Vapor Growth of Indium Iodide (InI) on the International Space Station

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Overview and Outline

Overall Objective: to determine the effects of microgravity crystal growth on the material properties of halide semiconductors relevant for radiation detector applications, thus exploring pathways for future heavy metal halide processing in microgravity

- InI crystal growth experiments were conducted in the SUBSA furnace facility in the Microgravity Science Glovebox (MSG) on the International Space Station (ISS) from 2019 through 2021.
- 4 melt growth and 2 vapor growth experiments were completed. This talk describes the results of the vapor growth experiments.

Outline

- Introduction to InI properties and crystal growth
- Ground-based crystal growth and characterization
- Flight facility and procedures
- Vapor growth flight results
- Summary and conclusions

InI Applications and Properties

Applications

- Reducing agent in organic synthesis
- Component in arc discharge metal halide lamps
- IR optical materials (0.62 – 51 mm)
- X-ray and γ-ray detector material

Room temperature X-ray and γ-ray direct conversion (semiconductor) requirements

- $1.5\ \mathrm{eV} < E_g < 2.5\ \mathrm{eV}$
- average $Z > 50$
- no or low radioactivity isotopes

Room Temperature γ-ray and X-ray Detector Materials

Material	(Cd,Zn)Te	BiI_3	InI	α-HgI_2	PbI_2
Average/High Z	49.1[a]/52	60.5/83	51/53	62/80	62.7/82
N [cm^{-3}] Density [g cm^{-3}]	$1.48\cdot10^{22}$ [a] 5.78[a]	$5.90\cdot10^{21}$ 5.78	$1.33\cdot10^{22}$ 5.31	$8.48\cdot10^{21}$ 6.4	$8.05\cdot10^{21}$ 6.16
Band Gap [eV]	1.5-1.6	1.67	2.00	2.14	2.32
Resistivity [Ω cm]	10^{10}	10^{11}	10^{12}	10^{13} -10^{14}	10^{13}
Space Group/ Structure	$F\bar{4}3m - T_d^2$ Zincblende type	$R\bar{3} - C_{3i}^2$ Layered[c] ⊥ **c**	$Cmcm - D_{2h}^{17}$ Layered ⊥ **b** TlI type[d]	$P4_2/nmc - D_{4h}^{15}$ Layered ⊥ **c**	$P\bar{3}m1 - D_{3d}^3$ Layered[f] ⊥ **c** CdI_2 type
Melting Point [°C]	1100	408	365	259[e]	410
Bond Energy [eV]	1.10	2.26	3.43	0.36	2.04
Hardness [MPa] Knoop/Vickers	HK 92	HV 12-15	HK 27	HK <10 HV 22	HgI_2<HK<10
Crystal Growth Methods	Bridgman, THM, PVT[b]	Bridgman, PVT	Bridgman, CZ, PVT	PVT, solution	Bridgman, CZ, PVT, solution, gel

[a] 10% Zn
[b] mostly CdTe

[c] Polytypism, stacking faults

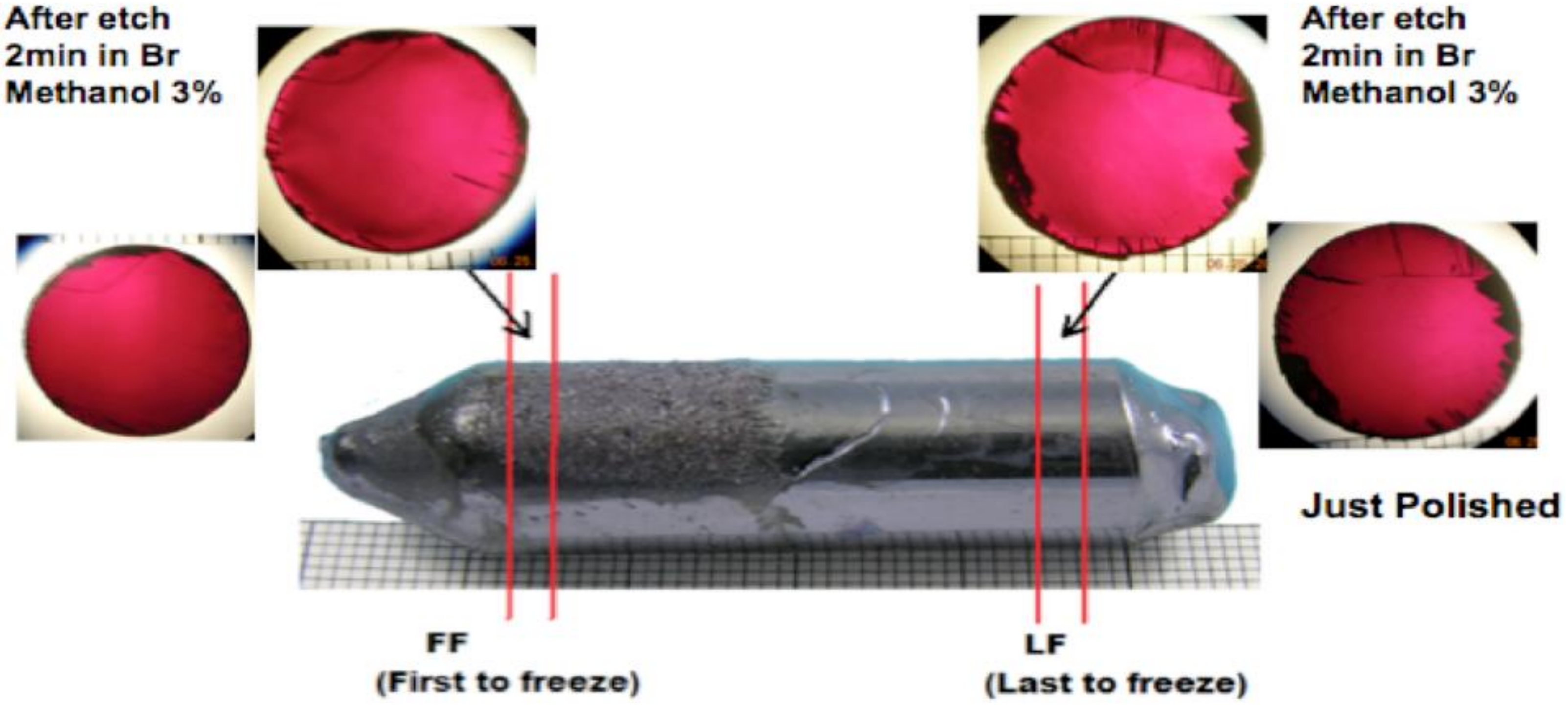
[d] distorted NaCl structure

[e] destructive phase transition at 127°C

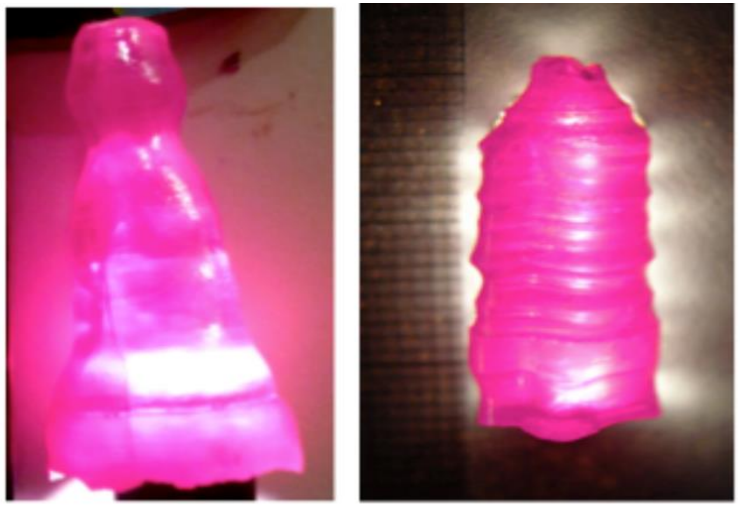
[f] Polytypism, stacking faults

InI Crystal Growth

- The low melting point and congruent sublimation of InI allow both melt growth and vapor growth.
- InI is not toxic



VB-grown crystal and wafers (IIT)



CZ-grown crystals (IIT)

Vapor Growth

Vapor growth

- Purifies the starting material
- Reduces the number of point defects due to the lower growth temperature

Vapor growth under µg

- Allows growth under purely diffusive conditions, as shown for the similar HgI_2 system [1, 2]
- Lead to a significantly increased μ-τ product in the case of HgI_2 [3]

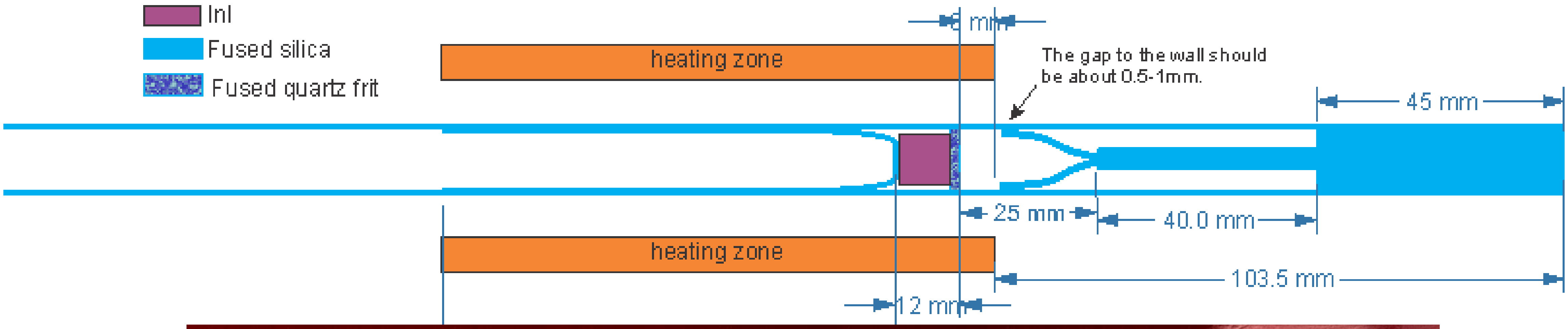
[1] M.Piechotka, E. Kaldis, G. Wetzel, H.-J. Schneider, W. Buff, M. Tardy, H. Stanna: Kinetics of physical vapor transport at low pressure under microgravity conditions: I. DCMF flight hardware and experimental conditions. J. Crystal Growth 193 (1998), 80-89

