Growth of Metal Silicides from Metal Flux Reactions

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I. Metal flux synthesis

II. Zintl phases and Thermoelectric materials

III. Metal silicides A/Mg/Si (A = Ca, Sr, Ba, Eu, Yb)

Metal Flux Synthesis

Metal flux synthesis: reaction where one low-melting metal reactant is present in large excess, acting as a solvent.

Common metal fluxes and products

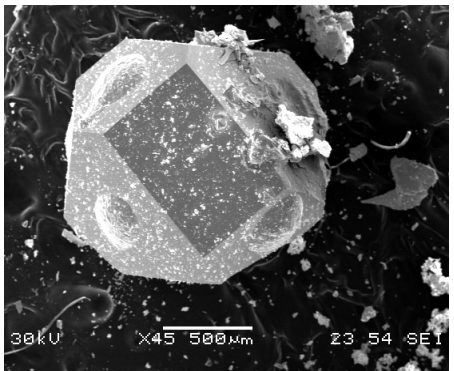
Tin flux: $PrCo_2P_2$, $BaFe_2As_2$, $Co_7Zn_3Sn_8$

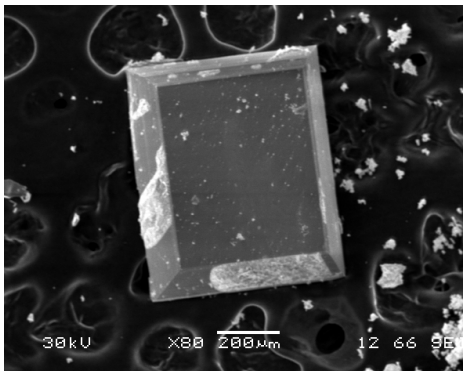
Aluminum flux: Co_4Al_{13}, $Y_2Al_3Si_2$, $CeNiAl_4Ge_2$, $U_8Al_{19}Si_6$

Gallium flux: $Mn_{123}Ga_{137}$, $Yb_3Ga_4Ge_6$, $Tb_{1.8}Si_8C_2B_{36}$

Flux synthesis advantages:

- Low temperatures--kinetic/metastable products
- Liquid state reaction--crystal growth
- Exploratory synthesis: allows reactants to find product with local energy minimum structure



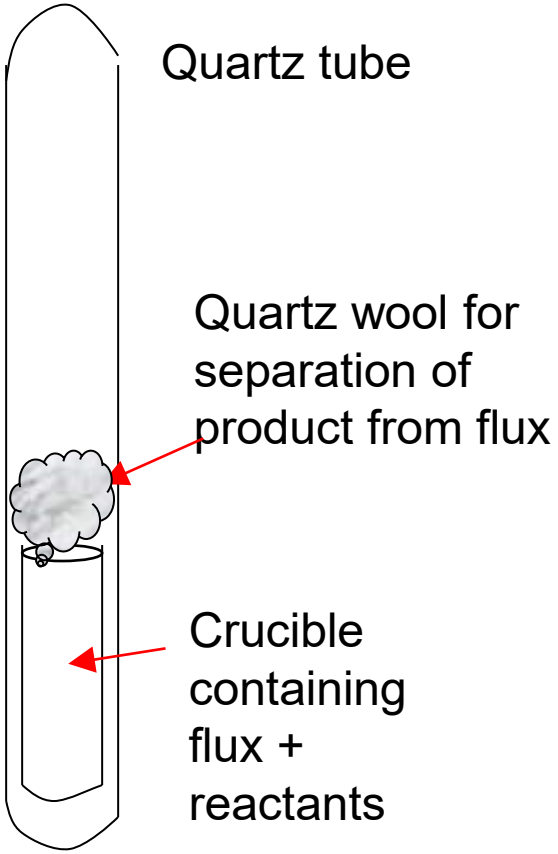


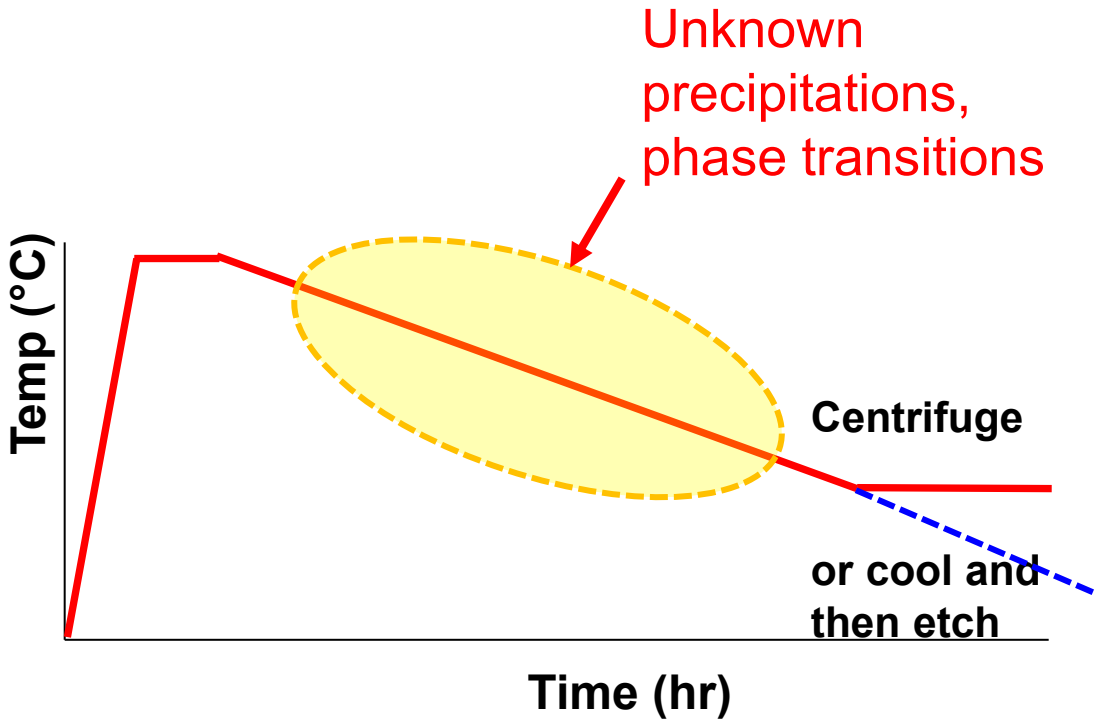
Metal Flux Synthesis

Combine reactants, add excess amount of suitable flux metal

Heat above mp of flux, slowly cool

Centrifuge while flux still molten





Characterization of product compounds

What's in it?

Elemental analysis to determine what elements were incorporated

SEM-EDS

What is the structure?

Single crystal XRD to determine positioning of elements

What other products were formed?

Powder XRD to determine purity, yield

What are its properties?

Band structure calculations to explore electronic structure

Magnetic susceptibility

Thermoelectric/transport measurements

Intermetallics and Zintl Phases

Intermetallic compounds: Compounds comprised of two or more metals or metalloids

Zintl phases: Subclass of Intermetallics. Compounds comprised of electropositive metal (Group 1, Group 2, some RE) and metalloid

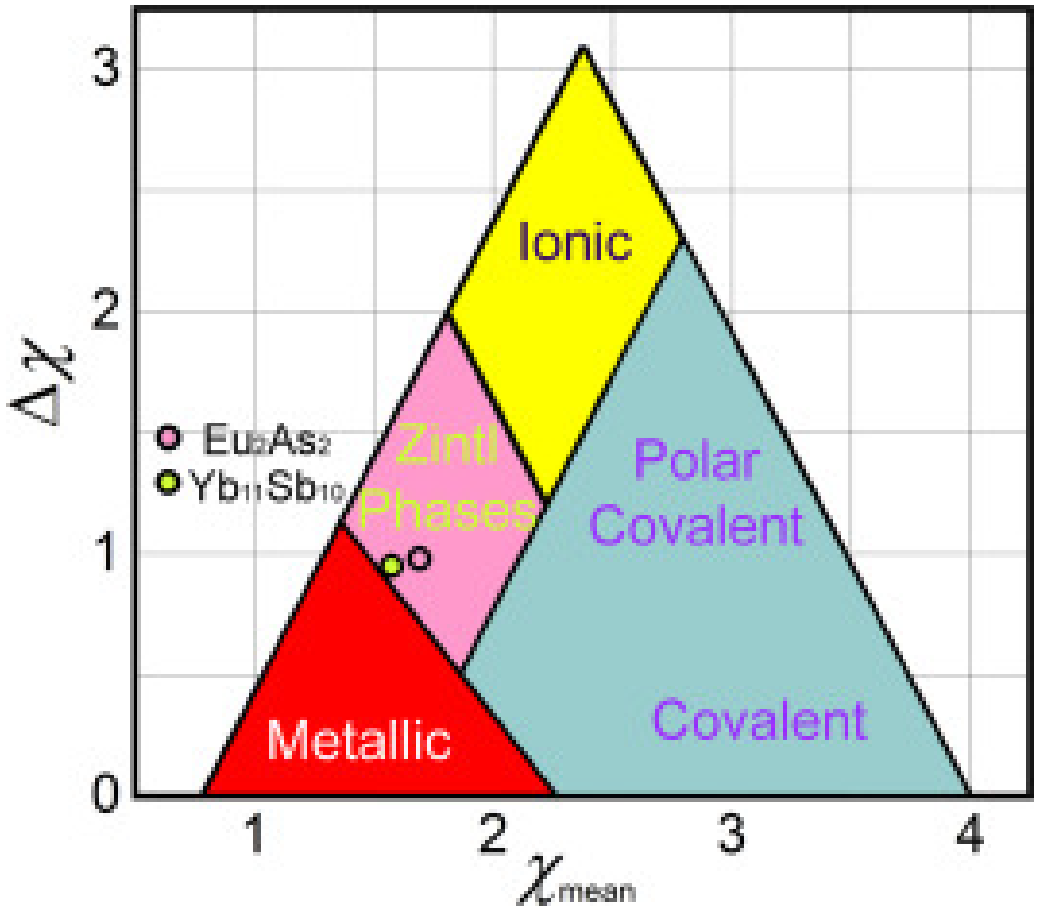
Charge transfer between electropositive metal and electronegative metalloids leads to metal cations and metalloid anions that are charge-balanced. Causes semi-metallic or semiconducting behavior

Often have complex structures

Metal + metal	metal + metalloid	metal + nonmetal
Alloys	Zintl phases	Ionic salts
Cu_xNi_{1-x}	Mg_2Si, Na_4Sn_9	MgO, NaCl
Metallic	semimetal/semiconductor	insulator

