

Thermal Conductivity and Optical Phonon Scattering of CMOS Compatible Aluminum Nitride-Based Ferroelectric Thin Films

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
See attachment

Reviewer #2

(Remarks to the Author)
Review report of "Thermal Conductivity and Optical Phonon Scattering of CMOS Compatible Aluminum Nitride-Based Ferroelectric Thin Films" by Makarem et al.

The authors investigate the effect of doping on the thermal transport and polarization of AlN-based ferroelectric thin films of Al_{1-x}B_xN and Al_{1-x}yB_xScyN using TDTR, IR-VASE, and picosecond ultrasonics. The authors argue that doping at concentrations above a threshold activates the silent B1 mode and facilitates polarization switching. Thermal transport remains controlled by phono-phonon scattering at low dopant concentration, but becomes impurity-dominated at intermediate concentrations. Thickness-dependent total thermal resistance measurements show a monotonic decrease, highlighting that dominant phonon mean free paths are below the lowest measured thickness value.

The author wants to emphasize that while doping may reduce the coercive field in this family, it also reduces thermal conductivity, which is not good for memory devices. The Al_{1-x}B_xN and Al_{1-x}yB_xScyN family, as the authors state, offers a relatively ideal combination of thermal conductivity and remnant polarization. The above conclusion is ok, but the discussion of the data is not well supported. Below are some of the major comments:

1. It is now well established in the literature that all modes, with different frequencies and group velocities, contribute to thermal conductivity. Measuring the lifetime of a single optical phonon (generally, their contribution is relatively low due to lower group velocity and shorter lifetimes) should not be taken as a definitive indicator of thermal conductivity.
2. I am unconvinced that the new mode that appears with the added doping concentration or increased thickness is of B1 symmetry. At high doping levels, localized vibrations of the B atom may also give rise to a new mode. For example, due to the heavy dopant (here, it is lighter), the resonance mode is observed experimentally in the FeSi system [Phys. Rev. B 91, 094307, 2015]. Absence of B1 symmetry mode in Al_{1-x}yB_xScyN further suggests that the B1 mode is not symmetry broken but rather from resonance. The existing discussion, which takes examples of N-doped ZnO and In_{1-x}GaxN alloys, is not convincing. Direct evidence is necessary.
3. The authors claim that "The emergence of the B1 phonon mode provides a compelling structural explanation for the enhanced ferroelectric behavior observed in Al_{1-x}B_xN films at intermediate boron concentrations" and "The appearance of this otherwise silent branch reflects symmetry breaking and disorder in the wurtzite lattice, where uncompensated antiparallel displacements endow the B1 vibrations with polar character". But the above claim has no supporting evidence. The authors do not show how uncompensated displacements relate to the B1 mode or how they directly correlate with ferroelectric behavior. The cited Ref. 61 talks about the role of weakened bond strength and enhanced Born effective charges, rather than the B1 mode.
4. The temperature-dependent thermal conductivity of alloys is characterized into three different scattering regimes as a function of dopant concentration. For dopant concentration < 5%, we see the effect of temperature-dependent phonon-

phonon scattering. For midrange (6%-25%) phonon-impurity scattering dominates, and there is no significant temperature dependence. However, at high concentrations (>25%), the increase in thermal conductivity with temperature is attributed to increasing heat capacity. At high concentrations, the authors should measure the heat capacity and show that the heat capacity of $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$ ($x = 33\%$ and $y = 20\%$) increases by nearly 50%, leading to an increase in thermal conductivity. Is it possible that at high concentrations, the composition is semi-metallic or metallic-like?

5. Thermal transport in 10-199 nm thick $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ films is characterized as diffusive, based on the observation that thermal resistance increases with thickness. However, in the quasi-ballistic regime, phonon lifetime, thermal conductivity, and total resistance can increase simultaneously with thickness. In a diffusive regime, the resistance would increase approximately linearly with thickness. Hence, the argument that measurements are in a diffusive regime needs to be re-examined.

Minor comments in supplementary information:

6. Q4. In Figure S3, the quantity plotted in contour maps is not stated. It means the mean squared error. A clarification is necessary.

7. Q5. On line 126 of the SI, the thickness of the transducer and its thermal conductivity are treated as independent variables with 5% uncertainty in both. However, if the thermal conductivity of the transducer is obtained from 4-point probe measurements, they are not independent. A clarification is necessary.

8. Q6. On line 127 in SI, the boundary resistance between film and substrate is also assigned a 5% uncertainty. However, it is a fitted parameter and not an input variable in the thermal model. A clarification is necessary.

Based on the above, I am unable to recommend the manuscript for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

The authors present detailed measurements of thermal conductivity and optical phonon lifetimes in AlN thin films with varying doping concentrations, utilizing time-domain thermoreflectance (TDTR) and infrared variable angle spectroscopic ellipsometry (IR-VASE). The activation of nominally silent B_1 modes is confirmed and interpreted as a signature of crystal symmetry breaking. The authors further claim a linear correlation between optical phonon lifetimes and measured thermal conductivity at room temperature. The work demonstrates reduced coercive fields associated with atomic disorder and the suppression of lattice thermal conductivity. However, the following issues must be addressed prior to publication:

Clarification is needed regarding whether the measured thermal conductivity represents in-plane or cross-plane values. At minimum, for the thinnest films (~13 nm), the lattice thermal conductivity is expected to be anisotropic. Please specify the measurement geometry and discuss potential anisotropy effects.

The Slack model is employed to explain the high thermal conductivity of AlN. However, significant advances have been made in high-thermal-conductivity material research, and the Slack model may not be appropriate for doped AlN given that the lattice structure is no longer simple upon alloying. Have the authors considered first-principles calculations (e.g., density functional theory) to accurately explain the high thermal conductivity of AlN? Relevant computational studies should be cited and discussed.

The manuscript states: "The structural perturbations introduced by boron and scandium doping serve as potent scattering centers, disrupting phonon coherence and severely limiting phonon transport." What specific physical meaning does "phonon coherence" denote in this context? Furthermore, what is the quantitative or qualitative relationship between phonon coherence and phonon transport efficiency?

Regarding the claim: "The hardening of the $E_1(\text{TO})$ mode indicates an overall lattice compression, likely arising from mass and bonding perturbations introduced by boron substitution, given its smaller atomic size compared to Al." Please provide additional experimental or computational evidence (e.g., X-ray diffraction data, lattice parameter calculations) to substantiate this assertion.

Concerning the statement: "...suggesting that optical phonon lifetimes can serve as an effective proxy for predicting thermal transport in these materials"—is this correlation expected to be universally applicable across material classes, or is it specific to this particular system? The reviewer notes that acoustic phonon lifetimes are generally considered more directly relevant to thermal conductivity than optical phonon lifetimes. Please clarify the rationale behind using optical phonon lifetimes as the predictive metric.

In Figures 2b and 2d, the experimental data points appear distributed above and below the dashed trend lines, respectively. Please explain the physical origin or statistical significance of these apparent systematic deviations.

The statement: "As shown in the inset of Fig. 2(b), the linear correlation is restored when only the E_1 mode lifetimes are considered, suggesting that the participation of B_1 modes in thermal transport does not change with concentration" requires clarification. Does this imply that B_1 modes contribute a constant offset to thermal conductivity regardless of doping concentration? Please elaborate on the interpretation.

The authors state: "As the temperature increases, additional phonon modes become thermally excited, and the range of phonons contributing to thermal conduction broadens in energy, causing the thermal conductivity to follow the temperature-dependent trends of heat capacity." Please provide additional experimental evidence or theoretical justification to solidify this conclusion.

Regarding: "In this regime, the crystal quality degrades to the extent that the vibrational eigenstates lose the periodic boundary conditions necessary to support symmetry-broken mode activation." Please provide the intensity ratio between the B_1 mode and the primary Raman-active mode for the 199 nm thickness sample. Additionally, when the thickness decreases to 30 nm, does the B_1 peak completely disappear or merely fall into the noise floor? This distinction is crucial for understanding the symmetry-breaking mechanism.

Both the Slack model and the kinetic theory expression $\kappa = (1/3)Cv\ell$ are relatively simple models that may be insufficient to capture the complex trends observed experimentally, particularly in doped systems with disorder-induced scattering. The

authors should discuss the limitations of these models or consider more sophisticated theoretical frameworks (e.g., Boltzmann transport equation with first-principles inputs).

Terminology consistency: "Phonon velocity" should be corrected to "phonon group velocity".

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have sufficiently addressed my comments and concerns. The data presented seems sound and the data plotting error was corrected. The conclusions and main take aways from their experimental data are appropriately presented now keeping a clear line between definitive claims and speculative claims that require more modeling, simulation or data.

Reviewer #2

(Remarks to the Author)

The authors have reasonably well addressed the critique, and I am largely satisfied with the response. I recommend the manuscript for publication.

Reviewer #3

(Remarks to the Author)

The authors have satisfactorily addressed all of my concerns. I have no further comments and recommend the manuscript for publication.

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

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We thank the Editor and Reviewers for their careful reading of the manuscript and for their constructive comments, which have aided in our revising our manuscript to result in a stronger version. We have made significant updates on our optical response analysis along with thermal conductivity measurement fittings and data analysis. Below, the Reviewers' comments are reproduced in bold, and our responses follows each comment, together with the specific revisions that we have made in the manuscript and Supporting Information.

Reviewer #1

Comment:

Thank you for the opportunity to review the manuscript “Thermal Conductivity and Optical Phonon Scattering of CMOS Compatible Aluminum Nitride-Based Ferroelectric Thin Films” by Makarem et al. I very much enjoyed reading it. They present a very well thought out and well executed data set on a relevant materials system.

I will say from the beginning that this is my first experience with IR-VASE data so I am unable to review the experimental details of that specific part of the paper. With that said, here is a point-by-point review of the rest of the paper. The experimental methodology as described is sound and meets the expected standards of the field, though I do note a possible small data error described below. I do disagree with some of the conclusions and claims made about the data as you will read below. Nonetheless, these experimental data contain several interesting, informative and important findings that could help guide implementation of this technology. I would imagine teams running FEA thermal models of next generation memory devices based on AlN would be interested in even just the raw data reported.

Broad impact on technology

While the paper includes a nice introduction, it is still unclear to me whether the decrease in κ shown here is a deal breaker for these materials in real technological applications. The paper would be greatly improved if the authors referenced real numbers regarding the usage of the next generation memory devices referenced, such as:

- What is the standard operating currents (or current densities) targeted for any of the next generation memory devices referenced.**
- How the thermal heating at these target currents is expected to be impacted by the change in electrical and thermal conductivities of the active material. Is there a critical temperature above which any of these next generation memories will not operate.**

A focus on questions of this nature is critical to keep the field focused on moving applications of these promising technologies forward. With the reference to CMOS in the title, I expected a more targeted technology-driven intro.

Response:

We thank the reviewer for this helpful suggestion. We agree that the introduction should more directly connect our measured thermal properties to device-level operation. In the revised manuscript, we add a paragraph that explains why thermal conductivity and thermal boundary resistance are relevant for nitride ferroelectric memory, especially because AlN-based wurtzite ferroelectrics combine large remanent polarization with relatively large coercive fields [1-6]. The dissipated electrical energy during polarization reversal is determined by the area of the polarization-electric field loop, with additional contributions from leakage and electrode or channel losses. These losses generate heat in a film whose thickness is often selected by voltage scaling rather than by thermal design [1,7-10].

We have not inserted one standard operating current density because a single number is not transferable across capacitor FeRAM, FeFETs, ferroelectric tunnel junctions, and diode-like stacks. In a ferroelectric capacitor, the switching current density depends on electrode area, pulse width, rise time, and dP/dt , while the energy loss is more directly obtained from the PE loop and leakage current.

In FeFETs, heat can also be generated in the channel and contacts. A universal current density could potentially be misleading. Instead, the revised introduction identifies the material and stack quantities that control self-heating: coercive field, remanent polarization, leakage current, film thickness, cross-plane thermal conductivity, and the thermal boundary conductance of the adjacent interfaces.

We also now state that there is not a single critical temperature above which all nitride ferroelectric memories fail. The relevant limit is architecture and material dependent, because temperature affects leakage, coercive field, retention, fatigue, electrode reactions, and backend thermal budgets. Prior work shows strongly temperature-dependent switching in AlN, AlScN, and AlBN films [11], while recent AlBN device-level thermal simulations show that self-heating and array thermal crosstalk can be severe for nanoscale FeRAM operation [4]. These points justify the central message of the paper: the measured decrease in κ is not automatically a deal breaker, but it is a first-order design constraint for memory-cell thermal engineering.

Revision to the manuscript:

We have added the following text to the introduction on page 2:

"These constraints are particularly important for wurtzite nitride ferroelectrics, which combine large remanent polarization with coercive fields that are often in the MV cm⁻¹ range [1-6,11]. Reaching low switching voltages therefore requires nanoscale active layers, while the energy dissipated during reversal is set by the area of the polarization-electric field loop with additional contributions from leakage, electrode resistance, and, in transistor geometries, channel current. A single operating current density is not transferable across capacitor FeRAM, FeFET, and tunnel-junction architectures; instead, the relevant thermal design parameters are the switching energy density, leakage, active-layer thickness, cross-plane thermal conductivity, and the thermal boundary resistances of the adjacent interfaces. Because leakage and switching kinetics are temperature dependent [11], and because array-level thermal crosstalk can exceed single-bit heating in nanoscale AlBN memory simulations [4], the measured decrease in thermal conductivity with alloying is not merely a materials-property trend but a device-level reliability and voltage-scaling constraint."

Comment:

κ , speed of sound, and lifetime data

The authors are disregarding the decrease in LA speed of sound (SoS) too quickly. From DFT based lattice dynamics or textbook analytical equations we have a relationship of $\kappa \approx A\nu^3$ when phonon-phonon scattering dominates and we are above the Debye temp. The representation given in the text of $\kappa = 1/3C\nu l$ is misleading since when one carries the calculation through, one does not get a $\kappa \propto \nu$ relationship. When one appreciates the cubic dependence, an 18% decrease in SoS may lead to a 45% decrease in κ .

Response:

We appreciate the reviewer's thorough analysis of these analytical expressions for phonon thermal conductivity. The high temperature Slack/Leibfried-Schlomann expressions for thermal conductivity do indeed give a simplified and straight forward representation of thermal conductivity as a function of Debye speed, as the ν^3 term in these expressions comes from the Debye temperature. And we also agree that by presenting only the Kinetic Theory expression for thermal conductivity and not this Slack/Leibfried-Schlomann expression, we leave an open question as to the origin of the reduction in thermal conductivity of AlBN that we observe in our measurements.

As you point out, this high temperature analytical expression for phonon thermal conductivity is valid above the Debye temperature, and, more importantly, when phonon-phonon scattering dominates the thermal transport processes. In the case of the films studied in this manuscript, we satisfy neither of these criteria. Our thermal conductivity measurements are conducted from room temperature to 400

deg. C (~673 K), where the Debye temperature of AlN is ~875 deg. C (~1,150 K), so our measurements are restricted to just over 1/2 of the Debye temperature. Additionally, as demonstrated from both the change in temperature dependence of the thermal conductivity and TO phonon lifetime, the trends in these values changes from an inverse dependence with temperature to approximately temperature independent. This is indicative of a transition from phonon-phonon scattering to phonon-impurity scattering, as discussed in various textbooks. Thus, these results point to the fact that phonon-impurity scattering (i.e., rooted from the inclusion of boron) dominates the reductions in thermal conductivity that we are observing with increased boron composition in the AIBN films.

