

Crossover in thermal transport properties of natural, perovskite-structured superlattices

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Atomic-level simulations are used to analyze the thermal-transport properties of a naturally layered material: the Ruddlesden–Popper phase, formed by interleaving perovskite layers of strontium titanate with strontium oxide rocksalt layers. The thermal conductivity parallel to the plane of structural layering is found to be systematically greater than that perpendicular to the layering. With decreasing number of perovskite blocks in the structure, a transition is seen from the thermal-transport properties of a bulk solid containing interfaces to that of an anisotropic monolithic material. The exact transition point should be temperature dependent and might enable tuning of the thermal conductance properties of the material. © 2009 American Institute of Physics. [doi:10.1063/1.3253421]

Low thermal conductivity materials are important for a variety of applications, including thermal barrier coatings and thermoelectric devices. Thermal control on the scale of the individual electronic devices (<100 nm) is becoming increasingly important with continuously scaling design rules. Superlattices are particularly interesting due to the possibility of lowering thermal conductivity, potentially even below the alloy limit.^{1,2} A number of explanations have been proffered for the low thermal conductivity of superlattice structures: reduction of the group velocity of the heat-carrying phonons due to the bands folding,^{3,4} mini-Umklapp processes⁵ and diffuse interface scattering.⁶ A full explanation, however, has yet to be developed.⁷ In addition, the thermal conductivity of synthetic semiconductor superlattices, as a function of the layer thickness, exhibits a minimum that has been explained as a result of a crossover between coherent and incoherent thermal transport.⁸

Artificial superlattices display strong anisotropy in structure and properties parallel and perpendicular to the layering. A similar structural anisotropy is also present in naturally layered material. An excellent example of such a natural superlattice is the Ruddlesden–Popper (RP) series of phases of the Sr–Ti–O system,^{9,10} formed by the interleaving of SrTiO₃ perovskite layers with SrO rocksalt layers. Just as engineered superlattices do, such natural superlattices can be expected to show significant anisotropy in thermal transport behavior, with the thermal conductivity through the layers being significantly lower than in parallel direction. Indeed, such a strong thermal anisotropy has recently been reported in another natural oxide superlattice, Bi₄Ti₃O₁₂.¹¹ Thermal conductivity below the Cahill limit¹² was observed in the layered material, WSe₂, both experimentally and in numerical simulations.¹³ Theoretical investigations¹⁴ for the same material based on modified Klemens theory provided a possible explanation for such a lowering of thermal conductivity in

anisotropic materials. In this letter, we use atomic-level simulation methods to show that the thermal transport behavior of the RP phase of SrTiO₃ undergoes a transition from that of a bulk material containing interfaces at large repeat lengths, to that of a monolithic anisotropic bulk system at short repeat lengths. This transition includes a minimum in thermal conductivity at repeat lengths comparable with the phonons mean free path.

The structure of a typical example of the RP-phase, the $n=2$ Sr₃Ti₂O₇ is presented in the inset of Fig. 1. It can be viewed as n layers of the SrTiO₃ perovskite, followed by a layer of the rocksalt structure of SrO, rotated by 45° about the [001] layering axis. This rocksalt layer is followed by another n layers of the perovskite, shifted in the $\langle 110 \rangle$ crystallographic direction by $a/\sqrt{2}$, where a is a lattice constant

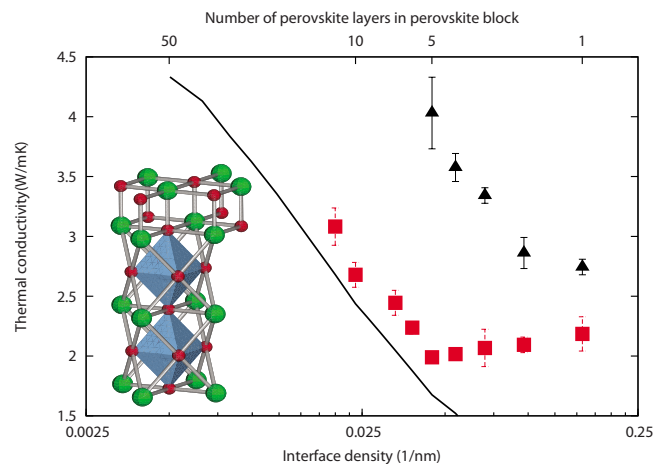


FIG. 1. (Color online) Thermal conductivity of the RP series of phases of the strontium titanate as a function of the number of the perovskite layers at 1250 K. (■) Across the layers, (▲) parallel to the layers. Solid line is the calculations based on the superlattice model, as described in the text. In the inset unit cell of the Sr₃Ti₂O₇ RP- $n=2$ phase material. The oxygen octahedra of the two perovskite unit cells are outlined. The single rocksalt layer is shown at the top.

