

Cite this: *J. Mater. Chem. C*, 2022,
10, 17557Local chemical origin of ferroelectric behavior
in wurtzite nitrides†Keisuke Yazawa,^{id} ab John S. Mangum,^{id} a Prashun Gorai,^{id} ab
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Ferroelectricity enables key modern technologies from non-volatile memory to precision ultrasound. The first known wurtzite ferroelectric $\text{Al}_{1-x}\text{Sc}_x\text{N}$ has recently attracted attention because of its robust ferroelectricity and Si process compatibility, but the chemical and structural origins of ferroelectricity in wurtzite materials are not yet fully understood. Here we show that ferroelectric behavior in wurtzite nitrides has local chemical rather than extended structural origin. According to our coupled experimental and computational results, the local bond ionicity and ionic displacement, rather than simply the change in the lattice parameter of the wurtzite structure, is key to controlling the macroscopic ferroelectric response in these materials. Across gradients in composition and thickness of $0 < x < 0.35$ and 140–260 nm, respectively, in combinatorial thin films of $\text{Al}_{1-x}\text{Sc}_x\text{N}$, the pure wurtzite phase exhibits a similar c/a ratio regardless of the Sc content due to elastic interaction with neighboring crystals. The coercive field and spontaneous polarization significantly decrease with increasing Sc content despite this invariant c/a ratio. This property change is due to the more ionic bonding nature of Sc–N relative to the more covalent Al–N bonds, and the local displacement of the neighboring Al atoms caused by Sc substitution, according to DFT calculations. Based on these insights, ionicity engineering is introduced as an approach to reduce coercive field of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ for memory and other applications and to control ferroelectric properties in other wurtzites.

Received 25th June 2022,
Accepted 12th October 2022

DOI: 10.1039/d2tc02682a

rsc.li/materials-c

1 Introduction

Ferroelectricity, which is a characteristic of materials possessing a spontaneous polarization that is reversible by applying an electric field, was discovered more than a hundred years ago.¹ Since that time ferroelectric materials have enabled and advanced ubiquitous electronic technologies in the forms of capacitors, piezoelectric actuators/sensors, energy harvesters, non-linear optics, pyroelectric sensors, and PTC thermistors.^{2–7} Thin film ferroelectrics have further enabled integrated devices such as FeRAM and PiezoMEMS.^{8,9} Research continues into use of ferroelectrics for multiferroic¹⁰ and photovoltaic^{11,12} applications as well as negative capacitance,¹³ and new concepts keep emerging.^{13–18} The race to develop new polar—and potentially ferroelectric—materials has seen significant recent expansion into nitride chemistries, most notably with the wurtzite and perovskite structures.^{19–23}

Among nitride ferroelectrics, the wurtzite aluminum scandium nitride alloy ($\text{Al}_{1-x}\text{Sc}_x\text{N}$) ferroelectric has received significant attention because of its enhanced piezoelectric response,²⁴ robust ferroelectricity,²⁰ and compatibility with both Si and III-N semiconductor processes. Chemistry, stress, strain, and film thickness have been rigorously investigated to control ferroelectricity in this material system.^{20,25–30} Higher Sc/Al ratio simultaneously reduces the crystallographic c/a ratio, spontaneous polarization, and coercive field,^{20,31} and in-plane tensile strain lowers the coercive field.^{20,27} Understanding how properties—particularly coercive field (voltage)—scale with film thickness is also important from a future device perspective.^{29,30}

The prior studies of ferroelectricity in $\text{Al}_{1-x}\text{Sc}_x\text{N}$ ^{20,25–30} included explicit and implicit variables such as residual strain state, process parameters, target condition, chamber type, substrate type/treatment, *etc.* These variables convolute experimental effects, and the resulting data scatter can easily mask important but unrepresented factors such as microstructure and defects. Combinatorial techniques reduce uncontrolled process variables because a single film library can include all samples of interest and also offer significant advantages for rapid screening.^{32,33} In such high-throughput methods, experimental variables (*e.g.*, composition, thickness, substrate

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2tc02682a>





Fig. 2 Grain and crystal growth direction analysis of $\text{Al}_{1-x}\text{Sc}_x\text{N}$. (a) Cross-sectional TEM micrographs for $\text{Sc} = 0.25$ (under Al target), $\text{Sc} = 0.38$ (middle of library), and $\text{Sc} = 0.50$ (under Sc target) showing oblique grain growth. (b) XRD omega-chi plan view map for (002) wurtzite peak with respect to substrate Pt (111) normal direction. (c) Omega and chi offsets across the sample library mapping out crystal growth direction with respect to Pt (111) normal.

on the thickness. Indeed, XRD profiles of thinner regions show smaller changes in the wurtzite phase peak intensity as a function of Sc content compared to that of thicker regions (Fig. 1(b)) as shown in Fig. S3 (ESI†).

