Application

Strong enhancement of piezoelectric constants in $Sc_xAl_{1-x}N$: First-principles calculations

Outline

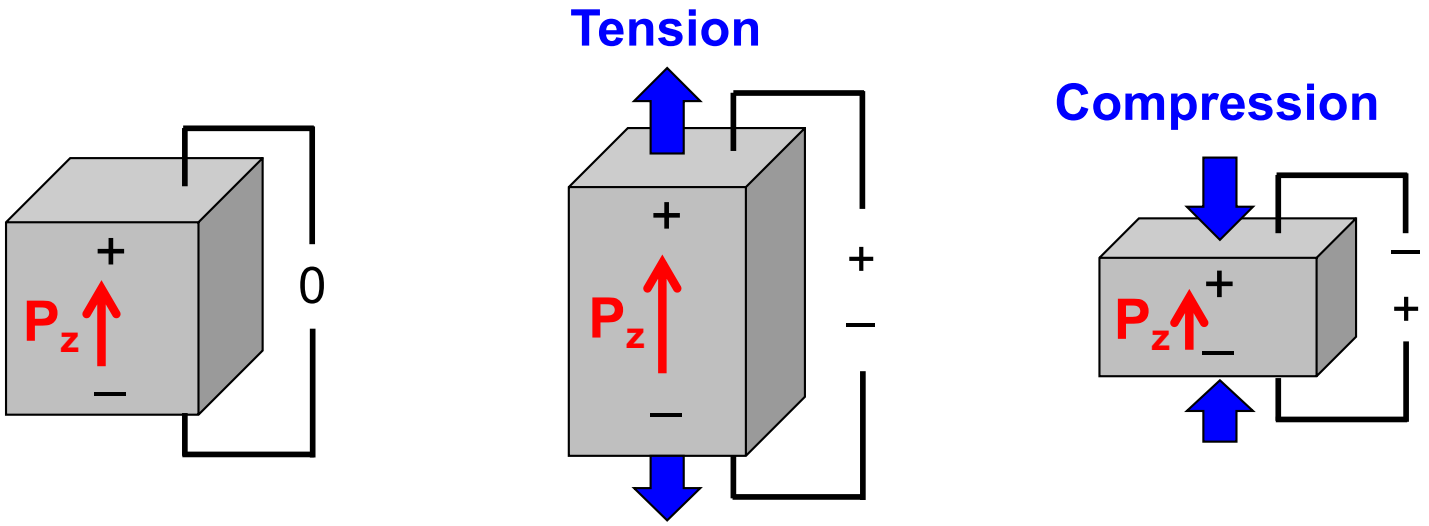
- Introduction
  - ✓ Piezoelectrics for high-temperature applications
- Piezoelectric enhancement in wurtzite $Sc_xAl_{1-x}N$
  - ✓ First-principles analysis
  - ✓ Descriptor for searching of high-piezo wurtzites
- Computational materials exploration

Electric Materials

- Dielectrics: insulators
- Piezoelectrics: non-polar/polar w. applied stress/strain
- Pyroelectrics: spontaneous polarization/unswitchable
- Ferroelectrics: switchable → FERAM

Piezoelectricity

- Electric polarization change by external stress/strain.



- Inversely, deformation can be induced by applying electric fields.

- Piezoelectric coefficients: *e*- and *d*-tensors

$$\underline{\Delta P_z} = e_{zz}\underline{\varepsilon_{zz}} = d_{zz}\underline{\sigma_{zz}}$$

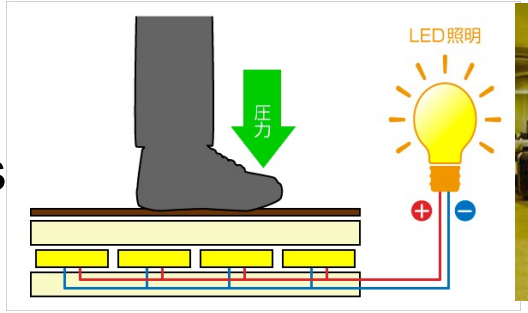
Electric Mechanical

⇒ **Energy Conversion**

Piezoelectric Devices

Mechanical ➔ Electric

- Piezoelectric ignition
- Acceleration or pressure sensors
- Piezoelectric microphone
- Floor electricity generation

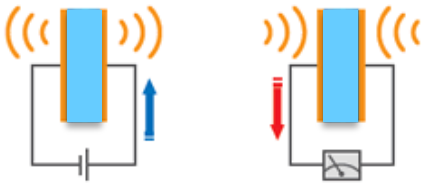


http://www.soundpower.co.jp

http://www.jreast.co.jp/development/theme/pdf/yukahatsuden.pdf

Electric ➔ Mechanical

- Piezoelectric actuator
- Piezoelectric buzzer and speaker
- Ultrasonic generator and sensor

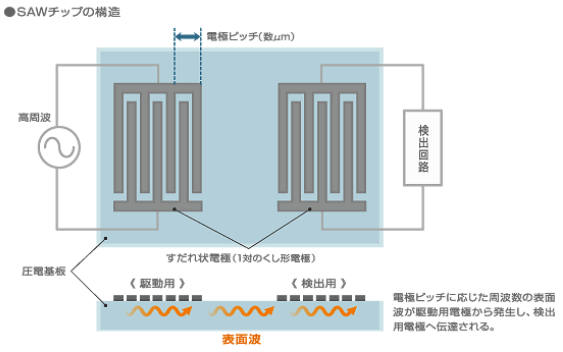


Voltage ⟷ Ultrasonic Waves

http://www.ndk.com/jp/sensor/ultrasonic/basic02.html

Surface acoustic wave (SAW) devices

- High-frequency SAW filter
- SAW touch screen

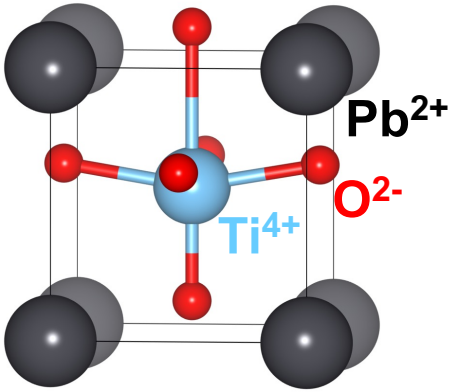


http://www.tdk.co.jp/techmag/inductive/201012/index2.htm

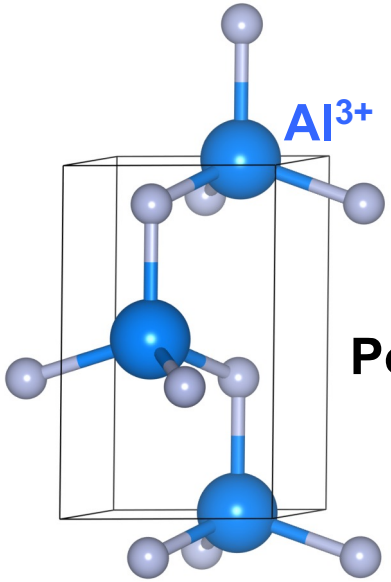
Piezoelectric Materials

- **Perovskite Materials**
  - $PbZr_xTi_{1-x}O_3$ (x~0.52)
    d ~ 410 pC/N, T_c~250ºC

Polar *P4mm*



- **Wurtzite Materials**
  - AlN
    d ~ 5 pC/N, T_C > 1000ºC
  - ZnO
    d ~ 12 pC/N



Polar *P63mc*

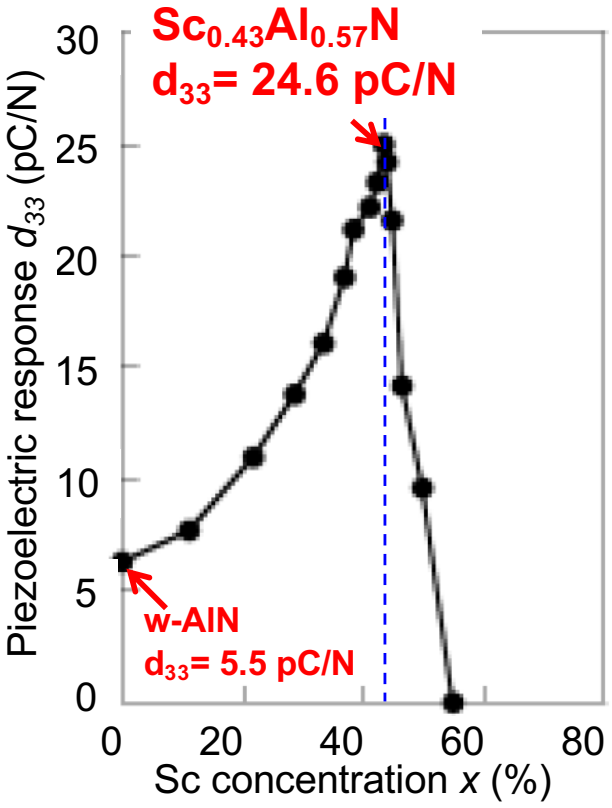
Wurtzite Materials:

- could be used at high-temperature environments.
- should increase piezoelectric constants.

