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补充材料

(111)取向无铅 $K_{0.5}Na_{0.5}NbO_3$ 外延薄膜的相变和电卡效应：外应力与错配应变效应

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为了探索(111)取向 $K_{0.5}Na_{0.5}NbO_3$ 铁电薄膜中的相变和电卡效应，首先建立了基于八阶朗道自由能的(111)取向铁电薄膜非线性热力学理论。钙钛矿块状铁电晶体的标准弹性吉布斯能量函数 G 由下式给出：

$$\begin{aligned}G=&\alpha_1\left(p_1^2+p_2^2+p_3^2\right)+\alpha_{11}\left(p_1^4+p_2^4+p_3^4\right)+\alpha_{12}\left(p_1^2p_2^2+p_1^2p_3^2+p_2^2p_3^2\right)+\alpha_{111}\left(p_1^6+p_2^6+p_3^6\right)\\&+\alpha_{112}\left[p_1^4\left(p_2^2+p_3^2\right)+p_2^4\left(p_1^2+p_3^2\right)+p_3^4\left(p_2^2+p_1^2\right)\right]+\alpha_{123}p_1^2p_2^2p_3^2+\alpha_{1111}\left(p_1^8+p_2^8+p_3^8\right)\\&+\alpha_{1112}\left[p_1^6\left(p_2^2+p_3^2\right)+p_2^6\left(p_1^2+p_3^2\right)+p_3^6\left(p_2^2+p_1^2\right)\right]+\alpha_{1122}\left(p_1^4p_2^4+p_1^4p_3^4+p_2^4p_3^4\right)+\\&\alpha_{1123}\left(p_1^4p_2^2p_3^2+p_1^2p_2^4p_3^2+p_1^2p_2^2p_3^4\right)-\frac{1}{2}s_{11}\left(\tilde{\sigma}_1^2+\tilde{\sigma}_2^2+\tilde{\sigma}_3^2\right)-s_{12}\left(\tilde{\sigma}_1\tilde{\sigma}_2+\tilde{\sigma}_1\tilde{\sigma}_3+\tilde{\sigma}_2\tilde{\sigma}_3\right)\\&-\frac{1}{2}s_{44}\left(\tilde{\sigma}_4^2+\tilde{\sigma}_5^2+\tilde{\sigma}_6^2\right)-Q_{11}\left(\tilde{\sigma}_1p_1^2+\tilde{\sigma}_2p_2^2+\tilde{\sigma}_3p_3^2\right)-Q_{44}\left(\tilde{\sigma}_4p_2p_3+\tilde{\sigma}_5p_1p_3+\tilde{\sigma}_6p_1p_2\right)\\&-Q_{12}\left[\tilde{\sigma}_1\left(p_2^2+p_3^2\right)+\tilde{\sigma}_2\left(p_1^2+p_3^2\right)+\tilde{\sigma}_3\left(p_2^2+p_1^2\right)\right],\end{aligned}\tag{S1}$$

其中 p_i 和 $\tilde{\sigma}_i$ 晶体参考系 x (x_1 , x_2 , x_3) （x_1 , x_2 , x_3 分别对应于立方晶胞的 [100] , [010]和[001]晶轴 ）中的极化矢量和应力张量的分量。 在（S1）式中，α_i, α_{ij}, α_{ijk} 和 α_{ijkl} 是介电刚度系数；s_{ij} 代表弹性柔量；Q_{ij} 是电致伸缩系数。这些材料参数列于表 S1。

为了得到(111)取向铁电外延薄膜的热力学势，必须知道不同参考系下极化矢量与应力张量的关系。可以使用矩阵 $\boldsymbol{t}_{ij}$ 来描述晶体参考系 x (x_1 , x_2 , x_3)和全局坐标系 X (X_1, X_2, X_3) 其中 X_1, X_2, X_3 分别对应伪立方晶胞的$[1\bar{1}0]$, $[11\bar{2}]$和[111]晶向：

$$\boldsymbol{t}_{ij}=\begin{bmatrix}\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0\\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{2}{\sqrt{6}}\\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}\end{bmatrix}.\tag{S2}$$

