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Natalie M. Dawley

Ella K. Pek

Che Hui Lee

Eugene J. Ragasa

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/phys_facwork/2084

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Natalie M. Dawley,¹  Ella K. Pek,² Che-Hui Lee,¹ Eugene J. Ragasa,³  Xue Xiong,^{3,4,5}  Kiyong Lee,⁶ Simon R. Phillpot,³  Aleksandr V. Chernatynskiy,⁷  David G. Cahill,²  and Darrell G. Schlom^{1,8,9,a)} 

AFFILIATIONS

¹Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

²Department of Materials Science and Engineering and Materials Research Laboratory
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

³Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, 32611, USA

⁴Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

⁵University of Chinese Academy of Sciences, Beijing 100049, China

⁶Inorganic Material Lab, Samsung Advanced Institute of Technology (SAIT), Samsung Electronics, 130 Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 16678, South Korea

⁷Department of Physics, Missouri University of Science and Technology, Rolla, Missouri 65409, USA

⁸Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA

⁹Leibniz-Institut für Kristallzüchtung, 12489 Berlin, Germany

^{a)} Author to whom correspondence should be addressed: schlom@cornell.edu

ABSTRACT

Unlike many superlattice structures, Ruddlesden–Popper phases have atomically abrupt interfaces useful for interrogating how periodic atomic layers affect thermal properties. Here, we measure the thermal conductivity in thin films of the $n = 1-5$ and 10 members of the $(\text{SrTiO}_3)_n\text{SrO}$ Ruddlesden–Popper superlattices grown by molecular-beam epitaxy and compare the results to a single crystal of the $n = 1$ Ruddlesden–Popper SrLaAlO_4 . The thermal conductivity cross-plane to the superlattice layering (k_{33}) is measured using time-domain thermoreflectance as a function of temperature and the results are compared to first-principles calculations. The thermal conductivity of this homologous series decreases with increasing interface density. Characterization by x-ray diffraction and scanning transmission electron microscopy confirms that these samples have a Ruddlesden–Popper superlattice structure.

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Materials with low thermal conductivity are of interest for a variety of applications including thermal barrier coatings^{1,2} and thermoelectric devices.^{3–5} Reducing dimensionality has been considered a promising approach to increase the effectiveness of a thermoelectric material.⁴ As the dimensionality of a material is decreased, quantum-confinement effects begin to affect material properties, providing an additional variable to control material properties. Quantum well systems^{6,7} and superlattices^{8,9} have been investigated to lower thermal conductivity by reducing dimensionality through the addition of internal epitaxial interfaces. An outstanding challenge in these layered materials is the quality of their interfaces, which can suffer from

internal surface roughness due to diffusion. The lack of atomically smooth interfaces can prevent accurate interpretation of a sample's thermal conductivity when compared to theoretical models. The $(\text{SrTiO}_3)_n\text{SrO}$ system we study in this Letter for its thermal conductivity properties naturally has atomically abrupt and smooth layers of $(\text{SrO})_2$ inserted into SrTiO_3 as these superlattice materials are stable in bulk form as the Ruddlesden–Popper phases for $n = 1-3$.^{10–13}

Several factors reduce thermal conductivity in superlattice structures. In general, internal interfaces inhibit the flow of heat. Across interfaces between dissimilar materials, differences in elastic properties impede the transfer of vibrational energy.¹⁴ Theoretical calculations

show that the average phonon velocity decreases with increasing superlattice period due to increased phonon band folding.¹⁵ Anharmonic phonon scattering due to the Umklapp process requires less energy in superlattices relative to the parent bulk materials due to a smaller reciprocal-lattice vector.¹⁶ These properties have been well studied experimentally in synthetic semiconductor superlattices of GaAs–AlAs for their unique thermal conductivity^{17,18} and phonon transport.¹⁹ In this system, the conductivity measured in the in-plane direction was found to decrease with reducing superlattice period¹⁷ and an even stronger reduction was found in the cross-plane direction (perpendicular to the layering).¹⁸ As an analog system to the semiconductor superlattices, oxide superlattices show potential for thermoelectric applications.²⁰

