Growth of InSb and InI crystals on Earth and in Microgravity

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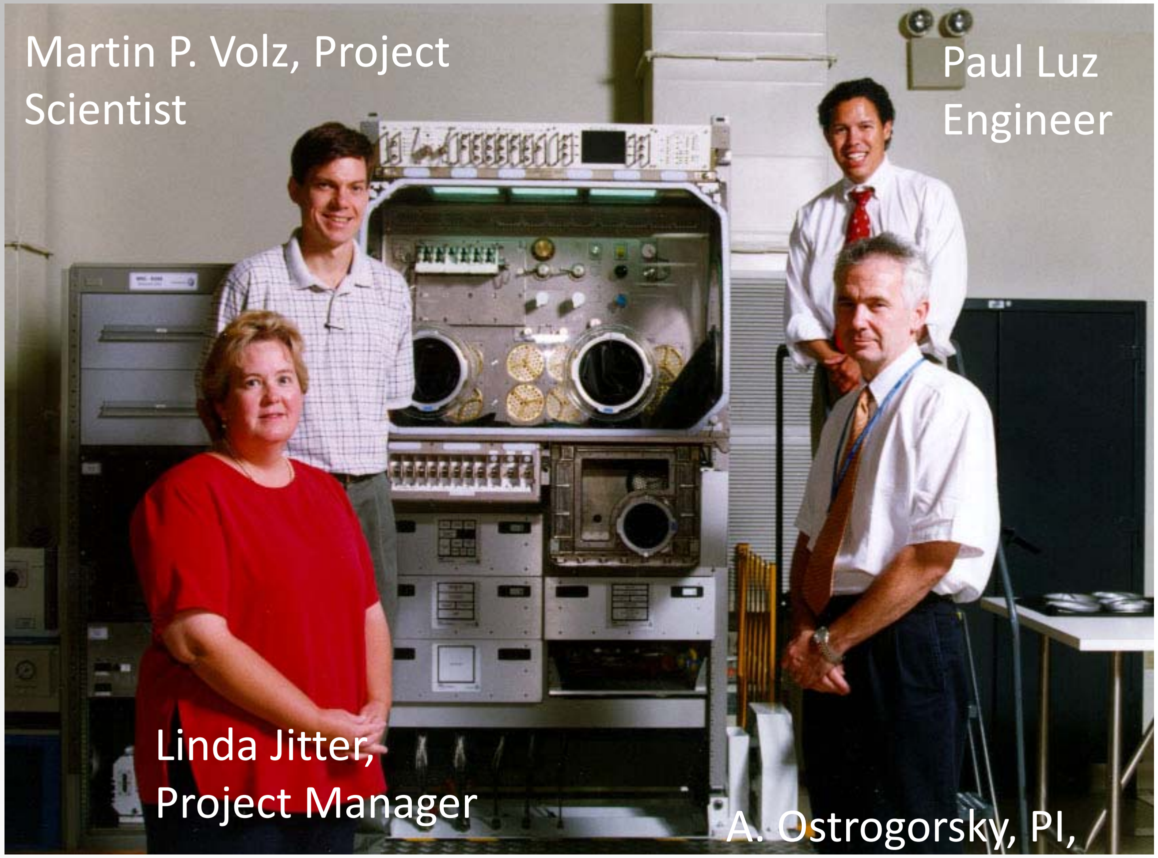
1. Te and Zn doped InSb: NASA (1995-2004)

2. InI DoE NNSA (2005-2015);
CASIS/NASA (2015-2017)

NNSA
National Nuclear Security Administration

SUBSA: Solidification Using a Baffle in Sealed Ampoules

- *1995-2004*
- SCR 1998
- Design review 2000
- Endeavour, Expedition 5, 2002.
- Seven Te- and Zn-doped InSb crystals were grown.



SUBSA Design review 6/8/2000

SUBSA HARDWARE AT AT GLANCE

TecMasters Inc

Cartridge head and 4 TCs

LabVIEW 6i processes data on MSG Laptop Computer

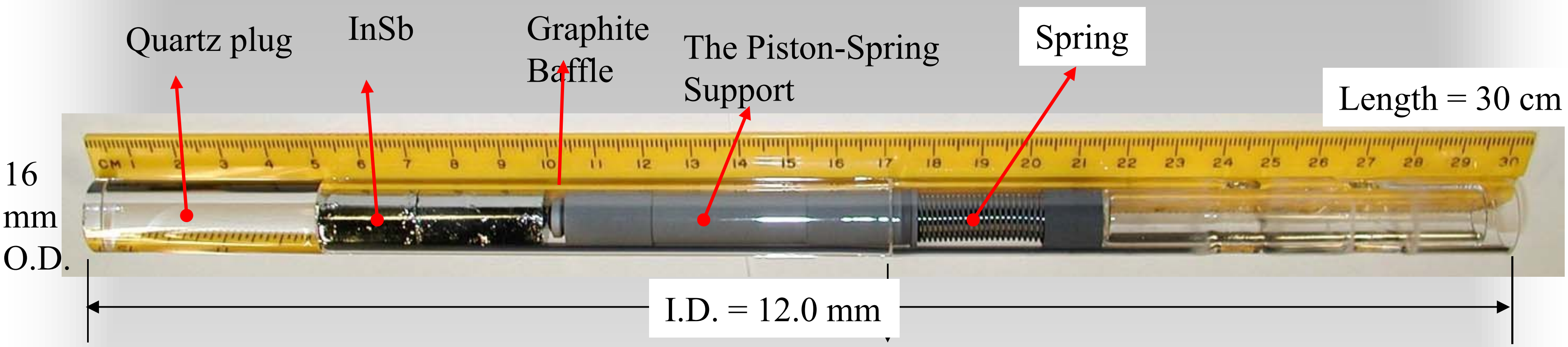
It's a Boy!!
Born May 8, 2001 at 10:35 p.m.
Weight: 14 lbs, 9 oz; Length: 15 inches