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of the perovskite block. The RP structures are thus prototypically tetragonal and exhibit space group $I4/mmm$. Experimentally, structures with periodicities of up to $n=5$ have been synthesized,^{15,16} thus providing a range of oxides with varying degrees of anisotropy: if n is large, one expects the material to behave as a regular isotropic perovskite, interspersed with planar defects. For small values of n , the system is expected to be a solid with properties rather different from the properties of the individual constituent layers. As the number of perovskite layers changes in between these two extreme compositions, we anticipate a transition in thermal-transport behavior.

We use atomic-level simulation methods to characterize the thermal properties of the RP phases. The interatomic forces are described with a classical Buckingham interatomic potential.¹⁷ The particular potential used in this study¹⁸ reproduces the mechanical and thermal properties of SrO and STO reasonably well. For SrO the simulations give a thermal expansion of $1.13 \times 10^{-5} \text{ K}^{-1}$ as compared with $1.4 \times 10^{-5} \text{ K}^{-1}$ obtained from experiment.¹⁹ The agreement for SrTiO₃ (Ref. 20) is even better: $0.99 \times 10^{-5} \text{ K}^{-1}$ versus $1.07 \times 10^{-5} \text{ K}^{-1}$.

Thermal conductivities are calculated at 1250 K using a standard nonequilibrium molecular dynamics simulation technique.²¹ In this approach the simulation cell is partitioned into a number of slices of equal thickness along the direction. Two of these slices, separated by half the simulation cell, serve as a heat source and a heat sink: an equal amount of energy is added to the source and removed at the sink, setting up a constant heat flow vector in the system. The temperature in the individual slices is used to calculate the temperature gradient, and thence the thermal conductivity from Fourier's law. It is important to estimate the computational errors associated with this type of simulation,²² the main source of which is the statistical error in the determination of temperature. Hence sufficiently long runs are required (we found ~ 200 ps to be sufficient). The statistical error is typically of the order of 6%–8%, in agreement with the error estimation of Stevens.²² As has been discussed extensively elsewhere,²³ because the length of the simulation cell is shorter than the phonon mean-free-path, a detailed size analysis is required in order to yield the best estimate of the thermal conductivity. This system size analysis was performed here: all results given are those extrapolated to infinite simulation cell size.

The results of the thermal conductivity calculations for the RP phases at 1250 K, as a function of number of perovskite layers, are presented in the Fig. 1. The thermal conductivity perpendicular to the layering (k_{\perp}) is significantly smaller than that parallel to layers (k_{\parallel}). k_{\parallel} appears to increase monotonically (in the limit of the infinite number of the perovskite layers it should converge to the SrTiO₃ value). k_{\perp} is more interesting, initially decreasing slightly with increasing number of perovskite layers, it then increases as the number of layers increases further. The minimum on the curve is at $n=5$ (Sr₅Ti₄O₁₃). This behavior is directly analogous to the thermal conductivity minimum reported for artificial superlattices.^{8,24} An analogous transition, from the thermal-transport properties of a polycrystalline system to that of an amorphous system, was observed in simulation of Si, with the crossover taking place at a grain size of about 3 nm.²⁵

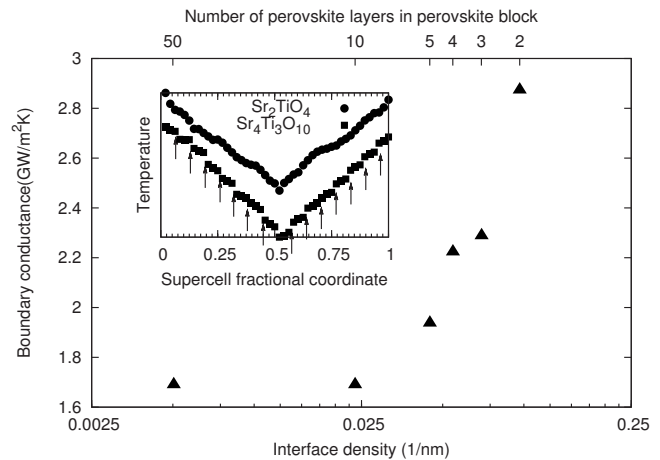


FIG. 2. Thermal boundary conductivity of the SrO layers as a function of the number of perovskite layers. Inset: temperature profiles of Sr₂TiO₄ and Sr₄Ti₃O₁₀ illustrating absence and presence of the jumps (arrowed) at the SrO layers.