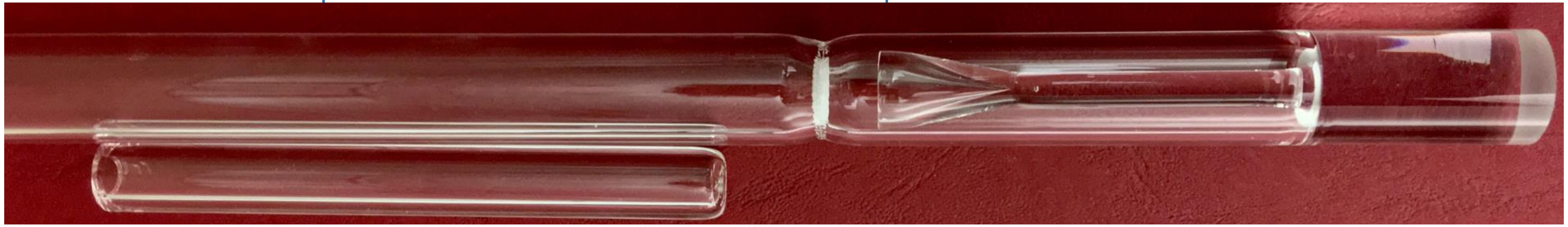
[2] M. Piechotka, E. Kaldis, G. Wetzel, A.Flisch: Kinetics of physical vapour transport at low pressure under microgravity conditions: II. Results of the DCMF space experiment. J. Crystal Growth 193 (1998), 90-100

[3] L. Van den Berg and W.F. Schnepple: Mercuric iodide crystal growth in space. Nucl. Instrum. A 283 (1989), 335-338

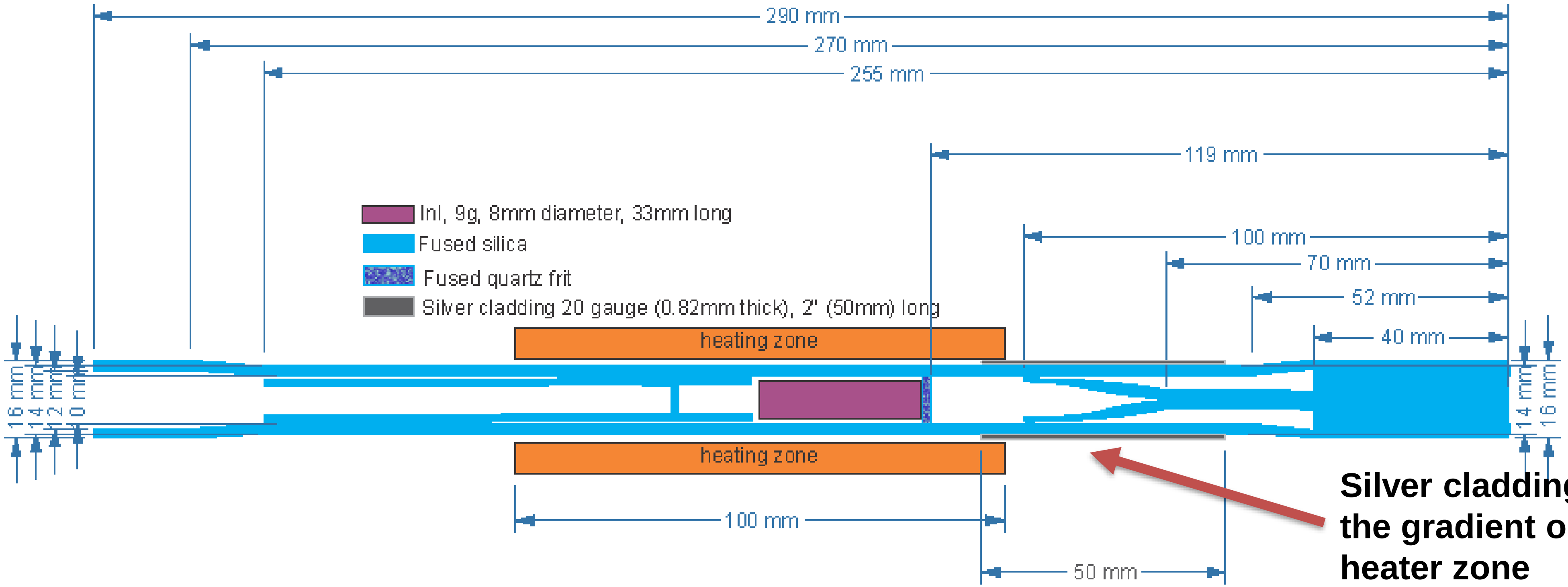
Vapor Phase Growth Process (Initial Design)

Modified Markov method setup (semi-closed system)

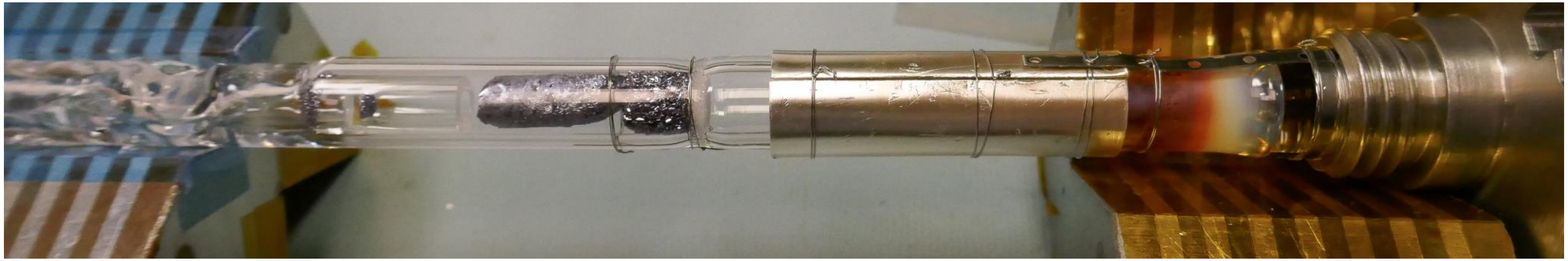




Vapor Phase Growth Process (Final Design)