This said, we use the reviewer's estimate as a transparent sensitivity check. An 18% decrease in velocity gives a reduction of approximately 45% under a v^3 scaling. This is substantial, but it remains smaller than the nearly 90% decrease in thermal conductivity across the AIBN series.

Revision to the manuscript:

With this, however, the reviewer's comment and insight is extremely important to discuss in our manuscript, and thus, we have added the following discussion to *page 5* of the revised manuscript:

"As shown in Fig. 1(d), the cross plane longitudinal sound velocity decreases by ~18% as the total dopant concentration increases from 1% to 33%. This decrease is not negligible because acoustic velocity enters both the harmonic spectrum and intrinsic scattering rates. In Debye Slack descriptions, these combined effects can yield an approximate κ proportional to v^3 sensitivity, although that limit assumes a branch averaged velocity and predominantly intrinsic phonon phonon scattering. The present measurement resolves only the cross plane longitudinal branch, and the measurement temperatures remain below the Debye temperature of crystalline AlN. Even when the v^3 relation is used as a sensitivity estimate, the measured velocity decrease corresponds to a conductivity reduction of ~45%, which is smaller than the nearly 90% decrease measured across the AIBN series. The remaining suppression therefore requires a substantial reduction in phonon mean free path from alloy, defect, and microstructural scattering."

Comment:

We do not expect much thermal energy to be carried by the TO modes. Therefore, I disagree with the statement that "optical phonon lifetimes can serve as an effective proxy for predicting thermal transport in these materials". There would need to be some argument for why the authors believe the optical lifetimes are tied to modes relevant for thermal conductivity. The authors show hardening of the E1(TO) mode along with the decrease in LA speed of sound, so for that property the two trends point in different directions.

Response:

We completely agree with the reviewer's comment that heat is not *carried* by the TO modes; we emphasize *carried*. Indeed, the higher velocity modes will "move" the energy through the material. However, this heat transfer is then limited by phonon scattering of different varieties. So for example, while an acoustic mode may be able to transfer energy to different locations in a material at some speed that is much higher than the TO (or any optical) mode, ultimately the distance (mean free path) that these acoustic modes can travel before their energy and momentum being redistributed will be limited by either scattering with another phonon (phonon-phonon scattering), or scattering with an impurity or defect in the crystal (phonon-impurity scattering).

Lindsay *et al.* discuss this in detail in their 2013 work (*Phys. Rev. B* **87**, 165201) [12], where they say, "We note that the importance of optic phonon scattering of heat-carrying acoustic phonons has been previously discussed in a number of papers, including Refs. 11, 15–17, 22, 28, 29, 51, and 54." These refs are: *Phys. Rev. B* **86**, 115203 [13]; *Phys. Rev. B* **85**, 184303 [14]; *Phys. Rev. Lett.* **109**, 095901 [15]; *Phys. Rev. B* **86**, 174307 [16]; *Phys. Rev. B* **82**, 161402(R) [17]; *Phys. Rev. B* **53**, 9064 [18]; *Nuovo Cimento Soc. Ital. Fis., D* **19**, 1537 [19]; *Phys. Rev.* **141**, 767 [20]; *Phys. Rev. B* **77**, 180302 (R) [21]. Further, in *Phys. Rev. B* **77**, 180302 (R) [21], conclude that "In summary, we have

demonstrated that, in contrast to the commonly accepted view, the optical phonon has an indirect, yet fundamental role, in thermal conductivity in semiconductors. We have illustrated our model with reference to set of AlN single crystals with different point defects densities and an excellent agreement with our experimental results, as well as with previously reported data, could be obtained.” And the aforementioned work by Lindsay *et al.* specifically state: “ Here, we show that the coupling of acoustic and optic phonons reduces the [lattice thermal conductivity] for the systems studied here [in reference to AlN].” Thus, the wealth of prior studies demonstrate that optical phonons indirectly impact thermal conductivity through scattering with acoustic phonons. Additionally, since phonon-defect scattering typically follows a quartic frequency dependence, the high frequency optical phonon models also readily scatter with crystal defects (e.g., in this case, defects that arise from the inclusion of boron in the AlBN).

Additionally, we have specifically studied this effect in AlN thin films of different thicknesses grown on sapphire (*Appl. Phys. Lett.* **125**, 262201) [22]. Specifically, in this work we measured the thermal conductance of AlN films with thicknesses from 1.6 - 2,440 nm demonstrating an increase in apparent thermal conductivity due to changes in the phonon scattering mechanisms (crystal quality, boundary, and phonon-phonon scattering). We used IR-VASE to monitor the anisotropic optical phonon mode lifetime in these films and demonstrated a trend of increase in phonon lifetime with thicknesses that followed the trend in thermal conductivity vs. thickness, further supporting our approach to use optical phonon lifetimes as a monitor of how the thermal conductivity of the film changes.

This said, we agree with the review in that the terminology that we have used in our manuscript to describe this correlation could be confusing. Specifically, optical phonon lifetimes are not related to the heat transport (i.e., the heat flux that is driven by acoustic phonons), but instead, the changes in optical phonon lifetimes can serve as an effective proxy to monitor the changes in the dominant phonon scattering rates and thus correlate to changes in thermal resistance of the films, which correlated to changes in thermal conductivity. We appreciate the reviewer highlighting our potentially confusing terminology.

Revision to the manuscript:

We have added the following discussion to page 8:

"The measured A1(TO) lifetime is not interpreted as the lifetime of the modes that dominate lattice heat conduction. Mode-resolved calculations and measurements on AlN show that most heat is carried by acoustic branches, while optical modes can influence thermal conductivity indirectly through acoustic-optic scattering and through their sensitivity to the same defect landscape that scatters heat-carrying modes [12,21,23-25]. In the present alloy series, the cross-plane A1(TO) linewidth provides a spectroscopic measure of disorder-induced vibrational damping. Its monotonic covariation with TDTR-measured cross-plane thermal conductivity should therefore be interpreted as a system-specific proxy for the strength of phonon scattering in AlBN and AlBScN, not as a universal conversion from optical phonon lifetime to thermal conductivity."

We have also updated Fig. 2 of the manuscript as follows:

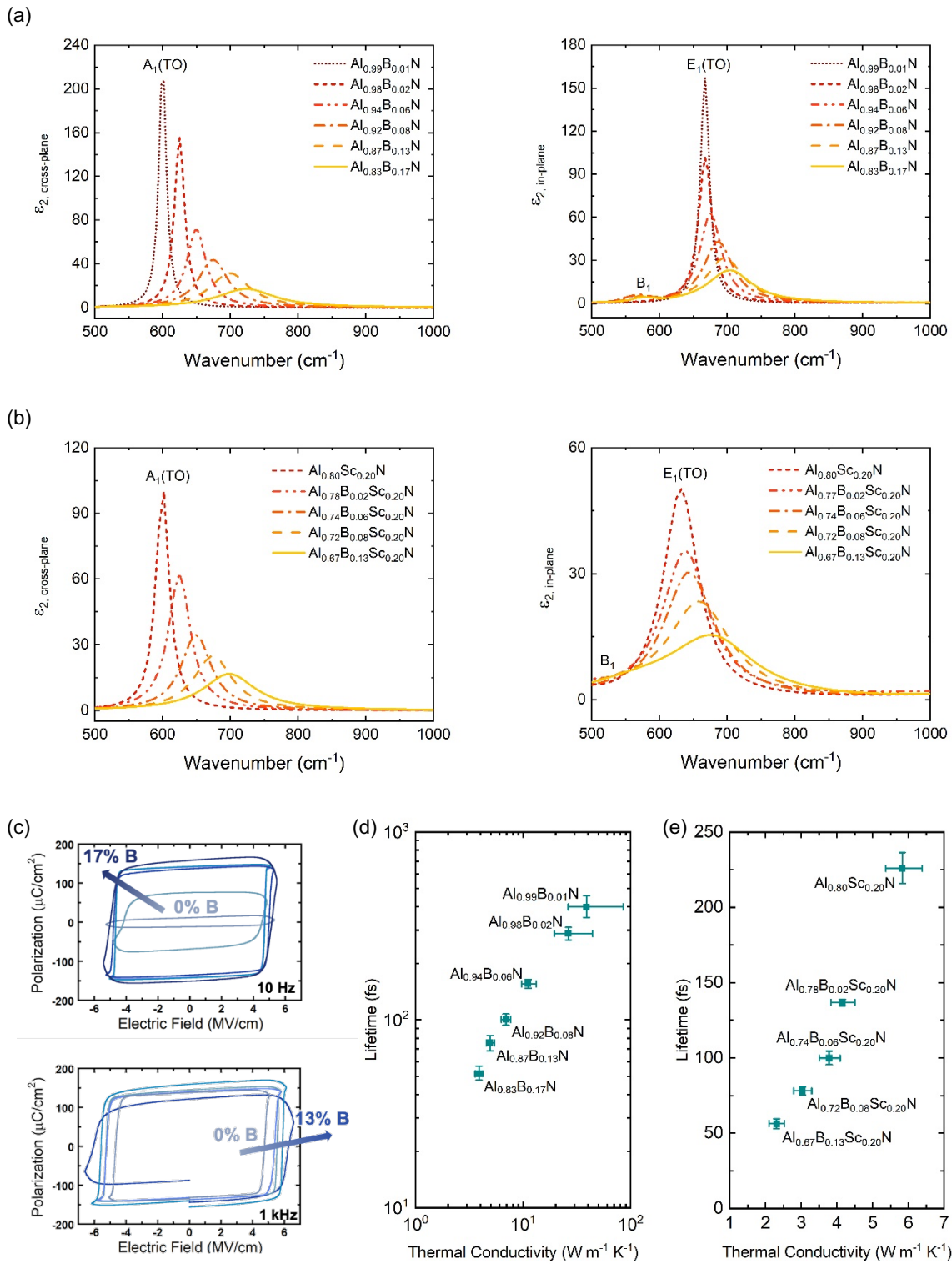


Figure 1 Imaginary parts of anisotropic infrared dielectric responses of (a) Al_{1-x}B_xN and (b) Al_{1-x-y}B_xSc_yN. Strong peaks in the in-plane and cross-plane imaginary parts correspond to A₁ and E₁ transverse optical phonon modes, respectively. The in-plane response includes the disorder-activated B₁ feature in the range of 500-600 cm⁻¹. The optical modes of the ferroelectrics with higher dopant concentration are broader, indicating greater anharmonicity from defect scattering. (c) Polarization hysteresis progression of ~200 nm Al_{1-x}B_xN (top) and Al_{1-x-y}B_xSc_yN films (bottom) with increasing B composition. (d,e) Thermal conductivity versus cross-plane A₁(TO) phonon lifetime of (d) Al_{1-x}B_xN and (e) Al_{1-x-y}B_xSc_yN. A linear correlation is observed between the extracted phonon lifetimes and independently measured room-temperature thermal conductivities. Increasing boron and scandium content broadens the phonon resonances, shortens the extracted lifetimes, and suppresses thermal conductivity.

Comment:

The authors report a relationship between decreased κ , decreased LA speed of sound, and decreased TO lifetime. We know from standard DFT based lattice dynamics, as well as textbook analytical thermal conductivity modeling, that thermal transport is dominated by acoustic modes. Therefore, the argument the authors can make with their data is that, for Al_{1-x}B_xN, adding B decreases the group velocities in the acoustic branches. If we take the decrease in LA sound speed as a proxy for transverse branches, this accounts for the decrease from about 30 to about 21 W/mK. The authors then observe a broadening of the TO mode, and while one would not expect that to directly decrease κ , it is an indication of the further phonon scattering introduced, which likely accounts for the remaining decrease in κ from about 21 to about 4 W/mK. In the Al_{1-x}B_xSc_{0.2}N system, virtually no acoustic softening is observed and the Sc point defect scattering dominates any additional B point defect scattering introduced. Another interesting story is that longitudinal sound speed decreases when substituting a lighter B for a heavier Al, particularly in Al_{1-x}B_xN. One might expect this trend to go the other way.

Response:

The reviewer is correct that this trend is rather counter-intuitive. However, something we must emphasize is that the uncertainty in our SoS measurements is quite large, and thus we cannot conclude that the SoS is changing at all for any of the films based on these measurements. We appreciate the reviewer highlighting this point, since we must clearly discuss the uncertainty and be clear about what we can conclude, which we do in our revisions.

This said, as the reviewer points out, it is very important for us to discuss the changes in the AIBN films' density and how it relates to our measured SoS and thermal conductivity. Indeed, there are a few competing factors that happen when boron is added to AlN. First, the light mass of the boron should reduce the density of the film. However, as boron is incorporated into the AlN wurtzite lattice, the unit cell decreases, by nearly 10% for ~15% boron in AIBN, as reported by Hayden *et al.* (*Phys. Rev. Mat.* **5**, 044412) [2]. Thus, with ~15% B incorporation, the ~10% reduction in average mass (averaged between Al and B) and the ~10% reduction in unit cell volume effectively cancel out, thus leading to a negligible change in atomic density in the AIBN films. Further, we note that as reported in the aforementioned Hayden *et al.* work, the unit cell volume linearly changes with addition of boron, thus we expect the average density of the AIBN films to remain relatively unchanged with increasing boron composition.

Now the sound speed should scale as the square root of modulus divided by density. Technically, we are measuring only the longitudinal speed of sound, and thus the sound speed should scale with C₁₁. So, if the density is unchanged, as per our discussion above, then the changes in stiffness should dictate change in sound speed, as the reviewer points out. To a rough approximation, if we then assume that the stiffening of the TO mode is indicative of an increase in C₁₁, then C₁₁ would increase by ~7% (as calculated by taking the ratio of TO mode energies). From this, assuming the sound speed is the square root of C₁₁ divided by density, we would only expect a 3% increase in sound speed. This change is not possible of being resolved in our SoS measurements with picosecond ultrasonics, as indicative of the nearly 10% error bars in our SoS measurements.

We very much appreciate the reviewer in bringing up this point, as we believe a discussion about this is warranted in the document. To this end, we have revised the discussion in the manuscript to read:

Revision to the manuscript:

We have added the following discussion to page 5:

"We note that substituting lighter B for Al might be expected to increase acoustic velocity, but B incorporation also contracts the wurtzite unit cell and modifies the elastic constants [2-3]. Because the

density depends on both average mass and unit-cell volume, these effects can partially compensate. The measured picosecond-acoustic velocity also probes only the cross-plane longitudinal branch and has uncertainties that are too large to resolve the small velocity increase that might be expected from local optical-mode hardening alone. We therefore use the sound-speed measurements as an experimental constraint on the acoustic spectrum, rather than as a complete description of all heat-carrying branches. The large residual decrease in κ beyond any plausible velocity effect requires strong mean-free-path suppression from substitutional disorder, force-constant disorder, and microstructural scattering."

