Pushing the limit of mechanical stiffness and glass-like thermal conductivity of crystalline materials via interfaces, Ruddlesden-Popper phases, and high entropy engineering

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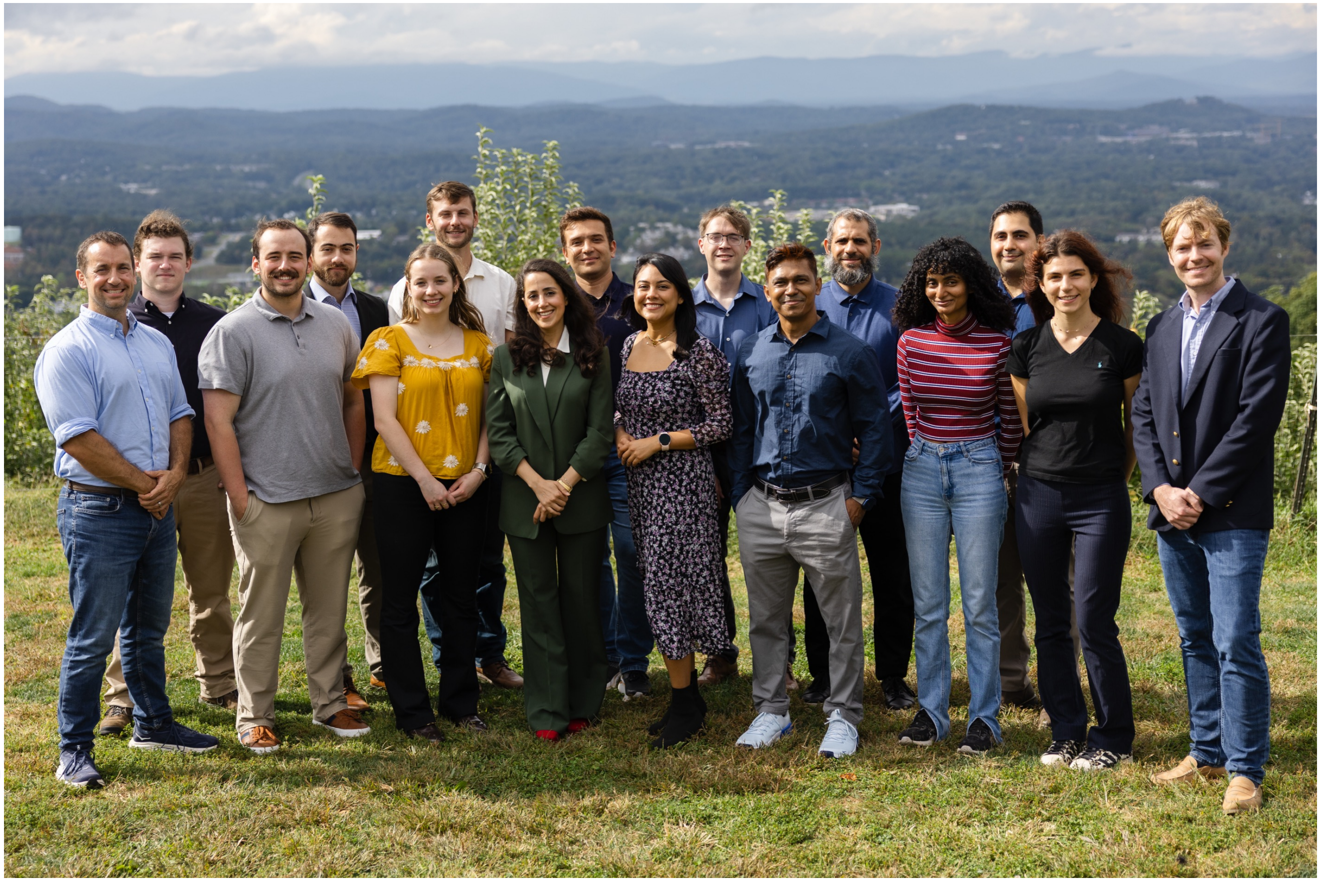
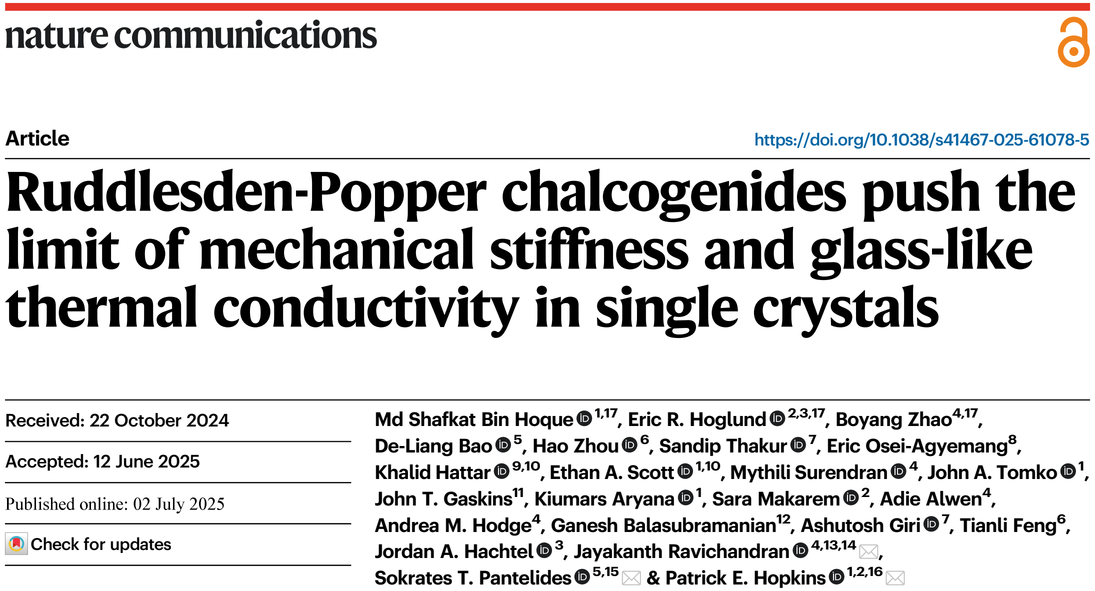
AT THE UNIVERSITY OF VIRGINIA



Students, publications, collaborators and funding



nature communications

Article

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Ruddlesden-Popper chalcogenides push the limit of mechanical stiffness and glass-like thermal conductivity in single crystals

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Check for updates

Md Shafkat Bin Hoque[1,17], Eric R. Hoglund[2,3,17], Boyang Zhao[4,17], De-Liang Bao[5], Hao Zhou[6], Sandip Thakur[7], Eric Osei-Agyemang[8], Khalid Hattar[9,10], Ethan A. Scott[1,10], Mythili Surendran[4], John A. Tomko[1], John T. Gaskins[11], Kiumars Aryana[1], Sara Makarem[2], Adie Alwen[4], Andrea M. Hodge[4], Ganesh Balasubramanian[12], Ashutosh Giri[7], Tianli Feng[6], Jordan A. Hachtel[3], Jayakanth Ravichandran[4,13,14] ✉, Sokrates T. Pantelides[5,15] ✉ & Patrick E. Hopkins[1,2,16] ✉

Unpublished work

"Phonon-mediated thermal transport and elastic modulus enhancement in TiN/TiC superlattices"

Led by: Rafiqul Islam (at Intel)

Collaboration w/ D. Gall (RPI)

COMMUNICATION

ADVANCED MATERIALS

Ceramics

www.advmat.de

Charge-Induced Disorder Controls the Thermal Conductivity of Entropy-Stabilized Oxides

*Jeffrey L. Braun, Christina M. Rost, Mina Lim, Ashutosh Giri, David H. Olson, George N. Kotsonis, Gheorghe Stan, Donald W. Brenner, Jon-Paul Maria, and Patrick E. Hopkins**

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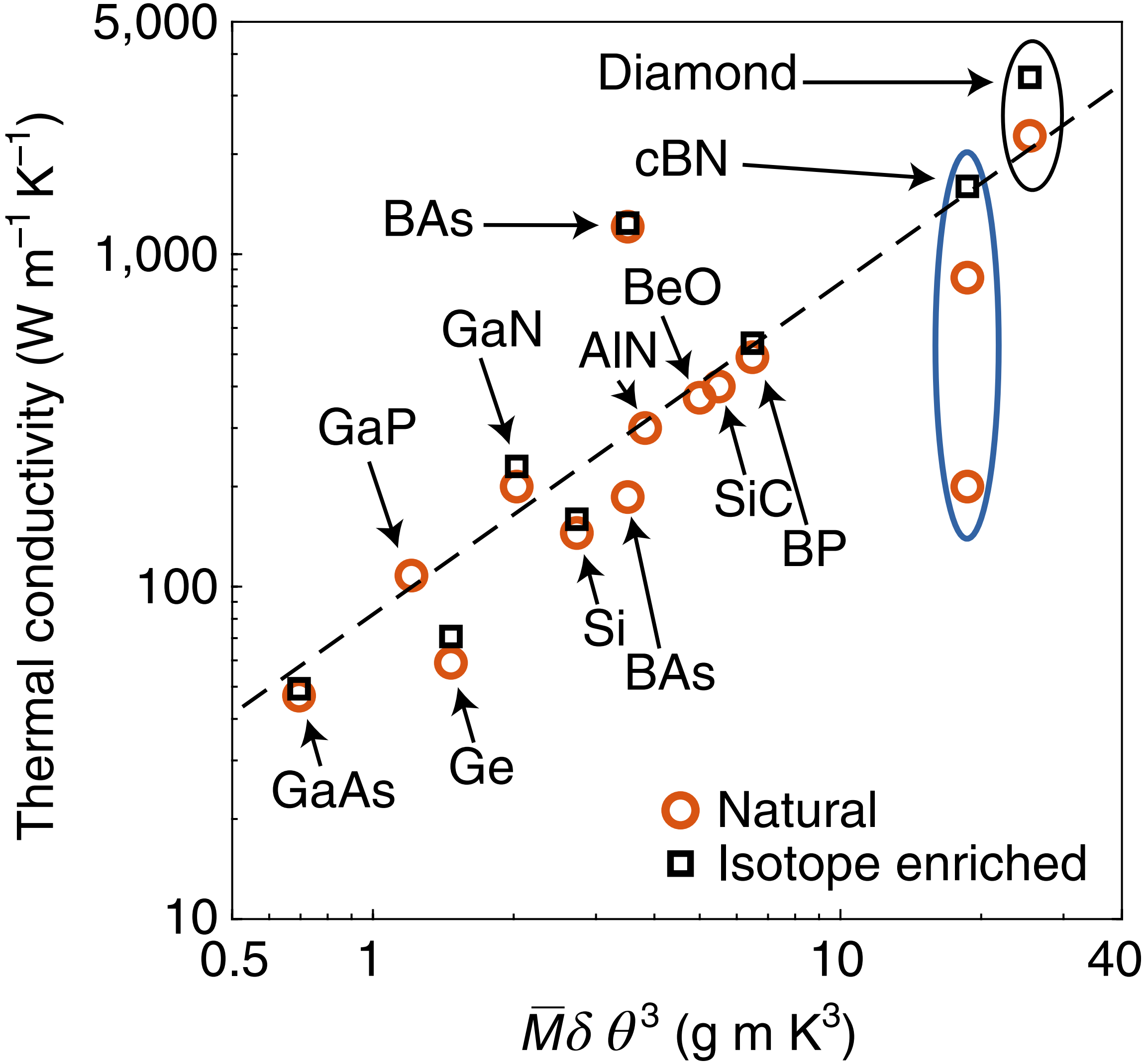
Stiffer crystalline materials - Larger λ - Larger v - Larger κ



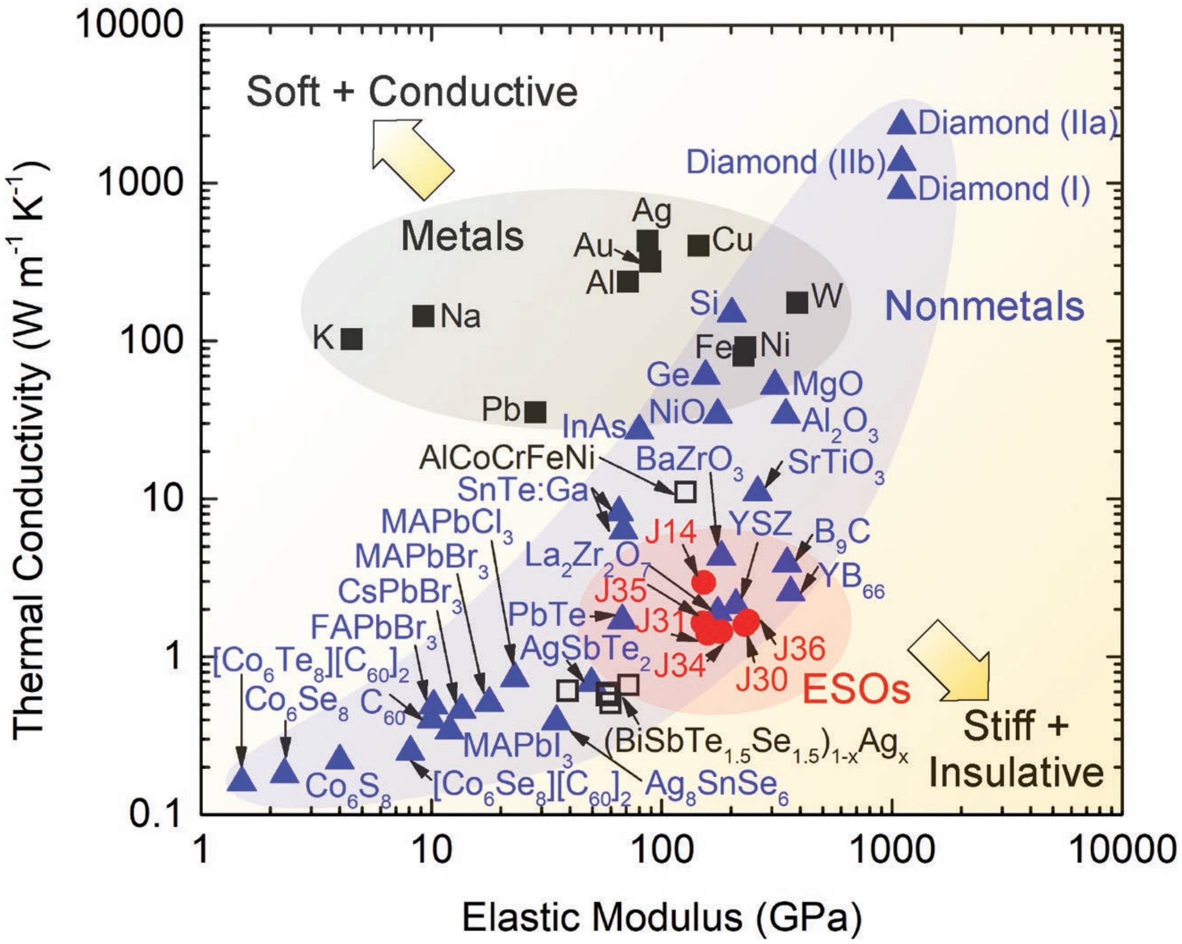
Nat. Mat. **19**, 481 (2020)

$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

- What makes a high κ material?

- Slack Criteria:
  - Strong bonds
  - Light masses
  - Small unit cell
  - Minimize defects!

