Metallic Composites Phase-Change Materials for High-Temperature Thermal Energy Storage

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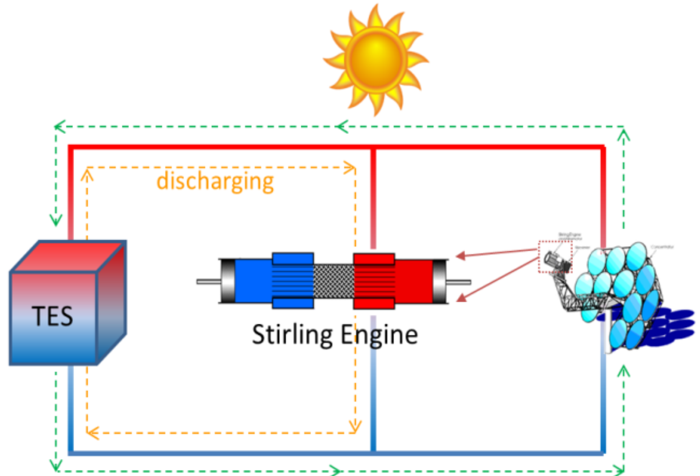
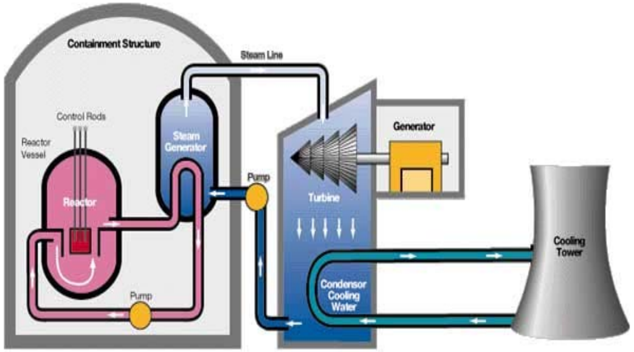
Background – Thermal Storage

Concentrated Solar Power



Affected by weather and night-time

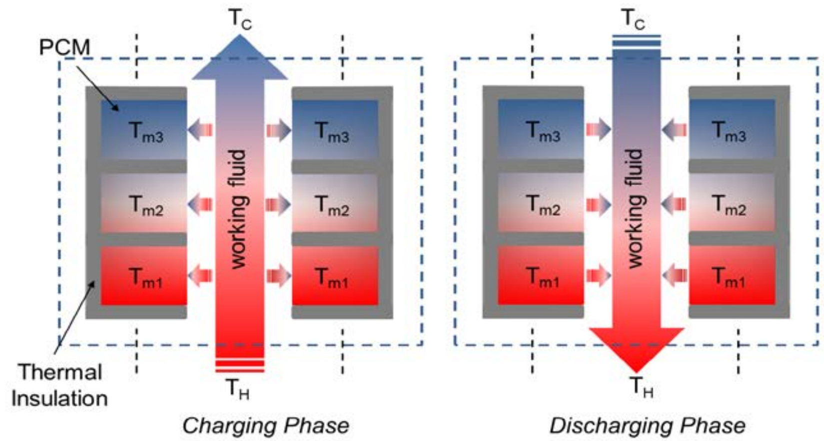
Nuclear Power Plant



Source: http://www.aaenvironment.com/GreenNuclear.htm

Lack peaking power capacity

Proposed Solution:
High temperature, high latent heat thermal storage materials



(T_m – melting point; $T_{m1}>T_{m2}>T_{m3}$)

Project Goals

- High temperature eutectic PCM *(550-900^{o}c)*
- High latent heat PCM *(> 400kJ/kg)*
- High thermal conductivity *(> 10W/mK)*

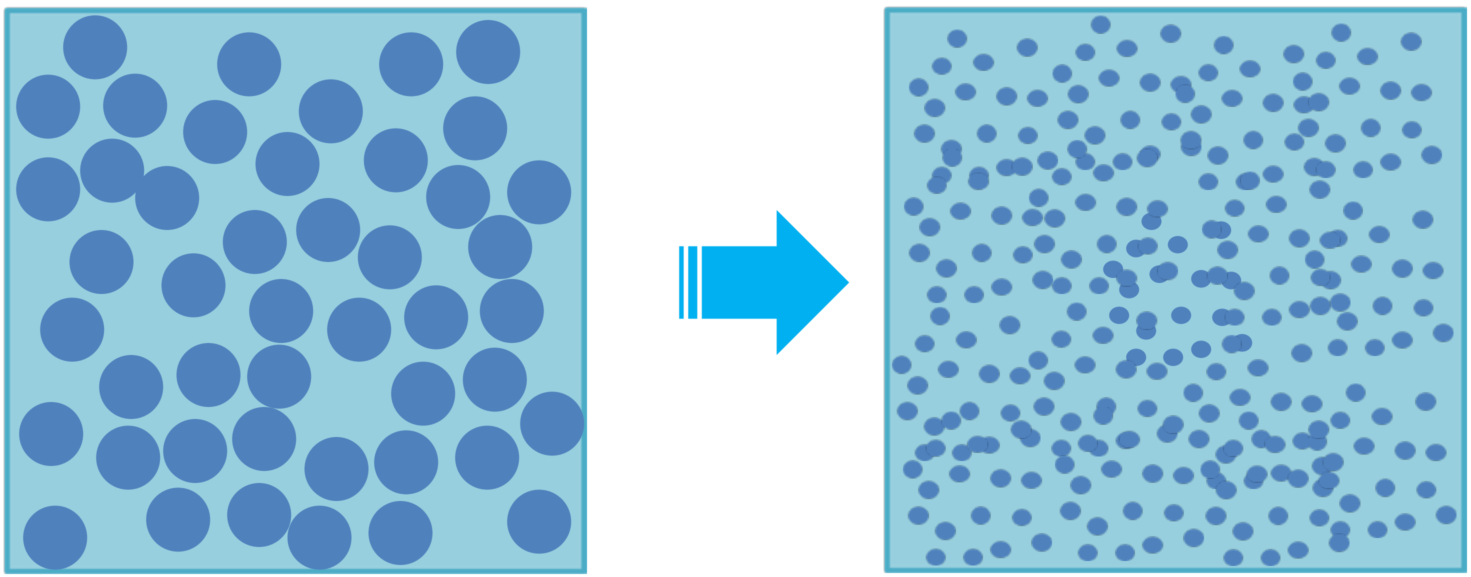
Strategies

- Nanoparticle/ternary increase latent heat *(50%)*
- Earth abundant materials
- Low cost materials

Direction for Increasing Latent Heat

High latent heat metallic composites with high thermal conductivity

Two Phase Separated in Solid | **Two Phase Mixed in Liquid**



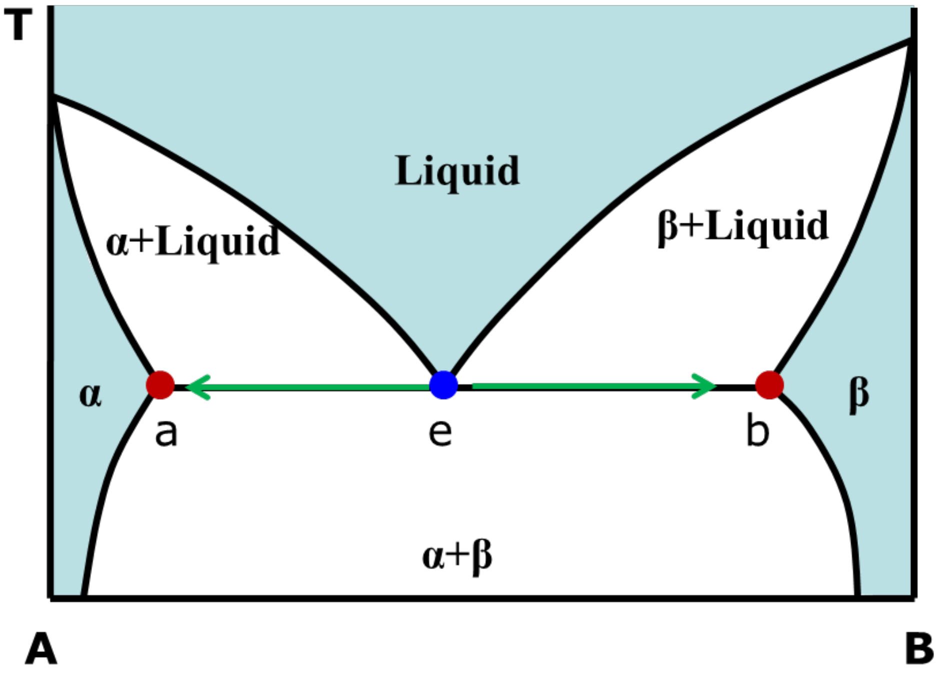
Latent Heat
(Enthalpy of Fusion *H*)

