2.00pm

Electron and Phonon Engineering in Nanostructured Thermoelectric Materials

Zhifeng Ren
Department of Physics, Boston College, Chestnut Hill, Massachusetts

Abstract

Thermoelectric materials in energy conversion, especially waste heat recovery, are more and more promising due to the recent breakthroughs in enhancing the dimensionless thermoelectric figure-of-merit (ZT) by nanostructuring approach. ZT enhancement involves both electron and phonon engineering at the atomic and nano scale. In this presentation, I will go through the principles of electron and phonon engineering and give a few examples to demonstrate the successful stories involving a few materials systems that are interest to power generation applications such as half-Heuslers, lead selenide, skutterudites, silicon-germanium alloys, etc., and also a successful case for potentially large scale application using thermoelectric materials.

Biography

Dr Zhifeng Ren is currently a professor of physics at Boston College. He obtained his PhD degree from the Institute of Physics Chinese Academy of Sciences in 1990, master degree from Huazhong University of Science and Technology in 1987, and bachelor degree from Sichuan Institute of Technology in 1984. He was a postdoc and then research faculty at SUNY Buffalo (1990-1999) before joining BC as an associate professor in 1999. He specializes in thermoelectric materials, solar thermoelectric devices & systems, photovoltaic materials & systems, carbon nanotubes and semiconducting nanostructures, nanocomposites, bio agent delivery and biosensors, and superconductors. He is a fellow of APS and AAAS, a recipient of R&D 100 award. He has published extensively, and was ranked the 49th of the top 100 Materials Scientists worldwide for the past decade 2000-2010. He has co-founded companies in the field of carbon nanotubes, thermoelectric materials, and photovoltaics.

Electron and Phonon Engineering in Nanostructured Thermoelectric Materials

Zhifeng Ren

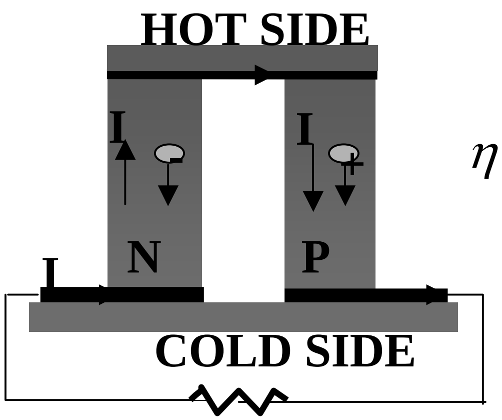
Boston College
Chestnut Hill
Massachusetts 02467

Email: renzh@bc.edu

Outline

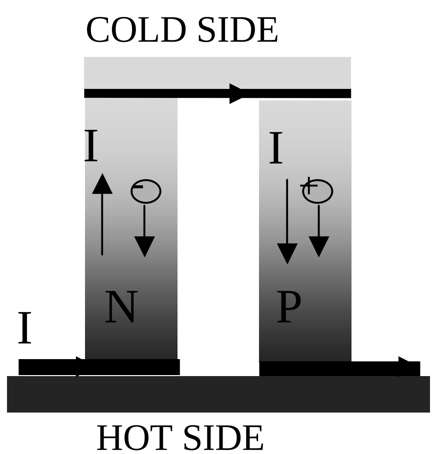
- Phonon Engineering
  –The effect of point defects and nanostructures on reducing thermal conductivity by phonon scattering in bulk materials
- Electron Engineering
  –The effect of density of states on increasing Seebeck coefficient through resonant doping
- Concurrent Phonon and Electron Engineering
  –The effect of modulation doping on improving mobility together with nanostructures in bulk materials

Thermoelectrics: Efficiency and ZT



$$\eta = \frac{W}{Q} = \frac{T_H - T_C}{T_H} \frac{(\sqrt{1 + Z\overline{T}} - 1)}{\sqrt{1 + Z\overline{T}} + \frac{T_C}{T_H}}$$

$$ZT = \frac{S^2 \sigma}{k} T$$



$$\varphi = \frac{Q}{W} = \frac{T_C}{T_H - T_C} \frac{\sqrt{1 + Z\overline{T}} - \frac{T_H}{T_C}}{\sqrt{1 + Z\overline{T}} + 1}$$

$S = -\Delta V / \Delta T$

$\sigma = ne\mu$

$\kappa = \kappa_e + \kappa_L$

$\kappa_L = L \sigma T$

$$S = \frac{\pi^2}{3} \frac{k_B}{e} k_B T \left\{ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F}$$

Zhifeng Ren · ***Boston College · Department of Physics***

Phonon Engineering decrease thermal conductivity

NATURE | VOL 413 | 11 OCTOBER 2001 **597**

Thin-film thermoelectric devices with high room-temperature figures of merit

Rama Venkatasubramanian, Edward Siivola, Thomas Colpitts & Brooks O'Quinn

Research Triangle Institute, Research Triangle Park, North Carolina 27709, USA

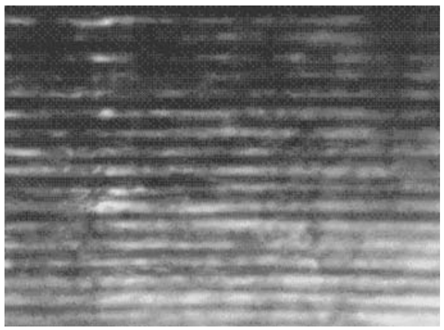


Table 1 Theoretical and experimental lattice thermal conductivities

Material	Thermal conductivity ($W m^{-1} K^{-1}$)
K_{min} of Bi_2Te_3 (*a-b* axis), Slack model[34]	0.55
K_{min} of Bi_2Te_3 (*c* axis), Slack model[34]	0.28
K_{min} of Bi_2Te_3 (*a-b* axis), Cahill model[35]	0.28
K_{min} of Bi_2Te_3 (*c* axis), Cahill model[35]	0.14
K_L of $Bi_{2-x}Sb_xTe_3$ alloy (*a-b* axis)	0.97
K_L of $Bi_{2-x}Sb_xTe_3$ alloy (*c* axis)	0.49
K_L of Bi_2Te_3/Sb_2Te_3 superlattice (*c* axis)	0.22

SCIENCE VOL 315 19 JANUARY 2007 **351**

Ultralow Thermal Conductivity in Disordered, Layered WSe_2 Crystals

Catalin Chiritescu,[1] David G. Cahill,[1*] Ngoc Nguyen,[2] David Johnson,[2] Arun Bodapati,[3] Pawel Keblinski,[3] Paul Zschack[4]

The cross-plane thermal conductivity of thin films of WSe_2 grown from alternating W and Se layers is as small as 0.05 watts per meter per degree kelvin at room temperature, 30 times smaller than the *c*-axis thermal conductivity of single-crystal WSe_2 and a factor of 6 smaller than the predicted minimum thermal conductivity for this material. We attribute the ultralow thermal conductivity of these disordered, layered crystals to the localization of lattice vibrations induced by the random stacking of two-dimensional crystalline WSe_2 sheets. Disordering of the layered structure by ion bombardment increases the thermal conductivity.

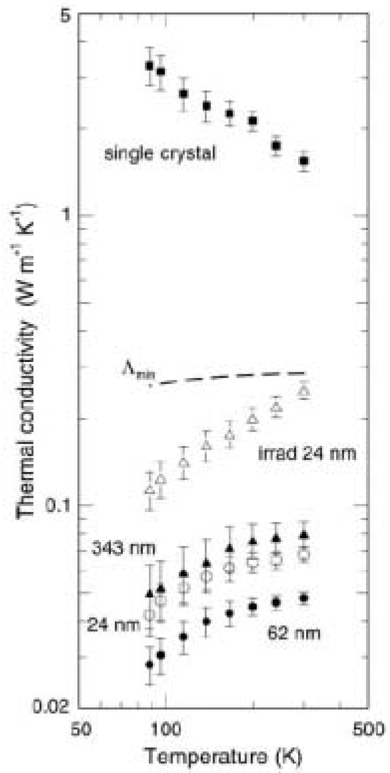


Fig. 2. Summary of measured thermal conductivities of WSe_2 films as a function of the measurement temperature. Each curve is labeled by the film thickness. Data for a bulk single crystal are included for comparison. Error bars are the uncertainties propagated from the various experimental parameters used to analyze the data (*6*). The ion-irradiated sample (irrad) was subjected to a 1-MeV Kr^+ ion dose of 3×10^{15} cm^{-2}. The dashed line marked Λ_{min} is the calculated minimum thermal conductivity for WSe_2 films in the cross-plane direction.

Electron Engineering increase Seebeck coeffcient

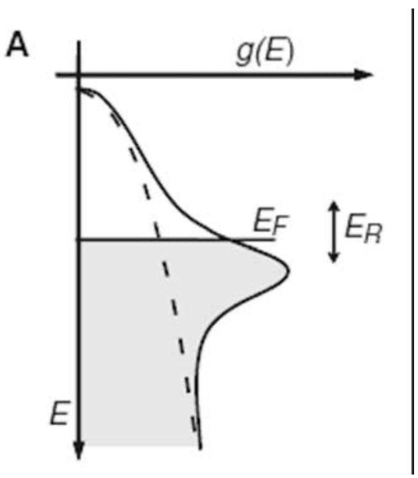
25 JULY 2008 VOL 321 SCIENCE 554

Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States

Joseph P. Heremans,[1,2]* Vladimir Jovovic,[1] Eric S. Toberer,[3] Ali Saramat,[3] Ken Kurosaki,[4] Anek Charoenphakdee,[4] Shinsuke Yamanaka,[4] G. Jeffrey Snyder[3]*

$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{d[\ln(\sigma(E))]}{dE}\right\}_{E=E_F}$$

$$= \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{1}{n}\frac{dn(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}_{E=E_F}$$



$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3}$$

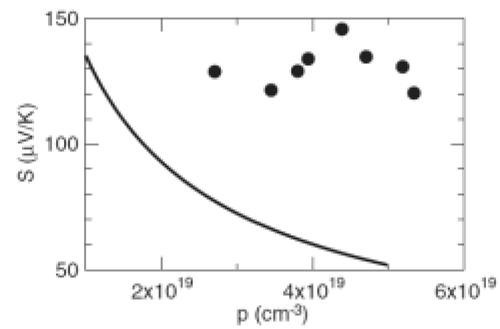
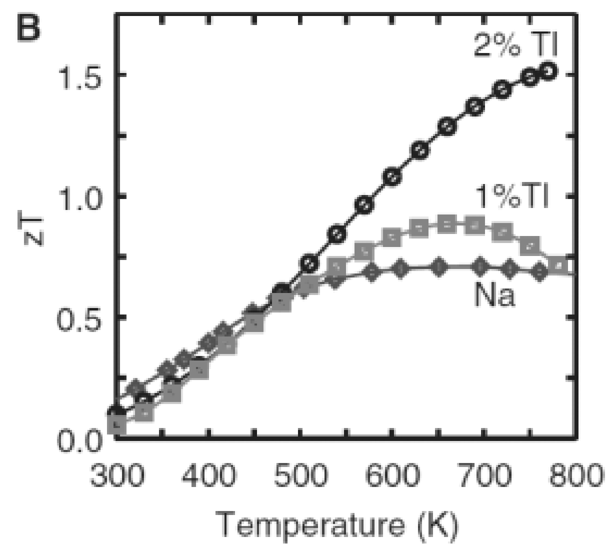


Fig. 3. Pisarenko relation of Seebeck coefficient at 300 K versus hole concentration for PbTe (solid line) compared to the results measured on every Tl-PbTe sample prepared for this study.



Electron Engineering modulation doping to increase power factor

665 Appl. Phys. Lett. 33(7), 1 October 1978

Electron mobilities in modulation-doped semiconductor heterojunction superlattices

R. Dingle, H. L. Störmer,[a] A. C. Gossard, and W. Wiegmann

Bell Laboratories, Murray Hill, New Jersey 07974
(Received 19 June 1978; accepted for publication 27 July 1978)

GaAs-$Al_xGa_{1-x}As$ superlattice structures in which electron mobilities exceed those of otherwise equivalent epitaxial GaAs as well as the Brooks-Herring predictions near room temperature and at very low temperatures are reported. This new behavior is achieved via a modulation-doping technique that spatially separates conduction electrons and their parent donor impurity atoms, thereby reducing the influence of ionized and neutral impurity scattering on the electron motion.

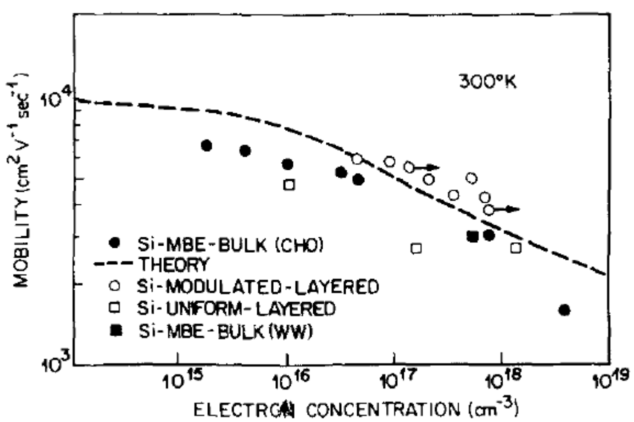


FIG. 2. 300 K mobilities of a range of Si-doped GaAs and Si-doped GaAs-$Al_xGa_{1-x}As$ superlattices. The filled circles and the theory [Brookes-Herring, $(N^+ + N^-)/n = 1$] are taken from Ref. 6. The horizontal arrows show electron concentration changes discussed in the text.

