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Composition dependence of piezoelectric constant and dielectric constant tunability in the ⟨001⟩-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ single crystals

Xiangyong Zhao[a,b,*], Jie Wang[b], Khian-Hooi Chew[b], Helen Lai-Wa Chan[b], Chung-Loong Choy[b], Zhiwen Yin[a], Haosu Luo[a]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 215 Chengbei Rd. Jiading, Shanghai 201800, China
[b] Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China

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Abstract

Composition dependence of room temperature piezoelectric constant d_{33} and dielectric constant tunability was investigated in the ⟨001⟩-poled single crystals of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ with x varying from 0.24 to 0.38. Temperature, frequency and composition dependence of the dielectric constant in the unpoled crystals shows that the critical composition for the relaxor state lies in the $0.69Pb(Mg_{1/3}Nb_{2/3})O_3-0.31PbTiO_3$ crystal. It has also the largest piezoelectric constant d_{33} of 2210 pC/N and highest dielectric constant tunability of 40.6% (at a dc bias of 1000 V/mm). The experiment results validate the prediction that the relaxor-based materials with the critical composition for the relaxor state will have the highest piezoelectric susceptibility.

Keywords: Ferroelectrics; Piezoelectric materials; PMN–PT; Critical composition; Relaxor; Piezoelectric constant; Dielectric constant tunability

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1. Introduction

Relaxor-based single crystals of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$, abbreviated as $(1-x)$PMN–xPT, and $(1-y)Pb(Zn_{1/3}Nb_{2/3})O_3-yPbTiO_3$ have been widely investigated due to their excellent piezoelectric and electro-optical (E-O) properties [1–3]. Moreover, the PMN–PT single crystals have been successfully grown in batches using a modified Bridgman technique [4–6]. The high piezoelectric susceptibility on the ⟨001⟩ direction and near the morphotropic phase boundary (MPB) between rhombohedral (FE_r) and tetragonal (FE_t) ferroelectric phases is related to electric field-induced engineered domain configurations [7,8] and polarization rotations through metastable monoclinic (FE_m) or orthorhombic (FE_o) ferroelectric phases [1,9,10]. Moreover, the local random fields in a relaxor have also been emphasized contributive to enhance piezoelectric susceptibility [11,12]. Pure PMN is a typical relaxor [13,14]. The degree of relaxor characteristics decreases with increasing x in the relaxor-based $(1-x)$PMN–xPT crystals [15]. Thus, a critical composition for the relaxor state arises. It has even been predicted that the best piezoelectric property would be found in the relaxor-based materials with the critical composition for the relaxor state due to the easiest rotation of the dipoles in the case [12].

In this paper, we will investigate the composition dependence of the piezoelectric constant and dielectric constant tunability in the ⟨001⟩-poled PMN–PT single crystals to evaluate the influence of a relaxor state on the properties.

2. Experiment

The $(1-x)$PMN–xPT single crystals used in this work were grown using a modified Bridgman technique with nominal composition x as 0.24, 0.30, 0.31, 0.33 and 0.38, respectively [4]. Various crystals oriented along the ⟨001⟩ direction were prepared with size of $5\times5\times1$ mm^3 and

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* Corresponding author. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 215 Chengbei Rd. Jiading, Shanghai 201800, China. Tel.: +86-21-39986059; fax: +86-21-59927184.

E-mail address: zhaoxiangyong@hotmail.com (X. Zhao).

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electroded with silver. The dielectric properties of the as-prepared unpoled crystals were measured using a HP4194A impedance analyzer at frequencies of 100 Hz, 1 and 10 kHz in the temperature range between 25 and 200 °C at a constant heating rate of 1 °C/min. Then, the crystals were poled for 15 min using a poling field of 1 kV/mm in silicone oil at room temperature. Piezoelectric constants d_{33} of the freshly poled crystals were measured by a Berlincourt-type quasistatic d_{33} meter at a frequency of 55 Hz at room temperature.

