Aerogels as a sublimation suppression layer for thermoelectric power system

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  - Thermoelectric system
  - Thermoelectric materials and sublimation
- Sublimation of thermoelectric materials
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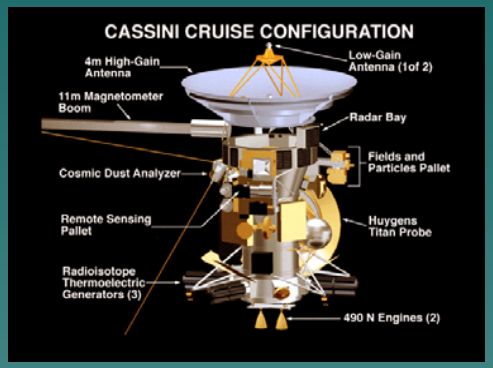
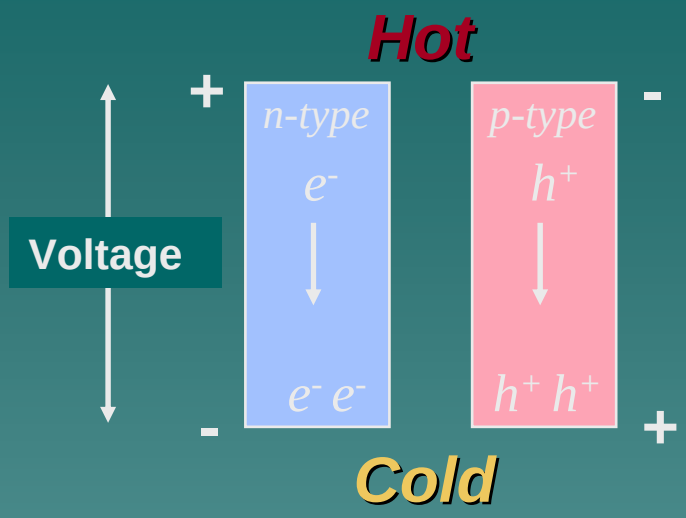
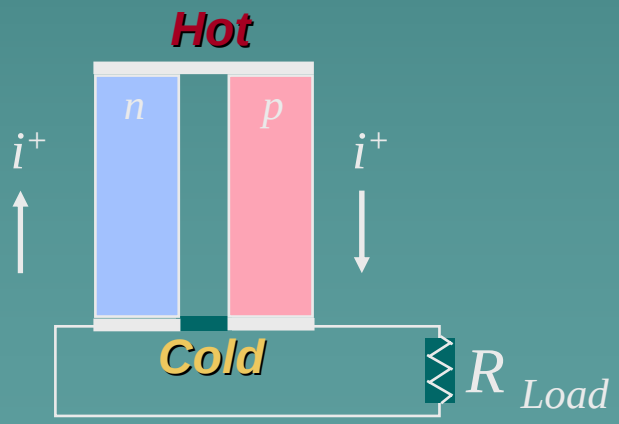
Thermoelectric system

Thermoelectric Power Generation





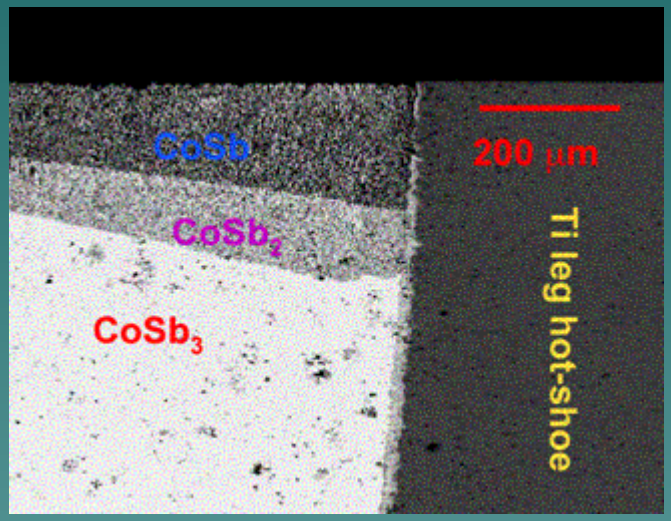
Thermoelectric Cooling



- Seebeck Voltage - Thermopower
  - Charge carriers move faster
  - Net diffusion to cold side
  - Produces Voltage
  - $V = \alpha \Delta T$
  - Proportional to Temperature Grad.
  - Power proportional to Heat Flux