Highest Piezoelectricity: $Sc_xAl_{1-x}N$

A. Teshigahara *et al.*, Proc. of International Ultrasonics Symposium 2012.

- Piezoelectric constant of $Sc_xAl_{1-x}N$



- $Sc_xAl_{1-x}N$ films synthesized by dual co-spattering techniques
- Piezoelectric constant
  - x < 43% : Enhance as x increases
  - 43% < x : Diminish rapidly by a structure transition
- Issues
  - Origin of the enhancement by Sc
  - Structural instability at x ~ ½
- Price of Sc ~ Pt

➠ Need to search for other candidates

First-Principles Methods

- **Density Functional Theory — GGA-PBE xc functional**

  Hohenberg–Kohn 1964, Kohn–Sham 1965
  Perdew–Burke–Ernzerhof 1996

- **All-electron Full-potential Linearized Augmented Plane Wave (FLAPW) method implemented in in-house HiLAPW code**

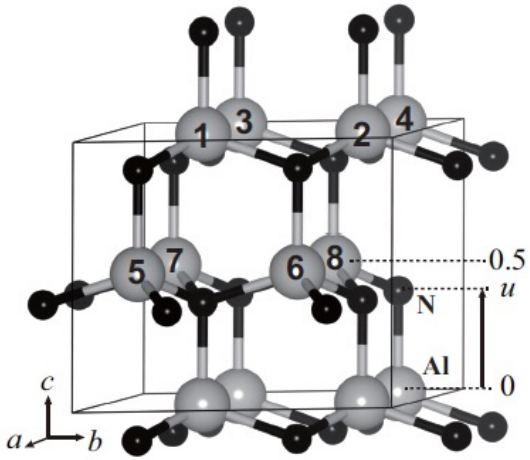
  Wimmer–Krakauer–Weinert–Freeman 1981
  Soler–Williams 1989

- **Berry–phase method for electric polarization**

  Resta 1992
  King-Smith–Vanderbilt 1993
  Zhong–Vanderbilt 1994

Models of $Sc_xAl_{1-x}N$

- **w-AlN (16 atom supercell)**



$Sc_xAl_{1-x}N$ models:
All possible configurations and concentrations of Sc at Al sites

- **Piezoelectric constants**

$$P_i = \sum_{j=1}^{6} e_{ij}\varepsilon_j$$

$$P_i = \sum_{j=1}^{6} d_{ij}\sigma_j$$

- **Calculation procedure**

1. Substitute Al by Sc and optimize structure

2. Piezoelectric *e* constants

Zhong–Vanderbilt 1994

$$e_{ij} = \left.\frac{\partial P_i}{\partial \varepsilon_j}\right|_u + \sum_{\alpha,k} \left.\frac{\partial P_i}{\partial u_{\alpha,k}}\right|_\varepsilon \frac{\partial u_{\alpha,k}}{\partial \varepsilon_j} = e_{ij}^{\text{clamp}} + e_{ij}^{\text{inter}}$$

Born effective charge $Z^*_{\alpha,ij} = \frac{V}{e}\frac{\partial P_i}{\partial r_{\alpha,j}}$

3. Elastic stiffness tensor

$$E(\varepsilon) - E(0) = \frac{V_0}{2}\sum_{i,j=1}^{6} C_{ij}\varepsilon_i\varepsilon_j$$

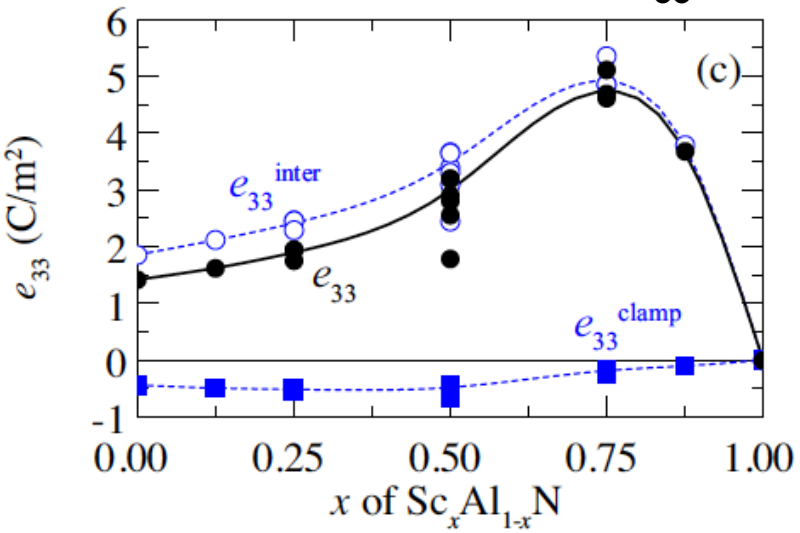
4. Elastic compliance tensor $S = C^{-1}$

5. Piezoelectric *d* constant $d_{ij} = \sum_{k=1}^{6} e_{ik}S_{kj}$

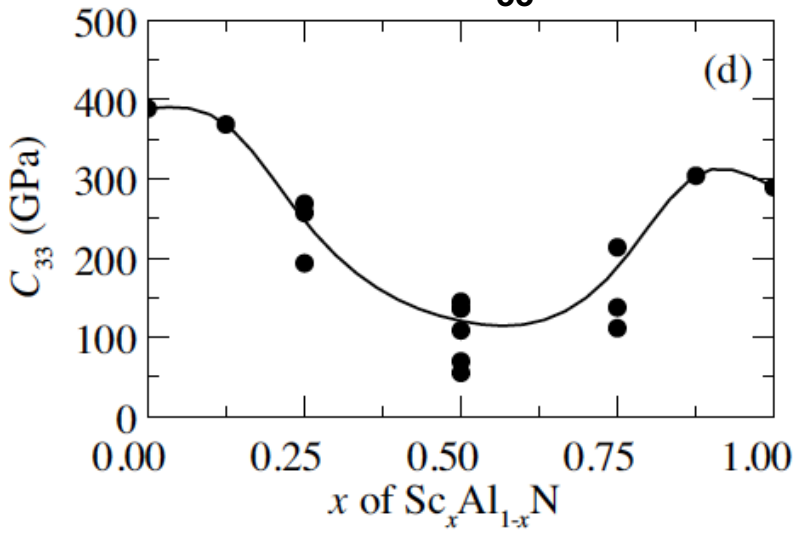
6. Canonical ensemble average over models at x