The dielectric response under a dc bias was measured by a multi-frequency LCR Meter (Model SR720 of Stanford Research Systems) at a frequency of 10 kHz while the crystal is placed in silicone oil. The applied dc bias varies from 0 to 1000 V/mm. The dc bias was applied on the samples in the same direction as the poling field to prevent occurrence of polarization reversal. After each time the dc bias was applied, a waiting time of 100 s was imposed before measuring the dielectric constant.

3. Results, discussions and conclusions

Fig. 1 shows the temperature, frequency and composition dependence of the dielectric constant of the ⟨001⟩-oriented unpoled $(1-x)$PMN–xPT single crystals. The temperature corresponding to the maximum of the dielectric constant is called the temperature T_m. In the 0.76PMN–0.24PT and 0.7PMN–0.3PT crystals, only one dielectric peak occurs at the temperature T_m of 110 and 128 °C, respectively, indicating a phase transition from the FE_r phase to paraelectric cubic phase near the T_m [6,14]. In the 0.62PMN–0.38PT crystal, there is also one dielectric peak at the T_m of 172 °C, indicating a phase transition from the FE_t phase to paraelectric cubic phase [2]. In both the 0.69PMN–0.31PT and 0.67PMN–0.33PT crystals, the dielectric curves show a peak with a shoulder joined on the left side near the lower temperatures T_{rt} indicated by dash arrow and point arrow, respectively, in Fig. 1. The T_{rt} shoulder indicates a FE_r–FE_t phase transition [4,5]. In the 0.69PMN–0.31PT and 0.67PMN–0.33PT crystals, the FE_r–FE_t phase transition takes place near the T_{rt} of 115 and of 75 °C, respectively. Corresponding FE_t-cubic phase transition occurs near the T_m of 135 and 158 °C, respectively. It can be seen that our dielectric results support the report that the PMN–PT system has a MPB composition x as $0.3<x<0.35$ [16].

Table 1
Summary of the composition dependence of the phase transition temperatures in the unpoled ⟨001⟩-oriented $(1-x)$PMN–xPT crystals, and of the room temperature piezoelectric constant d_{33} and dielectric constant tunability at a dc bias of 1000 V/mm in the ⟨001⟩-poled $(1-x)$PMN–xPT crystals

Composition	T_m (°C)	T_{rt} (°C)	d_{33} (pC/N)	Tunability of ε_r (%)
0.76PMN–0.24PT	110		770	25.9
0.7PMN–0.3PT	128		1760	32.9
0.69PMN–0.31PT	135	115	2210	40.6
0.67PMN–0.33PT	158	75	1870	34.2
0.62PMN–0.38PT	172		400	20.7

From Fig. 1, we can also observe the phenomenon of very evident frequency dispersion of dielectric constant in the ferroelectric phases in the $(1-x)$PMN–xPT crystals with $x\leq0.31$, indicating a dominant relaxor state. However, in the 0.67PMN–0.33PT and 0.62PMN–0.38P crystals, the frequency dispersion behavior is not obvious and could be only observed near the T_m. This shows that the composition x of 0.31 is a critical composition for the microdomain relaxor state. The crystals with a larger PT content ($x>0.31$) have a dominant macrodomain normal ferroelectric state. Our mea-

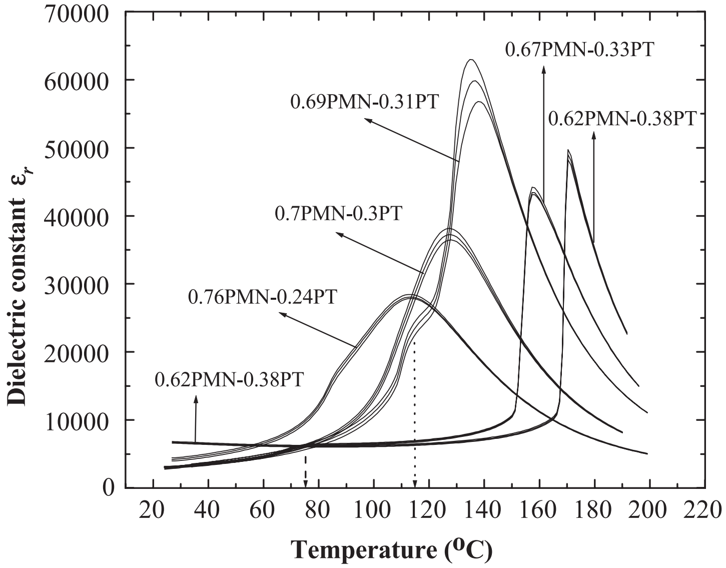

Fig. 1. Temperature and composition dependence of the dielectric constant ε_r in the unpoled ⟨001⟩-oriented $(1-x)$PMN–xPT crystals measured at frequencies of 100 Hz, 1 and 10 kHz.