1 DaqPad

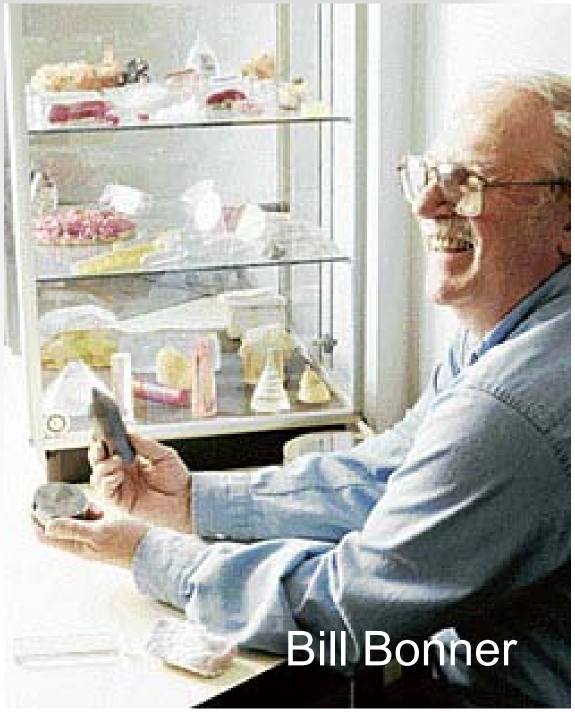
1 Process Control

Video Camera

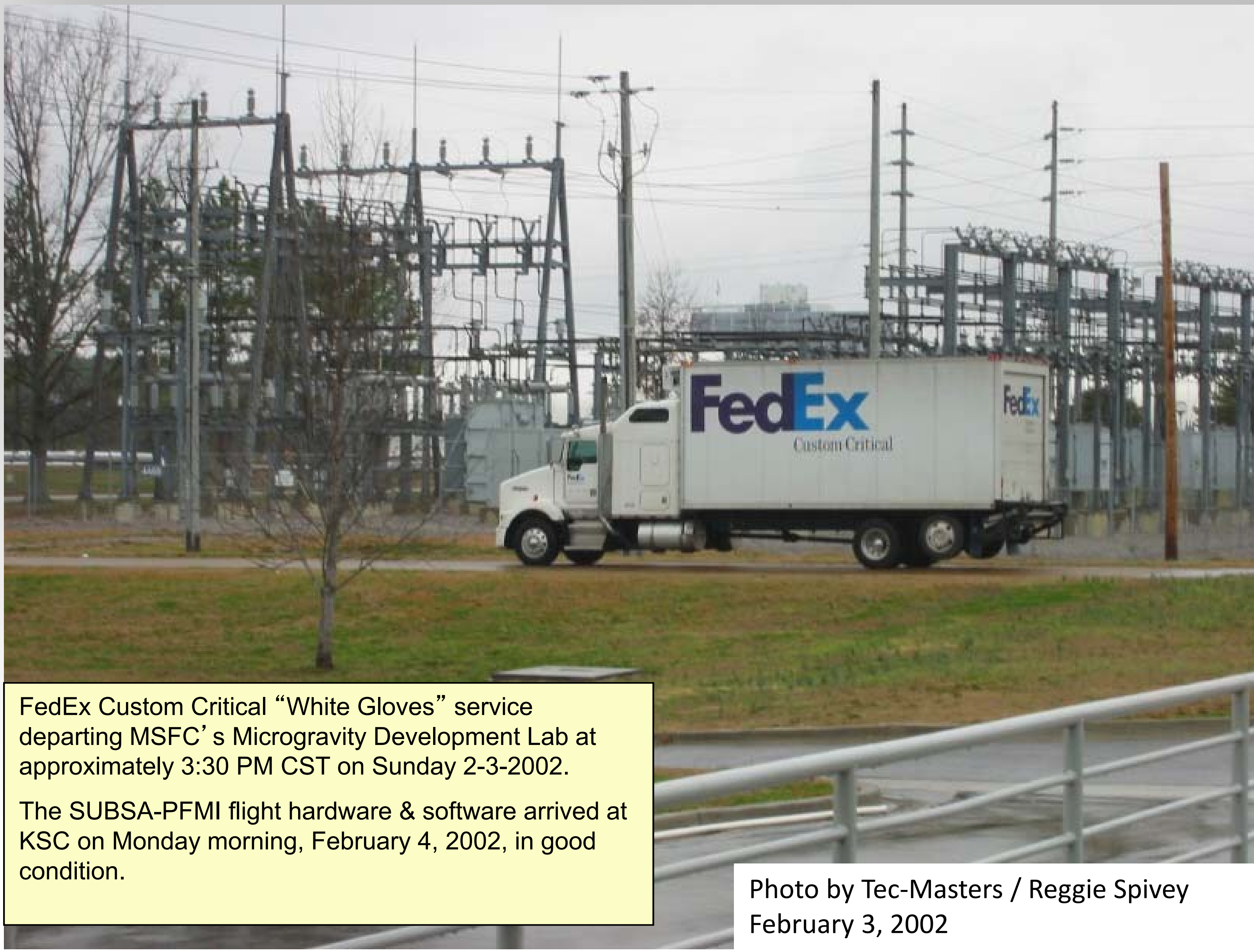
SUBSA AMPOULE ASSEMBLY



- InSb seed
- 50g InSb, doped with Te or Zn (MP 512 C)
- Sealed under vacuum.



SUBSA Status on Sunday 2/3/2002



FedEx Custom Critical “White Gloves” service departing MSFC’s Microgravity Development Lab at approximately 3:30 PM CST on Sunday 2-3-2002.

The SUBSA-PFMI flight hardware & software arrived at KSC on Monday morning, February 4, 2002, in good condition.

Photo by Tec-Masters / Reggie Spivey
February 3, 2002

Crew of the Expedition Five

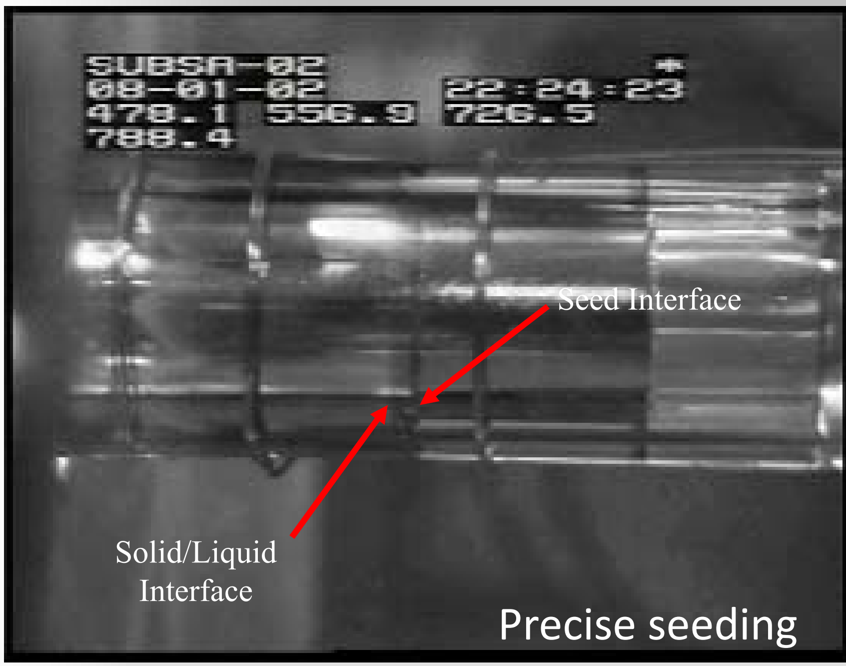
June 5, 2002. Shuttle Endeavour, Flight UF-2 -STS-111