Classifying compounds based on differences in electronegativity χ

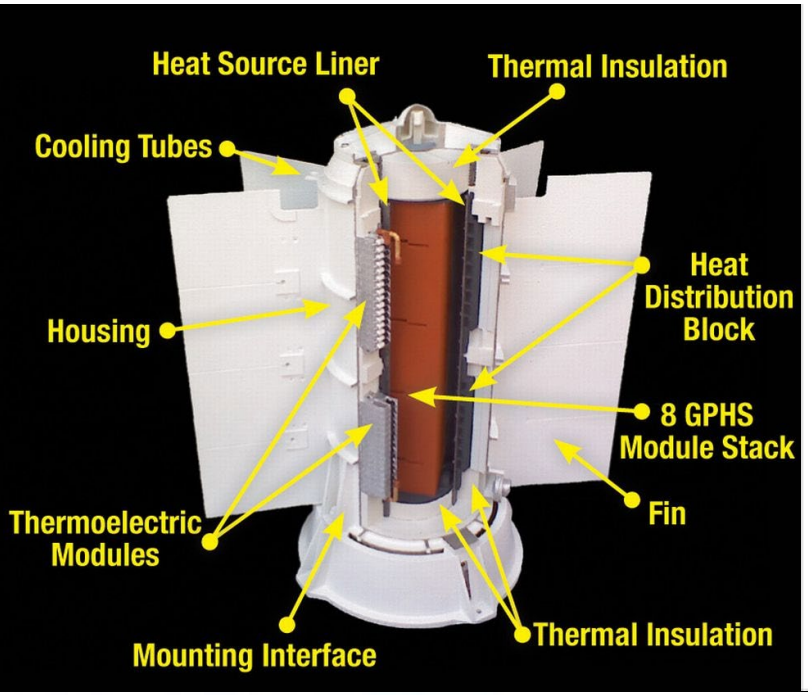
Electronegativity χ = 1 – 2 for metals χ = 2.5 – 4 for nonmetals

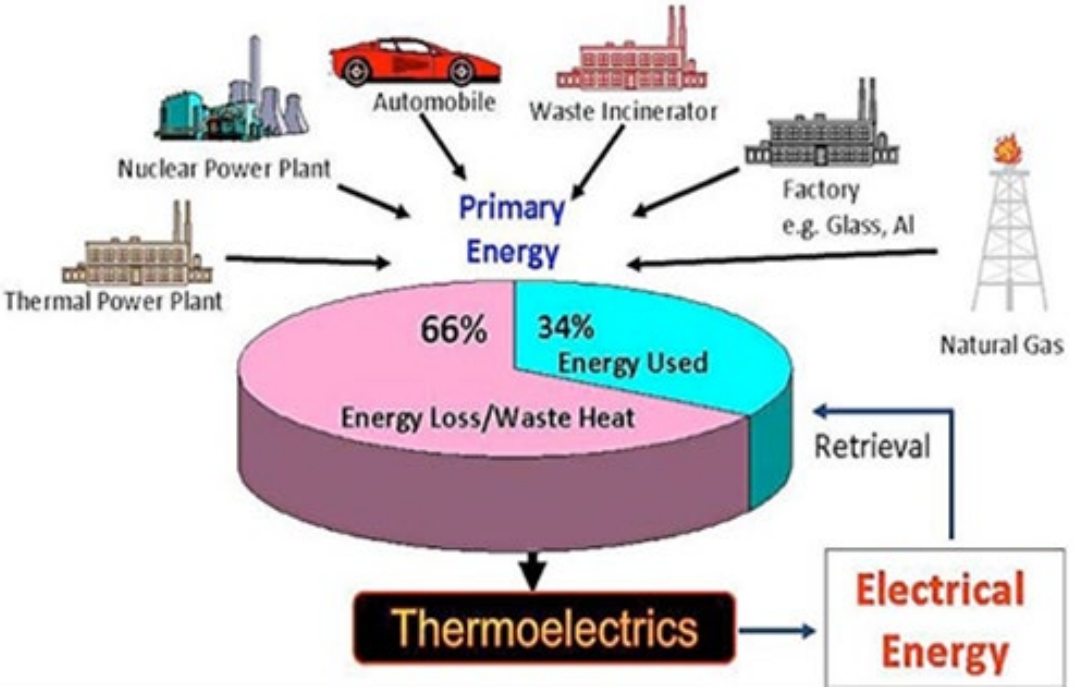


Thermoelectric materials

Generate a voltage when a temperature gradient is applied

Used as: power sources (makes use of waste heat)





Thermoelectric materials

To maintain thermal gradient while producing a voltage, compound must have:

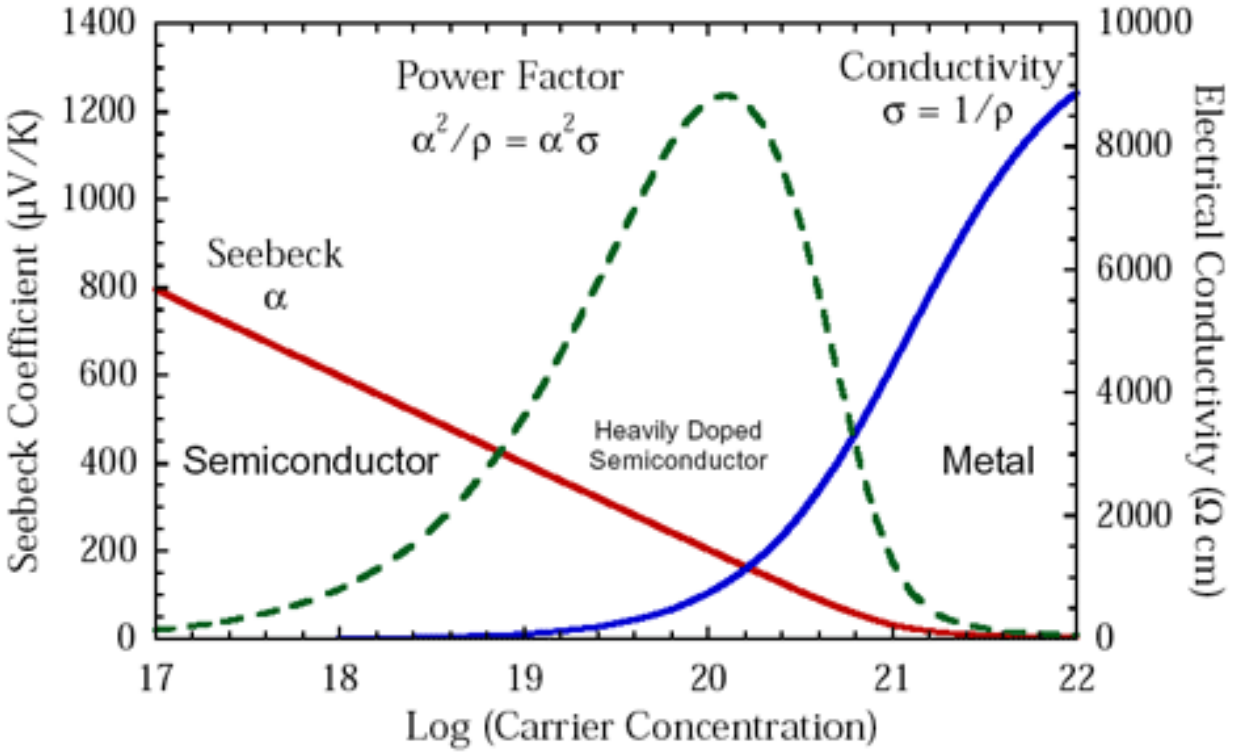
- Low thermal conductivity κ
- High electrical conductivity σ (low electrical resistivity ρ)
- High Seebeck coefficient S (voltage / ΔT)

Thermoelectric figure of merit:

$$zT = \frac{S^2}{\rho\kappa}T$$

Thermoelectric materials

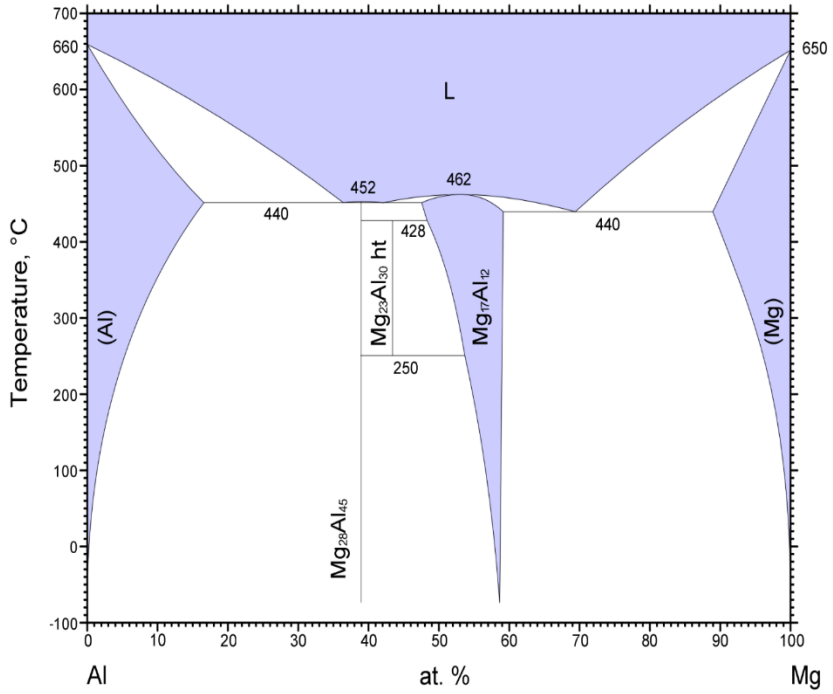
Problem: ρ and S are interrelated!

