Emerging Material Needs in Thermoelectrics

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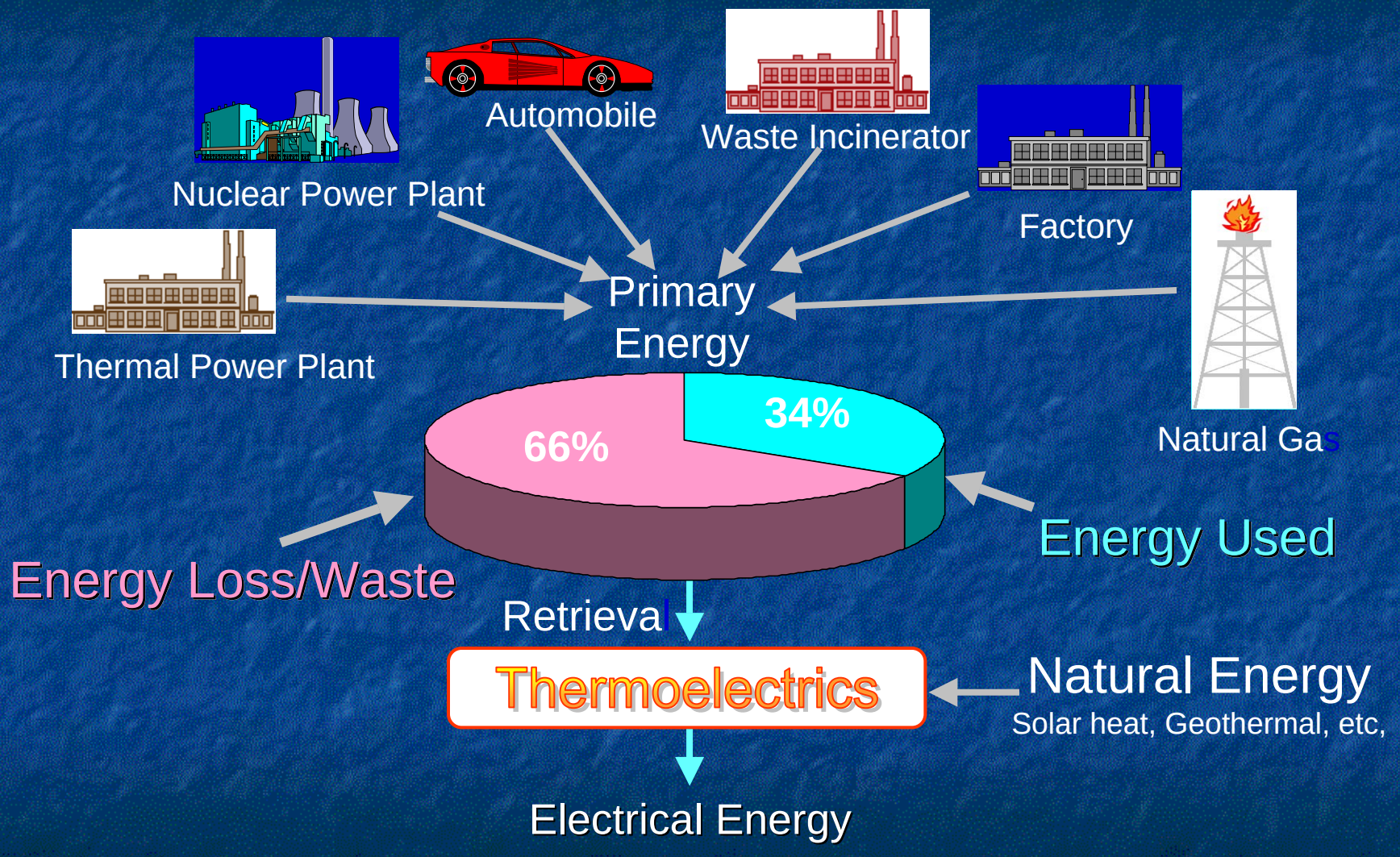
Introduction

- In recent years, there has been a resurgence of interest in the field of thermoelectrics driven by the need for more efficient materials for refrigeration and power generation.

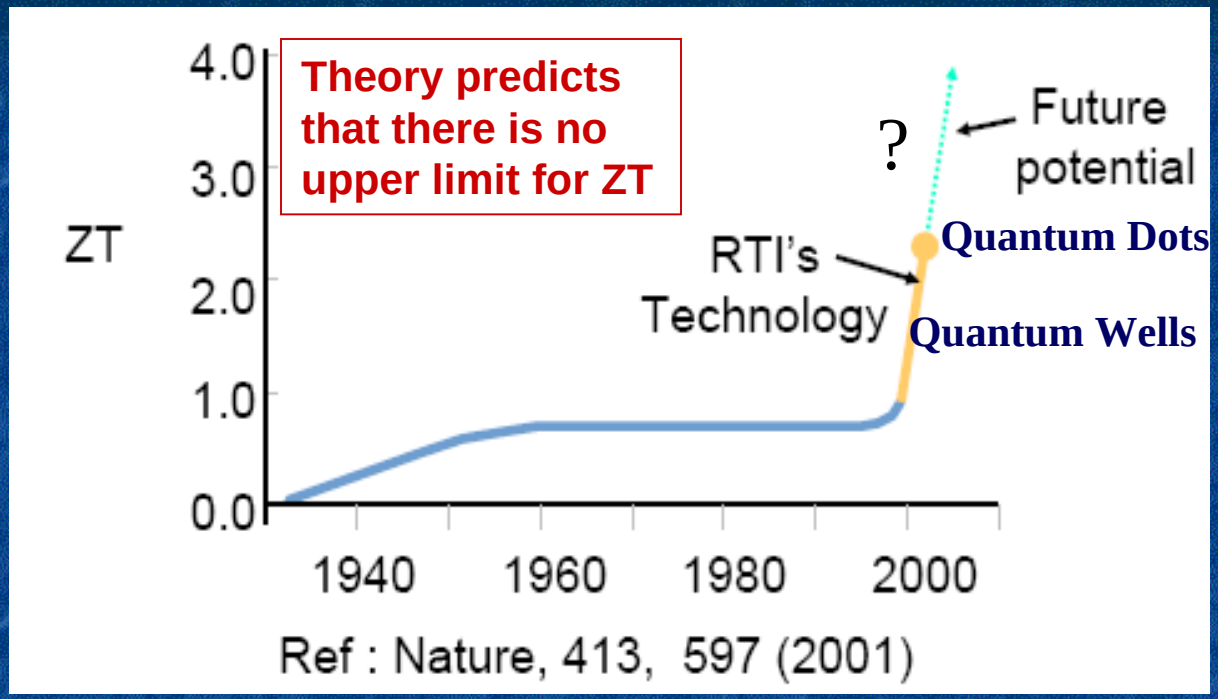
- ZT can be enhanced in novel complex materials such as mixed-valence Kondo metals, clathrates, skutterudites, superlattice quantum-well and quantum- dot structures and many others.

- Being natural superlattices, compounds with low-dimensional structures have been investigated actively as potential thermoelectric materials.

