A Landau – Devonshire Approach of Elastic Strain Effects on Ferroelectric $Al_{1-x}Sc_xN$

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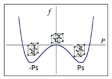
Background and Objectives

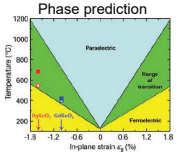
Thermodynamics of Ferroelectrics

- Phenomenological understanding of ferroelectric physics
- Prediction of ferroelectricity, stable phase and domain

$$f = a_{ij}P_iP_j + a_{ijkl}P_iP_jP_kP_l + a_{ijklmn}P_iP_jP_kP_lP_mP_n + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - q_{ijkl}\varepsilon_{ij}P_kP_l$$

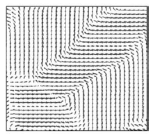


Phase prediction



Choi et al, Science (2004)

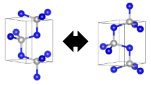
Phase field sim.

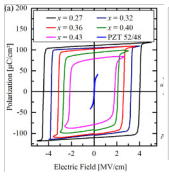


Wang et al, Acta Mater. (2005)

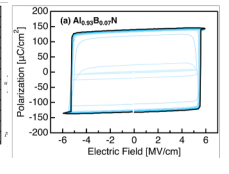
Novel Wurtzite Ferroelectrics

- Wurtzite material becomes ferroelectrics
  - $Al_{1-x}Sc_xN$, $Al_{1-x}B_xN$, $Zn_{1-x}Mg_xO$, and more
- Fundamental science questions unanswered

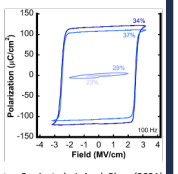




Fichtner, et al., J. Appl. Phys. (2019)



Hayden, et al., Phys. Rev. Mater. (2021)



Ferri, et al., J. Appl. Phys. (2021)

Objectives:

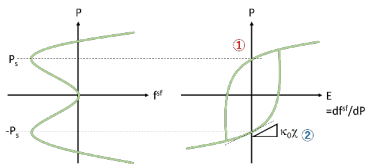
- **Describe Landau-Devonshire thermodynamics of wurtzite $Al_{1-x}Sc_xN$ ferroelectrics**
- **Predict ferroelectric properties under thermodynamic variables: elastic strain**

Thermodynamic Formulation for Wurtzite Ferroelectrics

- Determine and tabulate dielectric stiffness coefficient
- Predict first order phase transition at x = 0.2

Assumption: hBN prototype, $P_1 = P_2 = 0$, stress-free boundary condition then,

$$f^{sf} = a_{33}P_3^2 + a^*_{3333}P_3^4 + a_{333333}P_3^6$$



① Free energy local minima: P_s

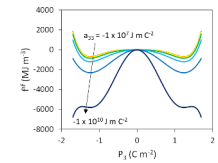
$$\left.\frac{\partial f^{sf}}{\partial P_3}\right|_{P_3=P_s} = 0$$

② Slope of P-E loop: susceptibility

$$\left.\frac{\partial^2 f^{sf}}{\partial P_3^2}\right|_{P_3=P_s} = \frac{1}{\kappa_0\chi_{33}}$$

Variable reduction: free energy is function of a_{33}

$$f^{sf} = a_{33}P_3^2 + \frac{8a_{33}\kappa_0\chi_{33}+1}{8P_s^2\kappa_0\chi_{33}}P_3^4 - \frac{4a_{33}\kappa_0\chi_{33}+1}{12P_s^4\kappa_0\chi_{33}}P_3^6$$

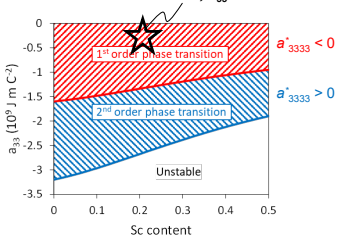


Condition for double well function formation: $\lim_{P\to\infty} f^{sf} = \frac{\infty(4a_{33}\kappa_0\chi_{33}+1)}{\mathrm{sgn}(\kappa_0\chi_{33})} > 0$

	Utmit	0*	0.1	0.2*	0.3	0.4	0.5
		Sc content x in $Al_{1-x}Sc_xN$					
a_{33}	GJ m C^{-2}	-1.84	>-2.97	-0.32	>-2.38	>-2.12	>-1.90
a^*_{3333}	GJ m^5 C^{-4}	0.33	<0.92	-0.66	<0.84	<0.89	<1.23
a_{333333}	GJ m^9 C^{-6}	0.12	>0	0.33	>0	>0	>0
a_{3333}	GJ m^5 C^{-4}	0.55	<1.13	-0.44	<1.19	<1.70	<3.28