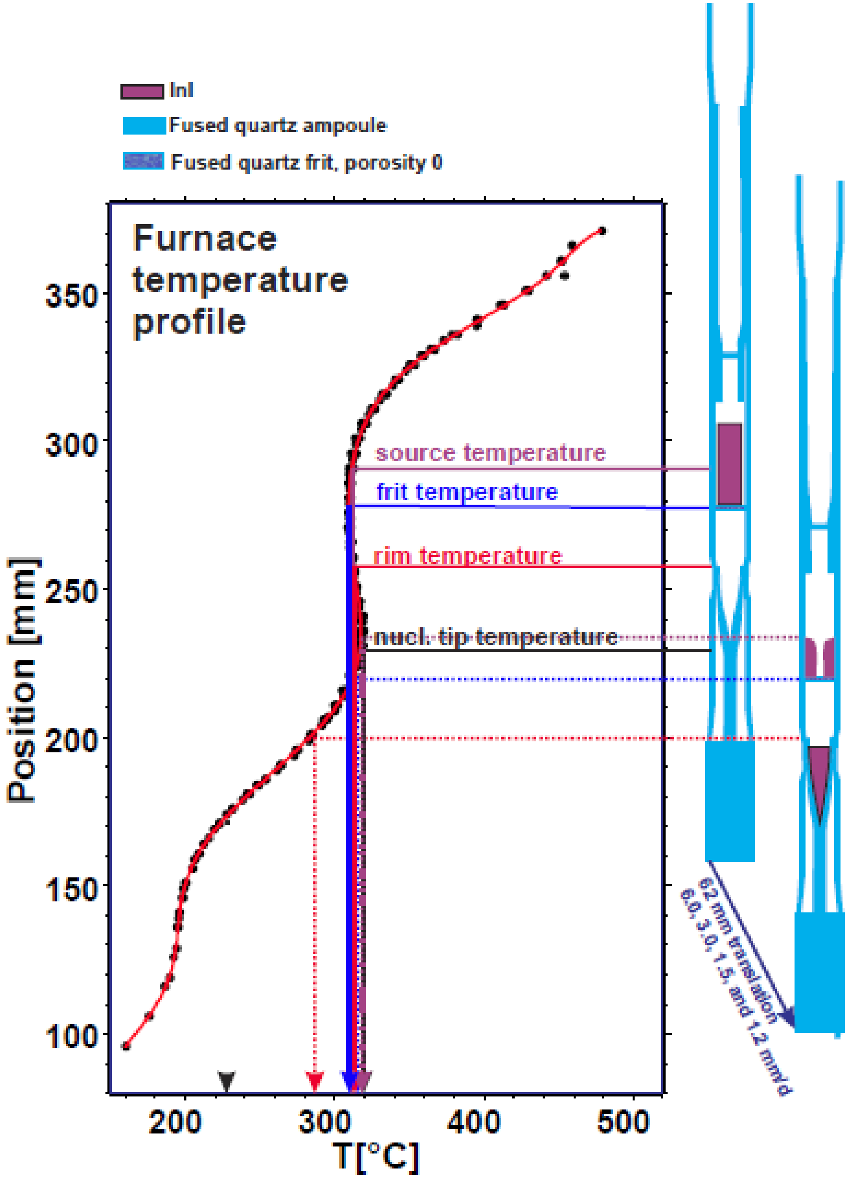


Silver cladding to reduce the gradient outside the heater zone

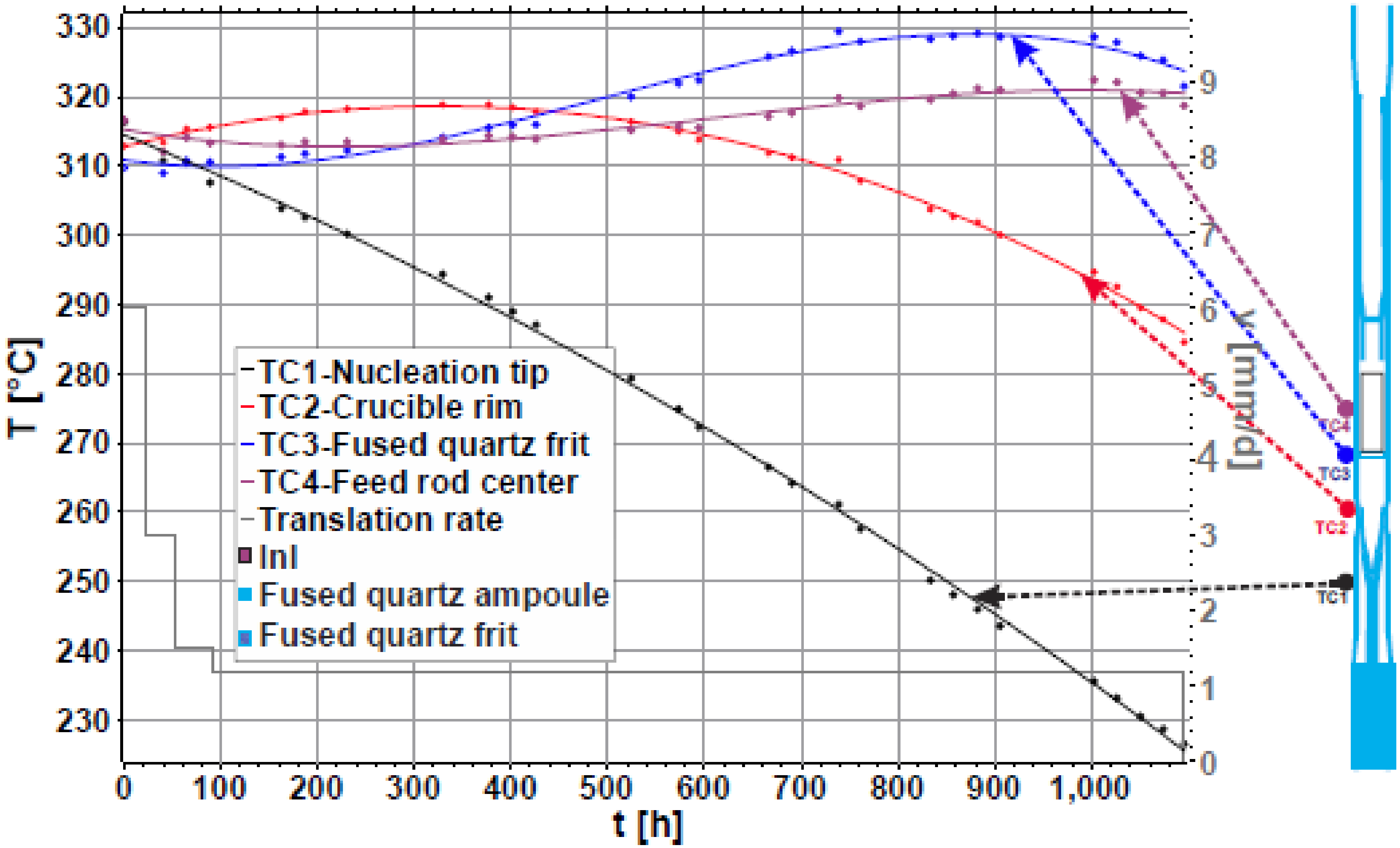


Furnace Temperature Profile in Earth Laboratory

- Furnace temperature profile resulted from 6-zone furnace at NASA Marshall Space Flight Center.
- Near isothermal conditions in source region.
- Temperature increase of 20-30K/cm above the source region to avoid or reduce sublimation into the empty space under the sealing plug.
- A temperature “hump” of 5-7 K between source and the growth region, including nucleation tip and crucible rim.
- A gradient zone to promote nucleation and growth in the translated ampoule with a gradient of approximately -20 K/cm.
- Translation rate: 1.2 – 1.5 mm/day.



Temperature Evolution During Growth



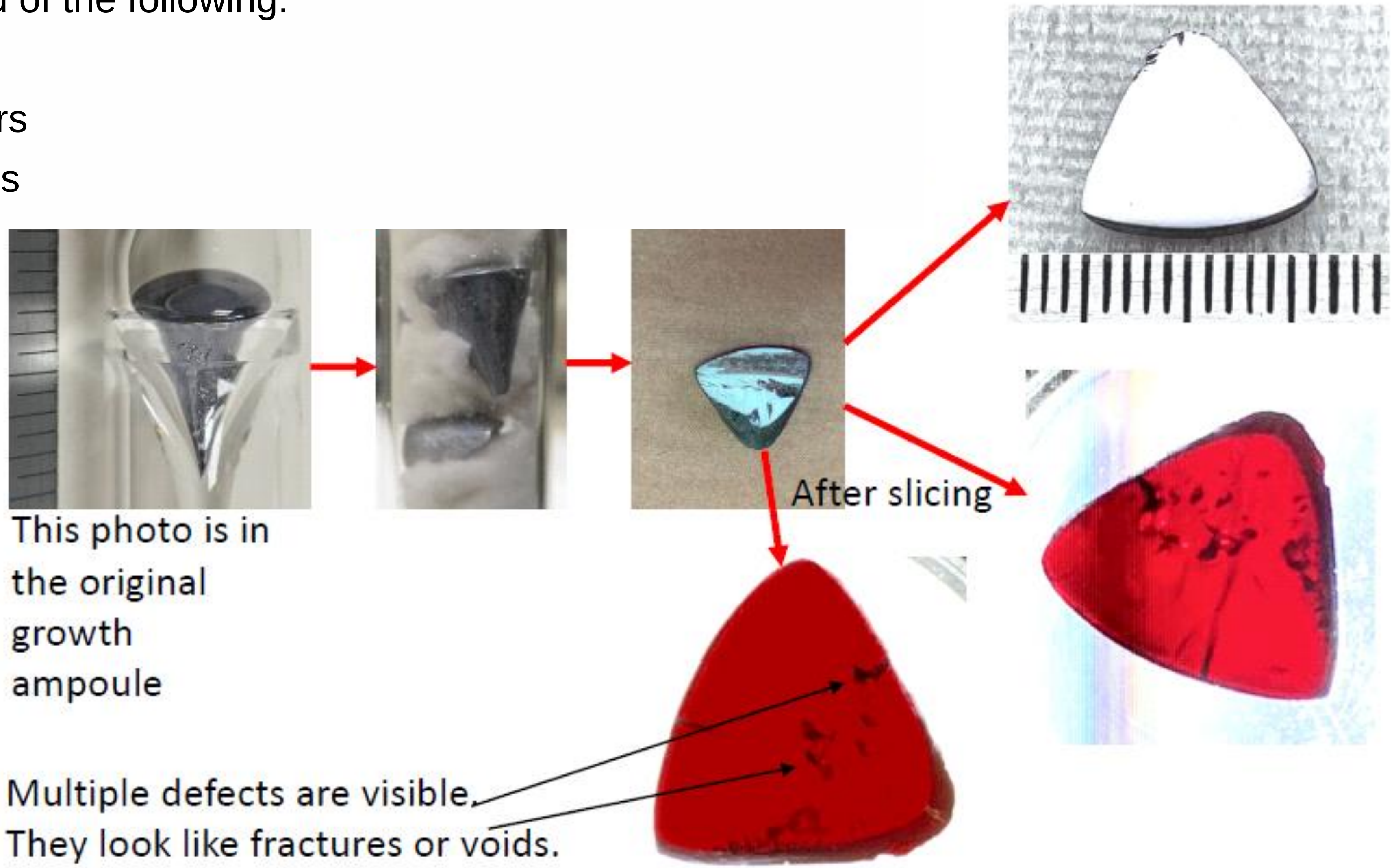
InI Single Crystals grown in Earth Laboratory