Piezoelectricity of $Sc_xAl_{1-x}N$

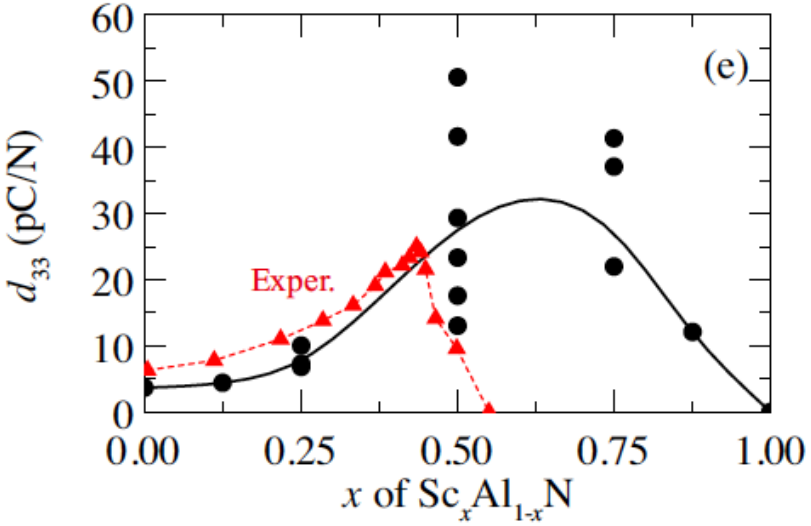
- Piezoelectric constant e_{33}



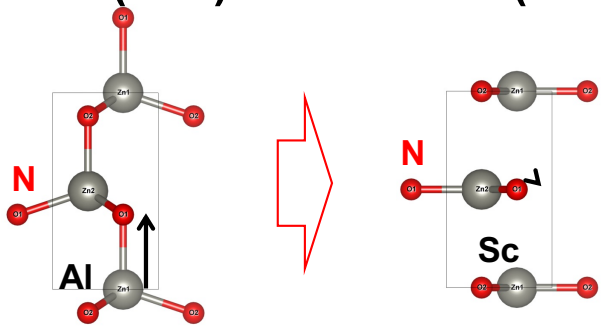
- Elastic constant C_{33}



- Piezoelectric constant $d_{33} \sim e_{33}/C_{33}$



- Hexagonal structures at both ends

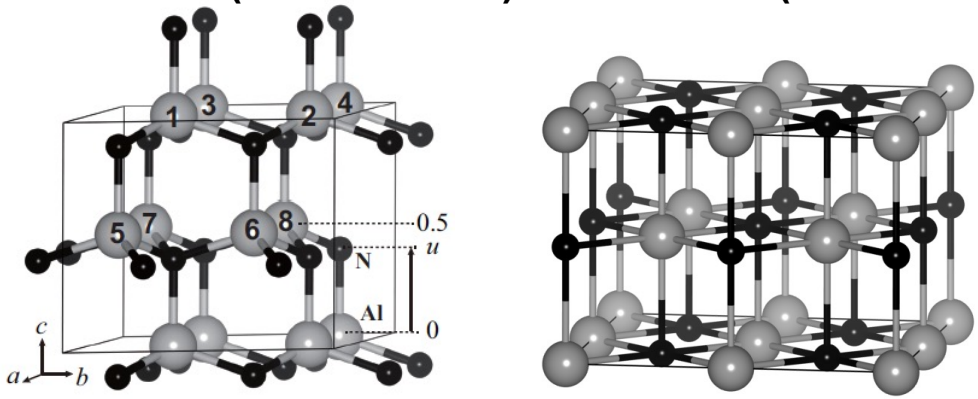


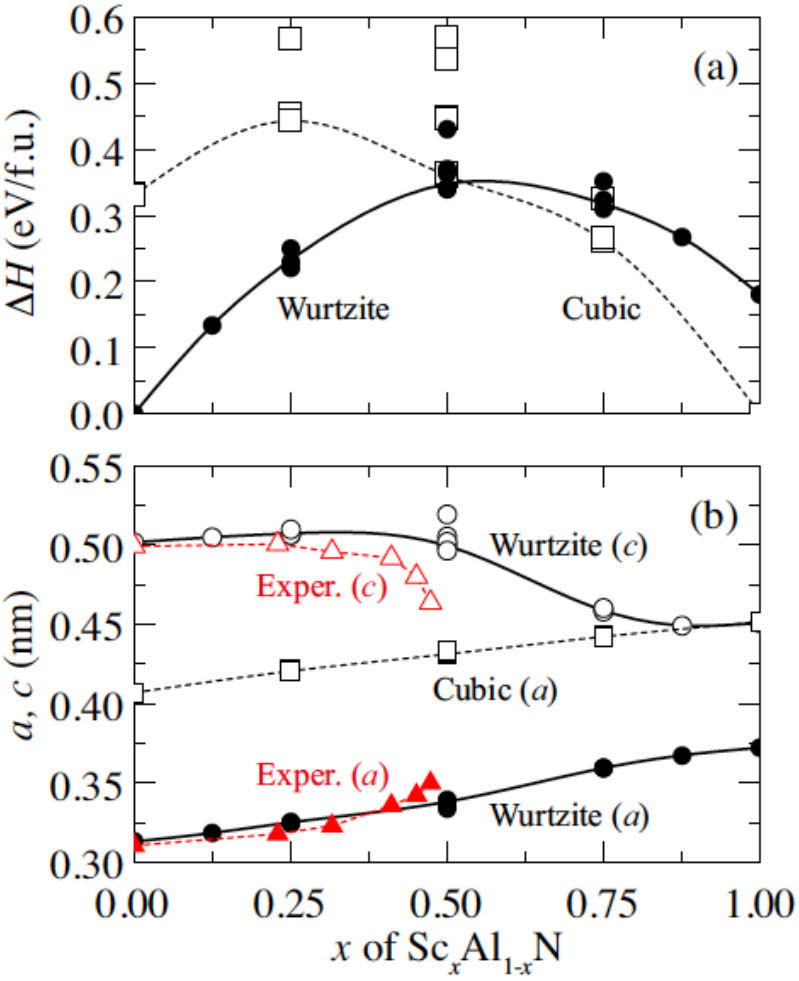
Structure Stability of $Sc_xAl_{1-x}N$

- **Most stable structures:**
  - AlN (x=0) : polar hexagonal wurtzite
  - ScN (x=1) : Non-polar cubic rock-salt

- **Two types of $Sc_xAl_{1-x}N$ models**

Wurtzite (16 atom/cell) Rock salt (16 atom/cell)





- **Structure stability analyses**

$$\Delta H = (1-x)E(\text{w-AlN}) + xE(\text{c-ScN}) - E(\text{Sc}_x\text{Al}_{1-x}\text{N})$$