Thermoelectric Materials and Sublimation

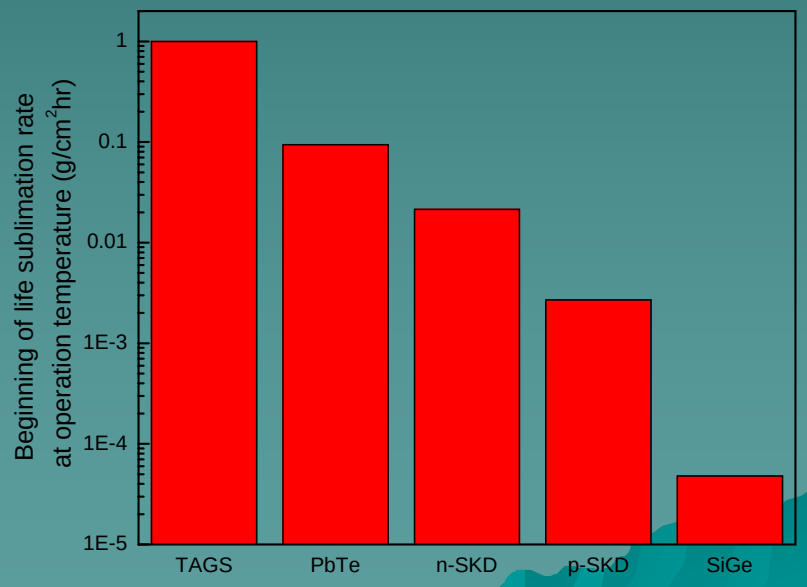
- Near Room Temperature
  - Bi_2Te_3 - Sb_2Te_3 semiconducting alloys
  - For cooling
  - For low temperature power generation
- Above Room Temperature
  - PbTe, TAGS, $CoSb_3$ semiconducting alloys (skutterudites)
  - Used for power generation
- High Temperature
  - Si-Ge alloys
  - Used for power generation



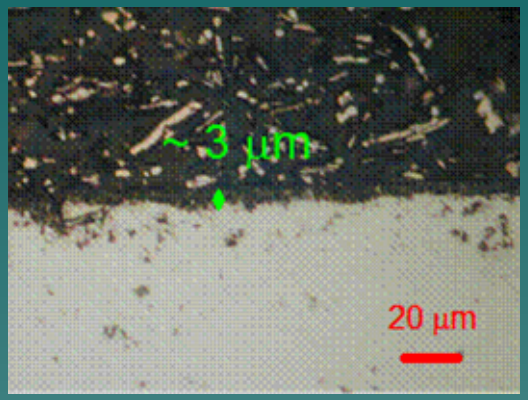
Photograph showing the decomposition of a $CoSb_3$ sample annealed at 875K for 3 months

Comparison of sublimation rates at the beginning of life in vacuum

	Beginning of life sublimation rate at operating temperature
TAGS at 500 °C	~ 1 g/cm^2·hr
PbTe at 500 °C	~ 9.4 × 10^{-2} g/cm^2·hr
n-SKD at 700 °C	~ 2.15 × 10^{-2} g/cm^2·hr
p-SKD at 700 °C	~ 2.7 × 10^{-3} g/cm^2·hr
SiGe at 1000 °C	~ 4.8 × 10^{-5} g/cm^2·hr

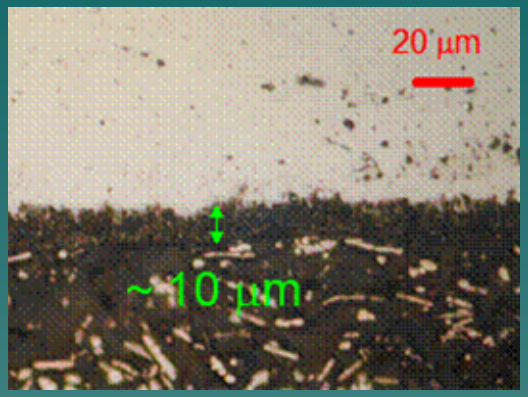


Depletion layers of p-SKD (skutterudite) discs after 700 ^{o}C heating (disc diameter : 6 mm, thickness : 2 mm)



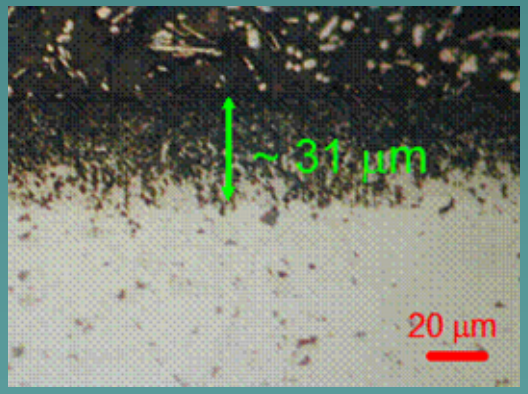
Depletion layer after 2 hr sublimation at 700 ^{o}C

Ave. sublimation rate : ~ 2.77×10^{-3} g/cm^{2}hr



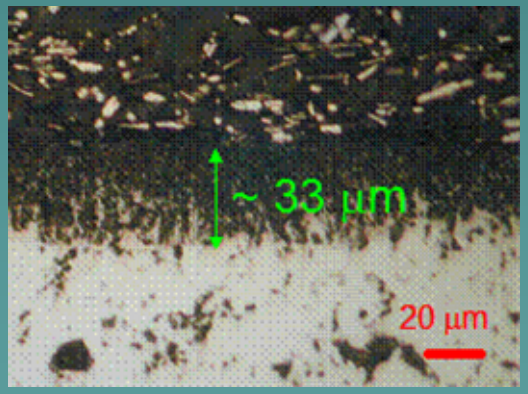
Depletion layer after 4 hr sublimation at 700 ^{o}C

