Solid Solutions Formation: Improving the Thermoelectric Properties of Skutterudites

A. Borshchevsky, 'J. Caillat, J.-P. Fleurial
Jet Propulsion Laboratory/California Institute of Technology
4800 Oak Grove Drive, MS ?'17-207, Pasadena, CA 91109

Materials with skutterudite structure have been know for a long time. Some of them are semiconductors. Typical skutterudite is $CoSb_3$ and its thermoelectric properties were partially studied in the 1 960's. Recently, it has been discovered that many skutterudite compounds are thermoelectrics with promising future. To make these materials more technically attractive for energy conversion purposes, their thermal conductivity should be decreased. Solid solutions formation is a well known way to reduce the thermal conductivity. Formation of solid solutions with skutterudite structure will be described. 11 will be shown that a substantial decrease of thermal conductivity can be achieved in some cases.

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- Skutterudite chemical compounds are known as attractive thermoelectric materials
- Room temperature thermal conductivity of skutterudites is ~10 $Wm^{-1}K^{-1}$ (80% lattice contribution)
- To achieve maximum ZT values the lattice thermal conductivity needs to be lowered
- Solid solution formation is a well known way to lower lattice thermal conductivity

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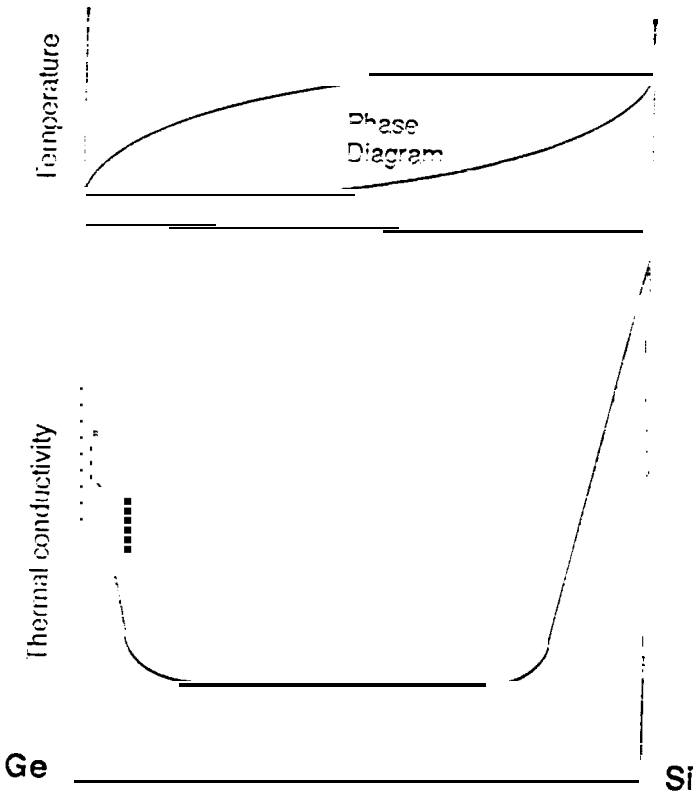
Si-Ge System



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Skutterudite Quasibinary Systems

- With full range of solid solutions:

  CoP_3-$CoAs_3$*

  $RhSb_3$-$IrSb_3$

  $IrSb_3$-$RuSb_2Te$

  $Fe_{0.5}Ni_{0.5}Sb_3$- $Ru_{0.5}Pd_{0.5}Sb_3$

- With partial range of solid solubility:

  $CoAs_3$- $CoSb_3$*

  $CoAs_3$- $IrAs_3$

  $CoSb_3$- $IrSb_3$

  $CoSb_3$- $Fe_{0.5}Ni_{0.5}Sb_3$

  $CoSb_3$- $FeSb_2Te$

  $IrAs_3$-$IrSb_3$

  $IrSb_3$- $Fe_{0.5}Ni_{0.5}Sb_3$

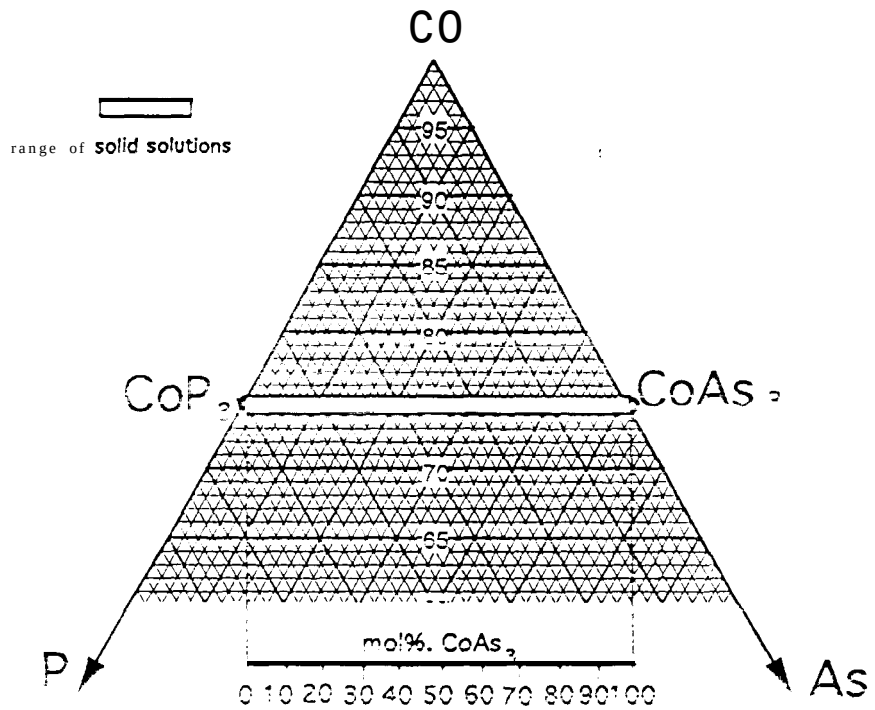
  $CoSb_3$- $Ru_{0.5}Pd_{0.5}Sb_3$

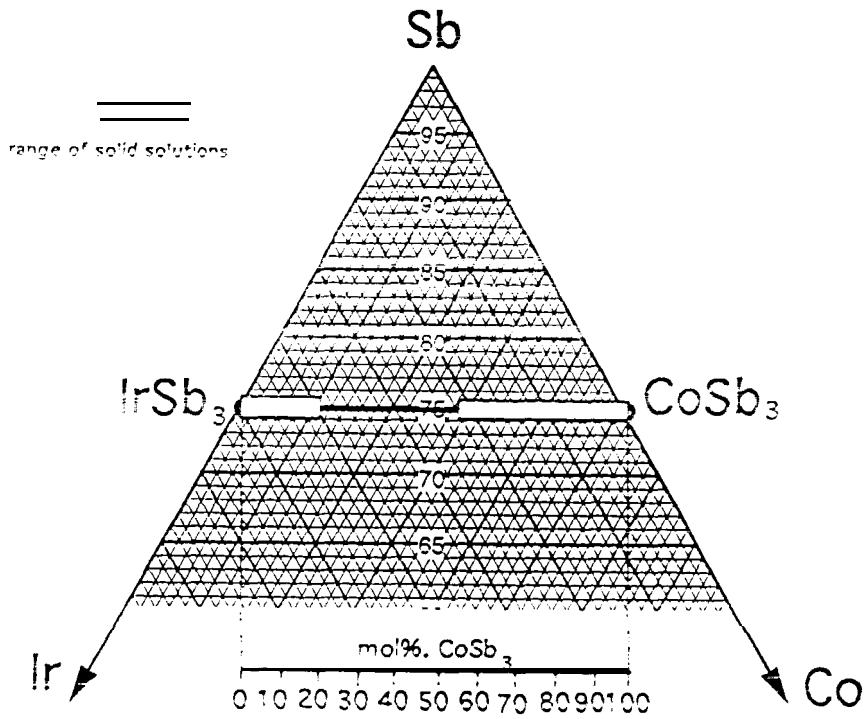
  $IrSb_3$- $Ru_{0.5}Pd_{0.5}Sb_3$

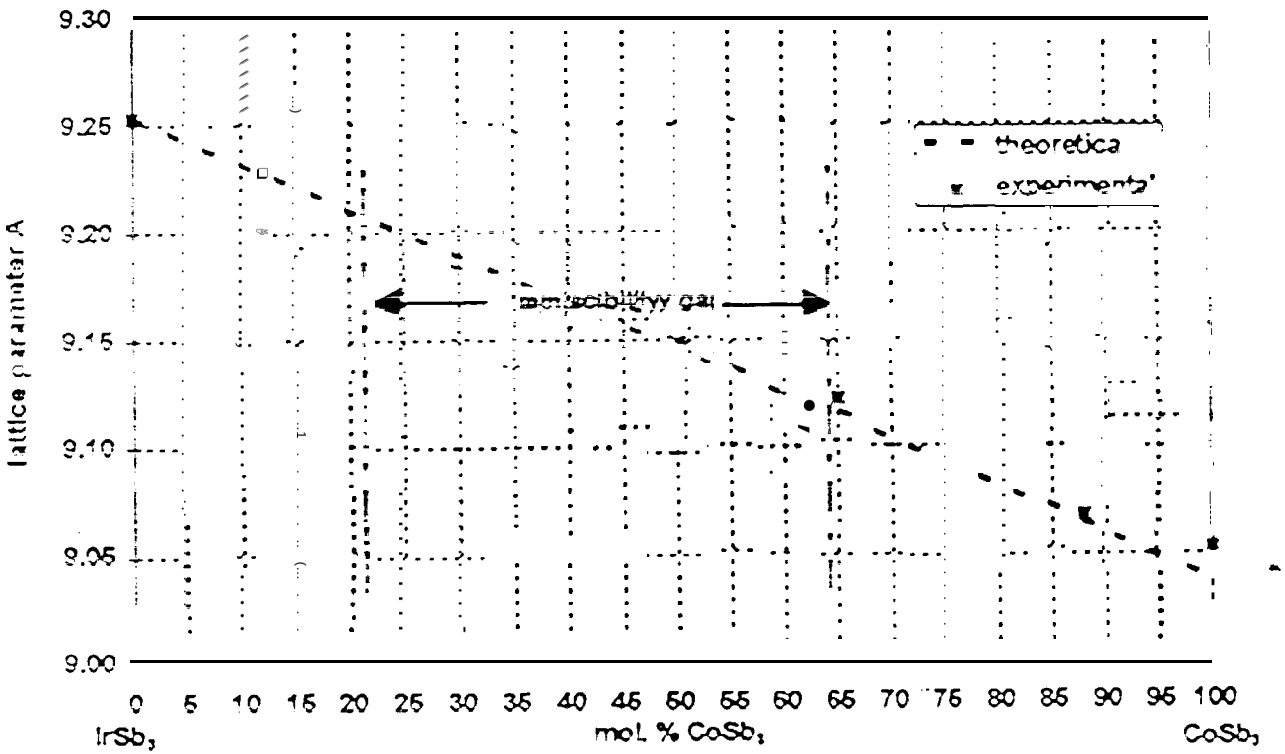
  $FeSb_2Te$- $RuSb_2Te$

  $IrSb_3$ -$RuSb_2Te$

*literature data


CO
range of solid solutions
95
90
85
80
CoP3
CoAs3
70
65
mol%. CoAs3
0 10 20 30 40 50 60 70 80 90 100
P
As


Sb
range of solid solutions
95
90
85
80
76
70
65
IrSb3
CoSb3
Ir
Co
mol%. CoSb3
0 10 20 30 40 50 60 70 80 90 100


9.30
9.25
9.20
9.15
9.10
9.05
9.00
lattice parameter A