The pure wurtzite phase region ($\text{Sc} < 0.35$) exhibits robust ferroelectric behavior. The compositional dependence of polarization–electric field hysteresis loops taken at 10 kHz for the similar thickness points ranging from 230–260 nm (same y position on the sample library) is shown in Fig. 3(c). Coercive field and polarization values decrease with increasing Sc content up to 0.35, in agreement with prior reports.^{20,25} A device at $\text{Sc} = 0.38$ (green loop) breaks down at 2500 kV cm^{-1} , which is below the coercive field, so that no hysteresis is observed. This breakdown field relates to the large leakage current when the rocksalt phase is present. Positive-up-negative-down (PUND) measurements are carried out to quantify the switched polarization without the leakage contribution^{53,54} (see ESI† Fig. S4 for the polarization values for each pulse sequence). Fig. 3(d) shows the remanent polarization ($+P_r - (-P_r)$) values as a function of applied electric field for each composition of the 230–260 nm thickness devices. The pulse width is 100 μs , and

duty cycle ratio is 10%. The decrease in switchable polarization with increasing Sc content is consistent with the P – E hysteresis measurements.

2.3 Correlation of crystal structure–ferroelectric properties

Fig. 4 summarizes the ferroelectric properties, c/a ratio (marker size) and film thickness (marker color) as a function of Sc content in our combinatorial library compared with homogeneous films reported in systematic composition–property studies (dotted and dashed lines),^{20,25} and from our chamber with nominally identical deposition condition and characterization method (black circles).^{27,42} The coercive field measured at 10 kHz and remanent polarization from PUND measurements both consistently decrease with Sc content (Fig. 4(a and b)). Note that the coercive fields of homogeneous films are results of our films using the same measurement condition, since the coercive field has a strong frequency dependence.⁵⁵ Despite the agreement in ferroelectric property change with literature, the c/a ratio in the library does not significantly change in the composition range as seen in the plot size in Fig. 4(a and b). As discussed above in Fig. 1(d), the c/a ratio is invariant with



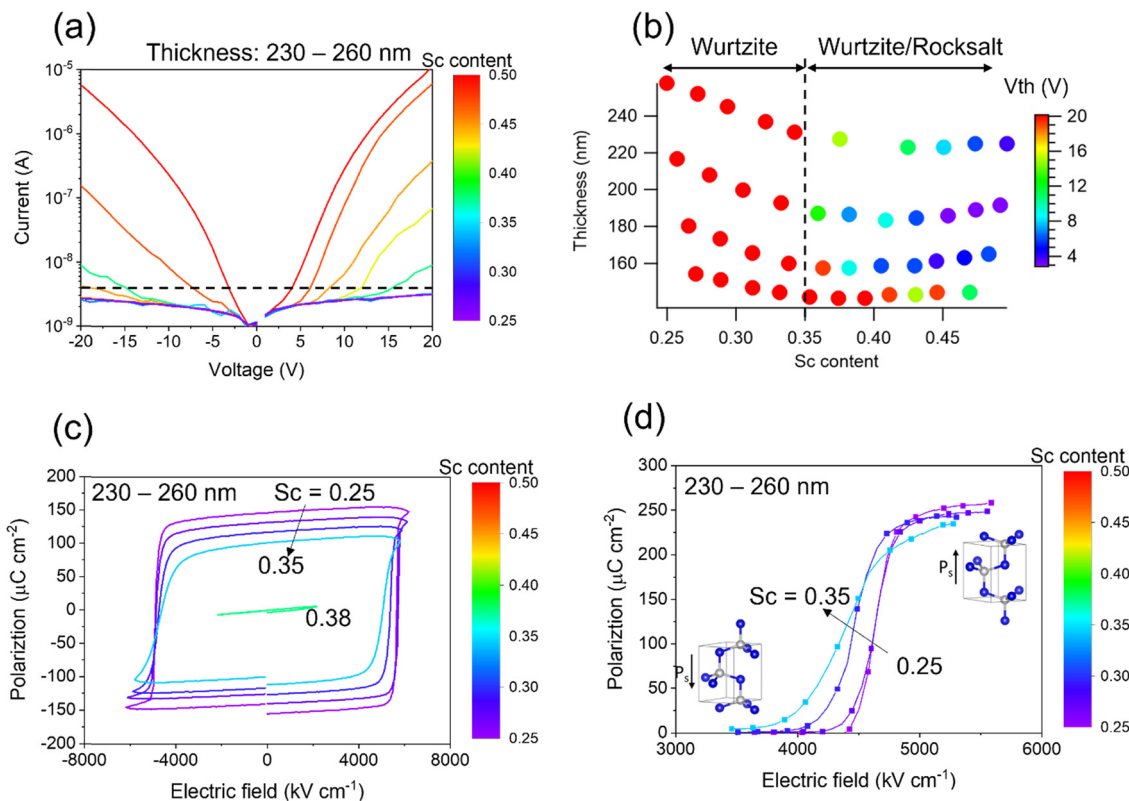


Fig. 3 Electrical properties of the $\text{Al}_{1-x}\text{Sc}_x\text{N}$ library. (a) Leakage current for films with varying Sc content from 0.25 to 0.5 and film thicknesses from 230–260 nm. (b) Threshold voltage V_{th} map in thickness–composition space showing significant conduction for Sc contents >0.35 . (c) P - E hysteresis loops for the subset of films with Sc contents from 0.25 to 0.38. (d) Switched polarization under various applied electric field pulses using the PUND method for films with Sc contents from 0.25 to 0.35.