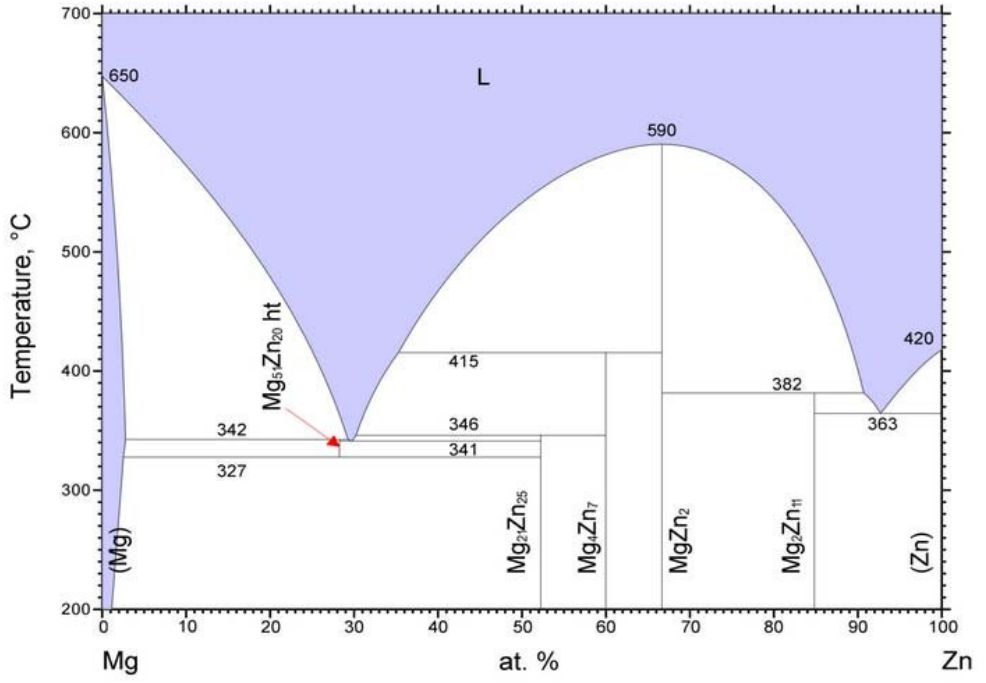


Best balance: Doped semiconductors/semimetals: Bi_2Te_3, $Yb_{14}MnSb_{11}$, PbTe. Or…Zintl phases!

κ is relatively independent, make as low as possible (heavy elements, complex structure, disorder)

Magnesium-based fluxes: Mg/Al or Mg/Zn





Adding Al or Zn lowers Mg m.p. Using 22 mmol Mg, 8 mmol of Zn or Al.

Silicon reacts with divalent metals (A = Ca, Sr, Ba, Eu, Yb) in Mg-rich melt

- Large family of new A/A'/Mg/Si compounds
- Charge-balanced Zintl phases
- Al or Zn not incorporated into products

Ternary A/Mg/Si products

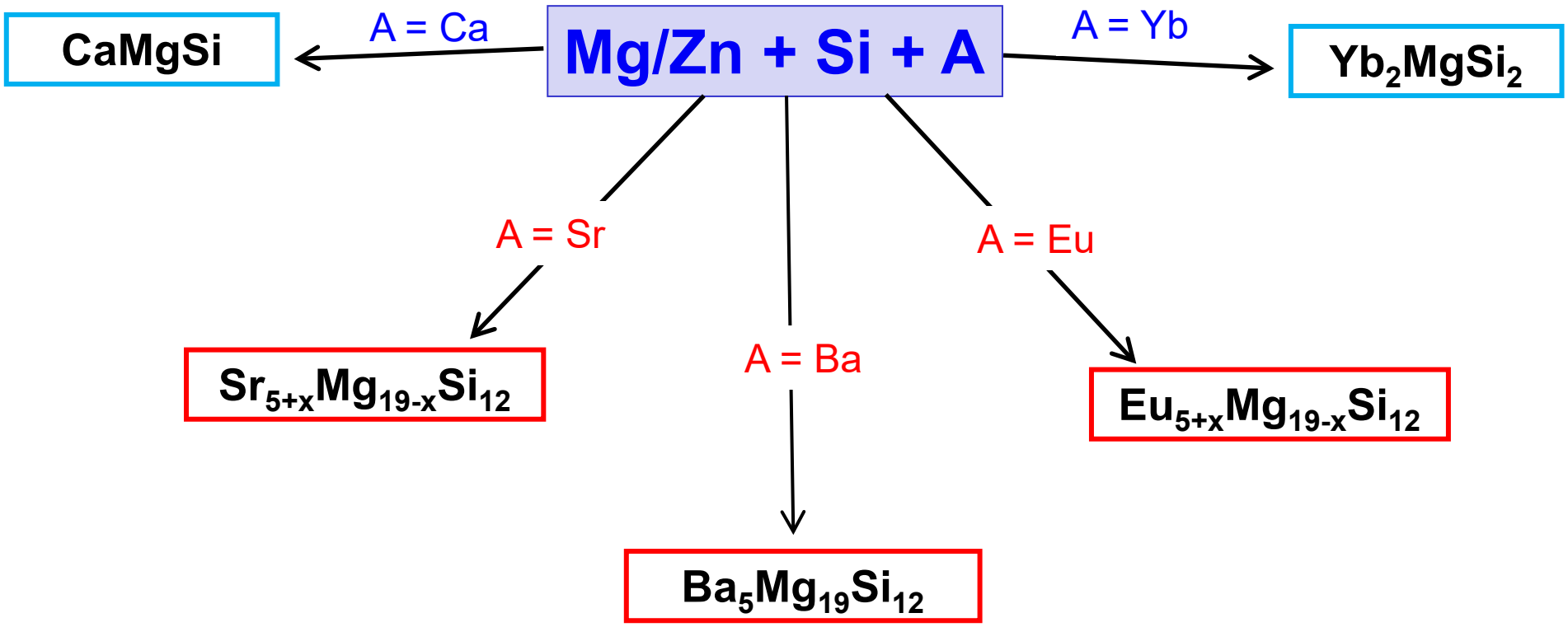
What determines structure and composition of product?

- Ionic radii of A^{2+} cations
- Reactant ratio
- Heating profile/cooling rate

Cation	Radius (Å)
Mg^{2+}	0.86
Ca^{2+}	1.14
Sr^{2+}	1.32
Ba^{2+}	1.49
Eu^{2+}	1.31
Yb^{2+}	1.16

Possible complication with Eu and Yb: They can be trivalent
Yb^{3+} radius: 1.01 Å
Eu^{3+} radius: 1.09 Å

Ternary A/Mg/Si products



Smaller A cations: give orthorhombic TiNiSi – type product (CaMgSi) or tetragonal U_3Si_2 – type product (Yb_2MgSi_2)

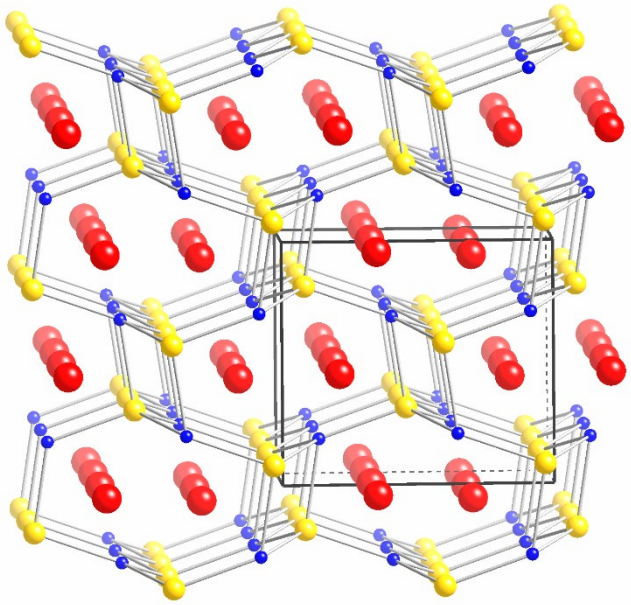
Larger A cations: give hexagonal $Ho_5Ni_{19}P_{12}$ – type products

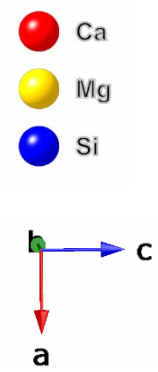
CaMgSi

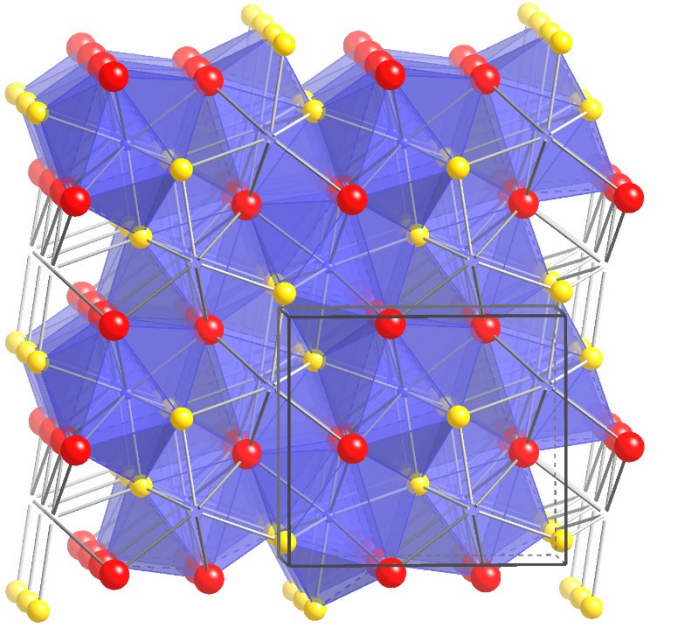
TiNiSi type
Orthorhombic
Space group *Pnma*
a = 7.4690(2)Å
b = 4.4255(1)Å
c = 8.3113(2)Å