Ave. sublimation rate : ~ 1.7×10^{-3} g/cm^{2}hr



Depletion layer after 10 hr sublimation at 700 ^{o}C

Ave. sublimation rate : ~ 1.49×10^{-3} g/cm^{2}hr

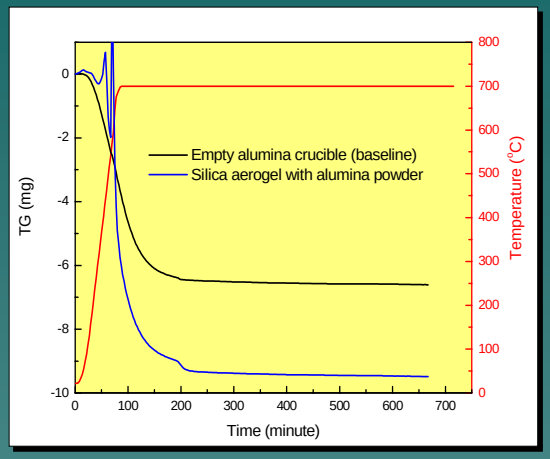


Depletion layer after 24 hr sublimation at 700 ^{o}C

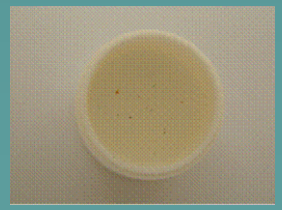
Ave. sublimation rate : ~ 1.45×10^{-4} g/cm^{2}hr

Thermal stability of aerogels (TGA results)

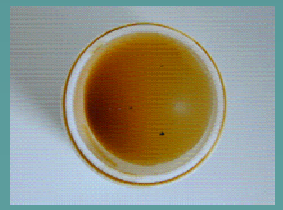
Silica aerogel with alumina powder



- Total weight loss : ~ 3.5 wt% (-2.85 mg / 81.4 mg)
- Most of weight loss before 700 °C isotherm
- Weight loss rate at 700 °C isotherm : ~6.11×10^{-10} g/sec (pressure :~2×10^{-6} Torr) (may be in the order of measurement error)

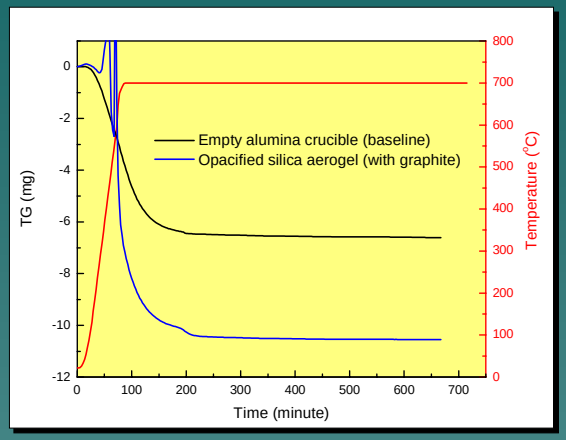


As made



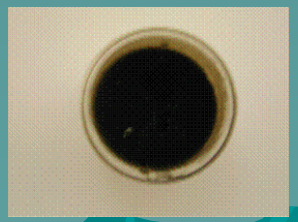
After TGA (700 °C)

Opacified silica aerogel with graphite

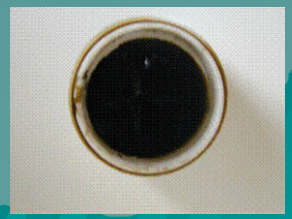


- Total weight loss : ~ 4.2 wt% (-3.8 mg / 92.6 mg)
- Most of weight loss before 700 °C isotherm
- Weight loss rate at 700 °C isotherm : ~2.11×10^{-9} g/sec (pressure :~2×10^{-6} Torr)

(may be in the order of measurement error)