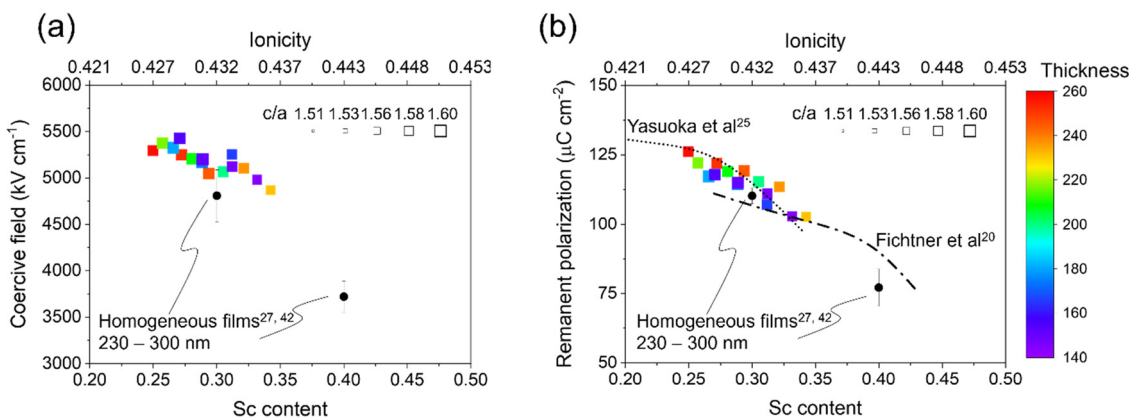


Fig. 4 Composition–structure–property relations in $\text{Al}_{1-x}\text{Sc}_x\text{N}$: (a) coercive field and (b) remanent polarization as a function of Sc content along with c/a and thickness in library, compared to reported homogeneous films.^{20,25,27,42}

composition across the pure wurtzite region due to elastic interaction in the composition gradient library.

The key findings of this work come from comparing our combinatorial library to literature values and trends relating composition, crystallography, and ferroelectric properties. Prior studies have observed consistent and simultaneous reductions in c/a ratio, coercive field, and switchable polarization with increases in Sc content.²⁵ Crucially, the fact that Sc content is

correlated with a reduction in c/a ratio has been repeatedly identified as the key mechanistic factor enabling ferroelectric polarization reversal in this system, but our results suggest that the underlying nature of the Sc–N chemical bonds is more important to enabling polarization reversal than simply *via* a change in the crystallographic c/a ratio. Indeed, Landau–Devonshire thermodynamic analysis suggests that the ferroelectric properties of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ are less sensitive to lattice strain



effects compared to classic perovskite ferroelectric PbTiO_3 .⁵⁶ Therefore, when learning from the $\text{Al}_{1-x}\text{Sc}_x\text{N}$ system to engineer other ferroelectric wurtzites, it is important to look beyond the simple lattice parameters.

2.4 $\text{Al}_{1-x}\text{Sc}_x\text{N}$ alloy calculations

The importance of bond chemistry on ferroelectric properties has long been recognized in the oxide ferroelectrics (e.g., see frequent references to cations such as Ti, Ta, and Nb as “ferroelectrically active” and Mg, Zn, and Sc as “ferroelectrically inactive” when in octahedral coordination⁵⁷), but such concepts require further consideration for the wurtzite nitrides. Considering classic Pauling electronegativity difference, the ionicity of the Al–N bond is 0.4 while the Sc–N bond is > 0.5 ionic.⁵⁸ Al–N bonding is dominated by directional sp^3 bonds whereas Sc–N is better described by non-directional ionic bonding, consistent with the endmember crystal structures (tetrahedral coordination in wurtzite AlN vs. octahedral coordination in rocksalt ScN). As shown on the secondary abscissa in Fig. 4(a and b), the average bond ionicity increases with increased Sc content. It stands to reason that the reduced directionality of such bonding would reduce barriers to polarization reversal.

We computationally modeled $\text{Al}_{1-x}\text{Sc}_x\text{N}$ alloys and performed density functional theory (DFT) calculations at 8 different compositions in the x range of 0.056–0.389 to better understand the differences in Al–N and Sc–N bonding character (see computational methods for details). Fig. 5(a) illustrates the average first nearest neighbor Al–N and Sc–N bond lengths as a function of composition x , with error bars representing the standard deviation of the bond lengths in the supercell at a given composition. The significant difference in the Al–N and Sc–N bond lengths could be attributed to the differences in the ionic radii of Al and Sc, and to the unfavorable tetrahedral coordination of Sc^{3+} (prefers octahedral coordination).