通过矩阵变换得到 $\boldsymbol{p}=(\boldsymbol{t}_{ij})^{-1}\boldsymbol{P}$ 和$\tilde{\boldsymbol{\sigma}}=(\boldsymbol{t}_{ij})^{-1}\cdot\boldsymbol{\sigma}\,\boldsymbol{t}_{ij}$, 其中 $\boldsymbol{p}$ 和 $\boldsymbol{P}$ 分别是晶体参考系 x 和薄膜参考系 X 中的极化矢量, $\tilde{\boldsymbol{\sigma}}$ 和 $\boldsymbol{\sigma}$ 分别是参考系 x 和 X 中的应力

张量矩阵。

对于(111)取向外延薄膜，面内失配应变为 u_1, u_2 和 u_6（全局坐标下），薄膜的热力学势 G_f 可以通过勒让德变换得到：

$$G_f = G + u_1\sigma_1 + u_2\sigma_2 + u_6\sigma_6. \tag{S3}$$

当面内双轴应变为等方双轴应变且切应变为零时，薄膜在垂直于薄膜方向受到一个外应力，那么薄膜受到混合机械边界条件为

$$u_1 = u_2 = u_m,\quad u_6 = 0,\quad \sigma_3 \neq 0,\quad \sigma_4 = \sigma_5 = 0,\quad u_i = -\partial G/\partial\sigma_i, \tag{S4}$$

根据(S4)式求出应力表达式，然后代入(S3)式中，得到(111)取向薄膜的自由能 G_f 的表达式为

$$\begin{aligned} G_f &= a_1^*(P_1^2+P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^2+P_2^2)^2 + a_{33}^*P_3^4 + a_{13}^*P_3^2(P_1^2+P_2^2) \\ &\quad + a_{2223}P_2P_3(P_2^2-3P_1^2) + G^{(6)} + G^{(8)} + \frac{3(4u_m+s_{44}\sigma_3)^2}{8(4s_{11}+8s_{12}+s_{44})} - \frac{8u_m+3s_{44}\sigma_3}{8}\sigma_3, \end{aligned} \tag{S5}$$

$$a_1^* = a_1 - \frac{4Q_{11}+8Q_{12}+Q_{44}}{4s_{11}+8s_{12}+s_{44}}u_m - \frac{s_{44}(Q_{11}+2Q_{12})-Q_{44}(s_{11}+2s_{12})}{4s_{11}+8s_{12}+s_{44}}\sigma_3, \tag{S6}$$

$$a_3^* = a_1 - \frac{4Q_{11}+8Q_{12}-2Q_{44}}{4s_{11}+8s_{12}+s_{44}}u_m - \frac{s_{44}(Q_{11}+2Q_{12})+2Q_{44}(s_{11}+2s_{12})}{4s_{11}+8s_{12}+s_{44}}\sigma_3, \tag{S7}$$

$$a_{11}^* = \frac{1}{4}(2a_{11}+a_{12}) + \frac{1}{24}\left[\frac{(4Q_{11}+8Q_{12}+Q_{44})^2}{4s_{11}+8s_{12}+s_{44}} + \frac{2(Q_{11}-Q_{12}+Q_{44})^2}{s_{11}-s_{12}+s_{44}}\right], \tag{S8}$$

$$a_{33}^* = \frac{1}{3}(a_{11}+a_{12}) + \frac{(2Q_{11}+4Q_{12}-Q_{44})^2}{6(4s_{11}+8s_{12}+s_{44})}, \tag{S9}$$

$$a_{13}^* = 2a_{11} + \frac{1}{6}\left[\frac{(2Q_{11}+4Q_{12}-Q_{44})(4Q_{11}+8Q_{12}+Q_{44})}{4s_{11}+8s_{12}+s_{44}} + \frac{(2Q_{11}-2Q_{12}-Q_{44})^2}{s_{11}-s_{12}+s_{44}}\right], \tag{S10}$$

$$a_{2223} = \frac{\sqrt{2}}{3}(a_{12}-2a_{11}) + \frac{(Q_{11}-Q_{12}+Q_{44})(-2Q_{11}+2Q_{12}+Q_{44})}{3\sqrt{2}(s_{11}-s_{12}+s_{44})}, \tag{S11}$$