Softer disordered materials - shorter λ - smaller v - smaller κ

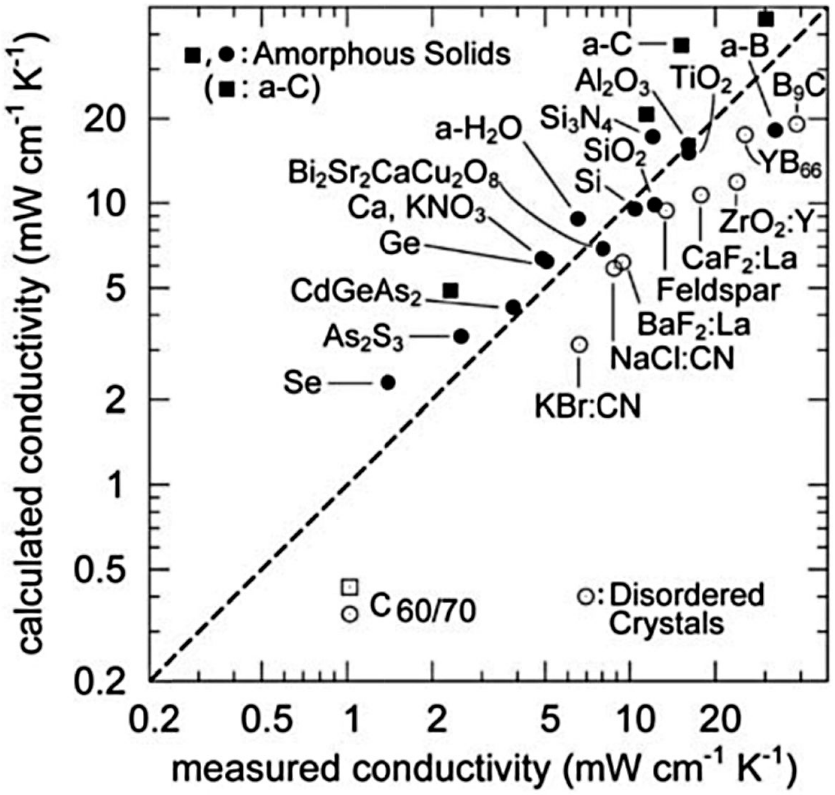


$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

- What makes a low κ material?
- Opposite of Slack Criteria:
  - Weak bonds
  - Heavy masses masses
  - Large unit cell
  - Increase “defects”!

Adv. Mater. **30**, 1805004 (2018)

Need electron crystal, but phonon glass – how?



- But often times making a low thermal conductivity material means disorder in crystal or even amorphous phase
- This can also reduce electron transport, which will reduce thermoelectric performance

REVIEW ARTICLE

CRYSTAL Research&Technology

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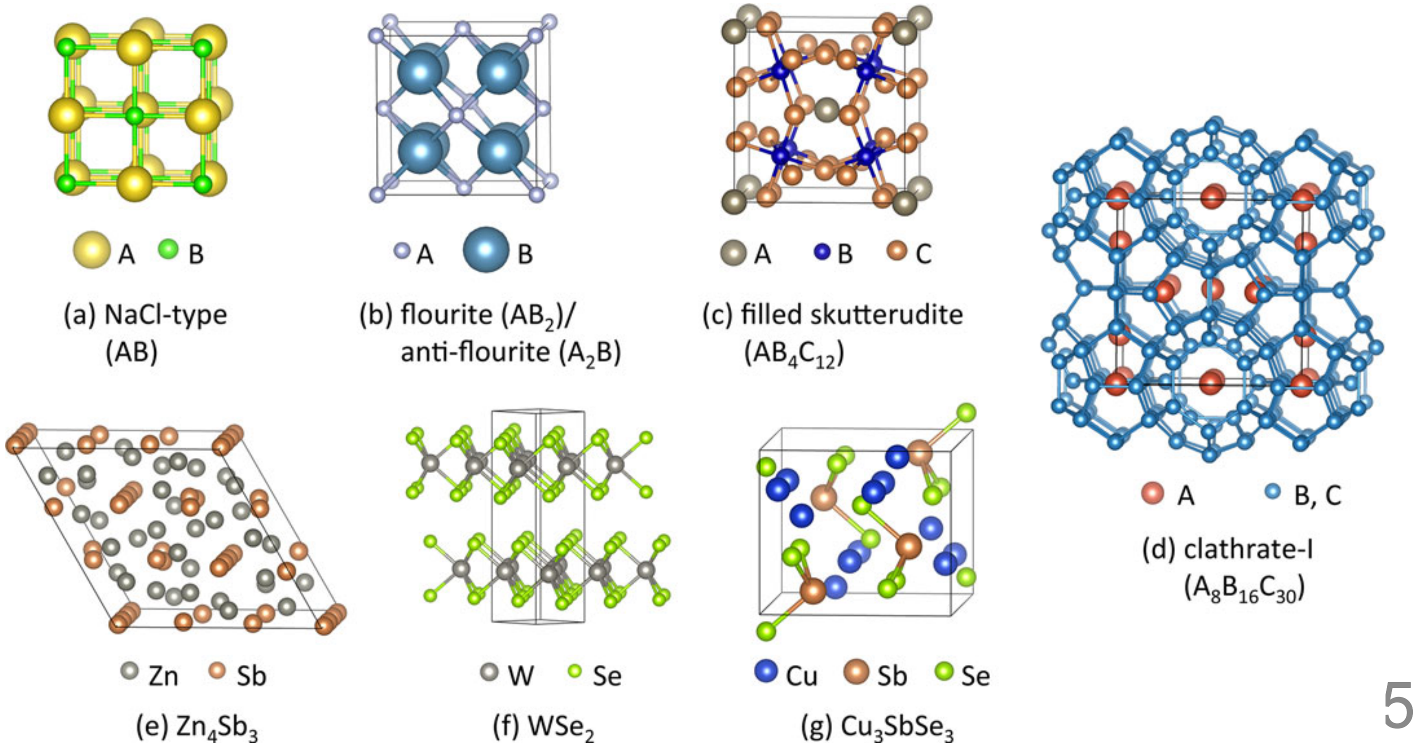
Inorganic Crystals with Glass-Like and Ultralow Thermal Conductivities†

Matt Beekman and David G. Cahill*



(a) NaCl-type (AB)

(b) flourite (AB_2)/ anti-flourite (A_2B)

(c) filled skutterudite (AB_4C_{12})

(d) clathrate-I ($A_8B_{16}C_{30}$)

(e) Zn_4Sb_3

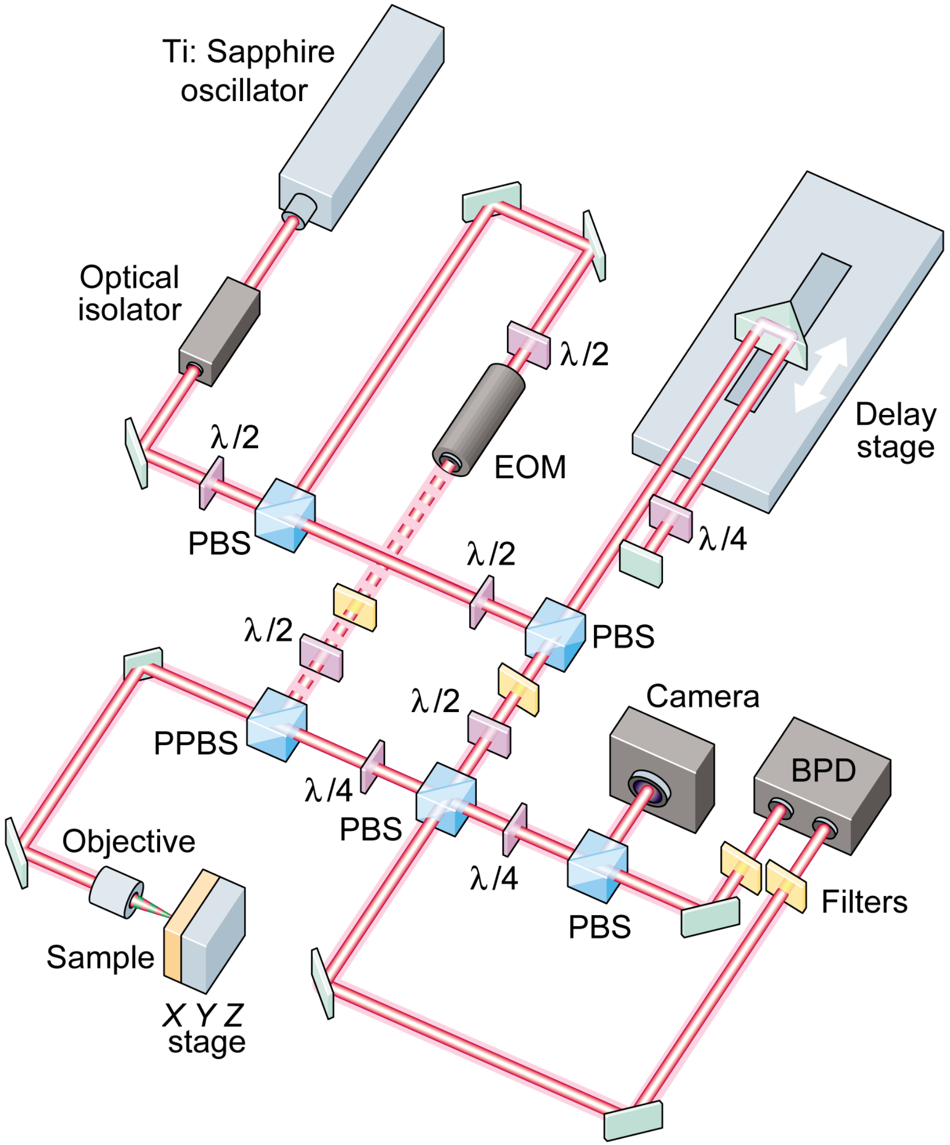
(f) WSe_2

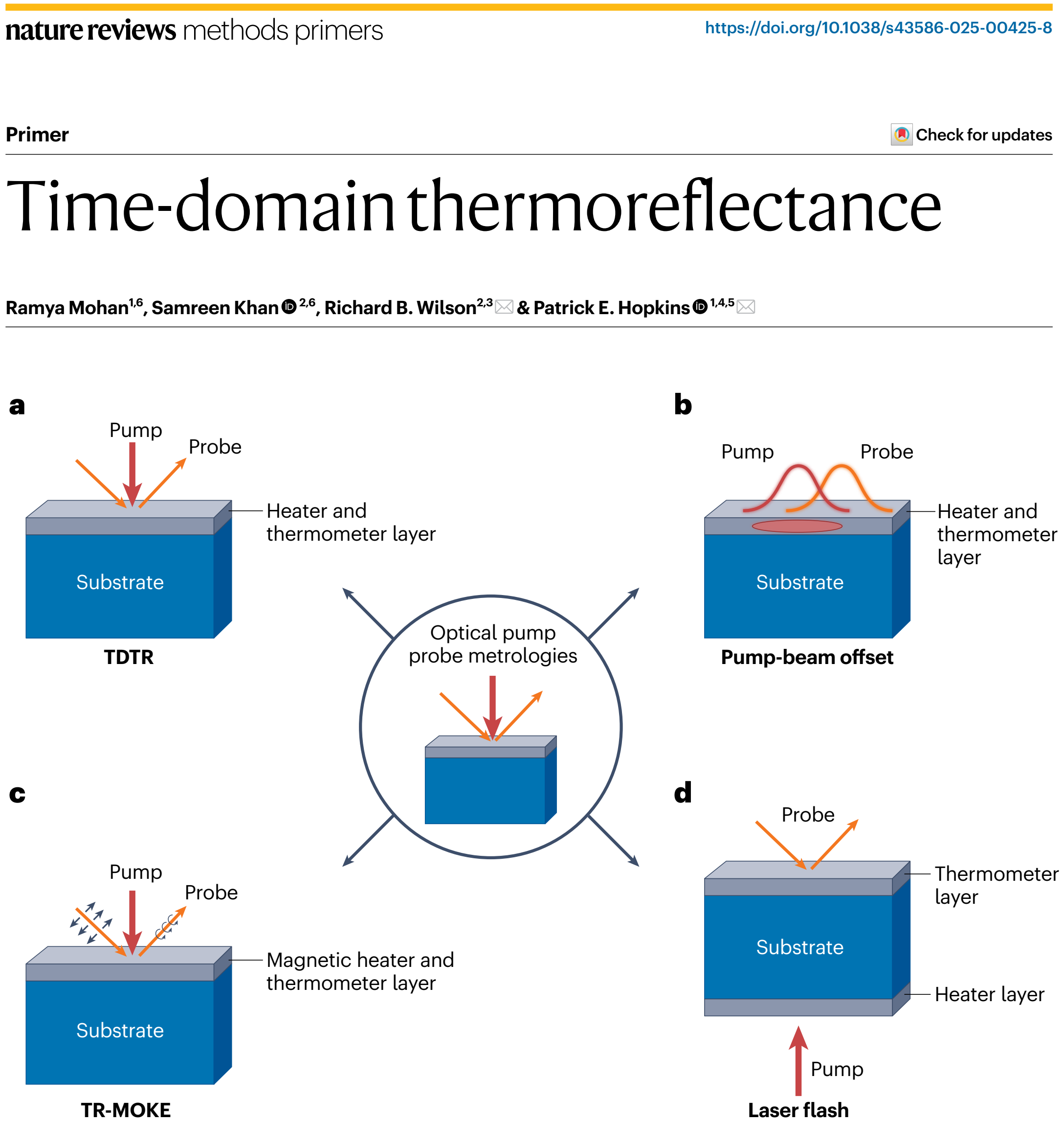
(g) Cu_3SbSe_3

Outline

- Question: How do we achieve low thermal conductivities in crystalline thin films with high modulus and crystal quality? How do we break the coupling of bonding and thermal conductivity dictated by Slack criteria?
- Thermal conductivity measurements with thermoreflectance
- Engineering defects in crystalline oxide films with entropy stabilization
- Phonon localization and reductions in group velocities with naturally layered crystals – Ruddlesden-Poper chalcogenides
- Interface phases in TiN/TiC superlattices that increase stiffness and reduce thermal conductivity