InI-7

Ground InI Crystal Characterization

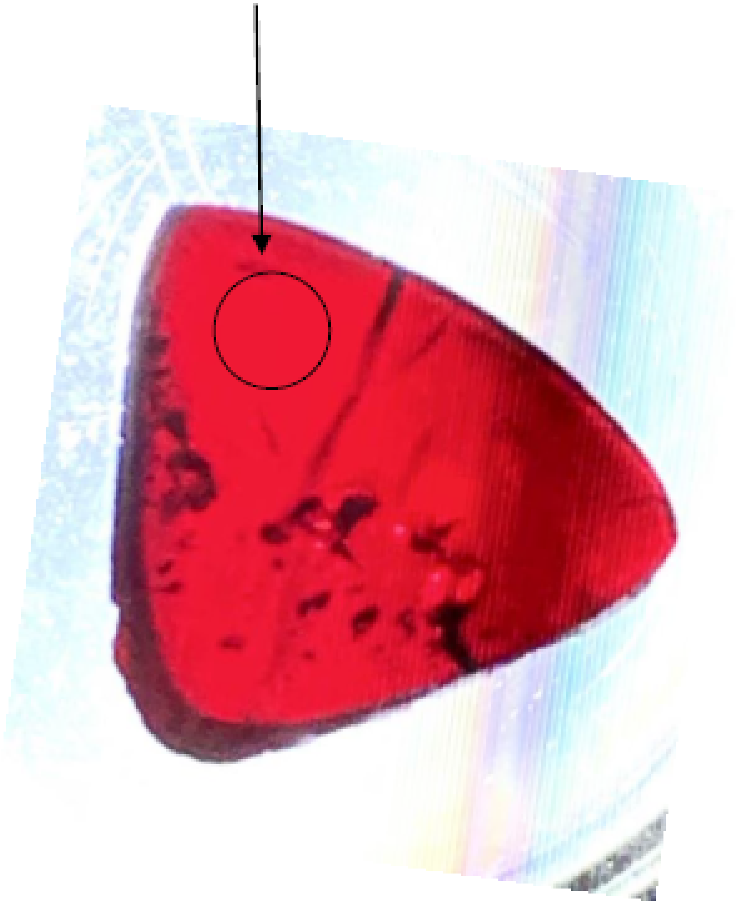
Ground characterization consisted of the following:

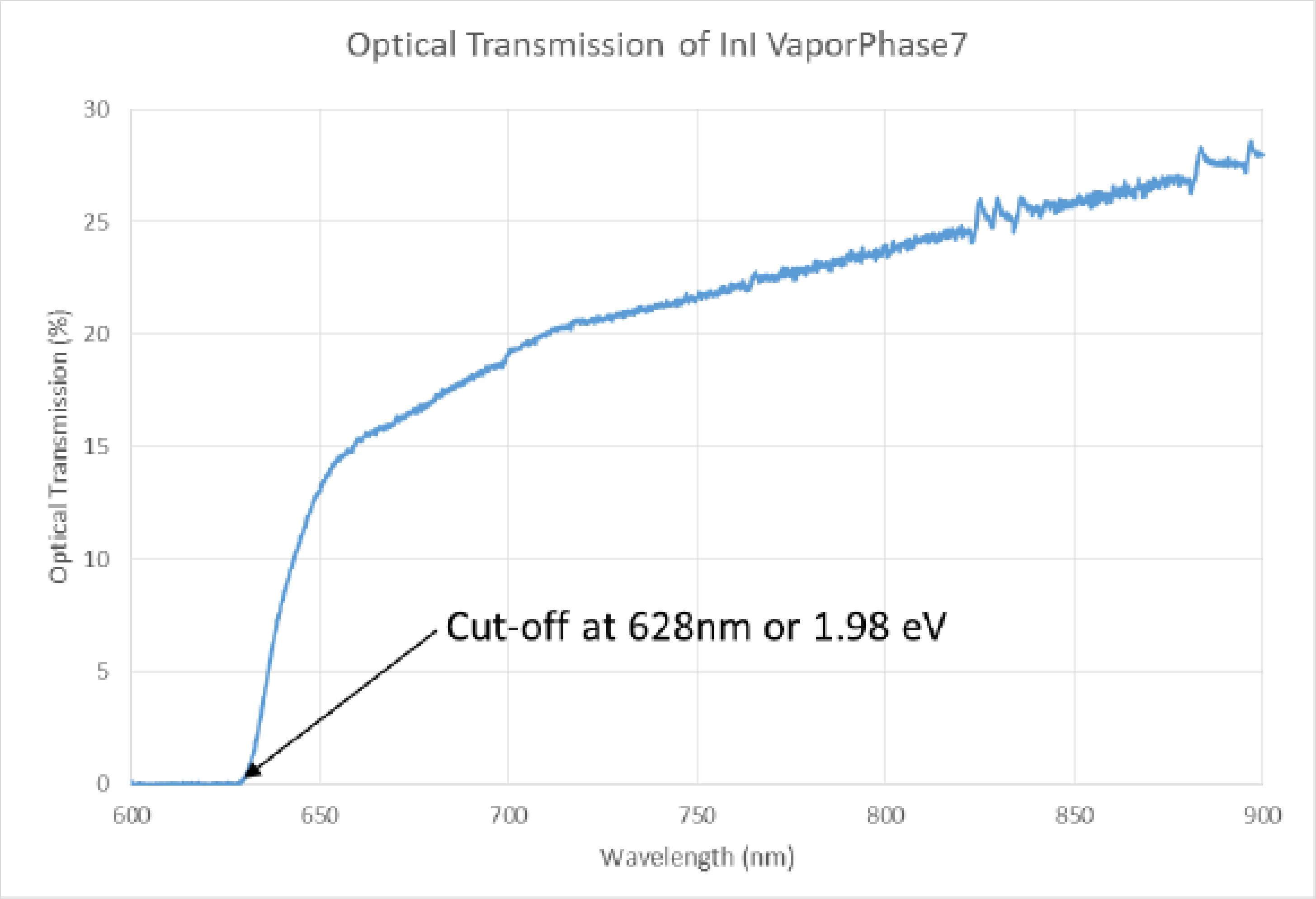
- Optical transmission
- Cutting and polishing into wafers
- Application of electrical contacts
- Electrical measurements



Ground InI Crystal Optical Transmission

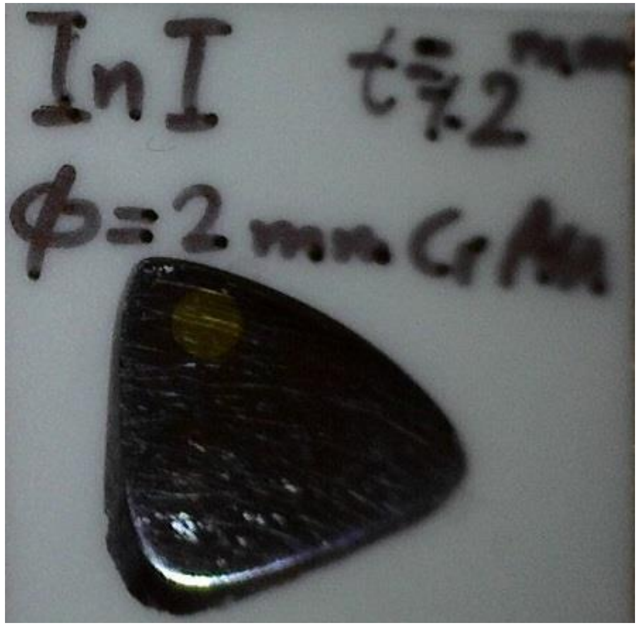
Location of electrical contact.



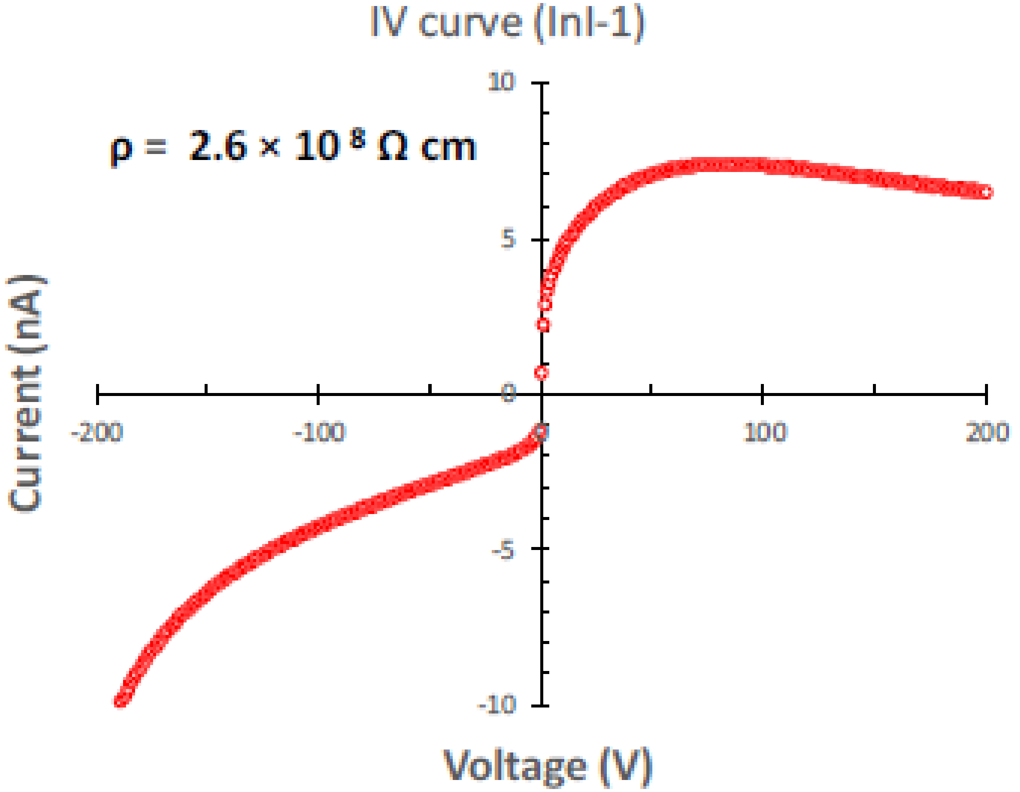


Electrical Contacts

- 2 mm diameter CrAu was deposited as contacts in an area of the wafer with few visible defects
- Pd wires and carbon paste were used to wire the sample
- No gamma response was observed from irradiation from Cs-137.