$\Delta H = T\Delta S \uparrow$

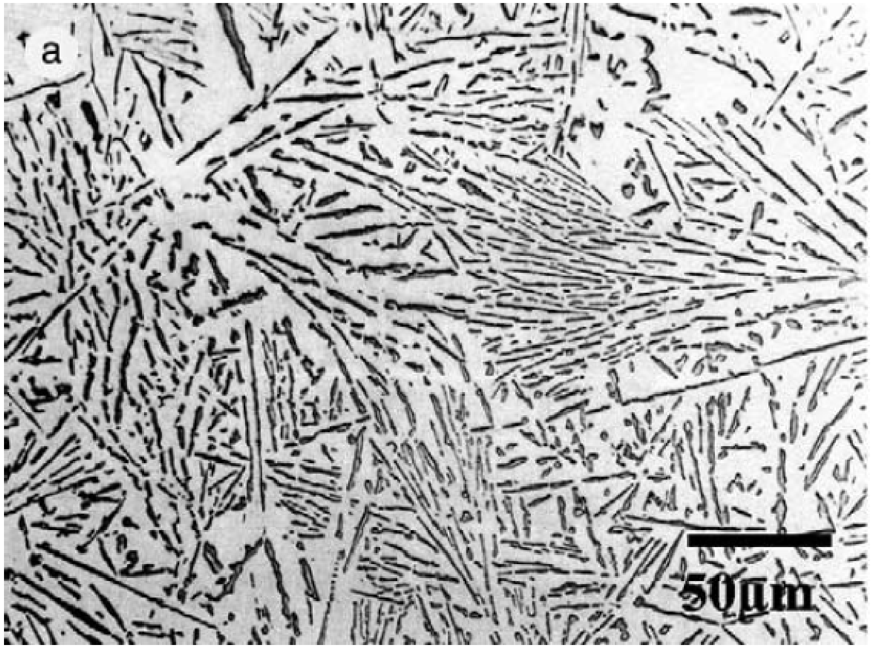
More Configuration
-> Configurational Entropy *S*

Eutectic Alloys as PCM

Typical Binary Phase Diagram with Eutectic Composition



Microstructure of Al-12Si eutectic alloy



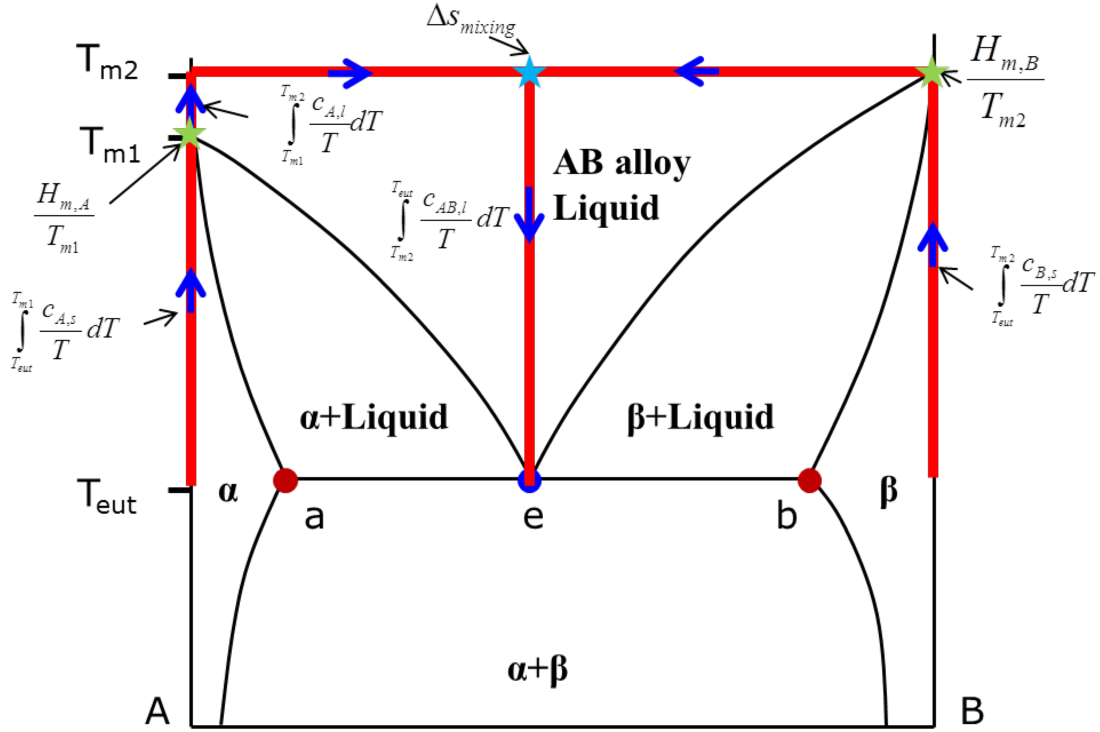
M.M. Makhlouf, H.V. Guthy, J. Light Metals 1, 2001