Thermoreflectance: thermal conductivity in thin films





nature reviews methods primers https://doi.org/10.1038/s43586-025-00425-8

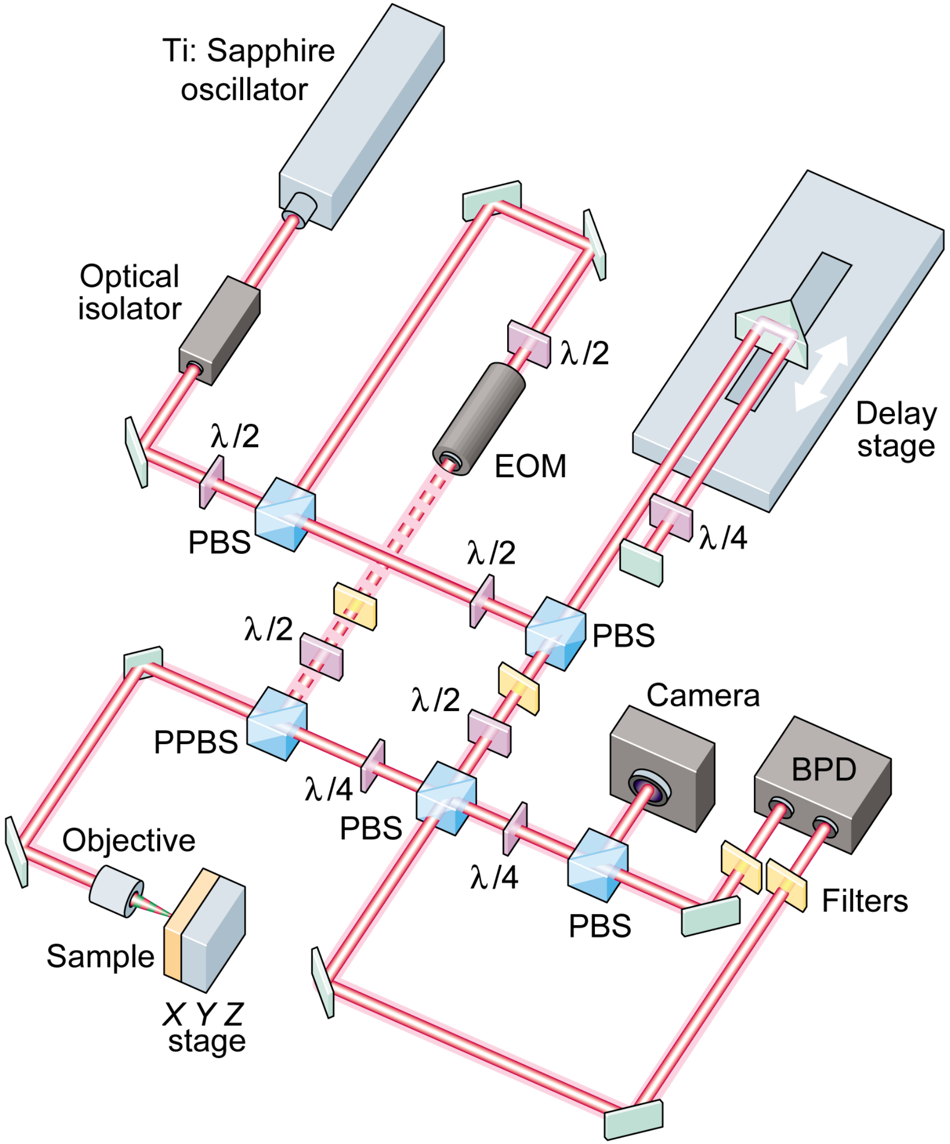
Primer Check for updates

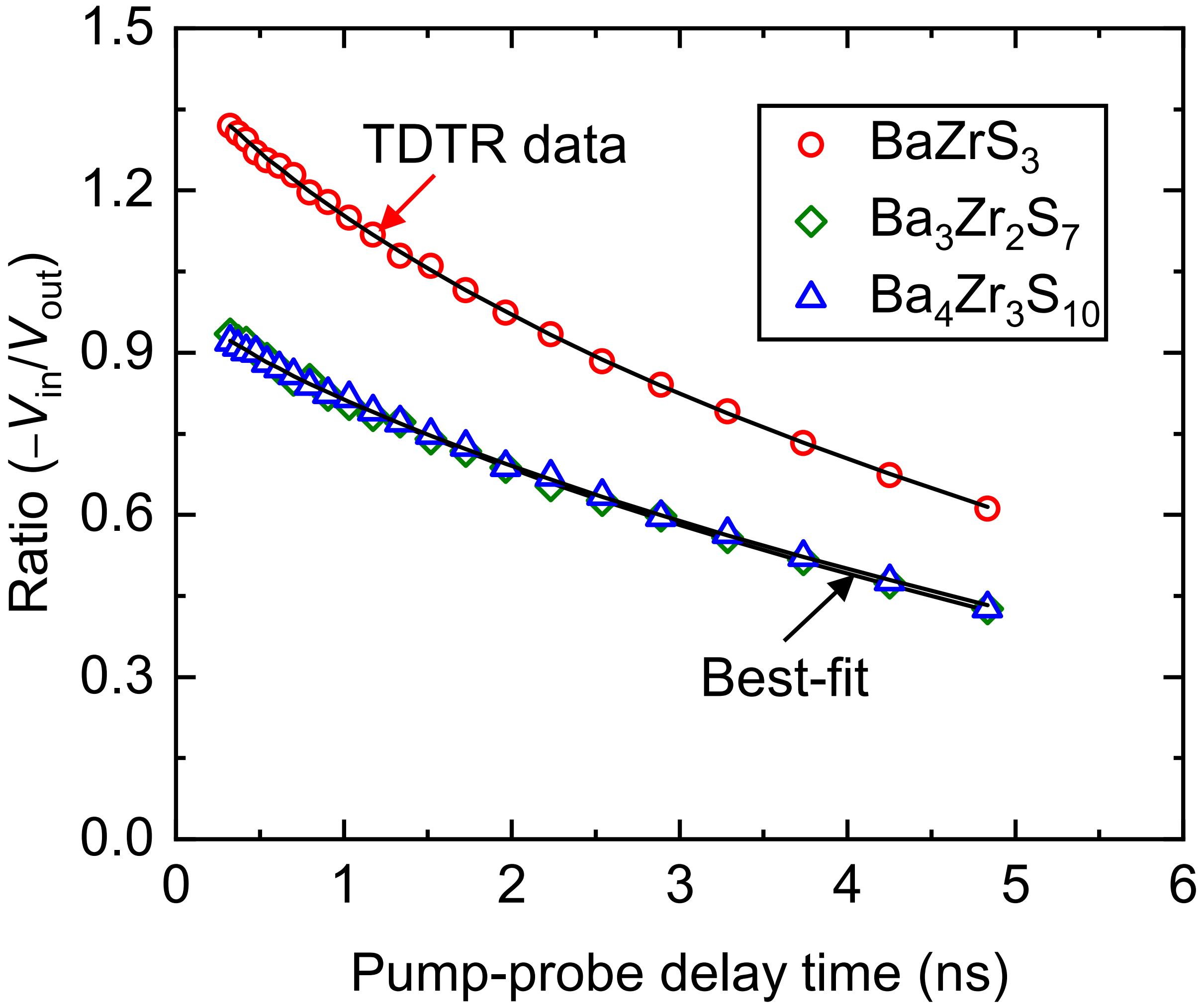
Time-domain thermoreflectance

Ramya Mohan[1,6], Samreen Khan[2,6], Richard B. Wilson[2,3] & Patrick E. Hopkins[1,4,5]

Nature Reviews Methods Primers **5**, 55 (2025).

Thermoreflectance: thermal conductivity in thin films





Nature Communications **16**, 6104 (2025)

Making complicated thermal conductivity metrologies easy

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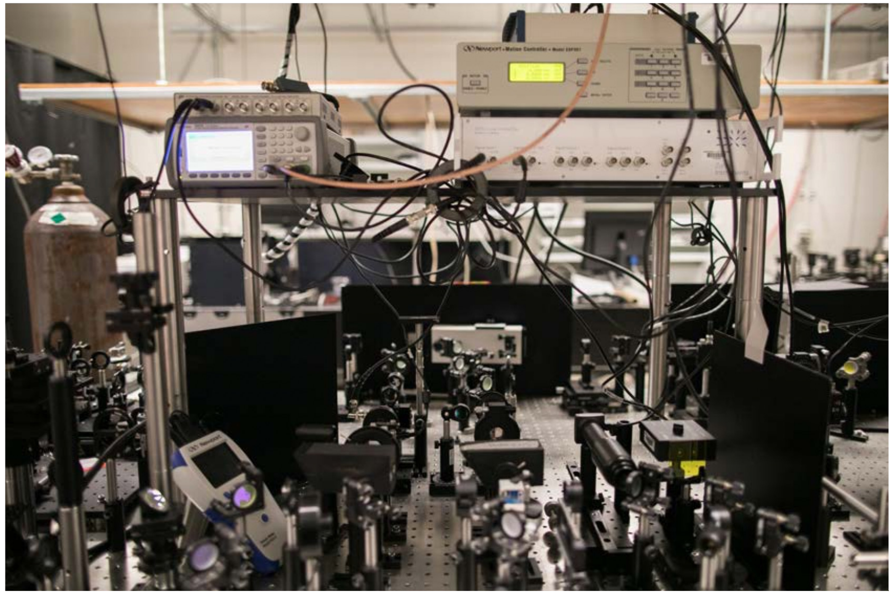
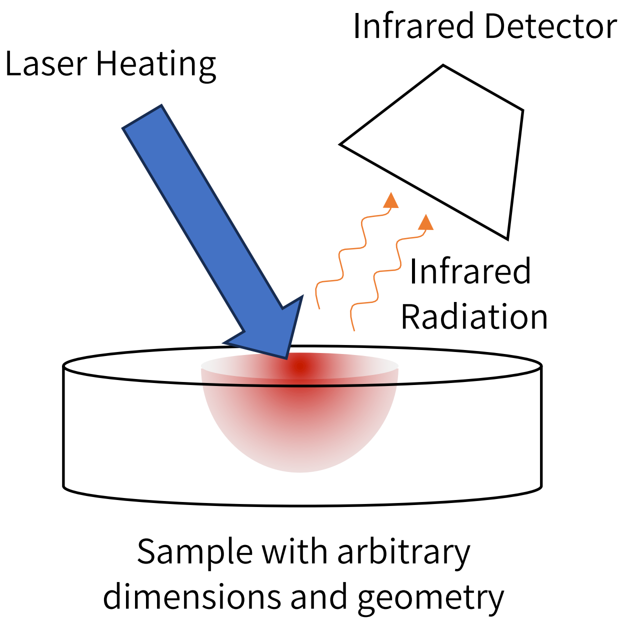
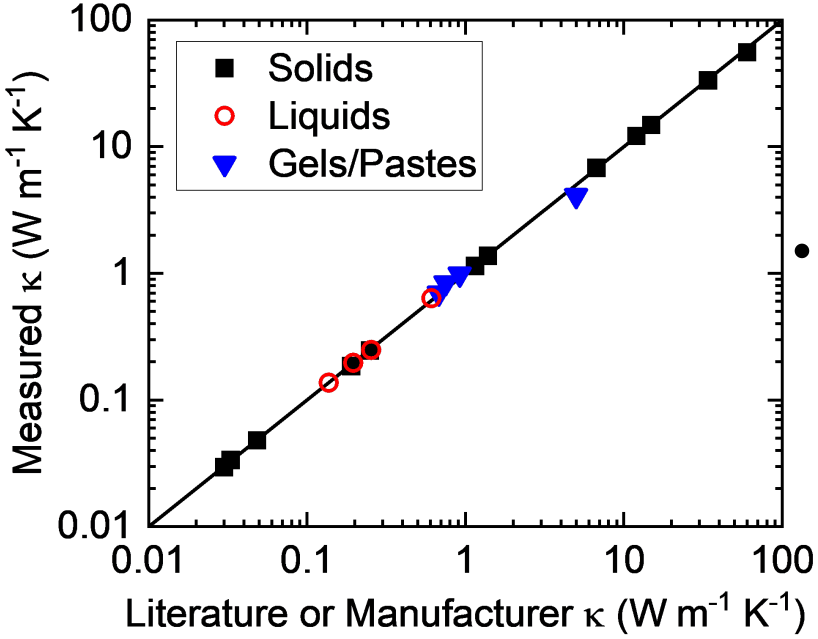


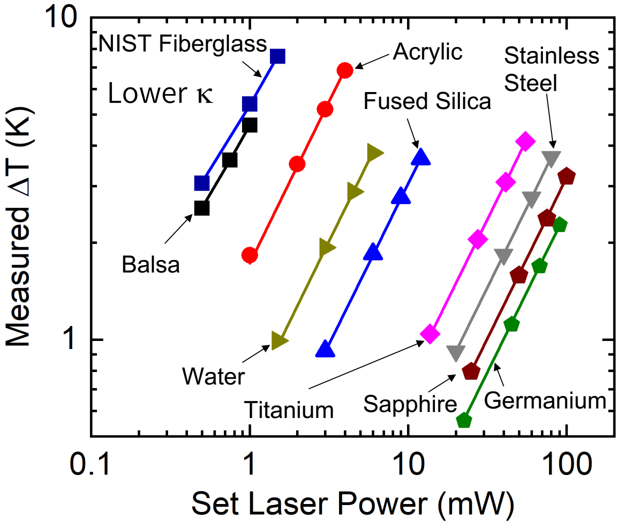
COI statement: Hopkins
co-founder of Laser thermal

To thick coatings and bulk materials (TOPS)





- Thermo-optical plane source (TOPS) ideal for measuring thermal conductivity of materials with length scales greater than ~0.5 – 1 mm.
- No surface roughness or material shape requirement since temperature monitored with IR thermography and not a reflected probe laser (as in thermoreflectance)




Review of Scientific Instruments ARTICLE pubs.aip.org/aip/rsi

A thermo-optical plane source method to measure thermal conductivity

Cite as: Rev. Sci. Instrum. 96, 074901 (2025); doi: 10.1063/5.0267492
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Jeffrey L. Braun,[1,a)] Bryan N. Baines,[1] John T. Gaskins,[1] and Patrick E. Hopkins[1,2,3,4]

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LASER THERMAL

COI statement: Hopkins co-founder of Laser thermal

Outline

- Question: How do we achieve low thermal conductivities in crystalline thin films with high modulus and crystal quality? How do we break the coupling of bonding and thermal conductivity dictated by Slack criteria?