While Fig. 5(a) suggests local structural differences in the neighborhood of Al and Sc cations, it does not provide insights into the nature of the chemical bonds. To investigate the cation–N bonding, we calculated the electron localization function (ELF). The calculated ELF at Sc content $x = 0.25$ is shown in Fig. 5(b) as a cross-section across the c -axis. Al–N bonds, indicated by black arrows, are characterized by large ELF values along the bonds suggesting directional polar covalent bonds consistent with sp^3 hybridization. In contrast, ELF contours are more isotropic and centered around Sc and neighboring N atoms, which is indicative of non-directional ionic bonds. We arrive at similar conclusions about the bonding nature when examining the ELF maps at other compositions.

The calculated Born effective charges (BECs) and Bader charges provide further evidence that Sc–N bonds are more ionic than Al–N bonds. The BECs of Al and N aggregated across the 8 compositions are presented in Fig. 5(c). There is a clear demarcation between Al and Sc BECs, with an average BEC of 2.62 ± 0.07 for Al and 3.03 ± 0.14 for Sc. BEC of Sc is closer to the formal charge of +3 while that of Al is much smaller than 3, again supporting the greater ionicity of Sc–N compared to polar

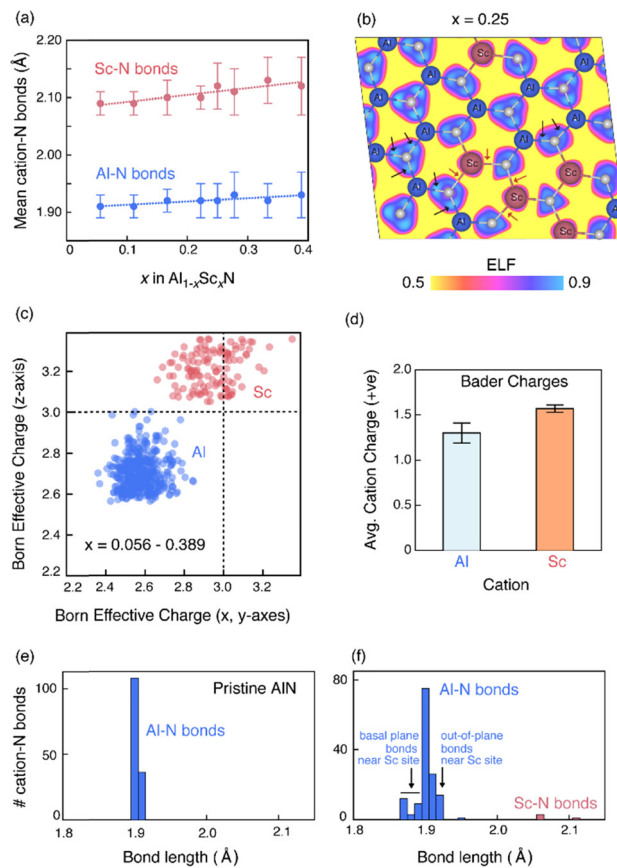


Fig. 5 Theoretical calculations of composition-dependent structural properties and local ionic distortions in $\text{Al}_{1-x}\text{Sc}_x\text{N}$: (a) average first nearest neighbor Al–N and Sc–N bond lengths as a function of composition x in DFT-relaxed SQS supercells. The errors bars are the standard deviations in the bond lengths. (b) Cross-sectional of isosurface of electron localization function (ELF) heat map computed at $x = 0.25$ composition. The black and red arrows point to representative Al–N and Sc–N bonds, respectively, showing the differences in ELF. (c) Calculated Born effective charges of Al and Sc aggregated across 8 different compositions in the range $x = 0.056$ – 0.389 . (d) Average Bader charges of Al and Sc (averaged across compositions). Error bars denote the standard deviation. The higher Bader charge of Sc is consistent with more ionic Sc–N bonds. (e) Histograms of bond lengths in pristine AlN and (f) dilute $\text{Al}_{1-x}\text{Sc}_x\text{N}$ alloy ($x = 0.028$) showing a wider distribution of Al–N bond lengths.

covalent Al–N bonds. Our calculations also show that Sc with an average Bader charge of 1.6 is more ionic than Al (~ 1.25). It has been previously argued that this well-known difference in the Bader charge^{59,60} and nominal charge is meaningful and reflects the degree of ionicity of the bond.⁵⁹ While both Al and Sc are cations in +3 formal oxidation states, the difference in their Bader charges (Sc 1.6 vs. Al 1.25) clearly indicates a difference in the Sc–N and Al–N bond ionicity.