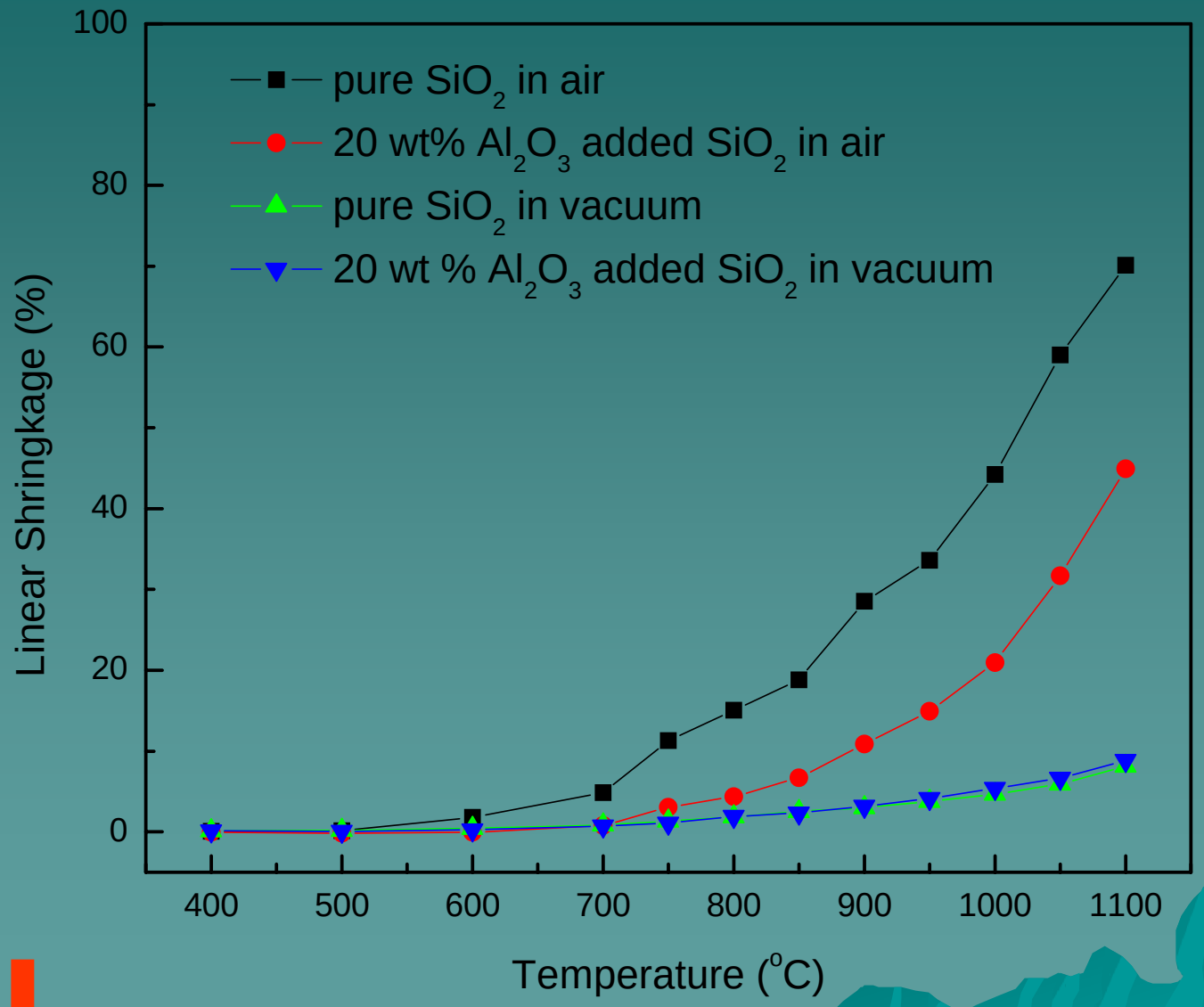


As made

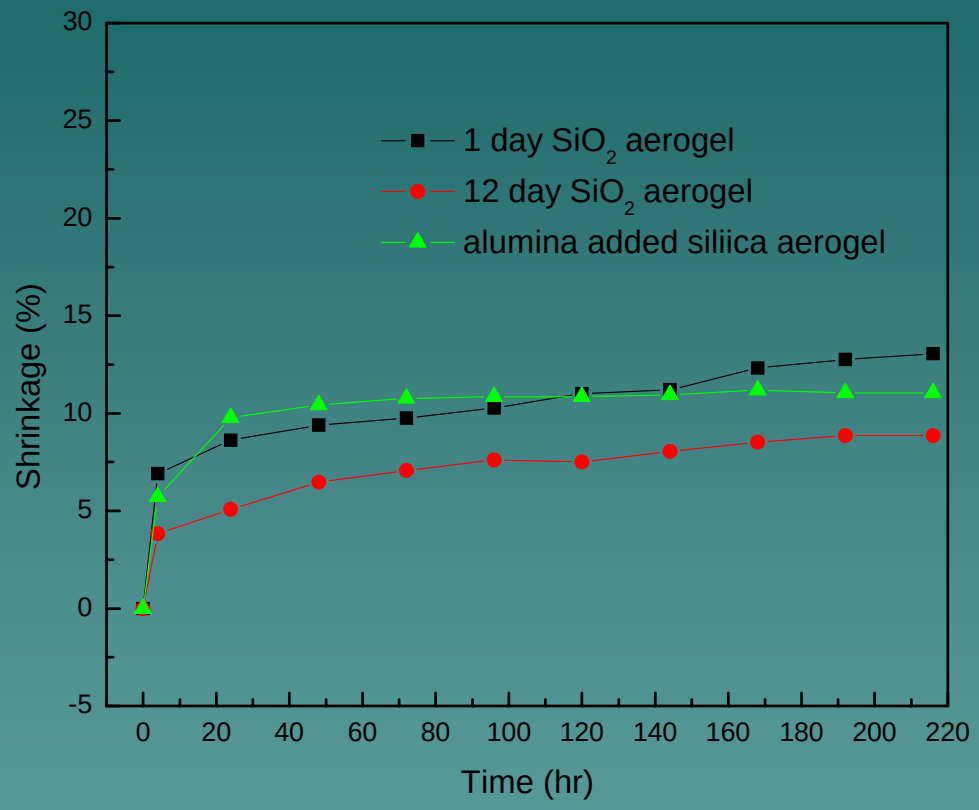


After TGA (700 °C)

Thermal stability of aerogels (shrinkage test)



Thermal stability of aerogels (life time)

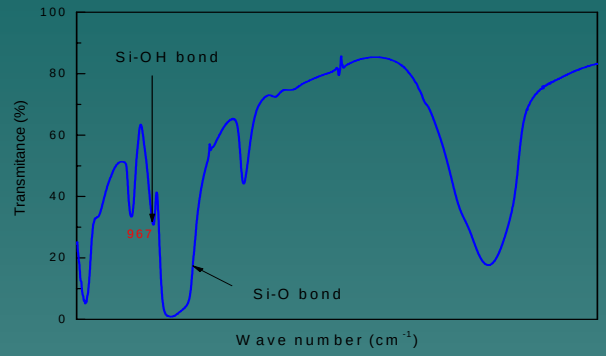


- Linear Shrinkage at 700 ^{o} C in vaccum is ~ 1 %.
- Aerogels with alumina particles shrink mostly in the beginning of heating and become stable without further noticeable shrinkage. It is believed that the addition of these particles increases viscosity, hence reducing viscous sintering.