Eutectic composition: phase separation for maximum mixing entropy

Understanding of Latent Heat

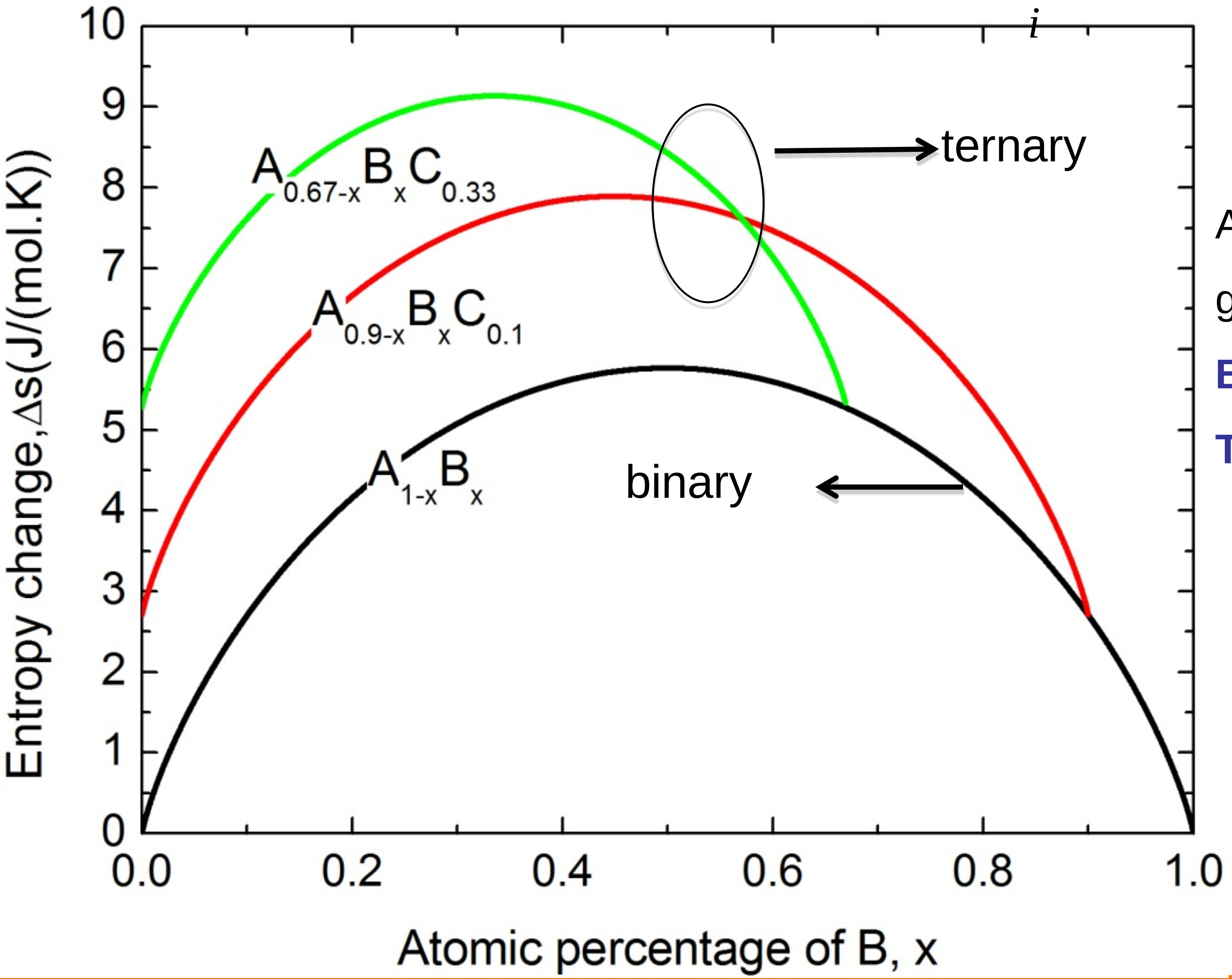
$$\Delta s = \Delta s_{mixing} + \Delta s_{c_p} + (1 - x_e)\frac{\Delta h_{f,A}}{T_{m,A}} + x_e \frac{\Delta h_{f,B}}{T_{m,B}}$$

Mixing entropy — **Sensible heat** — **Latent heat from each elements**



Latent Heat from Mixing Entropy

Ideal Mixing: $$\Delta s_{mixing} = -R\sum_i x_i \ln x_i$$

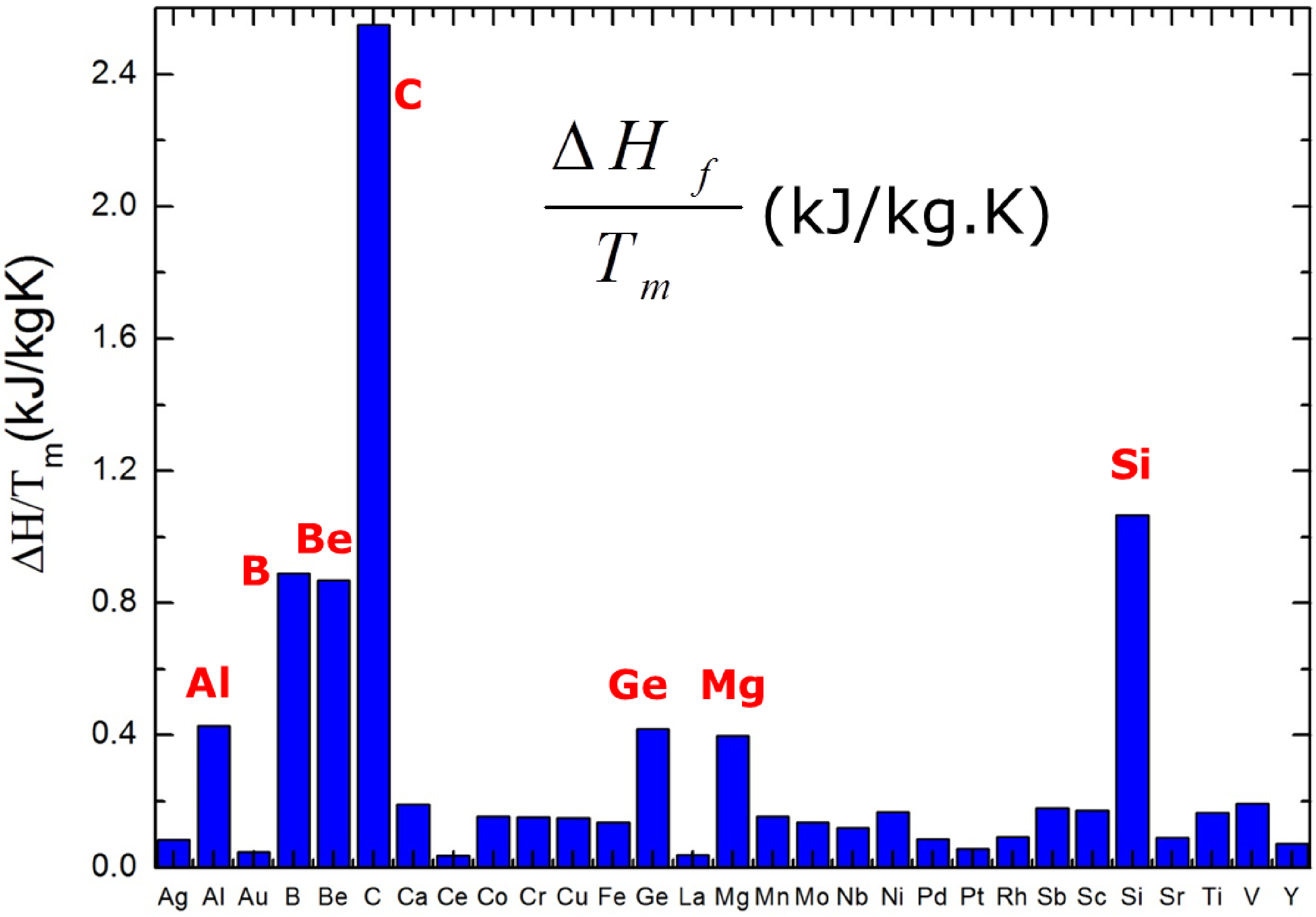


At 800K, with atomic mass of 30 g/mol, latent heat from mixing:

Binary alloy: 156 kJ/kg

Ternary alloy: 245 kJ/kg

Material Selection – Latent Heat



Material Selection – Vapor Pressure, Price

Instable Elements	Stable Elements for Melting
Vapor Pressure = 100 kPa	Vapor Pressure = 1 Pa