Hi ZT Thermoelectrics: Waste Heat



History of ZT



All thermoelectric programs, past and present, have concluded that the large-scale use of thermoelectrics require a significant improvement from the ZT=1 bulk limit established in the 1950's

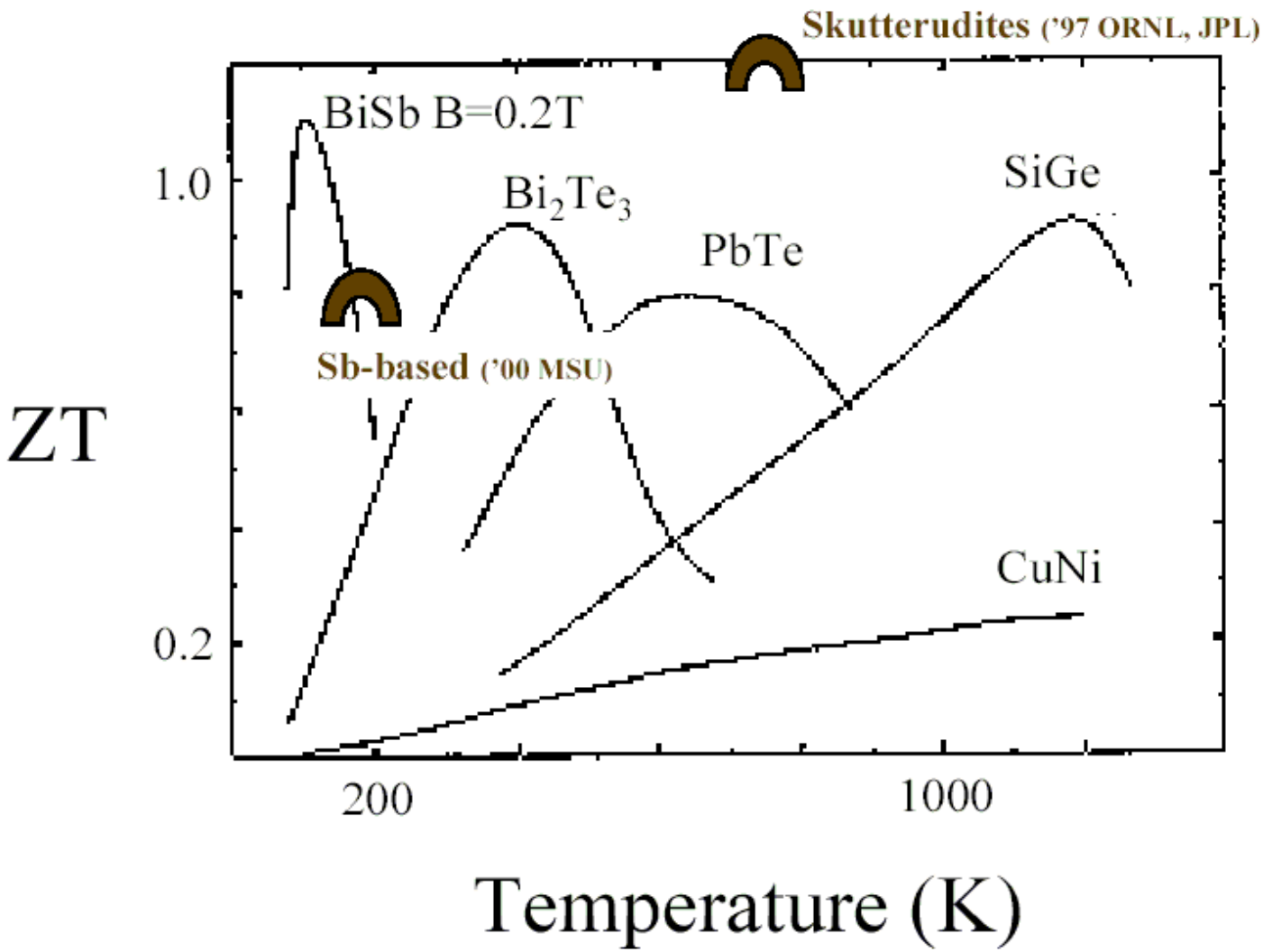
- MIT
- JPL
- RTI
- DOE
- MSU
- LLNL
- PNNL

- Toyota, Nissan
- Porsche, BMW,GM
- Westinghouse, GE
- Texas Instruments
- Gulf Atomics, IBM
- Borg-Warner
- Melcor, Teledyne
- 3-M, BASF, Exxon
- Aisin (Honda)
- Marlow Industries
- Amerigon, Motorola
- Tellurex Corp
- Caterpiller, Bell Labs
- Hi-Z Technology
- Ceramic Energy
- Delphi Corp
- Oak Ridge Nat Lab
- Sandia Nat Lab
- TE Technologies
- DuPont ???

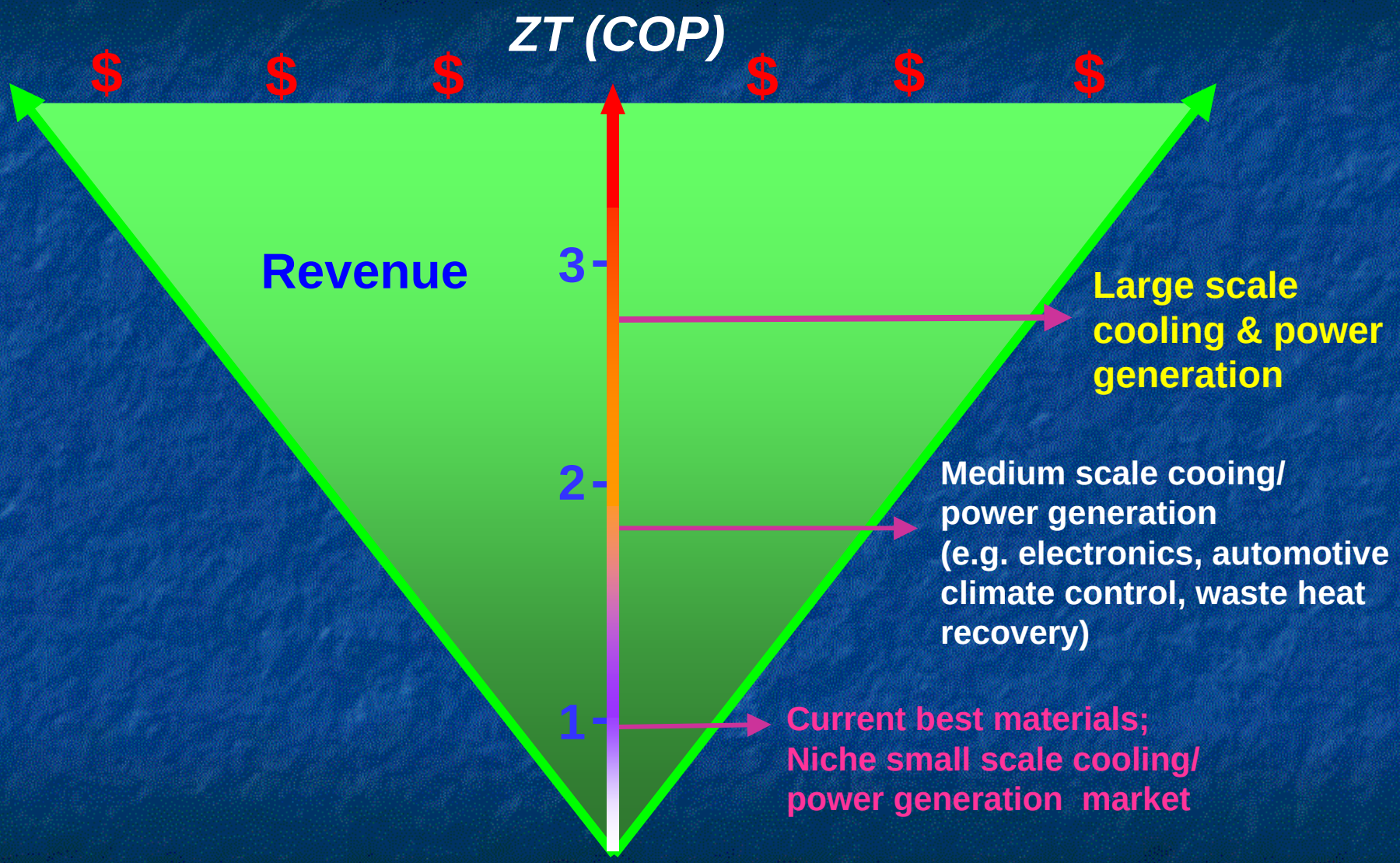
Recent Developments (superlattices and quantum dots)