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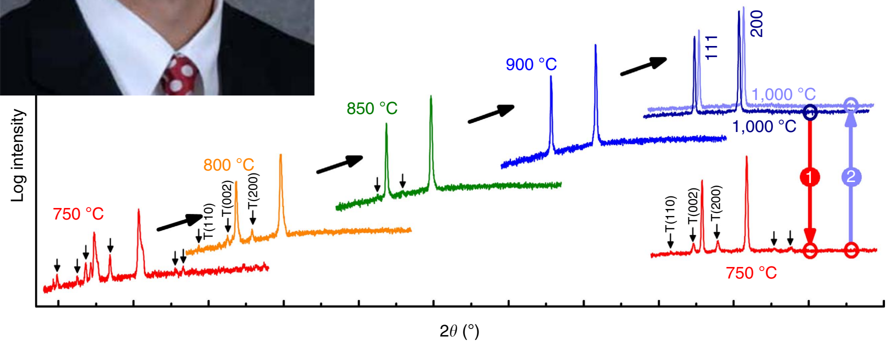
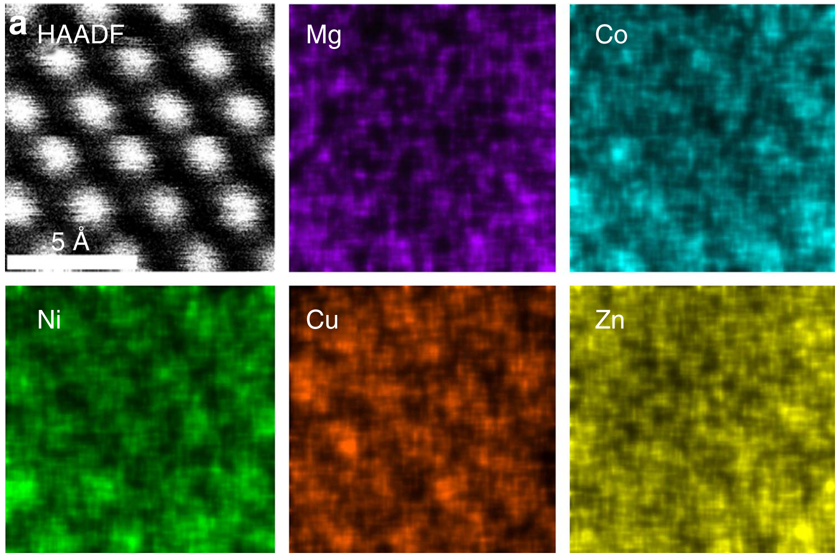
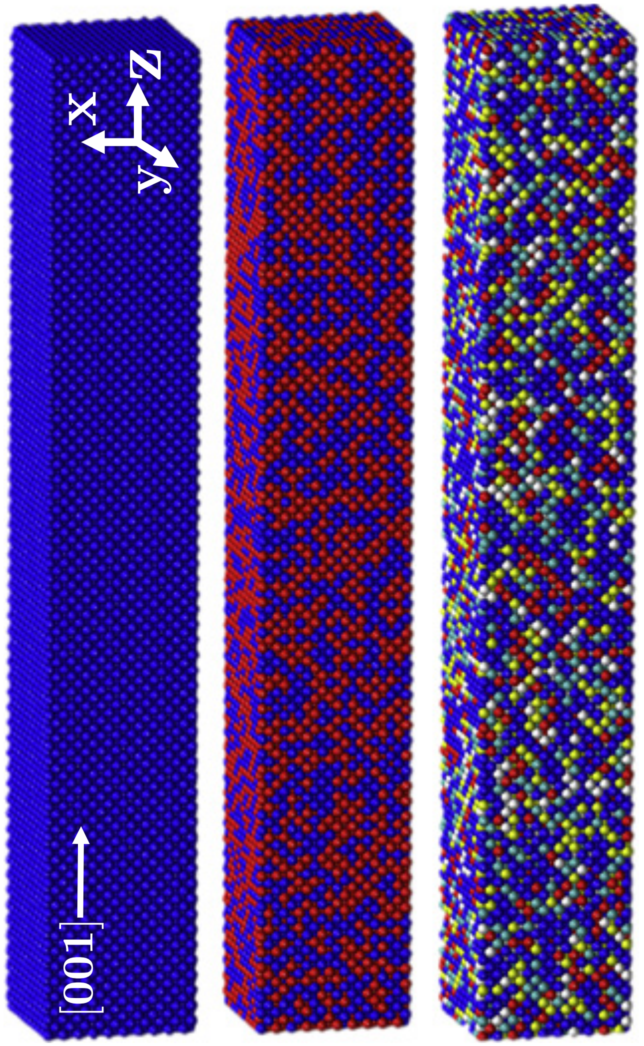
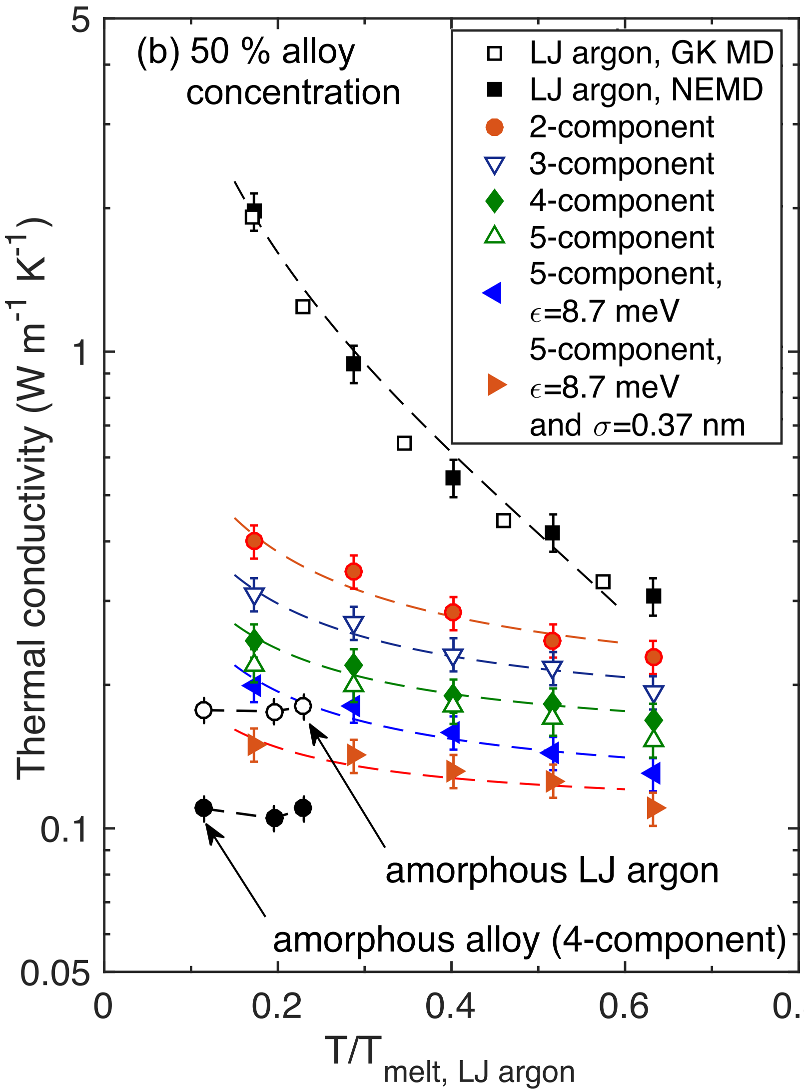
Entropy stabilized oxides: Cation disorder reduces κ





Nature Communications
6, 8485 (2015)

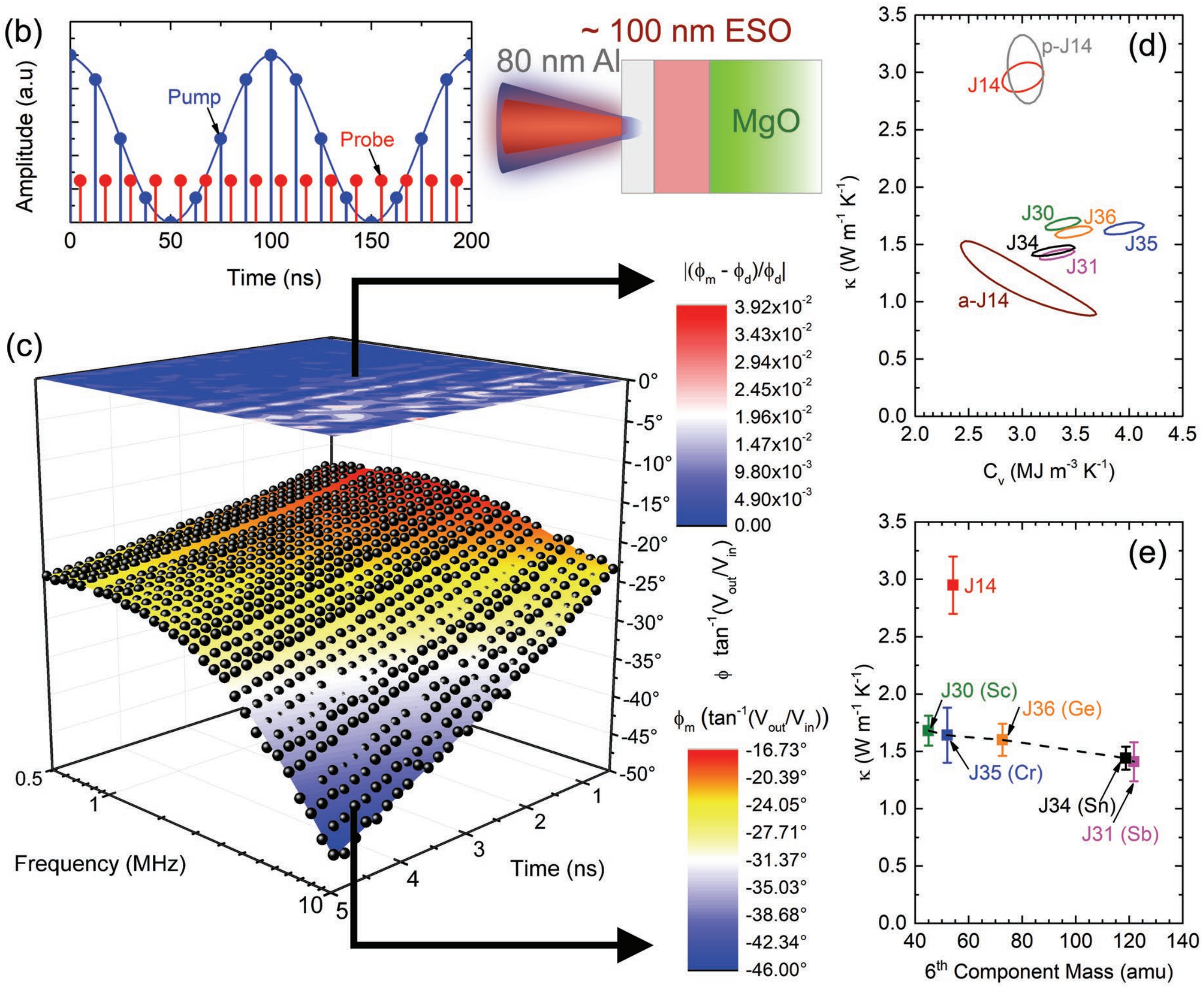




Scripta Materialia **138**, 134 (2017)

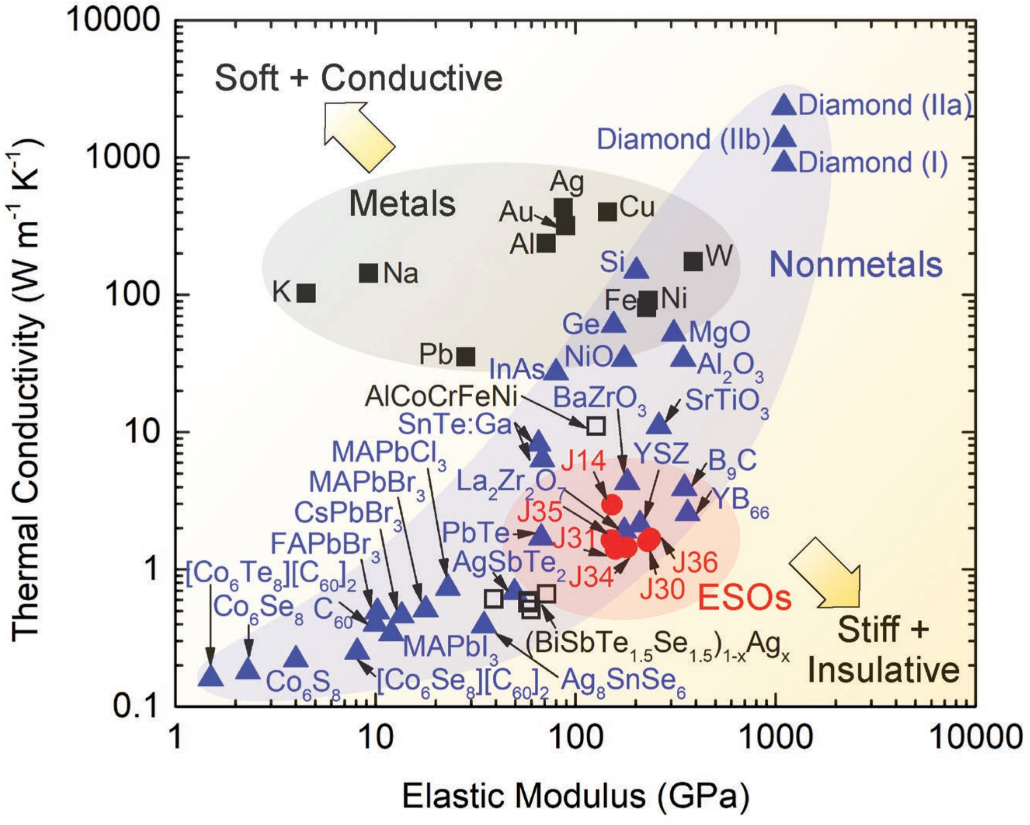
Entropy stabilized oxides: Cation disorder + local distortions

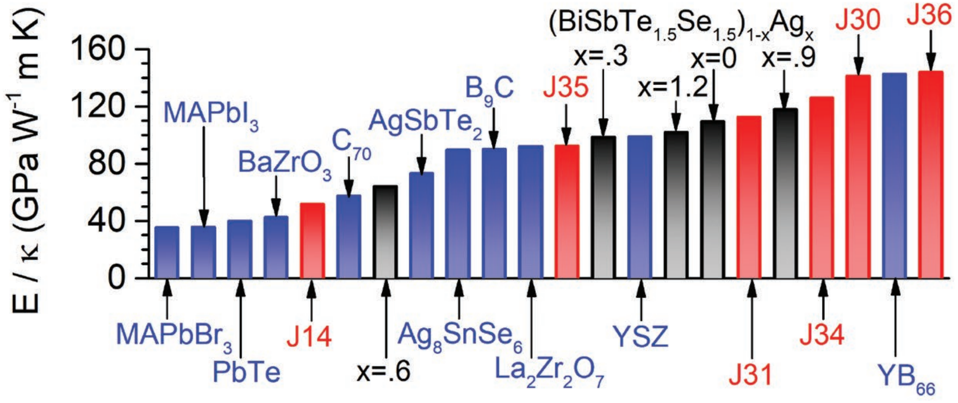
Name	Composition
J14	$Mg_xNi_xCu_xCo_xZn_xO$, $x = 0.2$
J30	$Mg_xNi_xCu_xCo_xZn_xSc_xO$, $x = 0.167$
J31	$Mg_xNi_xCu_xCo_xZn_xSb_xO$, $x = 0.167$
J34	$Mg_xNi_xCu_xCo_xZn_xSn_xO$, $x = 0.167$
J35	$Mg_xNi_xCu_xCo_xZn_xCr_xO$, $x = 0.167$
J36	$Mg_xNi_xCu_xCo_xZn_xGe_xO$, $x = 0.167$