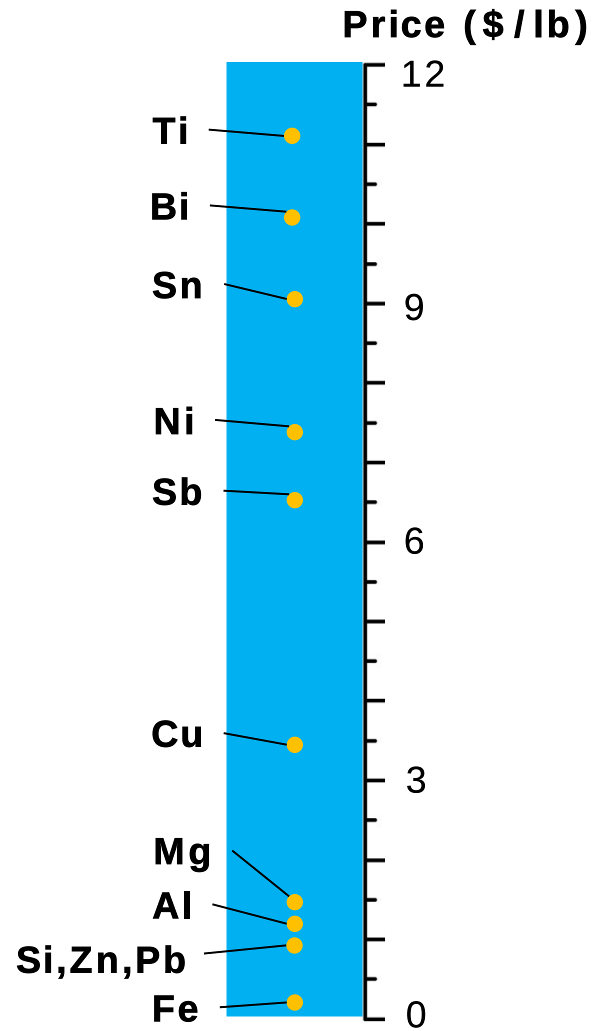
Instable Elements (Vapor Pressure = 100 kPa)

- Li @ 722 C
- Na @ 880 C
- Mg @1088 C
- P @ 276 C
- S @ 444 C
- K @ 756 C
- Ca @1482 C
- Zn @ 912 C
- Pb @1754 C
- Sb @1585 C

Stable Elements for Melting (Vapor Pressure = 1 Pa)

B @ 2075 C	Fe @ 1455 C
Al @1209 C	Co @ 1517 C
Si @1635 C	Ni @ 1510 C
Ti @1709 C	Cu @ 1236 C
V @ 1828 C	Ag @ 1010 C
Cr @ 1383 C	Mo @ 2469 C
Mn @ 955 C	Sn @ 1224 C

C - with 10 Pa @ 2566 C



Invariant Temperature of Binary Alloys

	B	C	Al	Si	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
B	2075	2435 2460	---	1362	1277 1877 2003 2040 2250	1540 2080 3225	1737 2035 2747	1605 1839 2083 2157	1142 1510 1630 1800 1580 1890 1990	1175 1510 1640	1133 1271 1353 1276 1462	1018 1025 1111 1093 1031 1125 1156	1013
C	2435 2460	3550	---	---	1722 2270	1647 2776 3066	1649 2606 2658	1530 1726 1765	1227	1153	1325	1326	NA
Al	---	---	660	575	1206 1201 1235 1246 1301 1425	---	---	---	656 1305	1162 1224 1184 1242	1130 1640	642 1365 1643	548
Si	1362	---	575	1410	1265 1285 2028	1330 1480 2130	1395 1631 1837 1914 1683 1921 1987	1328 1408 1664 1701 1439 1666 1780	1058 1152 1238 1283 1254	1193 1195 1210 1204 1219 1407	1202 1260 1304 1314 1327 1457 1320	949 966 1239 1142 993 1250 1289	803 820 859