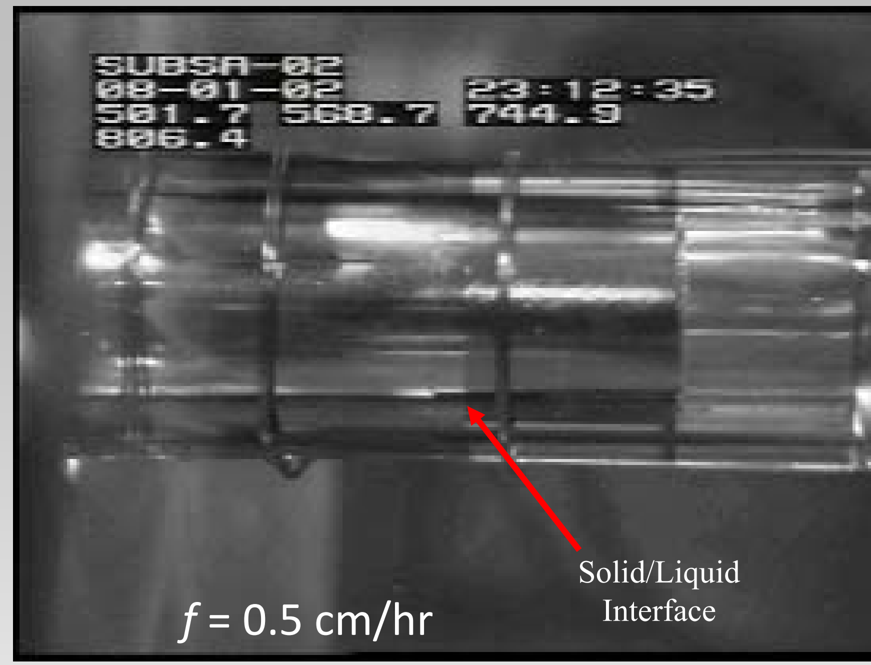
Valery Korzun
Expedition commander

Dr. Peggy Whitson,
flight engineer, USA,
payload specialist

Sergei Treschev
flight engineer

CONTROL OF seeding and growth



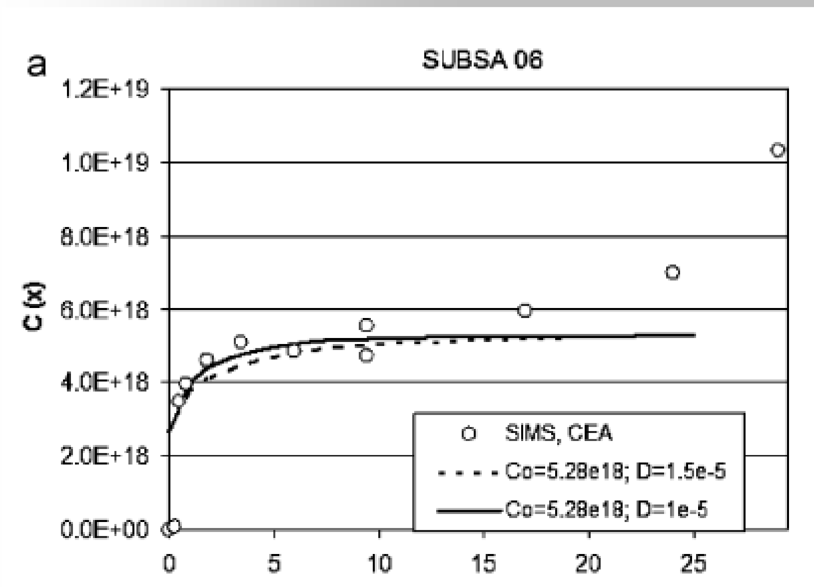


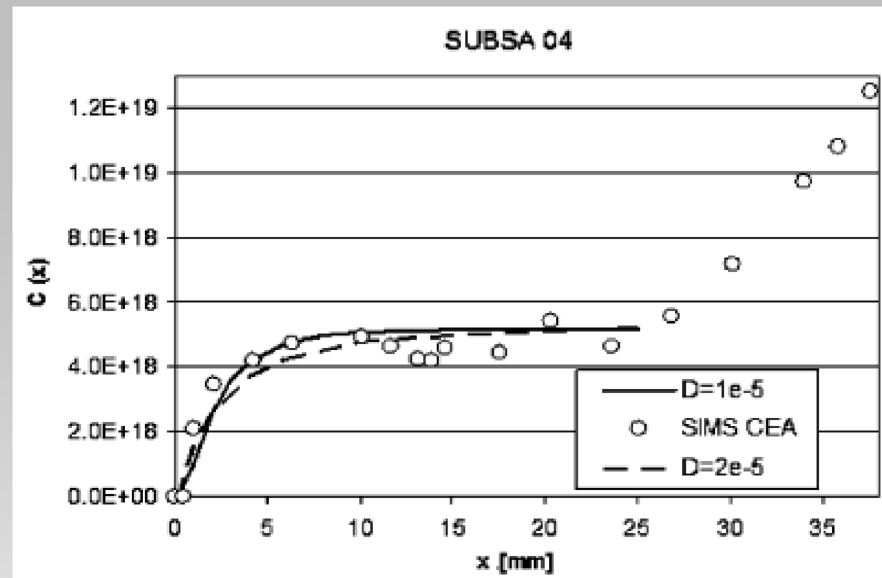
Dr. Whitson
July 11, 2002

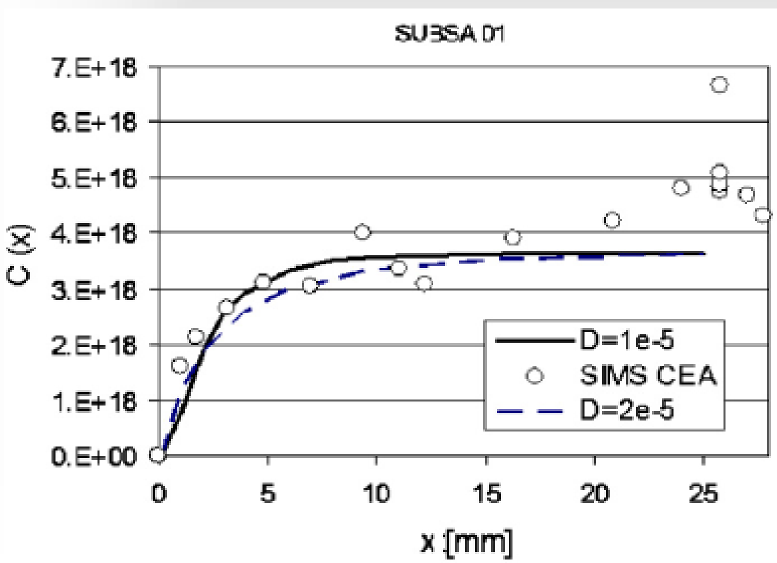
Monitoring room at RPI

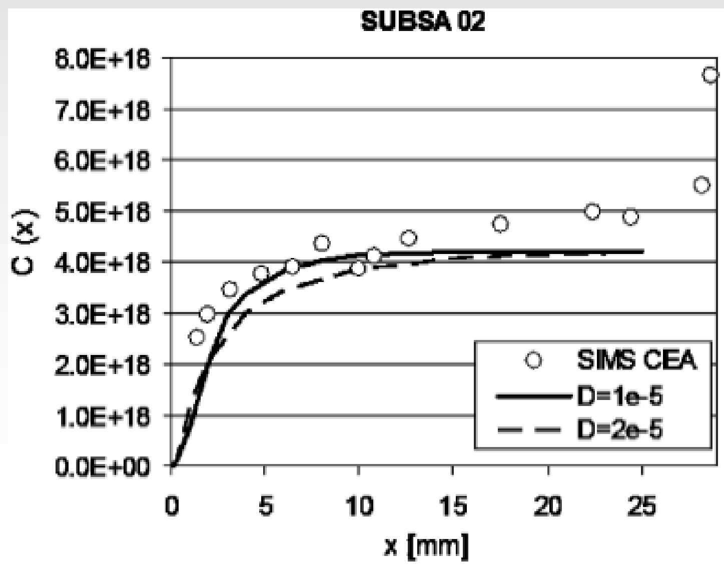
Results SUBSA: Te-doped InSb

$k_0=0.5<1$



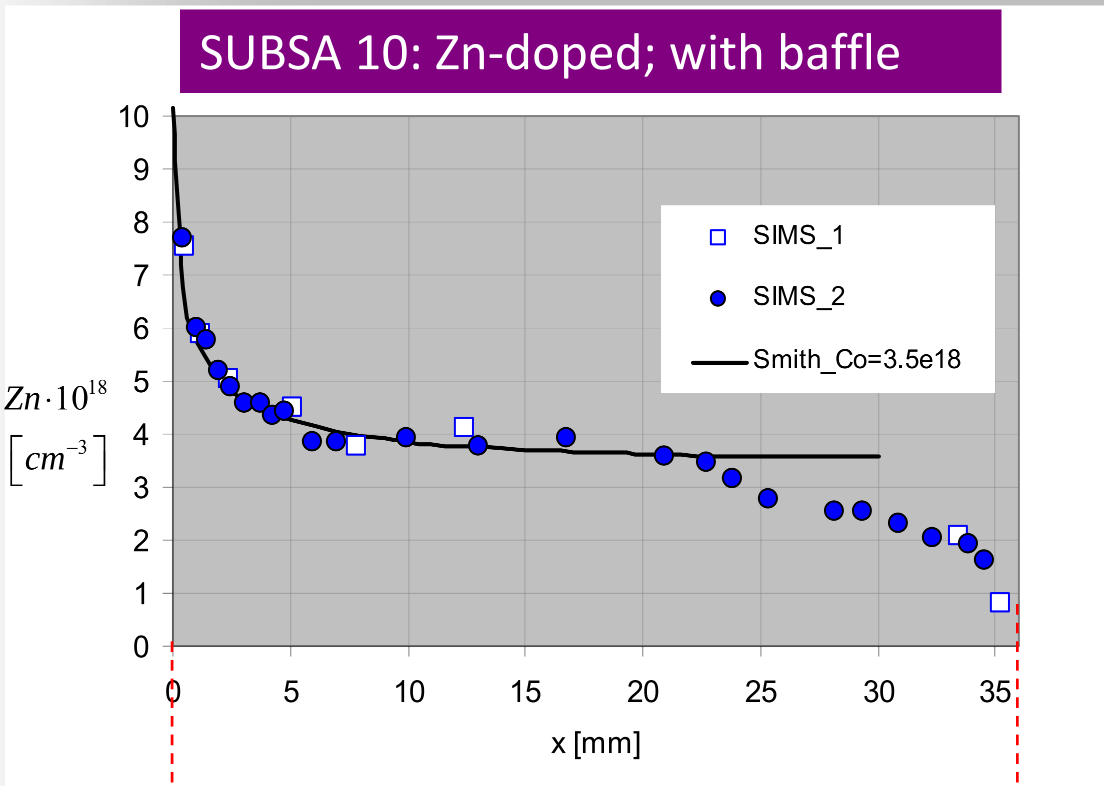


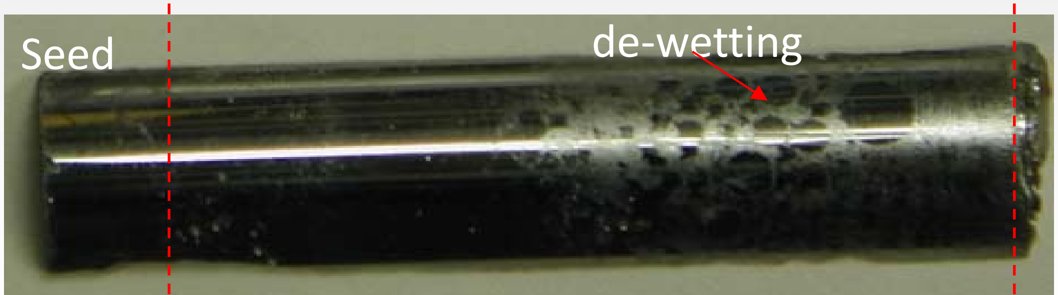




$$D=1\cdot 10^{-5}\left[\frac{cm^2}{s}\right]$$

Results SUBSA #10: Zn-doped InSb





Zn-doped => k_0=2.9> 1 !!

k_0 >1 is proffered for growth in microgravity.

D =1.2 x 10^{-4} cm^2/s

Results – k_{eff} model

All previous equations are based on δ:

1. BPS (1953) FC only.
2. Wilson (1978)-Garandet (2008) FC only.
3. Ostrogorsky-Muller, (OM, 1992, lateral convection, NC)
4. Yen and Tiller (1992, lateral convection considered).

. . .

$$\frac{C_S}{C_L} = k_{eff}\left(\delta\right)$$

$$\delta = 1.6\ D^{1/3} \nu^{1/6}\ \omega^{-1/2}$$

- *Laminar steady flow driven by a rotating disk*
- *g -driven flow ignored.*

*Equation based on **empirical** correlations for Nusselt (or Sherwood) Numbers (Ostrogorsky, 2012)*