surement results of the piezoelectric constants d_{33} of the poled crystals were summarized in Table 1. For the crystals with x as 0.3, 0.31 and 0.33, the metastable phases and polarization rotation have been emphasized on their capability to enhance the piezoelectric properties [1,9,10,17,18]. Correspondingly, these crystals all have large piezoelectric constant of larger than 1500 pC/N as shown in Table 1. Also, the FE_r 0.76PMN−0.24PT and FE_t 0.62PMN−0.38PT crystal have much lower piezoelectric constant. However, the most important point to note now is that the largest piezoelectric constant d_{33} of 2210 pC/N is found in the crystal with the critical composition x of 0.31 for the relaxor state, although the 0.67PMN−0.33PT crystal has a lower FE_r−FE_t phase transition temperature.

Fig. 2(a and b) shows the dc bias and composition dependence of the dielectric constant ε_r and tunability of ε_r, respectively, measured under various dc bias at room temperature. The tunability of ε_r at the dc bias of E_b is defined as $[\varepsilon_r(0)-\varepsilon_r(E_b)]\times 100\%/\varepsilon_r(0)$, where $\varepsilon_r(0)$ and $\varepsilon_r(E_b)$ are the dielectric constant ε_r at zero dc bias and at a bias of E_b, respectively. The data of $\varepsilon_r(0)$ and tunability of ε_r at the bias of 1000 V/mm in the $\langle 001\rangle$-poled crystals were also listed in Table 1. The results also reveal the largest tunability of ε_r, with a large value of 40.6% at the dc bias of only 1000 V/mm, in the 0.69PMN−0.31PT crystal with a critical composition for the relaxor state.

We have demonstrated the composition dependence of both piezoelectric constant and dielectric constant tunability in the $\langle 001\rangle$-poled PMN−PT crystals, both of which reveal the largest susceptibility in the 0.69PMN−0.31PT crystal with a critical composition for the relaxor state. The largest dielectric tunability reflects the most significant structure adaptivity of the engineered domain configuration, in which the applied electric field easily induces large lattice distortion with nullifying strain in the polar domains equivalent and symmetrically distributed along $\langle 001\rangle$ [7]. However, it should not be excluded that applied electric field should also induce polarization rotation from $\langle 111\rangle$ to $\langle 001\rangle$ in an advantageous path through metastable phases in the 0.69PMN−0.31PT crystal with also a MPB composition, which also produces high structure adaptivity [1]. In both cases, we believe the critical relaxor state plays an important role, as shown by the largest susceptibility of the 0.69PMN−0.31PT crystal. The local random fields in the relaxor state induce a random or spherical bond state and accordingly anisotropy is only metastably locked in under applied electric field [11]. Thus, the relaxor state contributes greatly to the sensitive engineered domain configuration and polarization rotation through metastable phases under electric field, and resultantly contribute greatly to the structure adaptivity, piezoelectric susceptibility and dielectric constant tunability. Egmai et al. [12] have also already predicted that the relaxor-based system will have the best piezoelectric susceptibility when possessing a critical composition for the relaxor state. Our results in this paper experimentally validate their prediction by revealing the largest piezoelectric constant d_{33} of 2210 pC/N and highest dielectric constant tunability of 40.6% in the 0.69PMN−0.31PT crystal with a critical composition for the relaxor state and also a MPB composition.