$$\begin{aligned} G^{(6)} &= a_{111}\left[(-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^6 + (\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^6 + (\frac{\sqrt{3}}{3}P_3-\frac{\sqrt{6}}{3}P_2)^6\right] \\ &\quad + a_{112}\Big\{[(-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^4 + (\frac{\sqrt{3}}{3}P_3-\frac{\sqrt{6}}{3}P_2)^4](\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^2 \\ &\quad + [(\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^4 + (\frac{\sqrt{3}}{3}P_3-\frac{\sqrt{6}}{3}P_2)^4](-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^2 \\ &\quad + (\frac{\sqrt{3}}{3}P_3-\frac{\sqrt{6}}{3}P_2)^2[(-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^4 + (\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^4]\Big\} \\ &\quad + \frac{a_{123}}{108}(P_3-\sqrt{2}P_2)^2(-3P_1^2+P_2^2+2\sqrt{2}P_2P_3+2P_3^2)^2, \end{aligned} \tag{S12}$$

$$
\begin{aligned}
G^{(8)} &= a_{1111}[\ (\frac{\sqrt{3}}{3}P_3-\frac{\sqrt{6}}{3}P_2)^8+(\frac{\sqrt{3}}{3}P_3-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2)^8+(\frac{\sqrt{3}}{3}P_3+\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2)^8\ ] \\
&+\frac{a_{1122}}{1679616}\{\ (-3\sqrt{2}P_1+\sqrt{6}P_2+2\sqrt{3}P_3)^4(3\sqrt{2}P_1+\sqrt{6}P_2+2\sqrt{3}P_3)^4 \\
&+144(P_3-\sqrt{2}P_2)^4[(-3\sqrt{2}P_1+\sqrt{6}P_2+2\sqrt{3}P_3)^4+(3\sqrt{2}P_1+\sqrt{6}P_2+2\sqrt{3}P_3)^4]\ \} \\
&+a_{1112}\{\ \frac{1}{81}(P_3-\sqrt{2}P_2)^6(3P_1^2+P_2^2+2P_3^2+2\sqrt{2}P_2P_3) \\
&+[\frac{1}{3}(P_3-\sqrt{2}P_2)^2+(-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^2](\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^6 \\
&+[\frac{1}{3}(P_3-\sqrt{2}P_2)^2+(\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^2](-\frac{\sqrt{2}}{2}P_1+\frac{\sqrt{6}}{6}P_2+\frac{\sqrt{3}}{3}P_3)^6\ \} \\
&+\frac{a_{1123}}{3888}(P_1^2+P_2^2+P_3^2)(P_3-\sqrt{2}P_2)^2(-3\sqrt{2}P_1+\sqrt{6}P_2+2\sqrt{3}P_3)^2(3\sqrt{2}P_1+\sqrt{6}P_2+2\sqrt{3}P_3)^2.
\end{aligned}
\tag{S13}
$$

极化平衡态可通过自由能 G_f 对极化 P_i 求极小值获得。介电常数可由方程 $\varepsilon_0\varepsilon_{ij} = \varepsilon_0 + \eta_{ij}$ (ε_0 为真空介电常数，η_{ij} 为介电极化率)获得。首先导出了介电极化率的倒数即介电刚度 $\eta_{ij}^{-1} = \partial^2 G_f /\partial P_i\, \partial P_j$ 的表达式，然后应用矩阵求逆得到介电常数，再根据 $d_{ij} = b_{kj}\eta_{ki}$ 计算压电系数 d_{ij}，其中 $b_{kj} = \partial u_j /\partial P_k$。

表 S1 $K_{0.5}Na_{0.5}NbO_3$ 的材料参数

Table S1. Parameters for $K_{0.5}Na_{0.5}NbO_3$, where T is the temperature in K.