- **For 0.5 < x, cubic phases are more stable than wurtzite phases.**

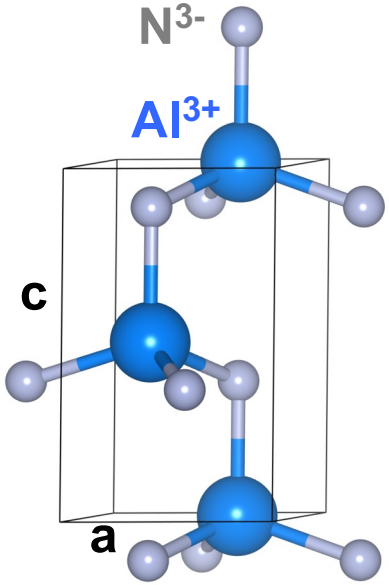
Search for High-Piezo Materials

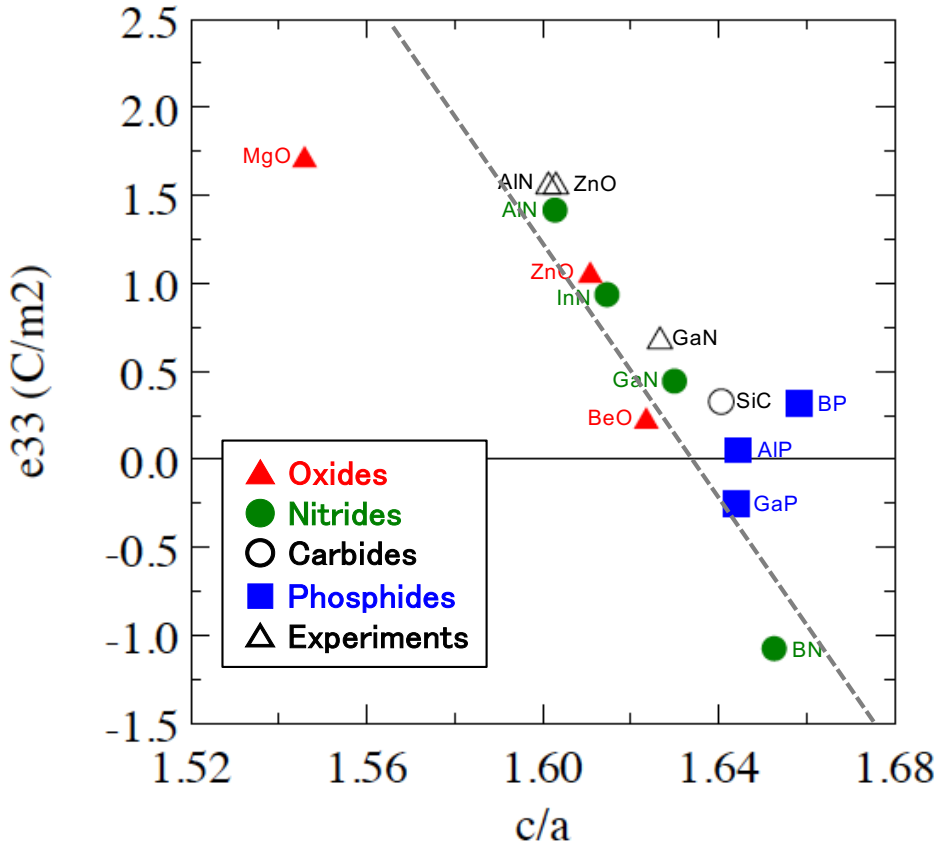
- $Sc_xAl_{1-x}N$ explained well from first principles 
- Search for novel materials with superior performances
  - Cation replacement:
    $A_xB_{1-x}N$ (*A* = Sc, Y, La & *B* = Al, Ga, In)
  - Anion replacement:
    $AlN_{1-x}P_x$ 
  - Long-range structure effect:
    Zinc-blende (111) stacking: AlP, GaP, InP
- **Need to get a simple guideline (descriptor) that measures the piezoelectricity of wurtzite materials.**

H. Momida, A. Teshigahara, TO, AIP ADVANCES 6, 065006 (2016)

Piezoelectricity of Wurtzite

- Stable wurtzite crystals: ZnO, BeO, AlN, GaN
- More than twelve wurtzite crystals reported