$$\frac{C_S}{C_L} = k_{eff}\left(k_0, Nu, Pe\right)$$

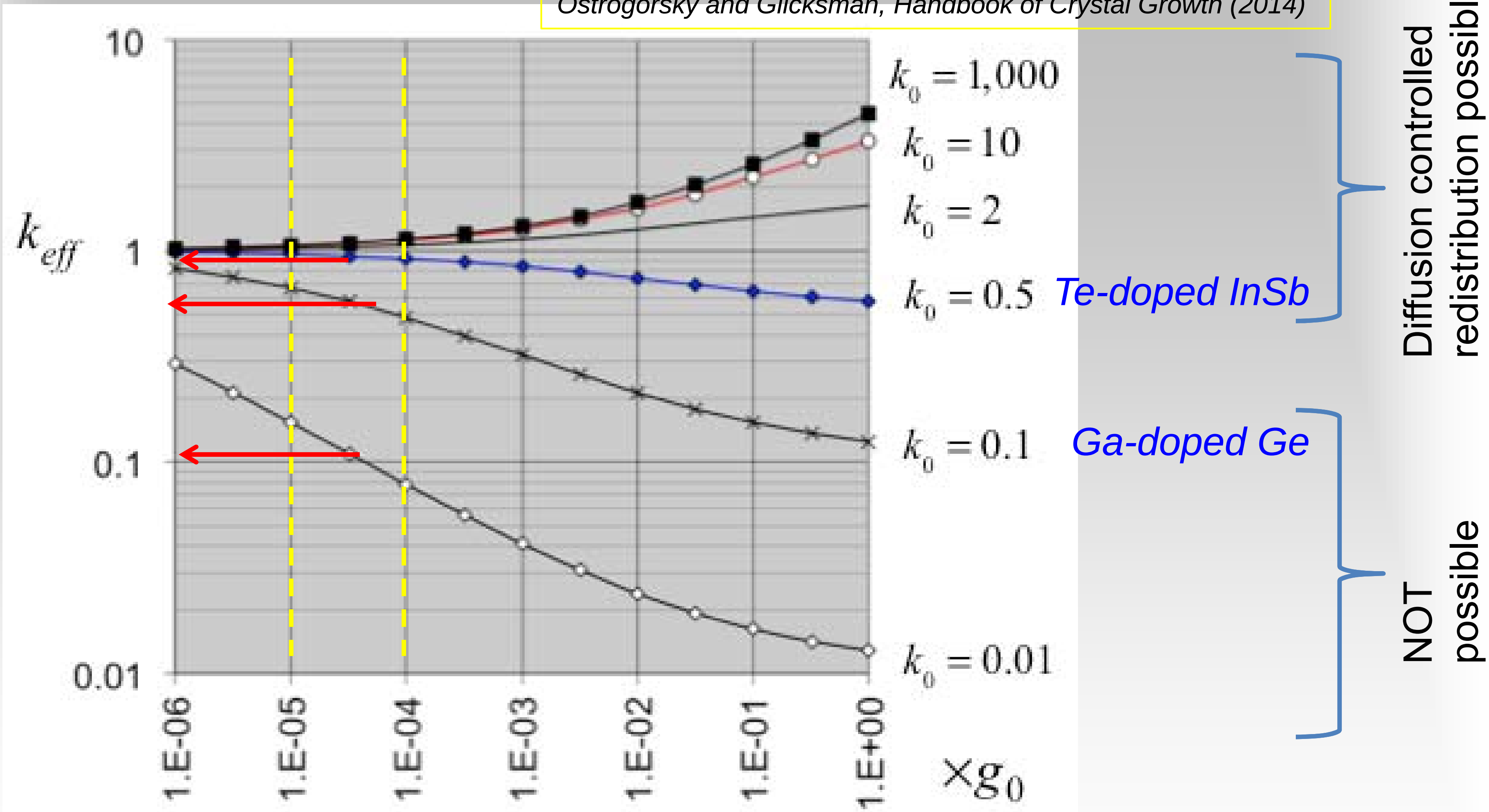
$$Nu \equiv \frac{h \cdot L}{D} = F\left(Gr, \Pr, Sc\right)$$

$$Gr = \frac{g\,\beta\,\Delta T\,L^3}{\nu^2} = \frac{F_{buyancy}}{F_{viscous}}$$

Chapter 25, *Handbook of Crystal Growth*, 2nd ed.

k_{eff} as a *function of* k_0 *and g- level*

Ostrogorsky and Glicksman, Handbook of Crystal Growth (2014)



- Diffusion-controlled melt growth on orbital platforms is practical only with systems $0.5 \le k_0 \le \infty$
- Not recognized in the 1970s and 1980s; attempts were made to grow Sb-doped Ge (k_0 = 0.003) and Sn-doped InSb (k_0 = 0.057)

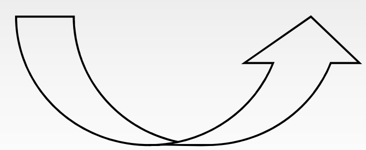
PART 2. InI DoE NNSA (2005-2015); CASIS/NASA (2015-2017)

HgI_2 (soft and grown from vapor phase)

- At in the vicinity of 130 ° C, tetragonal red α-HgI_2 crystals undergo a destructive phase transition to an orthorhombic yellow β-HgI_2 phase

Material	CdTe	ZnTe	$Cd_{0.9}Zn_{0.1}Te$	HgI_2	CdI_2	$HgBr_2$	InI
Av. Atomic Z_{eff}	50.16	46.21	49.1	59.9	51.3	50	51
ρ (g/cm^3)	5.85	6.34	5.78	6.4	5.640	6.05	5.31
Eg. (eV)	1.56	2.25	1.549	2.41	3.5	3.6	2.0
ρ [Ω cm]	~10^9		3x10^9	10^{13}			~10^{11}

GOALS: Investigate the potential of high-Z number binary and ternary iodides that have not received sufficient attention.