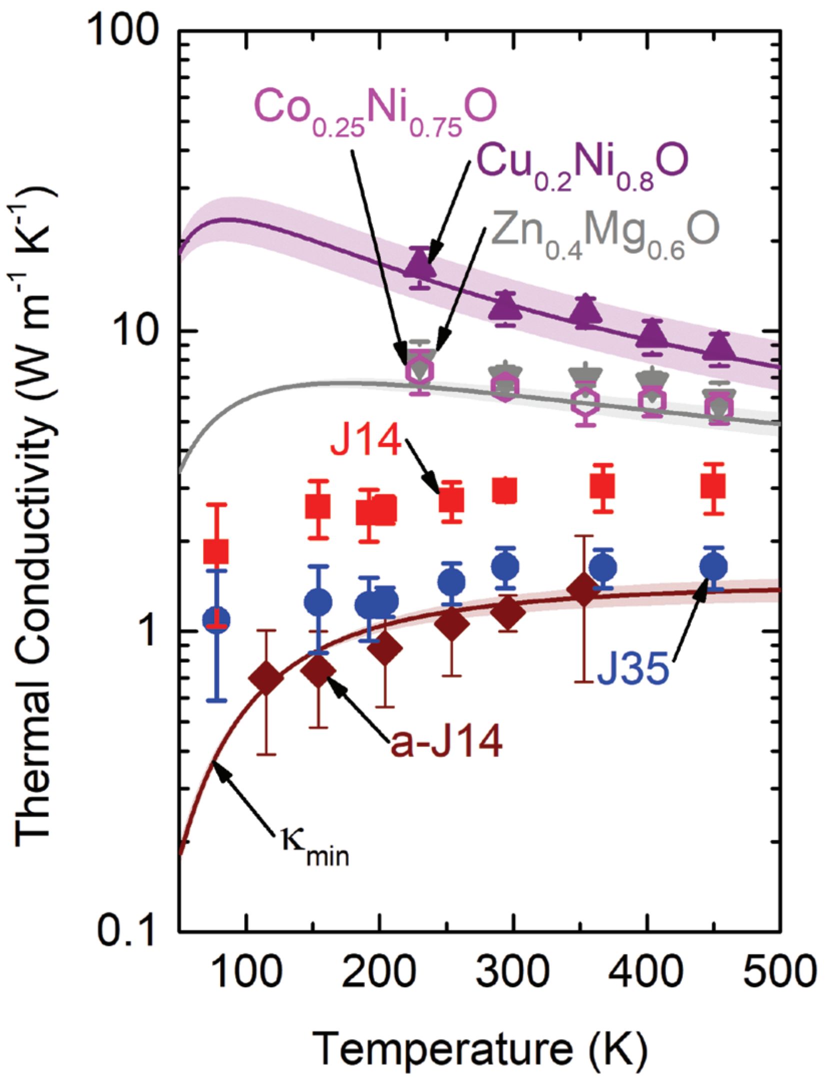


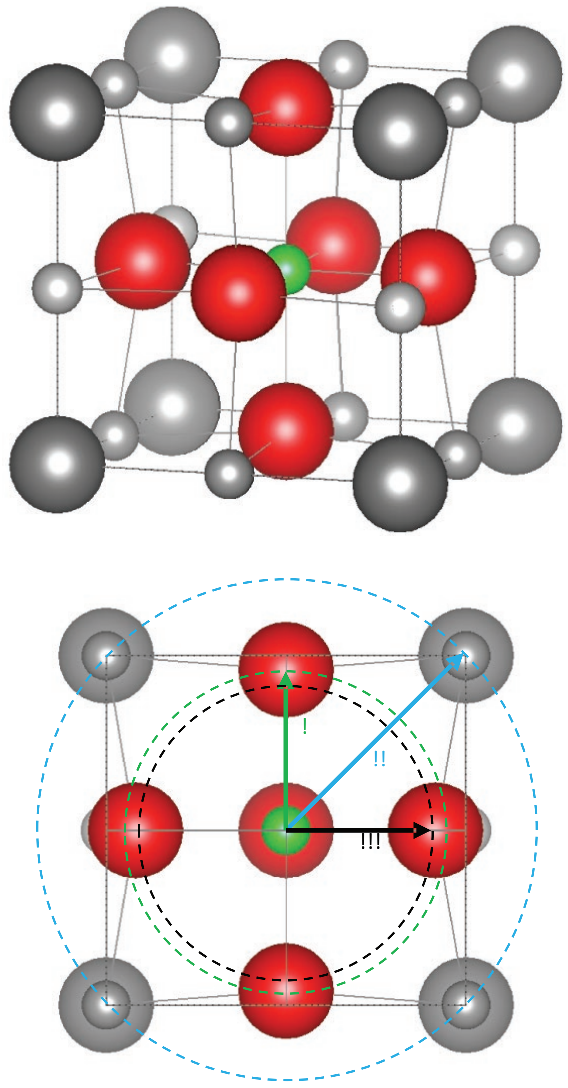
Adv. Mater. **30**, 1805004 (2018)

Entropy stabilized oxides: Cation disorder + local distortions



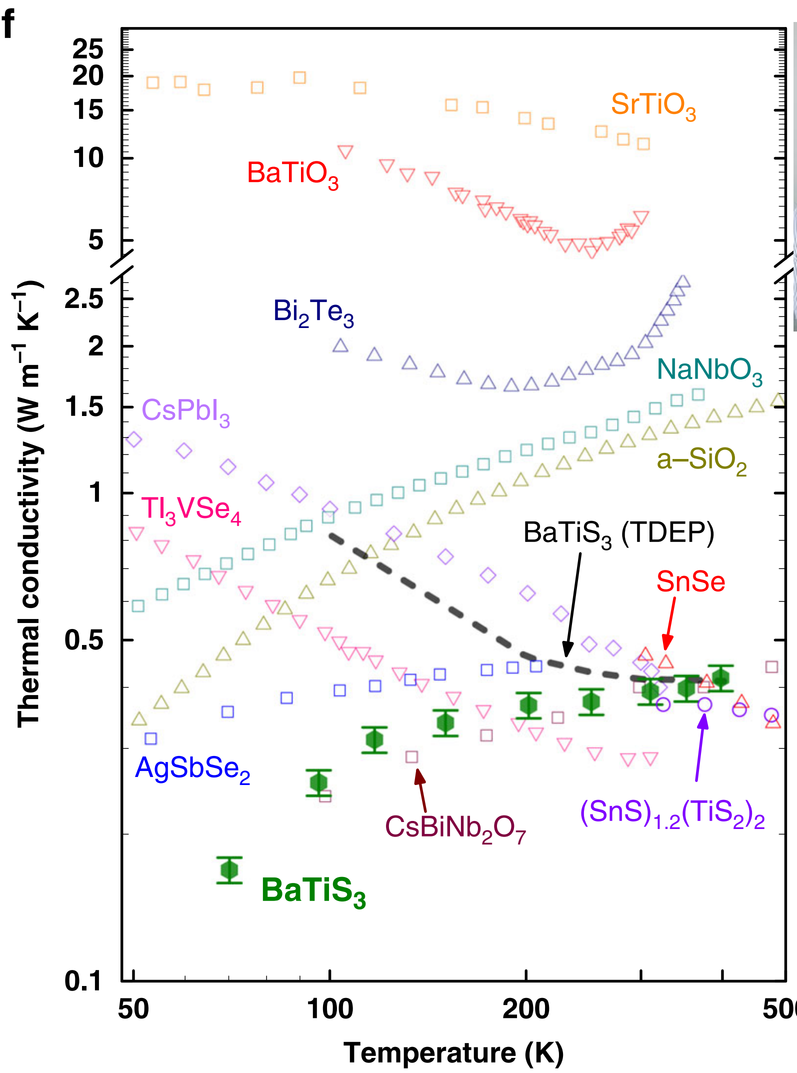


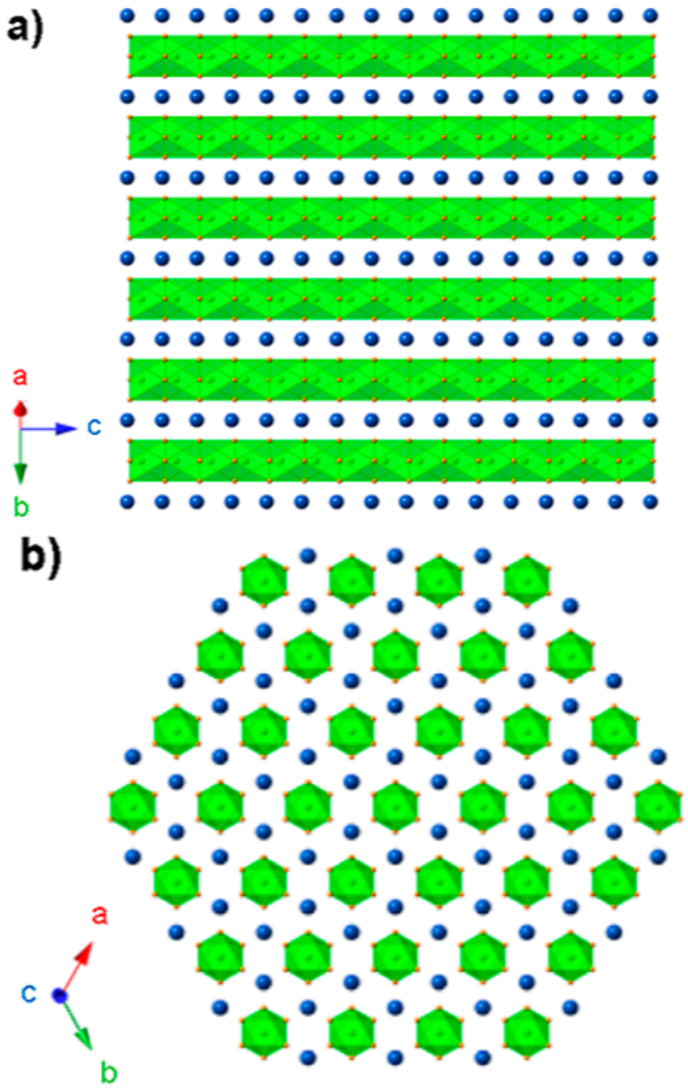




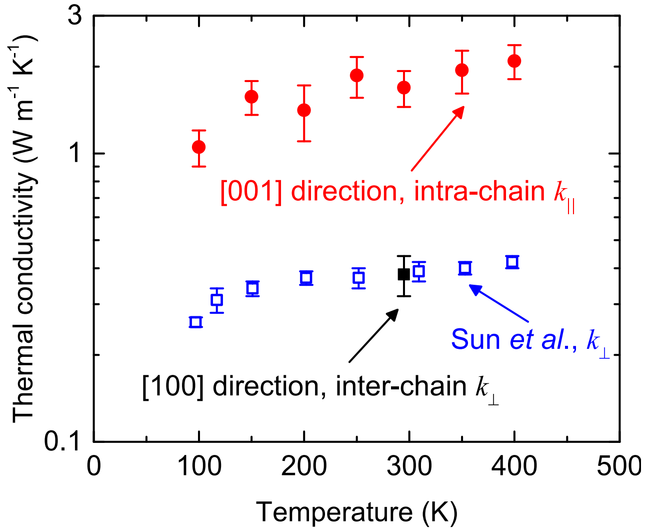
Adv. Mater. **30**, 1805004 (2018)

Sulfide-based chalcogenide single crystals

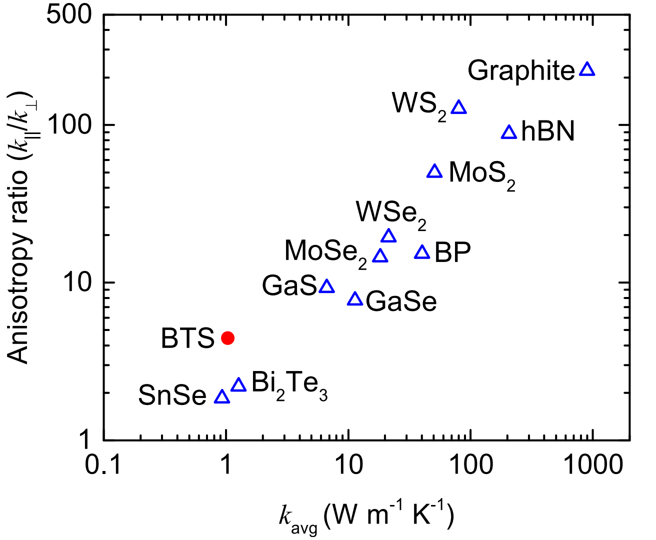




a)



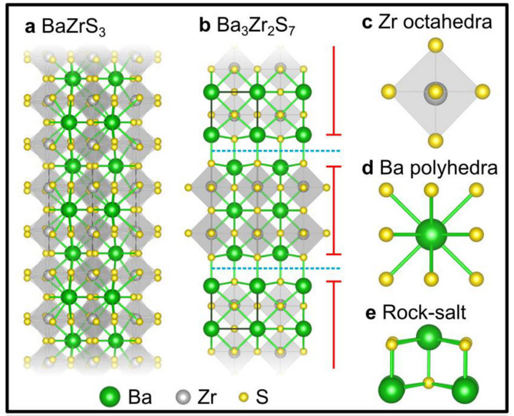
c)

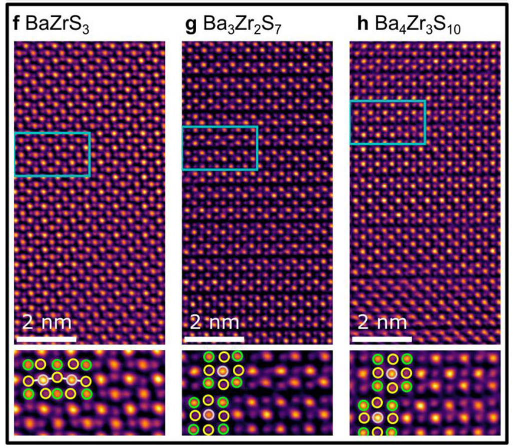


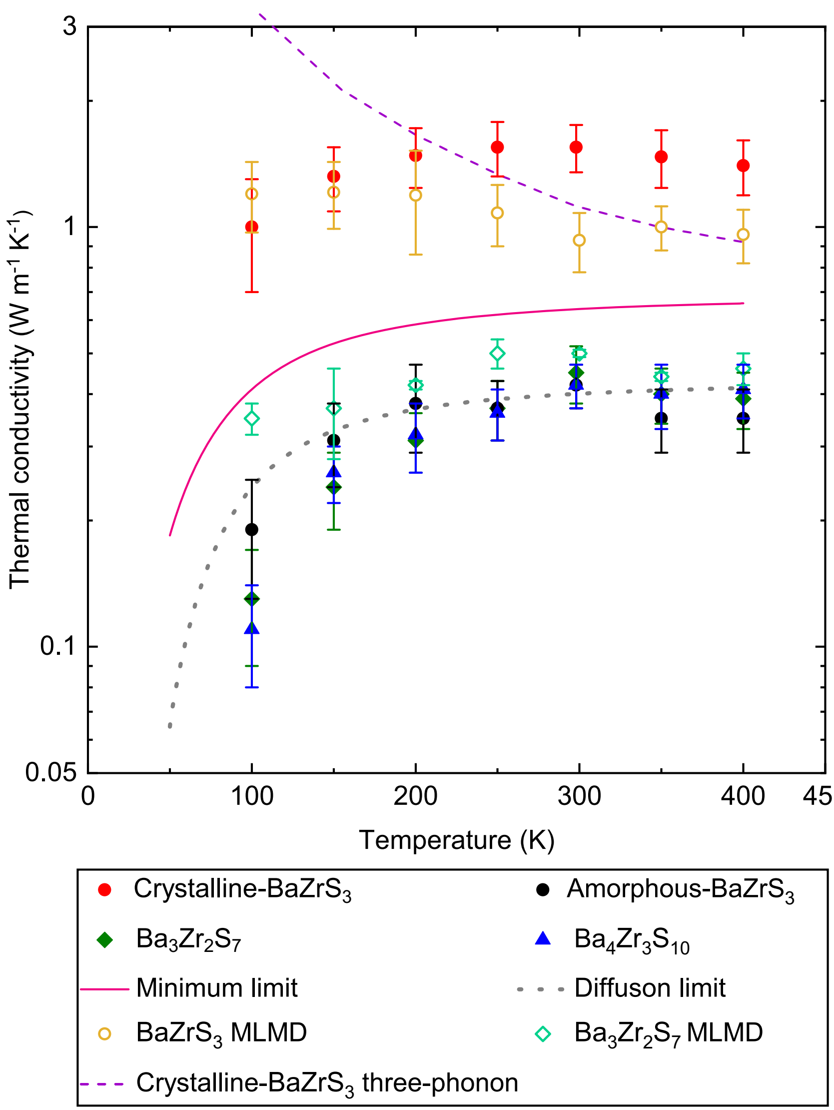
Nature Communications
11, 6039 (2020)