$(Ca^{2+})(Mg^{2+})(Si^{4-})$
Zintl phase, semimetal

Si anions surrounded by 9 cations
$Si@(Ca/Mg)_9$ shown in polyhedral mode







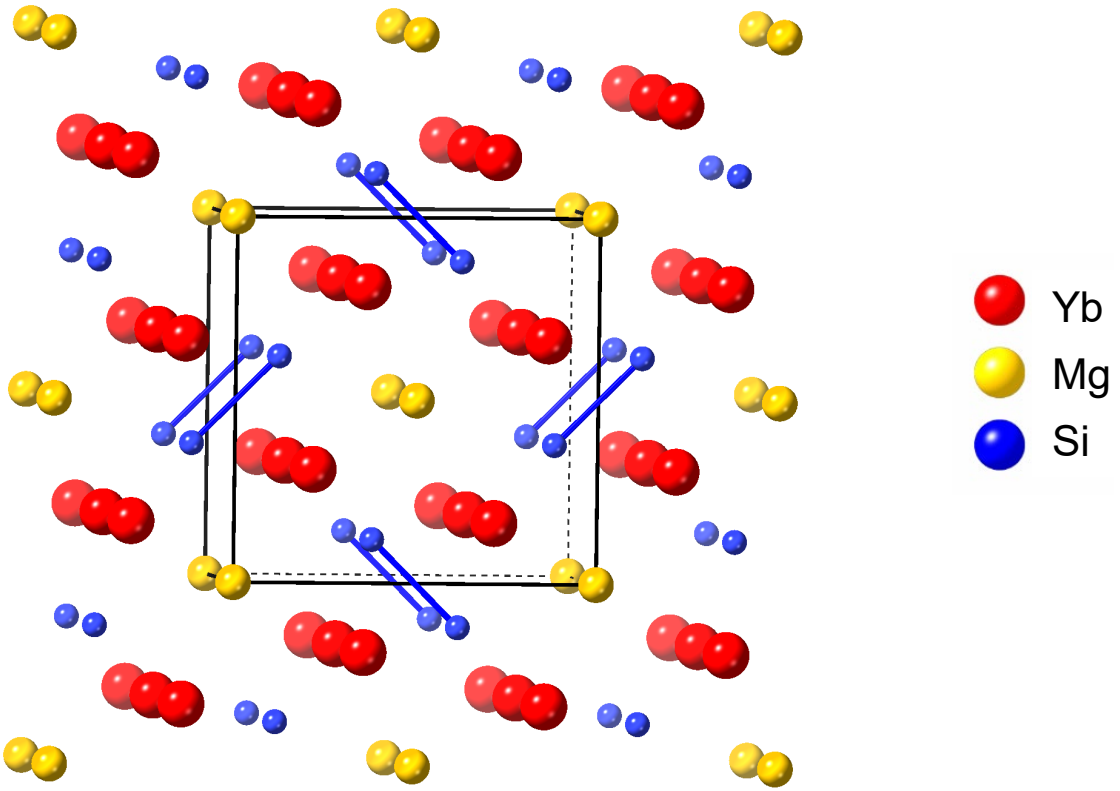
Yb_2MgSi_2

Mo_2FeB_2 type
Tetragonal
Space group *P4/mbm*
a = 7.0495(1)Å
c = 4.1313(1)Å

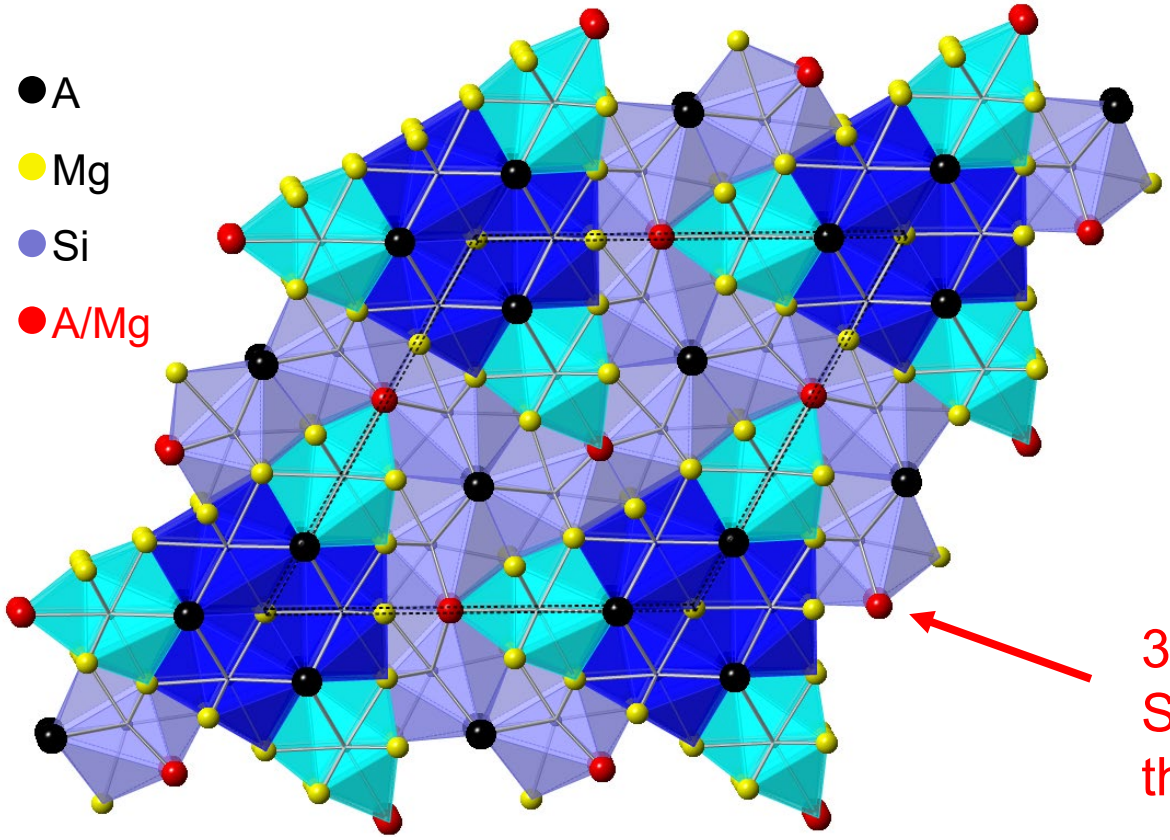
Contains Si-Si unit, formally $[Si_2^{6-}]$

Zintl phase:
$(Yb^{2+})_2(Mg^{2+})[Si_2^{6-}]$

…if the Yb is +2!
Reports indicate it is Yb^{3+}



$A_{5+x}Mg_{19-x}Si_{12}$ (A = Sr, Ba, Eu)



$Ho_5Ni_{19}P_{12}$ type

A in the Ho sites,

Mg in the Ni sites,

Si in the P sites

Hexagonal, *P*-62*m*

3f mixed site:
Smaller A^{2+} can mix on this Mg site (Ba^{2+} can't fit)

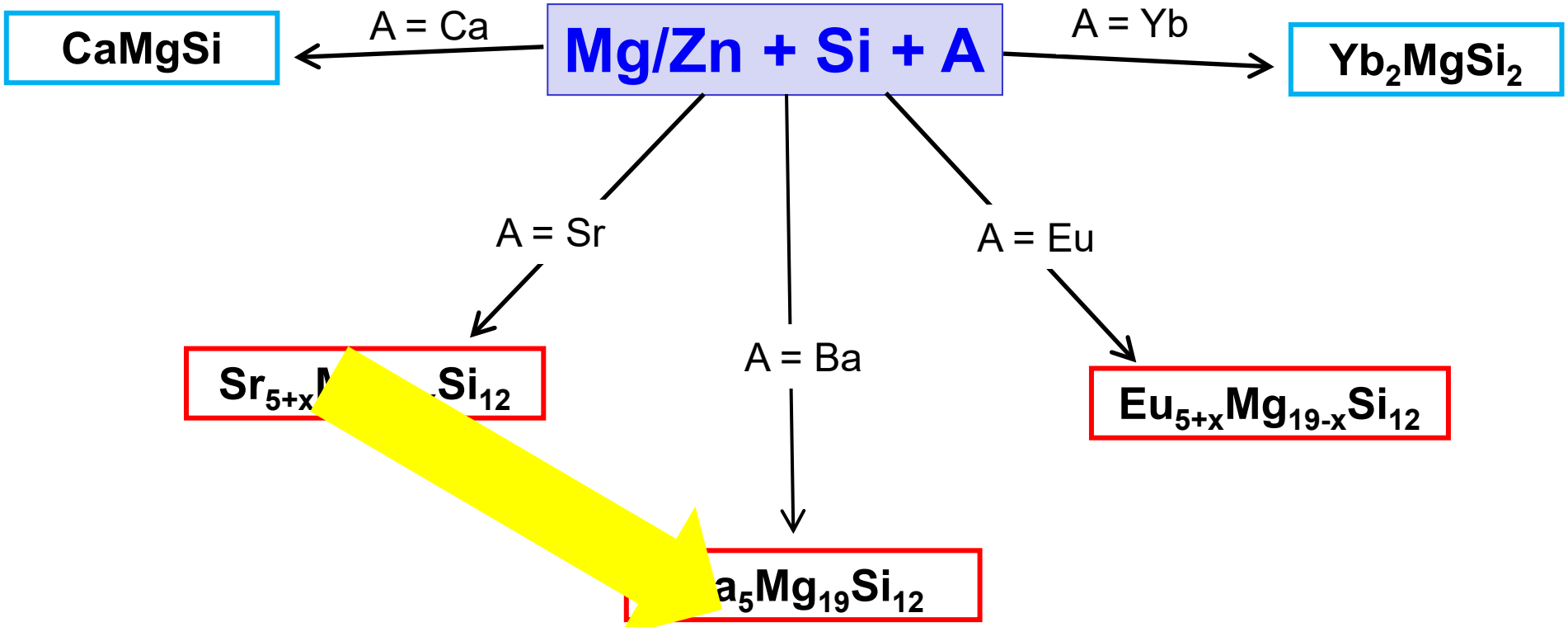
compound	Cell parameters (Å)
$Ba_5Mg_{19}Si_{12}$	a = 14.6392, c = 4.4775
$Sr_{7.82}Mg_{16.18}Si_{12}$	a = 14.8076, c = 4.4720
$Eu_8Mg_{16}Si_{12}$	a = 14.882, c = 4.4863

Charge-balanced:

$(A^{2+}/Mg^{2+})_{24}(Si^{4-})_{12}$

A/A'/Mg/Si semi-metallic silicides

What happens if you use more than one A element?