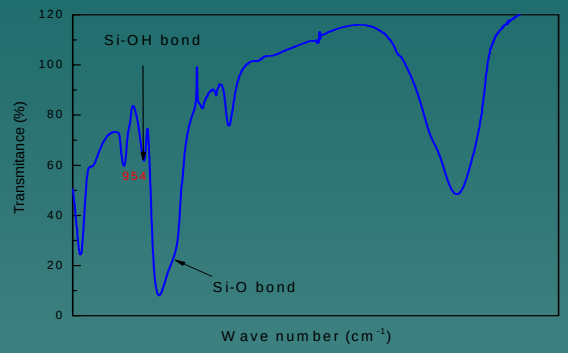
FTIR spectra of aerogels

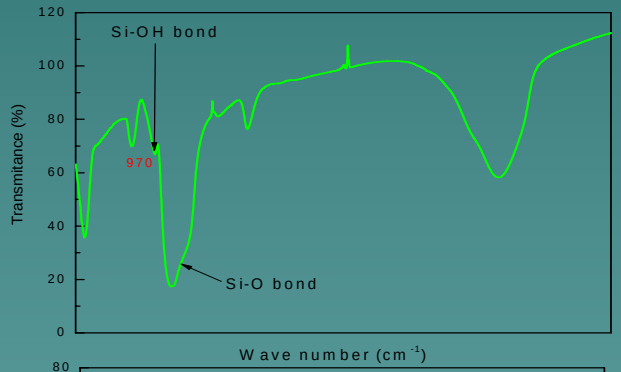
Pure SiO_2 aerogel

20 wt% Al_2O_3 added SiO_2 aerogel

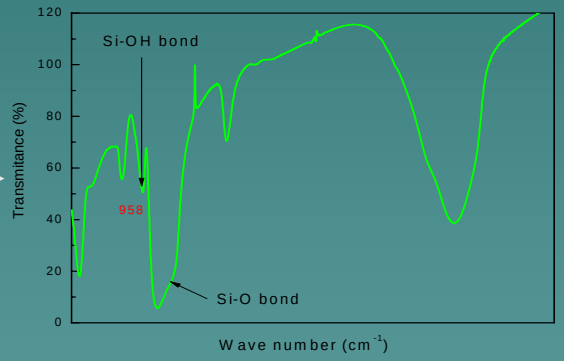


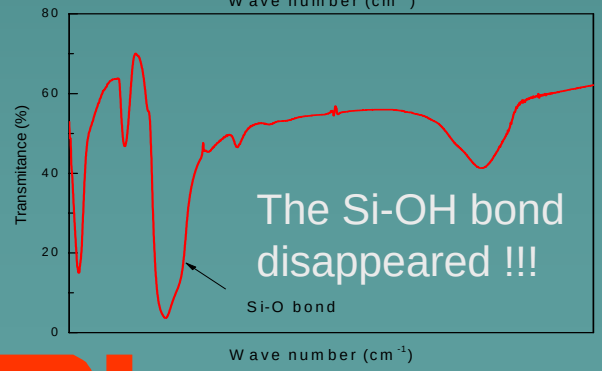
As made





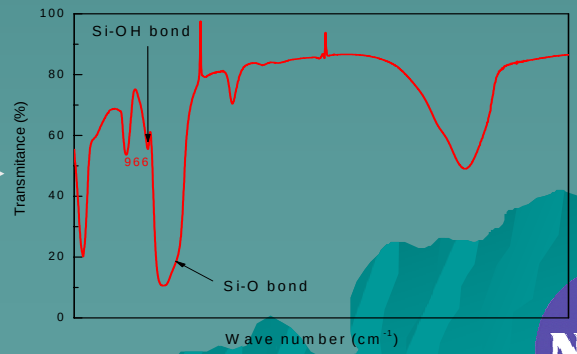
After 4hrs at 1000 ^{o}C in vacuum



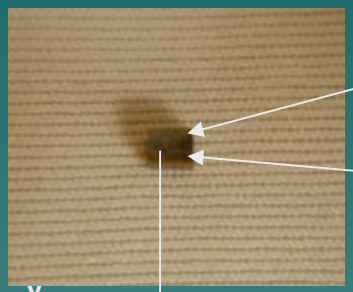


The Si-OH bond disappeared !!!