BiTe/SbTe Superlattice
(Venkatasubramanian et al. RTI)
ZT (300K)~2.4, Nature, 11 Oct. 2001

PbTe Q-Dots
(Harman et al. MIT Lincoln Lab)
ZT (500K)~2.0, estimated, J. Elect. Mat. 1999



ZT versus Revenue Potential



Exciting "new" technology with tremendous potential for growth

Why is DuPont Interested in TE ?

DuPont Automotive

- Replacement of fluorocarbons for cooling and heating, increased automotive electric power

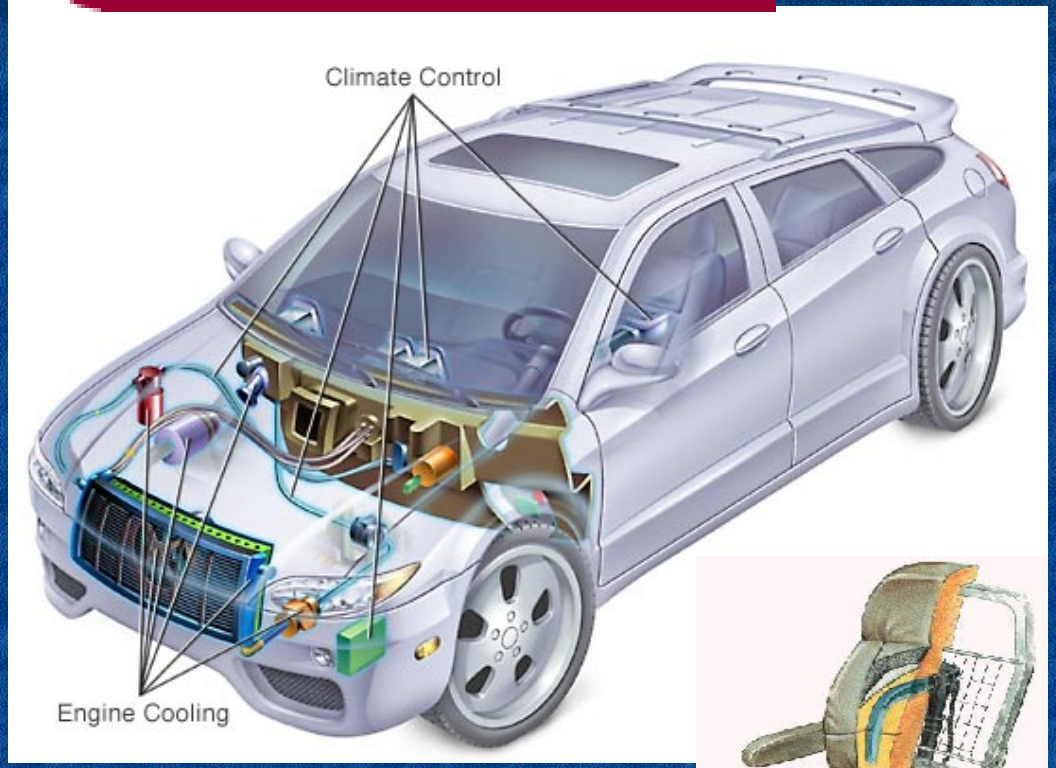
DuPont Fuel Cells

- Waste heat power generation, electronic safety features, portable backup power

DuPont Electronic and Communication Technologies

- Telecom towers, cell phones, portable generators, consumer and vehicle accessory electronics

DuPont Automotive



The miracles of science™

- Refrigerant replacement
  - Power generation, heating and cooling
  - Thermoplastic / nylon materials that can withstand extreme environments
  - Collision avoidance systems
  - Vehicle stability controls
  - Sensors and electronic subsystems
  - Electronic braking

Issues: Power Demands, TE Efficiency, Device Cost

DuPont Products

- DuPont™ Teflon® resins
- DuPont™ Lycra® brand spandex fiber
- DuPont™ Stainmaster® stain-resistant carpet
- DuPont™ Antron® carpet fiber
- DuPont™ Dacron® polyester fiber
- DuPont™ Kevlar® brand fiber
- DuPont™ Nomex® fire-retardant material
- DuPont™ Corian® solid surface material
- DuPont™ Tyvek® brand protective material
- DuPont™ Coolmax® textile fibers
- DuPont™ Cordura® textile fibers
- and
- DuPont™ Suva® chlorine-free refrigerants

DuPont™ Suva®
refrigerants

- **Alternative refrigerants** to replace CFCs.
- HFC compounds contain **no chlorine,** so have **zero ozone depletion potential (ODP).**
- HCFCs do contain chlorine, but have up to 98% less ODP than CFCs.
- The presence of one or more hydrogen atoms in HCFC molecules allows them to **break apart faster in the lower atmosphere** so that less chlorine reaches the ozone layer.

DuPont™ Suva® Refrigerants

DuPont™ Suva® refrigerants, which are composed of hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC) compounds, were developed as safe, effective alternatives to existing chlorofluorocarbon (CFC) refrigerants.

Suva® 123 (R-123) is the DuPont brand name for HCFC-123 refrigerant, which is a replacement for CFC-11 in centrifugal chillers.

Suva® 124 (R-124) is the DuPont brand name for HCFC-124 refrigerant, which will have application in some CFC-114 systems and is also a component of Suva® MP blends.

Suva® 125 (R-125) is the DuPont brand name for HFC-125, which is a component of some Suva® blends.

Suva® 134a (R-134a) and **Suva® 134a Auto** are DuPont brand names for HFC-134a refrigerant, which is a primary replacement for CFC-12.