In this work, we report an experimental study on the thermal properties of a broad spectrum ($n = 1$ –5 and 10) of $(\text{SrTiO}_3)_n\text{SrO}$ epitaxial films measured by the time-domain thermoreflectance (TDTR)

technique.³ The thermal conductivity of this homologous series shows decreasing thermal conductivity with n and is compared to first-principles calculations; the results of these first-principles calculations are consistent with those of our earlier analysis using empirical potentials.²¹ $(\text{SrTiO}_3)_n\text{SrO}$ Ruddlesden–Popper phases have drawn extensive attention due to their potential applications as tunable dielectrics^{22,23} and thermoelectric materials.²⁴ A similar system of the structurally related Dion–Jacobson homologous series, $A[A'_{n-1}B_nO_{3n+1}]$, was found to have an ultralow thermal conductivity ($\sim 0.4 \text{ W m}^{-1} \text{ K}^{-1}$) in $\text{CsBiNb}_2\text{O}_7$,²⁵ the $n = 2$ member. $(\text{SrTiO}_3)_n\text{SrO}$ Ruddlesden–Popper phases have similar structural features; these natural superlattices are composed of an alternate stacking of double layers of rock salt SrO and n layers of perovskite SrTiO_3 along the c -axis, Fig. 1(b). With decreasing n , the repeat distance between inserted additional SrO layers decreases and the structure undergoes a transition from a two-dimensional interfacial system to a three-