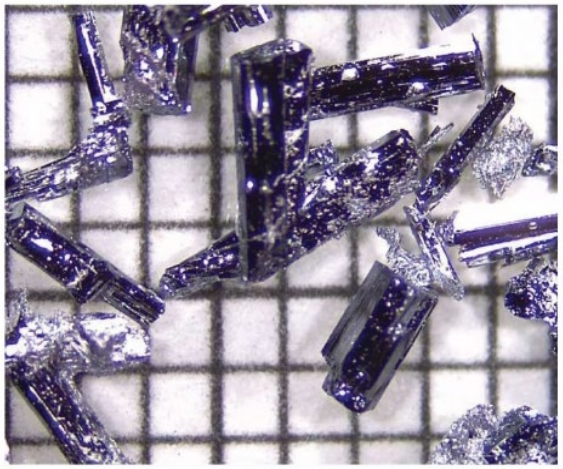


$A_{5+x}Mg_{19-x}Si_{12}$ (A = Sr, Ba)

Different amounts of Ba + Sr reacted with 3 mmol Si in Mg/Zn flux (22:8 mmol)

All products have $Ho_5Ni_{19}P_{12}$ structure type

Ba goes on Ho sites only
Sr goes on Ho sites and mixes on one Ni site



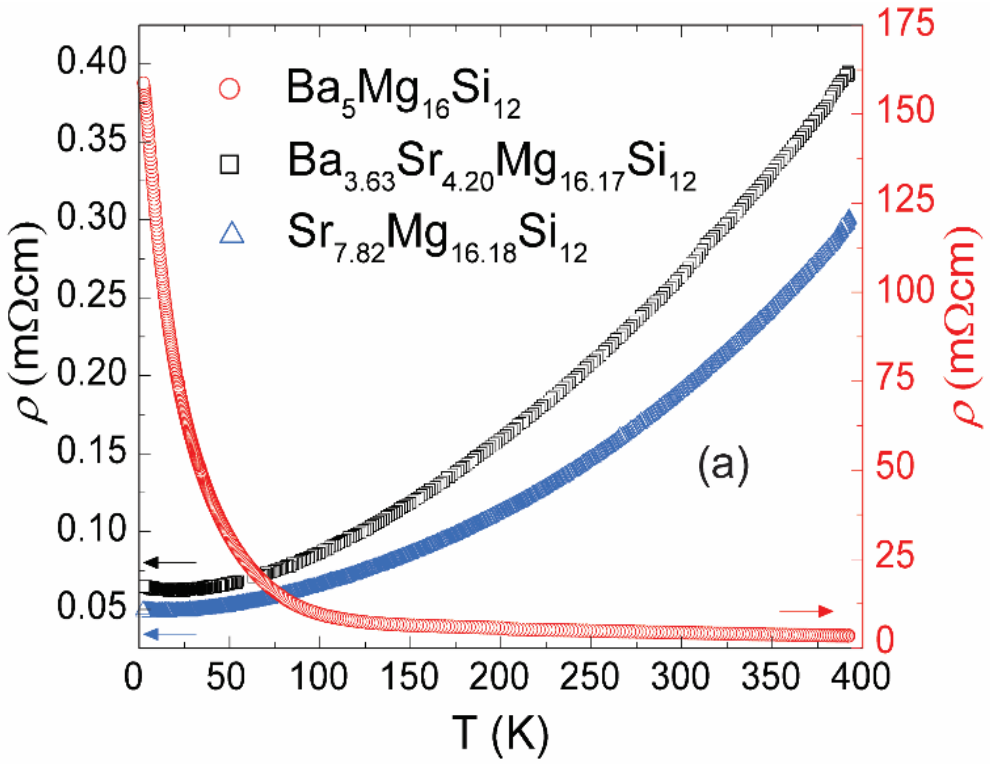
Ba mmol	Sr mmol	Product	*a* (Å)	*c* (Å)	Volume (Å^3)
3	0	$Ba_5Mg_{19}Si_{12}$	14.6392(2)	4.47754(9)	831.00(3)
2.25	0.75	$Ba_{4.86}Sr_{2.94}Mg_{16.20}Si_{12}$	14.9113(3)	4.5507(1)	876.27(4)
1.5	1.5	$Ba_{3.63}Sr_{4.20}Mg_{16.17}Si_{12}$	14.9063(2)	4.5382(1)	873.28(3)
0.75	2.25	$Ba_{1.93}Sr_{5.99}Mg_{16.08}Si_{12}$	14.8730(4)	4.5082(2)	863.64(6)
0	3	$Sr_{7.82}Mg_{16.18}Si_{12}$	14.8076(4)	4.4720(1)	849.18(5)

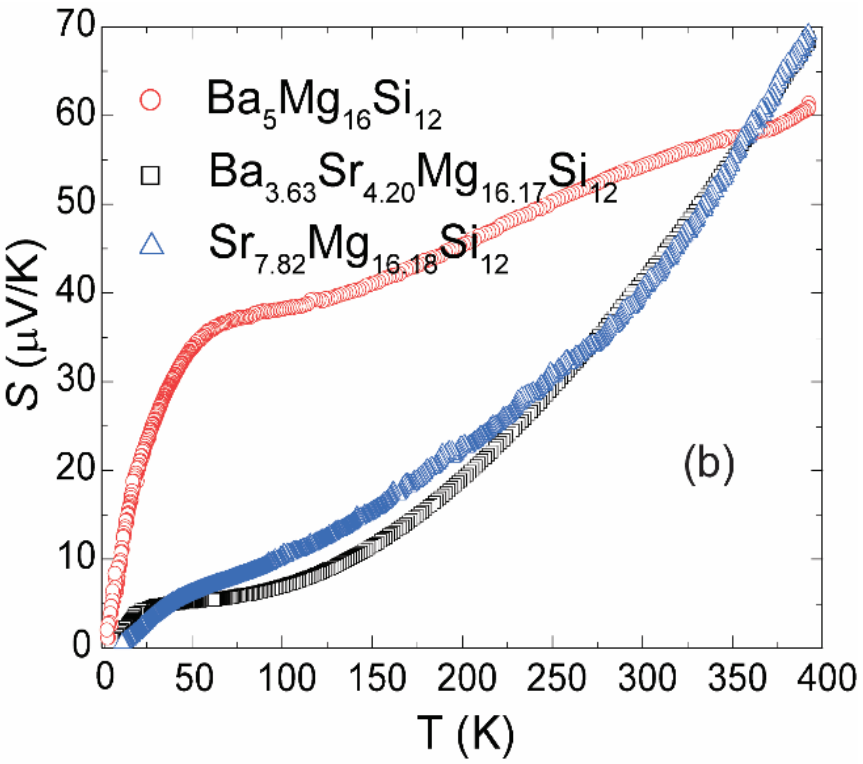
Zarei, A.; Uddin, M.S.; Baumback, R.; Wei, K.; Latturner, S.E.; *Inorg. Chem.*, **2024**, *submitted.*

$(Ba/Sr)_{5+x}Mg_{19-x}Si_{12}$ Electronic Properties

$Ba_5Mg_{19}Si_{12}$ (well ordered, no site mixing) is semiconducting with E_g = 0.02 eV.

$Sr_{7.82}Mg_{16.18}Si_{12}$ and $Ba_{3.6}Sr_{4.2}Mg_{16.2}Si_{12}$ are metallic



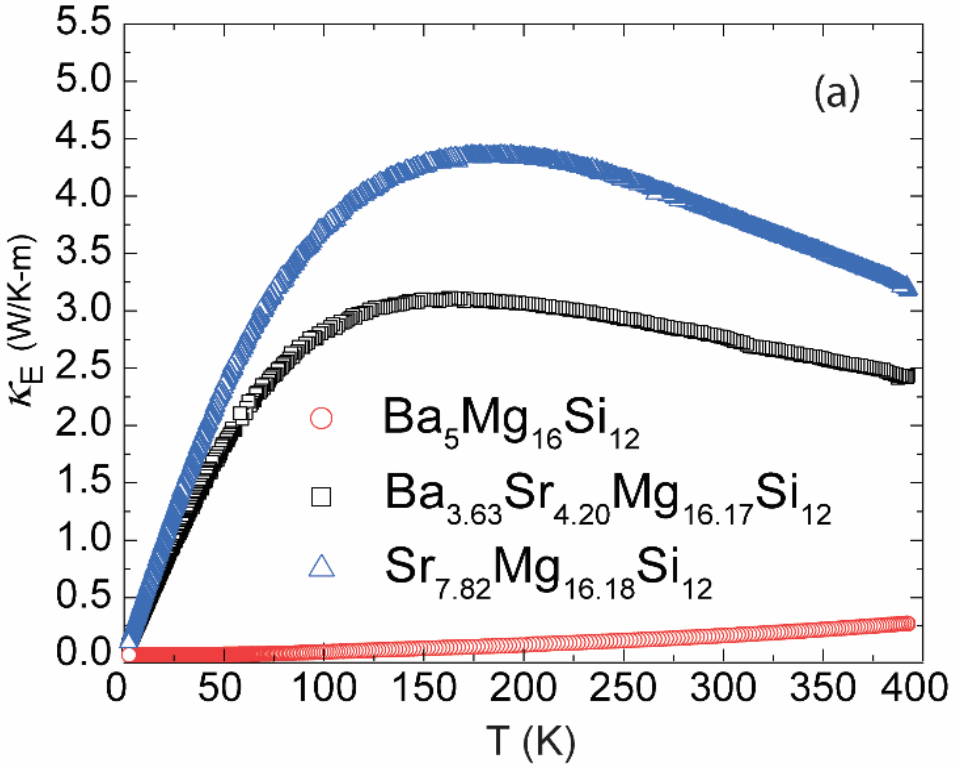


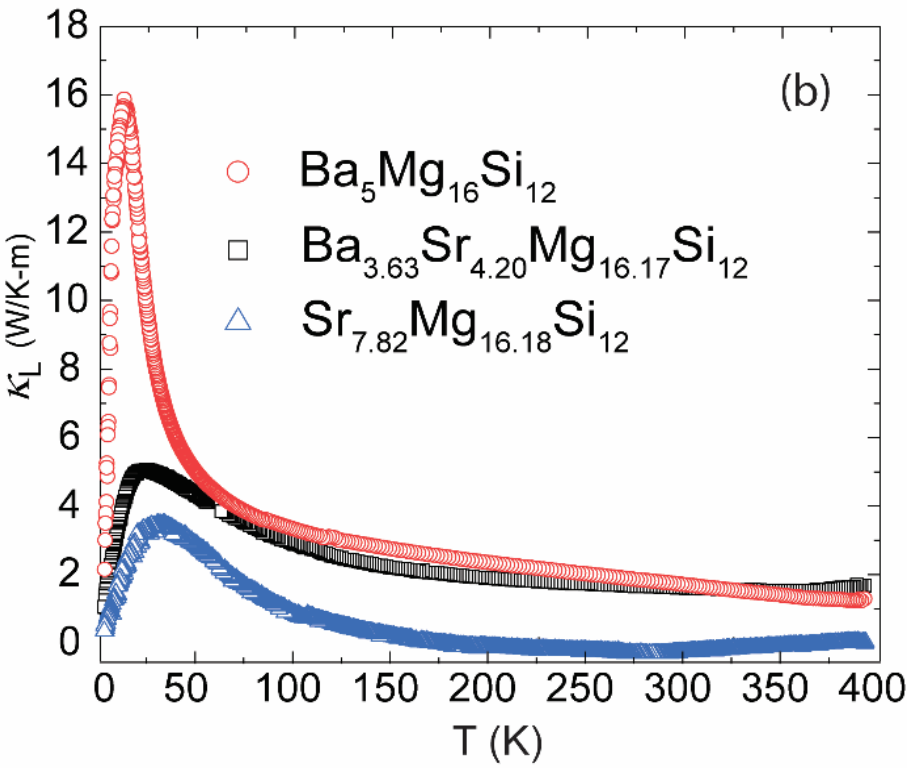
$(Ba/Sr)_{5+x}Mg_{19-x}Si_{12}$ Thermal Conductivity