2.5 Local bonding distortion hypothesis

To understand the effect of Al–N vs. Sc–N bonding differences on the local structure, we simulated dilute $\text{Al}_{1-x}\text{Sc}_x\text{N}$ alloys ($x = 0.028$) with 72-atom SQS supercells (see Methods) and relaxing the atomic positions with DFT while keeping the volume and cell shape fixed. In a dilute alloy, we ensure that



Al and Sc targets are located in a sputter-up configuration along the direction of the corners of the 2" Pt/TiO_x/SiO₂/Si substrate, resulting in orthogonal thickness and composition gradients (Fig. S6(b) in ESI†). Fig. S6(c and d) in ESI† show the thickness and composition map of the deposited film. The color is interpolated based on an array of discrete measurement points shown as white circles. The Sc content ranges from 0.25 to 0.5 across the *x* direction parallel to the Al and Sc target configuration, and film thickness varies between 140 and 260 nm across *y* direction, perpendicular to *x*. Other deposition conditions are as follows: 3 mtorr of Ar/N₂ (13.9/4.6 sccm flow), substrate temperature of 400 °C, 90 W on a 2" diameter Al target, and 98 W on a 2" diameter Sc target. The base pressure, partial oxygen and partial water vapor pressure at 400 °C are $< 5 \times 10^{-8}$ torr, $P_{O_2} < 2 \times 10^{-8}$ torr and $P_{H_2O} < 1 \times 10^{-8}$ torr, respectively.

4.2 Film characterization

The crystal structure of the film is investigated using X-ray diffraction (XRD) on Bruker D8 Discover and Panalytical Empyrean diffractometers. The lattice parameters are determined by pseudo-Voigt fitting of wurtzite 002 and 103 diffraction peaks (Fig. 1b and Fig. S1, ESI†) assuming a hexagonal lattice and taking into account the overlapped Au 220 diffraction peak. The cation composition is measured using X-ray fluorescence analysis calibrated with calibration standards and homogeneous Al_{0.7}Sc_{0.3}N and Al_{0.6}Sc_{0.4}N films. Cross-sectional transmission electron microscope (TEM) specimens were prepared by focused ion beam (FIB) in an FEI Nova NanoLab 200 dual beam FIB workstation using standard lift-out methods.⁷⁰ Final thinning of the TEM specimen was done in the FIB with a Ga+ beam energy of 5 kV and current of 41 pA. Cross-sectional TEM micrographs were acquired on a Philips CM30 TEM operated at 300 kV accelerating voltage. For electrical characterizations, top Au/Ti contacts are deposited on the film *via* electron beam evaporation through a shadow mask. Current–voltage (*I*–*V*) curves are measured using a bent probe whose gauge is ~300 μm contacting the bare surface of the library and a second probe contacting the exposed bottom Pt electrode. The applied voltage is a DC step function with delay time 0.1 s. Ferroelectric properties of the Au/Al_{1-x}Sc_xN/Pt stacks were collected using a Precision Multiferroic system from Radiant Technologies. High throughput data analysis is carried out using COMBigor,⁷¹ the files have been harvested using research data infrastructure (RDI),⁷² and will be made publicly available through High Throughput Experiment Materials Database (HTEM DB).⁷³

4.3 DFT calculation

Special quasirandom structures (SQS)⁷⁴ were used to model the wurtzite Al_{1-x}Sc_xN alloys at 8 different compositions in the range $x = 0.056$ – 0.389 . SQSs are constructed through a stochastic search over many possible configurations of local environments within the chosen supercell to best reproduce the pairwise correlation of random alloys. The SQS supercells at each composition were constructed with the Alloy Theoretic

Automated Toolkit (ATAT) code.⁷⁵ Following the methodology in a previous study,⁴³ we constructed 72-atom SQS supercells and performed structural relaxations (volume, cell shape, and atomic positions) with density functional theory (DFT). The DFT calculations were performed with the Vienna *Ab Initio* Software (VASP) package.⁷⁶ The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)⁷⁷ was used as the exchange–correlation functional with a plane-wave energy cutoff of 340 eV. The supercells were relaxed with Γ -centered *k*-point mesh. The electron localization function (ELF) and Bader charges were calculated on a dense *k*-mesh with a fixed number of *k*-points. The *k*-point grid is determined according to the equation $n_{kpts} \times n_{atoms} \approx 8000$, where n_{kpts} is the number of *k*-points and n_{atoms} is the number of atoms in the supercell. The Bader charges were calculated using the code developed by Henkelman and coworkers.⁷⁸ For calculating the Born effective charges, the SQS supercells were relaxed with stricter convergence criteria; a higher plane-wave energy cutoff of 520 eV and *k*-point grid corresponding to $n_{kpts} \times n_{atoms} \approx 2000$ was used. The structures were relaxed until the energies were converged to below 10^{-8} eV and forces below 0.005 eV Å⁻¹. Born effective charges were calculated with density functional perturbation theory, as implemented in VASP.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was co-authored by Colorado School of Mines and the National Renewable Energy Laboratory, operated by the Alliance for Sustainable Energy, LLC, for the US Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding was provided by the Office of Science (SC), Office of Basic Energy Sciences (BES) as part of the Early Career Award “Kinetic Synthesis of Metastable Nitrides” (material synthesis); and by the DARPA Tunable Ferroelectric Nitrides (TUFEN) program (DARPA-PA-19-04-03) as a part of Development and Exploration of FerroElectric Nitride Semiconductors (DEFENSE) project (structural and electrical characterization). K. Y., P. G., G. L. B., and A. Z. also acknowledge support for electrical measurements and theoretical calculations from NSF through the DMREF program award DMR-2119281. The data affiliated with this study are available from the corresponding author upon reasonable request. The views expressed in the article do not necessarily represent the views of the DOE or the US Government.