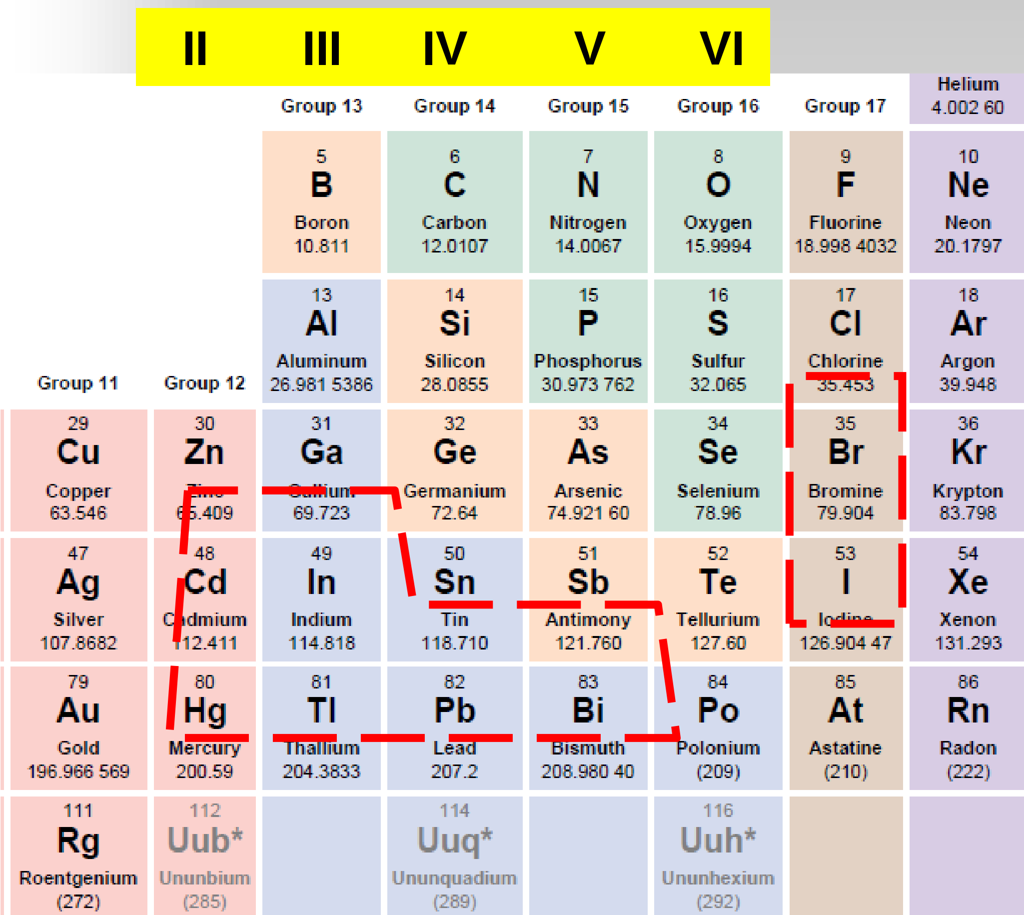
$HgCd_X I_{2-X}$ $HgBr_X I_{1-X}$

REQUIREMENTS FOR RT DETECTORS

<u>Room Temperature (RT) operation requirements</u>

energy gap: 1.5 eV< Eg <2.5 eV

Z>50



	Z	[eV]
Si	14	1.12
Ge	32	0.7
~~GaAs~~	~~33~~	~~1.43~~
~~InP~~	~~49~~	~~1.35~~
~~AlSb~~	~~51~~	~~1.6~~
CdTe	52	**1.49**
ZnTe	52	**2.25**
<u>HgI_2</u>	80	**<u>2.13</u>**
$HgBr_2$	80	3.6
PbI_2	82	2.55
BiI_3	83	1.75
TlBr	81	2.8
TlI	81	**2.15**
InI	53	**2**

III-V compounds (GaAs, InP, AlSb)

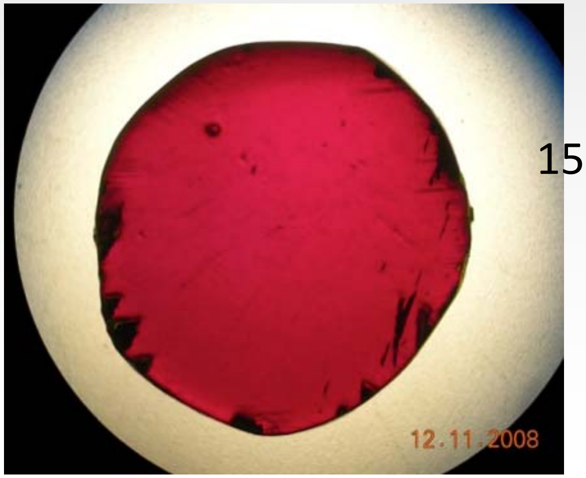
$Cd_{0.8}Zn_{0.2}Te$ "CZT" (CdTe, ZnTe)

Best (HgI_2)

Best (TlI)

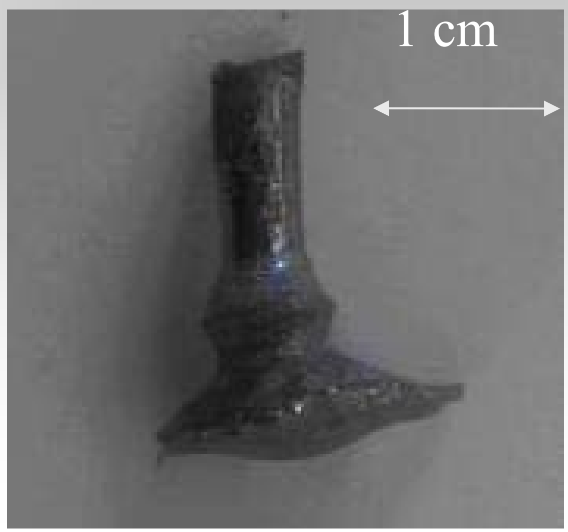
WHY INDIUM IODIDE?

- Promising semiconductor RT detector material + not toxic; MP= 360 C (perfect for SUBSA furnace)
- Developed procedures for synthesis, ZR, melt growth, vapor growth
- RPI (2006-2009); IIT (2009-present), RMD (2015).
- DoE, NNSA



15 mm diameter

Is CZ growth of InI possible ?



	Disassociation Energy , eV
I_2	1.542
BiI	0.3
HgI	0.35
HgBr	0.71
CdTe	1.2
PbI	2.0
PbBr	2.5
TlI	2.76
TlBr	2.34
InI	3.43
InBr	3.9

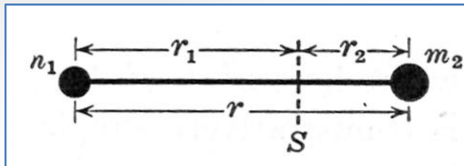


FIG. 38. Dumbbell Model of a Diatomic Molecule.

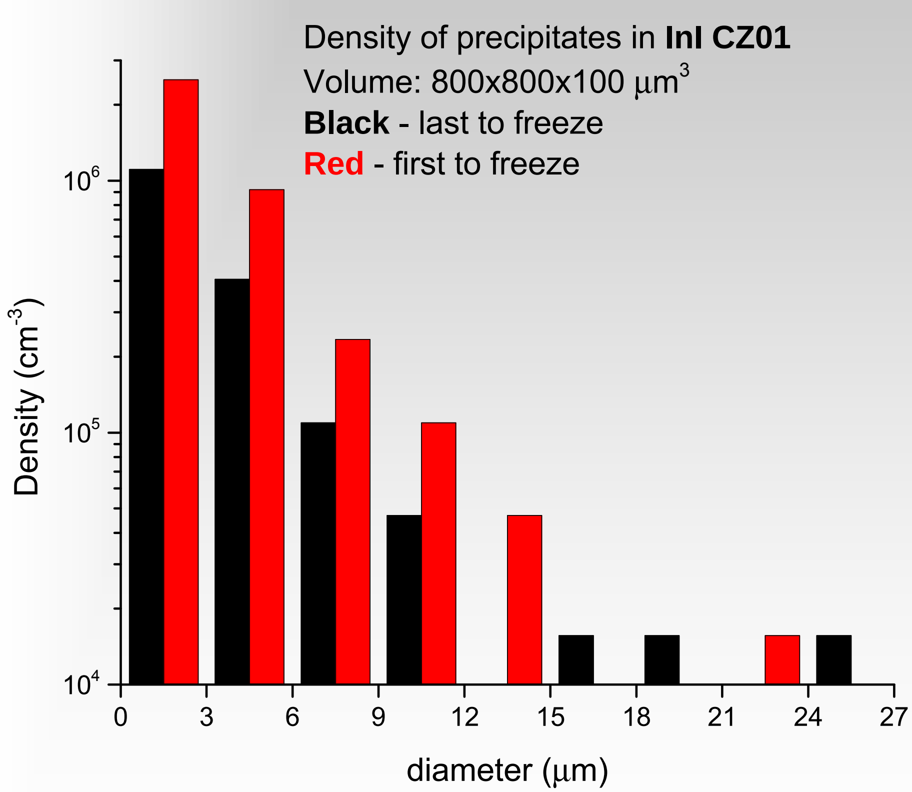
CZOCHRALSKI GROWTH OF InI

- Detector materials have high vapor pressure; growth in sealed ampoules.