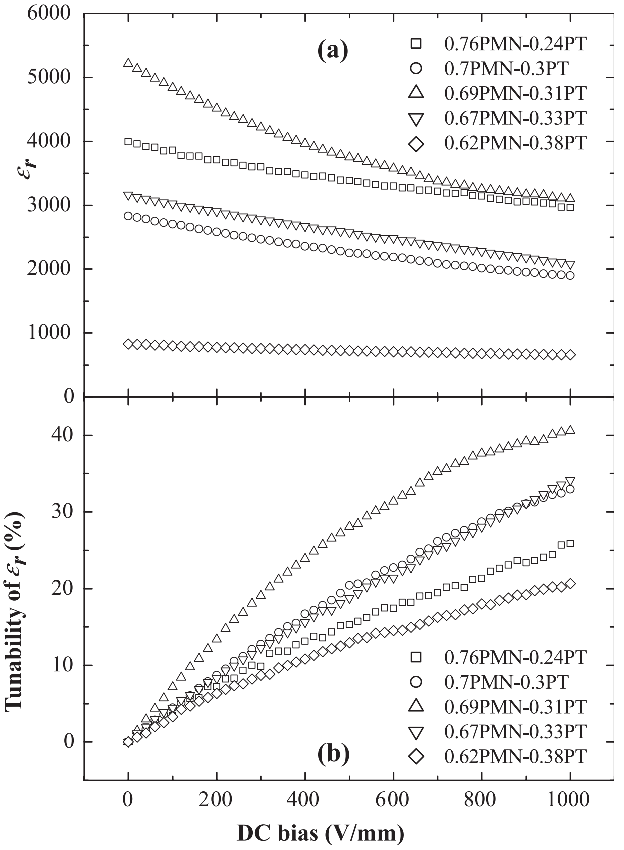

Fig. 2. DC bias and composition dependence of (a) the dielectric constant ε_r and (b) the tunability of ε_r in the $\langle 001\rangle$-poled $(1-x)$PMN−xPT crystals measured at a frequency of 10 kHz.

Acknowledgements

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References

[1] H. Fu, R.E. Cohen, Nature 403 (2000) 281.
[2] X. Wan, H. Xu, T. He, D. Lin, H. Luo, J. Appl. Phys. 93 (2003) 4766.
[3] Y. Barad, Y. Lu, Z.-Y. Cheng, S.-E. Park, Q.M. Zhang, Appl. Phys. Lett. 77 (2000) 1247.
[4] H. Luo, G. Xu, H. Xu, P. Wang, Z. Yin, Jpn. J. Appl. Phys. 39 (2000) 5581.
[5] G. Xu, H. Luo, P. Wang, H. Xu, Z. Yin, Chin. Sci. Bull. 45 (2000) 491.
[6] G. Xu, H. Luo, P. Wang, Z. Qi, Z. Yin, Chin. Sci. Bull. 45 (2000) 1380.

[7] S.-E. Park, T.R. Shrout, J. Appl. Phys. 82 (1997) 1804.
[8] S.-E. Park, T.R. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 44 (1997) 1140.
[9] D. Viehland, J. Appl. Phys 88 (2000) 4794.
[10] Y. Lu, D.-Y. Jeong, Q.M. Zhang, H. Luo, Z. Yin, D. Viehland, Appl. Phys. Lett. 78 (2001) 3109.
[11] D. Viehland, J. Powers, L.E. Cross, J.F. Li, Appl. Phys. Lett. 78 (2001) 3508.
[12] T. Egmai, S. Teslic, W. Dmowski, P.K. Davis, I.-W. Chen, J. Korean Phys. Soc. 32 (1998) S935.
[13] Z.-G. Ye, Key Eng. Mater. 155–156 (1998) 81.
[14] L.E. Cross, Ferroelectrics 76 (1987) 241.
[15] E.V. Colla, N.K. Yushin, D. Viehland, J. Appl. Phys. 83 (1998) 3298.
[16] A.K. Singh, D. Pandey, J. Phys., Condens. Matter 13 (2001) L931.
[17] K.-P. Chen, X.-W. Zhang, H. Luo, J. Phys., Condens. Matter 14 (2002) L571.
[18] B. Noheda, D.E. Cox, G. Shirane, J. Gao, Z.-G. Ye, Phys. Rev. B 66 (2002) 054104.