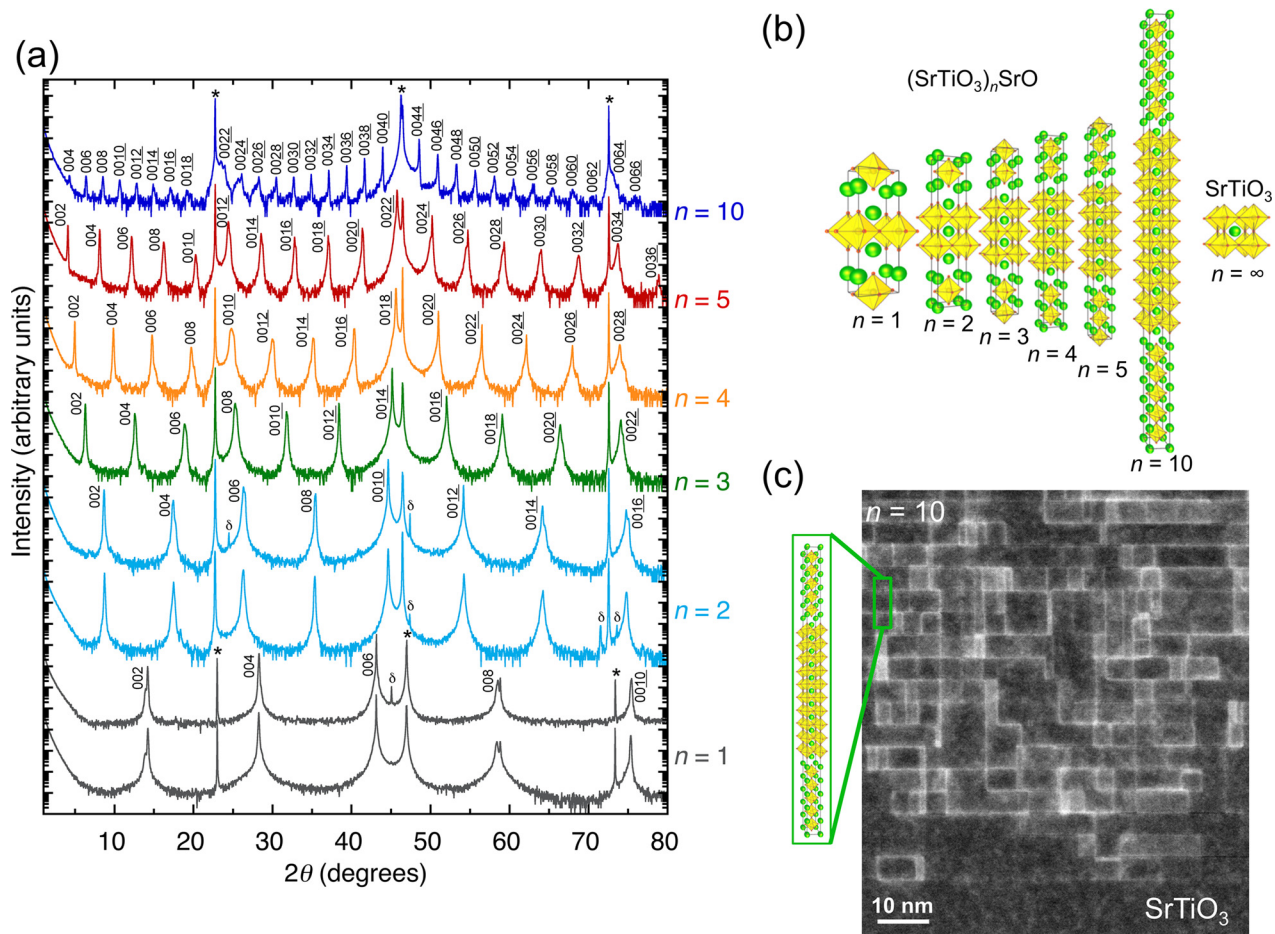


FIG. 1. (a) θ - 2θ x-ray diffraction scans of 300-nm-thick epitaxial $(\text{SrTiO}_3)_n\text{SrO}$ films grown on (001) SrTiO_3 for $n = 2$ –5 and 10 and 200-nm-thick films grown on (001) LSAT for $n = 1$. Substrate peaks are labeled with a (*), and the plots are offset for clarity. Peaks labeled “ δ ” denote hybrid diffraction peaks (see Ref. 39). (b) Schematic of the $(\text{SrTiO}_3)_n\text{SrO}$ series unit cells, $n = 1$ –5, 10, and ∞ , pure SrTiO_3 . Strontium atoms are shown in green and the TiO_2 oxygen coordination octahedra around each titanium ion are shown in yellow. (c) Low-angle annular dark-field scanning transmission electron microscopy (LAADF-STEM) of the $n = 10$ $(\text{SrTiO}_3)_n\text{SrO}$ film. A schematic of the $n = 10$ unit cell is shown on the left side of the image.

dimensional monolithic single crystal. The investigation of this homologous series provides an opportunity to tailor the thermal properties through changing dimensionality.

The synthesis of single-crystal $(\text{SrTiO}_3)_n\text{SrO}$ Ruddlesden–Popper phases is a challenging task. Conventional solid-state reactions only yield polycrystalline $n = 1$ –3 members^{10–13} due to the thermodynamic degeneracy of the higher- n phases of the series.^{26,27} Severe intergrowth of mixed- n phases is generally found in attempts to make higher n members.²⁸ Here, we use the precise layering ability of oxide molecular-beam epitaxy (MBE) to grow not only the first five but also $n = 10$ $(\text{SrTiO}_3)_n\text{SrO}$ single-phase epitaxial films of 300 nm thickness. Oxide MBE can supply incident species in any desired sequence with submonolayer composition control and essentially arbitrary n values can be synthesized even though nearby phases have similar formation energies.^{26–32}