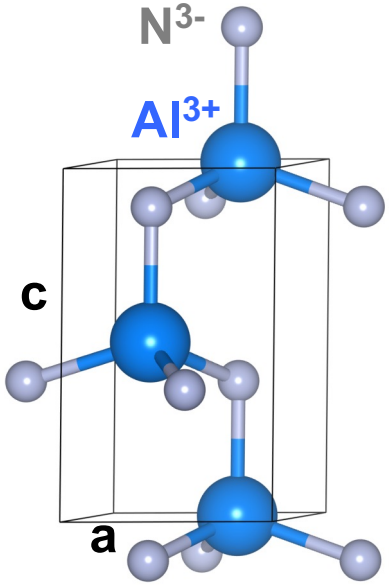


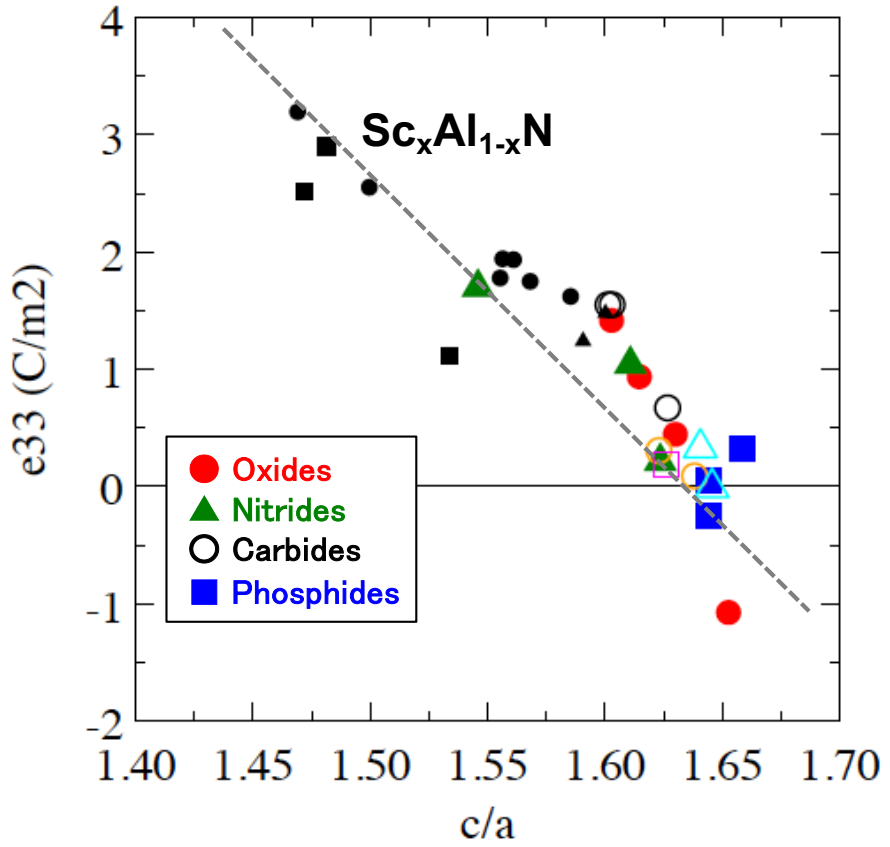


- Higher e_{33} for smaller *c*/*a*

Piezoelectricity of Wurtzite

- $Sc_xAl_{1-x}N$ results also support the e_{33}–*c*/*a* relation

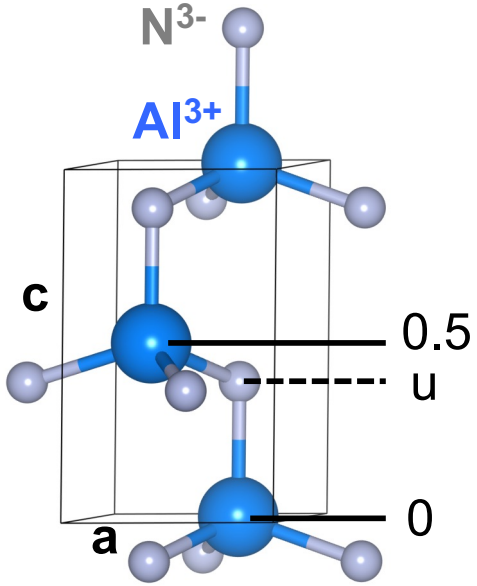


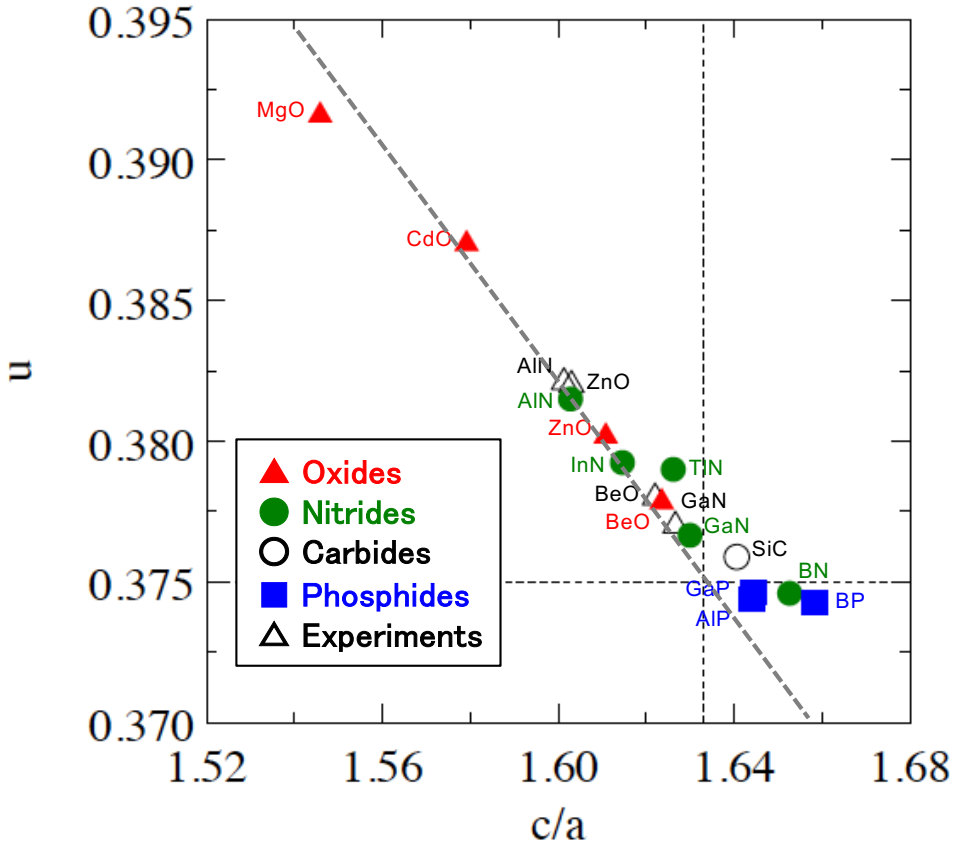


- Higher e_{33} for smaller *c*/*a*

Structure of Wurtzite

- **Atomic position parameter (*u*) and lattice constant ratio (*c*/*a*)**





- **Ideal wurtzite structure**
  - **Compose of regular tetrahedron**
  - ***c*/*a* = $(8/3)^{1/2}$ = 1.633**
  - ***u* = 0.375**
- **Higher *u* (tetrahedral → pyramidal) for smaller *c*/*a***

isotropic → anisotropic: must be preferable to high polarization

Mechanism of $e_{33} \propto c/a$

clamped-ion *internal-strain*

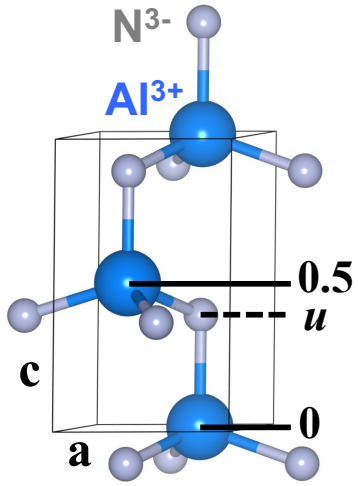
$$e_{33} = \left.\frac{\partial P_3}{\partial \varepsilon_3}\right|_u + \frac{ec}{V} Z^*_{\mathrm{Anion},33} \frac{\partial u}{\partial \varepsilon_3}$$

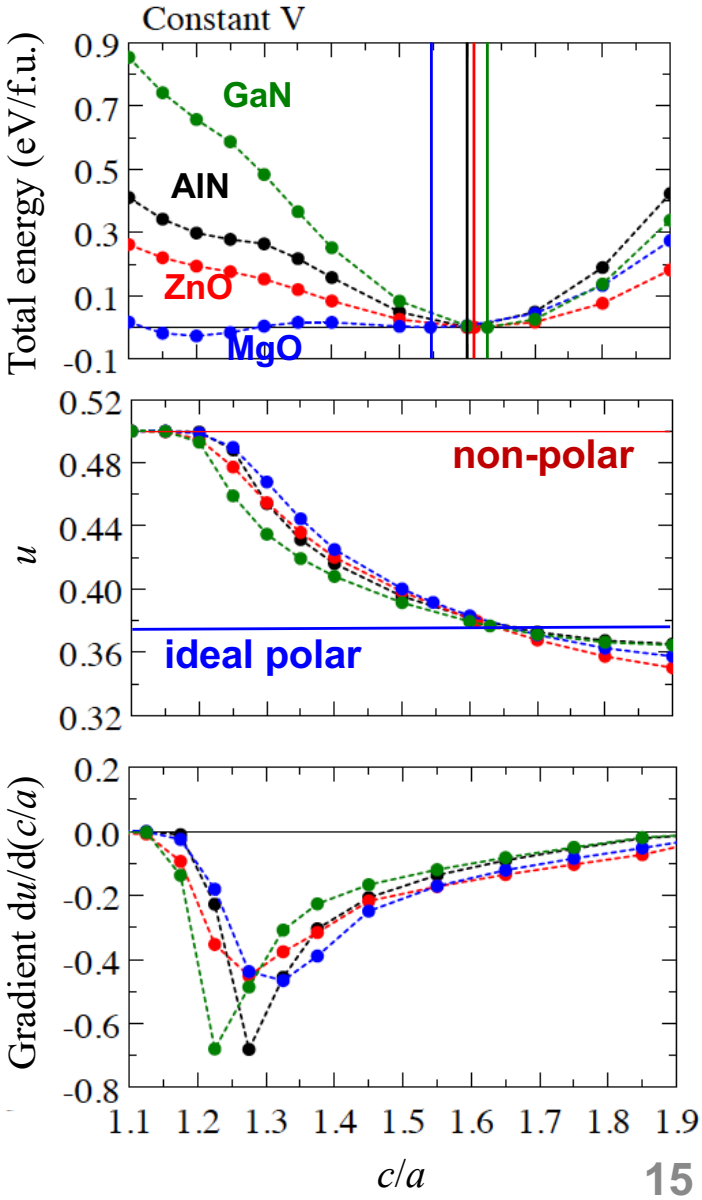
Small, independent of materials

Dominant !

$$e_{33} \propto Z^*_{\mathrm{Anion},33} \frac{\partial u}{\partial \varepsilon_3}$$

nearly nominal value





Instability of *u* in the transition region between ideal polar (*u*=0.375) and non-polar (*u*=0.5) structures leads to enhancement of $\partial u/\partial \varepsilon$.

$$\frac{\partial u}{\partial \varepsilon_3} \propto c/a \quad \text{for c/a > 1.45} \Rightarrow e_{33} \propto c/a$$

Predicted Data for Machine Learning

- Binary wurtzite materials found in literatures (mostly in metastable phases)

Material	e_{33} (C/m^2)	C_{33} (GPa)	d_{33} (pC/N)
MgO	1.70	164	10.35
AlN	1.42	388	3.65
ZnO	1.04	185	5.64
InN	0.94	215	4.36
GaN	0.44	290	1.53
SiC	0.33	501	0.65
BP	0.32	525	0.61
CdS	0.31	87	3.53
CuCl	0.26	80	3.20
CuH	0.22	144	1.50
BeO	0.22	485	0.44
MgTe	0.18	58	3.13
CdSe	0.15	69	2.14

Material	e_{33} (C/m^2)	C_{33} (GPa)	d_{33} (pC/N)
ZnS	0.09	144	0.62
CuBr	0.08	63	1.25
AlP	0.05	149	0.36
AgI	0.05	41	1.18
GeC	–0.01	430	–0.03
CdTe	–0.04	56	–0.67
CuI	–0.04	71	–0.61
ZnSe	–0.10	103	–0.92
ZnTe	–0.22	85	–2.55
GaP	–0.25	208	–1.21
BN	–1.08	1112	–0.97
TlN	Metallic		
CdO	Metallic		

- GGA
- $d_{33} \sim e_{33}/C_{33}$
- C/N = m/V

Method: Generalized Linear Models

- **Response (*y*) and explanatory (*x*) variables (target and descriptor)**

$$y = (y_1, y_2, \cdots, y_n)$$

$$x = (x_1, x_2, \cdots, x_p)$$

$$y = \beta x = \sum_{j=1}^{p} x_{ij}\beta_j$$

$$\left(L_p \text{ norm} \quad \|X\|_q = \left(\sum_{j=1}^{p} X_j^q \right)^{1/q} \right)$$