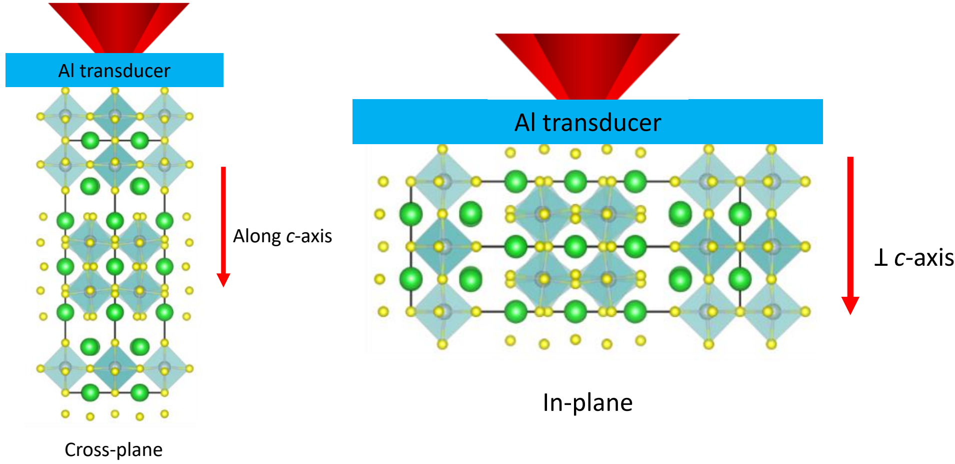
Chemistry of Materials **34**, 5680 (2022)

Ruddlesden-Popper $Ba_3Zr_2S_7$ and $Ba_4Zr_3S_{10}$

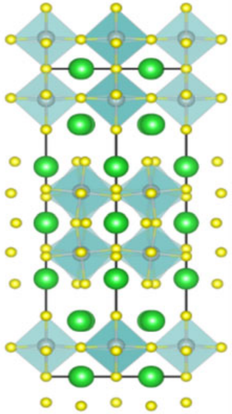








$Ba_3Zr_2S_7$

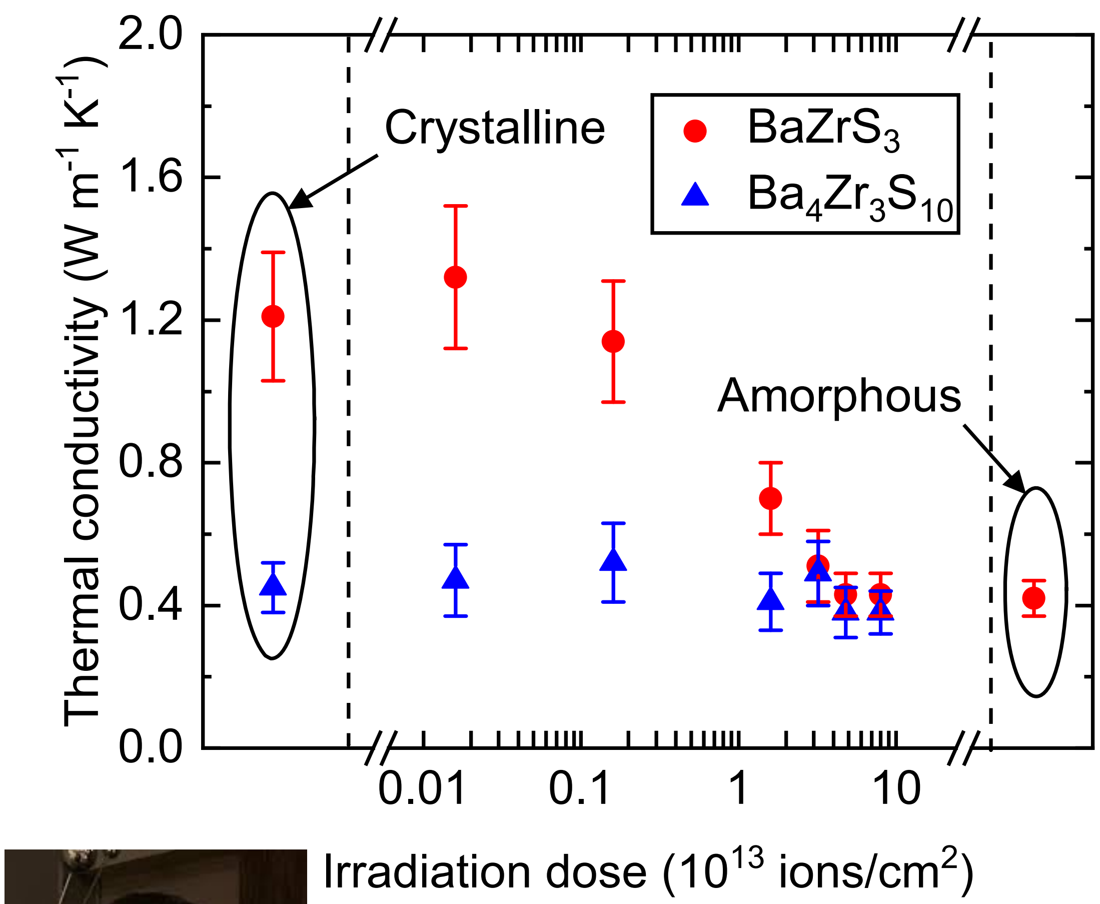


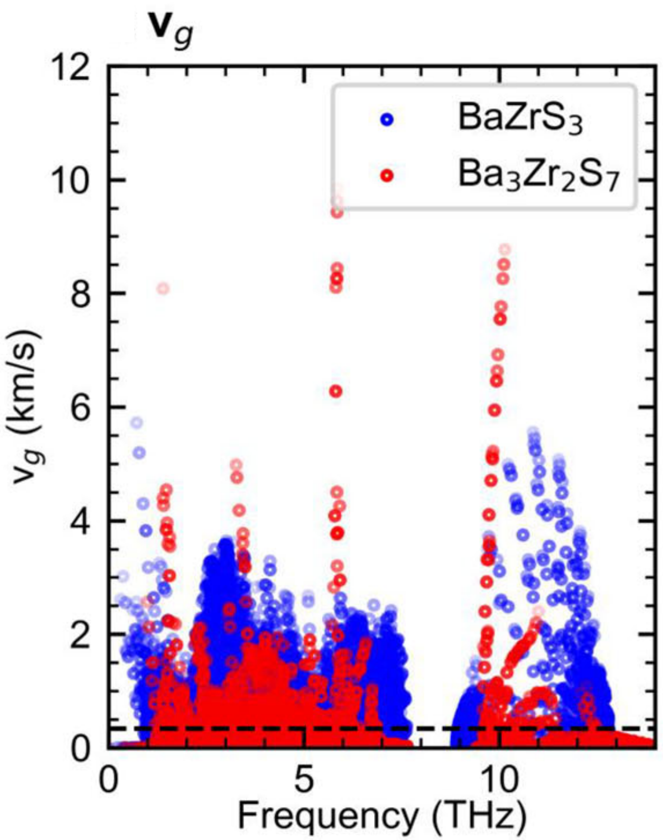
$k_{\perp} = 0.45 \pm 0.07$ $W\ m^{-1}\ K^{-1}$

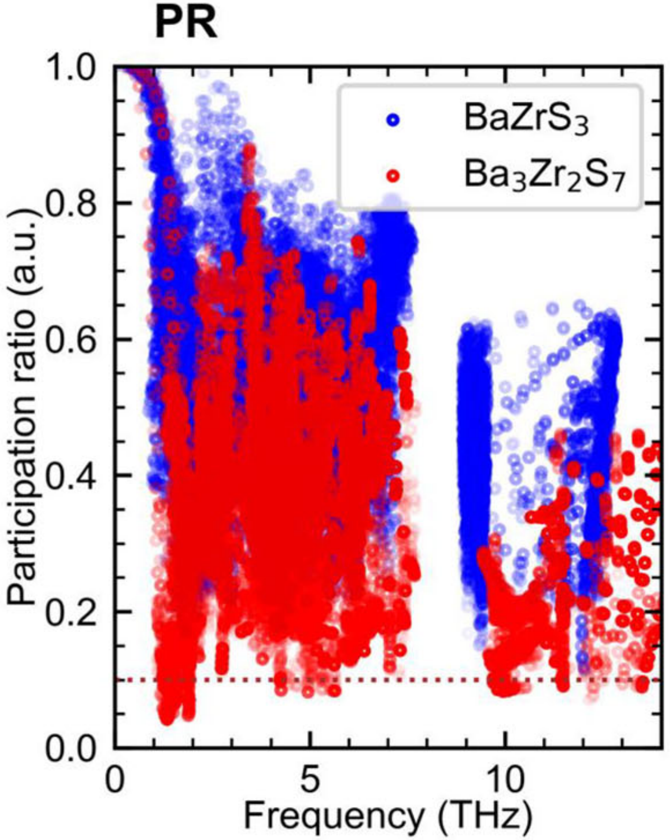
$k_{||} = 1.06 \pm 0.14$ $W\ m^{-1}\ K^{-1}$

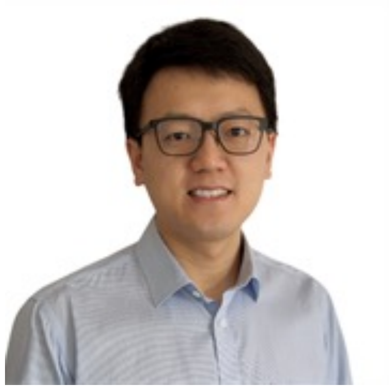
Nature Communications **16**, 6104 (2025)

Ruddlesden-Popper $Ba_3Zr_2S_7$ and $Ba_4Zr_3S_{10}$



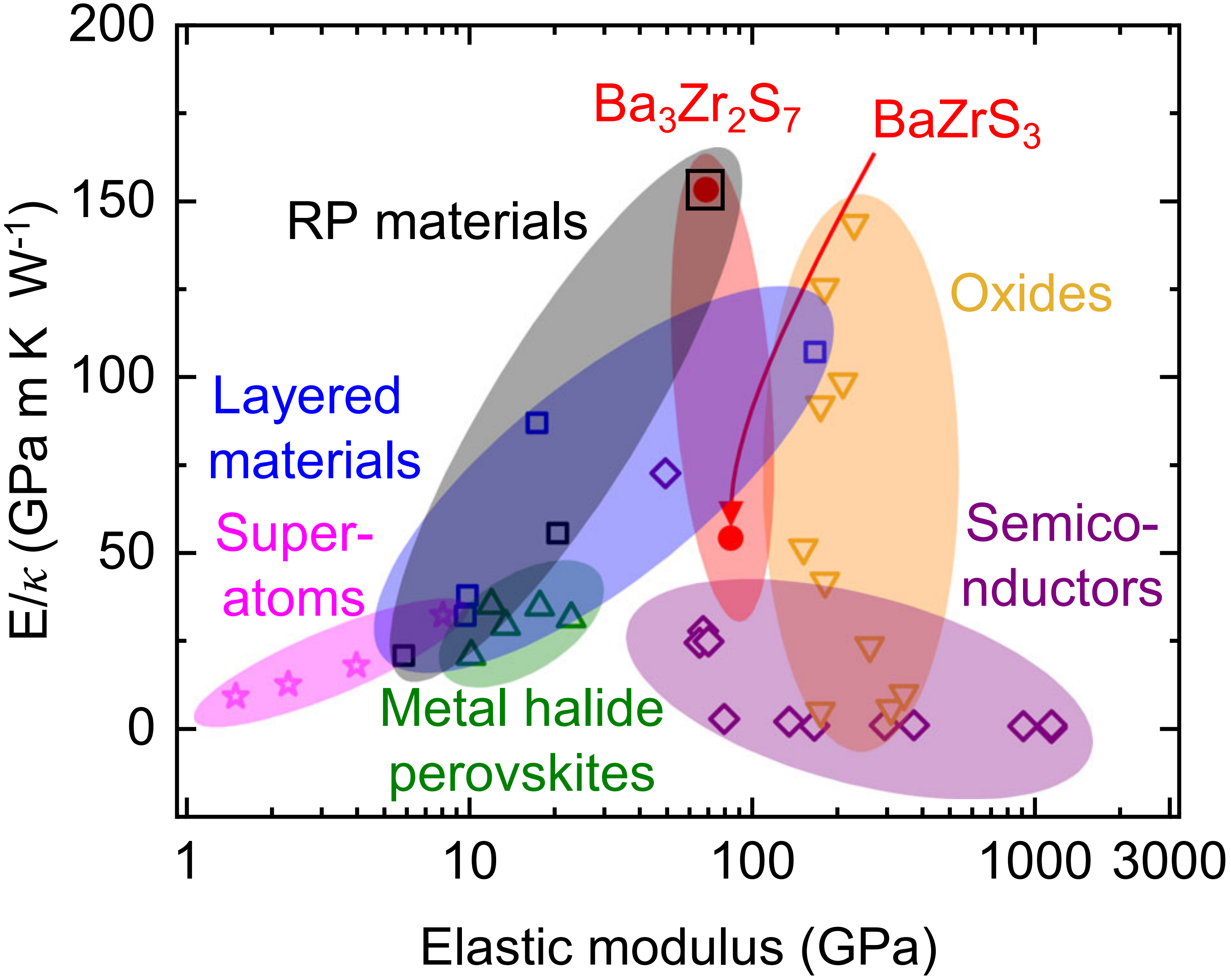






Nature Communications
16, 6104 (2025)

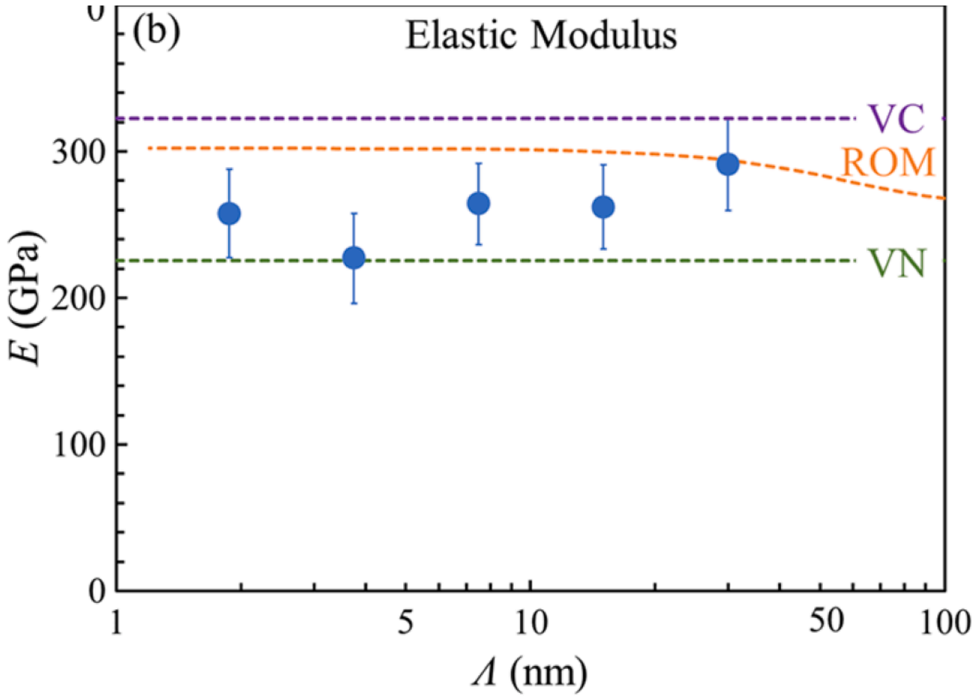
Ruddlesden-Popper $Ba_3Zr_2S_7$ and $Ba_4Zr_3S_{10}$