Suva® MP service refrigerants are ternary blends of HCFC-22, HFC-152a, and HCFC-124 that have been developed as replacements for CFC-12 and R-500 in a variety of applications.

DUPONT®
The miracles of science™

Thermoelectric Materials

- **Bi_2Te_3 - Sb_2Te_3** Solid Solutions
- **Lead Telluride** and its Alloys (Sn)
- **TAGS -** $(AgSbTe_2)_{1-x}(GeTe)_x$
- **Metal Disilicides-** (Fe, Mg, Mn, Cr, Re, Ru, Zr Hf… Sr,Na,Ca)
- **Semimetals** – Co(Ni)Si, $Mn_4Al_3Si_5$ (passive legs)
- **Silicon Germanium** - RTG
- **RE Compounds** - Chalcogenides, Pnictides, Oxides, Silicides
- High Pressure **Superconductors** - Copper Oxides
- **Boron Carbides** – Ti, Zr, W
- **Metals** - Pure, Alloys, Intermetallics, Kondo, Half-Heusler
- **Quasicrystals** – Al-Pd-Mn, Al-Cu-Tm
- **PGEC** – Skutterudites, Clathrates, Complex Pentatellurides
- **Low Dimensional** - Quantum Wells, Wires and Dots

Figure of Merit of Thermoelectrics

Figure of Merit (ZT)

Electrical conductivity ***Seebeck Coefficient S= ΔV/ΔT (mV/K)***

$$ZT = \frac{\sigma S^2}{\lambda_{total}} \bullet T$$

Total thermal conductivity
[lattice (phonon) + electronic(electron)]

The Goals

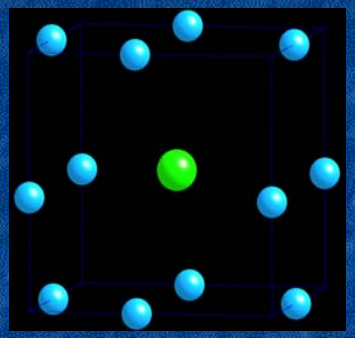
- High Energy Conversion Efficiency (> 5-10%)
- ZT ~ 3-4 to replace compressor refrigerators
- ZT ~ 2-3 for power conversion in vehicles

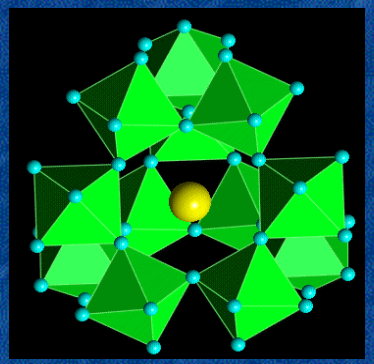
Oxide TE Materials

- **Advantage –**
  - High Seebeck coefficient
  - Low thermal conductivity
  - Excellent durability at high temperature in air –
  - Mostly nontoxic
- **Disadvantage –**
  - High electrical resistivity
  - Very Low ZT near room temperature
  - High ZT possible at high temperatures

Our Approaches to Higher ZT Materials

Lowering Lattice Thermal Conductivity of High Power Factor Materials





Phonon Engineering:

- atom disorder,
- chemical doping,
- intermediate valence,
- anharmonic atomic vibrations
- natural layered structures
- rattlers, grain boundary scattering

Band-gap engineering, quantum confinement, energy filtering off-sets, mobility enhancement, self-assembly nanoparticles and interface scattering have yet to be applied to BULK MATERIALS

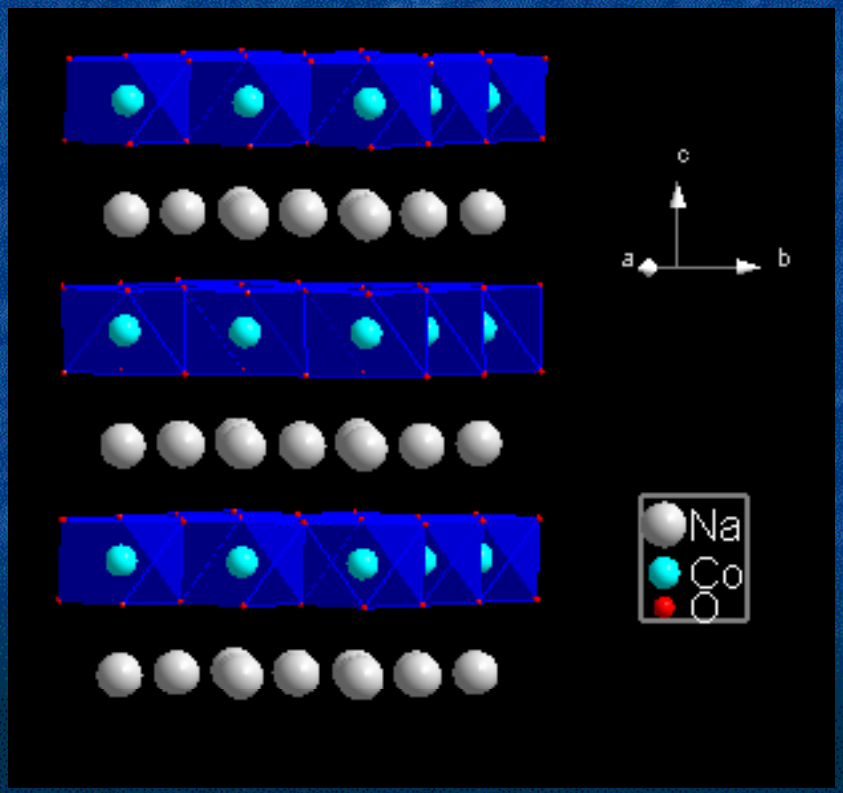
Minimizing Lattice Thermal Conductivities: Phonon Scattering Mechanism

- Void Fillers: “Rattlers”
- Mass and Strain Fluctuations - Atomic Disorder
- Interfaces: Superlattices
- Charge Carriers from Dopants
- Mixed-Valence Cations, Intermediate Valence
- Grain Boundaries, Defects, Dislocations
- Heavy Large Atoms (Bi, Pb, Te etc.)
- Complex Crystal Structure

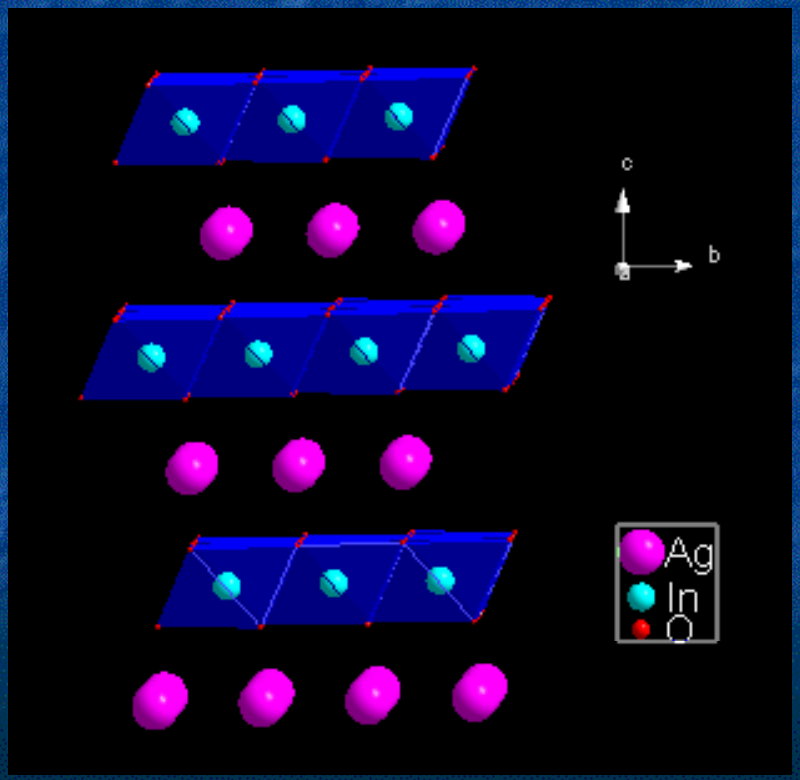
High efficiency TE material is an “electron metal – phonon glass”