After 4hrs at 1000 ^{o}C in air

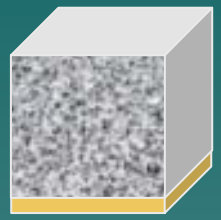


n-SKD cube for the sublimation test



SKD coupon

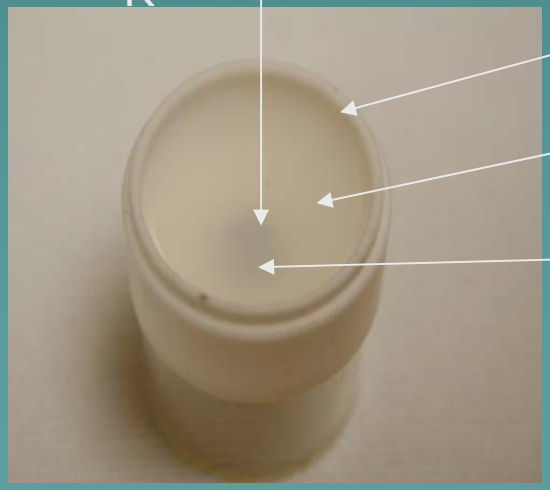
Ti



n-skd cube before aerogel encapsulation

type SKD

Aerogel encapsulation



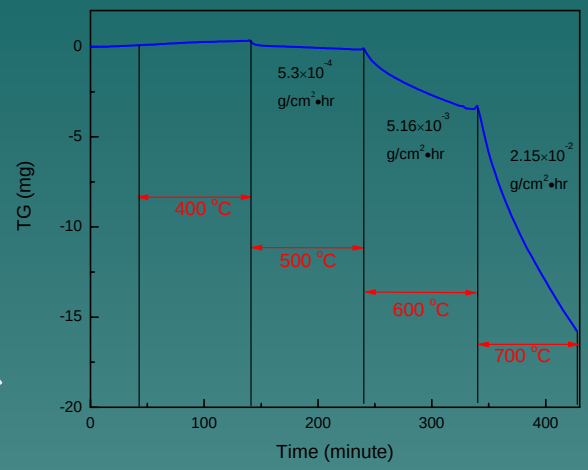
Alumina crucible

Alumina doped silica aerogel

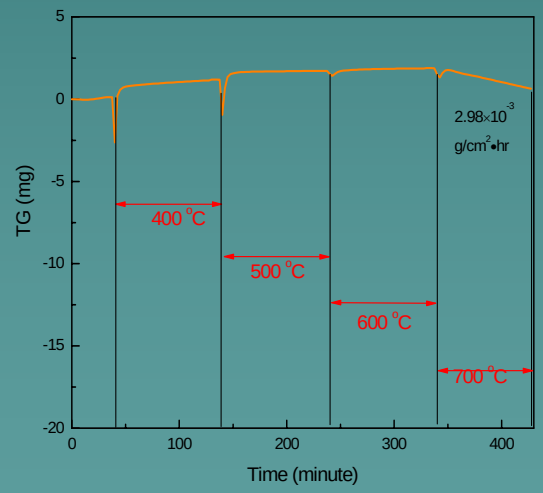
SKD covered with aerogel

TGA results of sublimation test

TG of n-SKD cube (Ti at the bottom)

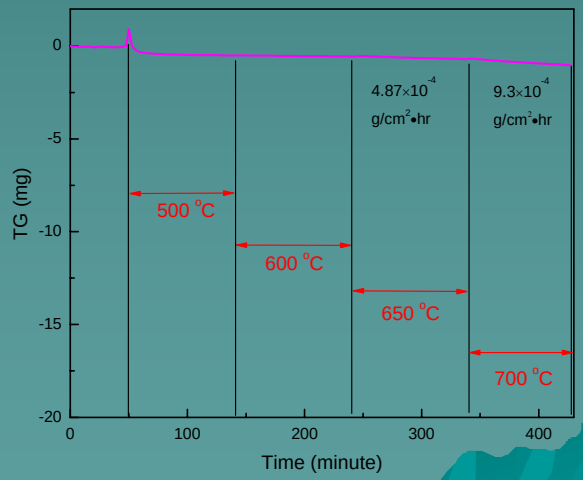


encapsulated with aerogel



TG of n-SKD cube (Ti at the bottom) encapsulated with aerogel (50 mg/cm^3)

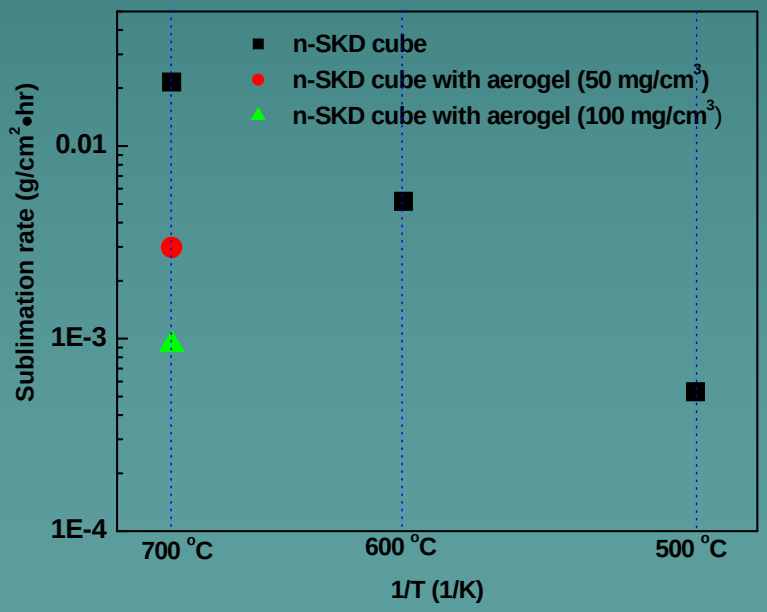
encapsulated with dense aerogel



TG of n-SKD cube (Ti at the bottom) encapsulated with aerogel (100 mg/cm^3)