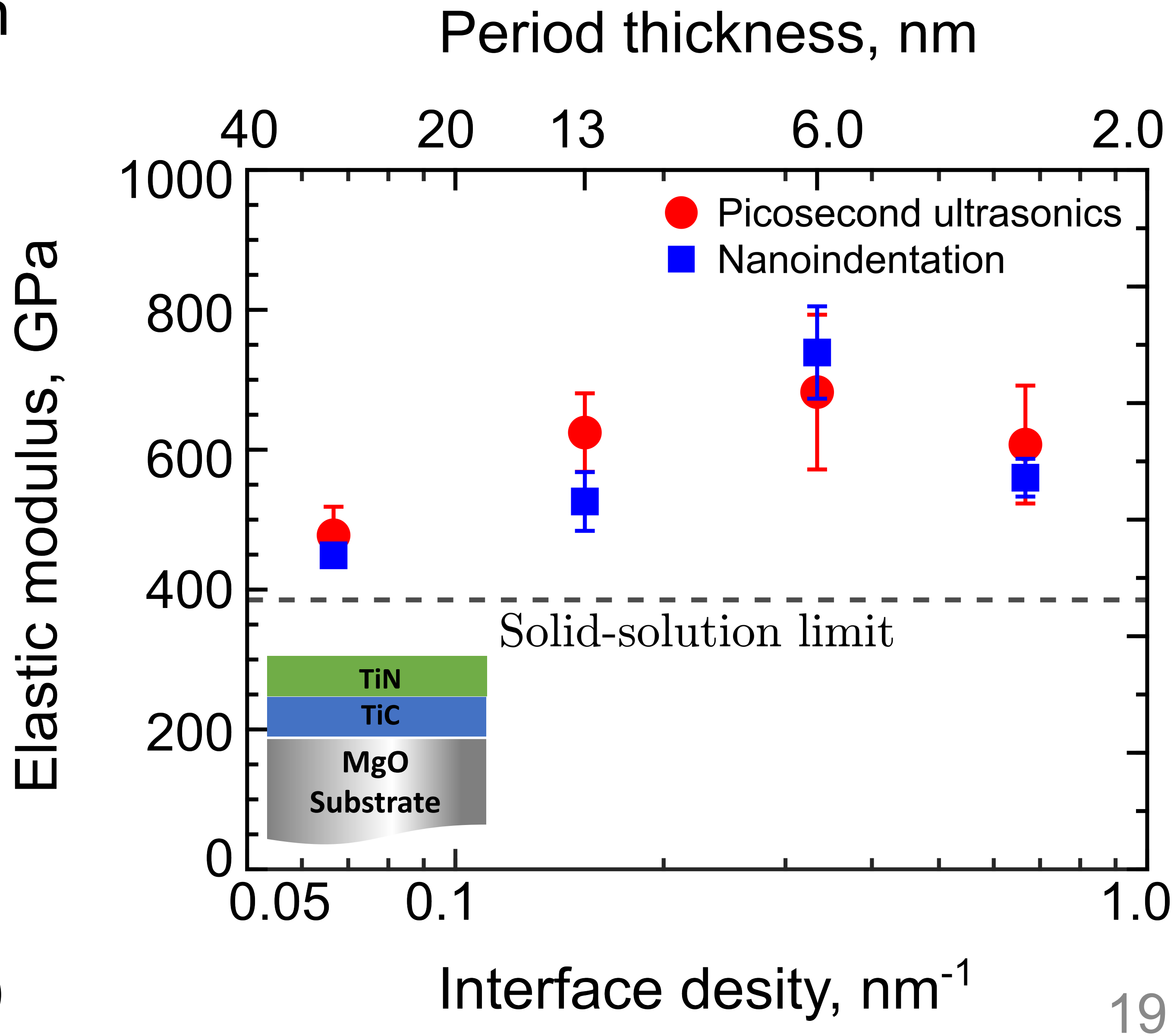
Nature Communications **16**, 6104 (2025)

Now how do we push to higher moduli independently of κ?

Controlling modulus with interfaces in refractory carbide/nitride superlattices

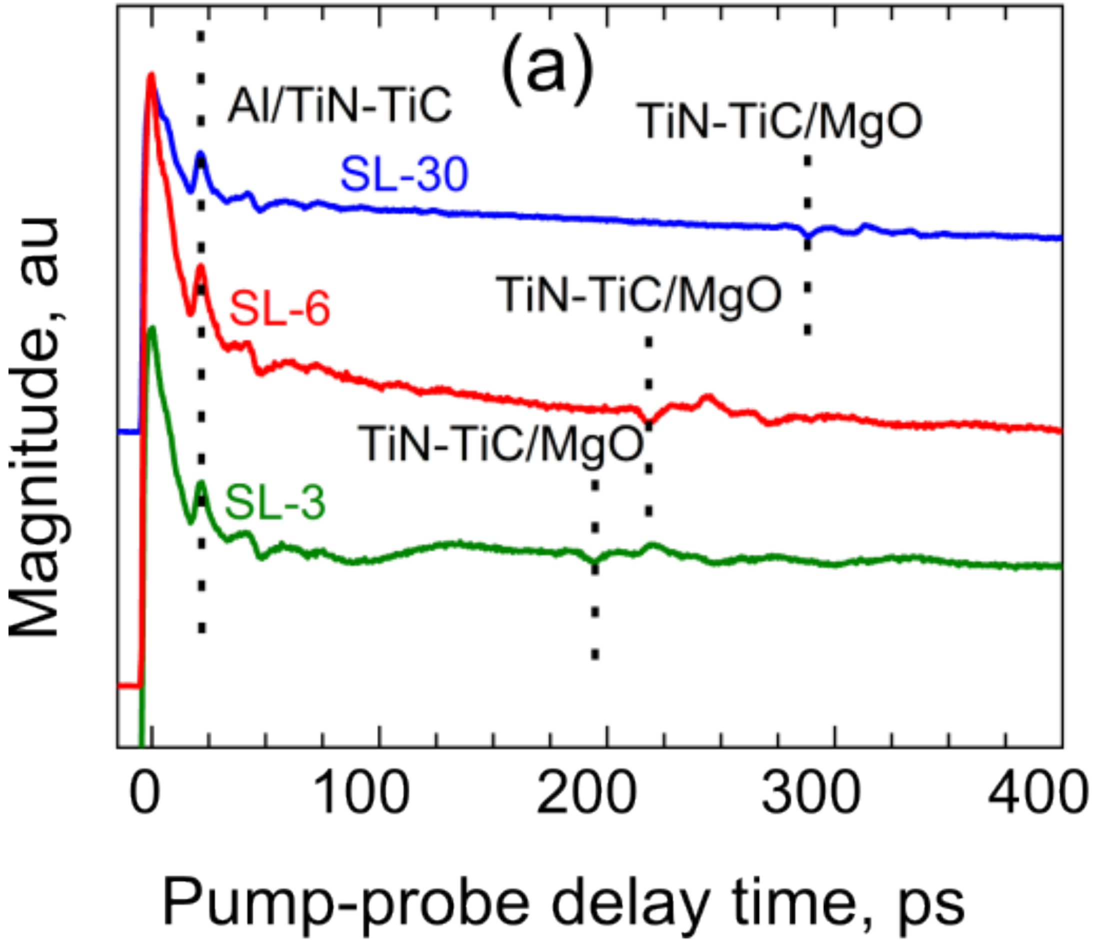


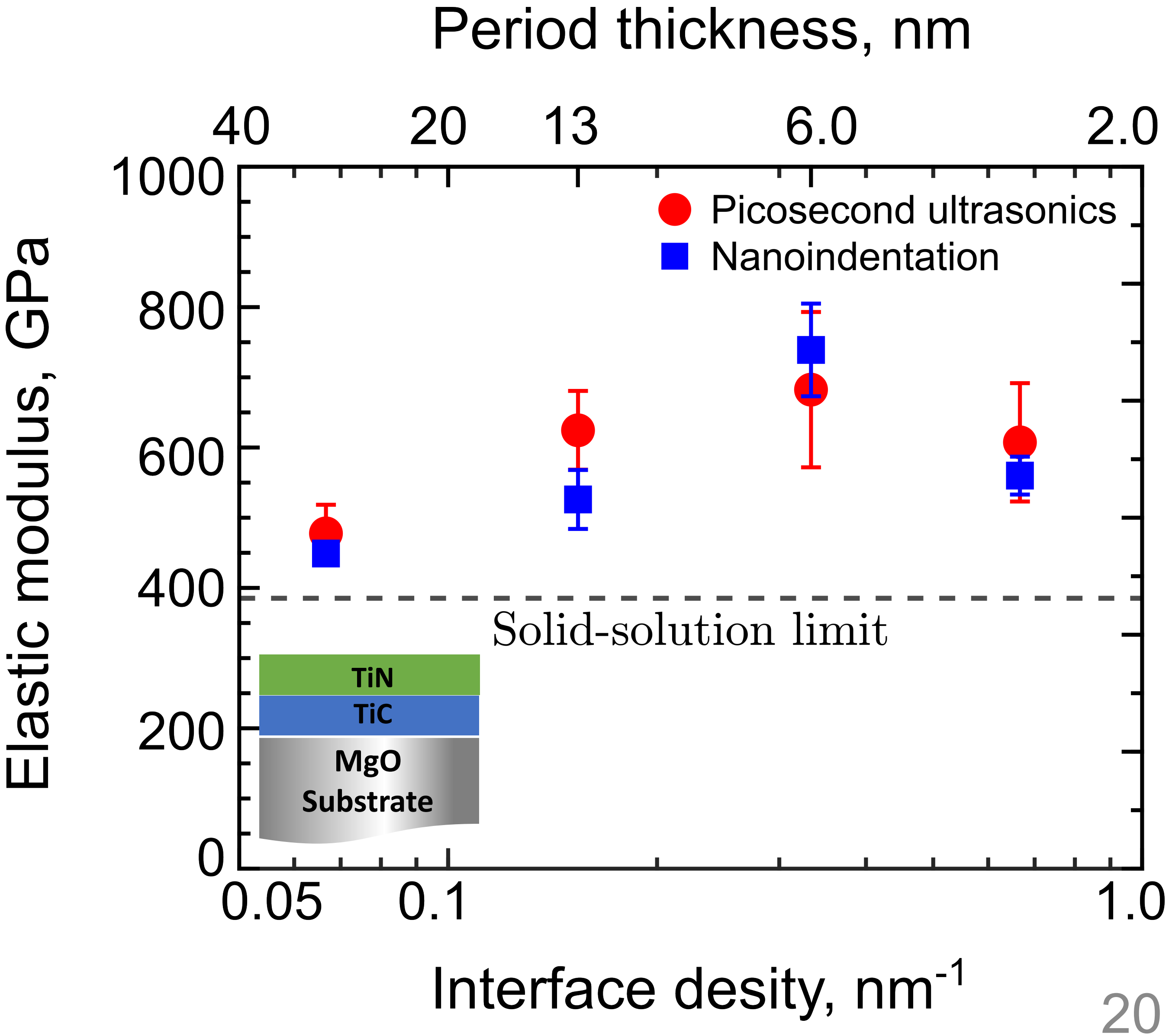
Acta Materialia **294**, 121135 (2025)



Now how do we push to higher moduli independently of κ?

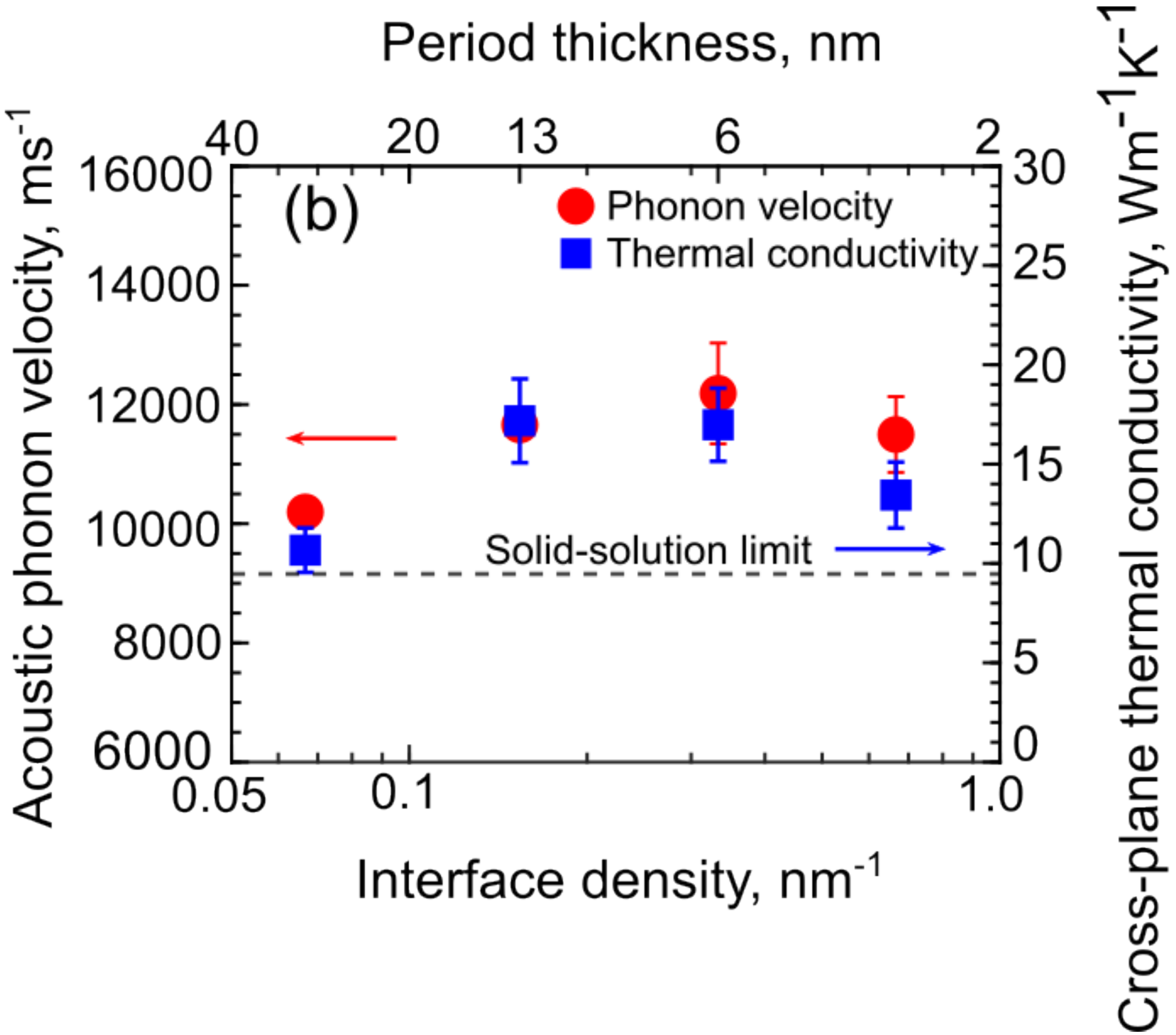
Picosecond ultrasonics





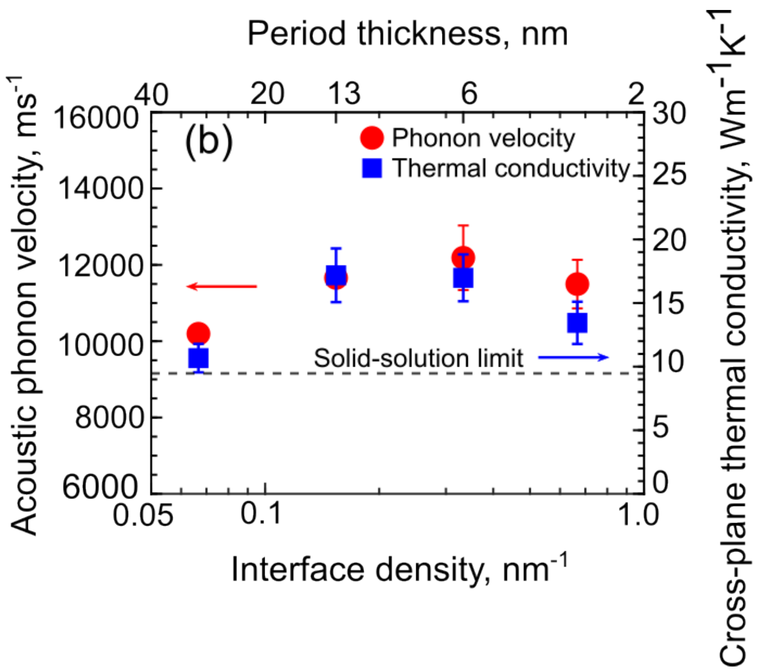
Increase in interface density increases *k* and velocity