Comment:

By "higher-order scattering events" I assume the authors mean 4-phonon scattering? I doubt 4-phonon scattering plays any meaningful role in this system. I recommend clarifying this statement or removing it.

Response:

We thank the reviewer for catching this comment. We agree that likely 4-phonon scattering is not playing any meaningful role. The present experiments do not isolate three phonon and four phonon rates, and the manuscript does not contain calculations that would justify such an assignment. We have removed the phrase higher order scattering events.

The revised text attributes the observed temperature dependence at low dopant concentration to increased anharmonic phonon phonon scattering in general. This retains the conclusion supported by the decreasing conductivity and lifetime without specifying an unmeasured scattering order.

Revision to the manuscript:

We have modified the discussion on page 10 to read:

"The reduction in thermal conductivity directly reflects a shortening of the phonon mean free path driven by enhanced Umklapp processes (ℓ_{Umklapp}), consistent with increasing anharmonic phonon phonon scattering at elevated temperatures."

Comment:

I am not convinced by the argument presented in the paragraph starting on line 201. This argument rests on the assumption there are modes relevant to thermal conductivity that are not yet thermally populated. At a minimum, this argument should be accompanied by a reference to the energy of the top of the acoustic modes in the system, or an estimation of it using the authors sound speed measurement, and a comparison to kBT.

Response:

We thank the reviewer for this critique. We agree that the original statement was too definitive and that the population argument requires more careful energetic framing. In the revision, we remove the implication that a large increase in thermal conductivity at high dopant concentration is necessarily caused by newly populated heat-carrying modes. Instead, we present a more cautious interpretation.

For crystalline AlN, reported phonon dispersions place the acoustic branches in the tens-of-meV range, while kBT is approximately 25.9 meV at 300 K and approximately 58 meV at 673 K (400 °C). Therefore, many acoustic modes are already thermally active at room temperature, and it is not correct to imply that the heat-carrying acoustic spectrum is mostly unpopulated at room temperature [12,23]. Elevated temperature can still increase heat capacity and alter mode populations, especially for higher-energy optical modes, but this effect cannot be claimed to be the sole origin of any increase in κ without a spectral calculation.

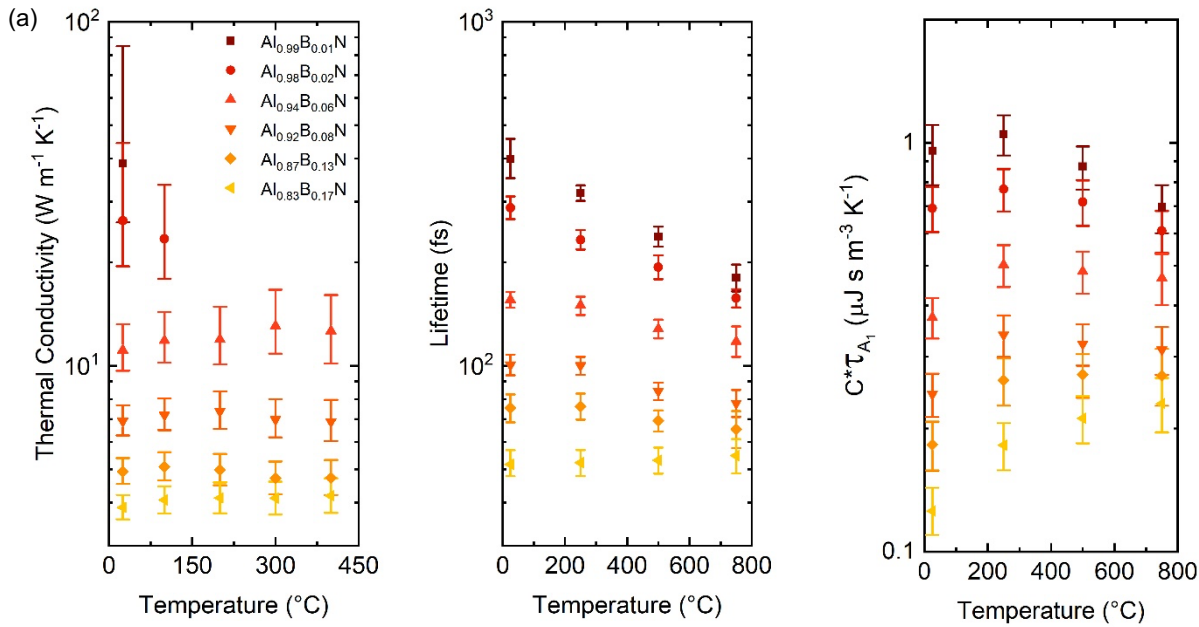
The revised manuscript therefore describes the high-dopant temperature trend as an apparent weak increase within a strongly disorder-limited regime. We state that it may reflect the combined effects of changing heat capacity, saturation of impurity-limited mean free paths, possible contributions from non-propagating or diffuson-like channels in the highly disordered limit, and measurement sensitivity. We do not claim a quantitative heat-capacity mechanism.

Revision to the manuscript:

We have added the following discussion to page 11:

“At the highest total dopant concentrations, the measured thermal conductivity shows a weak increase with temperature. We do not interpret this trend as evidence that acoustic heat-carrying modes are absent at room temperature. Reported AlN phonon dispersions show that the acoustic spectrum lies in an energy range comparable to kBT between room temperature and 400 °C, so many acoustic modes are already thermally populated [12,23]. The films are also not interpreted as metallic; the AlN-based alloys remain wide-band-gap nitride ferroelectrics, and no free-carrier evidence is available that would support a semimetallic transport mechanism. Instead, the weak increase is treated as an apparent trend in a strongly disorder-limited regime, where impurity and microstructural scattering substantially reduce the phonon mean free path and where changes in heat capacity, mode population, and non-propagating vibrational contributions may compete with anharmonic resistive scattering.”

We have also updated Fig. 3 of the manuscript as follows:



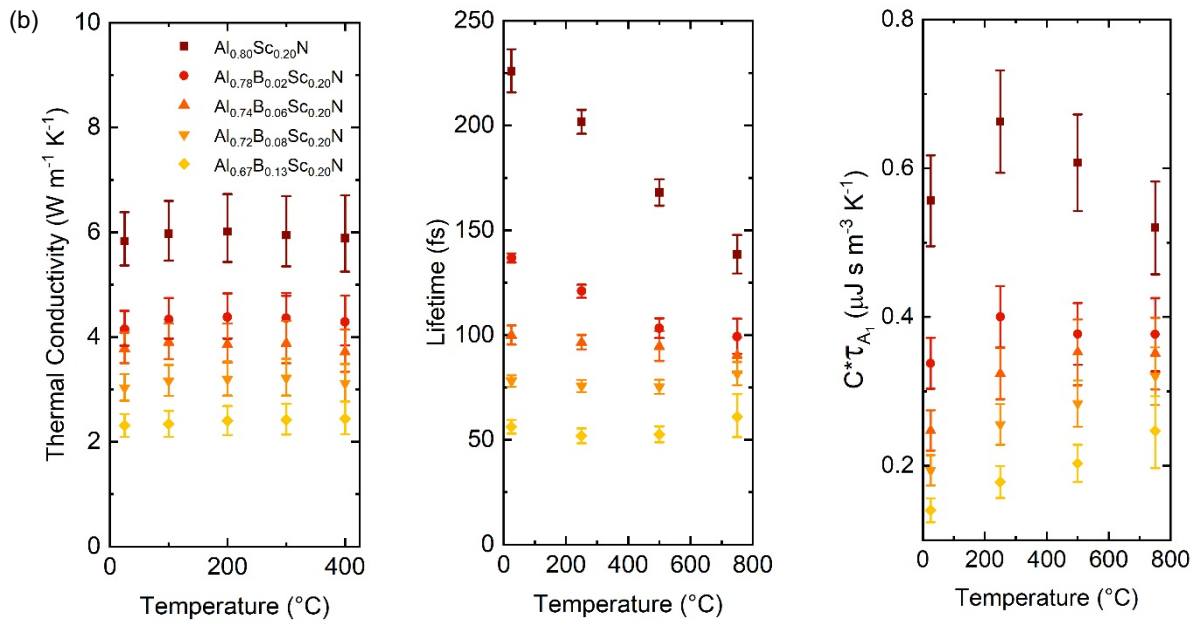


Figure 2 Thermal conductivity (left), Cross-plane A1(TO) phonon lifetime (middle), and product of heat capacity times A1 lifetime (right) as a function of temperature for (a) $Al_{1-x}B_xN$ and (b) $Al_{1-x-y}B_xSc_yN$ films.

Comment:

I recommend looking into two-channel lattice dynamics, where phonon contributions to kappa beyond the phonon-gas model are considered. These contributions increase with increasing temperature, so it is not clear whether the authors are seeing non-phonon-gas contributions or a heat capacity effect without more modeling or simulation. If the authors did see non-phonon-gas effects in this system, that would be of great interest to the community.

Response:

We appreciate this suggestion. We have added a discussion of the Wigner or two-channel framework, but we avoid claiming that the present data prove a non-phonon-gas contribution. The Wigner formulation unifies propagating Peierls-Boltzmann phonons and wave-like coupling between vibrational eigenstates and is especially important in complex or highly disordered crystals with ultralow or glass-like thermal conductivity [26-27].

Our most highly doped AIBN and AIBScN films have low thermal conductivities and substantial vibrational damping, so it is reasonable to mention this framework as a possible future modeling direction. However, the present data cannot distinguish among heat-capacity effects, diffuson-like contributions, and residual propagating phonon transport. We therefore include the Wigner framework only as a limitation and outlook, not as a claimed mechanism. This also addresses the reviewer concern that a heat-capacity-only explanation is not established.

Revision to the manuscript:

We have added the following discussion to page 5:

"This kinetic expression is used here to organize the dominant physical contributions to the measured thermal conductivity, rather than as a complete microscopic transport model. A fully quantitative

treatment would require spectral phonon transport calculations, such as first-principles Peierls-Boltzmann transport with composition-dependent force constants and realistic defect scattering."

We have added the following discussion to page 12:

"In the highly disordered limit, a complete description may also require transport channels beyond the conventional phonon-gas picture. Wigner and unified thermal-transport formulations show that wave-like coupling between vibrational eigenstates can contribute to thermal conductivity in complex or disordered crystals, and that this contribution can increase with temperature [26-27]. The present measurements do not isolate such a channel, and we therefore do not assign the high-dopant temperature trend uniquely to either heat capacity or non-phonon-gas transport. Instead, the data motivate future first-principles spectral calculations that include alloy disorder, finite size, and possible Wigner-channel contributions."

Comment:

I find the data shown in blue in Fig. 4b very interesting. I believe the authors are showing that the lifetime of the TO mode decreases with decreasing film thickness from about 30 nm to about 12 nm. At first glance I would not have expected the TO mode to have a long enough lifetime or mean free path to be influenced by film thicknesses of this magnitude. Is it driven by point defects, interfacial defects, or normal acoustic-mismatch interface scattering? Or perhaps it is following the trend seen in Figure 5b with the mosaic spread increase.

Response:

The reviewer is correct that the thickness dependence should not be interpreted as direct boundary limitation of the zone center optical mode. The A1(TO) group velocity near the Brillouin zone center is small, so the product of its group velocity and measured lifetime is far below a film thickness of tens of nanometers. A direct optical phonon mean free path explanation is therefore not credible.

The thickness series changes more than geometric confinement. The rocking curve broadens as thickness decreases, and the thermal conductivity rises toward a thickness independent value above approximately 40 nm. These observations indicate that the growth microstructure, mosaic spread, and defect density evolve with thickness. The A1 linewidth is consequently interpreted as a marker of this microstructural evolution, while the thermal conductivity can also be affected by boundary suppression of heat carrying acoustic modes.

We have revised the manuscript to separate these two roles. The lifetime trend is attributed to microstructure dependent damping rather than normal acoustic mismatch scattering of the optical mode itself. The transport regime below approximately 40 nm is treated as coupled size and microstructure dependence rather than uniformly diffusive.

Revision to the manuscript:

We have added the following discussion to page 12:

"The thickness dependence of the A1(TO) lifetime is not interpreted as direct boundary limitation of the optical phonon mean free path. Near the Brillouin zone center, the A1(TO) group velocity is small, so its propagation length is not expected to approach tens of nanometers. Instead, the lifetime trend follows the thickness dependent microstructure. Stacked θ - 2θ scans for the entire thickness series zoomed in around the (002) wurtzite reflection are presented in Fig. 5(a), and Fig. 5(b) presents FWHM rocking curve values for the same series, showing that the out-of-plane mosaic spread increases as film thickness decreases. The concurrent increase in mosaic spread and reduction in κ in the ultrathin films indicate that greater defect and orientational disorder increase vibrational damping, while heat carrying acoustic modes may also experience finite size suppression."

We have also updated Fig. 4 of the manuscript as follows:

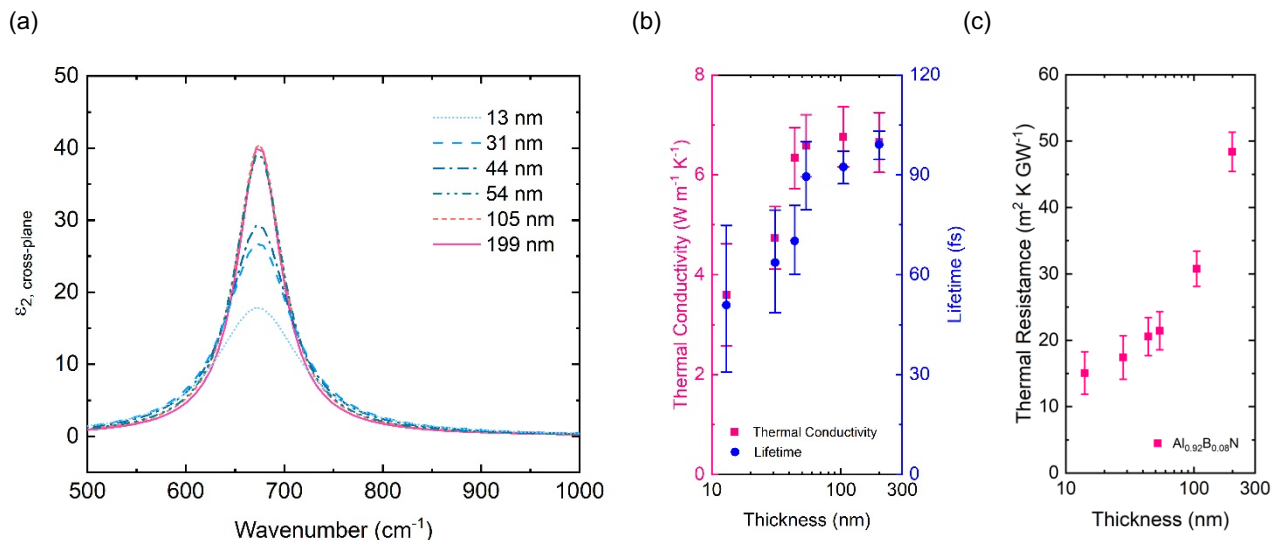


Figure 3 (a) The Imaginary part of the cross-plane dielectric function for $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ films with thicknesses from 13 nm to 199 nm. (b) thermal conductivity and phonon lifetime of $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ at various thicknesses. It can be seen that thermal conductivity at thicknesses ≥ 40 nm approaches a constant value of $\sim 7 \text{ W m}^{-1} \text{K}^{-1}$. (c) Total thermal resistance of the $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ films with increasing film thickness that is indicative of the diffusive transport.