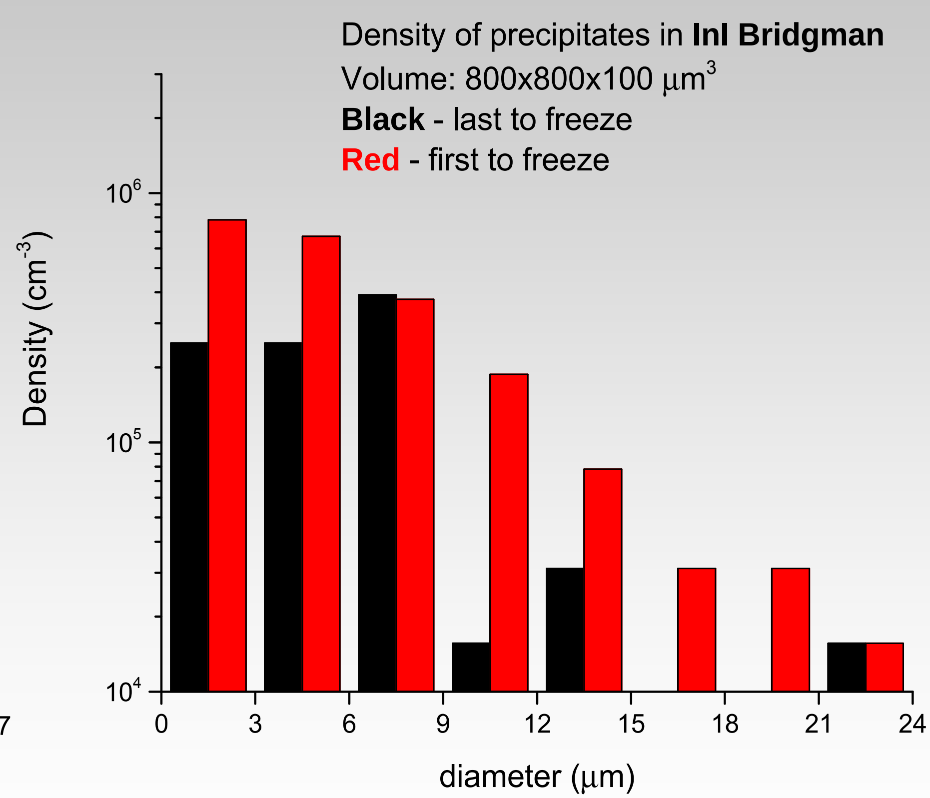
- **CZ growth of a detector crystal demonstrated for the first time**

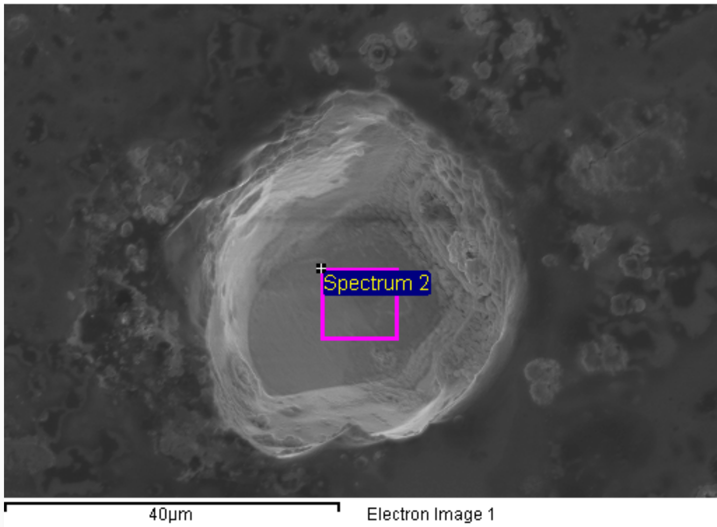
DISTRIBUTION OF PRECIPITATES

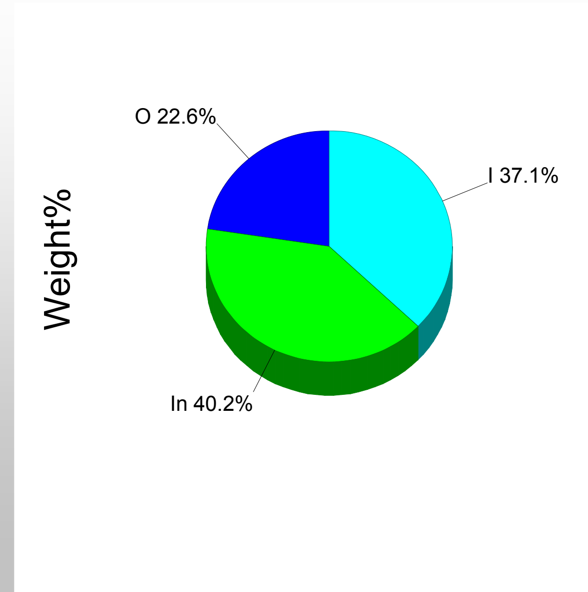
CZOCHRALSKI

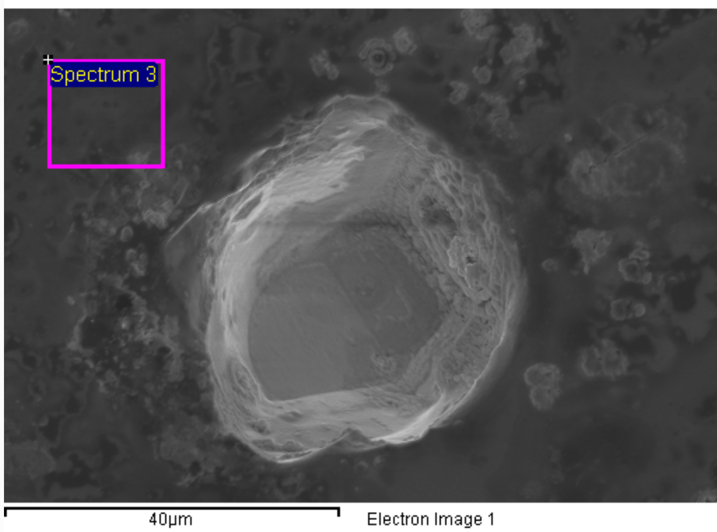


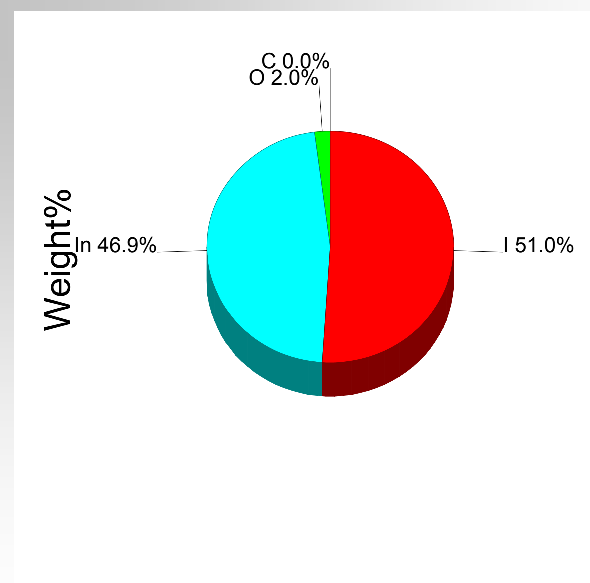
BRIDGMAN




Spectrum 2
40µm
Electron Image 1


Weight%
O 22.6%
I 37.1%
In 40.2%


Spectrum 3
40µm
Electron Image 1


Weight%
C 0.0%
O 2.0%
In 46.9%
I 51.0%

High Purity Indium (In) Metal

Analysis by Glow Discharge Mass Spectrometry

Tested by:	Institute for National Measurement Standards, National Research Council
Report Date:	14-Jul-10
Report NO:	31810
Lot Number:	92

Element	Analytical Result in ppb(mass)
Mg	<0.1
Al	<0.2
Si	0.7
S	2.8
Fe	0.5
Ni	18.4
Cu	8.3
Zn	<1.7
Ga	<0.4
Ge	<0.6
Ag	<0.8
Cd	79.3
Sn	13.4
Tl	7.1
Pb	61.4
Bi	<0.9
Total Detected Impurities:	**191.9**

Certicate of analysis iodine 5N metal basis (Alfa Aesar Inc.).