We used a Veeco GEN10 oxide MBE system to grow the $(\text{SrTiO}_3)_n\text{SrO}$ ($n = 1$ –5 and 10) films. The majority of the films were grown to a thickness of ~ 300 nm onto (001) SrTiO_3 ($a = 3.905$ Å) substrates; further growth details can be found in the [supplementary material](#). The lattice mismatch of the $(\text{SrTiO}_3)_n\text{SrO}$ ($n = 1$ –5 and 10) series to (001) SrTiO_3 decreases monotonically with n , from 0.6% for $n = 1$ to about 0.01% for $n = 10$. The mismatch for $n > 2$ was estimated from the weighted average of the in-plane lattice constants of bulk $n = 2$ $\text{Sr}_3\text{Ti}_2\text{O}_7$ ($a = 3.9026$ Å)³³ and bulk SrTiO_3 ($a = 3.905$ Å).³⁴ Two $n = 1$ samples ($a = 3.883$ Å) of 200 nm thickness were grown on (001) $(\text{LaAlO}_3)_{0.29}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.71}$ (LSAT) ($a = 3.869$ Å) for better lattice match (-0.4% vs 0.6% on (001) SrTiO_3) to allow us to grow a large enough volume of material for the accurate TDTR measurement without contribution from the substrate or added defects from lattice relaxation due to epitaxial stress as well as to approximate the bulk Sr_2TiO_4 lattice.³⁵ The predicted thermal penetration depth of TDTR in Sr_2TiO_4 at room temperature is 203 nm, $d = \sqrt{\Lambda/(\pi C f)}$, where thermal conductivity, Λ , was measured to be 2.9 W/m K, the heat capacity, C , of Sr_2TiO_4 is 2.41 J/cm³ K,³⁶ and the laser frequency, f , used in our TDTR experiments is 9.3 MHz.

The structural perfection of the $(\text{SrTiO}_3)_n\text{SrO}$ homologous series was examined by x-ray diffraction (XRD). [Figure 1](#) shows θ – 2θ scans of the 300-nm-thick $n = 2$ –5 and 10 films on (001) SrTiO_3 and the 200-nm-thick $n = 1$ films on (001) LSAT. Scans of each sample show all peaks corresponding to phase-pure $(\text{SrTiO}_3)_n\text{SrO}$ ($n = 1$ –5 and 10). X-ray rocking curves in ω confirm the high structural perfection of the films; the full width at half maximum (FWHM) of the $n = 1$ –5 and 10 films is less than 52 arc sec ($< 0.014^\circ$), comparable to the rocking curve FWHM of the 002 peak of the SrTiO_3 substrates themselves (see the [supplementary material](#), Fig. S1). Sample quality affects thermal conductivity from the addition of phonon-scattering defects. Multiple samples of $n = 1$ and 2 are shown here to demonstrate how small variations in superlattice quality affect the trend in thermal conductivity in both interface density and temperature. The $n = 10$ $(\text{SrTiO}_3)_n\text{SrO}$ thin film was examined by low-angle annular dark field scanning transmission electron microscopy (LAADF-STEM); a micrograph is shown in [Fig. 1\(c\)](#). The film has the expected Ruddlesden–Popper structure with the larger atomically spaced $(\text{SrO})_2$ layers appearing bright as compared to the surrounding SrTiO_3 . The film also shows vertical $(\text{SrO})_2$ intergrowths and projections through the sample seen as bright vertical lines and patches, respectively, forming a brick and mortar, patchwork structure of bulk SrTiO_3 and

$(\text{SrO})_2$ planes due to the low energy of formation of $(\text{SrO})_2$ in SrTiO_3 .^{30,37,38}

Cross-plane thermal conductivity (k_{33}) of the entire series of $(\text{SrTiO}_3)_n\text{SrO}$ ($n = 1$ –5 and 10) films was measured by TDTR.^{40,41} TDTR is a non-contact, pump-probe optical technique that can be used for measuring thermal properties of materials on nanometer length scales. In our implementation of TDTR, a thin aluminum layer is deposited on the surface of the thin film and is pumped with a short pulse of a 9.8 MHz laser beam. A small fraction of energy from each pulse in the pump beam produces a sudden temperature jump of ~ 3 K near the surface of a sample. Decay of this near-surface temperature is then examined by the reflected energy of the pulses in the probe beam, i.e., the temperature change of the sample is measured by its temperature-dependent reflectance. The results of these time-resolved measurements are analyzed to obtain the cross-plane thermal conductivities. Further details of the TDTR measurements can be found in the [supplementary material](#).