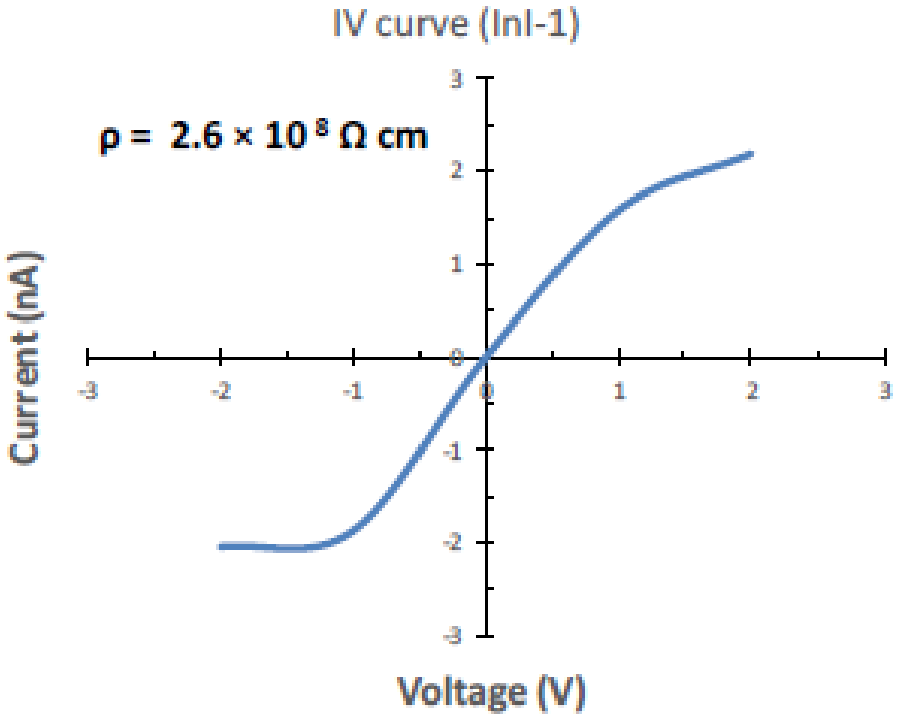
Resistivity Results



- The resistivity calculation was done based on the IV curve and the equation below.
- It is slope of the IV curve, was estimated based on a linear fitting to the curve near the origins and within +/- 2 V

$$R = \frac{\rho L}{A}$$

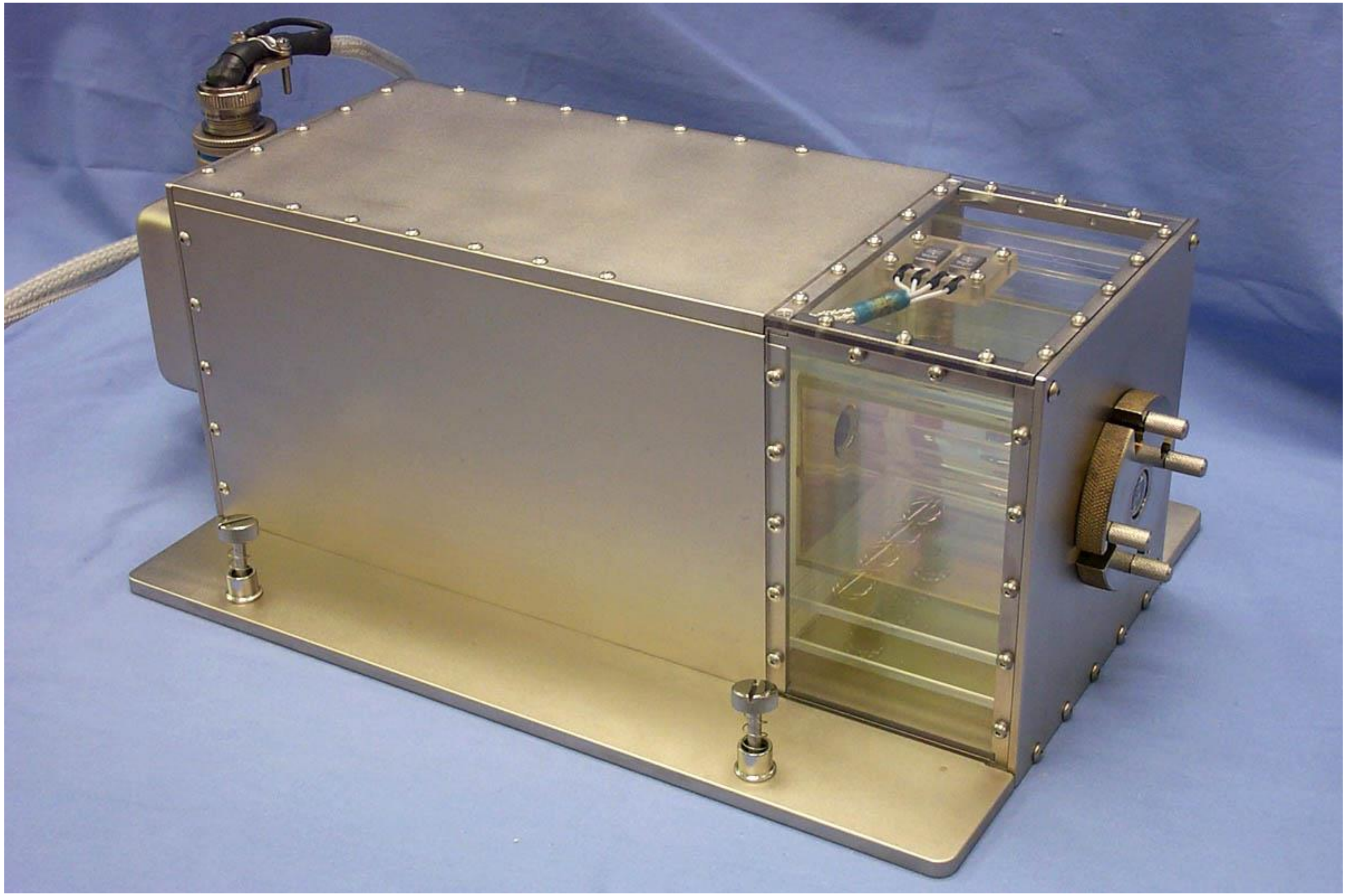
ρ = resistivity
L = length
A = cross sectional area



InI Flight Ampoule Processing

Sample	Method	Dopant	Cladding	Processing Date
SUBSA-01	Melt	Ga, 1%	Silver	4/11/2019
SUBSA-03	Melt	Ga, 1%	Silver	4/9/2019
SUBSA-05	Melt		Sapphire	4/19/2019; 1/4/2021
SUBSA-07	Melt		Sapphire	4/14/2019
SUBSA-09	Vapor		Silver	3/7/2019
SUBSA-10	Vapor		Silver	1/8/2021