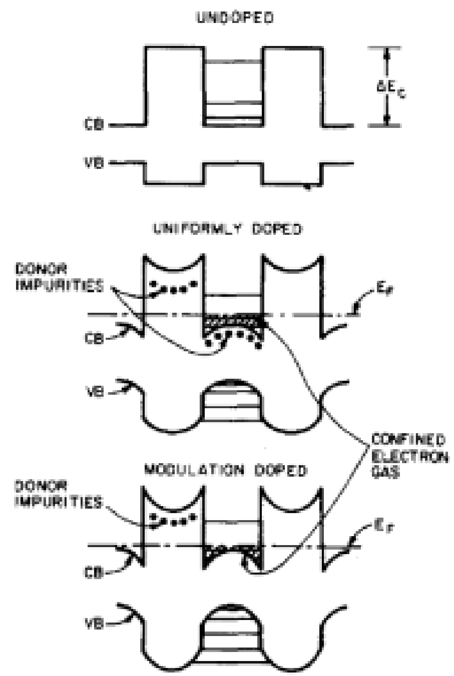
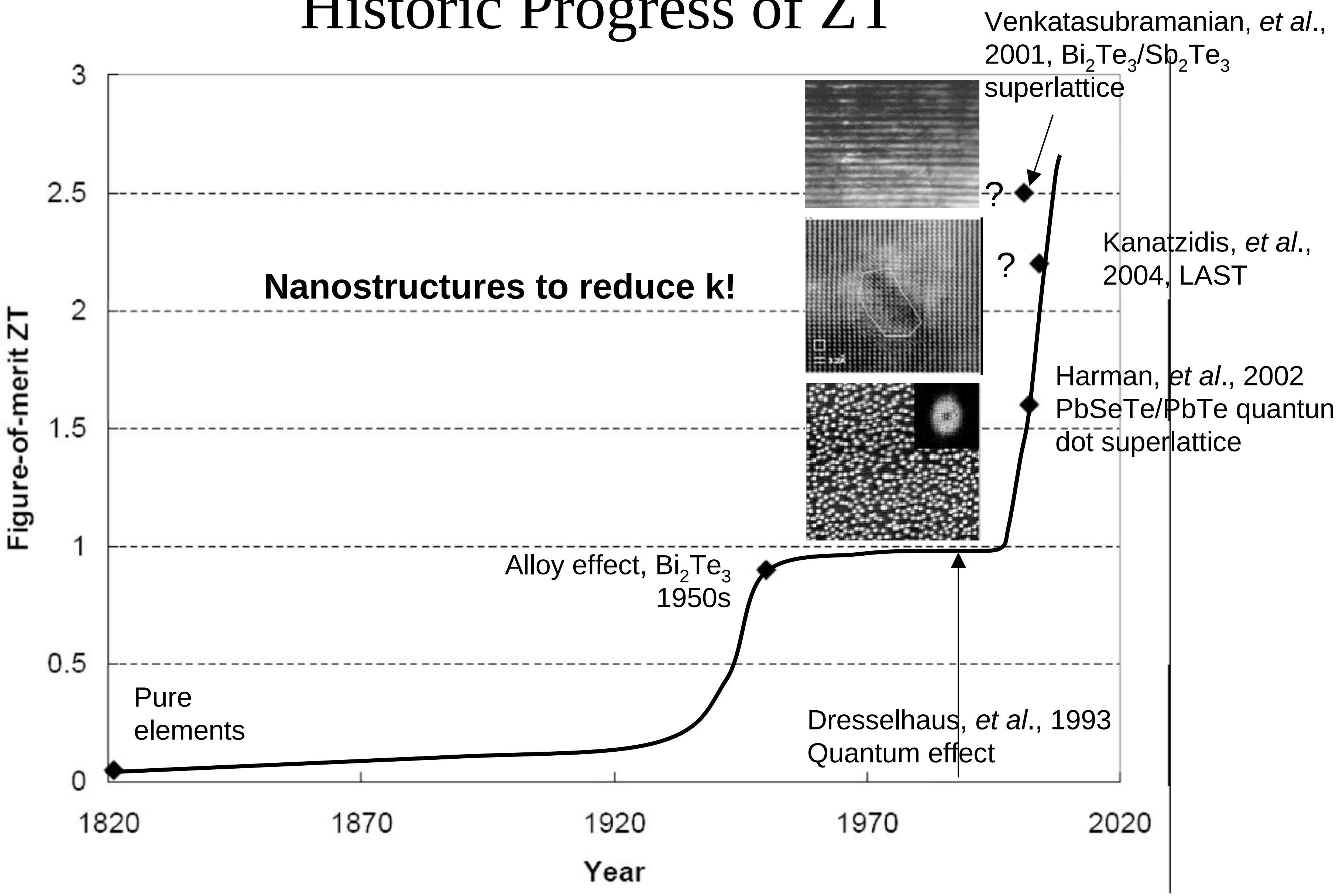
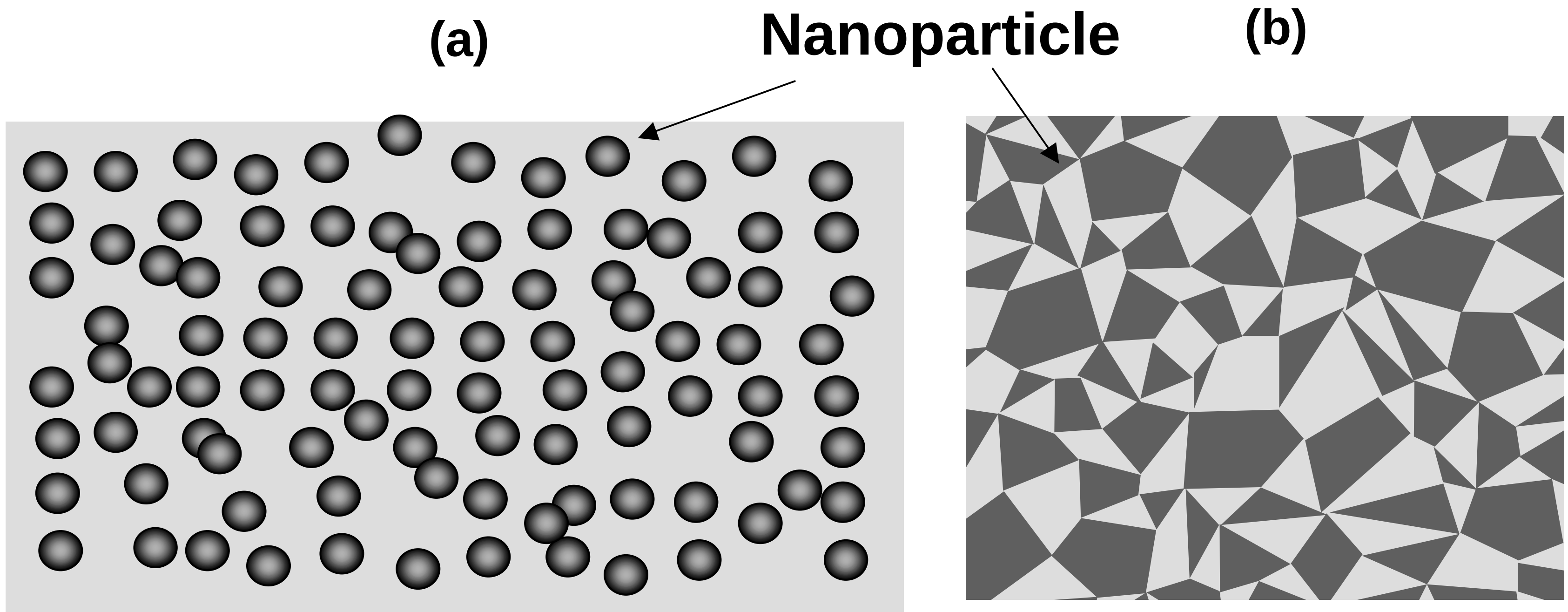


FIG. 1. Energy-band diagrams for n-doped and undoped GaAs-$Al_xGa_{1-x}As$ superlattices.

Historic Progress of ZT



Bulk Nanostructured Thermoelectric Materials



– Decrease thermal conductivity by phonon engineering

– Increase power factor by electron engineering

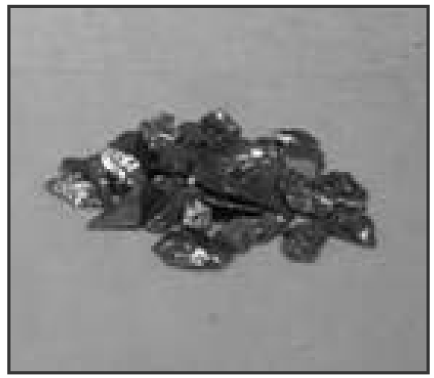
– Increase ZT by simultaneous electron and phonon engineering

How to Achieve Nanoparticles?

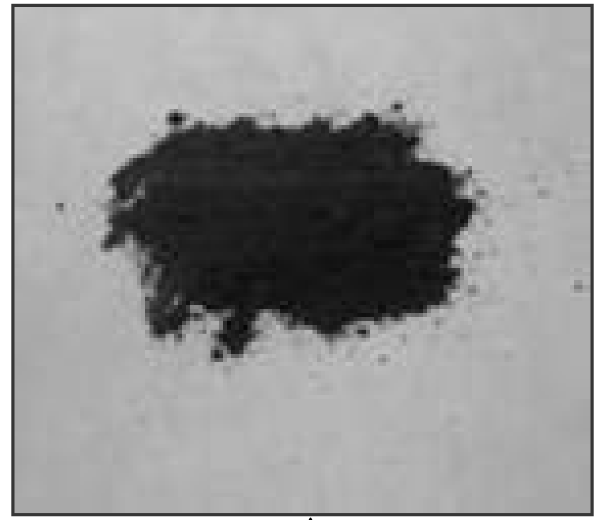
Ingot BiSbTe

Elements:

Bi, Sb, Te

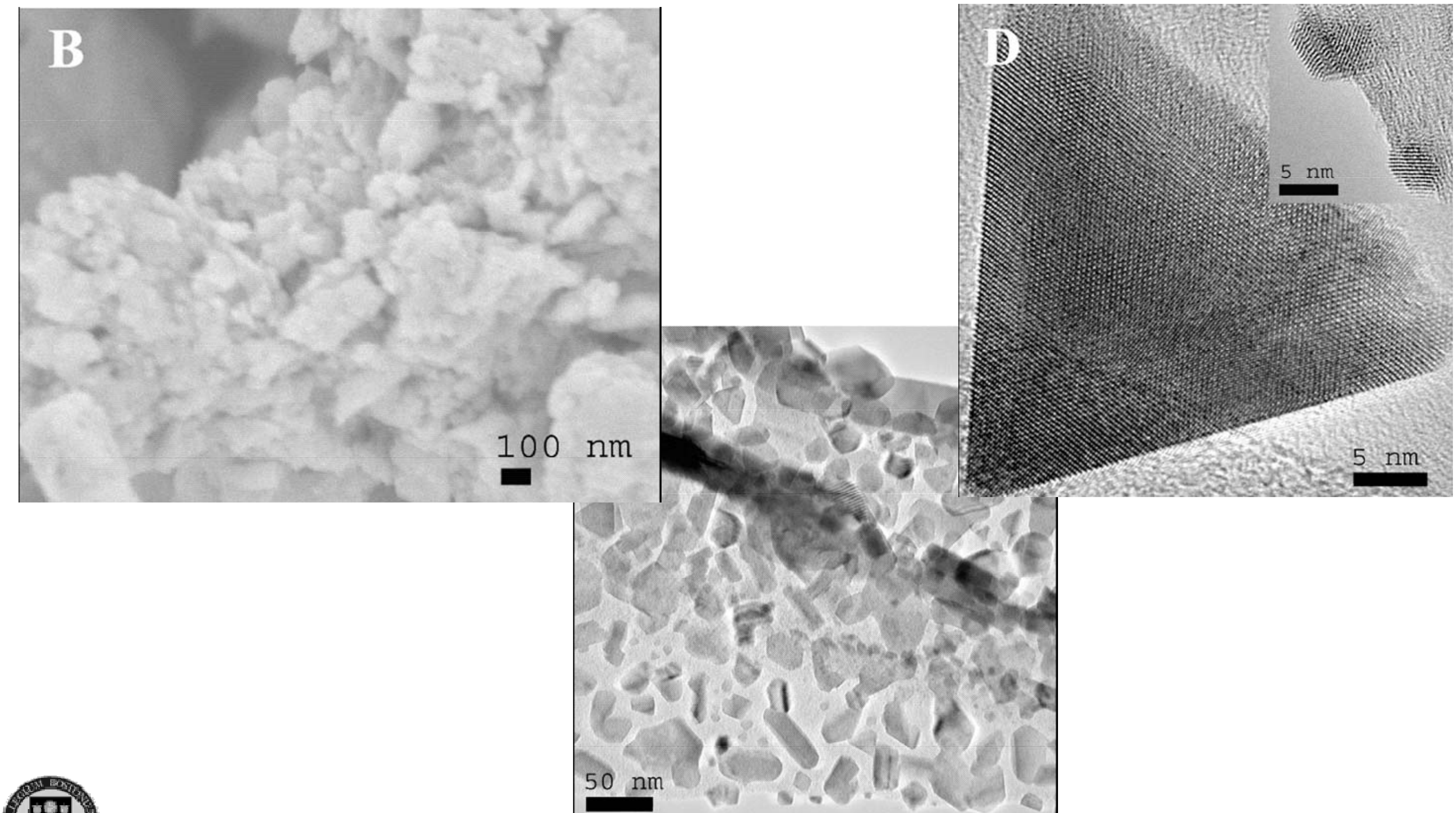


Ball milling



Particle Size of the Nanopowders

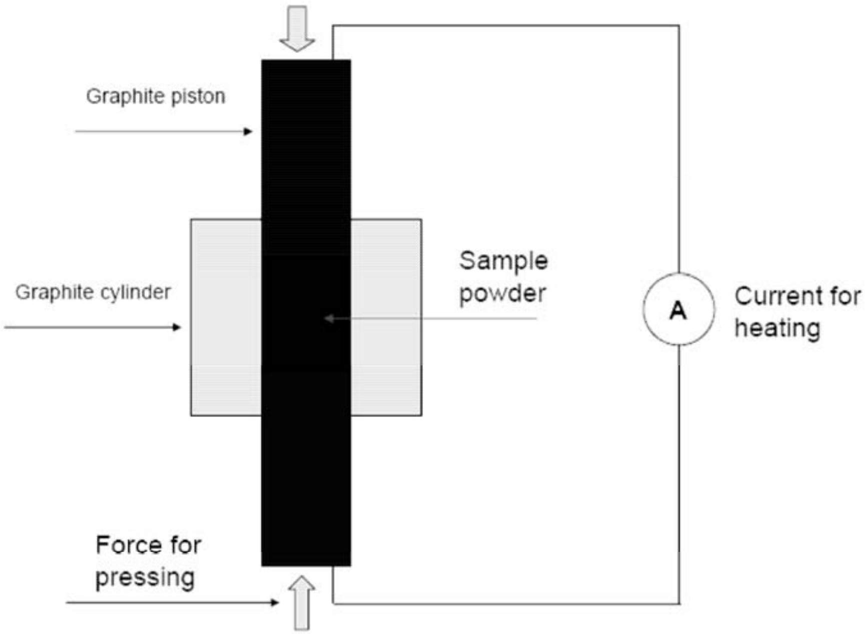
B. Poudel, *et al*., Science **320**, 634 (2008).



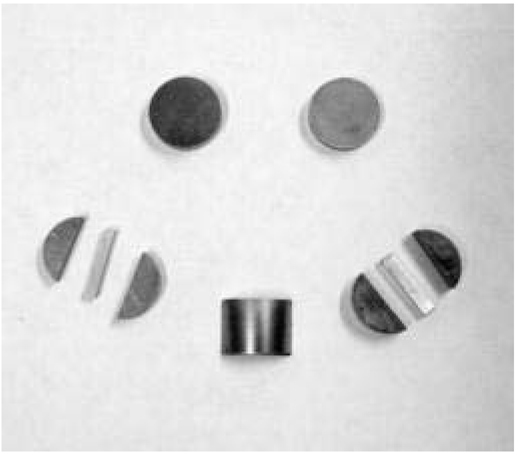
Zhifeng Ren · ***Boston College · Department of Physics***

How to Consolidate Nanopowders into bulk?

DC Induced Hot Press



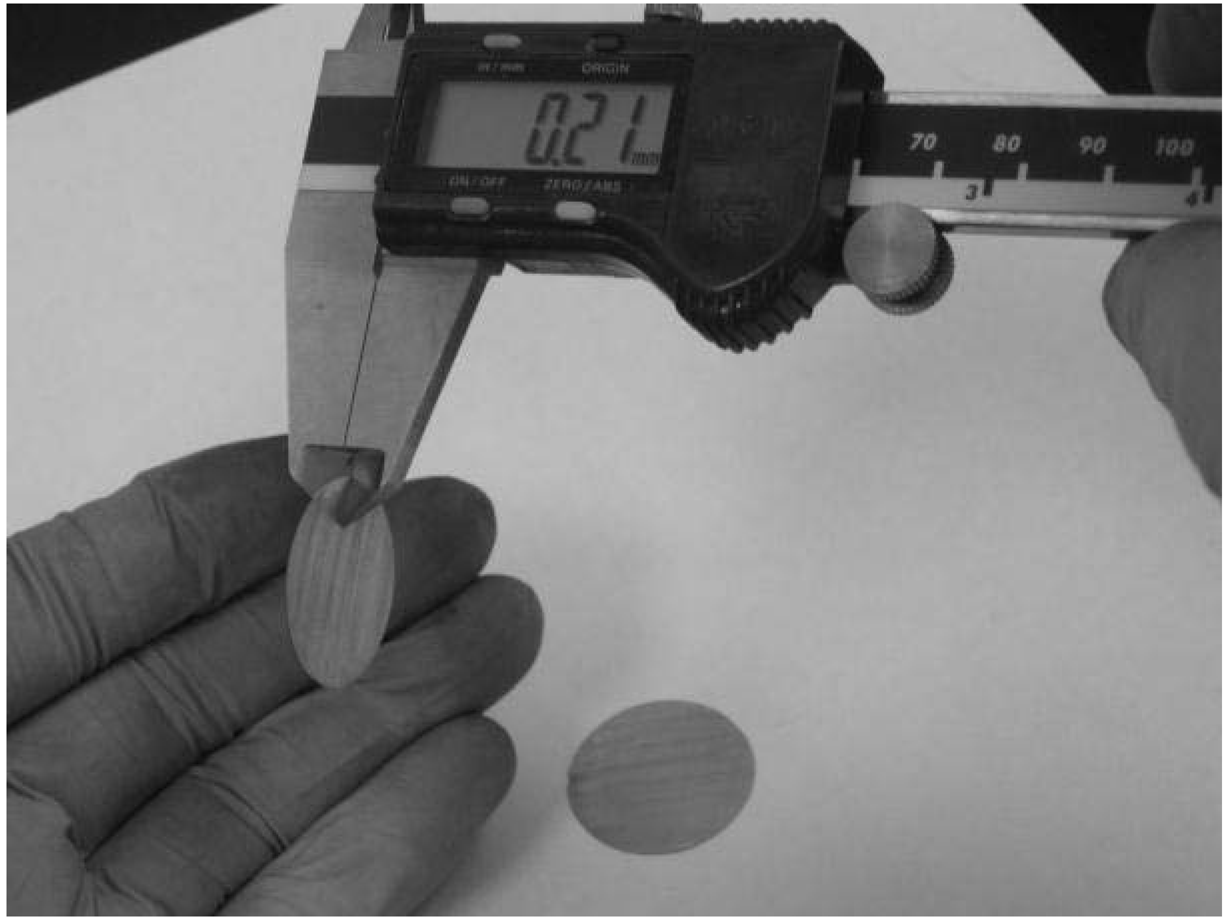
Disks, Bars, and Thin Wafers



Disks and bars are made for individual property measurements.

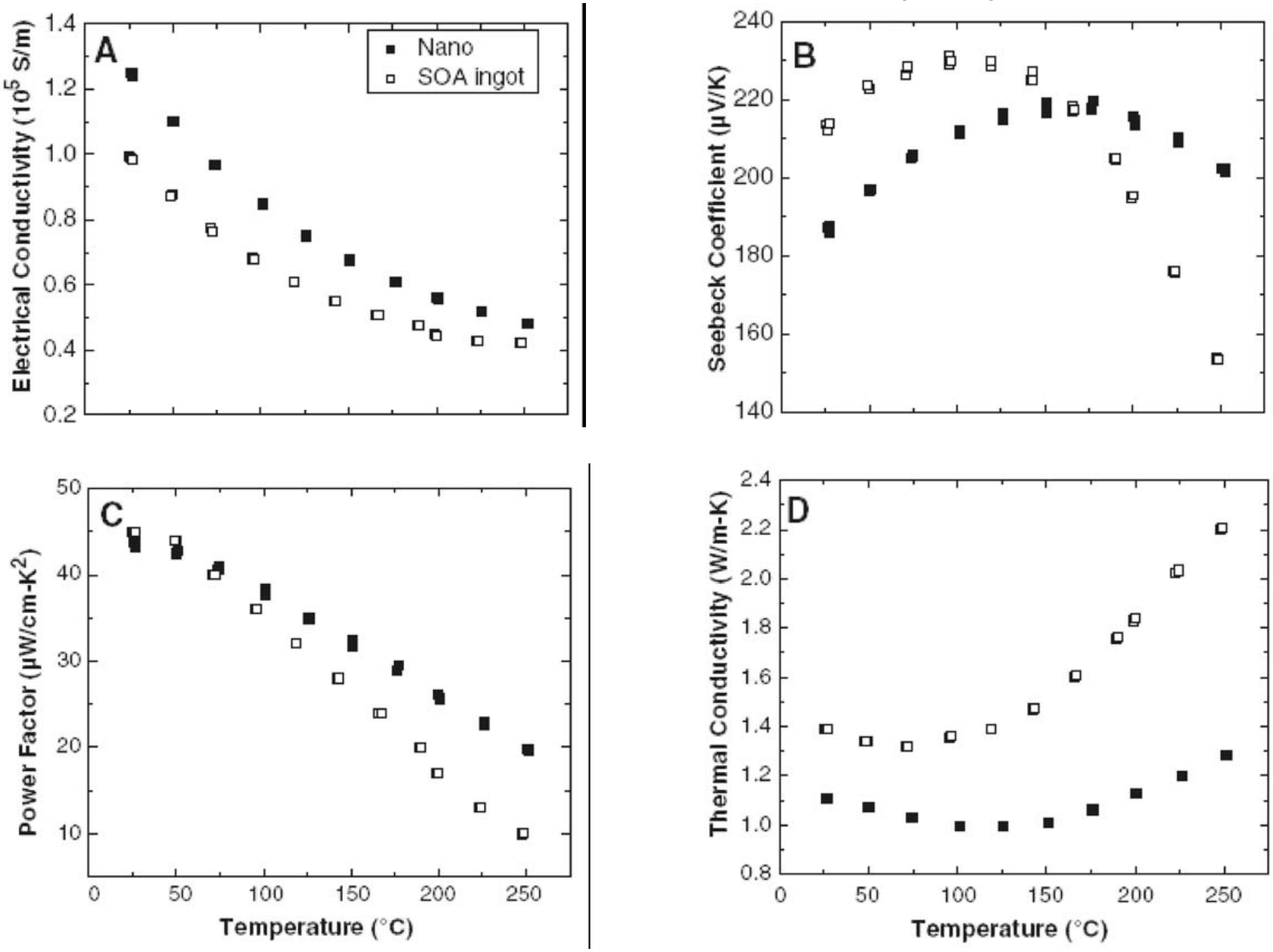
GMZ has capability of a few tons per year.

Thin wafers were made for testing the strength.



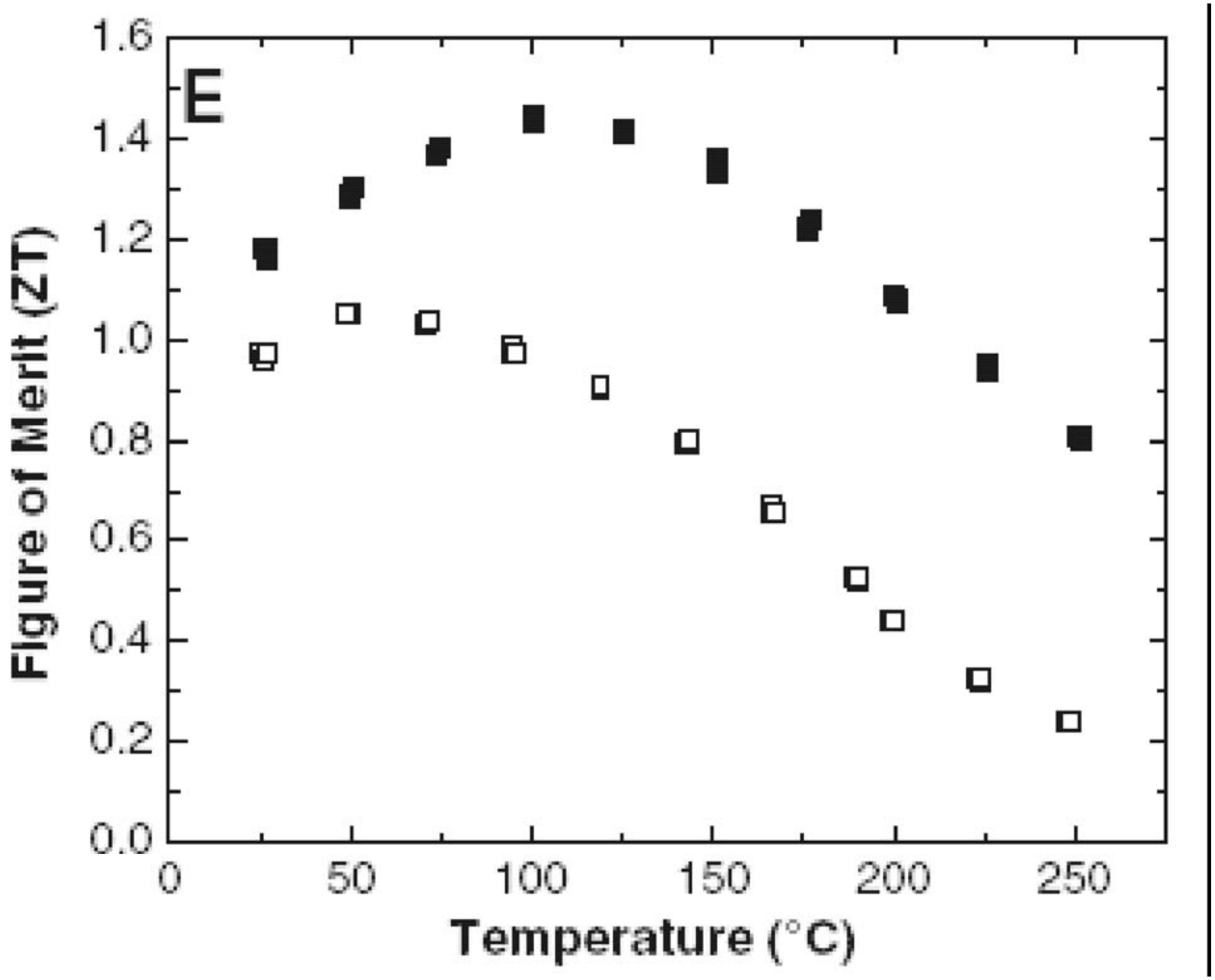
Thermoelectric Properties of p-type $Bi_{0.4}Sb_{1.6}Te_3$