[Figure 2\(a\)](#) compares the thermal conductivities of the $(\text{SrTiO}_3)_n\text{SrO}$ phases acquired from TDTR measurements at room temperature to conductivities calculated from first-principles methods for the same temperature. The MBE syntheses and the atomic-level simulations were performed for six ($n = 1$ –5 and 10) and four ($n = 1$ –4) members, respectively, and reveal significant agreement in trends, minima, and magnitude of the thermal conductivity across the series. All samples show the expected trend of the conductivity decreasing with increasing density of thermal-resistant interfaces. Very similar trends, albeit with slightly larger values of thermal conductivity, were seen in the earlier empirical calculations of this system.²¹ Phonons experience scattering at the interfaces between rock salt SrO and perovskite SrTiO_3 layers, which increases as n becomes smaller. For $n \leq 4$, the phonon mean free path is predicted to be larger than the spacing between the $(\text{SrO})_2$ layers sandwiching SrTiO_3 [[Fig. 2\(a\)](#) inset]. A transition in the thermal conductivity, [Fig. 2\(a\)](#), and phonon mean free path, [Fig. 2\(a\)](#) inset, is predicted by our theoretical calculations for the $n = 1$ member as the system changes from being best represented as SrTiO_3 with SrO interfacial layers to a well-defined monolithic Ruddlesden–Popper crystal with its own phonon spectrum and thermal transport properties (Sr_2TiO_4). From the current experimental data, it is unclear if the $n = 1$ member has an increase in thermal conductivity as compared to $n = 2$.

A similar trend with interface density was observed in SrTiO_3 - BaTiO_3 superlattice materials.⁴² Compared to the perovskite-on-perovskite system, the Ruddlesden–Popper superlattices not only have an atomic-mass variation, but also a structural variation between superlattice layers from the perovskite slabs interleaved with rock salt-type SrO layers. Structural changes from layer-to-layer are believed to provide additional contributions to phonon scattering at the internal interfaces.

We used the VASP suite to carry out all the *ab initio* calculations shown in [Fig. 2](#).^{43–46} Full details of the calculations can be found in the [supplementary material](#). In [Fig. 2\(b\)](#) at 300 K, excellent agreement between the *ab initio* calculations and experiment is observed for SrTiO_3 , while the calculations slightly overpredict the measured thermal conductivity of the Ruddlesden–Popper phases. The disagreement might be related to the calculations having been carried out for the perfect structure, while measurements were performed on thin films with defects that are evident in [Fig. 1\(c\)](#).