Iodine lump, ultra dry, 99.999% (metals basis)

Stock Number: 44857
Lot Number: J21W012

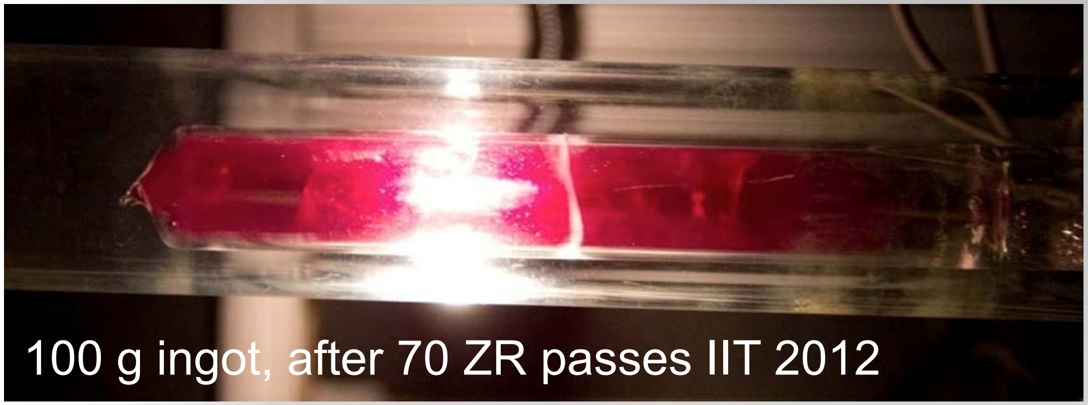
Analysis

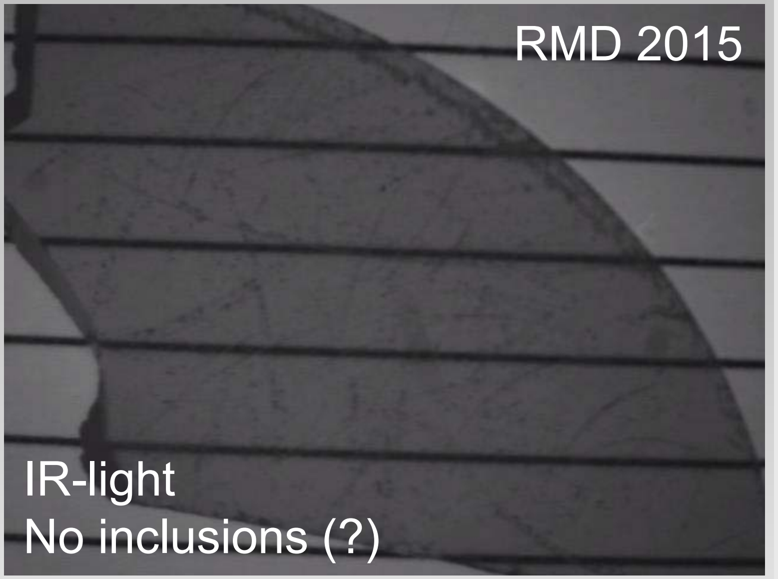
Purity > 99.999 % (metals basis)

Mg	< 0.5	Mn	< 0.2
Al	< 0.2	Fe	< 0.2
P	< 0.1	Ni	< 0.1
K	< 0.1	Cu	< 0.1
Ca	< 0.1	Zn	< 0.1
Ti	< 0.1	As	< 0.1
V	< 0.1	Sn	< 0.1
Cr	< 0.1	Pb	< 0.1

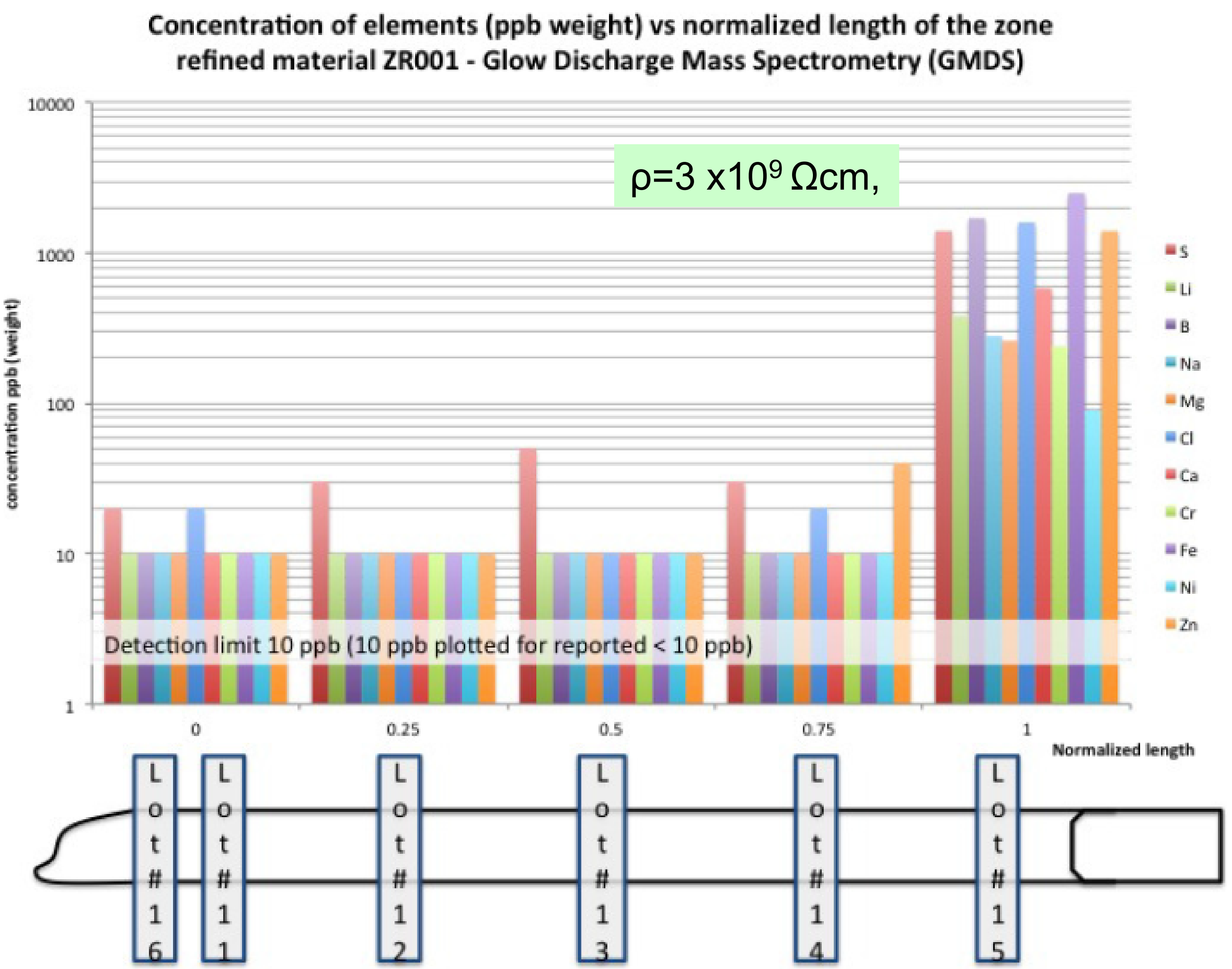
Values given in ppm unless otherwise noted
All other impurities are lower than detection limits (<0.01 ppm)
Analysis method: Mass spectrometry