B. Poudel, *et al*., Science **320**, 634 (2008).



Thermoelectric Properties of p-type $Bi_{0.4}Sb_{1.6}Te_3$

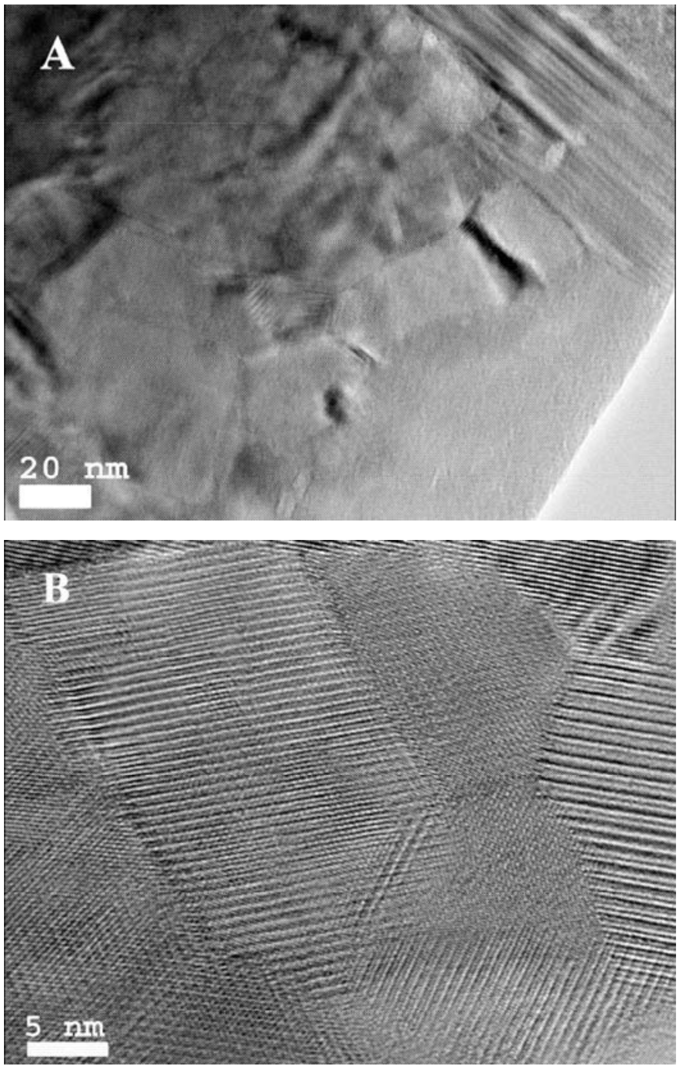
B. Poudel, *et al*., Science **320**, 634 (2008).



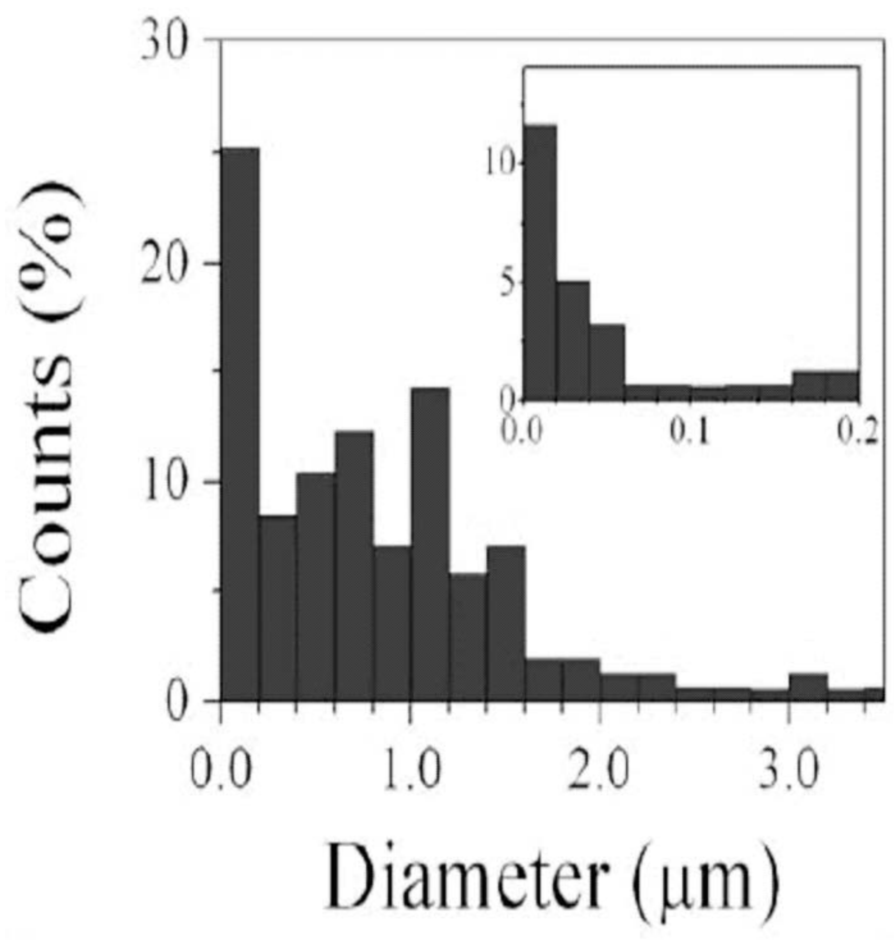
Zhifeng Ren · ***Boston College · Department of Physics***

Grain Size Distribution of p-type $Bi_{0.4}Sb_{1.6}Te_3$

B. Poudel, *et al*., Science **320**, 634 (2008).

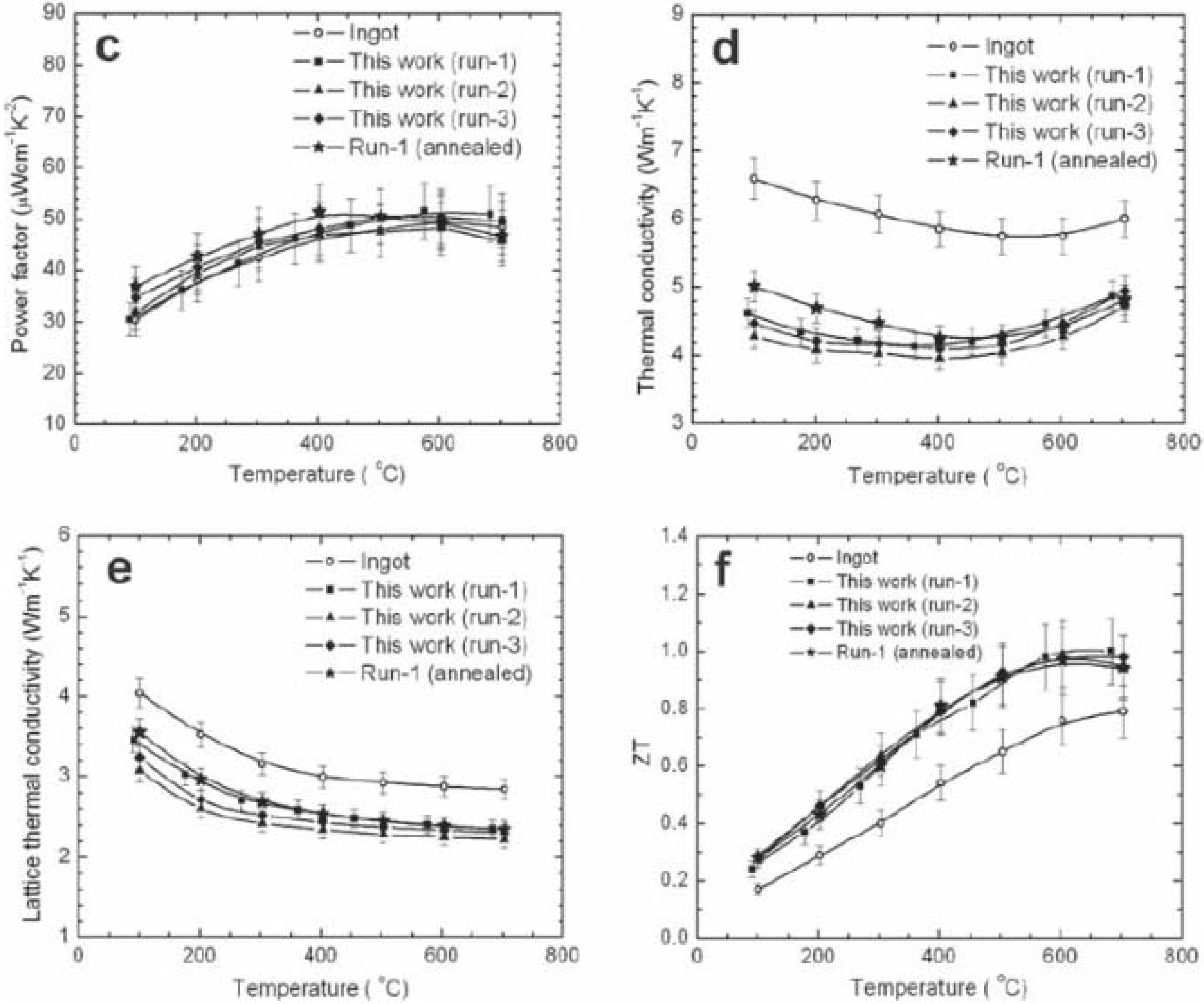


Y. C. Lan, *et al*., NanoLetters 9, 1419 (2009).



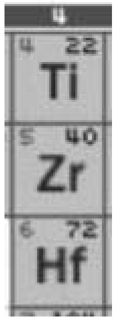
Phonon Engineering nanostructure in n-type half-Heusler