- **Least square fitting**

$$\hat{\beta} = \underset{\beta}{\operatorname{argmin}} \|y - \beta x\|_2^2 = \underset{\beta}{\operatorname{argmin}} \left[\sum_{i=1}^{n} (y_i - \sum_{j=1}^{p} x_{ij}\beta_j)^2 \right]$$

- **Elastic net penalization: Automatic variable selection**

$$\hat{\beta} = \underset{\beta}{\operatorname{argmin}} \left[\|y - \beta x\|_2^2 + \lambda \left\{ \alpha \|\beta\|_1 + \frac{1-\alpha}{2} \|\beta\|_2^2 \right\} \right] = \underset{\beta}{\operatorname{argmin}} \left[\|y - \beta x\|^2 + \lambda \left\{ \frac{1-\alpha}{2} \sum_{j=1}^{p} \beta_j^2 + \alpha \sum_{j=1}^{p} |\beta_j| \right\} \right]$$

  - **α = 0 : Ridge regression**
  - **α = 1 : Least absolute shrinkage and selection operator (LASSO)**

- **Best α giving a minimum error (0 ≤ α ≤1)**
- **Best λ selected with cross validation: Need many run**

Model: Target and Descriptor

Target variable

e_{33}	**Piezoelectric e constant**
C_{33}	Elastic constant
d_{33}	Piezoelectric d constant

$$e_{33} = \Sigma_i \beta_i D_i$$

Descriptors #1 (Material data)

E_g	Band gap
e_{33}^{cl}	Clamped piezoelectric e constant
e_{33}^{in}	Internal piezoelectric e constant
Z_{33}	Born effective charge of cation
$du/d\varepsilon$	Atomic position change by strain

5 descriptors ➔ **excluded**

Descriptors #2 (Structure data)

a	Lattice constant
c	Lattice constant
V	Volume of unit cell
c/a	Lattice constant ratio
u	Internal atomic position

5 descriptors

Descriptors #3 (Atomic data)

Z_v	Nominal ionic valence
(R_a, R_c)	Pauling's ionic radius
(X_a, X_c)	Pauling's electronegativity
(N_a, N_c)	Atomic number

+ 14 combinations of *R*, *X*, or *N*

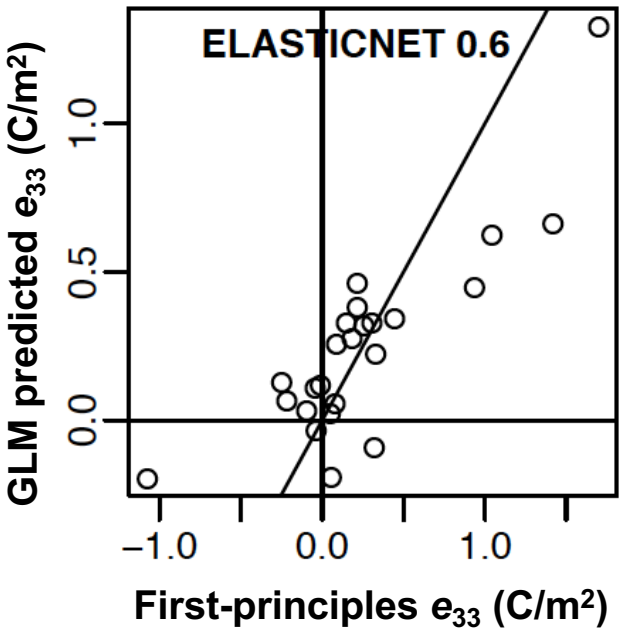
R_a+R_c	$R_aR_c/(R_a+R_c)$	$(R_a+R_c)^2$
R_a-R_c	$R_aR_c/(R_a-R_c)$	$(R_a-R_c)^2$
R_aR_c	$(R_a+R_c)/R_aR_c$	
$1/(R_a+R_c)$	$(R_a-R_c)/R_aR_c$	
$1/(R_a-R_c)$	$(R_a+R_c)/(R_a-R_c)$	
$1/(R_aR_c)$	$(R_a-R_c)/(R_a+R_c)$	

49 (=7+3*14) descriptors

Result: Target = e_{33}

- Dominant descriptors not significantly depend on α
- Minimum error for α=0.6, λ=0.186
- Only 5 descriptors selected

$$e_{33} \approx -6.82(c/a) + 0.19\left(\frac{\chi_A - \chi_C}{\chi_A \chi_C}\right) + 0.066\left(\frac{\chi_A - \chi_C}{\chi_A + \chi_C}\right) + 0.072(\chi_A - \chi_C)^2 - 0.618\left(\frac{1}{N_A - N_C}\right) + 11.27$$



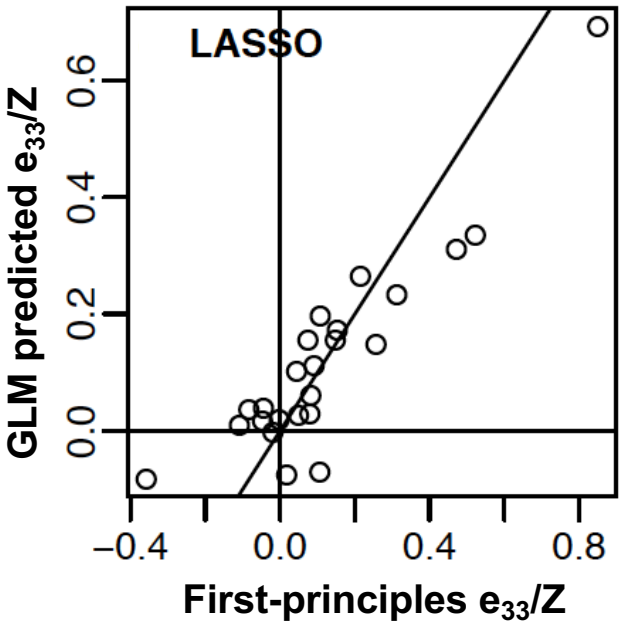
- GLM roughly explains the FP results
- Poorer agreements between GLM and FP than our expectation
- Missing information of ionic valences

- Changing target variable instead of expanding descriptors
- Target: e_{33} → e_{33}/Z
  e_{33} normalized with nominal ionic valences Z

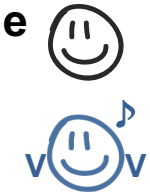
Result: Target = e_{33}/Z

- Dominant descriptors not significantly depend on α
- Minimum error for α=1, λ=0.041
- Only 4 descriptors selected

$$\frac{e_{33}}{Z} \approx -4.27(c/a) + 0.06\left(\frac{1}{R_A - R_C}\right) + 0.04(\chi_A - \chi_C)^2 - 0.20\left(\frac{1}{N_A - N_C}\right) + 6.99$$



- Linearity fairly improved compared with the target = e_{33} case
- *c*/*a* is always the predominated descriptor.



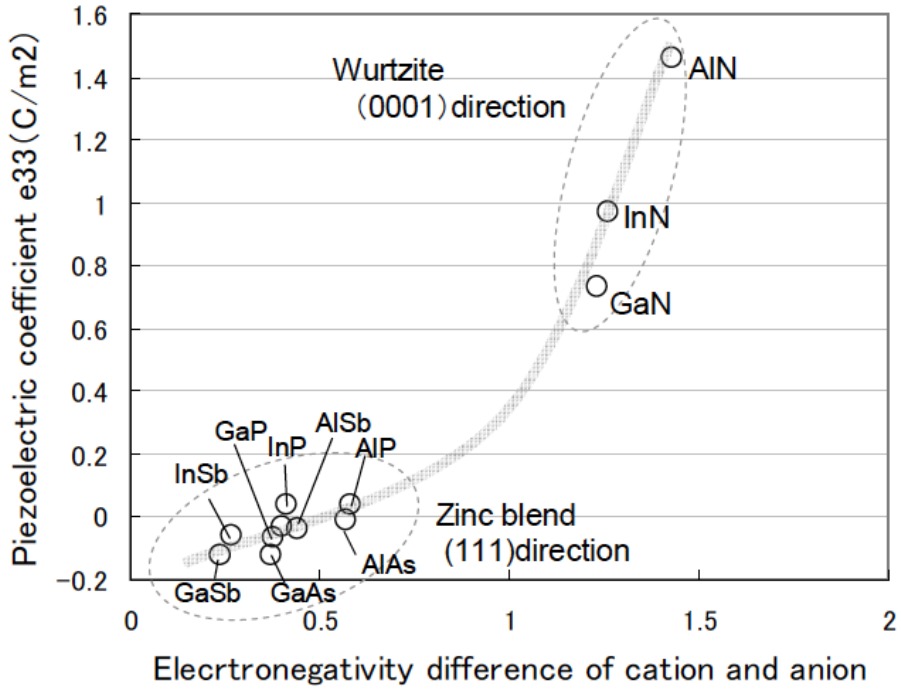
- A general guideline for enhancing e_{33} of wurtzites
  - Higher e_{33}/Z with decreasing lattice ratio (*c*/*a*)