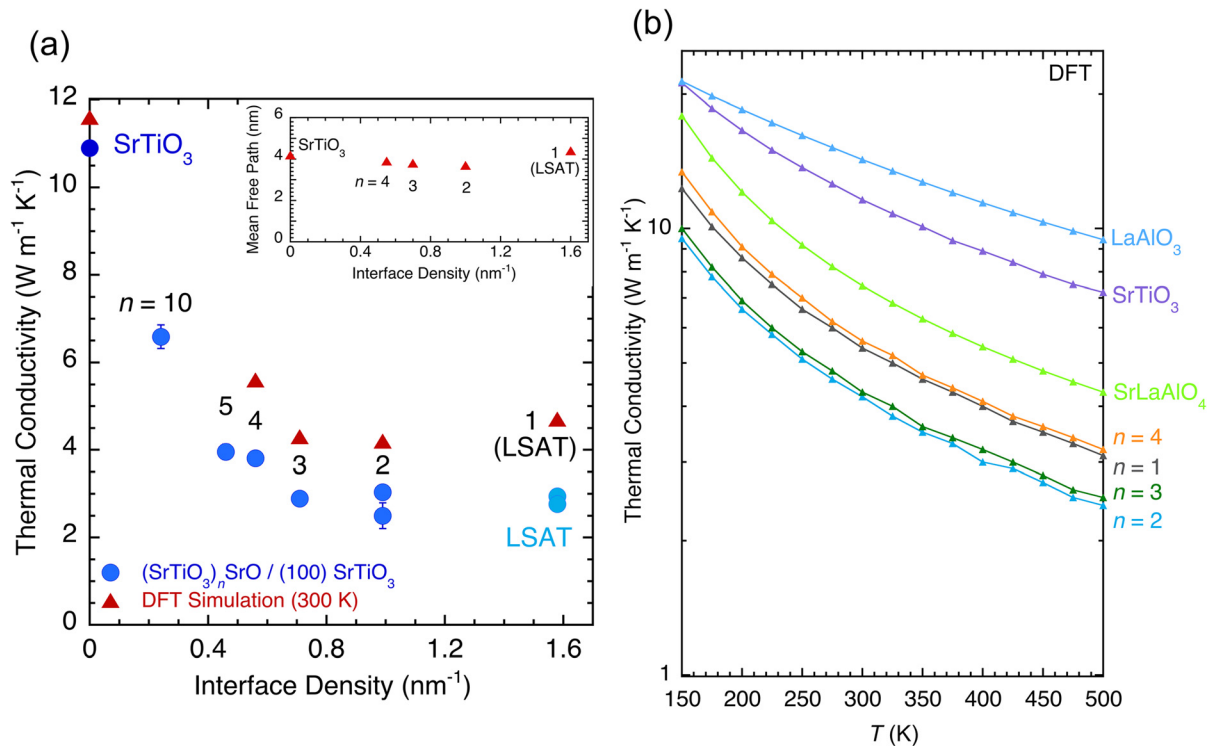


FIG. 2. (a) Summary of experimental and calculated cross-plane thermal conductivities (k_{33}) of the Ruddlesden–Popper $(\text{SrTiO}_3)_n\text{SrO}$ phases as a function of interface density at 300 K. The error bars of the experimental data taken at room temperature are the result of multiple measurements taken from different regions of the samples. To match our experimental series, the DFT simulation was performed for bulk SrTiO_3 , and biaxial strained structures of $n = 1$ – 4 to replicate the epitaxial strain of the substrates used in our experiment, (001) SrTiO_3 or (001) LSAT. Inset: the phonon mean free path as calculated by DFT. (b) The *ab initio* calculated cross-plane thermal conductivities (k_{33}) of the Ruddlesden–Popper $(\text{SrTiO}_3)_n\text{SrO}$ phases, the Ruddlesden–Popper SrLaAlO_4 , and its parent phase LaAlO_3 as a function of temperature.

The thermal conductivity was measured from 150 K to 500 K for all samples to investigate the temperature dependence of the thermal conductivity of superlattices with different interface densities. The experimental results are shown in Fig. 3(a). The thermal conductivities of $n = 1$ – 3 samples are relatively temperature independent. For $n = 4, 5, 10$ samples, the slope of the thermal conductivities at higher temperatures approaches that of bulk SrTiO_3 with increasing n . To compare our thin film superlattices to a single crystal, samples of single crystal SrLaAlO_4 , an $n = 1$ Ruddlesden–Popper, and its parent phase, LaAlO_3 (an $n = \infty$ Ruddlesden–Popper), were measured by TDTR from 150 K to 500 K. At room temperature, SrLaAlO_4 was observed to have a thermal conductivity of around $4 \text{ W m}^{-1} \text{ K}^{-1}$. The *ab initio* calculation of k_{33} for SrLaAlO_4 is $7.4 \text{ W m}^{-1} \text{ K}^{-1}$ and for LaAlO_3 , $14.3 \text{ W m}^{-1} \text{ K}^{-1}$. The *ab initio* calculated values were found to be systematically higher when compared to the TDTR measurements. The measured thermal conductivity of our Sr_2TiO_4 films, 2.8 – $3 \text{ W m}^{-1} \text{ K}^{-1}$, is significantly lower than the result of the *ab initio* calculations, $5.4 \text{ W m}^{-1} \text{ K}^{-1}$, likely due to interface disorder in our MBE-grown films. The lack of perfect single-crystal quality is further confirmed when the temperature dependence of k_{33} of our Sr_2TiO_4 films is compared to that of single-crystal SrLaAlO_4 . The two materials show a clear difference in trend, Fig. 3(b), indicating that our thin film samples have some atomic disorder possibly due to vertical $(\text{SrO})_2$ faults,^{22,36–38} flattening and lowering the temperature-dependent