Layered Crystal Structure

Best *p*-type oxide thermoelectric:
$NaCo_2O_4$
ZT ~ 0.78 at 780ºC



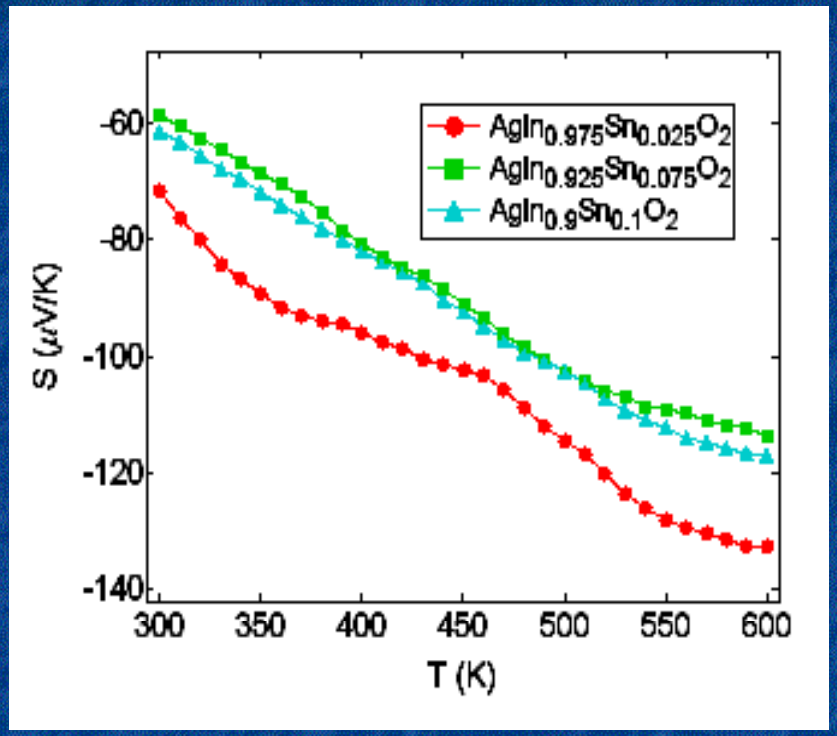
Delafossite structure
$AgInO_2$
Similar layered structure
- Good TE properties?

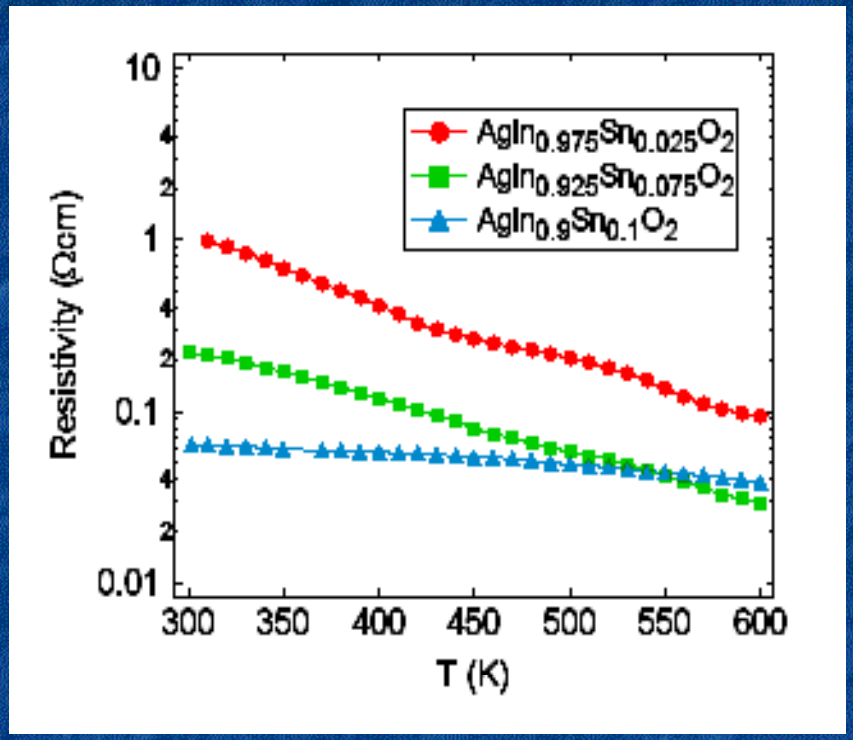


Synthesis of $AgIn_{1-x}Sn_xO_2$ ($0 \leq x \leq 0.1$)

- $NaIn_{1-x}Sn_xO_2$ ($0 \leq x \leq 0.1$) compounds were synthesized by solid state reaction.
- Cation exchange reactions were carried out by mixing $NaIn_{1-x}Sn_xO_2$, $AgNO_3$, and KNO_3 in 1:10:6 molar ratio, and heated at 300ºC for 96 hours.
- The resulted melts were washed, dried, and pressed into pellets. The pellets were heated for 12 hours at 350ºC in air, and used for characterization.

$AgIn_{1-x}Sn_xO_2$ ($0 \leq x \leq 0.1$)