Giri Joshi, Adv. Energy Mater. **2011**, *1*, 643–647

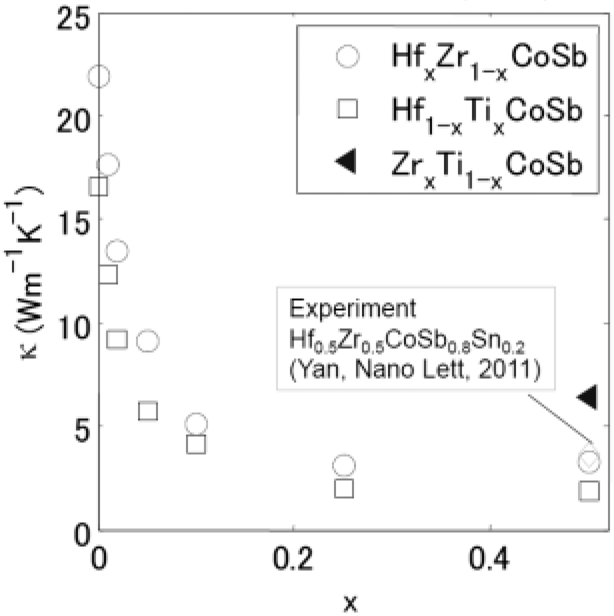


Phonon Engineering point defects in half-Heuslers

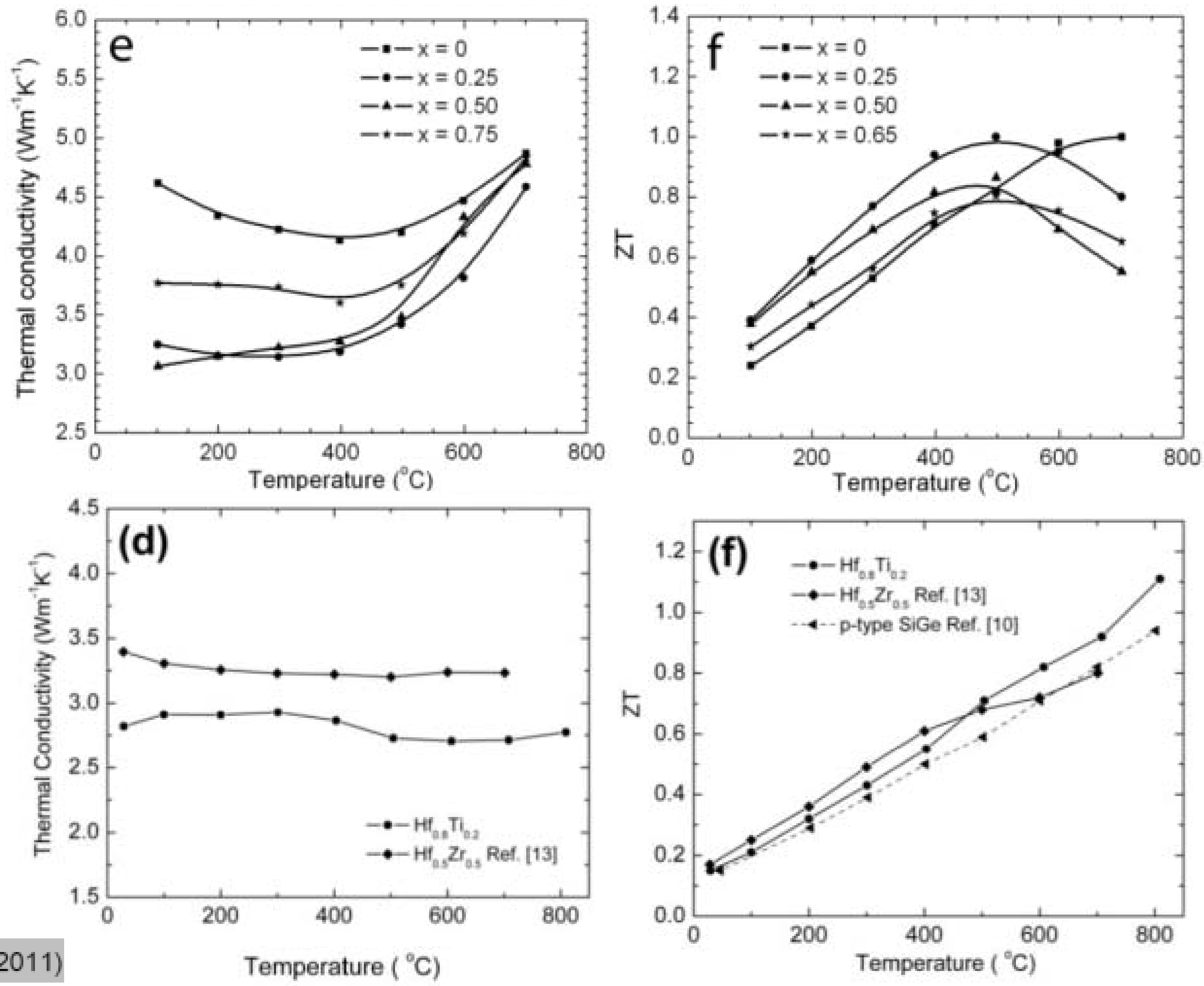
Giri Joshi *et al*. unpublished data and Yan *et al*., Nano Lett 11, 556-560 (2011)



Green Kubo Calculation (300 K)



Shiomi, Esfarjani, Chen, Phys. Rev. B 84, 104302 (2011)



Electron Engineering increase Seebeck coeffcient

25 JULY 2008 VOL 321 SCIENCE 554

Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States

Joseph P. Heremans,[1,2]* Vladimir Jovovic,[1] Eric S. Toberer,[3] Ali Saramat,[3] Ken Kurosaki,[4] Anek Charoenphakdee,[4] Shinsuke Yamanaka,[4] G. Jeffrey Snyder[3]*

$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{d[\ln(\sigma(E))]}{dE}\right\}_{E=E_F}$$

$$= \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{1}{n}\frac{dn(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}_{E=E_F}$$

$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3}$$

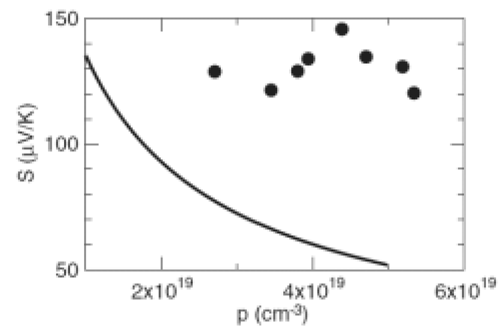
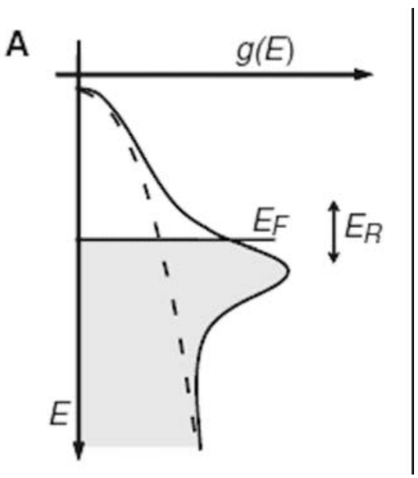
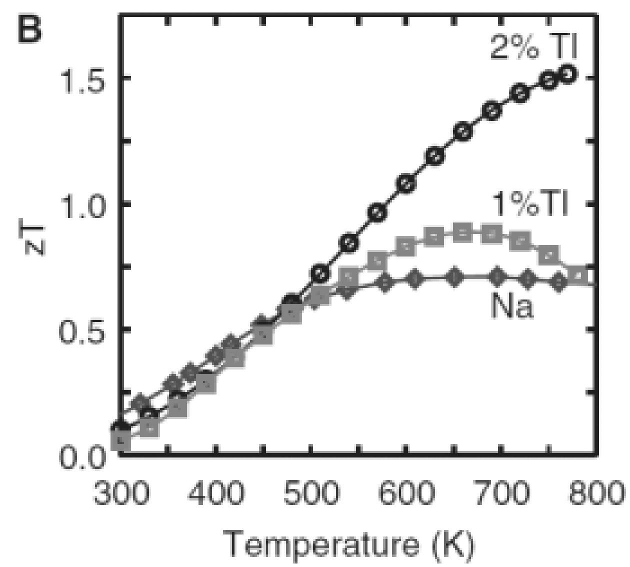


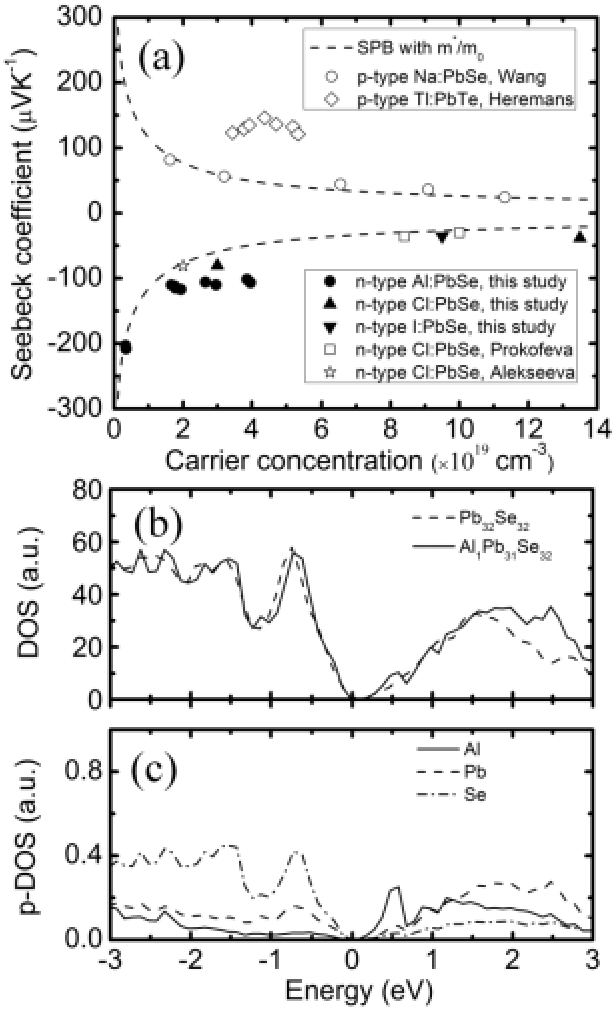
Fig. 3. Pisarenko relation of Seebeck coefficient at 300 K versus hole concentration for PbTe (solid line) compared to the results measured on every Tl-PbTe sample prepared for this study.

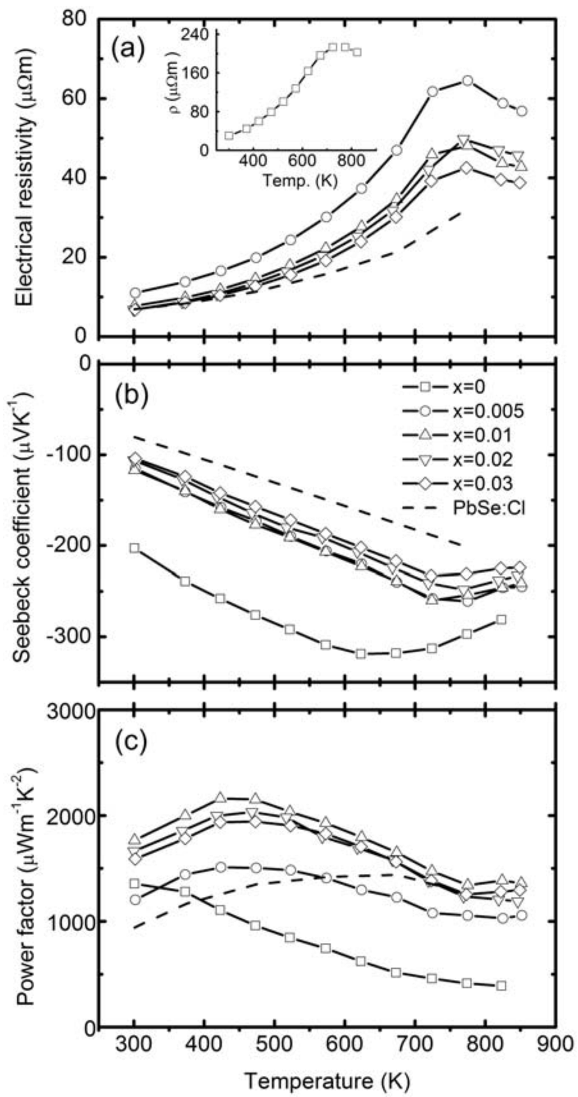


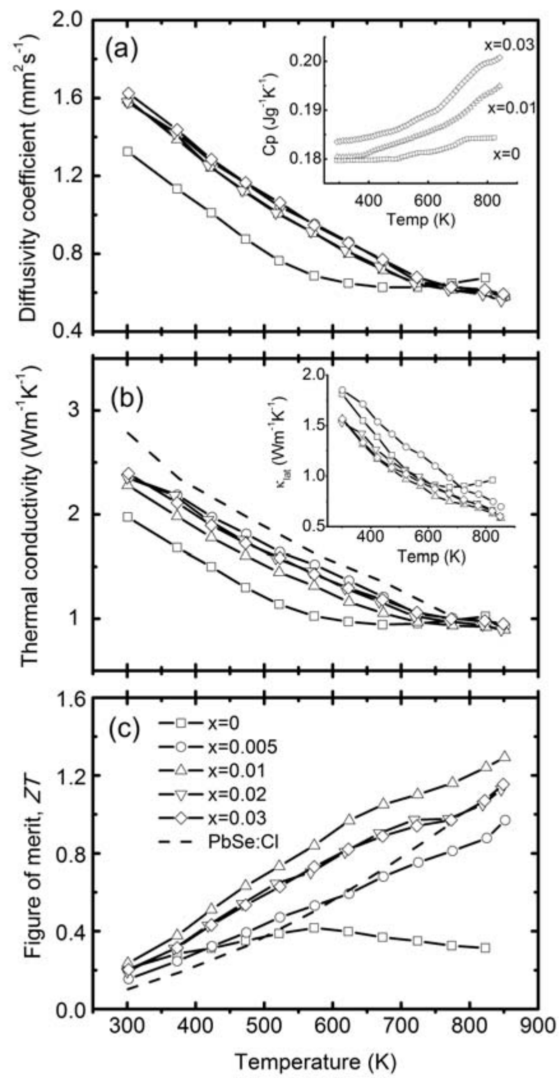


Electron Engineering resonant doping by Al in $Al_xPb_{1-x}Se$

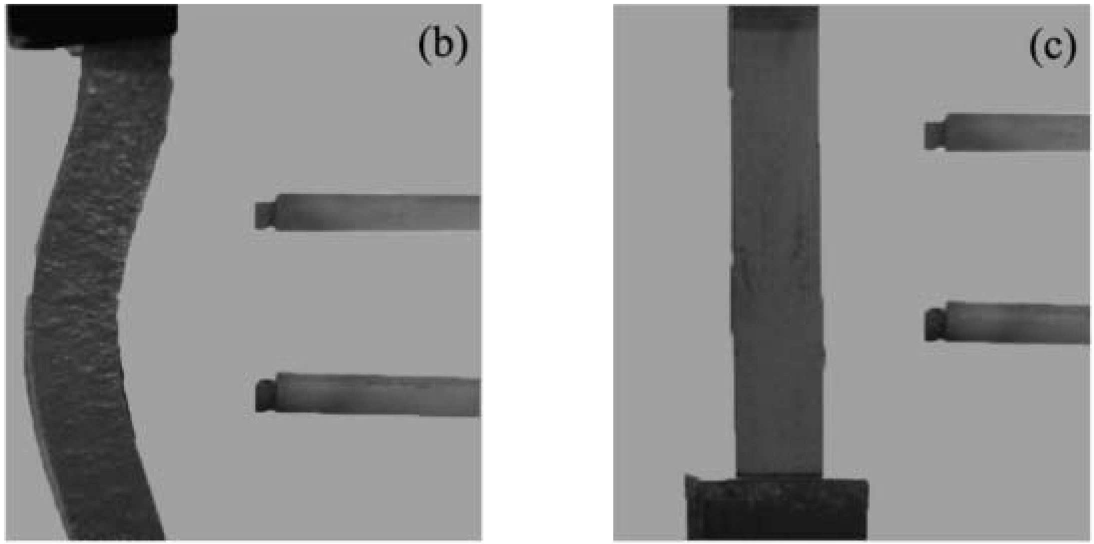
Qinyong Zhang *et al*. *Energy & Environmental Science* **5**, 5246-5251 (2012)

