13.13	23.10	13.48			
Piezoelectric coefficients: e_{ij} (C/m ²), d_{ik} (10 ⁻¹² C/N), g_{ik} (10 ³ Vm/N), and h_{ik} (10 ⁸ V/m)											
e_{15}	e_{24}	e_{31}	e_{32}	e_{33}	d_{15}	d_{24}	d_{31}^*	d_{32}^*	d_{33}^*		
13.84	52.30	5.82	-5.67	15.80	4324	1063	110	-291	229		
g_{15}	g_{24}	g_{31}	g_{32}	g_{33}	h_{15}	h_{24}	h_{31}	h_{32}	h_{33}		
66.93	6.78	9.90	-26.21	20.60	28.98	5.16	11.18	-10.89	30.36		
Dielectric constants: $\epsilon_{ij}(\epsilon_0)$ and $\beta(10^4/\epsilon_0)$											
ϵ_{11}^S	ϵ_{22}^S	ϵ_{33}^S	ϵ_{11}^T	ϵ_{22}^T	ϵ_{33}^T	β_{11}^S	β_{22}^S	β_{33}^S	β_{11}^T	β_{22}^T	β_{33}^T
540	11,450	588	7300	17,730	1256	18.54	0.87	17.00	1.37	0.56	7.96
Electromechanical coupling factors k_{ij} and density											
k_{15}	k_{24}	k_{31}^*	k_{32}^*	k_{33}^*	k_t^*	Density (kg/m ³)					
0.96	0.60	0.35	0.62	0.65	0.49	8198					