Sublimation suppression

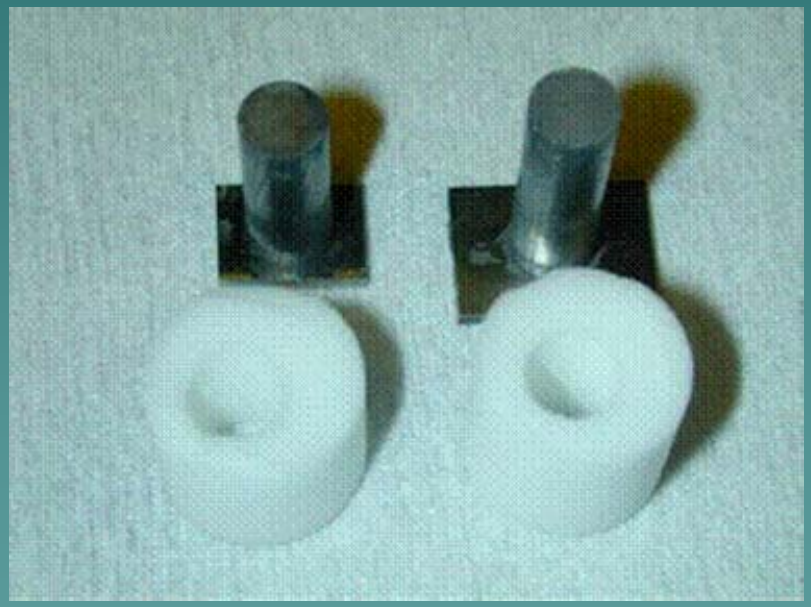
	Sublimation rate at 500 °C	Sublimation rate at 600 °C	Sublimation rate at 700 °C
n-SKD cube	5.3×10^{-4} g/cm²·hr	5.16×10^{-3} g/cm²·hr	2.15×10^{-2} g/cm²·hr
n-SKD cube encapsulated with aerogel (50 mg/cm³)	-	-	2.98×10^{-3} g/cm²·hr
n-SKD cube encapsulated with aerogel (100 mg/cm³)	-	-	9.3×10^{-4} g/cm²·hr

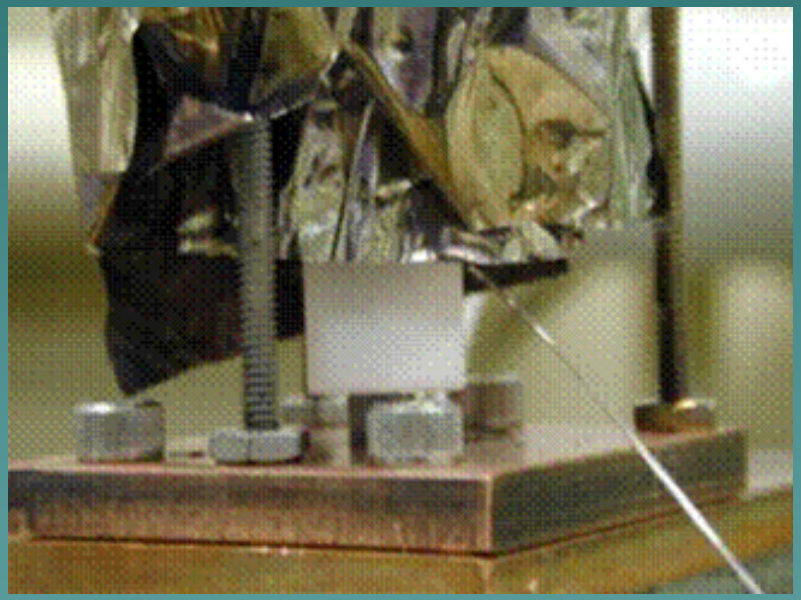


- No sublimation was detected with aerogel encapsulation at the temperature below 600 °C
- The value of sublimation rate was decreased by ~ 70 % with the use of dense aerogel (from 50 mg/cm³ to 100 mg/cm³).

Skutterudite legs coated with titania opacified aerogel tested in gradient (700 ^{o}C hot side and 25 ^{o}C cold side)

- Tested in gradient for several days, and no depletion layer detected.