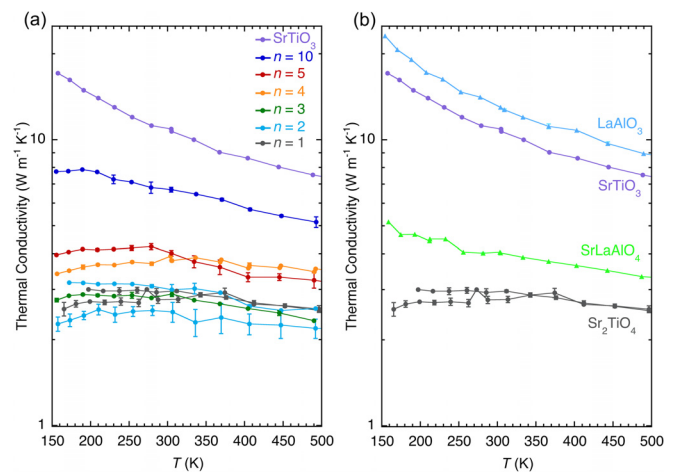


FIG. 3. (a) Experimental cross-plane thermal conductivities (k_{33}) of the Ruddlesden–Popper $(\text{SrTiO}_3)_n\text{SrO}$ phases measured from 500 K to 150 K. The error bars of the experimental data are the result of multiple measurements taken at different regions of the samples. (b) Comparison of experimentally measured k_{33} of $n = 1$ thin-film Sr_2TiO_4 with its parent ($n = \infty$) phase, a single crystal of SrTiO_3 . Also shown is a comparison of the experimentally measured k_{33} of an $n = 1$ single-crystal SrLaAlO_4 and a single crystal of LaAlO_3 ($n = \infty$).

thermal conductivity. The temperature-dependence of the calculated and measured k_{33} of the Ruddlesden–Popper superlattices [a comparison between Figs. 2(b) and 3(a)] also shows that the thin films have a flatter temperature dependence than predicted by theory. The variance between our experimental results and theory improves at higher temperatures where defects dominate less of the phonon scattering as seen from the converging of the multiple $n = 1$ and 2 films with temperature in Fig. 3.

The investigation of this Ruddlesden–Popper series provides an opportunity to tailor the thermal properties through changing dimensionality. In this Letter, we summarize the experimental and theoretical thermal conductivity cross-plane to the superlattice layering of $(\text{SrTiO}_3)_n\text{SrO}$ phases as a function of interface density. The minimum in the temperature-dependent thermal conductivity as a function of n allows the thermal conductivity and its temperature dependence to be tuned. A transition in k_{33} at room-temperature is predicted but experimentally inconclusive for the $n = 1$ member as the distance between interfaces becomes smaller than the phonon mean free path. Intergrowths and planar faults in Ruddlesden–Popper phases likely serve as additional scattering centers and lower the effective phonon mean free path as compared to single crystal samples.

See the [supplementary material](#) for additional details on the $(\text{SrTiO}_3)_n\text{SrO}$ thin film growth and XRD characterization, the TDTR experimental setup, and further details of the *ab initio* calculations.

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DATA AVAILABILITY

The data that support the findings of this study are available in the [supplementary material](#) or from the corresponding author upon reasonable request.

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