SUBSA Hardware

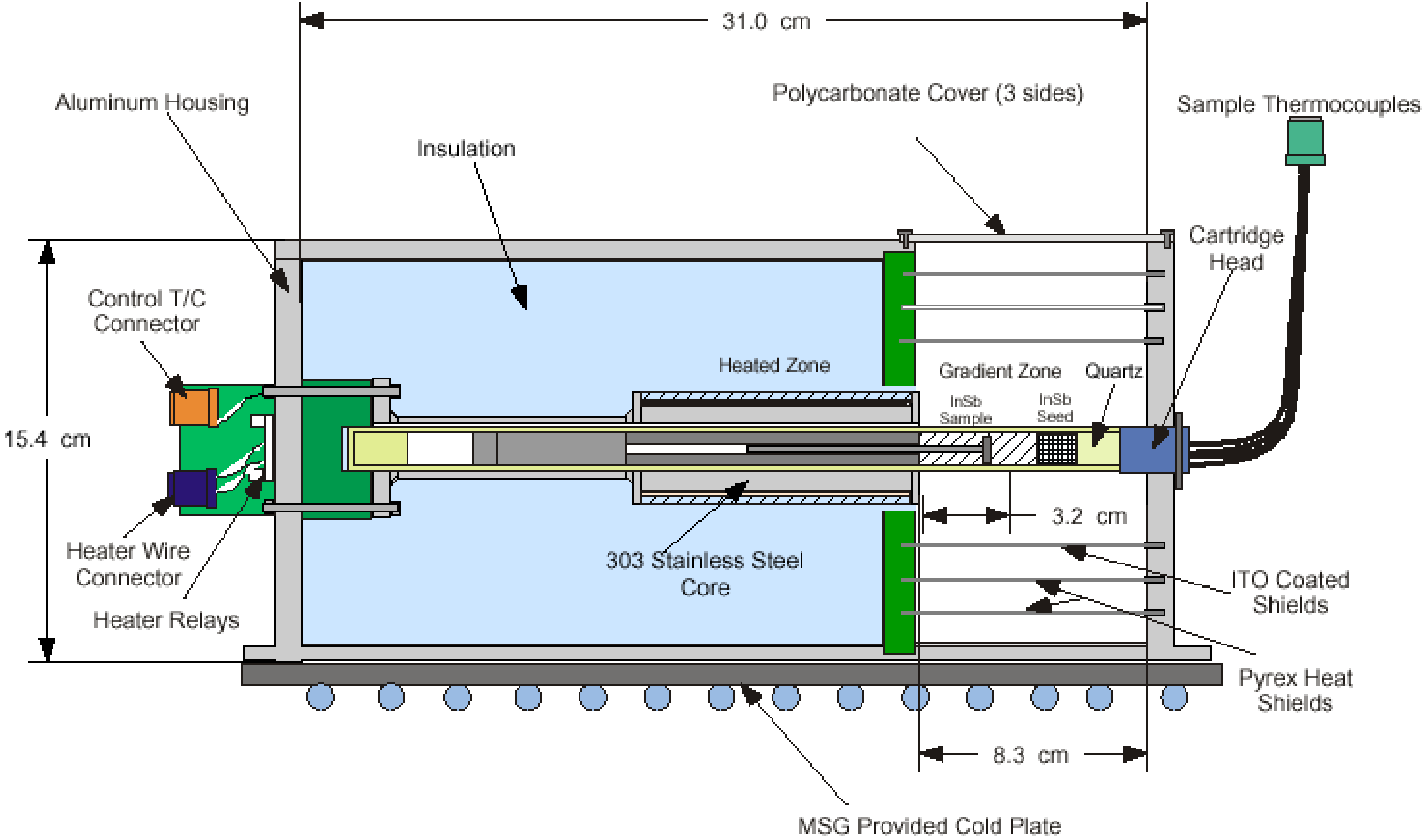


DaqPad

Process Control Module

The SUBSA hardware consists of a single zone furnace and other power control and data acquisition boxes that are designed to operate inside the ISS MSG

SUBSA Internal View

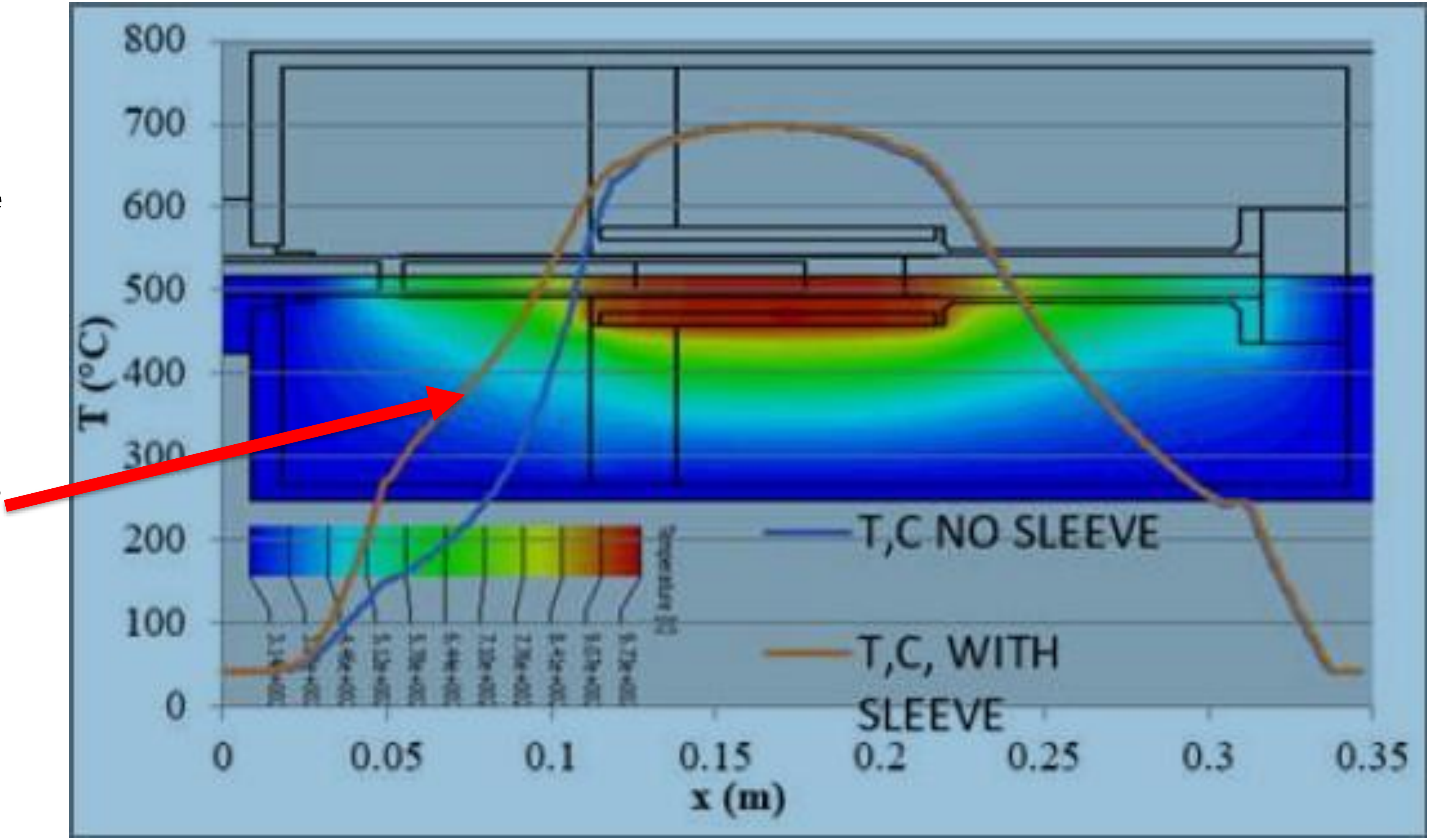


To Scale

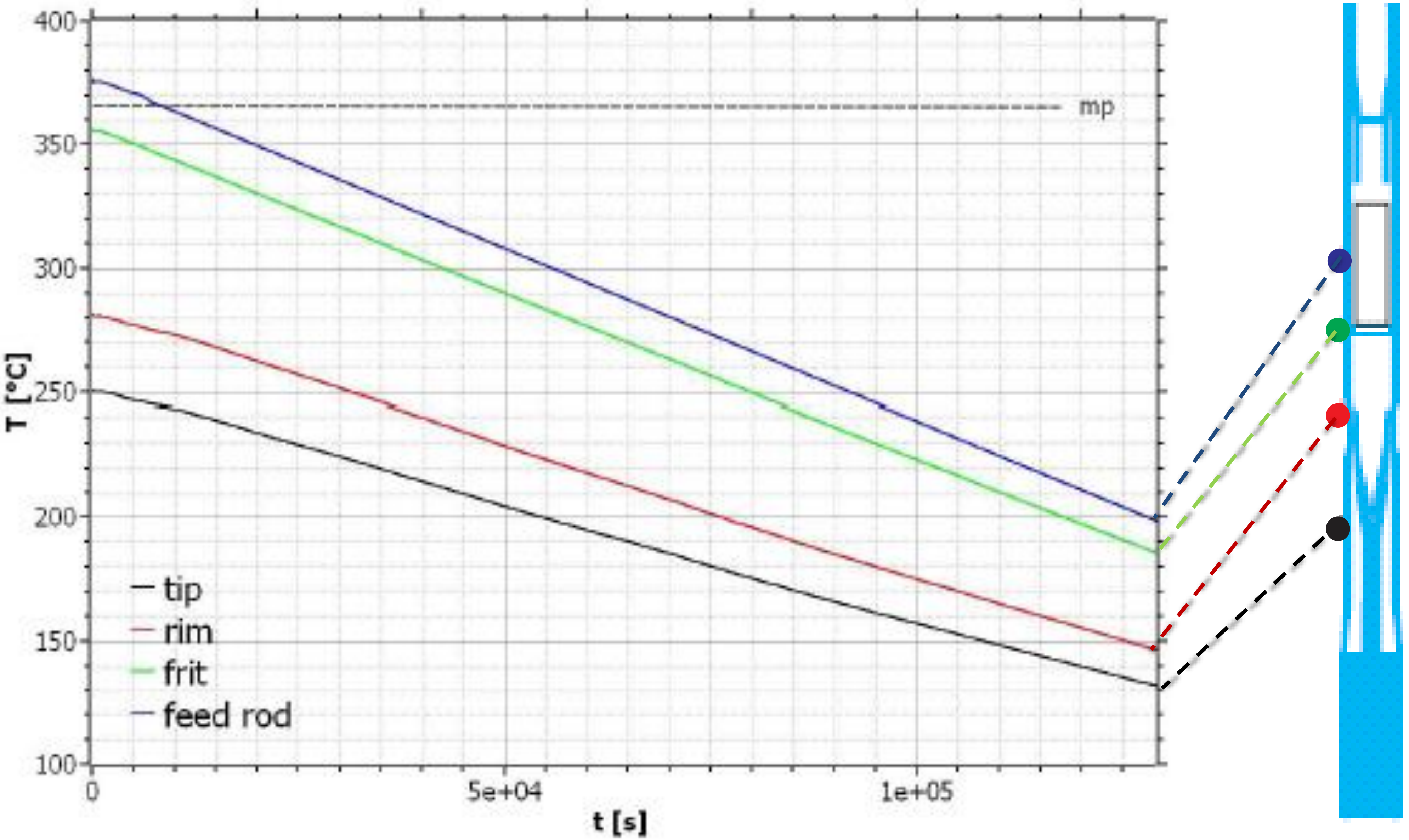
SUBSA Temperature Profile

Vertical Gradient Freeze: single heater temperature is lowered in time to cause position of melt point to move resulting in crystal growth