Invariant means the melting temperature does not change during phase change

Red: eutectic

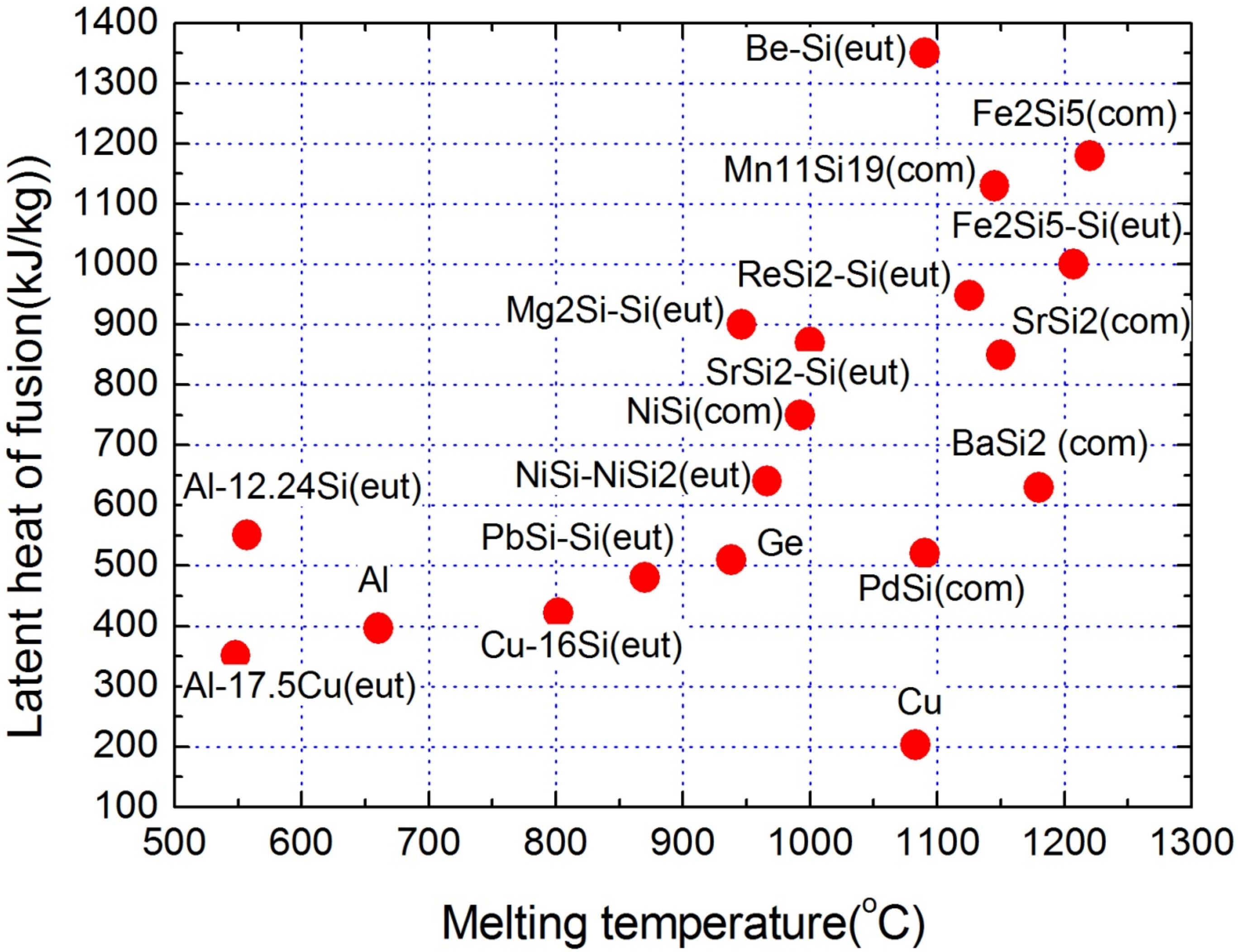
Green: compound

Black: element

---: no invariant temperature

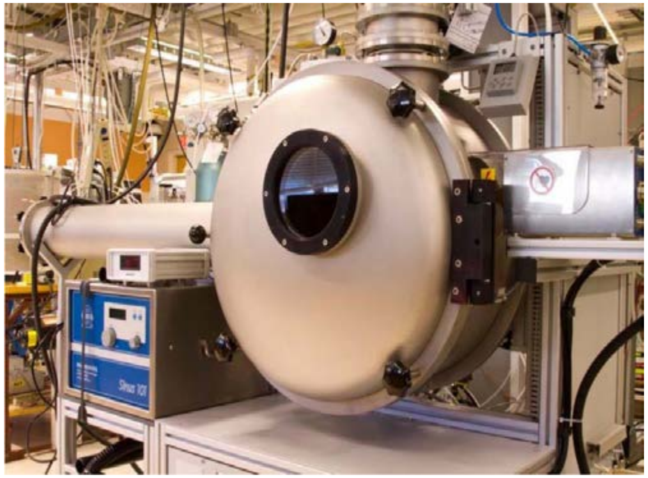
NA: phase diagram not identified

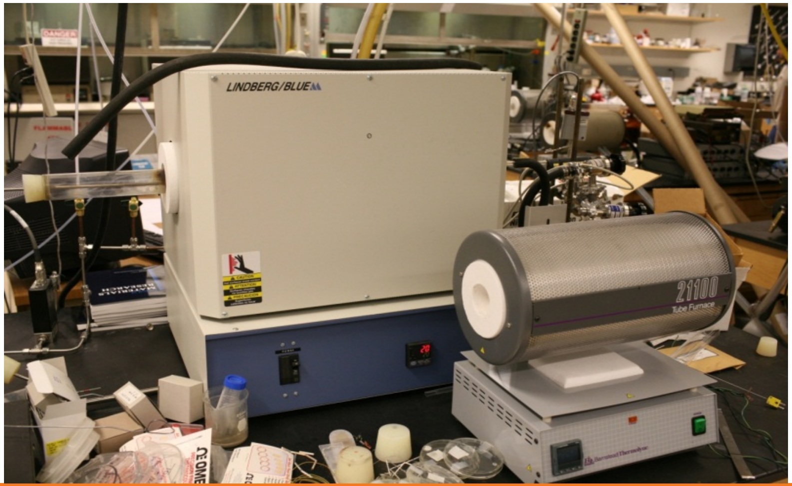
Latent Heat of Fusion ~ Melting T



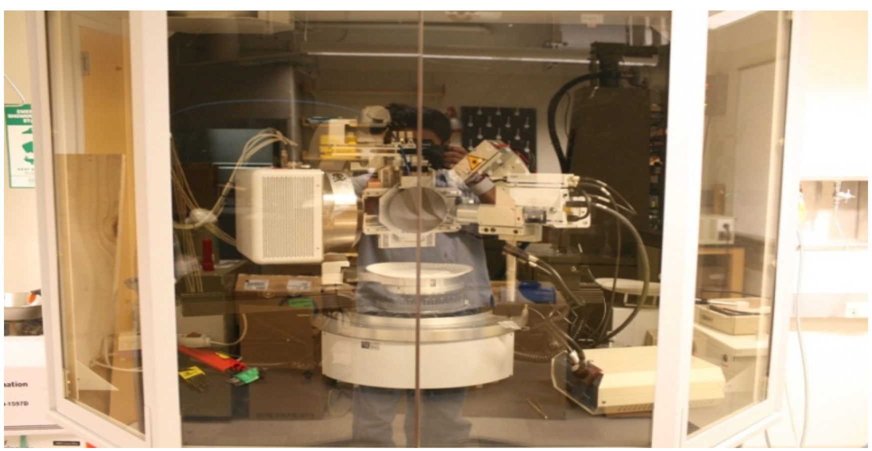
Data based on literature (not verified)