Parameters	Values	Units	References
α_1	$4.29\times10^7\times$[Coth(140/T)－Coth(140/657)]	$C^{-2}\ m^2\ N$	[S1]
α_{11}	-2.7302×10^8	$C^{-4}\ m^6\ N$	[S1]
α_{12}	1.0861×10^9	$C^{-4}\ m^6\ N$	[S1]
α_{111}	3.0448×10^9	$C^{-6}\ m^{10}\ N$	[S1]
α_{112}	-2.7270×10^9	$C^{-6}\ m^{10}\ N$	[S1]
α_{123}	1.5513×10^{10}	$C^{-6}\ m^{10}\ N$	[S1]
α_{1111}	2.4044×10^{10}	$C^{-8}\ m^{14}\ N$	[S1]
α_{1112}	3.7328×10^9	$C^{-8}\ m^{14}\ N$	[S1]
α_{1122}	3.3485×10^{10}	$C^{-8}\ m^{14}\ N$	[S1]
α_{1123}	-6.2017×10^{10}	$C^{-8}\ m^{14}\ N$	[S1]
Q_{11}	0.16	$C^{-2}\ m^4$	[S1]
Q_{12}	-0.072	$C^{-2}\ m^4$	[S1]
Q_{44}	0.084	$C^{-2}\ m^4$	[S1]
s_{11}	5.57×10^{-12}	m^2/N	[S1]
s_{12}	-1.57×10^{-12}	m^2/N	[S1]
s_{44}	13.1×10^{-12}	m^2/N	[S1]
ρ	4514	kg/m^3	[S2]
c_ρ	200	J/(kg K)	[S2]

表 S2 (111)取向 $K_{0.5}Na_{0.5}NbO_3$ 薄膜中可能出现的相结构

Table S2. Equilibrium phase structures appearing in (111) oriented $K_{0.5}Na_{0.5}NbO_3$ ferroelectric thin film.

相	全局坐标系(X)	晶体坐标系(x)
顺电相 PE	$P_1=P_2=P_3=0$	$p_1= p_2= p_3=0$
三方相 R	$P_1=P_2=0,\ P_3\neq0$	$p_1= p_2= p_3\neq0$
单斜相 M	$P_1=0,\ P_2\neq0,\ P_3\neq0$	$p_1= p_2\neq0,\ p_3\neq0$
正交相 O	$P_1\neq0,\ P_2=P_3=0$	$p_1=p_2\neq0,\ p_3=0$

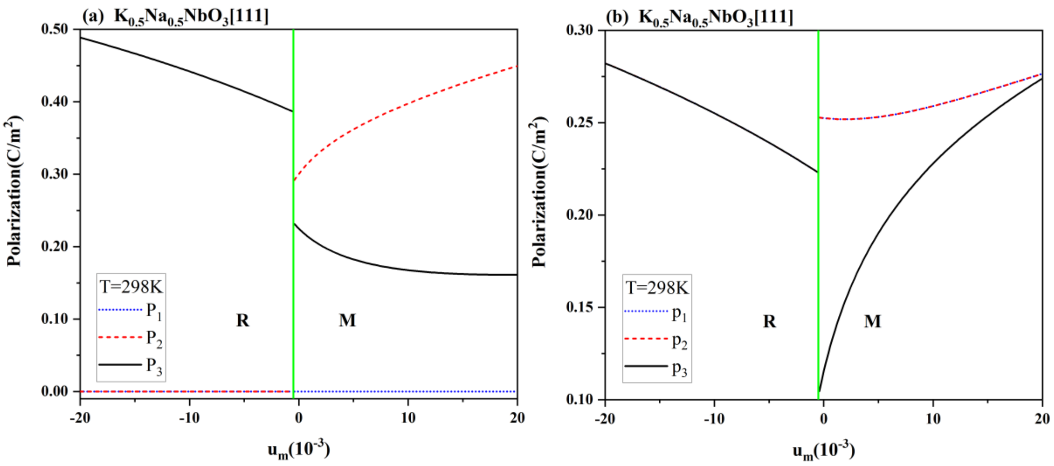

图 S1 室温 T = 298 K 下,（a）全局坐标系和（b）晶体坐标系中极化分量与失配应变的关系

Fig. S1. Polarization components as a function of misfit strain at room temperature T = 298 K in (a) global coordinate system and (b) crystal coordinate system, respectively.