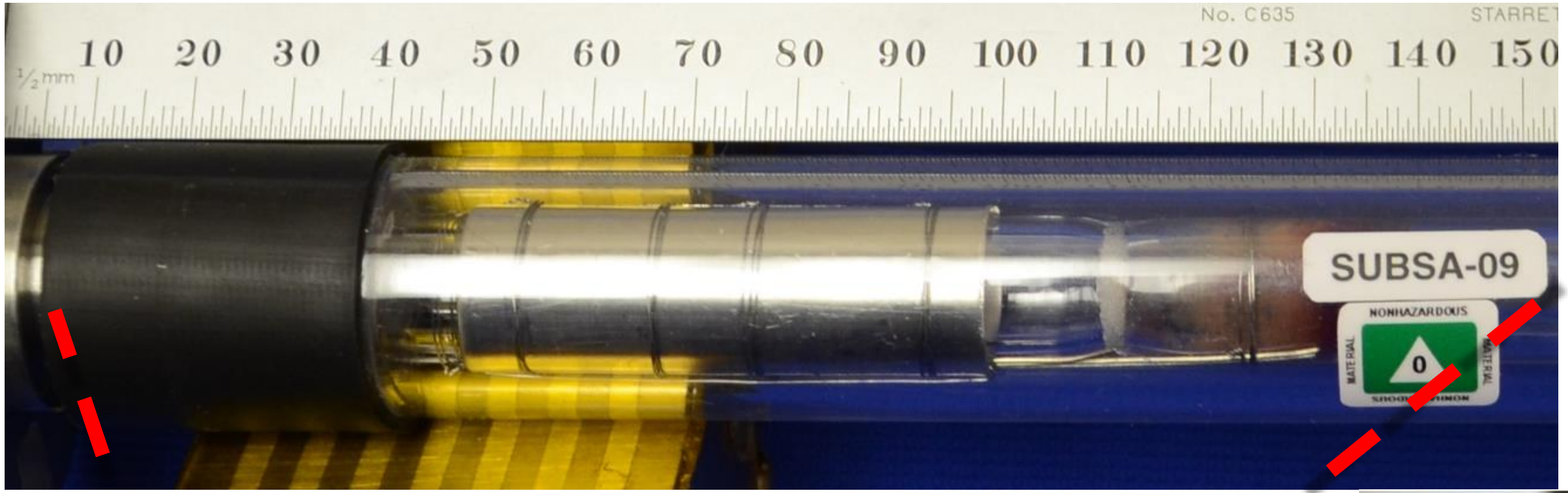
Thermally conducting sleeves added to ampoules to decrease thermal gradient over samples

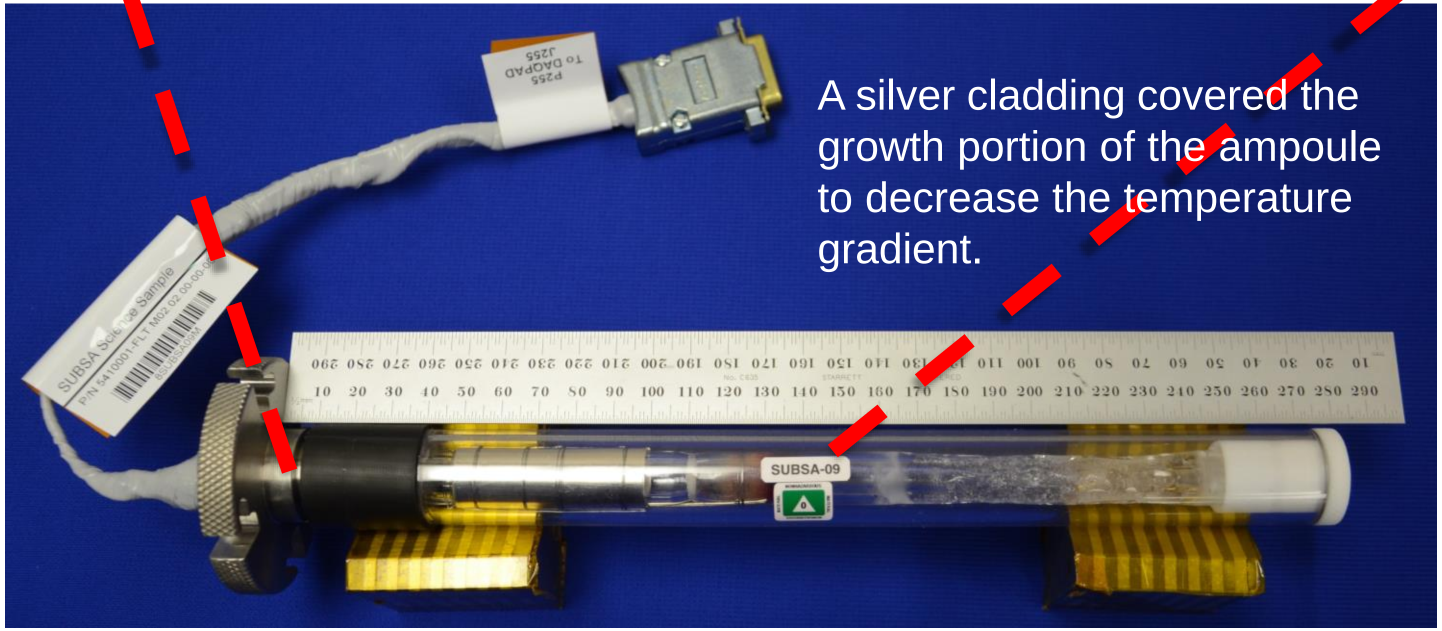


TC Temperatures During Growth in SUBSA with Ag Cladding



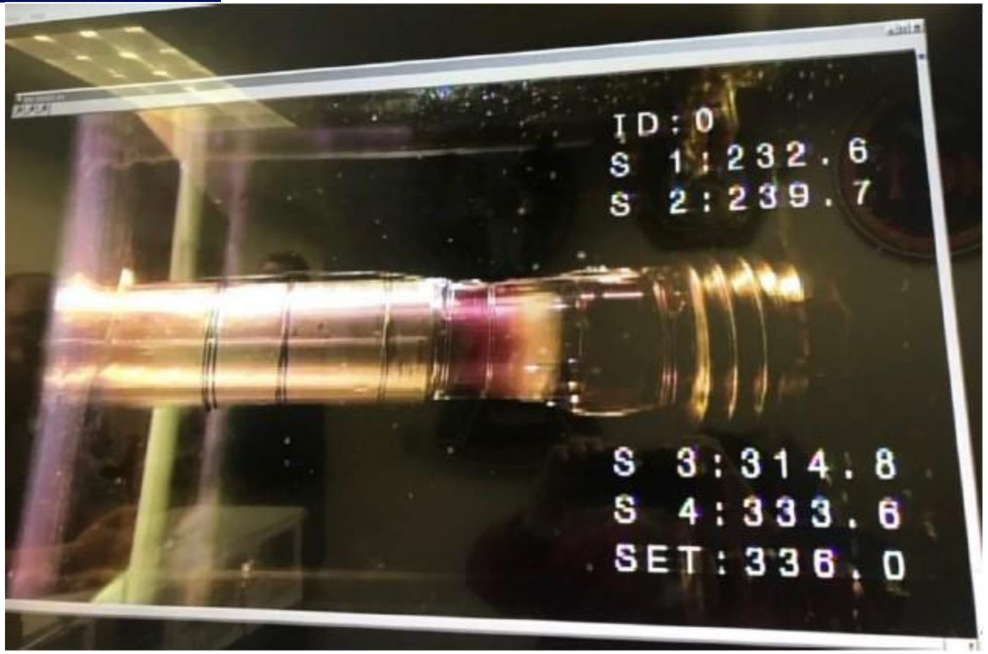
SUBSA PVT Flight Ampoule (SUBSA-09)





A silver cladding covered the growth portion of the ampoule to decrease the temperature gradient.