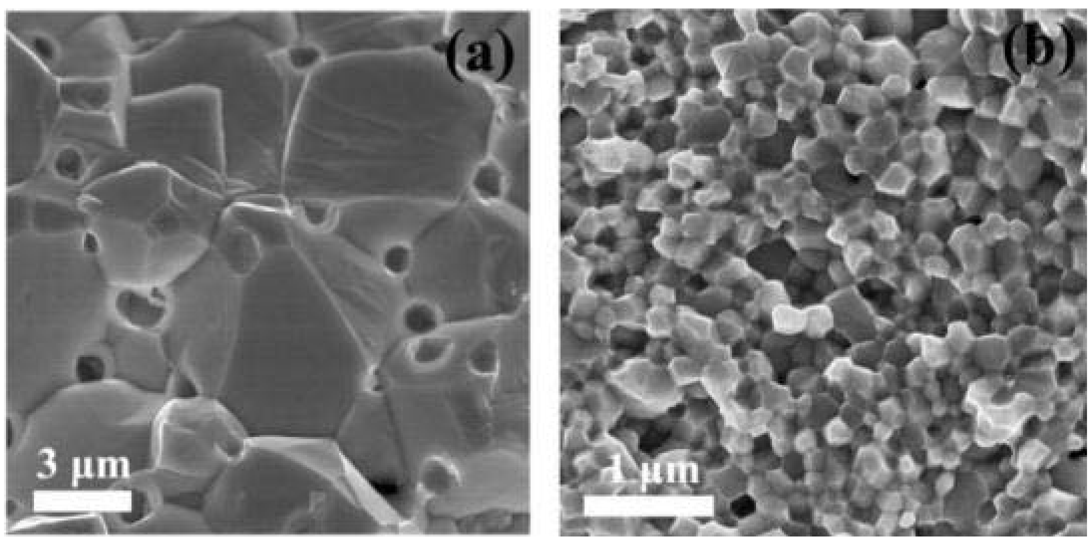




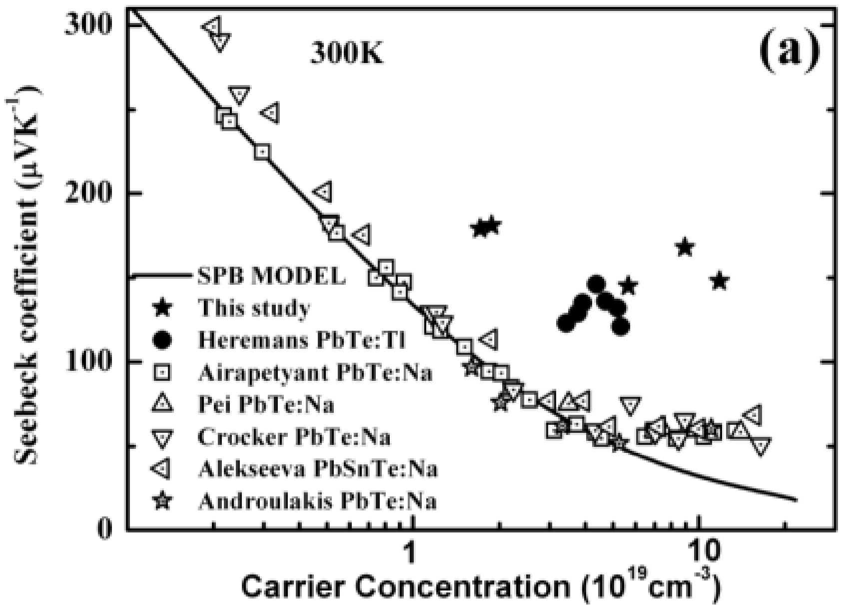


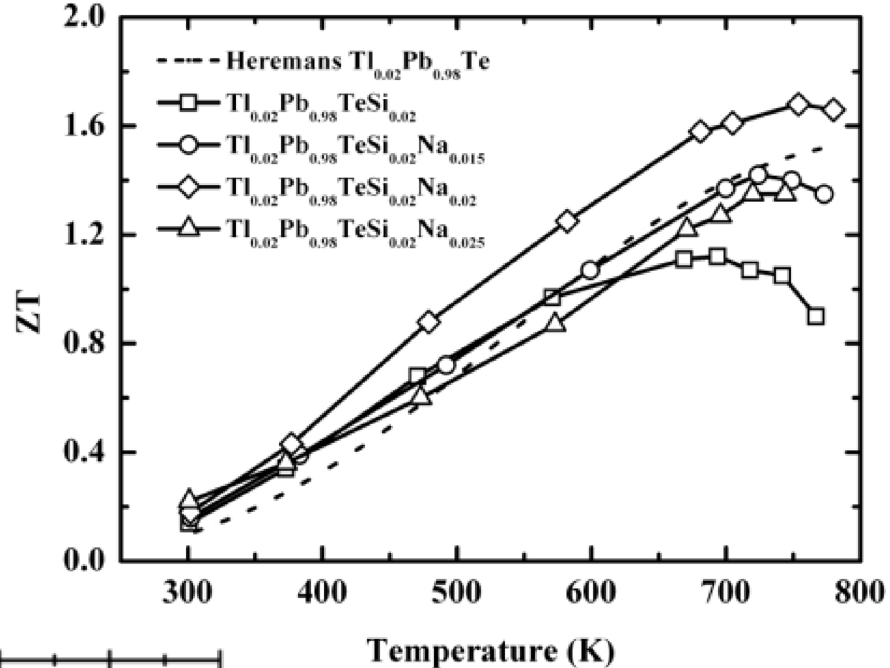
P-type $Tl_{0.02}Pb_{0.98}Te$ without/with Si and Na

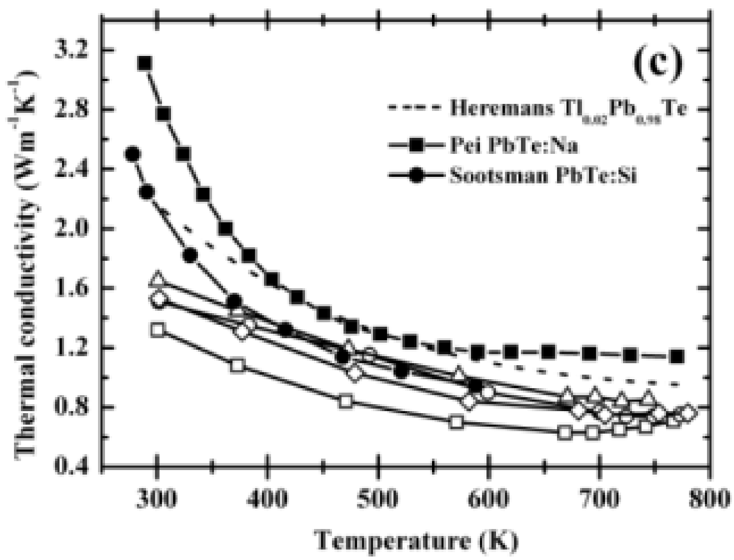




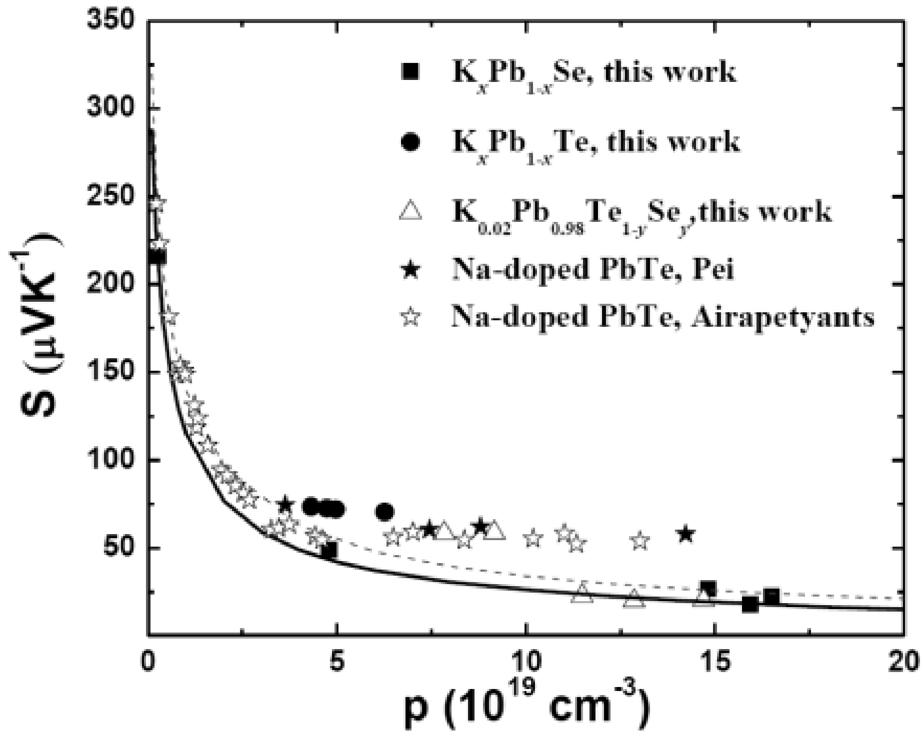
Concurrent Electron and Phonon Engineering

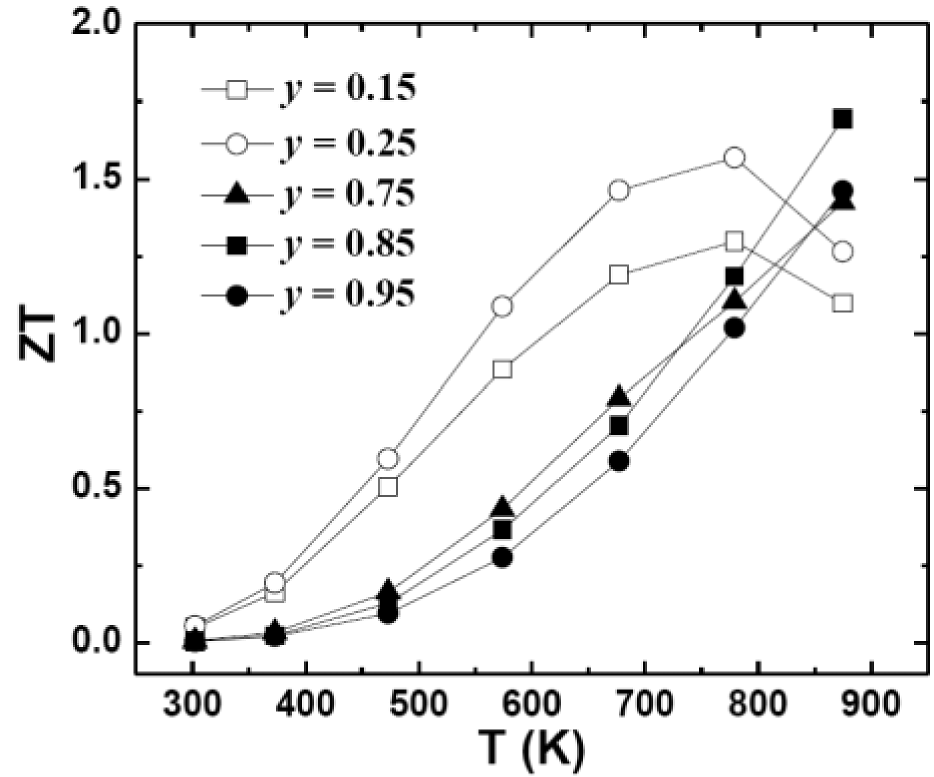






Electron Engineering two bands converging





Zhifeng Ren · ***Boston College · Department of Physics***

Electron Engineering modulation doping to increase power factor

665 Appl. Phys. Lett. 33(7), 1 October 1978

Electron mobilities in modulation-doped semiconductor heterojunction superlattices

R. Dingle, H. L. Störmer,[a] A. C. Gossard, and W. Wiegmann

Bell Laboratories, Murray Hill, New Jersey 07974
(Received 19 June 1978; accepted for publication 27 July 1978)

GaAs-$Al_xGa_{1-x}As$ superlattice structures in which electron mobilities exceed those of otherwise equivalent epitaxial GaAs as well as the Brooks-Herring predictions near room temperature and at very low temperatures are reported. This new behavior is achieved via a modulation-doping technique that spatially separates conduction electrons and their parent donor impurity atoms, thereby reducing the influence of ionized and neutral impurity scattering on the electron motion.

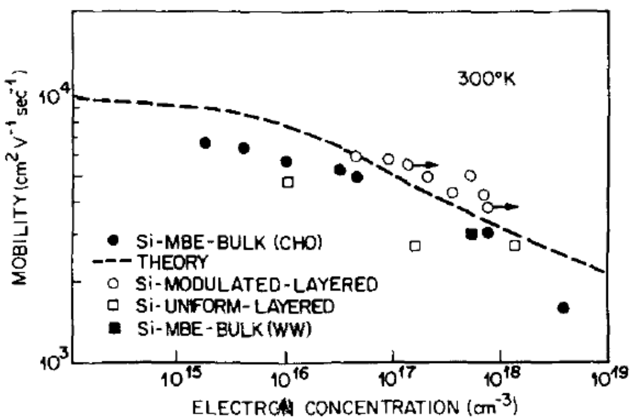


FIG. 2. 300 K mobilities of a range of Si-doped GaAs and Si-doped GaAs-$Al_xGa_{1-x}As$ superlattices. The filled circles and the theory [Brookes-Herring, $(N^+ + N^-)/n = 1$] are taken from Ref. 6. The horizontal arrows show electron concentration changes discussed in the text.