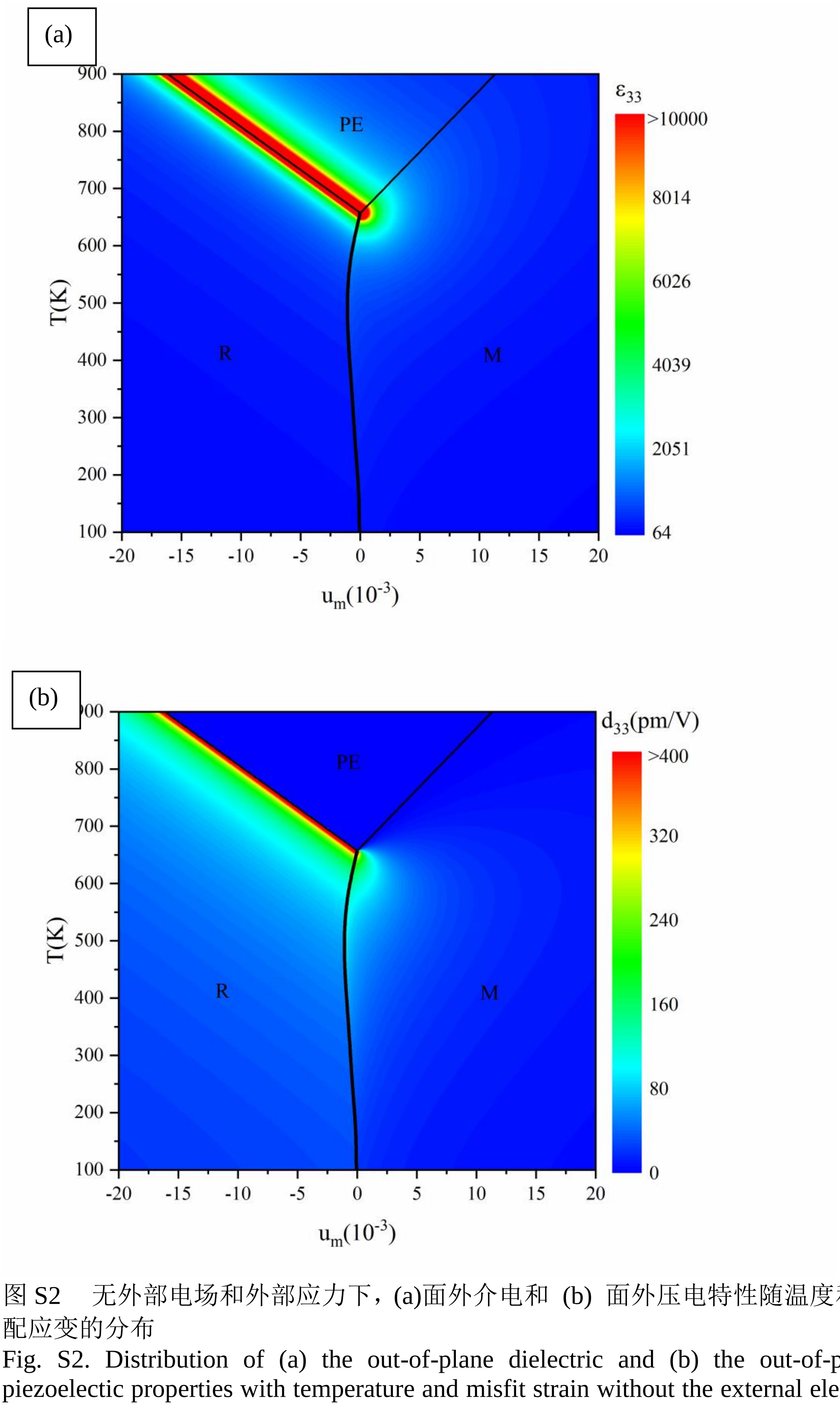

图 S2 无外部电场和外部应力下，(a)面外介电和 (b) 面外压电特性随温度和失配应变的分布

Fig. S2. Distribution of (a) the out-of-plane dielectric and (b) the out-of-plane piezoelectic properties with temperature and misfit strain without the external electric field without the external stress.