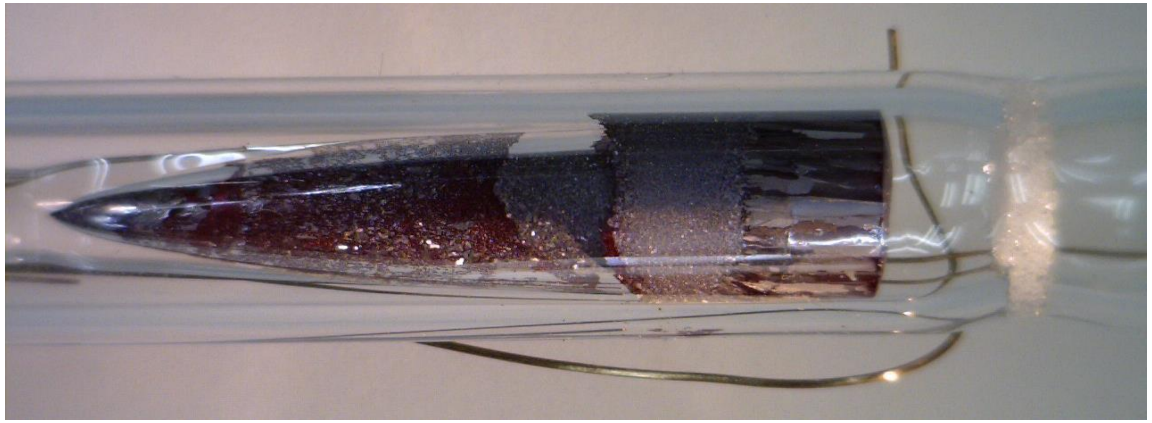
Screenshot of SUBSA-09 during flight operations

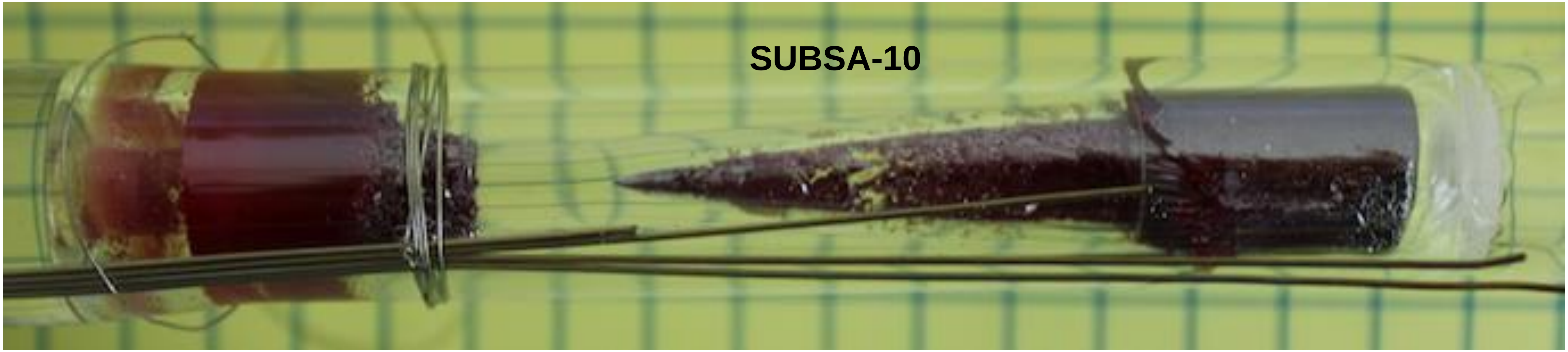


SUBSA PVT Flight Crystal Growth Results

SUBSA-09

SUBSA-09

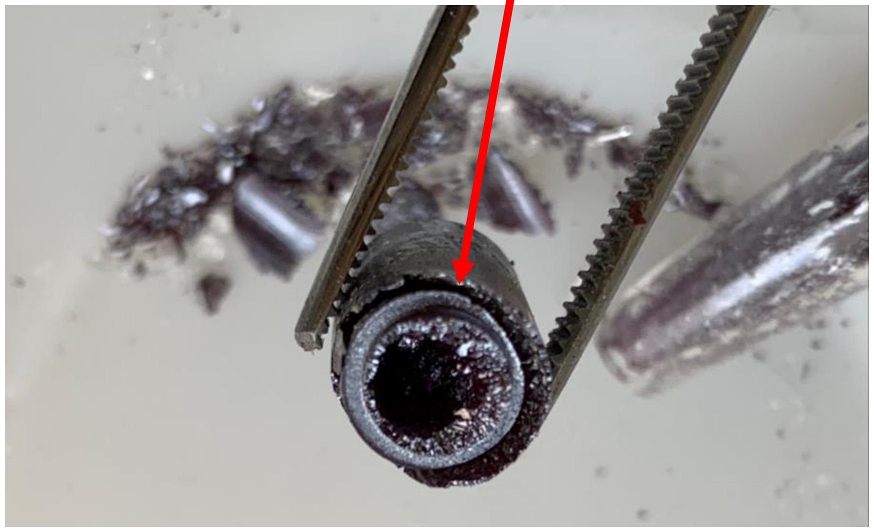




SUBSA PVT Flight Crystal Growth Results

Observations

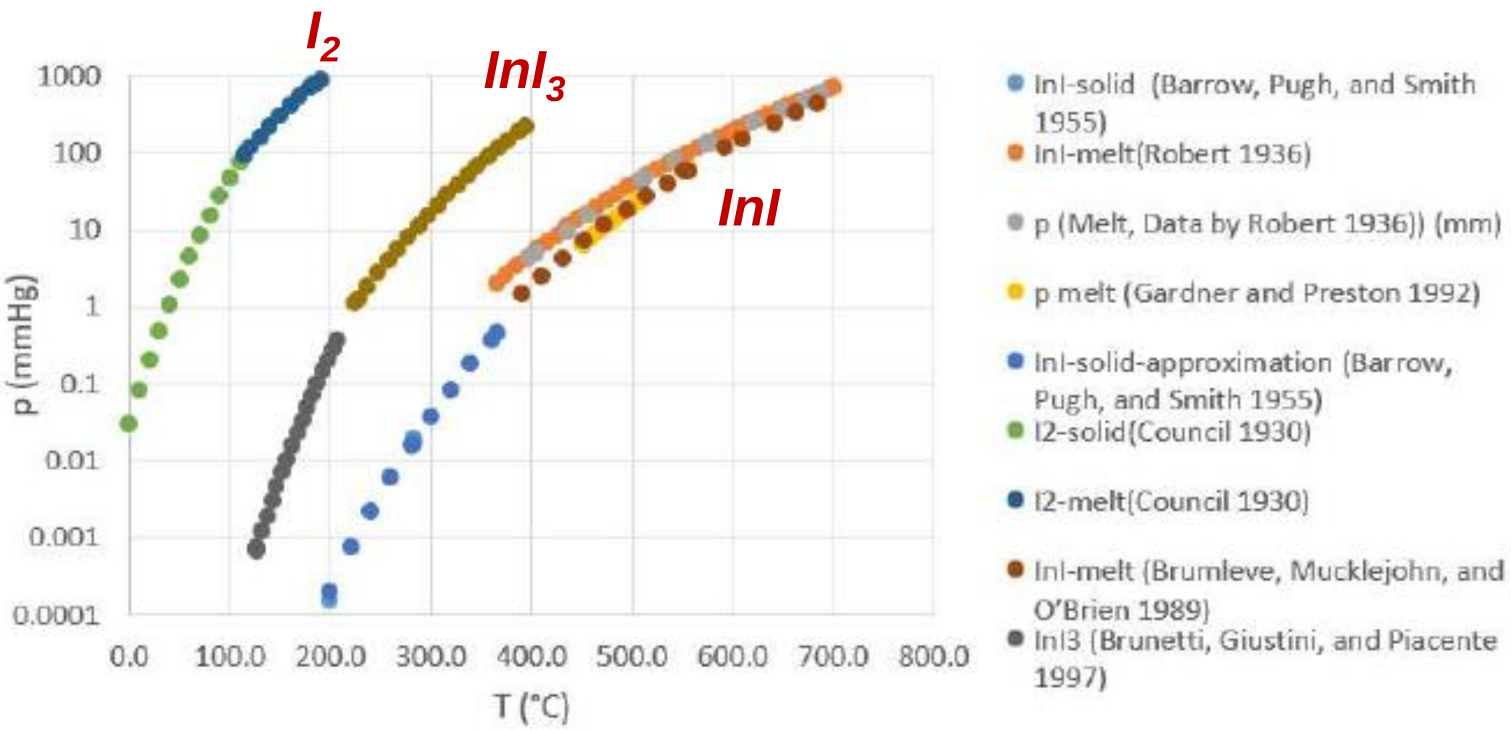
- SUBSA-09 and SUBSA-10 gave similar results under similar growth conditions
- Multiple nucleation sites between bottom of cone and rim
- Large amount of growth above rim and below frit on side of ampoule leaving void in center
- Not possible to obtain wafers for characterization
- Conclusion: the temperature gradient resulting from the single zone furnace is too large, even with silver cladding, to enable well-controlled single crystalline growth



Iodides InI, InI_2, InI_3

- InI_2 and InI_3 can be formed from InI oxidation.
- Higher vapor pressures of higher iodides will lead to earlier and larger vapor transport
- Existence of higher iodides will lead to formation of bubbles in the InI melt.
- On Earth, bubbles in melt growth are seldom observed, indicating that they float up due to density difference.
- In space, buoyancy is absent and bubbles are trapped.

$$4InI + 3O_2 \leftrightharpoons 2In_2O_3 + 2I_2;$$
$$4InI + 2I_2 \leftrightharpoons 2In^{+}In^{3+}I_4 = 2In_2I_4 = 4InI_2;$$
$$4InI + 2I_2 \leftrightharpoons 2InI_3;$$



Summary and Conclusions

- Growth of faceted transparent InI single crystals was achieved on Earth and attributed to the superior growth conditions including the optimized temperature profile in the multi-zone furnace and ampoule translation.
- Two InI vapor growth experiments were conducted on the ISS in the SUBSA furnace located in the Microgravity Science Glovebox (MSG).
- The flight SUBSA furnace had a single zone, growth by gradient freeze through lowering the furnace temperature, and no translation.
- Addition of a silver sleeve did lower the temperature gradient but not low enough for optimal crystal growth.
- The flight experiments resulted in polycrystalline samples.

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