Electronic Supplementary Material (ESI) for RSC Advances

SUPPLEMENTARY INFORMATION *for*

Effect of stress state on the domain configuration and switching behavior in ferroelectric thin films

Manoj Narayanan, Mengchun Pan, Shanshan Liu, Sheng Tong, Seungbum Hong, Beihai Ma, and Uthamalingam Balachandran

A. Stress Calculations:

Stresses in the films were calculated using the properties available in the literature for bulk PLZT materials. The stresses in PLZT films were determined using the properties given below and Eq (1).

Table of Properties used for films and substrates:

$\alpha_{PLZT} = 5.4 \times 10^{-6}$ /^{o}C; $\alpha_{LNO} = 12.5 \times 10^{-6}$ /^{o}C; $\alpha_{Si} = 3 \times 10^{-6}$ /^{o}C; $\alpha_{Ni} = 14.1 \times 10^{-6}$ /^{o}C; $E_{PZT} = 85$GPa; $\nu_{PZT} = 0.28$; $\Delta T = 625^{o}$C

Stress was calculated using Eq (1). Negative and positive values indicate compressive and tensile stress, respectively, observed in the films.

$$\sigma_{PLZT} = \frac{E_{PLZT}}{(1-\nu_{PLZT})}(\Delta\alpha \times \Delta T) \qquad \text{……}\textbf{Eq (1)}$$

B. Gibbs Free Energy Calculations:

Under the Landau-Ginzburg-Devonshire theory, Gibbs free energy is defined as

$$\begin{aligned}\Delta G &= \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_3^2P_1^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ &+ \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_3^2 + P_1^2) + P_3^4(P_1^2 + P_2^2)] + \alpha_{123}P_1^2P_2^2P_3^2 - \frac{1}{2}s_{11}(X_1^2 + X_2^2 + X_3^2) \\ &- s_{12}(X_1X_2 + X_2X_3 + X_3X_1) - \frac{1}{2}s_{44}(X_4^2 + X_5^2 + X_6^2) - Q_{11}(X_1P_1^2 + X_2P_2^2 + X_3P_3^2) \\ &- Q_{12}[X_1(P_2^2 + P_3^2) + X_2(P_3^2 + P_1^2) + X_3(P_1^2 + P_2^2)] - Q_{44}(X_4P_2P_3 + X_5P_3P_1 + X_6P_1P_2)\end{aligned}$$

……**Eq (2)**

For tetragonal compositions, $P_1 = P_2 = 0$, $P_3 \neq 0$; For two dimensional stress, $X_1 = X_2 \neq 0$; $X_3 = X_4 = X_5 = X_6 = 0$. Therefore ΔG reduces to:

$$\Delta G = \alpha_1 P_3^2 + \alpha_{11} P_3^4 + \alpha_{111} P_3^6 - \frac{1}{2} s_{11}(X_1^2 + X_2^2) - s_{12}(X_1 X_2) - Q_{12}(X_1 P_3^2) + X_2 P_3^2)$$

……**Eq (3)**

$$\left.\frac{\partial G}{\partial P}\right|_X = 0 = \sqrt{\frac{-\alpha_{11} + \sqrt{\alpha_{11}^2 - 3\alpha_1\alpha_{111} + 6Q_{12}\alpha_{111}X}}{3\alpha_{111}}}$$

……**Eq (4)**

PZT 50/50 Constants [S1]	
α_1 @ 25C, m/F	-2.669×10^7
α_{11}, m^5/C^2F	-1.431×10^7
α_{111}, m^9/C^4F	1.342×10^8
Q_{11}, m^4/C^2	6.50×10^{-2}
Q_{12}, m^4/C^2	-3.20×10^{-2}
s_{11}, m^2/N	6.785×10^{-12}
s_{12}, m^2/N	-2.50×10^{-12}

C. Second Order Phase Transition

For second order phase transition, the remnant polarization decreases to zero as temperature approaches the Curie Temperature and is defined by Eq (5) [S2]

$$P_r = \left[\kappa_P (T_c - T) / \beta'_P\right]^{1/2}$$

……**Eq (5)**

Measured data was fitted with this equation to achieve correlation coefficient of >0.99 and the respective curie temperatures are reported in the communication.

References

[S1] A. Amin, R. E. Newnham and L. E. Cross, Phys. Rev. B. 34 (3), 1595, 1986

[S2] H. Zhu, D. P. Chu, J. Phys. Condens. Matter. 23, 495901, 2011