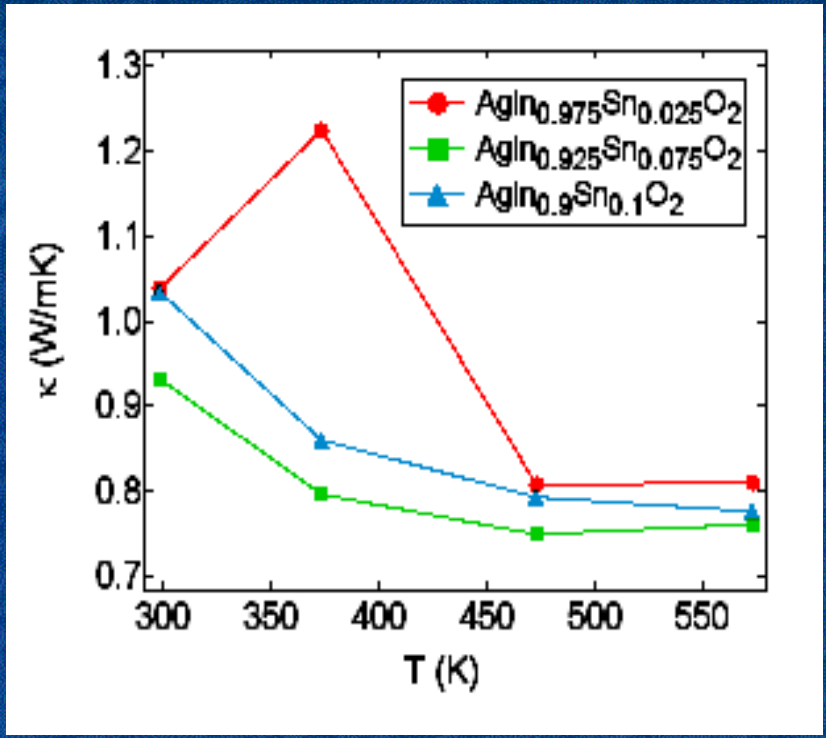


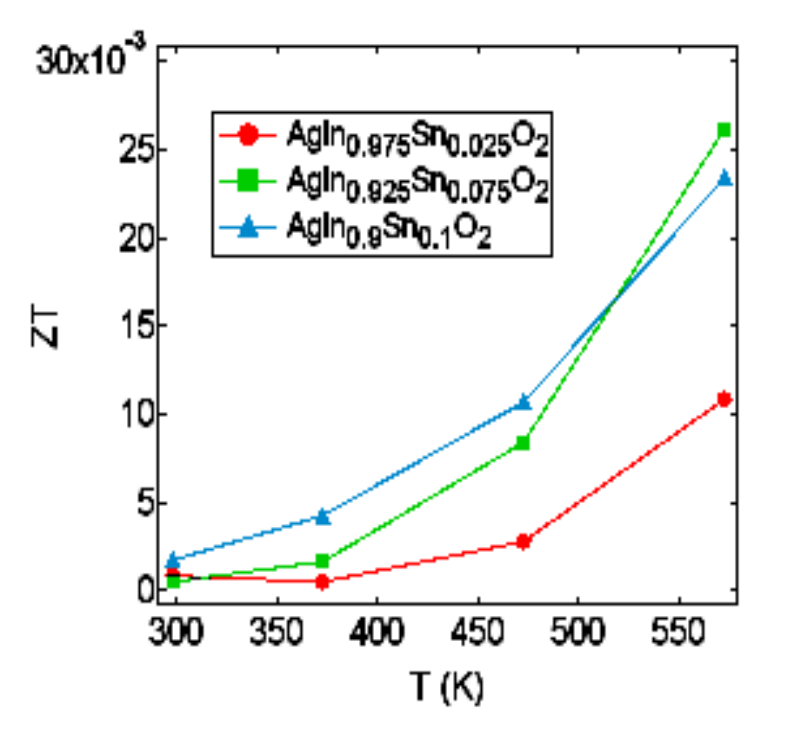


The large negative Seebeck coefficients indicate *n*-type conduction in these samples. The absolute values of Seebeck coefficients increase with increasing temperature.

Doping Sn in $AgInO_2$ lowers the electrical resistivity dramatically, by almost five orders of magnitude than that of nondoped $AgInO_2$.

$AgIn_{1-x}Sn_xO_2$ ($0 \leq x \leq 0.1$)





The thermal conductivity is relatively low at high temperatures (Less than that of Bi_2Te_3 ~ 1 W/mK).

The highest ZT achieved in this system at 573 K is ~ 0.025.

Oxide Summary

Compound	S (μV/K)	ρ (Ωcm)	κ (W/Km)	ZT @ 300°C	ZT_{Max}
(Zn,Al)O	-145	0.0018	18	0.04	0.3 @ 1000°C
$AgIn_{0.925}Sn_{0.075}O_2$	-118	0.0357	0.76	0.026	?

This system has comparable ZT values at 300°C to the best *n*-type oxide TE materials up to date, i.e., Zn1-xAlxO.

- Doping Sn in AgInO2 enhances the electrical conductivity dramatically.
- The large negative Seebeck coefficients indicates *n*-type conduction.
- The thermal conductivity is relatively low (< 1 W/mK).

Thermoelectric Issues

Seebeck Coefficient -- Thermal Conductivity -- Resistivity

- **Bi_2Te_3 - Sb_2Te_3** Solid Solutions
- **Lead Telluride** and its Alloys (Sn)
- **TAGS -** $(AgSbTe_2)_{1-x}(GeTe)_x$
- **Metal Disilicides-** (Fe, Mg, Mn, Cr, Re, Ru, Zr Hf… Sr,Na,Ca)
- **Semimetals** – Co(Ni)Si, $Mn_4Al_3Si_5$ (passive legs)
- **Silicon Germanium -** RTG
- **RE Compounds -** Chalcogenides, Pnictides, Oxides, Silicides
- High Pressure **Superconductors** - Copper Oxides
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- **Metals -** Pure, Alloys, Intermetallics, Kondo, Half-Heusler
- **Quasicrystals** – Al-Pd-Mn, Al-Cu-Tm
- **PGEC** – Skutterudites, Clathrates, Complex Pentatellurides
- **Low Dimensional -** Quantum Wells, Wires and Dots

Thermoelectric Needs

- **Materials:** Structure, Synthesis, Compatibility, Reproducibility, COP, ZT … *Costs*
- **Devices:** Engineering, Fabrication, Performance, Efficiency, Reliability, Heat Load …*Costs*
- **Systems:** Design, Competitive Pricing, Market Demand, Mass Production … *Costs*

"One of the milestones along the [discovery] pathway is when new blood shows up [for rejuvenation of thermoelectric research]. You're going to see a whole bunch of new faces with new ideas. They don't have to accept the old ZT as a limit." Hylan Lyon 1997

There was some discussion during the **ICT96** panel session about the prospects for thermoelectrics if break-throughs were made in ZT. I have also participated in workshops in Washington, D.C., where the discussion was, **"where should we set the goal for ZT: 3,4,7?" Set it high enough and the multi-million dollar R&D programs will go to the biggest liars!** According to a recent world survey of the world's best TE cooling module manufacturers, the **highest room-temperature ZT was 0.9**. If we aim too high, we could miss the target altogether and spend the next few decades trying to **establish credibility - AGAIN!**

Don't get me wrong, though. I am just as optimistic as any other thermoelectrician. I am excited (well, "cautiously excited") about the new possibilities that are emerging. Just remember, though, that it was not those who promised the most 30-40 years ago who got us to where we are. It was the hard work, dedication and commitment of companies like Melcor and Marlow who started when the entire industry had zero credibility and established a practical, economic and solid business base for the TE cooling industry from which we all now benefit.