*The dielectric stiffnesses are determined by energy barrier height of a DFT result at x = 0 and 0.2
H. Wang, et al, J. Appl. Phys. **130**, 104101 (2021)

x = 0.2, a_{33} = -0.32



First order phase transition

Electromechanical Coupling

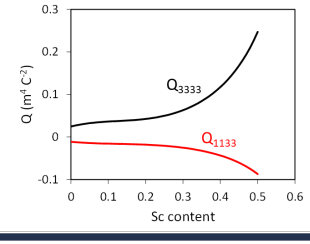
- Determine electrostrictive coefficient

Piezoelectric vs electrostrictive coefficients in wurtzite structure

$$d_{311} = d_{322} = 2Q_{1133}P_s\chi_{33} \qquad d_{333} = 2Q_{3333}P_s\chi_{33}$$

	Utmit	0*	0.1	0.2*	0.3	0.4	0.5
		Sc content x in $Al_{1-x}Sc_xN$					
Q_{3333}	m^4 C^{-2}	0.025	0.036	0.043	0.063	0.117	0.247
Q_{1133}	m^4 C^{-2}	-0.011	-0.016	-0.018	-0.025	-0.043	-0.087

d values are from M.A. Caro, et al, J. Phys. Condens. Matter **27**, 245901 (2015).



Elastic Strain Effects on Ferroelectricity

- f(P,ε) is explicitly expressed for understanding strain – ferroelectric property coupling
- Elastic strain sensitivity of energy barrier is one order of magnitude higher than that of polarization
- Both free energy barrier and polarization are much less sensitive to elastic strain compared to $PbTiO_3$ ->in good agreement with experimental results*

*K. Yazawa et al, J. Mater. Chem. C (2022)

Restarting from full description of free energy density ***to consider strain term*** (with symmetry consideration: hBN prototype)

$$f = a_{33}P_3^2 + a_{3333}P_3^4 + a_{333333}P_3^6 + \frac{1}{2}c_{1111}(\varepsilon_{11}^2+\varepsilon_{22}^2) + \frac{1}{2}c_{3333}\varepsilon_{33}^2 + c_{1122}\varepsilon_{11}\varepsilon_{22} + c_{1133}(\varepsilon_{11}\varepsilon_{33}+\varepsilon_{22}\varepsilon_{33}) - q_{1133}(\varepsilon_{11}+\varepsilon_{22})P_3^2 - q_{3333}\varepsilon_{33}P_3^2$$

Spontaneous polarization satisfies (as a function of strain)

$$\left.\frac{\partial f}{\partial P_3}\right|_{P_3=P_s^*} = 0$$

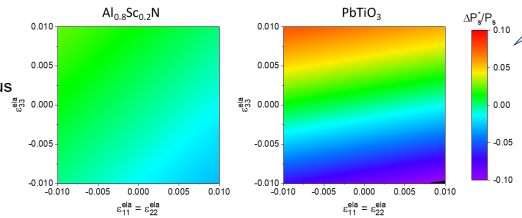
Free energy barrier between $+P_s$ and $-P_s$

$$f_b = f(0) - f(P_s^*)$$

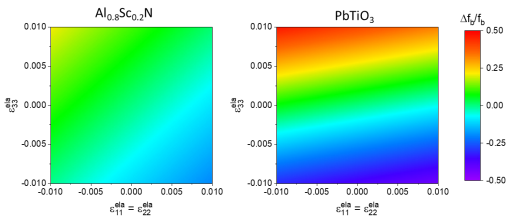
Elastic strain: total strain – spontaneous strain

$$\varepsilon_{ij}^{ela} = \varepsilon_{ij} - Q_{ij33}P_s^2$$

Spontaneous polarization at x = 0.2

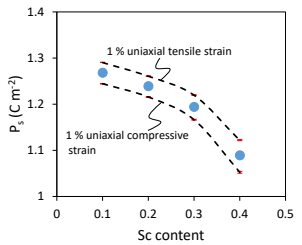


Free energy barrier at x = 0.2



A strain state **ε** gives unique data set of spontaneous polarization, free energy barrier, and elastic strain

Spontaneous polarization vs Sc content



Summary and Acknowledgement

- Describe Landau-Devonshire thermodynamics for $Al_{1-x}Sc_xN$ with hBN prototype assumption
- Tabulate dielectric stiffness and electrostrictive coefficients for future use
- Predict first order phase transition based on dielectric stiffness coefficient (T_c is unknown)
- Elastic strain sensitivity of free energy barrier and polarization is significantly smaller than $PbTiO_3$

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