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
IrSb3
mol. % CoSb3
CoSb3
theoretical
experimental
miscibility gap

Lattice thermal conductivity values for some skutterudite alloys

10^{-3} W $cm^{-1}K^{-1}$

Skutterudite Alloys	Alloy	1st member	2nd member
$(CoSb_3)_{0.96}$-$(IrSb_3)_{0.04}$	45	100	100
$(CoSb_3)_{0.90}$-$(IrSb_3)_{0.10}$	32	100	100
$(CoSb_3)_{0.88}$-$(IrSb_3)_{0.12}$	29	100	100
$(CoAs_3)_{0.98}$-$(CoSb_3)_{0.02}$	57	134-150	100
$(CoSb_3)_{0.90}$-$(IrAs_3)_{0.10}$	25	100	134-150
$(CoSb_3)_{0.9}$-$(FeSb_2Se)_{0.1}$	31	100	-
$(CoSb_3)_{0.79}$-$(Fe_{0.5}Ni_{0.5}Sb_3)_{0.21}$	35	100	~30
$(IrSb_3)_{0.90}$-$(RuSb_2Te)_{0.10}$	42	100	32
$(Ru_{0.5}Pd_{0.5}Sb_3)_{0.5}$-$(Fe_{0.5}Ni_{0.5}Sb_3)_{0.5}$	24	14	~30