Academic progress is nice, but we don't need more "museum pieces." **My optimism and expectations for thermoelectric break-through is one which has practical application, economic soundness and the elements needed for solid business success.**

Thermoelectric News Richard J. Buist, Editor

Kandace R. Kalnbach, Assistant Editor

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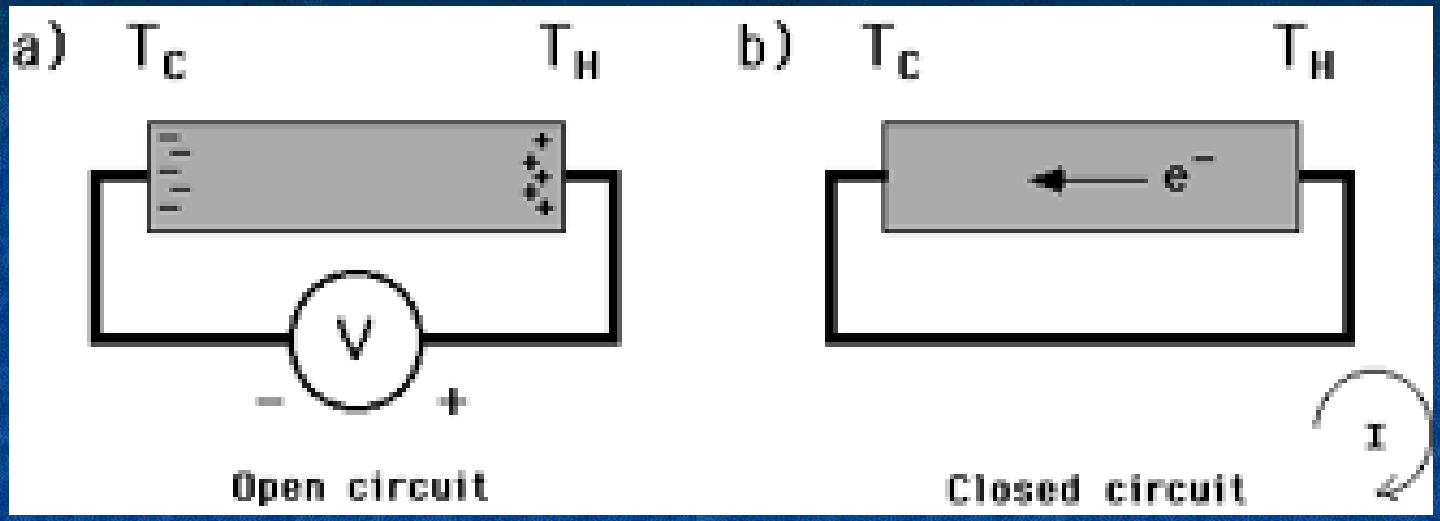
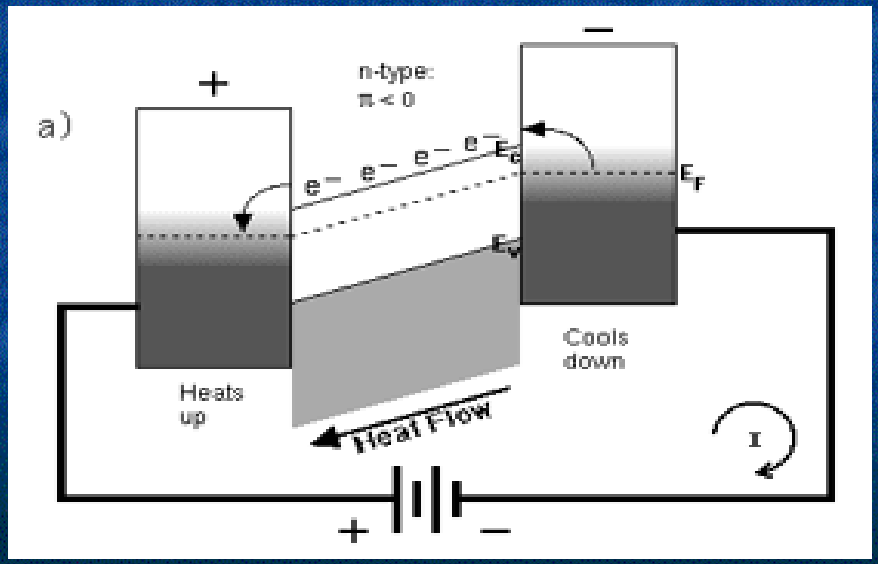
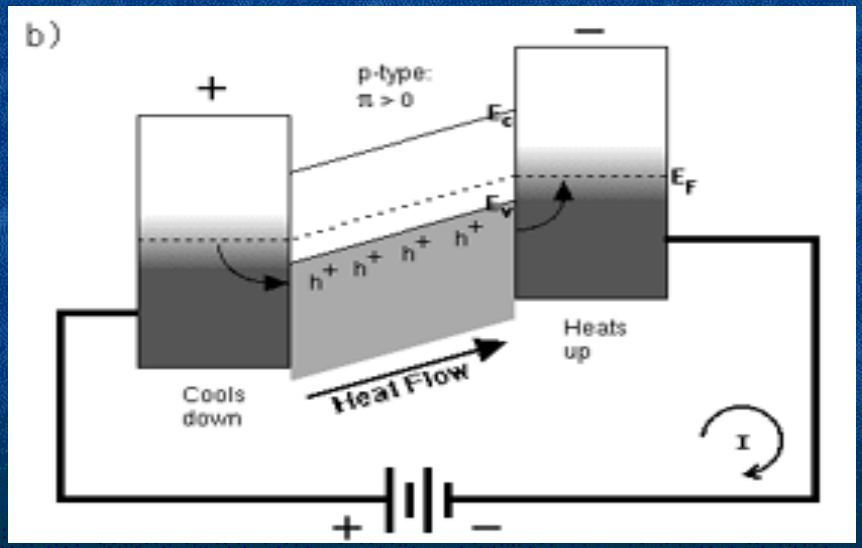
Seebeck Effect