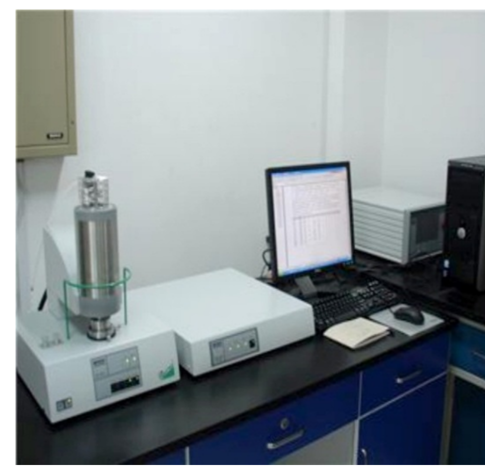
Materials Fabrication Facilities





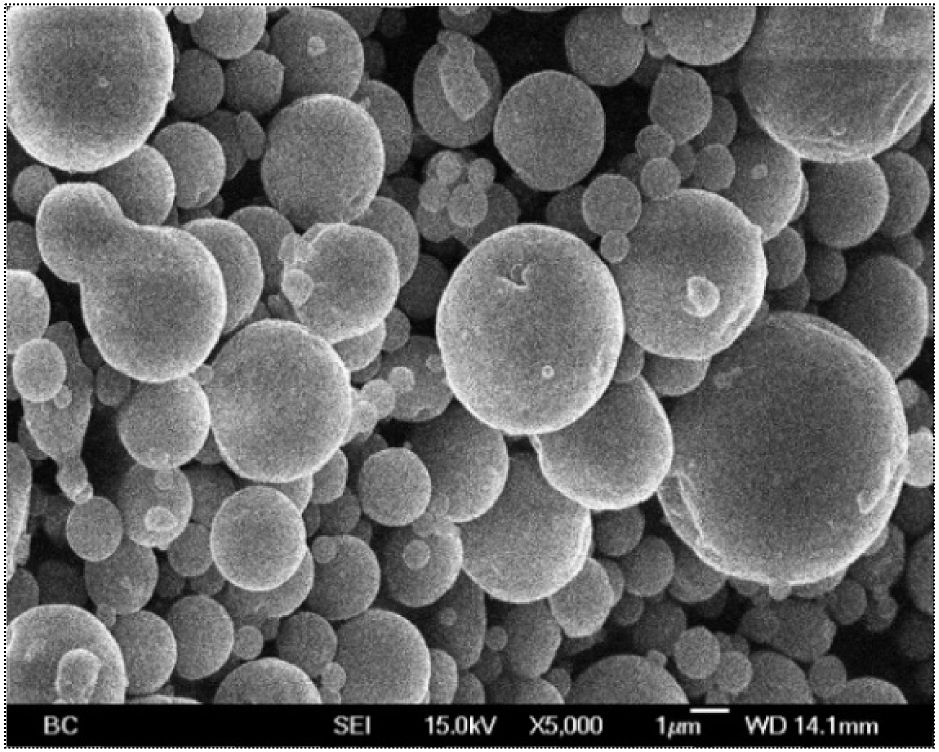
Materials Characterization Facilities





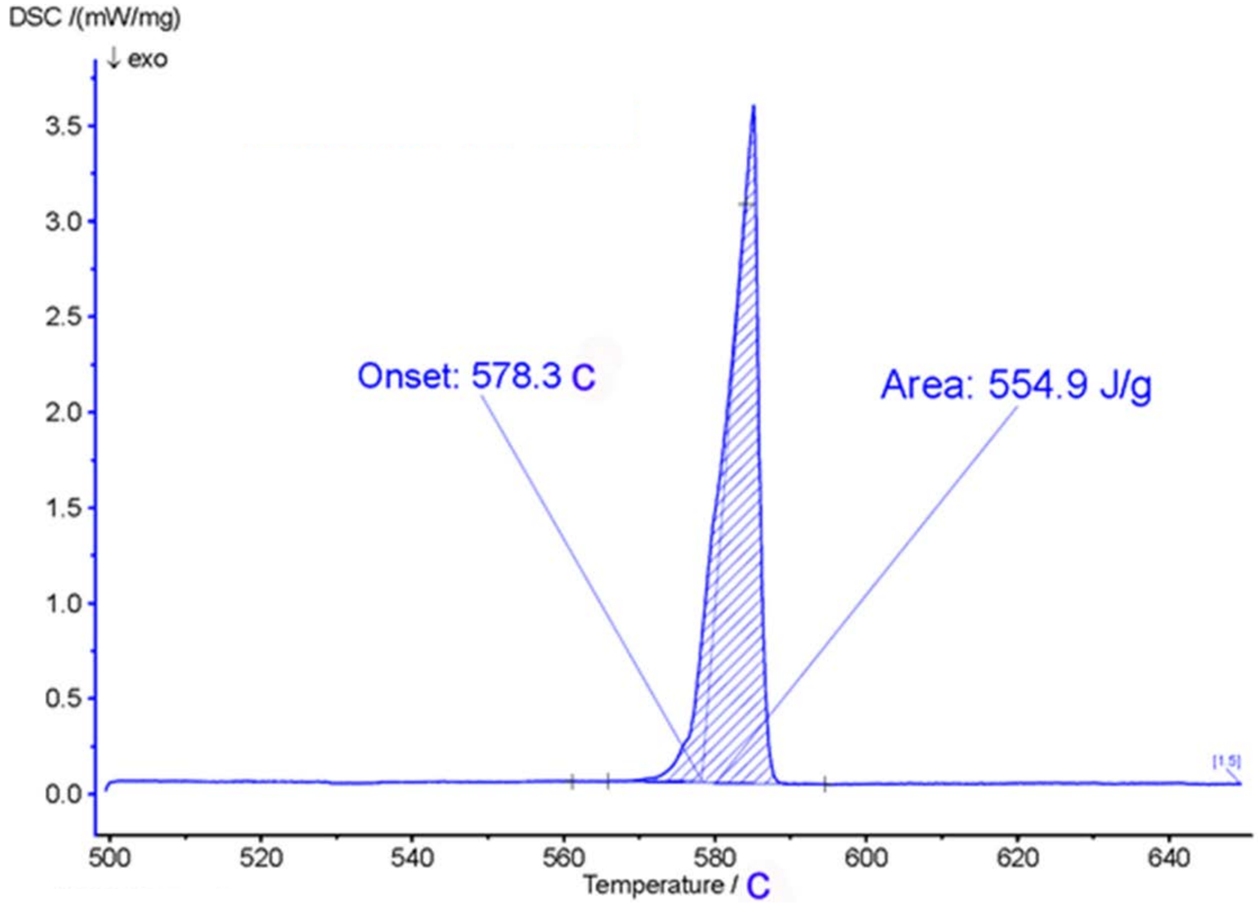
Al-12Si (at%) Eutectic Alloy

Hot-Press: Pressure: 80 Mpa, Temperature: 577 °C



Diameter: 12.7 mm
Thickness: 1.5-2.8 mm

Latent Heat of Al-12Si Alloy

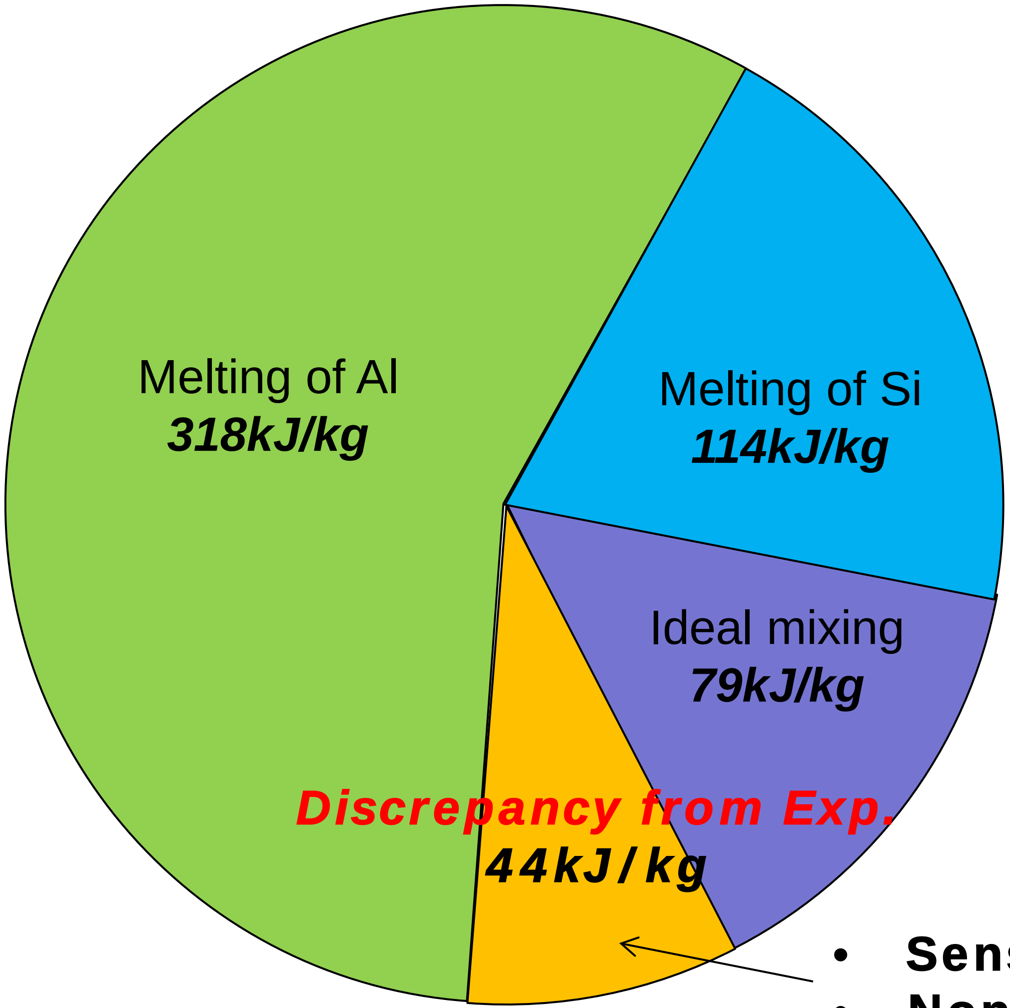


	Melting T (°C)	Latent Heat(kJ/kg)
Measured value	**578.3**	**554.9**
Reference value	576	560

SunShot U.S. Department of Energy

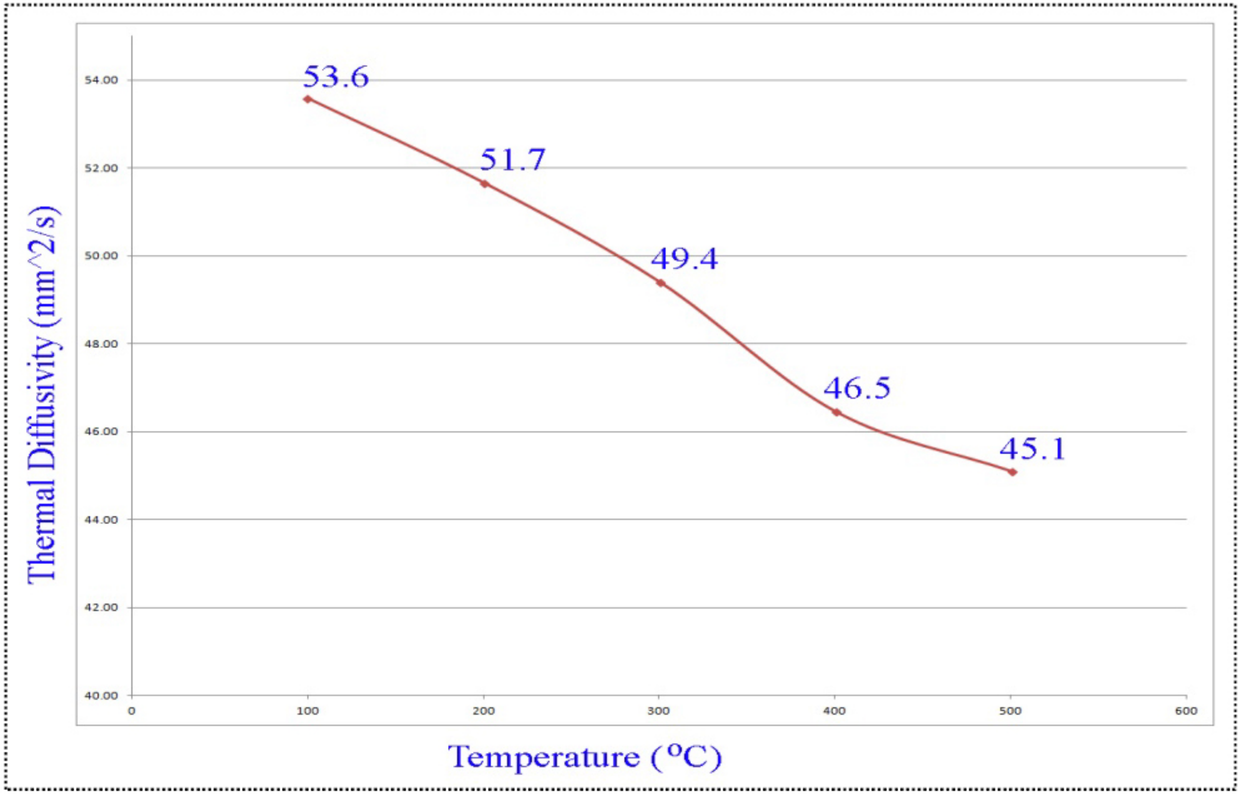
Estimation of Al-12.2Si (at%)