- Confirmation of the correlation between e_{33} and *c*/*a*

- As minor effects,
  - ✓ $1/(R_A - R_C)$: ionic radius difference
  - ✓ $(X_A - X_C)^2$: electronegativity difference
  - ✓ $1/(N_A - N_C)$: atomic number difference

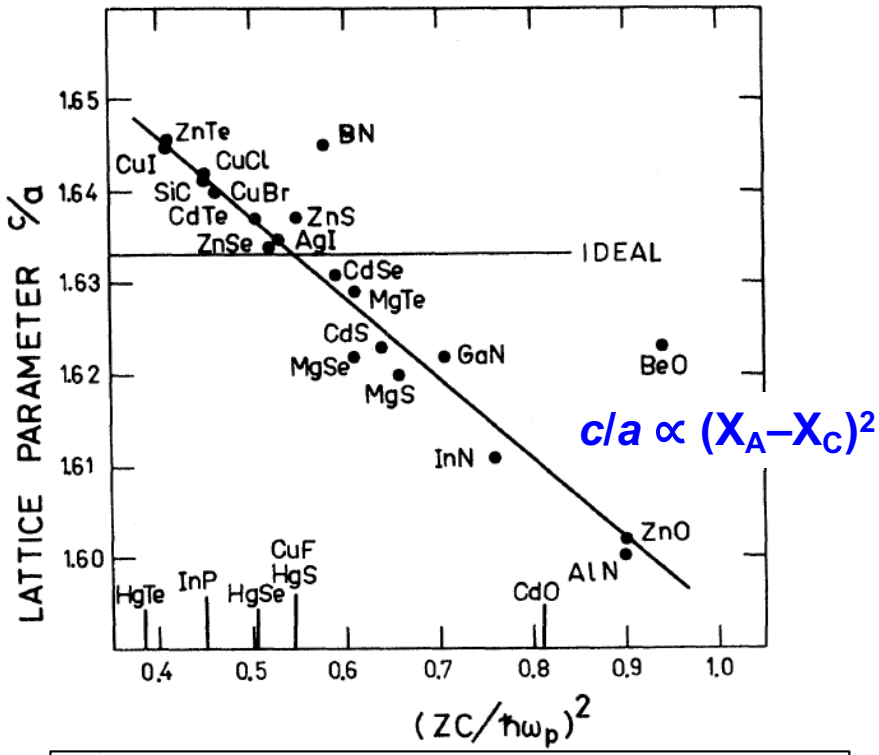
Previous Reports

A. Teshigahara et al., IEEE Int. Ultrasonics Symp. Proc. (2012).



e_{33} : nonlinear dependence on $(X_A–X_C)$

P. Lawaetz, Phys. Rev. B 5, 4039 (1972).



$c/a \propto (X_A–X_C)^2$

Z	: Valence
C	: Phillips's electronegativity difference
$\hbar\omega_p$	: Plasma energy of valence electron gas

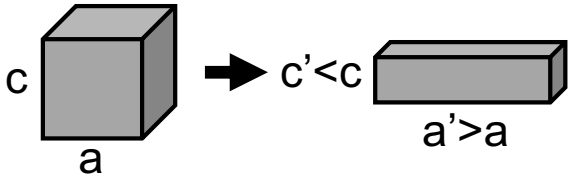
Strategy of Material Exploration

Search for higher-piezoelectric wurtzite materials

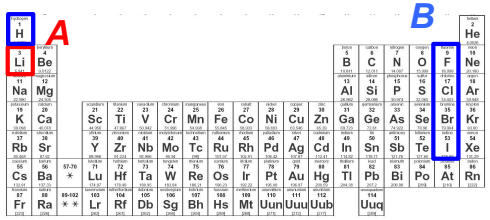
⬇

Search for wurtzite materials with small c/a

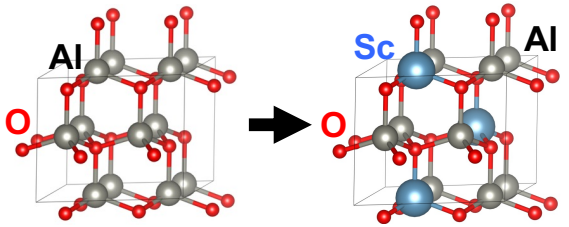
1. **Artificial reduction of *c*/*a* ratio by strain**
   - In-plane strains of AlN
   - Films on substrates with lattice mismatch



2. **Binary *AB* materials with small *c*/*a* (or larger X_A–X_C)**
   - MgO
   - Hypothetical materials: LiH, LiF, LiCl

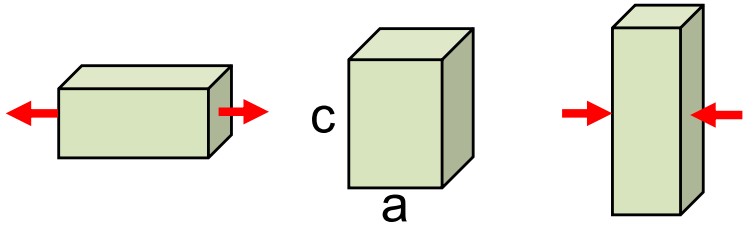


3. **Third-element doping into practical materials**
   - Experimentally reported "Sc in AlN"
   - Alkaline-earth metals doping in ZnO
   - $Ca_xZn_{1-x}O$

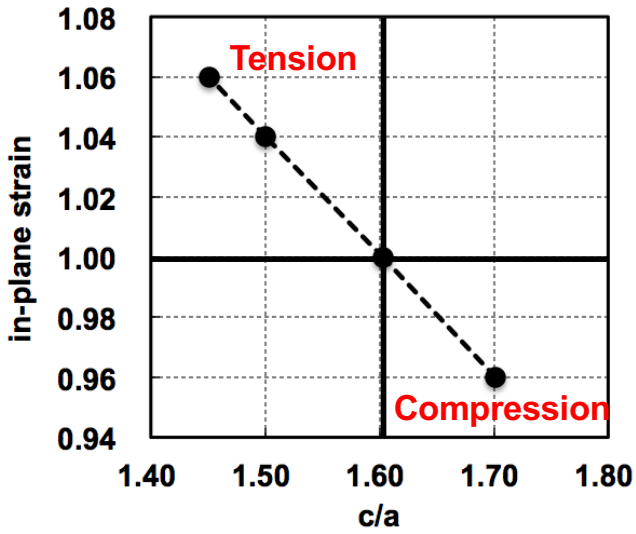


Result 1 : Strained AlN

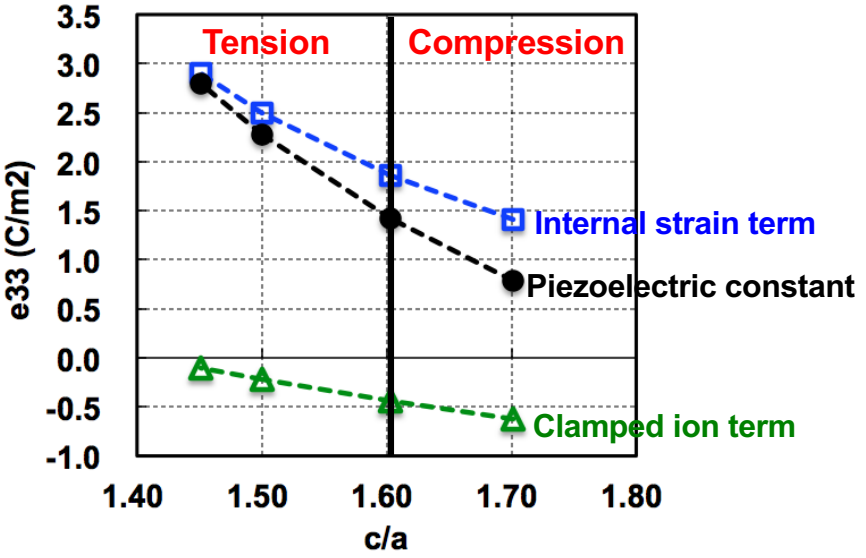
- *c/a* artificially controlled by in-plane strain