Comment:

Crystal symmetry breaking. Is the only evidence of symmetry breaking the IR-VASE data? I suspect the appearance of a mode could arise from interfacial effects or phase impurities. The authors highlight this quite prominently in the abstract, so if it is going to be a main focus of the paper, I would expect more discussion and possible corroborating data such as XRD, Raman, or TEM.

Response:

We thank the reviewer for requesting a more rigorous basis for the symmetry related claim. The original manuscript described the feature too definitively. The updated anisotropic analysis provides additional evidence that was not available in the submitted version. A lower wavenumber contribution is required in the in plane dielectric response of both AIBN and AIBScN, with the AIBScN feature shifted to lower wavenumber. Its evolution with alloy composition and the absence of additional crystalline phases in the XRD scans argue against a fixed substrate feature or a readily detectable secondary crystalline phase.

The assignment is also consistent with prior work on wurtzite nitrides showing that disorder can relax selection rules and activate nominally silent B1 branches. The systematic redshift in the Sc containing series follows the broader softening of the host optical spectrum. A purely mass driven local vibration from lighter B would generally be expected toward higher frequency if local force constants were comparable. The observed lower wavenumber feature and its host dependent shift are therefore not naturally explained by mass contrast alone, although mixed local and host character cannot be excluded. This argument favors a B1 related assignment but does not uniquely establish the eigenvector.

We have therefore narrowed the language. The revised text now uses B1 related feature and consistent with disorder relaxed selection rules. We do not claim that IR VASE alone proves a specific local symmetry breaking mechanism, and we identify polarized Raman or first principles eigenvector calculations as the direct tests needed for a conclusive assignment.

Revision to the manuscript:

Per the reviewer's comment, we have revised the text on page 7 in the manuscript as:

"At higher boron concentrations, a lower wavenumber feature develops in the in-plane dielectric response of both AIBN and AIBScN samples in the range of 500-600 cm^{-1} , located at lower frequencies than the $E1(\text{TO})$ modes. The spectral position of this feature is close to the calculated silent $B1$ branch of wurtzite nitrides, it evolves systematically with alloy composition, and no secondary crystalline phase is detected by XRD. These observations favor a disorder activated $B1$ related assignment over a fixed interfacial or secondary phase origin. However, IR-VASE measurements alone do not uniquely determine the mode eigenvector, so we describe the feature as $B1$ related and consistent with disorder relaxed selection rules rather than as definitive proof of a specific symmetry breaking mechanism."

Comment:

Possible data error. The lowest-x pink square is shifted between Fig. 1c and Fig. 1d. This is apparent when comparing x values of blue and pink points. Is this correct? Maybe a bug in the plotting script.

Response:

We thank the reviewer for catching this potential plotting issue. We rechecked the plotting script and the composition arrays used for Fig. 1(c) and Fig. 1(d). The revised figures use the same composition values in both panels for each sample series and the same labels as in the composition table. We also updated the figure source files to ensure that all low-x points for AIBN and AIBScN are plotted consistently.

We have updated Fig. 1 of the manuscript as follows:

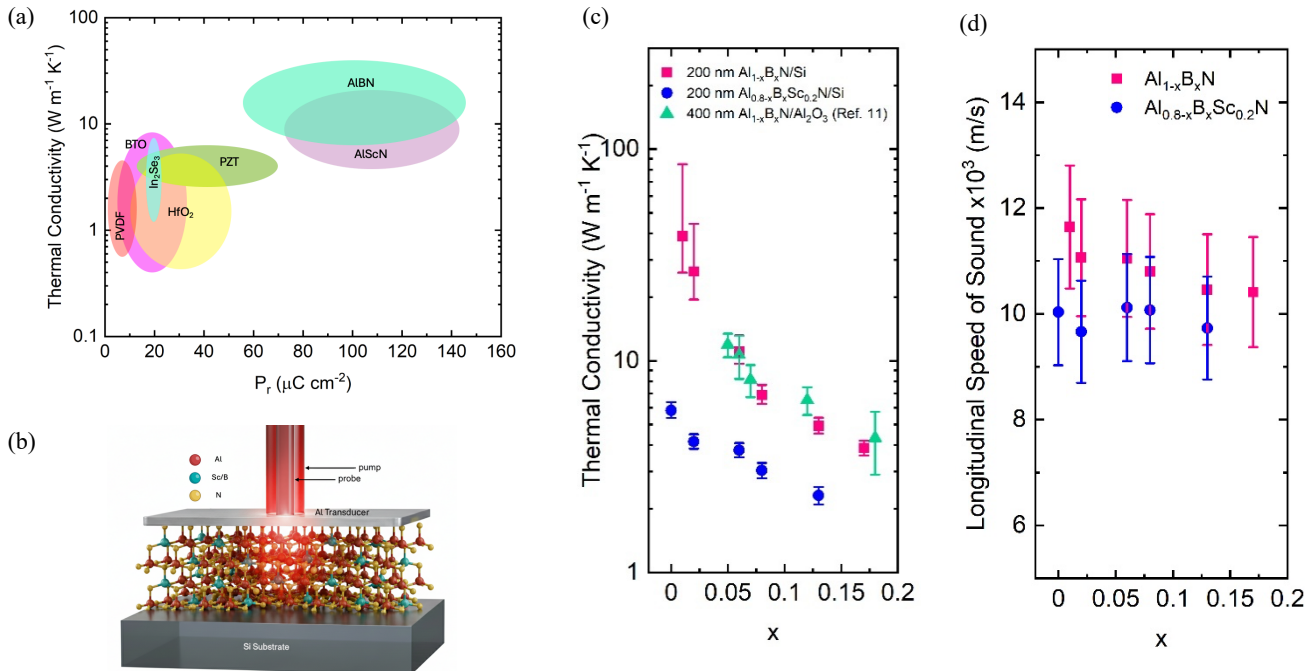


Figure 4 (a) The Ashby plot of thermal conductivity versus remnant polarization, P_r , for various ferroelectric materials (ref.⁴). $\text{Al}_{1-x}\text{B}_x\text{N}$ ferroelectrics exhibit the highest thermal conductivity ever measured in a ferroelectric thin film: Thermal conductivity of $\text{Al}_{1-x}\text{B}_x\text{N}$ (measured in this work and (ref.¹⁴); HfO₂ (ref.³⁷); In_2Se_3 (ref.³⁸); PZT (refs.³⁹⁻⁴¹); PVDF (refs.^{42,43}); $\text{Al}_{1-x}\text{Sc}_x\text{N}$ (ref.¹⁵); BTO (refs.⁴⁴⁻⁴⁷). (b) Schematic of $\text{Al}_{1-x}\text{B}_x\text{N}$ and $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$ sample geometry and pump-probe experiment. (c) Room temperature thermal

conductivity of $Al_{1-x}B_xN$ and $Al_{1-x-y}B_xSc_yN$ as a function of boron concentration, x . Data from Kang et al.¹⁴ from ~ 400 nm $Al_{1-x}B_xN$ films on sapphire substrate is presented for comparison. (d) Sound velocity in $Al_{1-x}B_xN$ and $Al_{1-x-y}B_xSc_yN$ as a function of boron concentration, x .

Reviewer #2

Review report of “Thermal Conductivity and Optical Phonon Scattering of CMOS Compatible Aluminum Nitride-Based Ferroelectric Thin Films” by Makarem et al.

The authors investigate the effect of doping on the thermal transport and polarization of AlN-based ferroelectric thin films of $\text{Al}_{1-x}\text{B}_x\text{N}$ and $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$ using TDTR, IR-VASE, and picosecond ultrasonics. The authors argue that doping at concentrations above a threshold activates the silent B1 mode and facilitates polarization switching. Thermal transport remains controlled by phonon-phonon scattering at low dopant concentration, but becomes impurity-dominated at intermediate concentrations. Thickness-dependent total thermal resistance measurements show a monotonic decrease, highlighting that dominant phonon mean free paths are below the lowest measured thickness value.

The author wants to emphasize that while doping may reduce the coercive field in this family, it also reduces thermal conductivity, which is not good for memory devices. The $\text{Al}_{1-x}\text{B}_x\text{N}$ and $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$ family, as the authors state, offers a relatively ideal combination of thermal conductivity and remnant polarization. The above conclusion is ok, but the discussion of the data is not well supported. Below are some of the major comments:

1. It is now well established in the literature that all modes, with different frequencies and group velocities, contribute to thermal conductivity. Measuring the lifetime of a single optical phonon, whose contribution is generally low due to lower group velocity and shorter lifetime, should not be taken as a definitive indicator of thermal conductivity.

Response:

We agree. The revised manuscript no longer states or implies that a single optical phonon lifetime is a definitive indicator of thermal conductivity. Acoustic modes dominate heat conduction in AlN-based materials because of their larger group velocities, and a full microscopic description would require mode-resolved phonon transport [12,23].

Our revised interpretation is that the cross-plane $\text{A1}(\text{TO})$ linewidth provides a directional, spectroscopic measure of composition-dependent vibrational damping. In this particular alloy series, the same disorder that broadens the IR-active modes also scatters the acoustic phonons that dominate cross-plane heat flow. Thus, the $\text{A1}(\text{TO})$ lifetime is useful as a system-specific marker of the evolving disorder landscape, not as a universal predictor of κ . This distinction has been made throughout the Abstract, Results, and Conclusions.

Revision to the manuscript:

We have revised the Abstract to now state:

"A monotonic relationship between cross-plane $\text{A1}(\text{TO})$ lifetime and TDTR-measured cross-plane thermal conductivity is observed at room temperature, indicating that IR-VASE can serve as a system-specific spectroscopic probe of disorder-induced vibrational damping in these AlN-based alloy films. "

We have added the following discussion to page 8:

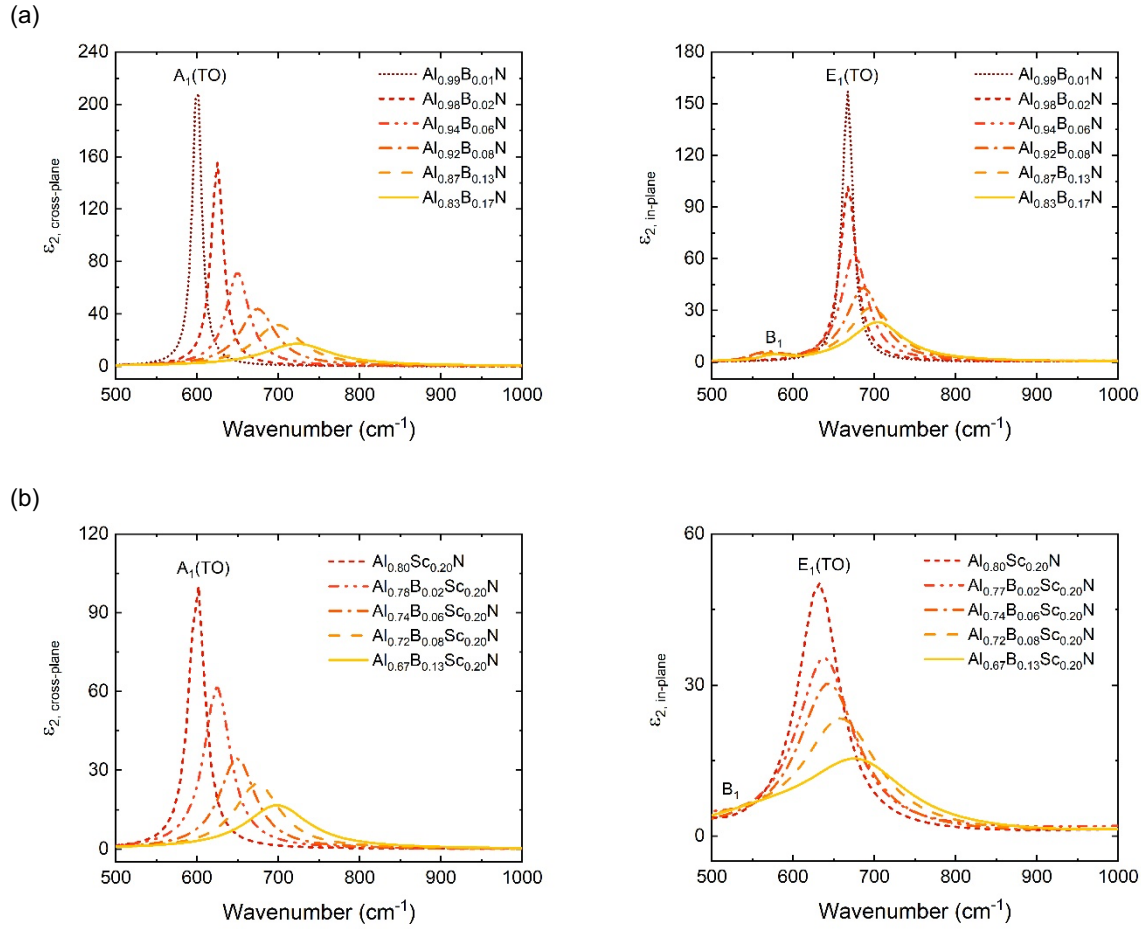
"The measured $\text{A1}(\text{TO})$ lifetime is not interpreted as the lifetime of the modes that dominate lattice heat conduction. Mode-resolved calculations and measurements on AlN show that most heat is carried by acoustic branches, while optical modes can influence thermal conductivity indirectly through acoustic-optic scattering and through their sensitivity to the same defect landscape that scatters heat-carrying modes [12,21,23-25]. In the present alloy series, the cross-plane $\text{A1}(\text{TO})$ linewidth provides a spectroscopic measure of disorder-induced vibrational damping. Its monotonic covariation with TDTR-measured cross-plane thermal conductivity should therefore be interpreted as

a system-specific proxy for the strength of phonon scattering in AIBN and AIBScN, not as a universal conversion from optical phonon lifetime to thermal conductivity."

We have revised the conclusion to read:

"A strong correlation between optical phonon lifetimes and thermal conductivity establishes IR-VASE as a spectroscopic probe of vibrational damping induced by defects in these AlN-based films."