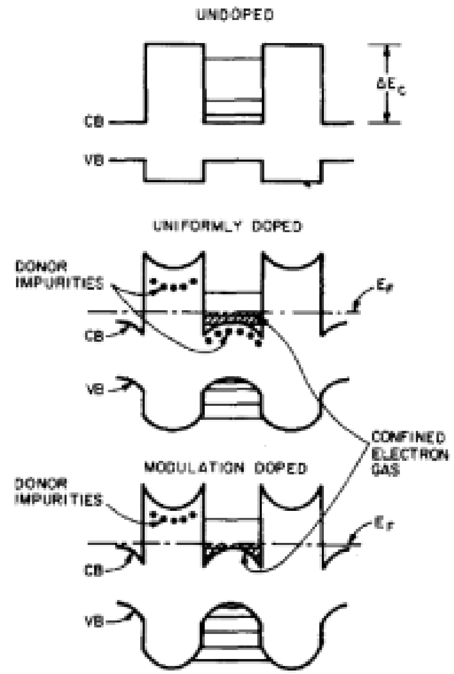
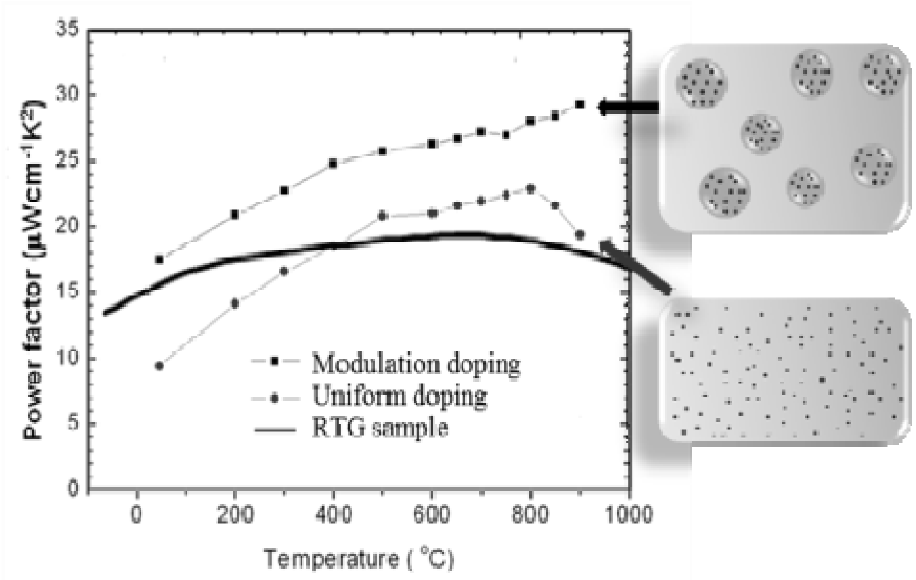
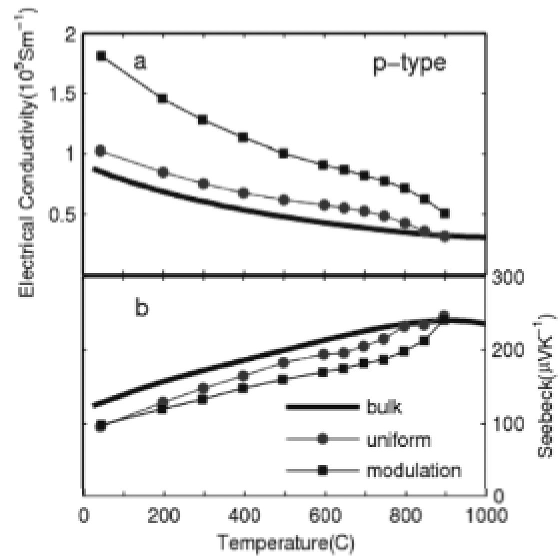


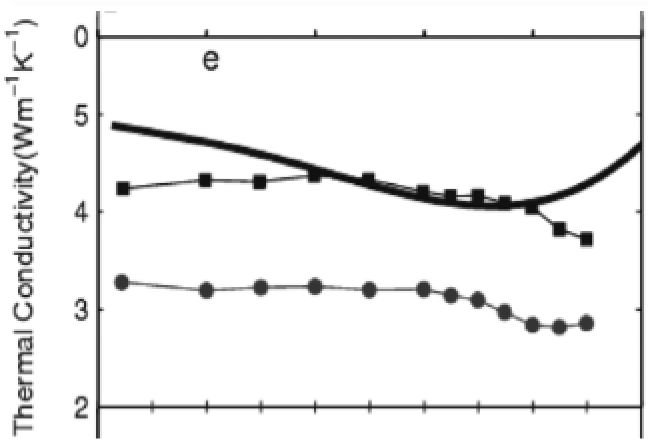
FIG. 1. Energy-band diagrams for n-doped and undoped GaAs-$Al_xGa_{1-x}As$ superlattices.

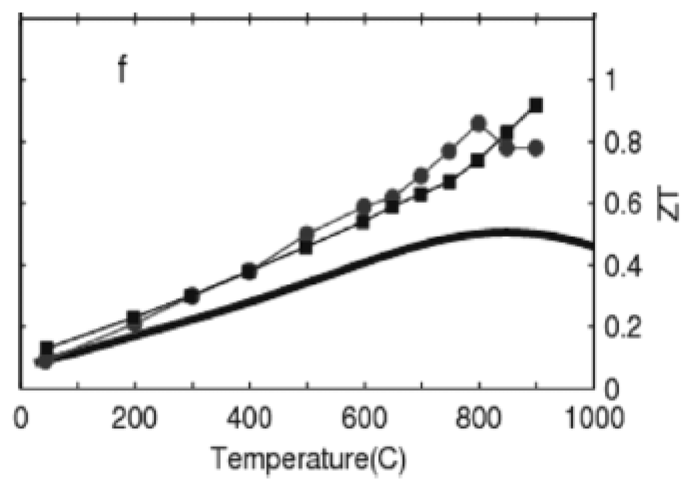
Concurrent Electron and Phonon Engineering: modulation doping

Mona Zebarjadi et al., Nano Lett 11, 2225-2230 (2011)



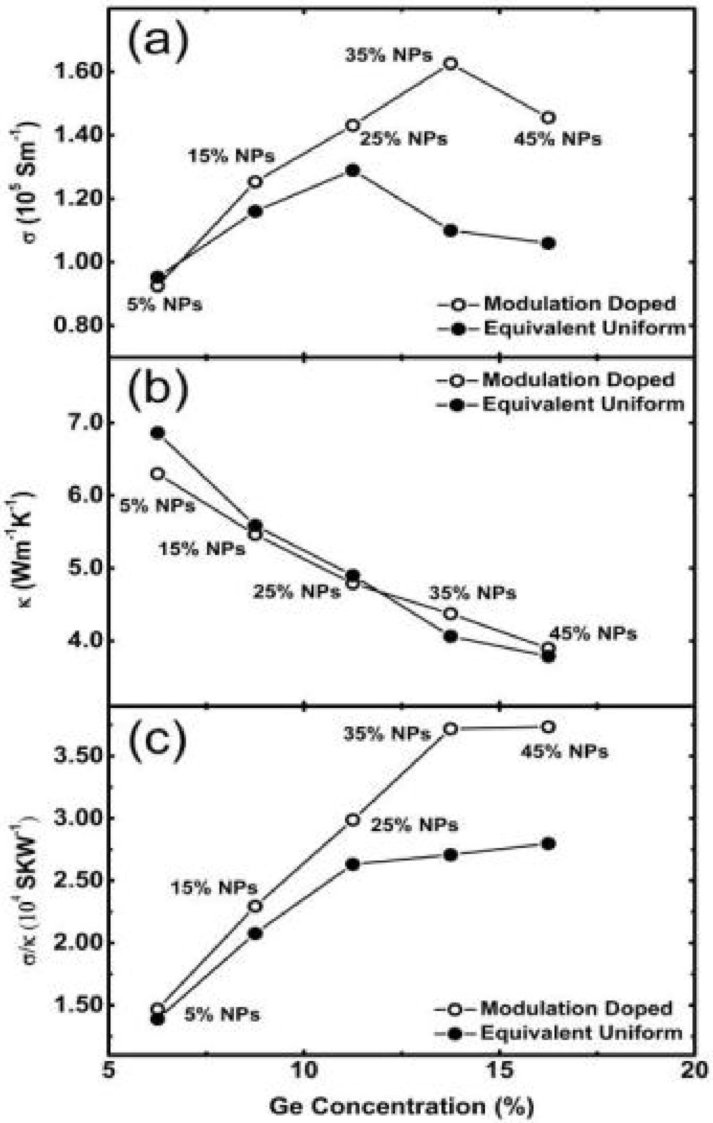


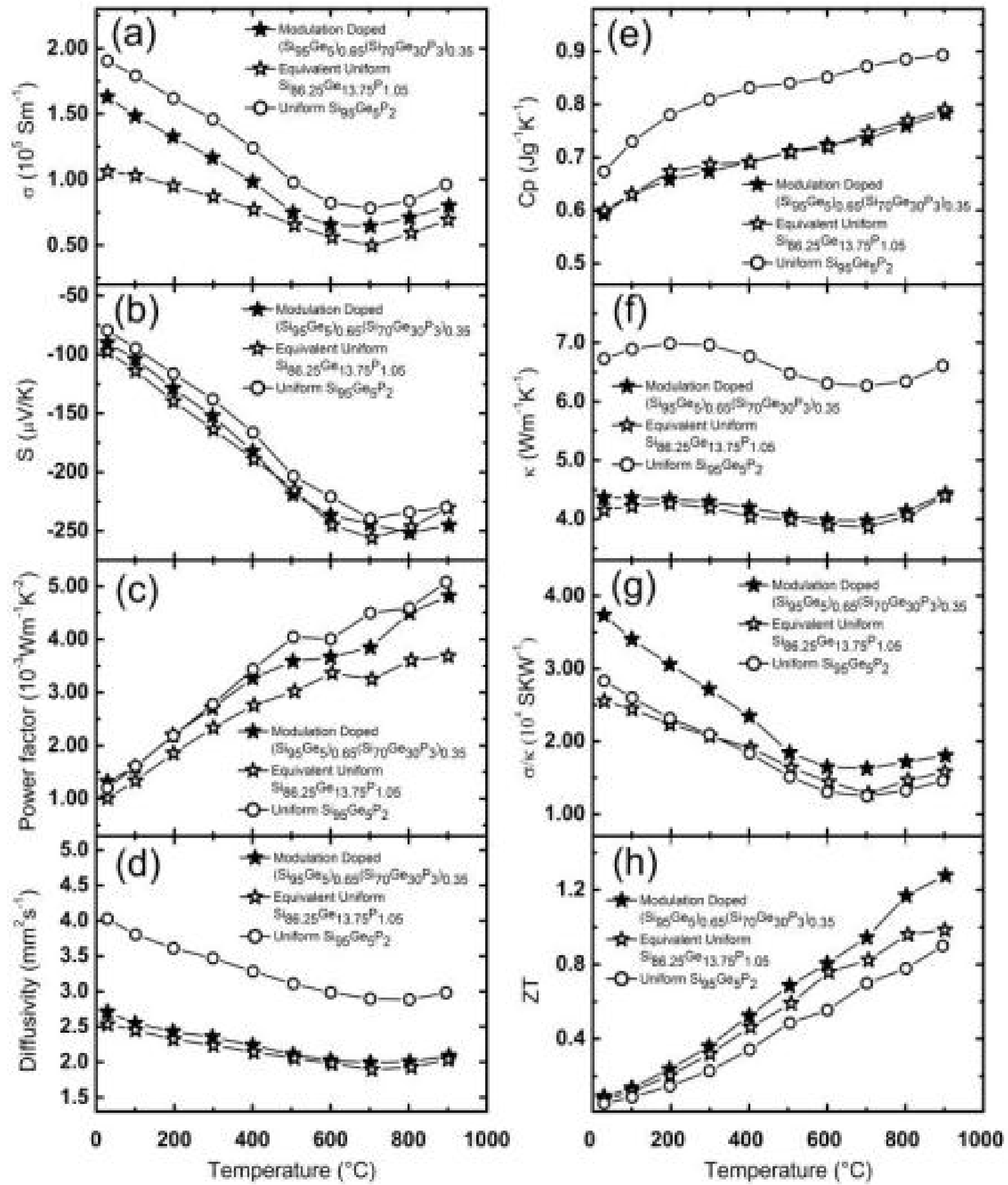




Concurrent Electron and Phonon Engineering modulation doping

Bo Yu et al. (under review)