One can view the structure of the RP phases as a series of perovskite layers separated by SrO planar defects. The interfacial thermal resistance of these planar defects should give rise to distinct temperature jumps at the position of the SrO layers in the simulated thermal profiles. We indeed observe these temperature jumps for $n \geq 2$. One such example, for $n=3$ Sr₄Ti₃O₁₀, is presented in the inset to Fig. 2. From this data and corresponding data for other large n values, we calculate the values of the effective boundary conductance shown in Fig. 2. The limiting value of 1.7 GW/m² K at large n ($n=50$) corresponds to the interfacial conductance of an individual isolated interface, namely an SrO layer in bulk SrTiO₃. Even $n=10$ yields the same conductance, indicating that the $n=10$ RP phase behaves thermally as a bulk perovskite containing a discrete interface. As the number of perovskite layers decreases further, the thermal conductance increases, an effect previously seen experimentally in the AlN-GaN system.²⁶ This dependence arises from a qualitative change in the role of the SrO layer on the thermal transport behavior from being a planar defect in bulk SrTiO₃ for large n , to being an integral part of an intrinsically layered material for small n . Indeed, when only one perovskite layer is present ($n=1$), there are no jumps in the temperature profile (see inset on Fig. 2). However, as the number of perovskite layers increases, the SrO layer behaves more and more as an embedded interface. This interface effect is present despite the fact that the interface between the SrO and perovskite layers is crystallographically coherent. In turn, this suggests that the boundary conductance is a result of the differences in the anharmonicity of the interactions at the interface and the differences in the atomic masses at the interface.

The view that RP-phases are a number of perovskite blocks separated by interfaces allows the calculation of the thermal conductivity in the regime of the large repeat length by the simple standard formula for adding thermal conductivities: $k = k_0 \cdot [1 + k_0 / (R \cdot d)]^{-1}$. Here k_0 is the thermal conductivity of the perovskite block that has thickness d and R is the interfacial boundary conductance. k_0 is obtained using the Mathiessen rule that takes into account contributions from the intrinsic thermal conductivity of the bulk SrTiO₃ and final thickness of the perovskite block. The result of

application of this formula is given on Fig. 1 by the solid line. It matches reasonably well with the simulation data for large values of n (low interface density), though it slightly underestimates thermal conductivity. For small n , the Matthiessen rule fails completely, indicative of the transition from an interfacial system to a monolithic single crystal.

In this Letter we have presented molecular dynamics simulation studies of the anisotropic thermal conductivity in the RP-phases of the SrO–SrTiO₃ system at 1250 K. The results indicate that these systems may be viewed as natural superlattice systems with ideal interfaces between the SrO and perovskite blocks. The observed behavior fits very well to what is known about thermal transport in synthetic superlattices. In particular, the minimum of the thermal conductivity perpendicular to the layering structure, as a function of the thickness of the layers, is attributed to a transition between two different mechanisms of the thermal transport: coherent transport, when the boundary between the layers is a part of the crystal structure, which affects strongly the phonon structure, and incoherent transport, in which case one can consider phonons to be completely determined by the perovskite layers and experience scattering at the interface between the SrO and perovskite layers. Thermal transport parallel to the layers, on the other hand, shows monotonic increase with the number of layers. As a result there is a maximum anisotropy in the thermal conductivity, a factor of 2, for the $n=5$ RP-phase, Sr₆Ti₅O₁₆.

It is interesting to consider the position of the minimum of k_{\perp} as a function of temperature. We estimated the effective mean free path in pure SrTiO₃ from the kinetic formula for the thermal conductivity ($k=vc_v l_{\text{eff}}/3$) to be $l_{\text{eff}} \approx 1.5$ nm which corresponds to $n=4$ perovskite layers (lattice parameter=0.39 nm), which is approximately where the simulated thermal conductivity minimum is observed. We therefore expect that because the mean free path increases with decreasing temperature, the minimum will be shifted toward thicker perovskite layers. The opposite would then be true for the high temperatures, with the minimum in thermal conductivity being shifted to thinner perovskite layers. Such behavior might allow further tuning toward better thermal insulator behavior for a given temperature.

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