Estimated Latent Heat: 511kJ/kg



- **Sensible Heat?**
- **Non-ideal Mixing?**

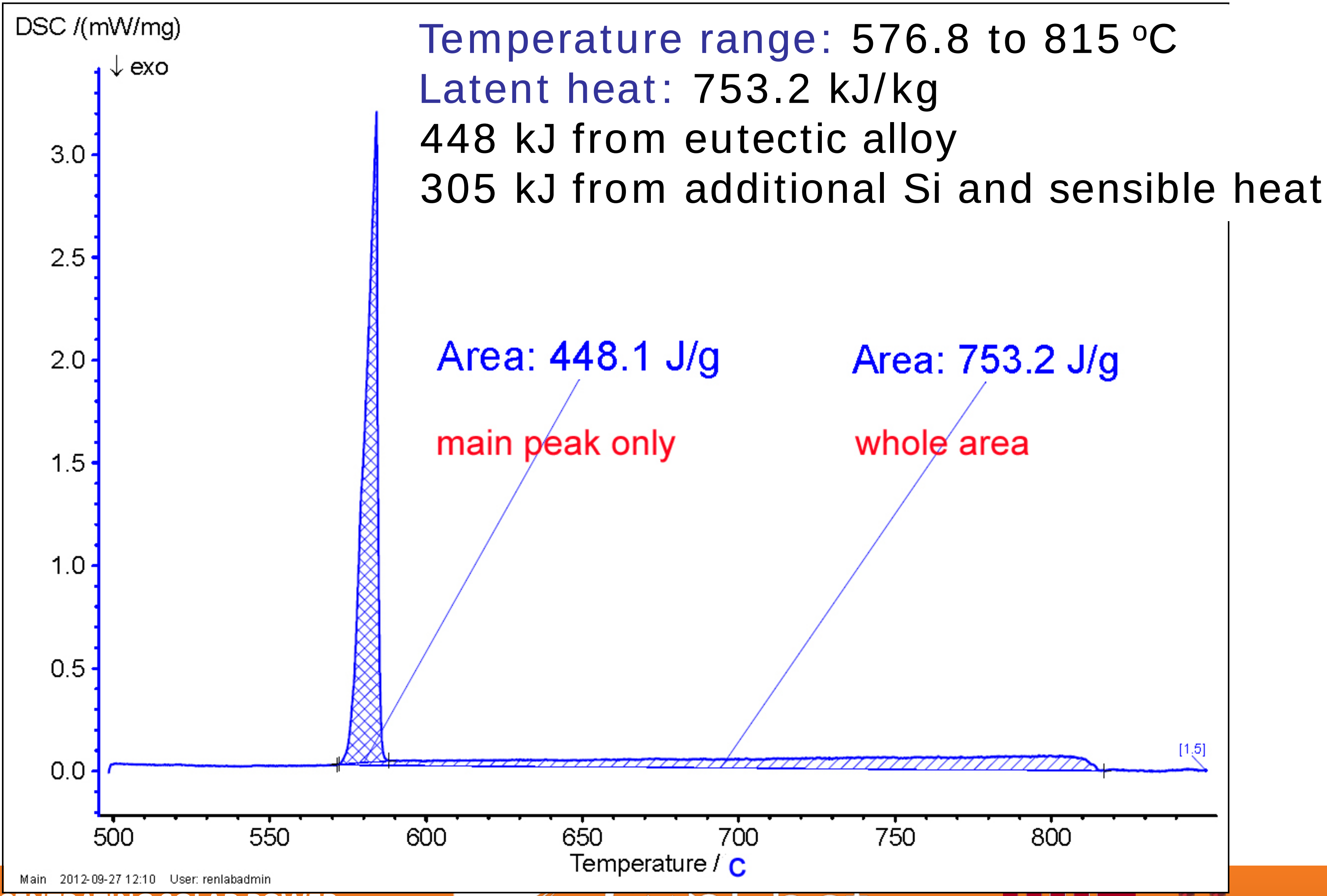
Thermal Conductivity of Al-12Si Alloy



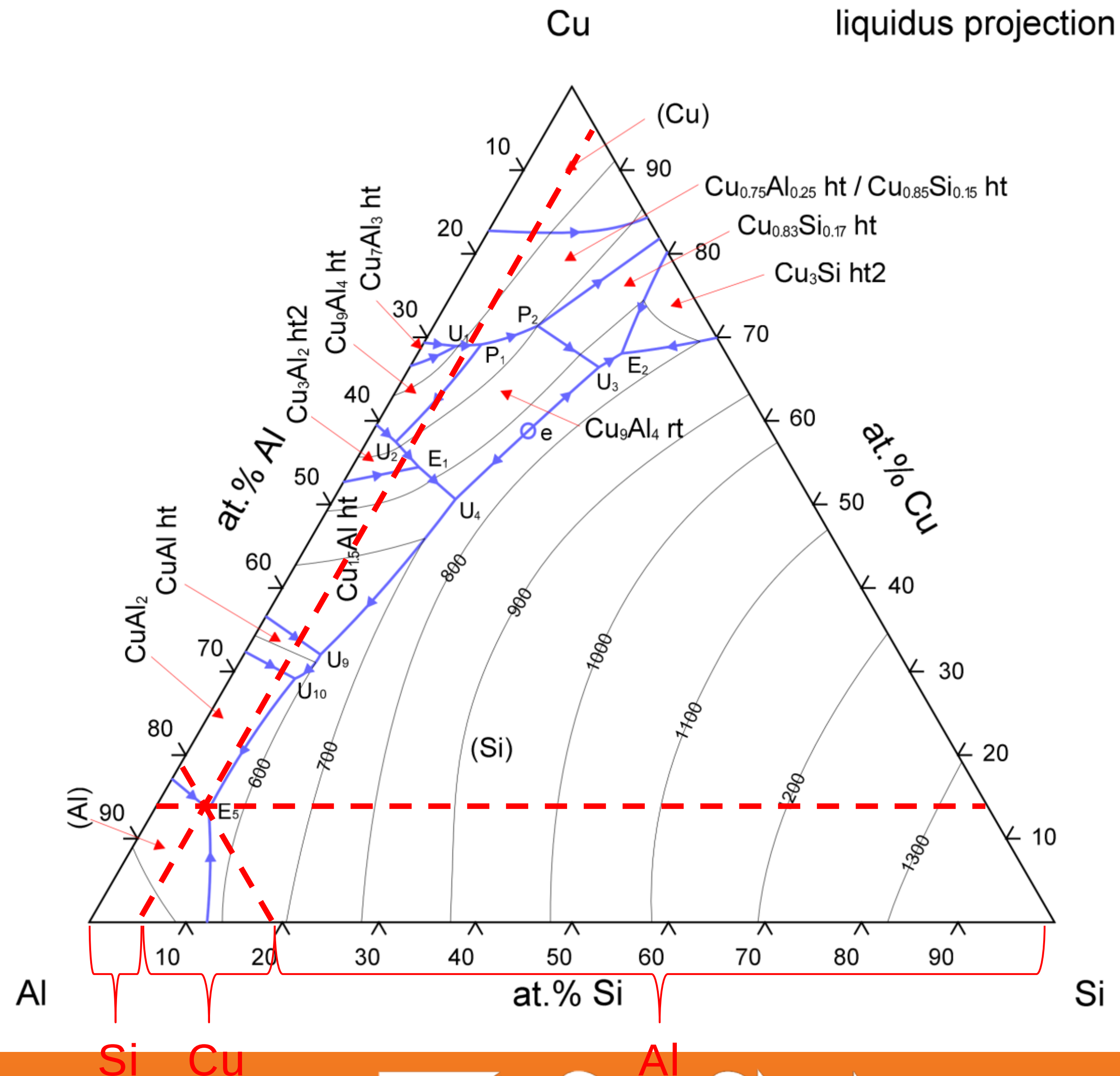
Thermal diffusivity of eutectic Al-12Si alloy (LFA 457 MicroFlash, Netzsch)