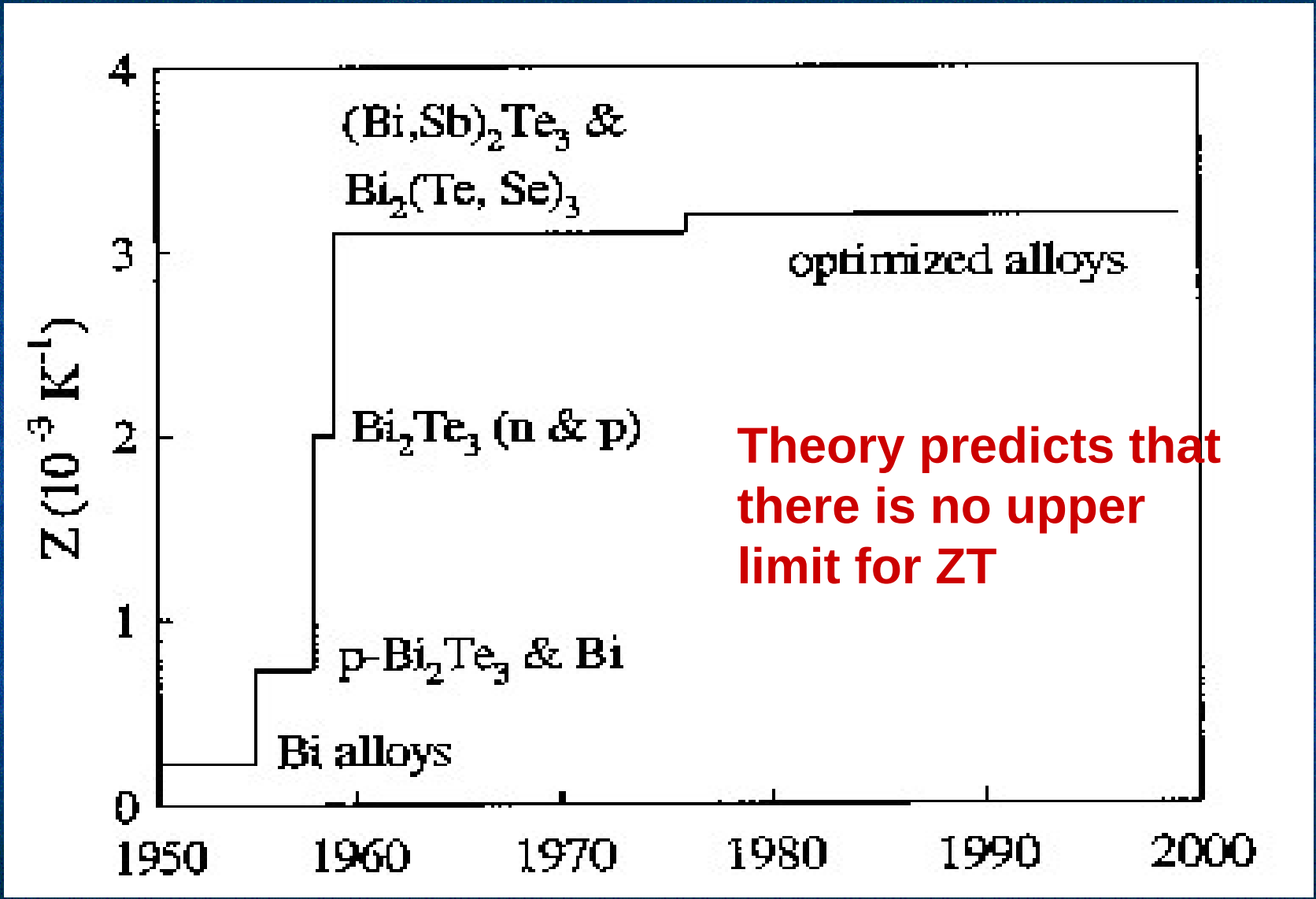






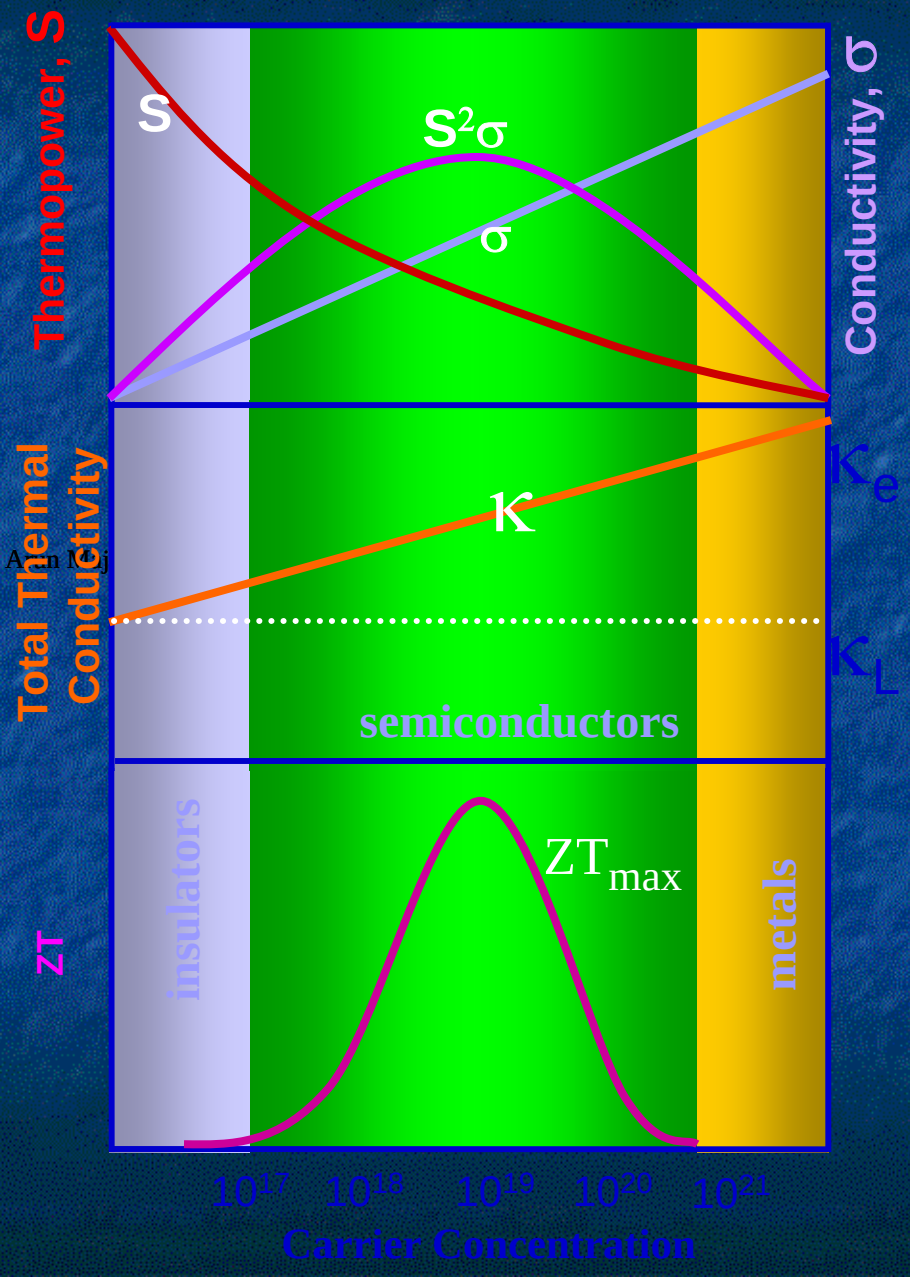
Peltier Effect

PROGRESS IN FIGURE OF MERIT AT ROOM TEMPERATURE



Theory predicts that there is no upper limit for ZT

Optimum Transport Coefficients for Thermoelectrics



$$ZT = \frac{S^2\sigma}{\kappa_{e+L}} T$$

Wiedemann-Franz "Law"

$\uparrow \sigma : \uparrow \kappa_e$

$\uparrow S : \downarrow \sigma \quad \uparrow ZT : \uparrow S\,\sigma \quad \downarrow \kappa$

Thin grain boundaries

- electron tunneling
- short range disorder
- phonon scatter at boundaries
- longer range order

By Arun Mj

Characterization

- The electrical resistivity was measured from 300 to 600 K by the four-probe technique.
- The Seebeck coefficient was measured using a commercial apparatus produced by MMR technology.
- Thermal conductivity was derived by:

  Conductivity = Diffusivity · Density · Specific heat. Thermal diffusivity obtained with a Holometrix Laser Flash Technology.