We have also updated Fig. 2 of the manuscript as follows:



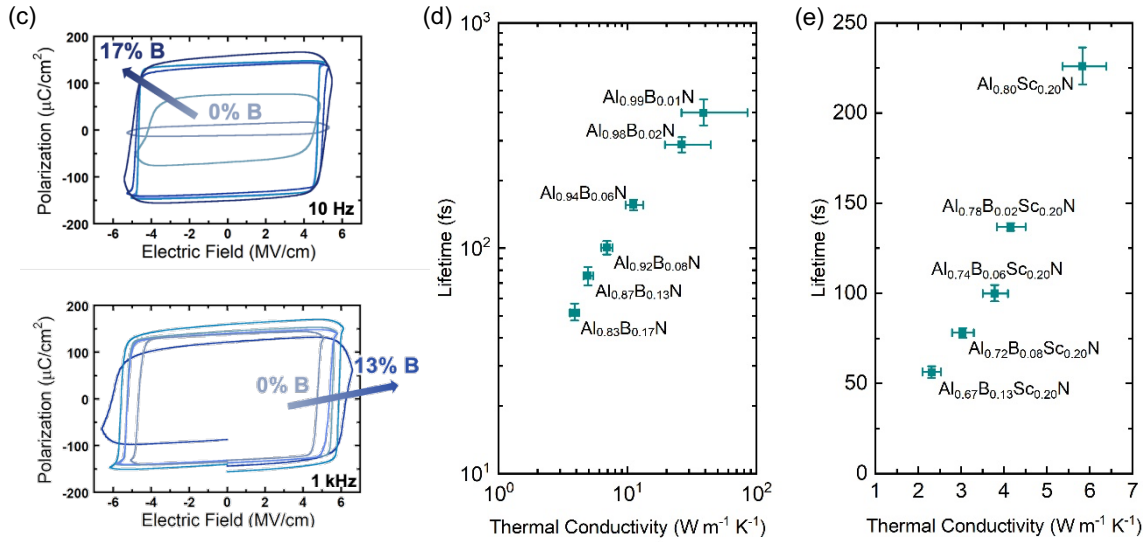


Figure 5 Imaginary parts of anisotropic infrared dielectric responses of (a) $Al_{1-x}B_xN$ and (b) $Al_{1-x-y}B_xSc_yN$. Strong peaks in the in-plane and cross-plane imaginary parts correspond to A_1 and E_1 transverse optical phonon modes, respectively. The in-plane response includes the disorder-activated B_1 feature in the range of $500-600\text{ cm}^{-1}$. The optical modes of the ferroelectrics with higher dopant concentration are broader, indicating greater anharmonicity from defect scattering. (c) Polarization hysteresis progression of $\sim 200\text{ nm}$ $Al_{1-x}B_xN$ (top) and $Al_{1-x-y}B_xSc_yN$ films (bottom) with increasing B composition. (d,e) Thermal conductivity versus cross-plane $A_1(TO)$ phonon lifetime of (d) $Al_{1-x}B_xN$ and (e) $Al_{1-x-y}B_xSc_yN$. A linear correlation is observed between the extracted phonon lifetimes and independently measured room-temperature thermal conductivities. Increasing boron and scandium content broadens the phonon resonances, shortens the extracted lifetimes, and suppresses thermal conductivity.

2. I am unconvinced that the new mode that appears with added doping concentration or increased thickness is of B1 symmetry. At high doping levels, localized vibrations of the B atom may also give rise to a new mode. Absence of B1 symmetry mode in $Al_{1-x-y}B_xSc_yN$ further suggests that the B1 mode is not symmetry broken but rather from resonance. Direct evidence is necessary.

Response:

We appreciate the reviewer's alternative assignment and agree that IR VASE alone cannot provide direct eigenvector identification. However, we respectfully note the following: First, the updated anisotropic analysis does reveal a lower wavenumber B1 related contribution in AIBScN. It is broader and shifted to lower wavenumber relative to AIBN, but it is present in the in plane response. Second, the feature is not observed only at one high B composition. It develops systematically with alloying in both material families.

A defect resonance remains a possible microscopic description, but the observed trends are not naturally explained by a purely mass driven B local mode. Because B is lighter than Al, a localized vibration produced only by mass contrast would generally be expected toward higher frequency if the local force constants were comparable. The measured feature instead occurs below the dominant $E_1(TO)$ resonance and shifts to still lower wavenumber when Sc is added, following the softening of the host optical spectrum. This host dependent evolution favors a disorder activated host branch, although it does not by itself exclude a mixed or localized character.

Additional evidence also weighs against an interface or secondary crystalline phase origin. The samples have comparable thickness and substrate stacks across each composition series, the contribution is required only in the in plane dielectric response, and XRD does not show an additional

crystalline phase. None of these observations is individually conclusive. We therefore maintain the physically motivated B1 related assignment but explicitly acknowledge that polarized Raman spectroscopy or first principles eigenvector calculations would be required for definitive symmetry identification.

Revision to the manuscript:

To clarify this important point raised by the reviewer, we have revised the text on page 7 to read:

"At higher boron concentrations, a lower wavenumber feature develops in the in-plane dielectric response of both AIBN and AIBScN samples in the range of 500-600 cm⁻¹, located at lower frequencies than the E1(TO) modes. In the Sc containing series, the feature is shifted to lower wavenumber together with the broader softening of the host optical response. The spectral position of this feature is close to the calculated silent B1 branch of wurtzite nitrides, it evolves systematically with alloy composition, and no secondary crystalline phase is detected by XRD. These observations favor a disorder activated B1 related assignment over a fixed interfacial or secondary phase origin. However, IR-VASE measurements alone do not uniquely determine the mode eigenvector, so we describe the feature as B1 related and consistent with disorder relaxed selection rules rather than as definitive proof of a specific symmetry breaking mechanism."

3. The authors claim that "The emergence of the B1 phonon mode provides a compelling structural explanation for the enhanced ferroelectric behavior observed in Al_{1-x}B_xN films at intermediate boron concentrations" and "The appearance of this otherwise silent branch reflects symmetry breaking and disorder in the wurtzite lattice, where uncompensated antiparallel displacements endow the B1 vibrations with polar character". But the above claim has no supporting evidence. The authors do not show how uncompensated displacements relate to the B1 mode or how they directly correlate with ferroelectric behavior. The cited Ref. 61 talks about weakened bond strength and enhanced Born effective charges, rather than the B1 mode.

Response:

We thank the reviewer for this critique and agree that the original wording overstated the mechanistic role of the B1-related feature. The reviewer is correct that the cited reference discusses bonding, strain, and Born effective charges rather than proving that a B1 mode directly drives ferroelectric switching. We have therefore removed the claim that the B1 mode provides a compelling structural explanation for enhanced ferroelectric behavior.

The revised interpretation is correlation based and more defensible. Boron and scandium substitution introduce local bonding disorder, strain-field variations, altered coordination, and reduced switching barriers, as reported in prior structural and ferroelectric studies of AIBN and related wurtzite ferroelectrics [2-3,34-35]. These structural changes can both reduce the switching barrier and activate otherwise silent or weakly allowed vibrational responses. The B1-related feature is therefore treated as a spectroscopic marker of the local disorder environment that coincides with improved switching behavior, not as a direct causal mechanism.

This revision preserves the importance of the data. The manuscript still shows that the same compositional changes that enable saturated ferroelectric hysteresis also strongly damp vibrational modes and suppress thermal conductivity. That trade-off remains central to the paper, while the revised B1 language avoids claiming a microscopic switching pathway that was not directly measured.

Revision to the manuscript:

We revise the manuscript to account for this important point by the reviewer by including the following:

"The B1 related feature appears over the same composition range in which polarization switching becomes experimentally accessible. This co-occurrence does not establish that the mode causes ferroelectric switching. Instead, both observations are consistent with the broader local structural disorder and symmetry lowering introduced by substitution. We therefore use the B1 related feature as a spectroscopic marker of the changing vibrational environment, while the reduction in switching barrier is discussed in terms of previously reported changes in bonding, local coordination, and polarization energetics [2-3,34-35]."

4. The temperature-dependent thermal conductivity of alloys is characterized into three different scattering regimes. At high concentrations, the increase in thermal conductivity with temperature is attributed to increasing heat capacity. The authors should measure heat capacity and show that the heat capacity of $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$ increases by nearly 50%, leading to an increase in thermal conductivity. Is it possible that at high concentrations, the composition is semimetallic or metallic-like?

Response:

We thank the reviewer for identifying an overstatement in the original text. We have revised the high-dopant discussion so that it no longer requires or implies a measured heat-capacity increase. The heat capacity used in the TDTR model is not sufficient to establish that heat capacity is the sole origin of the observed trend, and we have not measured composition-specific heat capacity at high temperature.

We also do not interpret the high-dopant films as semimetallic or metallic. AlN, AlBN, and AlScN are wide-band-gap nitride systems, and the measurements are performed on ferroelectric nitride films on highly doped Si bottom electrodes. The TDTR transducer response is optical and thermal, not an electrical transport measurement of the film. A metallic interpretation would require independent electrical conductivity, optical free-carrier absorption, or carrier-density evidence, which is not present. Prior reports on AlBN and AlScN describe these as insulating or semiconducting wide-band-gap ferroelectric nitrides, with leakage affecting device behavior but not indicating metallic conduction [1-6,11].

To qualitatively capture the competing effects of heat capacity and vibrational lifetime, we have added a figure showing the temperature dependence of the product of heat capacity and lifetimes, where heat capacity is estimated through composition-weighted alloy averaging. At low boron concentrations, the decrease in lifetime with increasing temperature is largely offset by the increase in heat capacity, resulting in a relatively weak temperature dependence of the product. At high boron concentrations, the lifetime remains nearly constant with temperature, while the heat capacity increases, causing the product to increase. This trend is qualitatively similar to the measured temperature dependence of thermal conductivity. This product can help us to provide a qualitative comparison of how the competing temperature dependences of heat capacity and lifetime evolve with boron concentration.

The weak increase in apparent κ , however, may arise from a combination of changing vibrational heat capacity, saturation of impurity-limited mean free paths, altered interface sensitivity at very low film conductivity, and possible wave-like or diffuson-like vibrational contributions in highly disordered films [26-27]. So, we no longer assign it to heat capacity alone.

Revision to the manuscript:

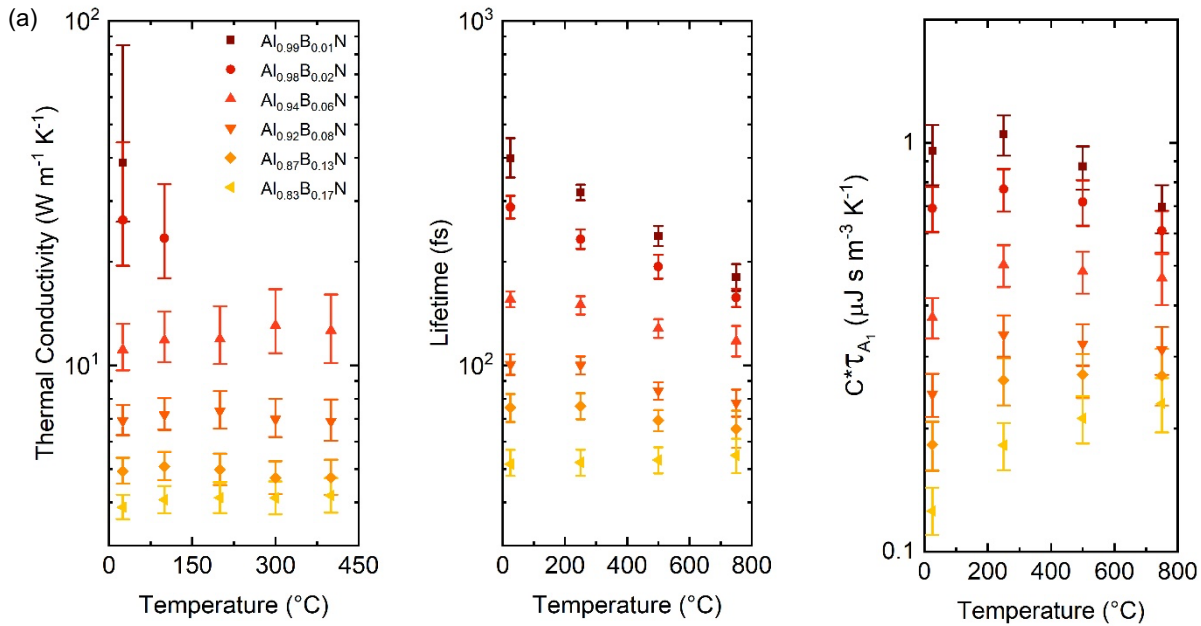
We revise the manuscript to account for this point raised by the reviewer by including the following paragraphs:

"At the highest total dopant concentrations, the measured thermal conductivity shows a weak increase with temperature. We do not interpret this trend as evidence that acoustic heat-carrying

modes are absent at room temperature. Reported AlN phonon dispersions show that the acoustic spectrum lies in an energy range comparable to kBT between room temperature and 400 °C, so many acoustic modes are already thermally populated [12,23]. The films are also not interpreted as metallic; the AlN-based alloys remain wide-band-gap nitride ferroelectrics, and no free-carrier evidence is available that would support a semimetallic transport mechanism. Instead, the weak increase is treated as an apparent trend in a strongly disorder-limited regime, where impurity and microstructural scattering substantially reduce the phonon mean free path and where changes in heat capacity, mode population, and non-propagating vibrational contributions may compete with anharmonic resistive scattering.

To qualitatively examine the competing effects of heat capacity and vibrational lifetime, Figure 3 presents the temperature dependence of $C\tau_{A1}$, where C is the volumetric heat capacity estimated through composition-weighted alloy averaging and τ_{A1} is the measured cross-plane A1-mode lifetime. At low boron concentrations, the decrease in lifetimes with increasing temperature is largely offset by the increase in heat capacity, producing a relatively weak temperature dependence of their product. At high boron concentrations, lifetime remains nearly constant, while heat capacity increases with temperature, causing the product to increase. This evolution is qualitatively similar to the measured thermal-conductivity trend. However, this product should not be interpreted as a quantitative thermal-transport model because it combines the total estimated heat capacity with the lifetime of a single optical phonon mode and does not account for mode-dependent group velocities or the full vibrational spectrum. The comparison instead illustrates how the relative temperature dependences of heat capacity and vibrational lifetime change with boron concentration.”

We have also updated Fig. 3 of the manuscript as follows:



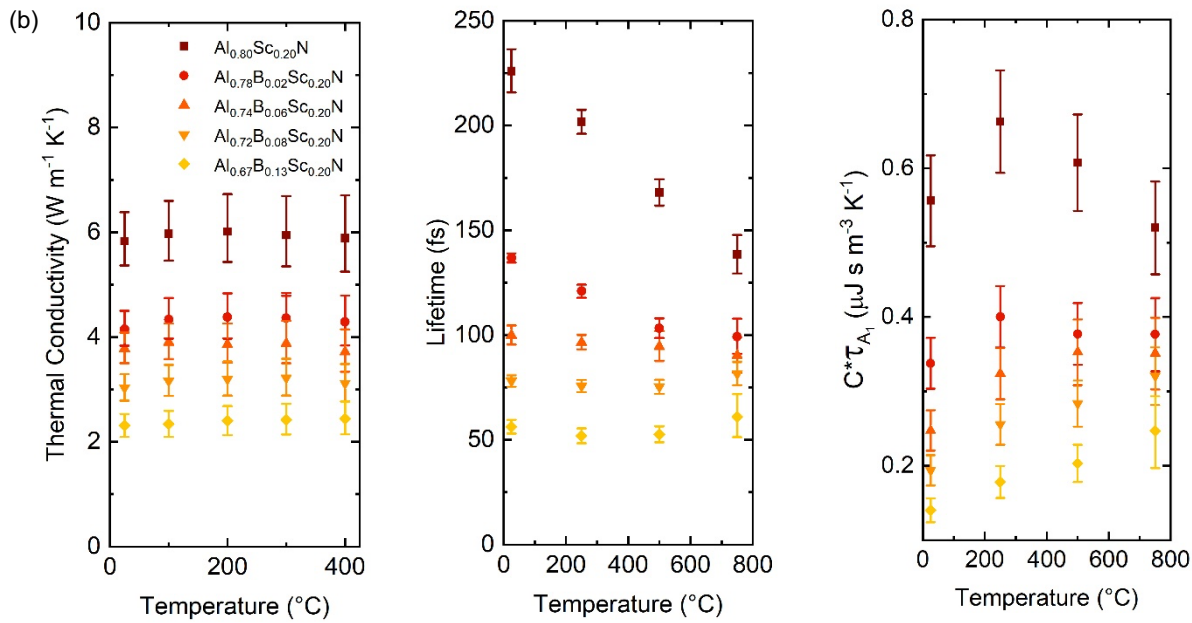


Figure 6 Thermal conductivity (left), Cross-plane A1(TO) phonon lifetime (middle), and product of heat capacity times A1 lifetime (right) as a function of temperature for (a) $Al_{1-x}B_xN$ and (b) $Al_{1-x-y}B_xSc_yN$ films.