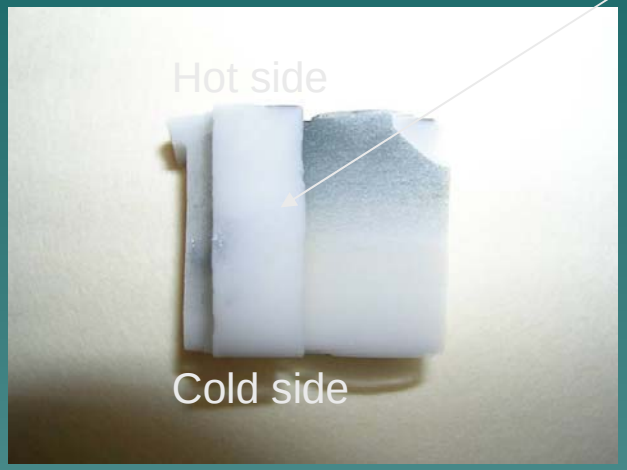


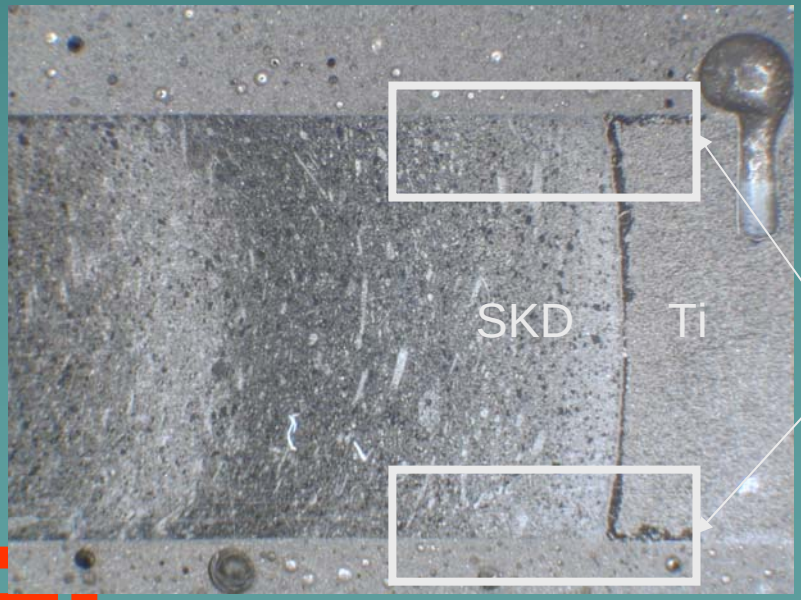


Post analysis of aerogel encapsulated n-type skutterudite

Hot side

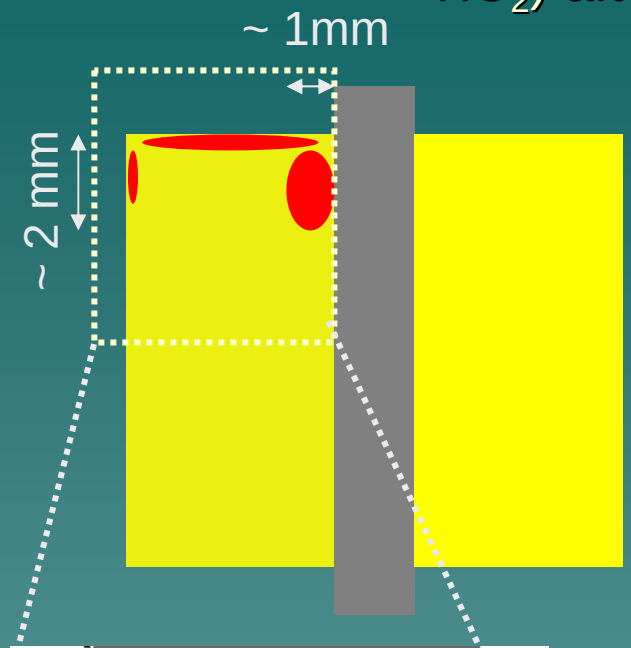
cross-sections don't indicate significant condensation



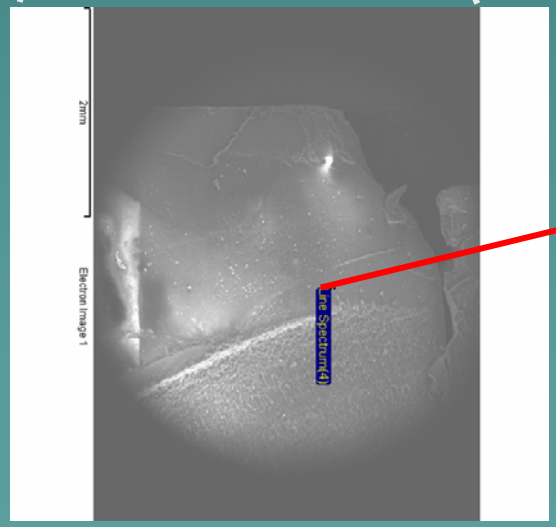


This is where depletion would be expected, but there is no apparent depletion.

EDS results (machined aerogel (150mg/cc SiO_2 and < 4 mg/cc TiO_2) after 5 day in-gradient test (n-type))



- Area represented as red color shows antimony trace.
- The antimony amount is ~ 0.2 at %
- Penetration depth is very shallow (< 1 mm after 5 day in-gradient testing)
- Top and outside skin of aerogel is believed to show antimony trace from lateral antimony sublimation.



Element	Weight %	Atomic %
C	5.02	7.86
Si	37.82	25.31
Ti	0.42	0.16
O	56.74	66.67

Summary and Future work

Summary

✓ Accurate sublimation rate measurement with the use of TGA system

✓ Promising result of sublimation suppression with aerogels

✓ Excellent thermal stability of aerogels

Future work

- Optimization of aerogel
  - Further investigation of the stability of aerogels and transport mechanism of sublimed species through aerogels
  - Developing optimized opacified aerogel with titania
  - Life time test