References

- 1 J. Valasek, *Phys. Rev.*, 1921, **17**, 475–481.
- 2 K. Uchino, *Ferroelectric Devices*, Marcel Dekker; New York, 2000.
- 3 I. Burn and D. M. Smyth, *J. Mater. Sci.*, 1972, **7**, 339–343.
- 4 P. Muralt, *J. Micromech. Microeng.*, 2000, **10**, 136–146.



- 5 H. A. Sodano, D. J. Inman and G. Park, *Shock Vib. Dig.*, 2004, **36**, 197–205.
- 6 M. DiDomenico and S. H. Wemple, *J. Appl. Phys.*, 1969, **40**, 720–734.
- 7 M. H. Lee, R. Guo and A. S. Bhalla, *J. Electroceram.*, 1998, **2**, 229–242.
- 8 J. F. Scott and C. A. Paz De Araujo, *Science*, 1989, **246**, 1400–1405.
- 9 S. Trolier-Mckinstry and P. Muralt, *J. Electroceram.*, 2004, **12**, 7–17.
- 10 R. Ramesh and N. A. Spaldin, *Nat. Mater.*, 2007, **6**, 21–29.
- 11 S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C. H. Yang, M. D. Rossell, P. Yu, Y. H. Chu, J. F. Scott, J. W. Ager, L. W. Martin and R. Ramesh, *Nat. Nanotechnol.*, 2010, **5**, 143–147.
- 12 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050–6051.
- 13 M. Hoffmann, F. P. G. Fengler, M. Herzig, T. Mittmann, B. Max, U. Schroeder, R. Negrea, L. Pintilie, S. Slesazek and T. Mikolajick, *Nature*, 2019, **565**, 464–467.
- 14 A. K. Yadav, C. T. Nelson, S. L. Hsu, Z. Hong, J. D. Clarkson, C. M. Schlepütz, A. R. Damodaran, P. Shafer, E. Arenholz, L. R. Dedon, D. Chen, A. Vishwanath, A. M. Minor, L. Q. Chen, J. F. Scott, L. W. Martin and R. Ramesh, *Nature*, 2016, **530**, 198–201.
- 15 C. Dai, V. A. Stoica, S. Das, Z. Hong, L. W. Martin, R. Ramesh, J. W. Freeland, H. Wen, V. Gopalan and L. Chen, *Adv. Mater.*, 2022, **34**, 2106401.
- 16 L. Qi, S. Ruan and Y. Zeng, *Adv. Mater.*, 2021, **33**, 2005098.
- 17 H. Ishiwara, Y. Aoyama, S. Okada, C. Shimamura and E. Tokumitsu, *Comput. Electr. Eng.*, 1997, **23**, 431–438.
- 18 S. Oh, H. Hwang and I. K. Yoo, *APL Mater.*, 2019, **7**, 091109.
- 19 Y. W. Fang, C. A. J. Fisher, A. Kuwabara, X. W. Shen, T. Ogawa, H. Moriwake, R. Huang and C. G. Duan, *Phys. Rev. B*, 2017, **95**, 014111.
- 20 S. Fichtner, N. Wolff, F. Lofink, L. Kienle and B. Wagner, *J. Appl. Phys.*, 2019, **125**, 114103.
- 21 C. Gui and S. Dong, *Phys. Rev. B*, 2020, **102**, 180103.
- 22 K. R. Talley, C. L. Perkins, D. R. Diercks, G. L. Brennecke and A. Zakutayev, *Science*, 2021, **374**, 1488–1491.
- 23 R. Sherbondy, R. W. Smaha, C. J. Bartel, M. E. Holtz, K. R. Talley, B. Levy-Wendt, C. L. Perkins, S. Eley, A. Zakutayev and G. L. Brennecke, *Chem. Mater.*, 2022, **34**, 6883–6893.
- 24 M. Akiyama, T. Kamohara, K. Kano, A. Teshigahara, Y. Takeuchi and N. Kawahara, *Adv. Mater.*, 2009, **21**, 593–596.
- 25 S. Yasuoka, T. Shimizu, A. Tateyama, M. Uehara, H. Yamada, M. Akiyama, Y. Hiranaga, Y. Cho and H. Funakubo, *J. Appl. Phys.*, 2020, **128**, 114103.
- 26 J. Hayden, M. D. Hossain, Y. Xiong, K. Ferri, W. Zhu, M. V. Imperatore, N. Giebink, S. Trolier-Mckinstry, I. Dabo and J. P. Maria, *Phys. Rev. Mater.*, 2021, **5**, 044412.
- 27 K. Yazawa, D. Drury, A. Zakutayev and G. L. Brennecke, *Appl. Phys. Lett.*, 2021, **118**, 162903.