5. Thermal transport in 10-199 nm thick $Al_{0.92}B_{0.08}N$ films is characterized as diffusive, based on the observation that thermal resistance increases with thickness. However, in the quasi-ballistic regime, phonon lifetime, thermal conductivity, and total resistance can increase simultaneously with thickness. In a diffusive regime, the resistance would increase approximately linearly with thickness. Hence, the argument that measurements are in a diffusive regime needs to be re-examined.

Response:

We thank the reviewer for this important point. We agree that the monotonic increase in total resistance alone is not sufficient to prove a fully diffusive regime across the entire 10 to 200 nm thickness range. In ultrathin films, thickness-dependent microstructure, interface disorder, and possible quasi-ballistic effects can cause thermal conductivity, lifetime, and total resistance to evolve together.

The data instead show two coupled trends. Thermal conductivity approaches an approximately thickness independent value above about 40 nm, while the cross plane A1 lifetime and XRD mosaic spread also evolve most strongly in the ultrathin range. This means that size effects and thickness dependent microstructure are not separable below about 40 nm. In the thicker range, the saturation of κ and increasing resistance are consistent with predominantly diffusive transport, but a quantitative ballistic to diffusive crossover would require a suppression function analysis with a thickness independent microstructure.

We have replaced the all thickness diffusive claim with a crossover interpretation. The revised text does not infer a 10 nm upper bound on the dominant mean free paths and does not use the optical lifetime as a direct MFP measurement. This revision is consistent with prior AlN thin-film work showing a ballistic-to-diffusive transition and strong coupling between film thickness, defects, and boundary scattering [22-23].

Revision to the manuscript:

We have replaced the original diffusive claim with:

"The thickness dependence does not establish a uniformly diffusive regime across the full 10 to 200 nm range. Above approximately 40 nm, the thermal conductivity approaches an approximately constant value while the total resistance continues to increase with thickness, which is consistent with predominantly diffusive transport in the thicker films. Below approximately 40 nm, thermal conductivity, A1(TO) lifetime, and mosaic spread change concurrently, indicating that finite size effects and thickness dependent microstructure are coupled. The present data therefore identify a crossover from an ultrathin microstructure and size sensitive regime to near thickness independent conductivity at larger thickness, rather than demonstrating that the dominant phonon mean free paths are shorter than 10 nm."

We have also updated Fig. 4 of the manuscript as follows:

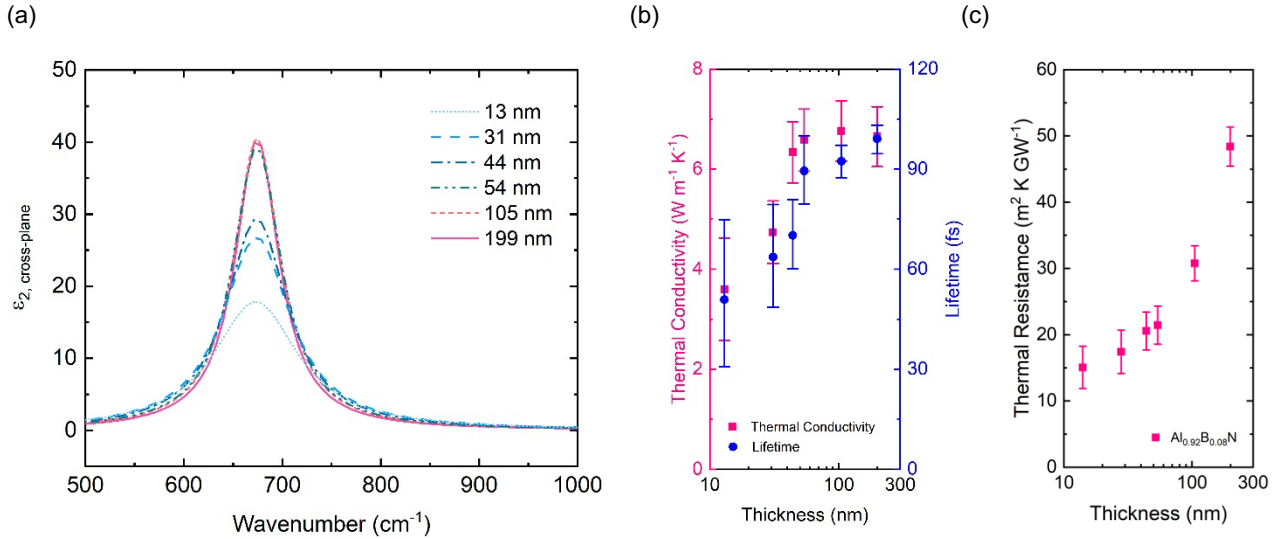


Figure 7 (a) The Imaginary part of the cross-plane dielectric function for $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ films with thicknesses from 13 nm to 199 nm. (b) thermal conductivity and phonon lifetime of $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ at various thicknesses. It can be seen that thermal conductivity at thicknesses ≥ 40 nm approaches a constant value of $\sim 7 \text{ W m}^{-1} \text{K}^{-1}$. (c) Total thermal resistance of the $\text{Al}_{0.92}\text{B}_{0.08}\text{N}$ films with increasing film thickness.

6. Minor comment in Supporting Information: In Figure S3, the quantity plotted in contour maps is not stated. It means the mean squared error. A clarification is necessary.

Response:

We thank the reviewer for the comment. We have since reanalyzed our sensitivities and determined we have sufficient sensitivity to the fitted parameters for all compositions and temperatures reported. As such, we have edited our thermal conductivity measurement section to reflect our now sufficient sensitivity at low compositions as well as remove the contour analysis information and the representative figures.

7. Minor comment in Supporting Information: On line 126 of the SI, the thickness of the transducer and its thermal conductivity are treated as independent variables with 5% uncertainty in both. However, if the thermal conductivity of the transducer is obtained from 4-point probe measurements, they are not independent. A clarification is necessary.

Response:

We thank the reviewer for this point. We have revised the uncertainty-analysis language to clarify how the Al transducer properties were treated. The Al thickness was measured independently via picosecond acoustics, while the Al thermal conductivity was obtained from four-point-probe electrical resistivity using the Wiedemann-Franz relation. These are distinct measurements, but they are both properties of the same deposited Al transducer and should not be described as statistically independent in a rigorous covariance sense. We have revised the supporting information to clarify this point.

Revision to the manuscript:

We have edited the corresponding section of the supporting information to reflect this:

“An uncertainty of +/- 3 nm was assumed for the transducer thickness. The uncertainty in Al thickness was propagated jointly with the measured sheet resistance when calculating the Al thermal conductivity through the Wiedemann–Franz relation.”

8. Minor comment in Supporting Information: On line 127 in the SI, the boundary resistance between film and substrate is also assigned a 5% uncertainty. However, it is a fitted parameter and not an input variable in the thermal model. A clarification is necessary.

Response:

We appreciate the comment from the reviewer, though would like to clarify that the boundary resistance between the film and substrate is not a fitted parameter as we are much less sensitive to it compared to the parameters we are fitting for (thermal conductivity of the film (κ_1) and thermal boundary resistance between the transducer and film, $R_{Al/1-xBxN/Si}$ and $R_{Al/1-x-yBxScyN/Si}$) in all composition and temperature cases. In prior fitting iterations, we had previously fitted for the thermal boundary resistance between the film and substrate using a high thermal conductivity AlN sample and then used this measured value as an input variable for all compositions. We have revisited our fitting since receiving these comments and have determined both that the AlN we had received with our samples is not of sufficiently high quality to give sufficient sensitivity to thermal boundary resistance between the film and substrate and also that we are not as sensitive to the thermal boundary resistance between the film and substrate as we had originally stated for all compositions. As such, we assume a constant value (with a 10% uncertainty) for the thermal boundary resistance between the film and substrate as given in Perez *et al.* [23]. We have made edits to clarify what parameters we are fitting for and separately also updated the Uncertainty Analysis section to reflect our new fittings and error analysis.

Revision to the manuscript:

We have removed all text on contour analysis as well as the representative figures. We have edited Table S2 as well as the error analysis information to:

“An uncertainty of 5% was assumed for the film’s heat capacity and 10% uncertainty was assumed for both the thermal boundary resistance between the film and substrate ($R_{Al/1-xBxN/Si}$ & $R_{Al/1-x-yBxScyN/Si}$) as well as the thermal conductivity of the substrate (κ_3).”

Reviewer #3**Comment:**

Clarification is needed regarding whether the measured thermal conductivity represents in-plane or cross-plane values. At minimum, for the thinnest films, the lattice thermal conductivity is expected to be anisotropic. Please specify the measurement geometry and discuss potential anisotropy effects.

Response:

We thank the reviewer for this important clarification. The TDTR measurements reported in the manuscript represent the cross-plane thermal conductivity of the thin films. Because the films are approximately 10 to 200 nm thick and the pump and probe radii are much larger than the film thickness, the TDTR signal is primarily sensitive to heat flow normal to the film plane. The films are c-axis textured and their intrinsic thermal conductivity can be anisotropic.

The updated anisotropic IR-VASE analysis also directly addresses the reviewer's concern. We now extract in-plane and cross-plane dielectric functions separately and compare the TDTR thermal conductivity with the cross-plane $A_1(\text{TO})$ lifetime. We also acknowledge that the lattice thermal conductivity may be anisotropic, especially in the thinnest films. The present TDTR geometry does not independently determine in-plane thermal conductivity, so we do not claim that the reported values represent isotropic thermal transport.

Revision to manuscript:

We have revised the main text, figure captions, and methods to state this explicitly.

Results section:

"Under the present spot sizes and modulation frequency, the TDTR signal is dominated by through thickness heat flow. The reported film conductivities are therefore effective cross plane values."

Methods section:

"The film thicknesses measured in this study are 10 to 200 nm, which are much smaller than the pump and probe radii. Sensitivity analysis confirms that the fitted film parameter is dominated by cross plane heat transport. In-plane thermal conductivity is not independently extracted, so possible conductivity anisotropy is not included as a measured quantity."

Comment:

The Slack model is employed to explain the high thermal conductivity of AlN. However, significant advances have been made in high-thermal-conductivity material research, and the Slack model may not be appropriate for doped AlN given that the lattice structure is no longer simple upon alloying. Have the authors considered first-principles calculations, such as DFT, to accurately explain the high thermal conductivity of AlN? Relevant computational studies should be cited and discussed.

Response:

We thank the reviewer for this useful suggestion. We agree that the Slack model should not be presented as a *quantitative* model for the doped alloys. Its assumptions are most appropriate for relatively simple, ordered crystals, while the present AlBN and AlBScN films contain alloy disorder, finite-thickness effects, and interfaces. We have therefore revised the manuscript to describe the Slack framework as qualitative motivation for why AlN begins from a high-thermal-conductivity baseline, not as a full model for the composition-dependent trends.

We added discussion of first-principles and experimental studies of AlN thermal conductivity. Crystalline AlN has high thermal conductivity because of strong bonding, high acoustic group velocities, and long phonon mean free paths [12,23,25]. First-principles and analytical studies also

show that point defects and impurities can strongly suppress AlN thermal conductivity, with vacancies and mass disorder having particularly large effects [23-25]. These prior studies support our interpretation that lightly B-substituted AlN can retain relatively high thermal conductivity, while increasing B and Sc substitution introduces disorder that shortens phonon mean free paths.

We did not perform new first-principles calculations in this revision. However, we now explicitly state that a full quantitative description of the alloyed films would require mode-resolved lattice dynamics with alloy disorder, force-constant disorder, finite thickness, and interfaces. This clarification addresses the limitation of the Slack model while keeping the manuscript focused on the experimental contribution. We now state this explicitly as a future direction.

Revision to the manuscript:

We have revised the Slack model paragraph on page 3 to read:

"This framework is useful as a qualitative starting point for lightly substituted $\text{Al}_{1-x}\text{B}_x\text{N}$ because the Al-N backbone is retained and the films remain strongly textured wurtzite nitrides. The Slack criteria are used here as qualitative motivation for why the AlN parent lattice provides an unusually favorable thermal-transport baseline, not as a quantitative model for the alloyed films. First-principles calculations and thermal measurements on crystalline AlN show that its high thermal conductivity originates from stiff bonding, high acoustic group velocities, and long mean-free-path acoustic phonons, while vacancies, impurities, and alloy disorder strongly reduce κ [12,23-25]. The present data are consistent with this picture. Lightly boron-substituted AlN retains a comparatively high conductivity among ferroelectric thin films, while increased boron and scandium incorporation progressively introduces mass disorder, bond-length disorder, and microstructural disorder that shorten phonon mean free paths. Thus, the Slack criteria explain why AlN-based ferroelectrics begin from an unusually favorable thermal-transport baseline."

Comment:

The manuscript states: "The structural perturbations introduced by boron and scandium doping serve as potent scattering centers, disrupting phonon coherence and severely limiting phonon transport." What specific physical meaning does "phonon coherence" denote in this context? Furthermore, what is the quantitative or qualitative relationship between phonon coherence and phonon transport efficiency?

Response:

We thank the reviewer for flagging this terminology. The phrase phonon coherence was too vague in the original text. We did not intend to introduce a separate measured coherence length or a formal phase-coherence analysis. We have therefore removed the phrase from this section.

The revised manuscript describes the mechanism in terms of phonon lifetime, mean free path, and mode relaxation, which are directly connected to the measurements and to standard phonon-scattering models [23,36]. Boron and scandium substitution introduce mass disorder, bond-length disorder, and force-constant disorder. These perturbations increase scattering rates and reduce the mean free paths of heat-carrying phonons. This wording is more precise and directly connected to the TDTR, picosecond acoustics, and IR-VASE measurements.

Revision to the manuscript:

We have replaced the sentence on page 6 to read:

"These local mass and force-constant perturbations increase phonon scattering rates and reduce the mean free paths of heat-carrying modes."

Comment:

Regarding the claim: "The hardening of the E1(TO) mode indicates an overall lattice compression, likely arising from mass and bonding perturbations introduced by boron substitution, given its smaller atomic size compared to Al." Please provide additional experimental or computational evidence, such as X-ray diffraction data or lattice parameter calculations, to substantiate this assertion.