Thermal Conductivity: 122 W/mK (500 °C, Cp from literature)

Hypereutectic Al-28Si Alloys

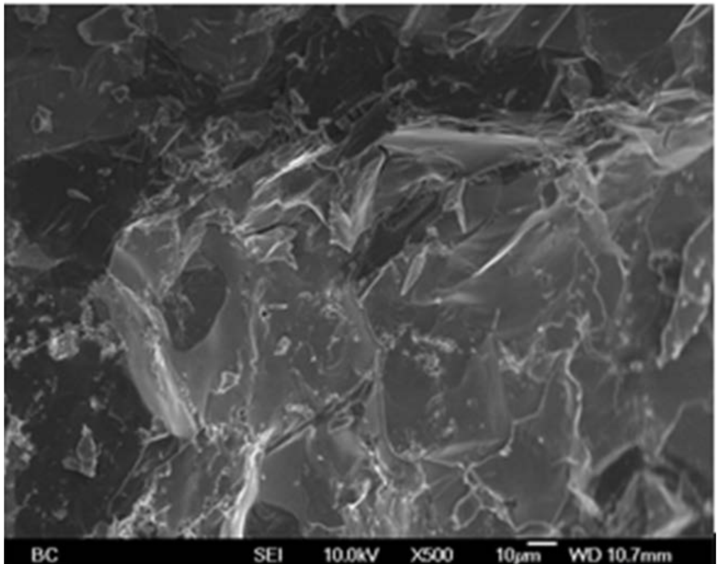


Ternary Phase Diagram



Ternary Alloy # 1

Ternary alloy A-B-C



Latent heat: 867 kJ/kg

Estimated: 964 kJ/kg

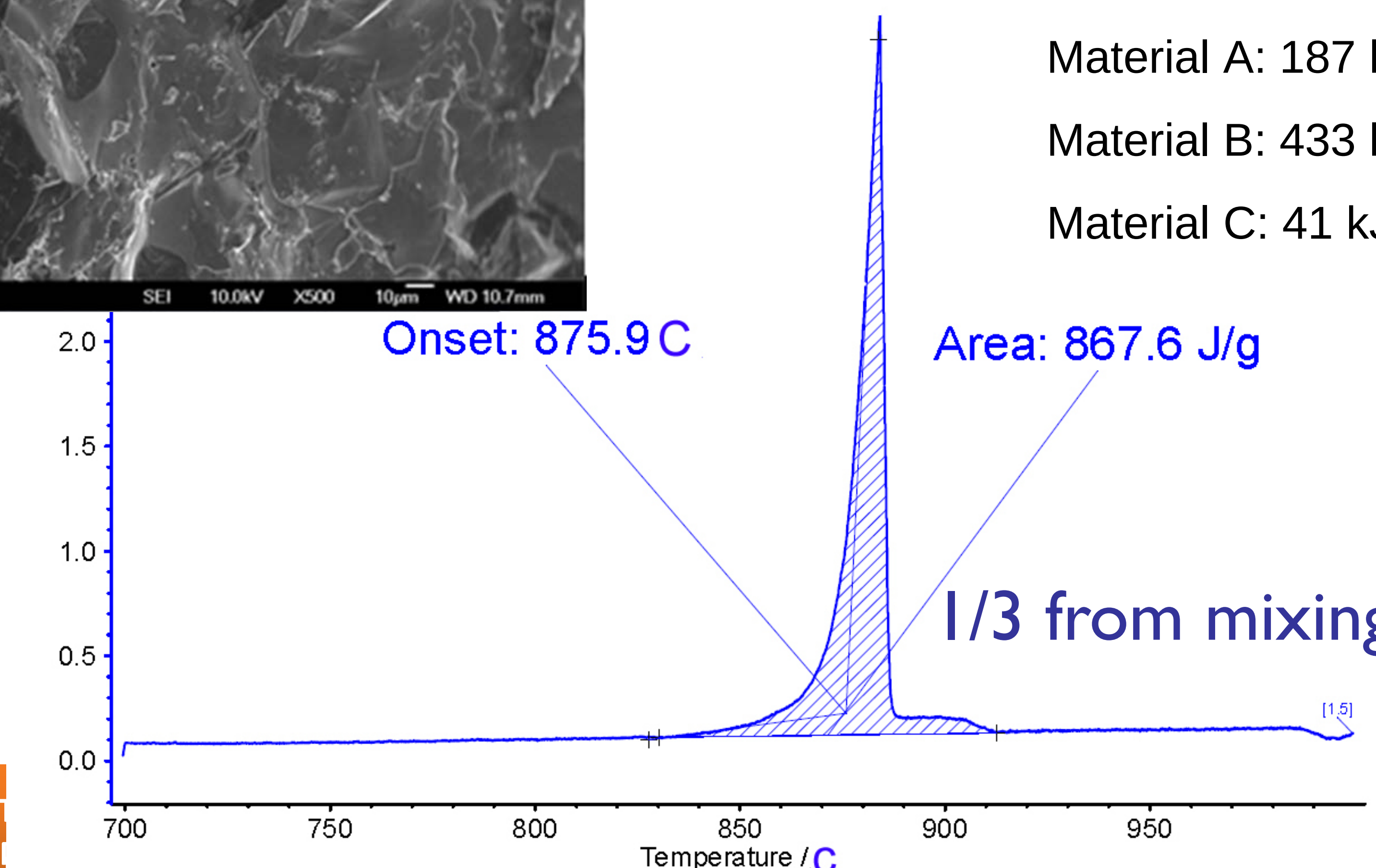
Contribution from:

Mixing entropy: 304 kJ/kg

Material A: 187 kJ/kg

Material B: 433 kJ/kg

Material C: 41 kJ/kg



1/3 from mixing entropy!

Summary

- Systematically investigated metallic PCMs from unary to ternary alloys.
- Binary 87.8Al-12.2Si (at%) alloy: **554.9 kJ/kg at 578.3 ^{o}C**
- Ternary alloy # 1: **865 kJ/kg around 850 ^{o}C**
- Thermal conductivity > 100 W/m.K

Future Directions

- **Further improving materials**
  - Quaternary alloys and eutectics
  - Compounds + eutectics
  - Additives
- **Packaging of materials**
- **Systems and applications**