- 28 S. Rassay, F. Hakim, C. Li, C. Forgey, N. Choudhary and R. Tabrizian, *Phys. Status Solidi RRL*, 2021, **15**, 2100087.
- 29 S. L. Tsai, T. Hoshii, H. Wakabayashi, K. Tsutsui, T. K. Chung, E. Y. Chang and K. Kakushima, *Jpn. J. Appl. Phys.*, 2021, **60**, SBBA05.
- 30 R. Mizutani, S. Yasuoka, T. Shiraishi, T. Shimizu, M. Uehara, H. Yamada, M. Akiyama, O. Sakata and H. Funakubo, *Appl. Phys. Express*, 2021, **14**, 105501.
- 31 S. Yasuoka, T. Shimizu, A. Tateyama, M. Uehara, H. Yamada, M. Akiyama and H. Funakubo, *Phys. Status Solidi A*, 2021, **218**, pssa.202100302.
- 32 R. C. Pullar, in *Springer Series in Materials Science*, Springer Verlag, 2015, vol. 225, pp. 241–270.
- 33 M. L. Green, I. Takeuchi and J. R. Hattrick-Simpers, *J. Appl. Phys.*, 2013, **113**, 231101.
- 34 I. Takeuchi, H. Chang, C. Gao, P. G. Schultz, X. D. Xiang, R. P. Sharma, M. J. Downes and T. Venkatesan, *Appl. Phys. Lett.*, 1998, **73**, 894–896.
- 35 H. Chang, C. Gao, I. Takeuchi, Y. Yoo, J. Wang, P. G. Schultz, X. D. Xiang, R. P. Sharma, M. Downes and T. Venkatesan, *Appl. Phys. Lett.*, 1998, **72**, 2185–2187.
- 36 M. Murase, T. Yoshimura and N. Fujimura, *Jpn. J. Appl. Phys.*, 2020, **59**, SPPC05.
- 37 S. Fujino, M. Murakami, V. Anbusathaiah, S. H. Lim, V. Nagarajan, C. J. Fennie, M. Wuttig, L. Salamanca-Riba and I. Takeuchi, *Appl. Phys. Lett.*, 2008, **92**, 202904.
- 38 D. Kan, R. Suchoski, S. Fujino and I. Takeuchi, in *Integrated Ferroelectrics*, Taylor & Francis Group; 2009, vol. 111, pp. 116–124.
- 39 K. W. Kim, M. K. Jeon, K. S. Oh, T. S. Kim, Y. S. Kim and S. I. Woo, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 1134–1139.
- 40 M. Sasaki, S. Ju, Y. Xu, J. Shiomi and M. Goto, *ACS Comb. Sci.*, 2020, **22**, 782–790.
- 41 D. Solonenko, C. Lan, C. Schmidt, C. Stoeckel, K. Hiller and D. R. T. Zahn, *J. Mater. Sci.*, 2020, **55**, 17061–17071.
- 42 D. Drury, K. Yazawa, A. Mis, K. Talley, A. Zakutayev and G. L. Brennecke, *Phys. Status Solidi RRL*, 2021, **15**, 2100043.
- 43 K. R. Talley, S. L. Millican, J. Mangum, S. Siol, C. B. Musgrave, B. Gorman, A. M. Holder, A. Zakutayev and G. L. Brennecke, *Phys. Rev. Mater.*, 2018, **2**, 063802.
- 44 K. Furuta, K. Hirata, S. A. Anggraini, M. Akiyama, M. Uehara and H. Yamada, *J. Appl. Phys.*, 2021, **130**, 024104.
- 45 Y. Lu, M. Reusch, N. Kurz, A. Ding, T. Christoph, M. Prescher, L. Kirste, O. Ambacher and A. Žukauskaitė, *APL Mater.*, 2018, **6**, 076105.
- 46 G. Arlt, *Ferroelectrics*, 1990, **104**, 217–227.
- 47 C. A. Randall, N. Kim, J.-P. Kucera, W. Cao and T. R. Shrout, *J. Am. Ceram. Soc.*, 1998, **81**, 677–688.
- 48 F. Xu, S. Trolier-Mckinstry, W. Ren, B. Xu, Z.-L. Xie and K. J. Hemker, *J. Appl. Phys.*, 2001, **89**, 1336–1348.
- 49 K. Yazawa, H. Uchida and J. E. Blendell, *Adv. Funct. Mater.*, 2020, **30**, 1909100.
- 50 S. Yang, J. Li, Y. Liu, M. Wang, L. Qiao, X. Gao, Y. Chang, H. Du, Z. Xu, S. Zhang and F. Li, *Nat. Commun.*, 2021, **12**, 1–10.
- 51 D. Gall, M. Städele, K. Järrendahl, I. Petrov, P. Desjardins, R. T. Haasch, T. Y. Lee and J. E. Greene, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 1251191–1251199.