Response:

We agree that this claim needed additional support and more precise wording. We have revised the text to avoid stating that the IR mode hardening alone proves overall lattice compression. Instead, we connect the observed E1(TO) and A1(TO) hardening to prior structural measurements showing that B incorporation in AIBN reduces lattice dimensions and modifies local bonding [2-3]. We also refer to the XRD data in the Supporting Information, which show systematic changes in the (002) peak and rocking-curve width with B incorporation.

The revised interpretation is that mode hardening is consistent with local bond stiffening and structural contraction associated with B substitution, but it is not treated as a standalone measurement of lattice parameter. This distinction is important because optical phonon frequencies depend on both force constants and effective masses, and alloy disorder can broaden and shift modes in ways that are not captured by a simple compression picture.

Revision to the manuscript:

We have added the following discussion to page 7:

"The blue shift of the A1(TO) and E1(TO) resonances with increasing B content is consistent with prior structural studies showing that B incorporation contracts the AlN-based wurtzite lattice and changes local bond environments [2-3]. Because optical mode frequencies depend on both force constants and reduced mass, we interpret the hardening as evidence of local bonding changes rather than as a standalone measurement of macroscopic lattice compression."

Comment:

Concerning the statement that optical phonon lifetimes can serve as an effective proxy for predicting thermal transport in these materials, is this correlation universally applicable across material classes, or is it specific to this particular system? Acoustic phonon lifetimes are generally more directly relevant to thermal conductivity than optical phonon lifetimes. Please clarify the rationale behind using optical phonon lifetimes as the predictive metric.

Response:

We thank the reviewer for raising this important point. We agree that the measured IR-active optical phonon lifetimes should not be interpreted as the lifetimes of the dominant heat-carrying phonons. Acoustic modes carry most of the lattice thermal conductivity because of their larger group velocities, and our revised text now states this explicitly. Our intended claim was not that TO modes dominate heat flow, but that the IR-measured TO linewidths provide an experimentally accessible measure of the same disorder and vibrational damping that also suppresses acoustic phonon transport in this alloy series.

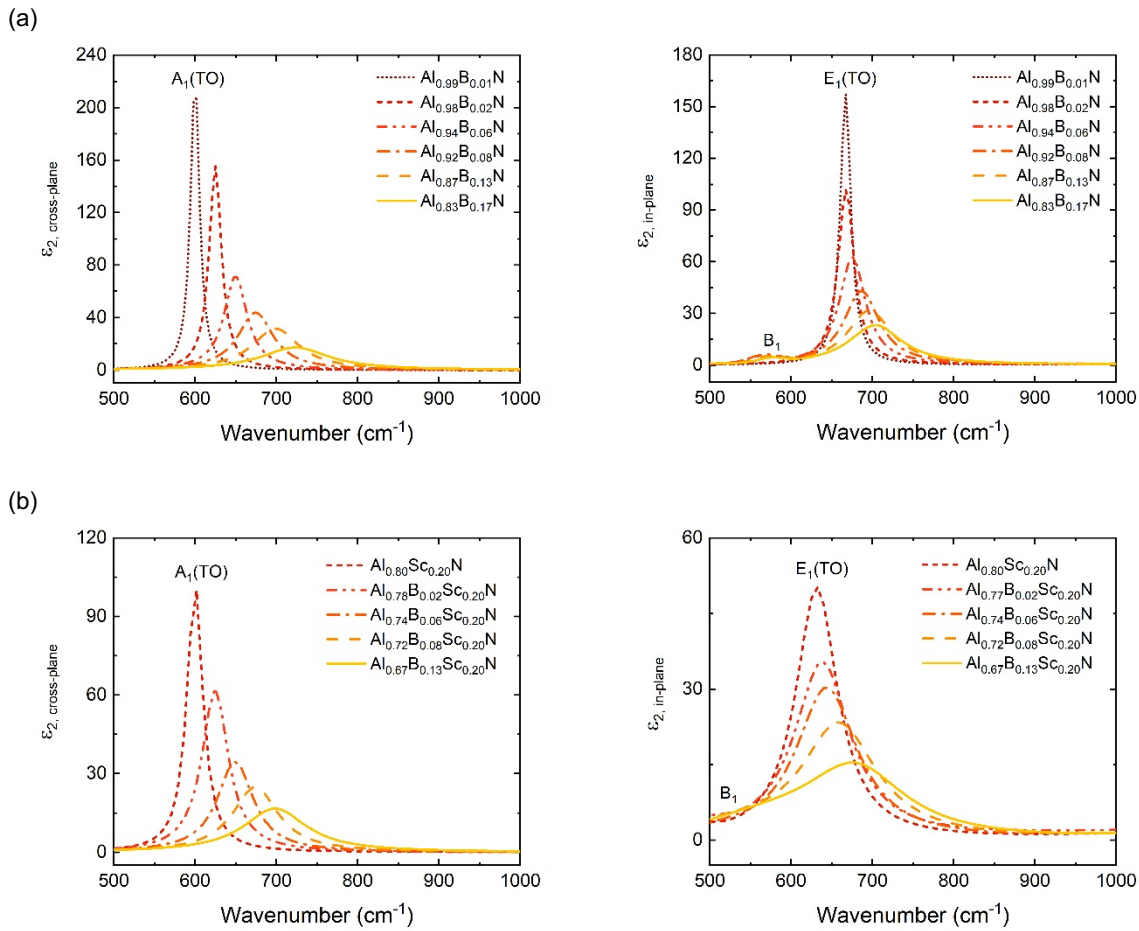
In AIBN and AIBScN, B and Sc substitution introduce mass disorder, force-constant disorder, bond-length disorder, and local strain fields. These perturbations broaden the IR-active A1 and E1 modes, but they also scatter the acoustic phonons that dominate cross-plane thermal conductivity. The observed correlation between cross-plane A1(TO) lifetime and TDTR-measured cross-plane thermal conductivity is therefore interpreted as a system-specific proxy for composition-dependent phonon scattering, not as a universal relationship between optical phonon lifetime and thermal conductivity. We have revised the manuscript as follows to make this distinction clear and to avoid implying universal applicability across all material classes.

Revision to the manuscript:

We have added the following paragraph to page 9:

" The measured $A_1(\text{TO})$ lifetime is not interpreted as the lifetime of the modes that dominate lattice heat conduction. Mode-resolved calculations and measurements on AlN show that most heat is carried by acoustic branches, while optical modes can influence thermal conductivity indirectly through acoustic-optic scattering and through their sensitivity to the same defect landscape that scatters heat-carrying modes [12,21,23-25]. In the present alloy series, the cross-plane $A_1(\text{TO})$ linewidth provides a spectroscopic measure of disorder-induced vibrational damping. Its monotonic covariation with TDTR-measured cross-plane thermal conductivity should therefore be interpreted as a system-specific proxy for the strength of phonon scattering in AlBN and AlBScN, not as a universal conversion from optical phonon lifetime to thermal conductivity."

We have also updated Fig. 2 of the manuscript as follows:



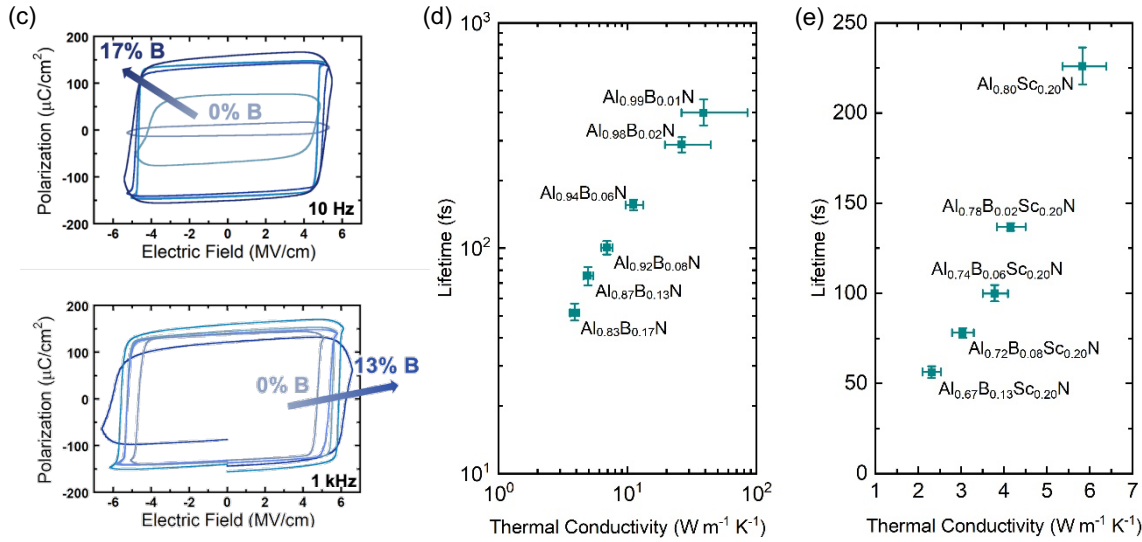


Figure 8 Imaginary parts of anisotropic infrared dielectric responses of (a) $\text{Al}_{1-x}\text{B}_x\text{N}$ and (b) $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$. Strong peaks in the in-plane and cross-plane imaginary parts correspond to A_1 and E_1 transverse optical phonon modes, respectively. The in-plane response includes the disorder-activated B_1 feature in the range of $500\text{--}600\text{ cm}^{-1}$. The optical modes of the ferroelectrics with higher dopant concentration are broader, indicating greater anharmonicity from defect scattering. (c) Polarization hysteresis progression of $\sim 200\text{ nm}$ $\text{Al}_{1-x}\text{B}_x\text{N}$ (top) and $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$ films (bottom) with increasing B composition. (d,e) Thermal conductivity versus cross-plane $A_1(\text{TO})$ phonon lifetime of (d) $\text{Al}_{1-x}\text{B}_x\text{N}$ and (e) $\text{Al}_{1-x-y}\text{B}_x\text{Sc}_y\text{N}$. A linear correlation is observed between the extracted phonon lifetimes and independently measured room-temperature thermal conductivities. Increasing boron and scandium content broadens the phonon resonances, shortens the extracted lifetimes, and suppresses thermal conductivity.

Comment:

In Figures 2b and 2d, the experimental data points appear distributed above and below the dashed trend lines, respectively. Please explain the physical origin or statistical significance of these apparent systematic deviations.

Response:

We thank the reviewer for this observation. The lines shown in Figs. 2b and 2d of the original manuscript are empirical guides to show the composition-dependent correlation between cross-plane lifetime and cross-plane thermal conductivity. The scatter reflects uncertainty in both TDTR thermal conductivity and IR-VASE lifetime extraction, as well as differences in how each measurement samples disorder and interfaces. Given the small number of compositions and the size of several uncertainty bars, the previous residual pattern should not be assigned statistical or physical significance.

The updated anisotropic analysis changes the plotted quantities and removes the need for a linear regression. The revised panels show cross plane $A_1(\text{TO})$ lifetime against cross-plane κ with measurement uncertainties and no dashed trend lines. We now describe a monotonic relationship and do not claim a universal linear law. The IR-VASE analysis is extensively revised on pages 7 through 11 of the manuscript.

Comment:

The statement "As shown in the inset of Fig. 2(b), the linear correlation is restored when only the E_1 mode lifetimes are considered, suggesting that the participation of B_1 modes in thermal transport does not change with concentration" requires clarification. Does this imply

that B1 modes contribute a constant offset to thermal conductivity regardless of doping concentration? Please elaborate on the interpretation.

Response:

We thank the reviewer for identifying this unclear statement. In the original manuscript, the IR-VASE response was treated with an effective dielectric model, and the discussion of the B1-related oscillator was therefore coupled to the same lifetime analysis used for the thermal-conductivity comparison.

In the revised manuscript, we have replaced this analysis with an anisotropic IR-VASE model that treats the wurtzite films as optically uniaxial layers with separate in-plane and cross-plane dielectric functions. This revision allows the cross-plane A1(TO) lifetime and the in-plane E1(TO) lifetime to be extracted separately. Because the TDTR measurements in this thin-film geometry are primarily sensitive to cross-plane heat flow, the revised thermal-conductivity comparison is now made specifically between the TDTR-measured cross-plane thermal conductivity and the cross-plane A1(TO) lifetime. This is the more physically appropriate comparison and removes the need for the previous inset-based analysis.

The B1-related feature is now modeled only in the in-plane dielectric response, where it appears as a disorder-activated feature at lower wavenumber than the primary E1(TO) mode. We do not use the B1 lifetime to construct the thermal-conductivity correlation, nor do we claim that the B1 mode provides a constant offset to thermal conductivity. Instead, the revised text treats the B1 feature as a spectroscopic signature of local symmetry breaking and disorder, while the quantitative comparison to thermal transport is based on the cross-plane A1(TO) mode. This distinction has been added to the manuscript to clarify that the optical lifetime correlation is directional, system-specific, and tied to the same disorder environment that suppresses cross-plane phonon transport.

Revision to the manuscript:

We have revised the discussion on page 9 to read:

"Because the TDTR geometry is primarily sensitive to cross-plane heat flow, the thermal-transport comparison is made with the cross-plane A1(TO) lifetime extracted from the anisotropic IR-VASE model. The E1(TO) mode and lower-wavenumber B1-related feature appear in the in-plane dielectric response and is discussed as a marker of disorder-relaxed selection rules, not as a separate contribution to thermal conductivity."

Comment:

The authors state: "As the temperature increases, additional phonon modes become thermally excited, and the range of phonons contributing to thermal conduction broadens in energy, causing the thermal conductivity to follow the temperature-dependent trends of heat capacity." Please provide additional experimental evidence or theoretical justification to solidify this conclusion.

Response:

We thank the reviewer for identifying an overstatement in the original text. We have revised the high-dopant discussion so that it no longer requires or implies a measured heat-capacity increase. The heat capacity used in the TDTR model is not sufficient to establish that heat capacity is the sole origin of the observed trend, and we have not measured composition-specific heat capacity at high temperature. The weak increase in apparent κ , however, may arise from a combination of changing vibrational heat capacity, saturation of impurity-limited mean free paths, altered interface sensitivity at very low film conductivity, and possible wave-like or diffuson-like vibrational contributions in highly disordered films [26-27]. So, we no longer assign it to heat capacity alone.

To qualitatively capture the competing effects of heat capacity and vibrational lifetime, we have added a figure showing the temperature dependence of the product of heat capacity and lifetimes, where heat capacity is estimated through composition-weighted alloy averaging. At low boron

concentrations, the decrease in lifetime with increasing temperature is largely offset by the increase in heat capacity, resulting in a relatively weak temperature dependence of the product. At high boron concentrations, the lifetime remains nearly constant with temperature, while the heat capacity increases, causing the product to increase. This trend is qualitatively similar to the measured temperature dependence of thermal conductivity. This product can help us to provide a qualitative comparison of how the competing temperature dependences of heat capacity and lifetime evolve with boron concentration.