Thermal conductivity is sum of electron contribution and lattice contribution $\kappa_{tot} = \kappa_{elec} + \kappa_{latt}$

κ_{elec} directly proportional to conductivity; can be calculated; subtracted from κ_{tot} to get lattice contribution

More disorder and rattling atoms → lower κ_{latt}





$(Ba/Sr)_{5+x}Mg_{19-x}Si_{12}$

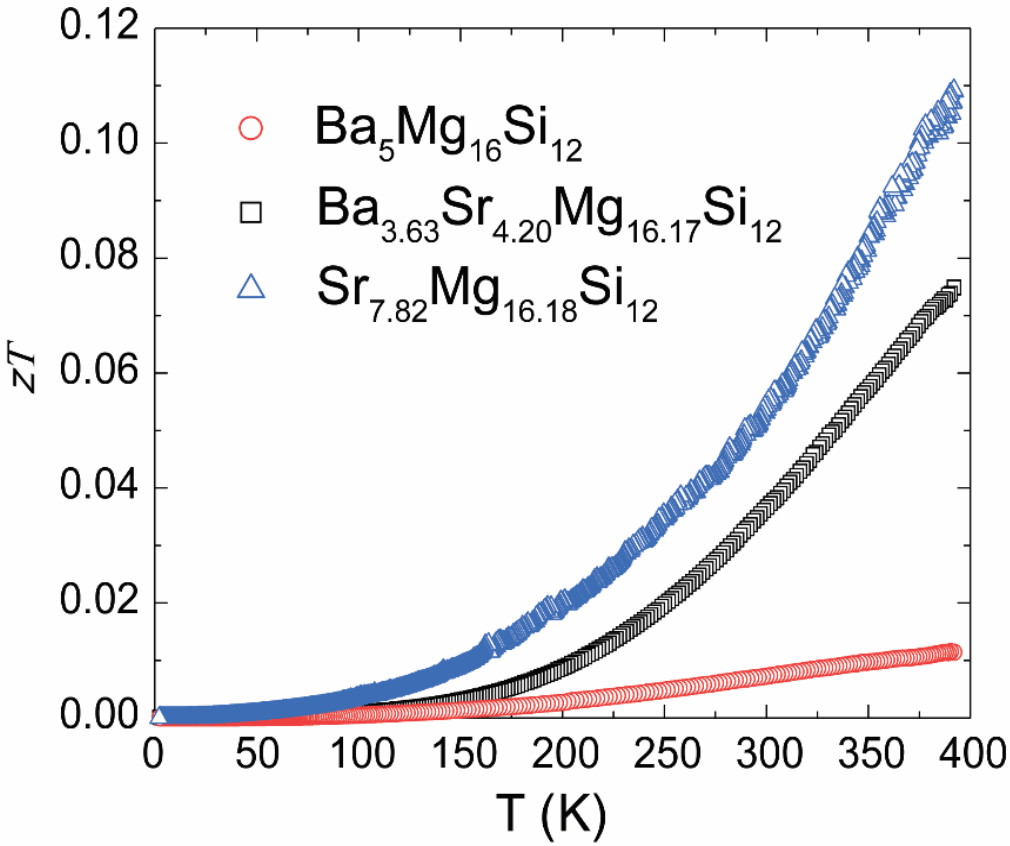
Thermoelectric figure of merit: $zT = \frac{S^2}{\rho\kappa}T$

Lowest for $Ba_5Mg_{19}Si_{12}$
Higher for the analogs with more disorder (Sr/Mg and Sr/Ba mixing)

Need high temp measurements!

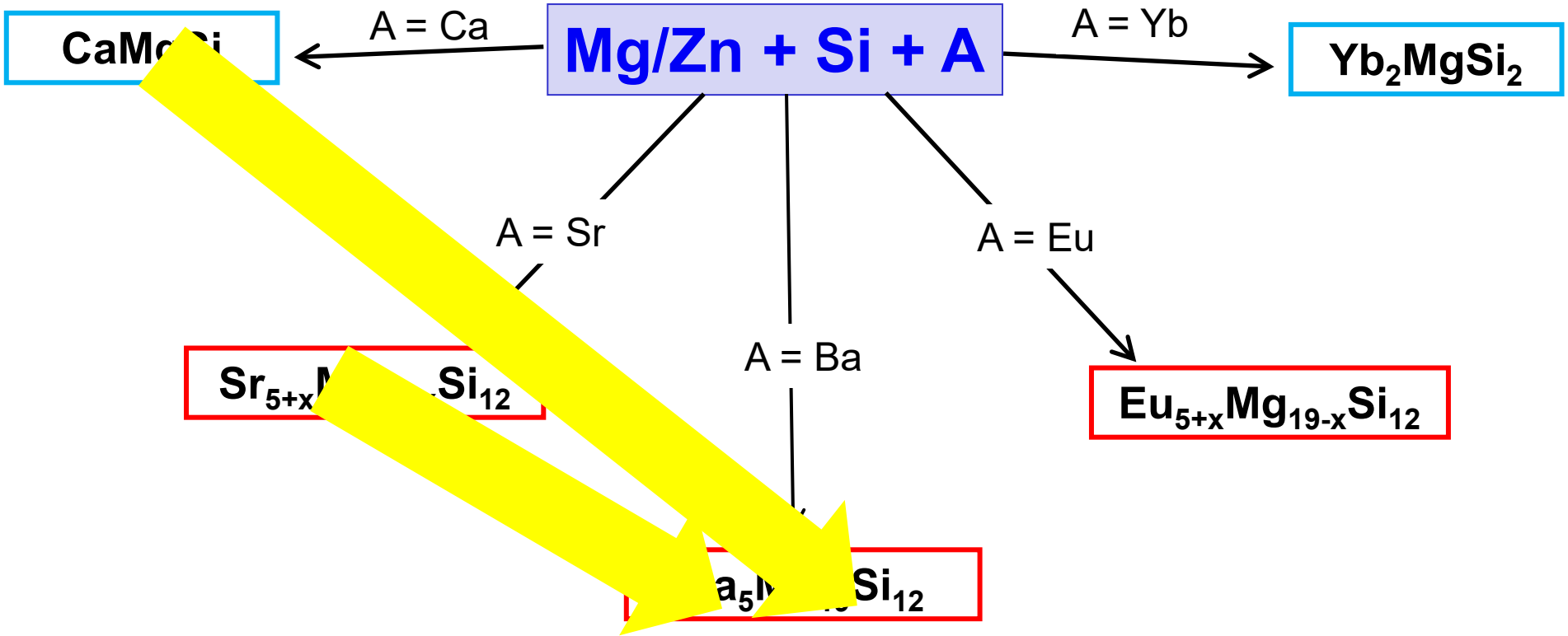
Improve zT by lowering κ_{latt}

- Heavier atoms (Yb, Eu?)
- More rattling (Ca mixing?)
- More complex structures?



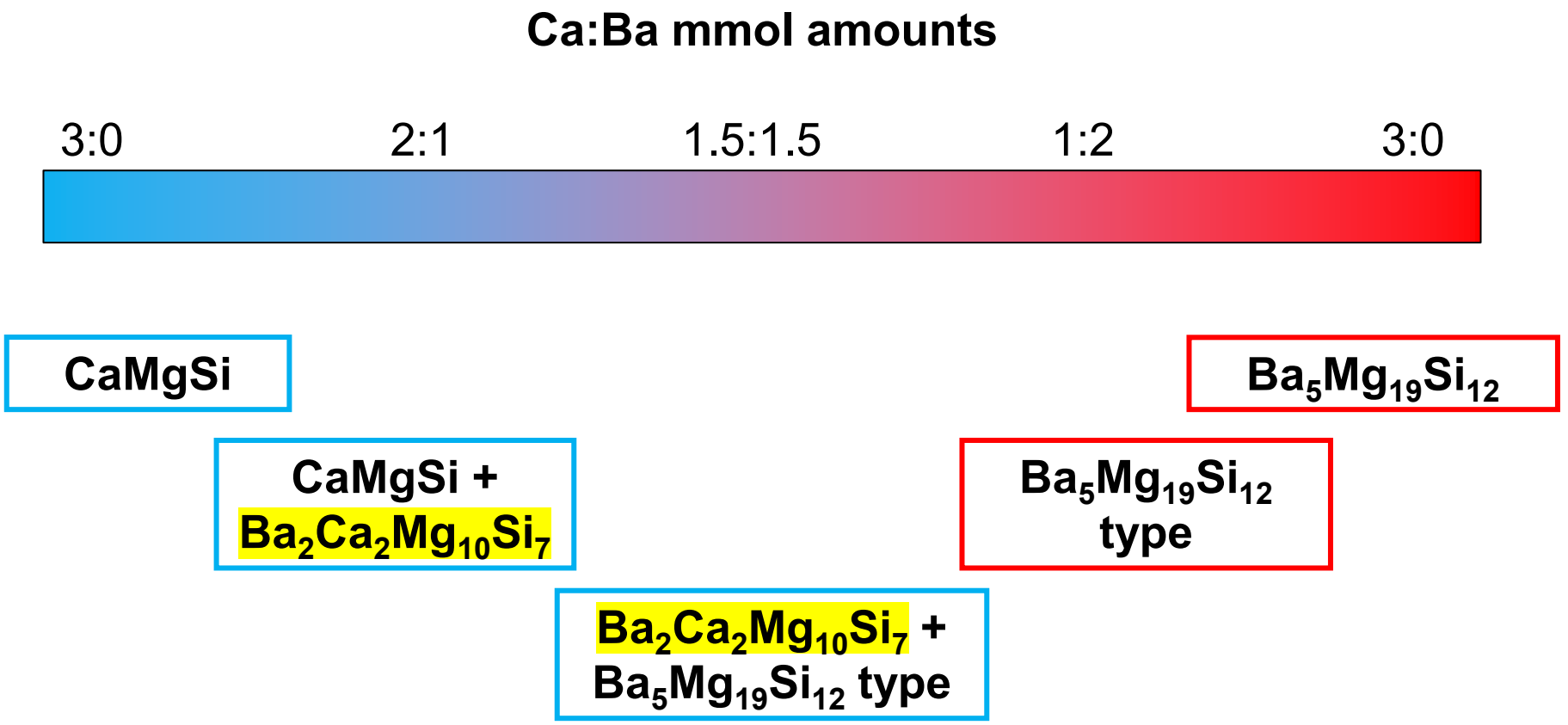
$(A/A'/Mg)_2Si$ semi-metallic silicides

What happens if you use more than one A element?