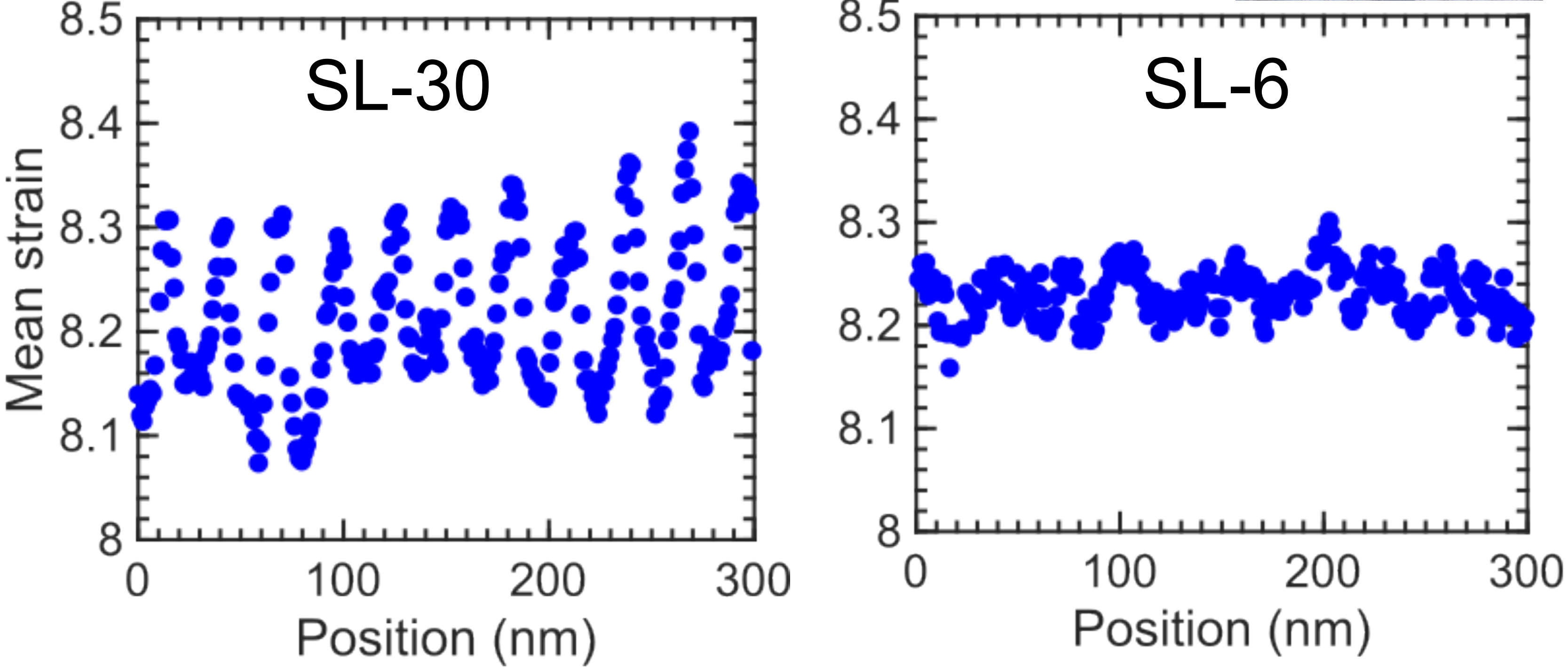
- Increased interface density *increases* thermal conductivity until highest interface density sample when interfaces are no longer distinct
- Trends follow stiffness change, but still we know that interfaces should scatter shorter wavelength phonons



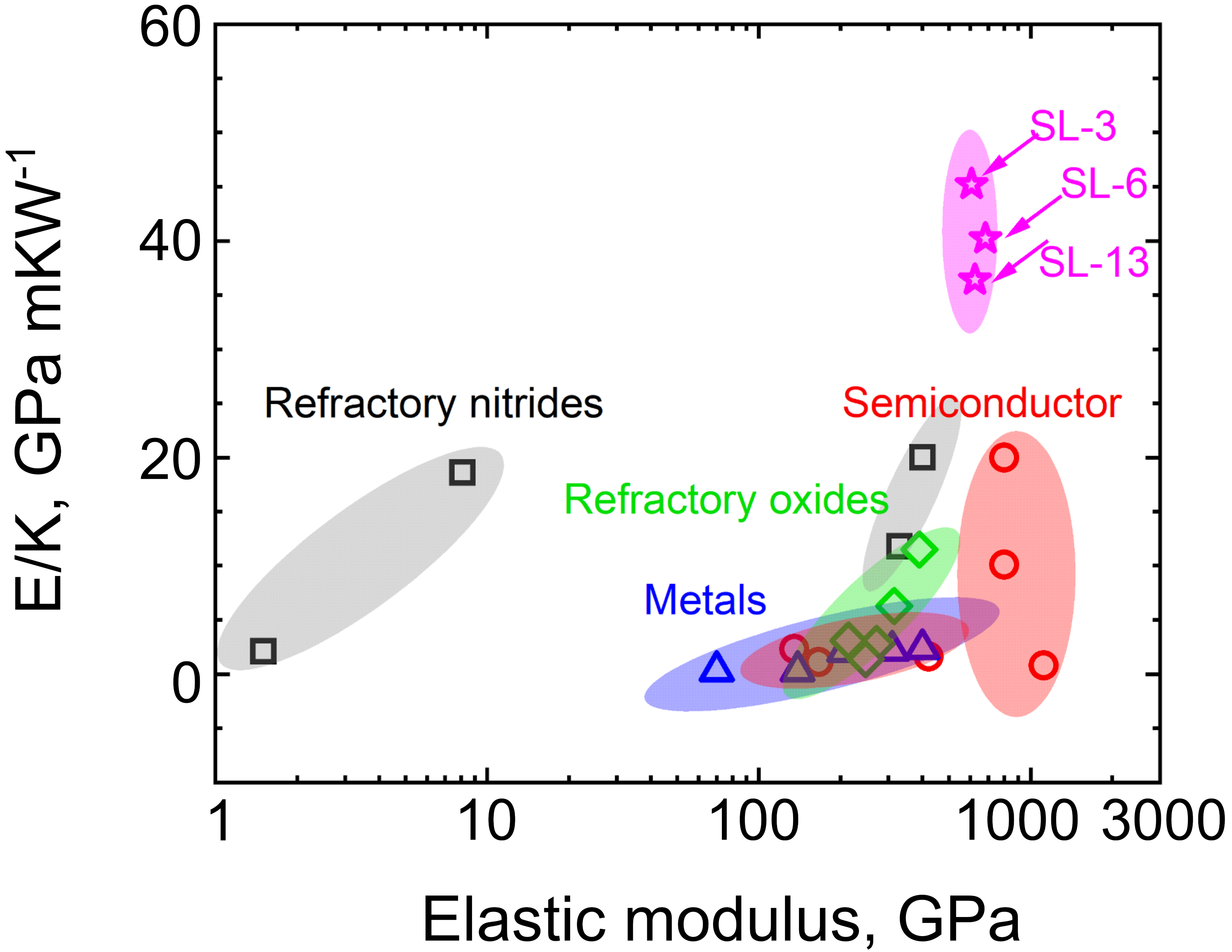
TiNC interfacial phases increase stiffness

- Interfacial TiNC phase “stiffer” (evidence from refractories)
- Increased interface density reduces strain difference between layers, thus reducing phonon scattering (increased density of interfacial phase)

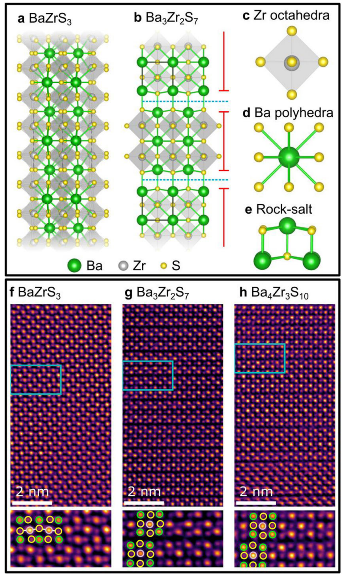




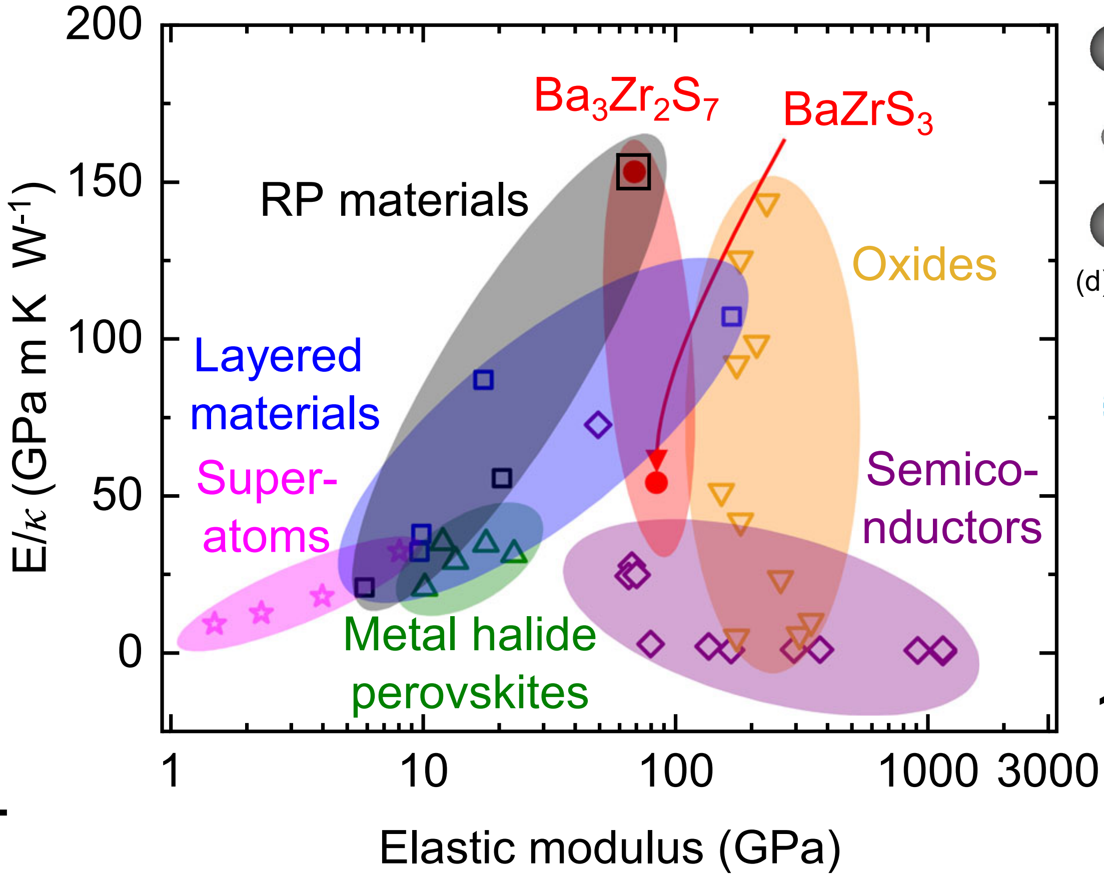
Pushing the limits of *E*/κ for refractories and high κ materials

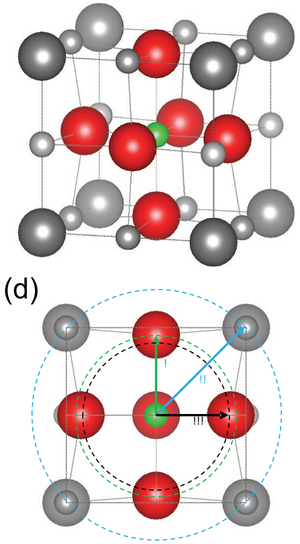


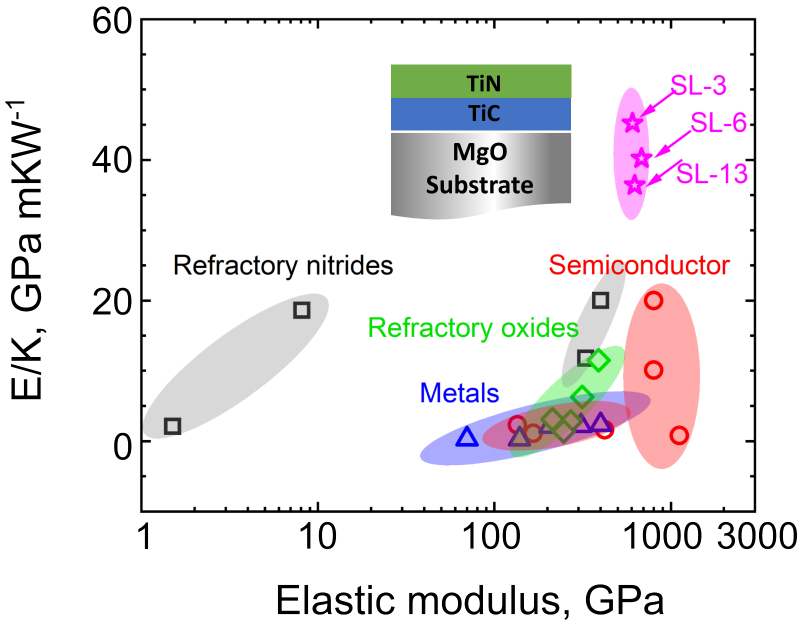
Summary



Nature Comm. **16**, 6104 (2025)







Adv. Mater. **30**, 1805004 (2018)

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