- 52 H. A. Al-Britthen, H. Yang and A. R. Smith, *J. Appl. Phys.*, 2004, **96**, 3787–3792.
- 53 S. Y. Yang, F. Zavaliche, L. Mohaddes-Ardabili, V. Vaithyanathan, D. G. Schlom, Y. J. Lee, Y. H. Chu, M. P. Cruz, Q. Zhan, T. Zhao and R. Ramesh, *Appl. Phys. Lett.*, 2005, **87**, 102903.
- 54 H. Naganuma, Y. Inoue and S. Okamura, *Appl. Phys. Express*, 2008, **1**, 0616011–0616013.
- 55 J. F. Scott, *Integr. Ferroelectr.*, 1996, **12**, 71–81.
- 56 K. Yazawa, A. Zakutayev and G. L. Brennecke, *Appl. Phys. Lett.*, 2022, **121**, 042902.
- 57 I. W. Chen, *J. Phys. Chem. Solids*, 2000, **61**, 197–208.
- 58 L. Pauling, *J. Am. Chem. Soc.*, 1932, **54**, 3570–3582.
- 59 N. Mammen, L. Spanu, E. C. Tyo, B. Yang, A. Halder, S. Seifert, M. J. Pellin, S. Vajda and S. Narasimhan, *J. Phys.: Condens. Matter*, 2019, **31**, 144002.
- 60 J. P. Allen, D. O. Scanlon and G. W. Watson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 161103.
- 61 H. Moriwake, R. Yokoi, A. Taguchi, T. Ogawa, C. A. J. Fisher, A. Kuwabara, Y. Sato, T. Shimizu, Y. Hamasaki, H. Takashima and M. Itoh, *APL Mater.*, 2020, **8**, 121102.
- 62 N. A. Spaldin, *J. Solid State Chem.*, 2012, **195**, 2–10.
- 63 C. E. Dreyer, A. Janotti, C. G. Van de Walle and D. Vanderbilt, *Phys. Rev. X*, 2016, **6**, 021038.
- 64 O. Ambacher, B. Christian, N. Feil, D. F. Urban, C. Elsässer, M. Prescher and L. Kirste, *J. Appl. Phys.*, 2021, **130**, 045102.
- 65 H. Wang, N. Adamski, S. Mu and C. G. Van de Walle, *J. Appl. Phys.*, 2021, **130**, 104101.
- 66 M. A. Caro, S. Zhang, T. Riekkinen, M. Ylilammi, M. A. Moram, O. Lopez-Acevedo, J. Molarius and T. Laurila, *J. Phys.: Condens. Matter*, 2015, **27**, 245901.
- 67 K. Ferri, S. Bachu, W. Zhu, M. Imperatore, J. Hayden, N. Alem, N. Giebink, S. Trolier-McKinstry and J.-P. Maria, *J. Appl. Phys.*, 2021, **130**, 044101.
- 68 J. Jia and T. Yanagitani, *Phys. Rev. Appl.*, 2021, **16**, 044009.
- 69 K. Hirata, Y. Mori, H. Yamada, M. Uehara, S. A. Anggraini and M. Akiyama, *Materials*, 2021, **14**, 309.
- 70 L. A. Giannuzzi, J. L. Drown, S. R. Brown, R. B. Irwin and F. A. Stevie, in *Materials Research Society Symposium - Proceedings*, MRS; 1997, vol. 480, pp. 19–27.
- 71 K. R. Talley, S. R. Bauers, C. L. Melamed, M. C. Papac, K. N. Heinselman, I. Khan, D. M. Roberts, V. Jacobson, A. Mis, G. L. Brennecke, J. D. Perkins and A. Zakutayev, *ACS Comb. Sci.*, 2019, **21**, 537–547.
- 72 K. R. Talley, R. White, N. Wunder, M. Eash, M. Schwarting, D. Evenson, J. D. Perkins, W. Tumas, K. Munch, C. Phillips and A. Zakutayev, *Patterns*, 2021, **2**, 100373.
- 73 A. Zakutayev, N. Wunder, M. Schwarting, J. D. Perkins, R. White, K. Munch, W. Tumas and C. Phillips, *Sci. Data*, 2018, **5**, 1–12.
- 74 A. Zunger, S. H. Wei, L. G. Ferreira and J. E. Bernard, *Phys. Rev. Lett.*, 1990, **65**, 353–356.
- 75 A. van de Walle, *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, 2009, **33**, 266–278.
- 76 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 77 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 78 W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens. Matter*, 2009, **21**, 7.