Ca/Ba/Mg/Si (Taylor's version)

Different amounts of Ba + Ca reacted with 3 mmol Si in either Mg/Al or Mg/Zn flux (22:8 mmol)



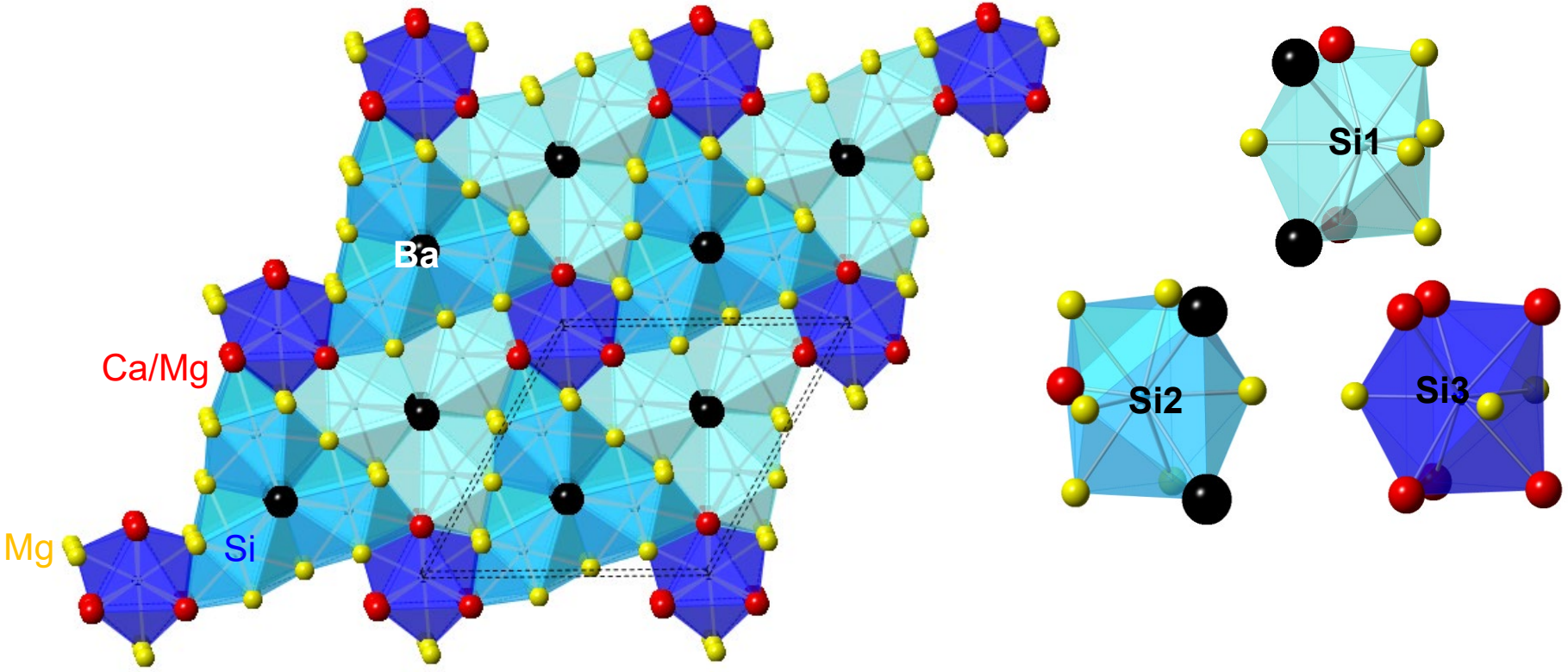
$Ba_2Ca_{2.3}Mg_{9.7}Si_7$

$Zr_2Fe_{12}P_7$ type

hexagonal, P-6; a = 11.196(2) Å, c = 4.4595(9) Å

Ba in the Zr sites, Si in the P sites, Mg in the Fe sites

Ca mixes on one Mg site

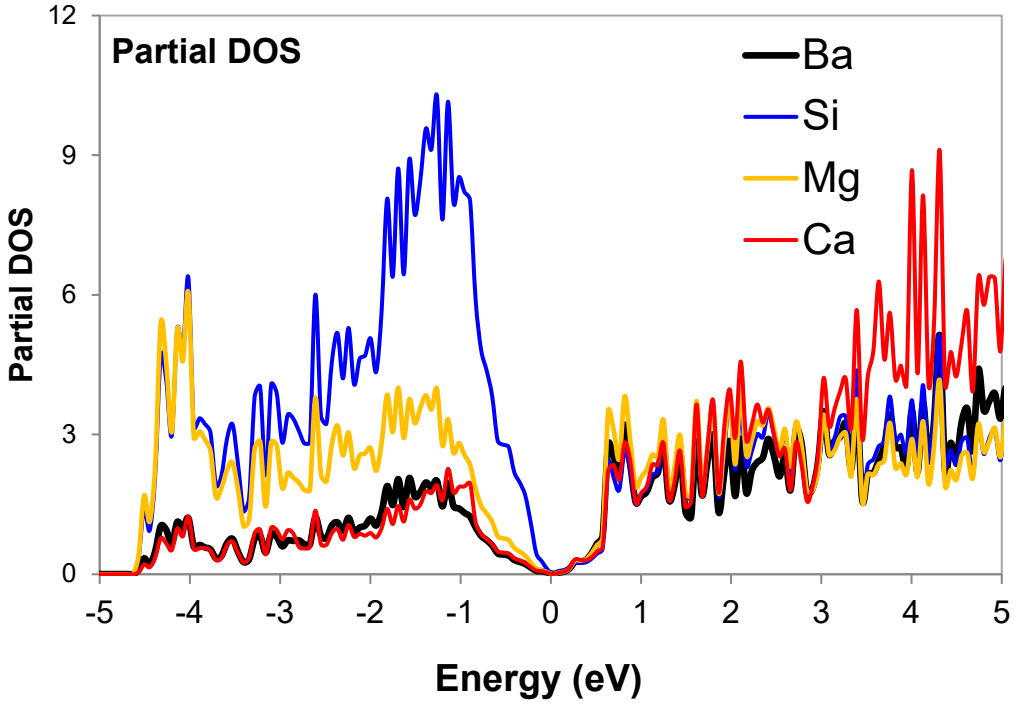


Silsby, K.; Latturner, S.E.; Kauzlarich, S.M. *Chem. Mater.*, **2015**, *27,* 6708-6716

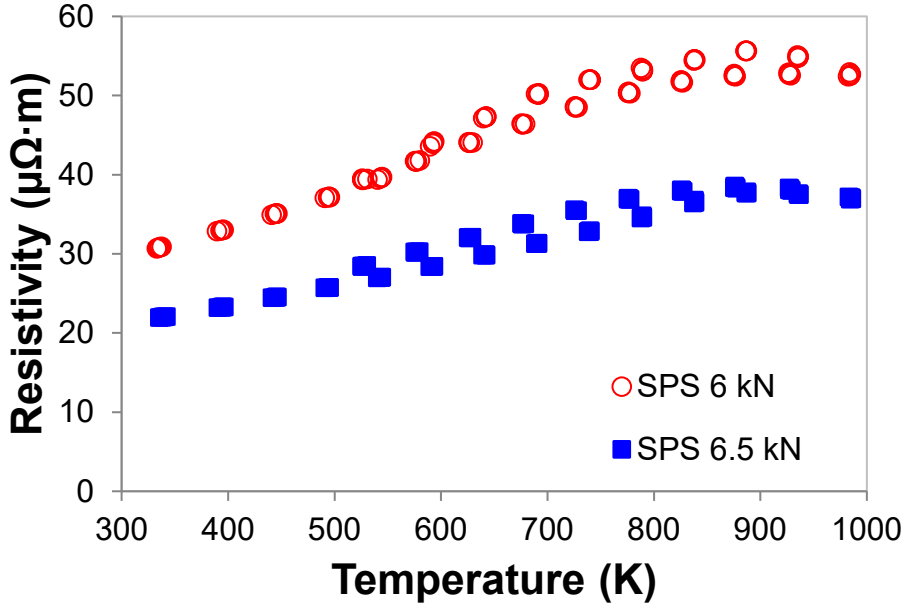
$Ba_2Ca_{2.3}Mg_{9.7}Si_7$

Charge-balanced Zintl phase: $(Ba^{2+}/Ca^{2+}/Mg^{2+})_{14}(Si^{4-})_7$

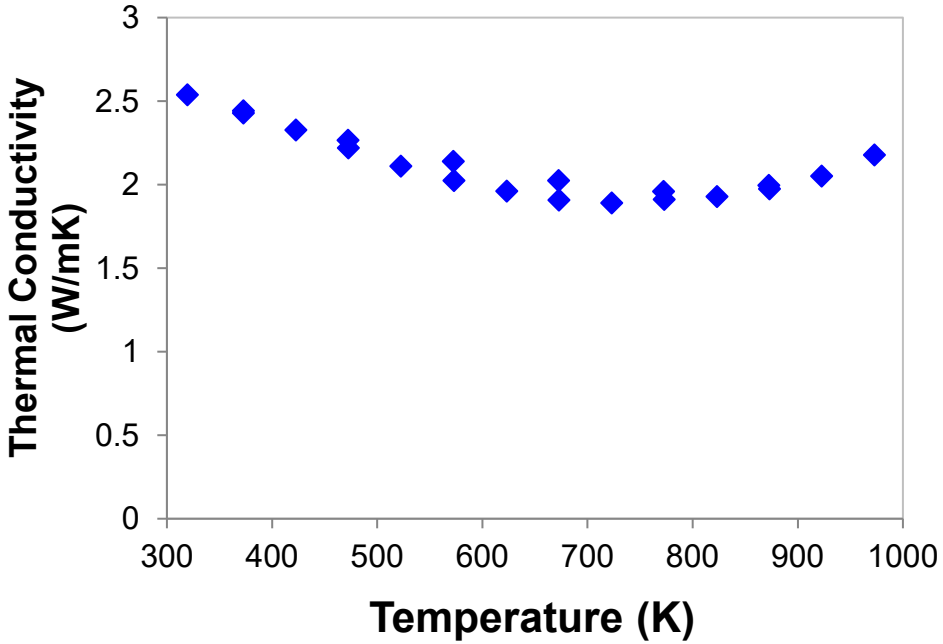
Band structure calculations indicate semiconductor/semimetal