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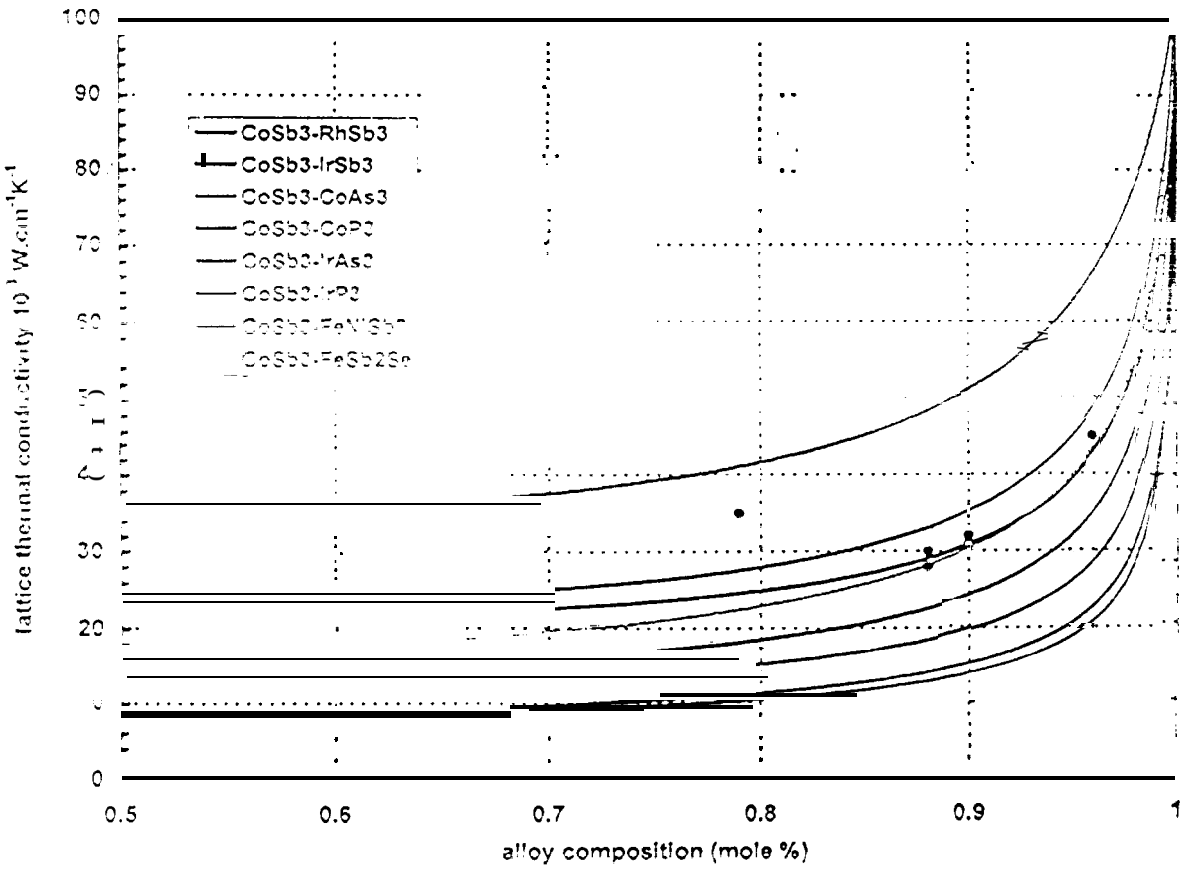
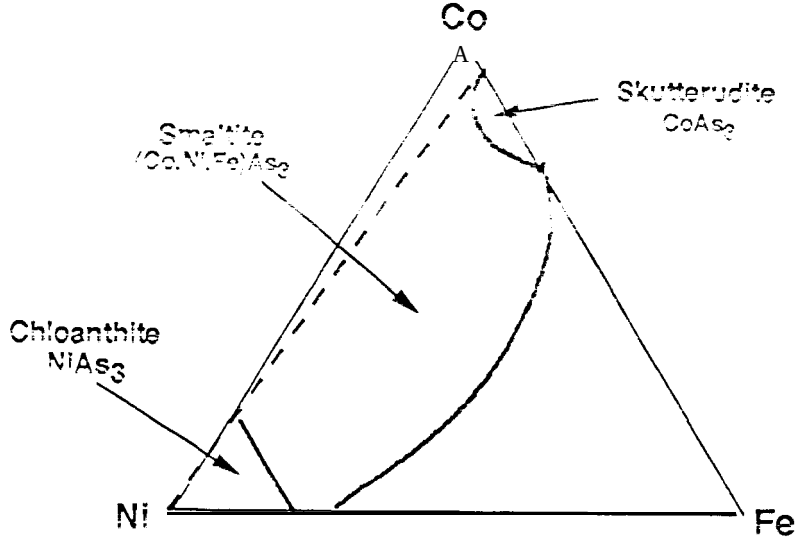
Effect of Alloy Scattering on the Room Temperature Thermal Conductivity of $CoSb_3$



Skutterudite Group **of Minerals**



All are solid solutions

(Compositions are idealized)

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Conclusions

- There exist many solid solutions in skutterudite family of compounds
- 3 quasibinary systems have been studied at JPL: 4 with full range of solubility and 9 with partial range of solubility
- Significant reduction in thermal conductivity of compounds has been achieved by solid solution formation
- Theoretical calculation of thermal conductivity for different systems of skutterudite solid solutions, at room temperature, has been performed and the lowest possible thermal conductivity value of about 8×10^{-3} $Wcm^{-1}K^{-1}$ was predicted for $CoSb_3$-IrP_3 system
- Much more solid solutions within skutterudite group of materials are available for their thermoelectric properties evaluation