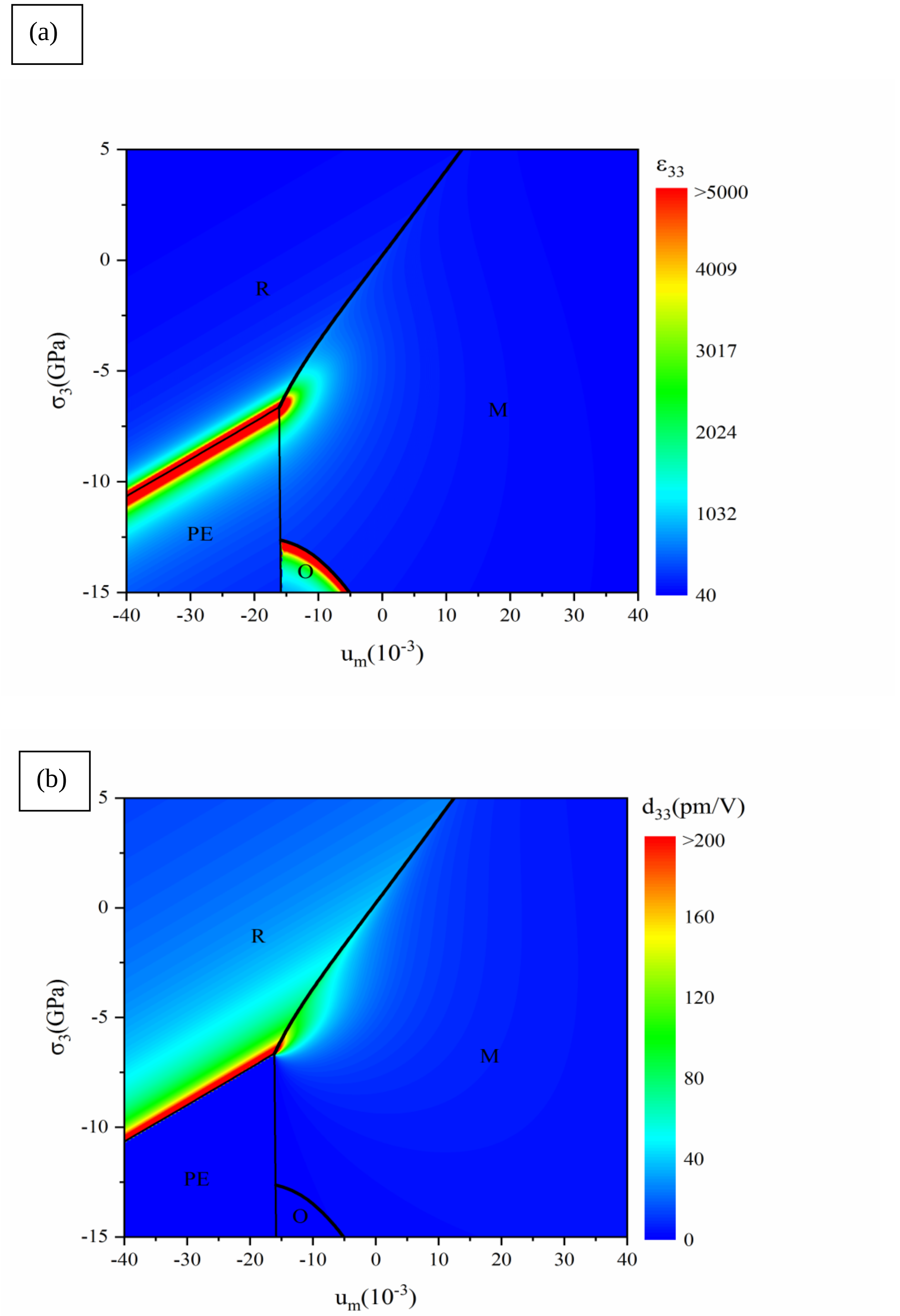

图 S3　室温下无外部电场时，(a)面外介电和(b)面外压电特性随外部应力和失配应变的分布

Fig. S3. Distribution of (a) the out-of-plane dielectric and (b) the out-of-plane piezoelectic properties with a wide range of external stress and misfit strain without the external electric field under room temperature (T = 298 K).

参考文献

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[S2]Li C, Huang Y, Wang J, et al. 2021 *Npj Comput. Mater.* **7** 1.