$Ba_2Ca_{2.3}Mg_{9.7}Si_7$ electrical properties



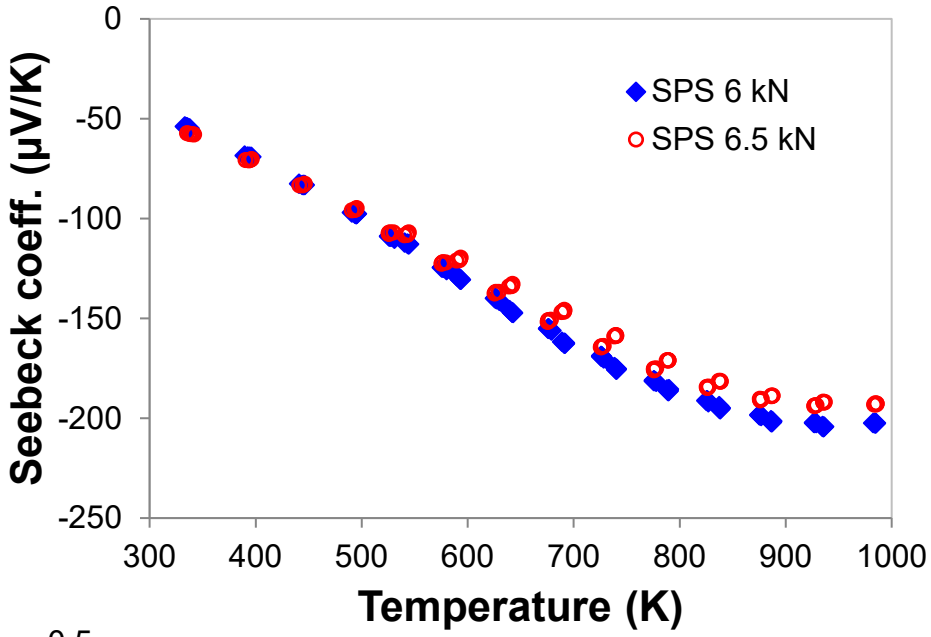
Increasing resistivity as temperature rises (metallic/semimetallic)



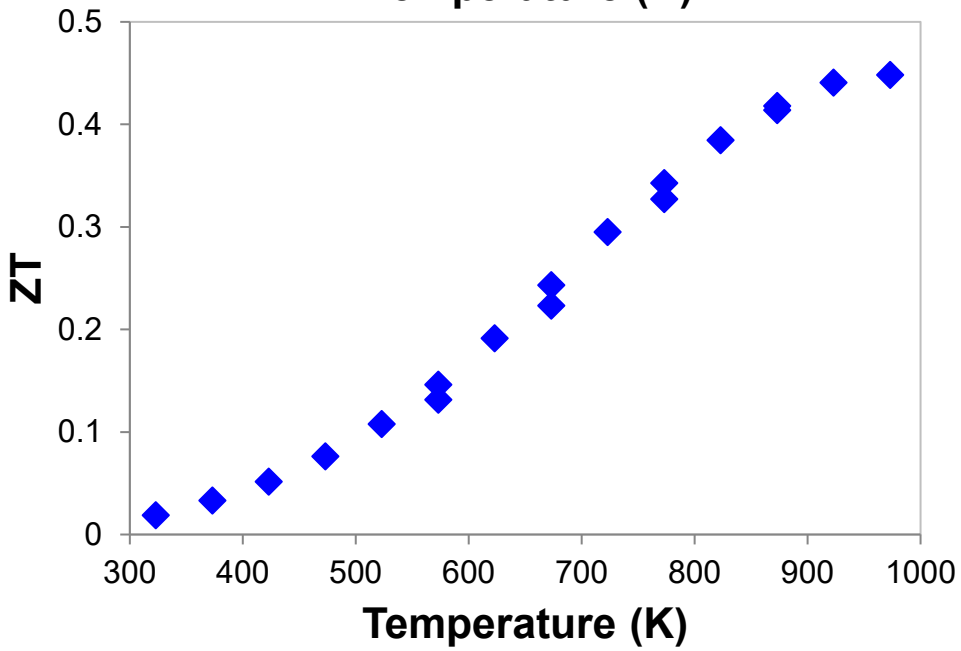
Low thermal conductivity

Silsby, K.; Kauzlarich, S.M.; Latturner, S.E. *Chem. Mater.*, **2015**, *27,* 6708-6716

$Ba_2Ca_{2.3}Mg_{9.7}Si_7$ thermoelectric properties



High Seebeck coefficient; n-type



$ZT = S^2T/\rho\kappa$

Maximum of 0.4 at 900 K

Improvements likely if substituted or doped

Conclusions / Future Work

Flux reactions enable crystal growth of metal silicides

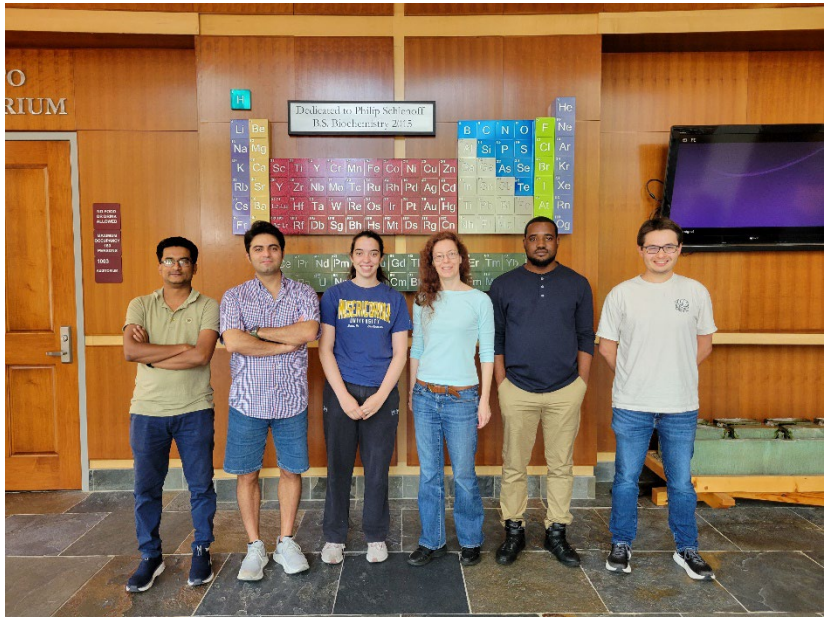
Semi-metallic silicide Zintl phases show promise as thermoelectric compounds

Improve zT by lowering κ_{latt}

- Heavier atoms (Yb, Eu?)
- More disorder (site mixing)
- Rattling of small cations mixed on large cation sites
- More complex structures?

zT likely higher at high temperature; need high temp measurements!

Acknowledgments



Xiaowei Ma, Kurt Silsby, Milorad Stojanovic, Jeff Whalen, Guillermo Vasquez, Jo Haddock, Olufemi Araoyimbo, Amir Zarei, Taylor Walker

Susan Kauzlarich (UC Davis)

Kaya Wei and Ryan Baumbach (NHMFL)

NATIONAL HIGH MAGNETIC FIELD LABORATORY

NSF

OAK RIDGE National Laboratory

Large family of $(A/A'/Mg)_2Si$ from flux growth

Compound	Structure type	Space group	Unit cell parameters (Å)	
$Ba_{1.9}Ca_{2.4}Mg_{9.7}Si_7$	$Zr_2Fe_{12}P_7$	*P*-6	*a* = 11.196(2)	*c* = 4.4595(9)
$Ba_2Yb_{0.88}Mg_{11.12}Si_7$			*a* = 11.0830(6)	*c* = 4.4150(3)
$Eu_2Yb_{1.11}Mg_{10.89}Si_7$			*a* = 10.9910(7)	*c* = 4.3250(3)
$Sr_5Mg_{19}Si_{12}$	$Ho_5Ni_{19}P_{12}$	*P*-62*m*	*a* = 14.457(1)	*c* = 4.3713(4)
$Ba_5Mg_{19}Si_{12}$			*a* = 14.5874(8)	*c* = 4.4662(2)
$Eu_{7.5}Mg_{16.5}Si_{12}$			*a* = 14.668(5)	*c* = 4.428(1)
$Ba_5Eu_{2.85}Mg_{16.15}Si_{12}$			*a* = 14.857(2)	*c* = 4.5225(5)
$Ba_{3.4}Sr_{4.5}Mg_{16}Si_{12}$			*a* = 14.862(9)	*c* = 4.521(2)
$Sr_{4.8}Ca_{3.2}Mg_{16}Si_{12}$			*a* = 14.666(2)	*c* = 4.4187(7)
$Ba_5Yb_{2.26}Mg_{16.73}Si_{12}$			*a* = 14.8223(8)	*c* = 4.5174(3)
$Eu_5Yb_2Mg_{17}Si_{12}$			*a* = 14.526(2)	*c* = 4.3800(6)
$Sr_5Eu_{1.39}Mg_{17.61}Si_{12}$			*a* = 14.553(2)	*c* = 4.4102(7)
$Ba_6Yb_{1.84}Mg_{18.16}Si_{13}$	$Zr_6Ni_{20}P_{13}$	*P*-6	*a* = 15.455(1)	*c* = 4.5046(3)
$Ba_6Eu_3Mg_{17}Si_{13}$			*a* = 15.482(1)	*c* = 4.5082(3)
$Ba_{20}Yb_{4.7}Mg_{61.3}Si_{43}$	$Ho_{20}Ni_{66}P_{43}$	$P6_3/m$	*a* = 27.928(4)	*c* = 4.4808(6)
$Ba_{20}Eu_{5.6}Mg_{60.4}Si_{43}$			*a* = 27.988(3)	*c* = 4.4915(6)
$Ba_{20}Mg_{66}Si_{43}$			*a* = 27.805(4)	*c* = 4.4741(6)