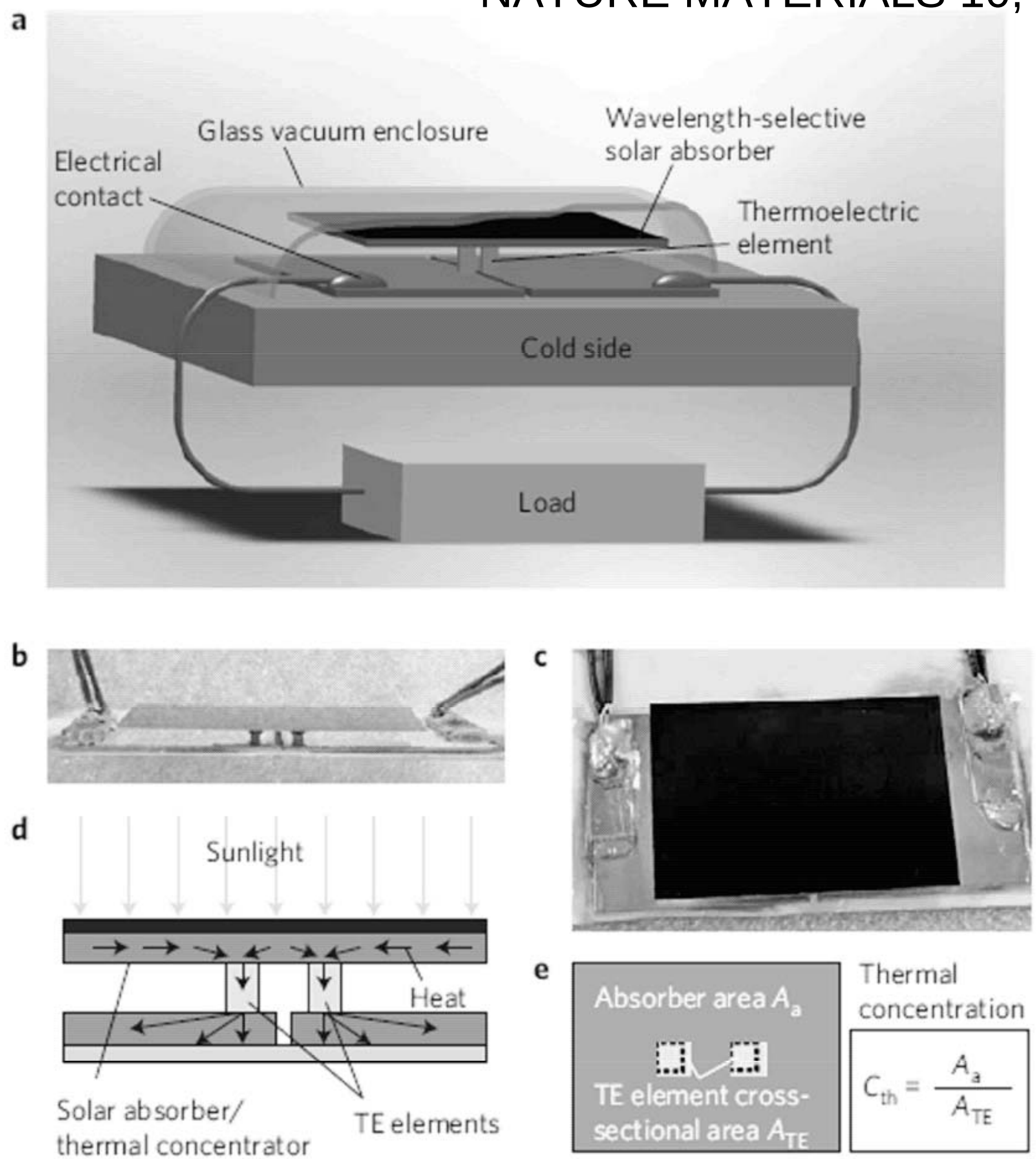




Zhifeng Ren · ***Boston College · Department of Physics***

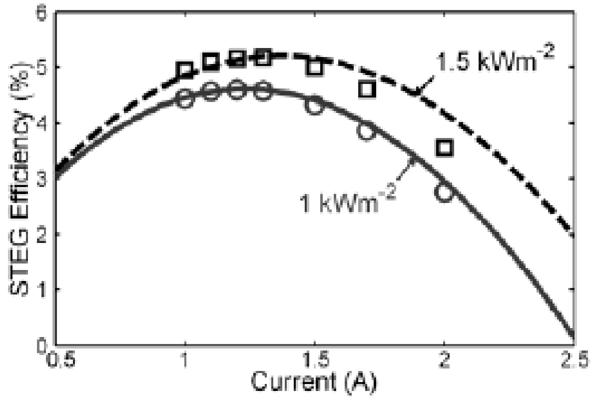
Solar Panels Using Thermoelectric Nano Materials

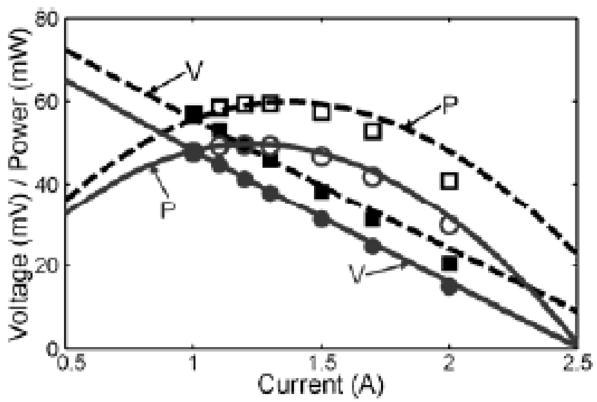
NATURE MATERIALS 10, 532-538 (2011)

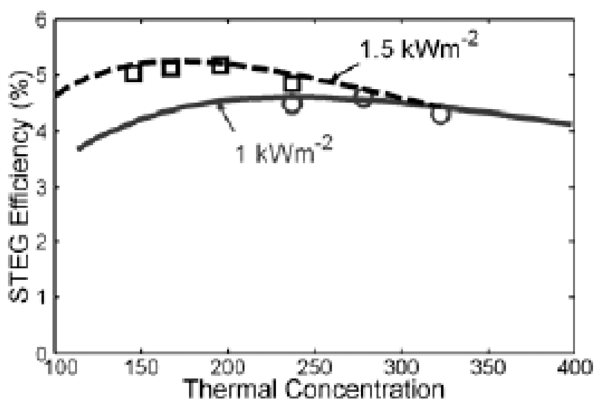


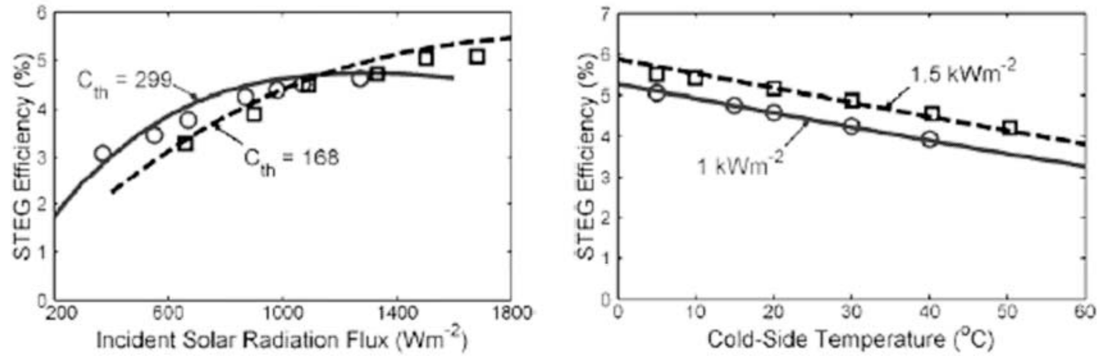
Zhifeng Ren · ***Boston College · Department of Physics***

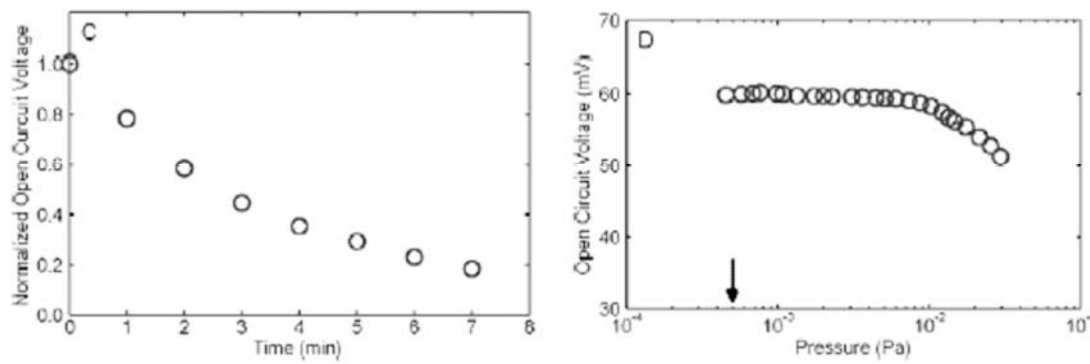
Efficiency and Thermal Momentum







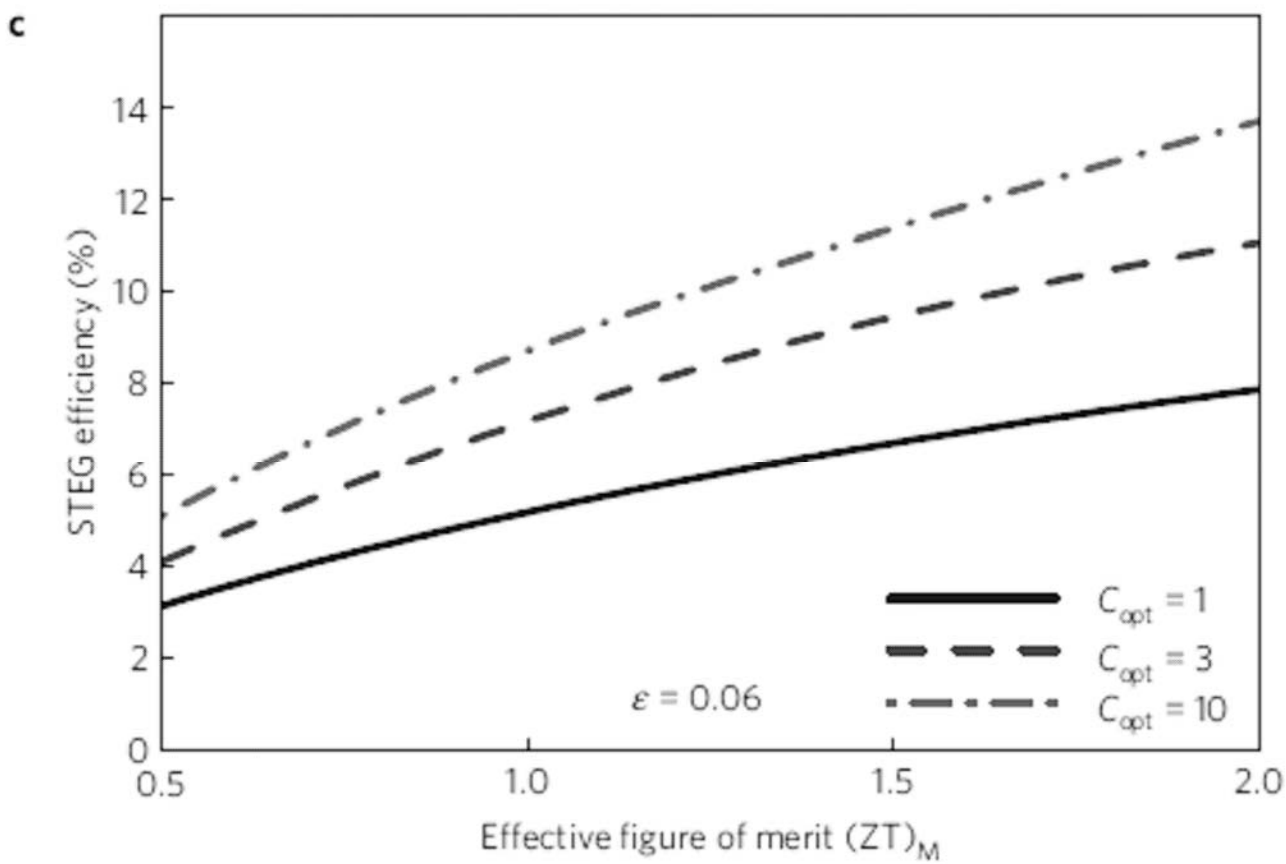




NATURE MATERIALS 10, 532-538 (2011)

Zhifeng Ren · ***Boston College · Department of Physics***

Potential of Thermoelectrics



Summary

- Physics is very fundamental, understanding
- Materials science is very essential, processing
- Interdisciplinary is very important.
- Solar energy is very large.
- Thermoelectric materials may be very useful.
- The area is very open.
- The future is very bright.
- Your attention is very much appreciated!

Acknowledgments

Former PhD students

Dr. B. Poudel
Dr. Y. Ma
Dr. X. W. Wang
Dr. J. Yang
Dr. X. Yan
Dr. G. Joshi
Dr. T. Paudel
Dr. Gaohua Zhu

Former postdocs

Dr. W. Z. Wang
Dr. B. Q. Zeng
Dr. Q. Y. He
Dr. Q. Y. Zhang

Current PhD students

Mr. B. Yu
Mr. T. Y. Sun
Mr. Tulashi Dahal

Current postdocs

Dr. H. Z. Zhao
Dr. H. Z. Wang
Dr. Y. C. Lan
Dr. W. S. Liu
Dr. Q. Zhang
Dr. Q. Jie
Dr. X. Yan
Dr. Zhaoui Shu
Dr. Shuo Chen
Dr. Chuanfei Guo

Colleagues at BC

Prof. D. Broido, Prof. C. Opeil, and their students

Collaborators

Prof. G. Chen and his students, MIT
Prof. M. Dresselhaus and her students, MIT

$$$

DOE, NSF, ARO, NASA, DOD, etc.