- $\varepsilon^{\text{in-plane}}$ vs. c/a



- e_{33} vs. c/a

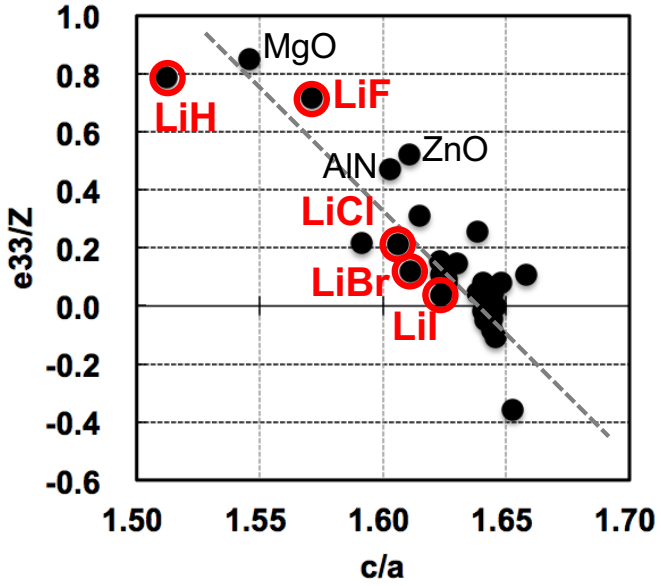


Result 2 : Element Combination

- Binary wurtzite *AB*
  1. Equi-valence for cation and anion ($A^{+Z}B^{-Z}$) to be insulating
  2. Higher electronegativity difference (X_A–X_C)

- An example: *A* = Li

	X_A–X_C	R_A–R_C	C.N. *	c/a	e_{33} (C/m²)
LiH	1.22	1.48	4	1.512	0.79
LiF	3.00	0.76	4–6	1.571	0.72
LiCl	2.18	1.21	4	1.606	0.21
LiBr	1.98	1.35	4	1.611	0.12
LiI	1.68	1.56	4	1.624	0.04



* C.N. : Coordination number guessed by critical radius ratio

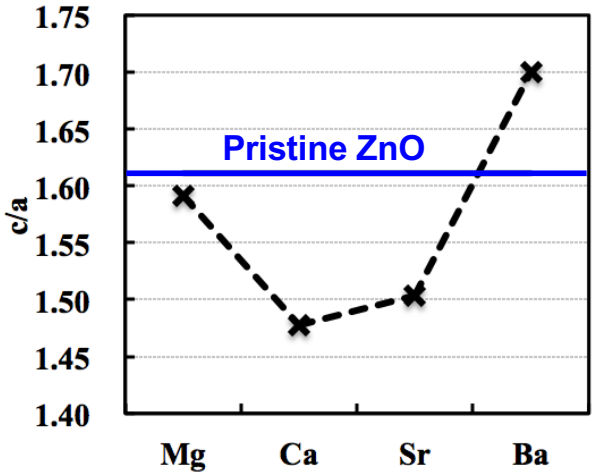
8 (CsCl-type)	6 (NaCl-type)	4 (ZnS-type)	3 (Triangle)
$R_A/R_C < 1.366$	$1.366 < R_A/R_C < 2.414$	$2.414 < R_A/R_C < 4.449$	$4.449 < R_A/R_C < 6.464$

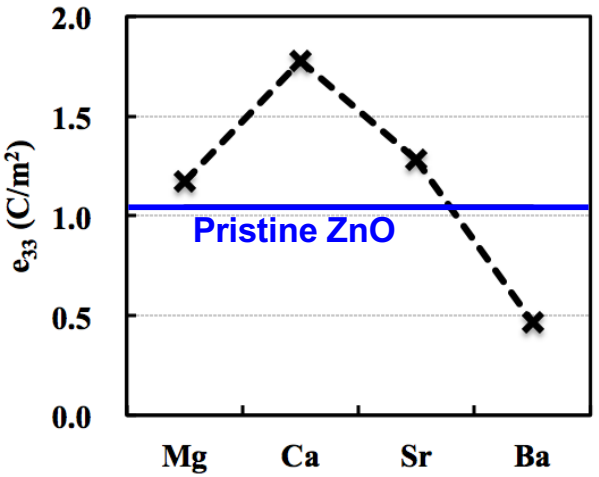
- Note that thermodynamically stable phase is NaCl structure, unfortunately.

Result 3 : Third-Element Doping

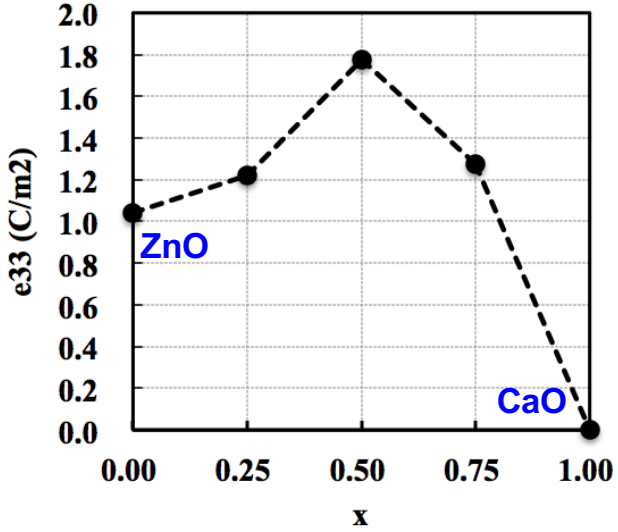
- **Base material: Technologically useful ZnO**
- **Substitute Zn by *A* : $A_xZn_{1-x}O$**
- **Information obtained through vast published papers**
  - **Ca substitution reduces c/a in ZnO** X. F. Fan *et al.*, J. Phys.: Cond. Mat. 20, 235221 (2008).

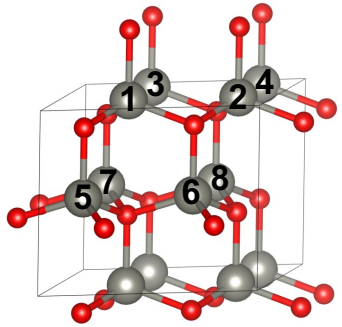
- ***c*/*a*** and e_{33} of $A_{0.5}Zn_{0.5}O$ (*A* = Mg, Ca, Sr, Ba)





- **Optimization of x in $Ca_xZn_{1-x}O$**





- **16 atom super-cell**
- **All possible atomic configurations of *A* and Zn**
- **Results averaged over the models**

Summary

- First-principles study on piezoelectricity of wurtzites
- Understanding of enhanced piezoelectricity in $Sc_xAl_{1-x}N$
  - Strong correlation between e_{33} and c/a

    H. Momida, A. Teshigahara, TO, AIP ADVANCES 6, 065006 (2016)
- Conformation by machine-learning analysis
- Materials exploration of highly piezoelectric wurtzites
  - Strain
  - Element combinations
  - Doping → a promising candidate $Ca_{0.5}Zn_{0.5}O$
    → Need to check thermodynamical stability

    H. Momida, TO, Appl. Phys. Express 11, 041201 (2018).