Revision to the manuscript:

We revise the manuscript to account for this point raised by the reviewer by including the following paragraphs:

“At the highest total dopant concentrations, the measured thermal conductivity shows a weak increase with temperature. We do not interpret this trend as evidence that acoustic heat-carrying modes are absent at room temperature. Reported AlN phonon dispersions show that the acoustic spectrum lies in an energy range comparable to $k_B T$ between room temperature and 400 °C, so many acoustic modes are already thermally populated [12,23]. The films are also not interpreted as metallic; the AlN-based alloys remain wide-band-gap nitride ferroelectrics, and no free-carrier evidence is available that would support a semimetallic transport mechanism. Instead, the weak increase is treated as an apparent trend in a strongly disorder-limited regime, where impurity and microstructural scattering substantially reduce the phonon mean free path and where changes in heat capacity, mode population, and non-propagating vibrational contributions may compete with anharmonic resistive scattering.

To qualitatively examine the competing effects of heat capacity and vibrational lifetime, Figure 3 presents the temperature dependence of $C \cdot \tau_{A1}$, where C is the volumetric heat capacity estimated through composition-weighted alloy averaging and τ_{A1} is the measured cross-plane A1-mode lifetime. At low boron concentrations, the decrease in lifetimes with increasing temperature is largely offset by the increase in heat capacity, producing a relatively weak temperature dependence of their product. At high boron concentrations, lifetime remains nearly constant, while heat capacity increases with temperature, causing the product to increase. This evolution is qualitatively similar to the measured thermal-conductivity trend. However, this product should not be interpreted as a quantitative thermal-transport model because it combines the total estimated heat capacity with the lifetime of a single optical phonon mode and does not account for mode-dependent group velocities or the full vibrational spectrum. The comparison instead illustrates how the relative temperature dependences of heat capacity and vibrational lifetime change with boron concentration.”

We have also updated Fig. 3 of the manuscript as follows:

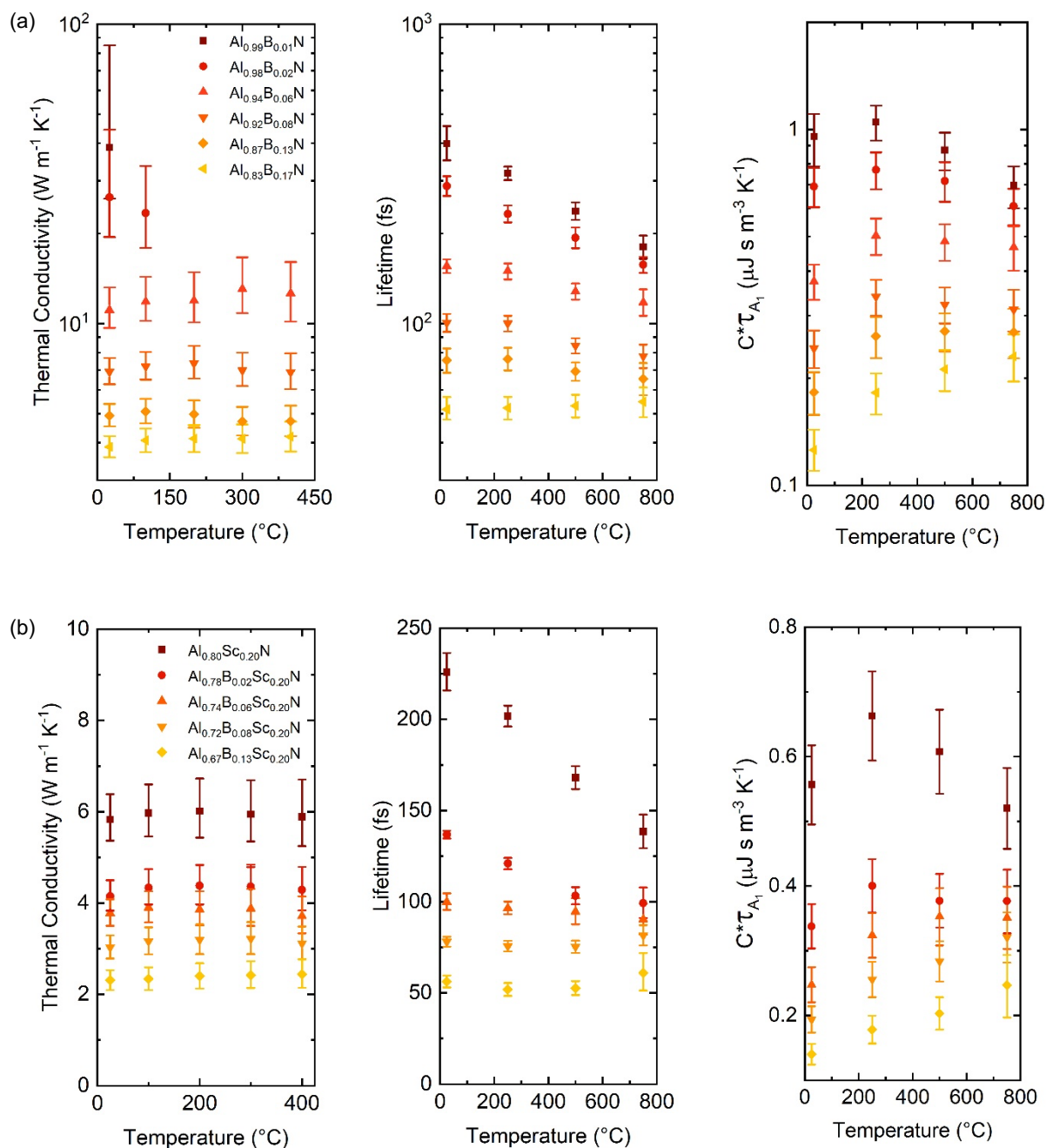


Figure 9 Thermal conductivity (left), Cross-plane A1(TO) phonon lifetime (middle), and product of heat capacity times A1 lifetime (right) as a function of temperature for (a) $Al_{1-x}B_xN$ and (b) $Al_{1-x-y}B_xSc_yN$ films.

Comment:

Regarding: "In this regime, the crystal quality degrades to the extent that the vibrational eigenstates lose the periodic boundary conditions necessary to support symmetry-broken mode activation." Please provide the intensity ratio between the B1 mode and the primary Raman-active mode for the 199 nm thickness sample. Additionally, when the thickness decreases to 30 nm, does the B1 peak completely disappear or merely fall into the noise floor?

Response:

We thank the reviewer for this careful point. We have removed this statement from the revised manuscript. The original language about loss of periodic boundary conditions was speculative and was not supported by a quantitative intensity-ratio analysis. Furthermore, the B1-related feature is measured by IR-VASE in this work, not by Raman, so an intensity ratio to a primary Raman-active mode is not directly available from the present data.

In the revised manuscript, we do not use the thickness series to support the B1-related assignment. The thickness discussion now focuses on cross-plane A1(TO) lifetime, cross-plane thermal conductivity, total thermal resistance, and XRD mosaic spread. This avoids overinterpreting whether the B1-related feature disappears or falls below the noise floor in ultrathin films.

Comment:

Both the Slack model and the kinetic theory expression $\kappa = (1/3)Cv\ell$ are relatively simple models that may be insufficient to capture the complex trends observed experimentally, particularly in doped systems with disorder-induced scattering. The authors should discuss the limitations of these models or consider more sophisticated theoretical frameworks (e.g., Boltzmann transport equation with first-principles inputs).

Response:

We thank the reviewer and agree. We agree that neither the Slack framework nor the simple kinetic expression $\kappa = 1/3 C v \ell$ is sufficient to quantitatively describe thermal transport in these doped, anisotropic, nanometer-scale alloy films. In the manuscript, these expressions were not intended as predictive models for the measured conductivities. Rather, they were used as physically transparent frameworks to motivate why AlN can have high intrinsic thermal conductivity and to separate the possible origins of the observed conductivity reduction into changes in heat capacity, phonon group velocity, and phonon mean free path. A complete description would require mode-resolved Peierls-Boltzmann transport with composition-dependent force constants, alloy scattering, defect scattering, boundary scattering, and interface thermal conductance. In the most disordered limit, Wigner or unified transport approaches may also be relevant [26-27].

We have revised the manuscript to state explicitly that Slack-type arguments and kinetic theory are used as interpretive frameworks, not as quantitative models for the full doped thin-film system. The Slack criteria are retained only as qualitative descriptors of the AlN parent lattice. The kinetic expression is retained only to organize the roles of heat capacity, group velocity, and mean free path.

Revision to the manuscript:

We have added the following discussion to page 5:

"This kinetic expression is used here to organize the dominant physical contributions to the measured thermal conductivity, rather than as a complete microscopic transport model. A fully quantitative treatment would require spectral phonon transport calculations, such as first-principles Peierls-Boltzmann transport with composition-dependent force constants and realistic defect scattering."

We have also added the following discussion to page 12:

"In the highly disordered limit, a complete description may also require transport channels beyond the conventional phonon-gas picture. Wigner and unified thermal-transport formulations show that wave-like coupling between vibrational eigenstates can contribute to thermal conductivity in complex or disordered crystals, and that this contribution can increase with temperature [26-27]. The present measurements do not isolate such a channel, and we therefore do not assign the high-dopant temperature trend uniquely to either heat capacity or non-phonon-gas transport. Instead, the data motivate future first-principles spectral calculations that include alloy disorder, finite size, and possible Wigner-channel contributions."

Terminology consistency: "Phonon velocity" should be corrected to "phonon group velocity".

Response:

Thank you for the terminology correction. We have replaced phonon velocity with phonon group velocity when discussing heat carrying modes. We retain longitudinal sound velocity when referring specifically to the picosecond ultrasonic measurement because that is the measured acoustic propagation speed.

Reviewer #4

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Response:

We thank the co-reviewer for their contribution to the review process and appreciate their participation in this peer-review training initiative. The comments provided by the reviewers have helped us substantially improve the clarity, rigor, and scope of the manuscript.

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Peer Review: Thermal Conductivity and Optical Phonon Scattering of CMOS Compatible Aluminum Nitride-Based Ferroelectric Thin Films

Thank you for the opportunity to review the manuscript “Thermal Conductivity and Optical Phonon Scattering of CMOS Compatible Aluminum Nitride-Based Ferroelectric Thin Films” by Makarem et al. I very much enjoyed reading it. They present a very well thought out and well executed data set on a relevant materials system.

I will say from the beginning that this is my first experience with IR-VASE data so I am unable to review the experimental details of that specific part of the paper. With that said, here is a point-by-point review of the rest of the paper.

The experimental methodology as described is sound and meets the expected standards of the field, though I do note a possible small data error described below. I do disagree with some of the conclusions and claims made about the data as you will read below. Nonetheless, these experimental data contain several interesting, informative and important findings that could help guide implementation of this technology. I would imagine teams running FEA thermal models of next generation memory devices based on AlN would be interested in even just the raw data reported.

Broad impact on technology

While the paper includes a nice introduction, it is still unclear to me whether the decrease in κ shown here is a deal breaker for these materials in real technological applications. The paper would be greatly improved if the authors referenced real numbers regarding the usage of the next generation memory devices referenced, such as:

- What is the standard operating currents (or current densities) targeted for any of the next generation memory devices referenced.
- How the thermal heating at these target currents is expected to be impacted by the change in electrical and thermal conductivities of the active material.

- Is there a critical temperature above which any of these next generation memories will not operate.

A focus on questions of this nature is critical to keep the field focused on moving applications of these promising technologies forward. With the reference to CMOS in the title, I expected a more targeted technology-driven intro.

κ , speed of sound, and lifetime data

The authors are disregarding the decrease in LA speed of sound (SoS) too quickly. From DFT based lattice dynamics or textbook analytical equations we have a relationship of $\kappa \approx Av^3$ when phonon-phonon scattering dominates and we are above the Debye temp. The representation given in the text of $\kappa = 1/3Cvl$ is misleading since when one carries the calculation through, one does not get a $\kappa \propto v$ relationship. When one appreciates the cubic dependence, an 18% decrease in SoS may lead to a 45% decrease in κ .

We don't expect much thermal energy to be carried by the TO modes. Therefore, I disagree with the statement that "optical phonon lifetimes can serve as an effective proxy for predicting thermal transport in these materials". There would need to be some argument for why the authors believe the optical lifetimes are tied to modes relevant for thermal conductivity. In fact, the authors show hardening of the E1(TO) mode along with the decrease in LA speed of sound, so for that property the two trends point in different directions.

The authors report a relationship between decreased kappa, decreased LA speed of sound, and decreased TO lifetime. We know from standard DFT based lattice dynamics, as well as textbook analytical thermal conductivity modeling, that thermal transport is dominated by acoustic modes. Therefore, the argument the authors can make with their data is that, for $\text{Al}_{1-x}\text{B}_x\text{N}$, adding B decreases the group velocities in the acoustic branches. If we take the decrease in LA SoS as a proxy for transverse branches (often TA soften more than LA), this accounts for the decrease from ~ 30 to ~ 21 W/mK. The authors then observe a broadening of the TO mode, and while one would not expect that to directly decrease kappa, it is an indication of the further phonon scattering introduced, which likely accounts for the remaining decrease in kappa from ~ 21 to ~ 4 W/mK. In the $\text{Al}_{1-x}\text{B}_x\text{Sc}_{0.2}\text{N}$ system, virtually no acoustic softening is observed and the Sc point defect scattering dominates any additional B point defect scattering introduced (a point the authors already make).

Another interesting story is that longitudinal SoS decreases when substituting a lighter B for a heavier Al, particularly in the $\text{Al}_{1-x}\text{B}_x\text{N}$. One might expect this trend to go the other way.

By "higher-order scattering events" I assume the authors mean 4-phonon scattering? I doubt 4-phonon scattering plays any meaningful role in this system. I recommend clarifying this statement or removing it.

I agree with the paragraph in lines 195–200.

I'm not convinced by the argument presented in the paragraph starting on line 201. This argument rests on the assumption there are modes relevant to thermal conductivity that are not yet thermally populated. At a minimum, this argument should be accompanied by a reference to the energy of the top of the acoustic modes in the system (or an estimation of it using the authors' SoS measurement), and a comparison to $k_B T$. I recommend looking into two-channel lattice dynamics, where phonon contributions to κ beyond the phonon-gas model are considered (quantum coherence/diffuson-channel). These contributions increase with increasing temp, so it's not clear to me whether the authors are seeing non-phonon-gas contributions or a heat capacity effect without more modeling or simulation. If the authors did see non-phonon-gas effects in this system, that would be of great interest to the community.

I find the data shown in blue in Fig. 4b very interesting. I believe the authors are showing that the lifetime of the TO mode decreases with decreasing film thickness from ~ 30 nm to ~ 12 nm. At first glance I would not have expected the TO mode to have a long enough lifetime/MFP to be influenced by film thicknesses of this magnitude. Is it driven by point defects, interfacial defects, or normal acoustic-mismatch interface scattering? Or perhaps it is following the trend seen in Figure 5b with the mosaic spread increase.

Crystal symmetry breaking

Is the only evidence of symmetry breaking the IR-VASE data? I suspect the appearance of a mode could arise from interfacial effects or phase impurities. The authors highlight this quite prominently in the abstract, so if it is going to be a main focus of the paper, I would expect more discussion and possible corroborating data (e.g. XRD, Raman, TEM).

Possible data error

The lowest- x pink square is shifted between Fig. 1c and Fig. 1d. This is apparent when comparing x values of blue and pink points. Is this correct? Maybe a bug in the plotting script.