PURIFICATION BY ZONE REFINING (ZR)



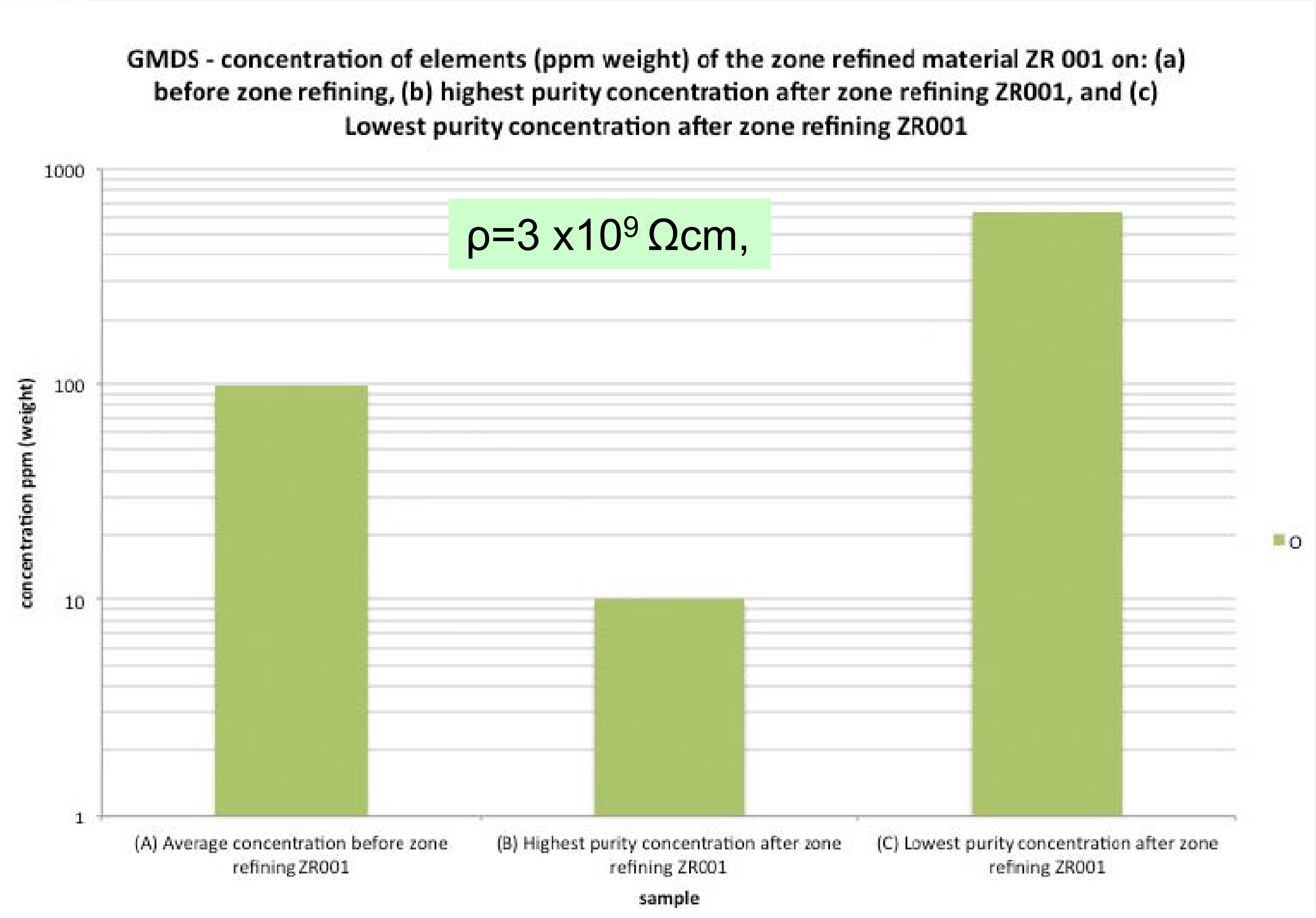


350 g ingot, was ZR and grown in an open boat, under dynamic gas flow 5% H_2 +95 %Argon, RMD 2015.



IIT 2012: Final concentration of S, Li, B, Na, Mg, Cl, Ca, Cr, Fe, Ni and Zn (ppb by weight) vs normalized length of the zone refined material ZR001 - Glow Discharge Mass Spectrometry (GMDS) by Evans Analytical Group.

Instrumental Gas Analysis (IGA) by Evans Analytical Group.



Comparison of concentrations of oxygen (ppm by weight) of the zone refined (ZR) material ZR 001 on: (a) before zone refining, (b) highest purity concentration after ZR, and (c) Lowest purity concentration after ZR.

2012, IIT:

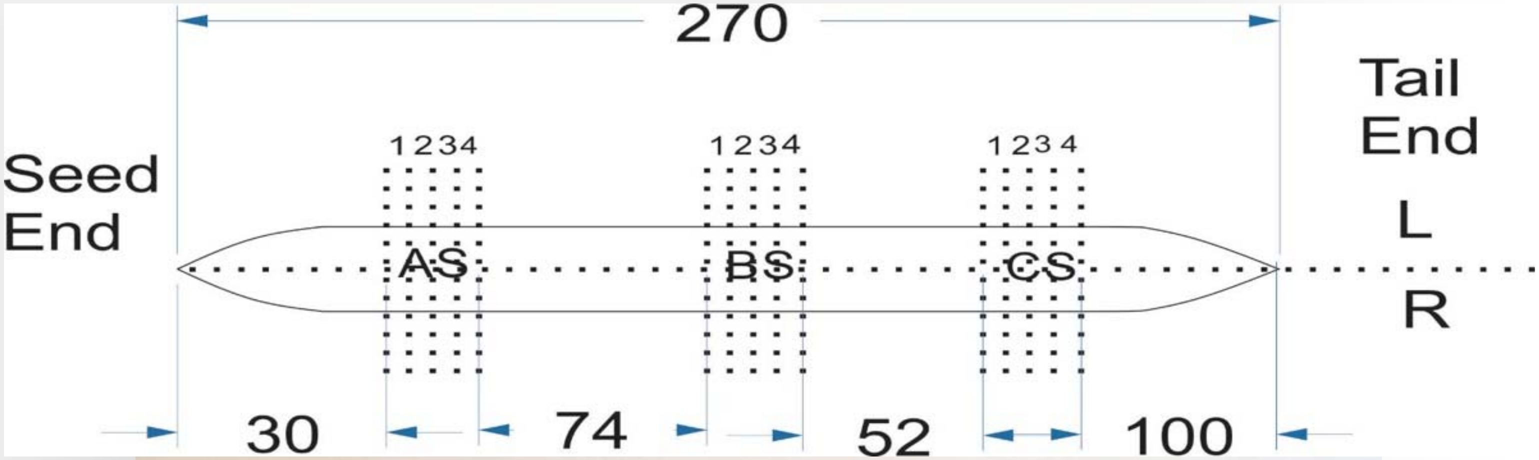
Concentration of oxygen and selected elements in ZR 001

Oxygen: Instrumental Gas Analysis (IGA)
All others elements: GDMS

	Before		After
	Sample 1	Sample 2	
O_2	16 ppm	180 ppm	< 10 ppm
Li	< 10 ppb	< 10 ppb	< 10 ppb
B	< 10 ppb	11 ppb	< 10 ppb
Na	30 ppb	20 ppb	< 10 ppb
Mg	30 ppb	20 ppb	< 10 ppb
Al	30 ppb	180 ppb	< 10 ppb
Si	230 ppb	620 ppb	530 ppb
S	220 ppb	240 ppb	20 ppb
Cl	50 ppb	130 ppb	20 ppb
Ca	60 ppb	50 ppb	20 ppb
Ti	120 ppb	10 ppb	< 10 ppb
Cr	10 ppb	< 10 ppb	< 10 ppb
Fe	40 ppb	80 ppb	< 10 ppb
Ni	< 10 ppb	10 ppb	< 10 ppb
Cu	20 ppb	10 ppb	< 10 ppb
Zn	50 ppb	80 ppb	< 10 ppb

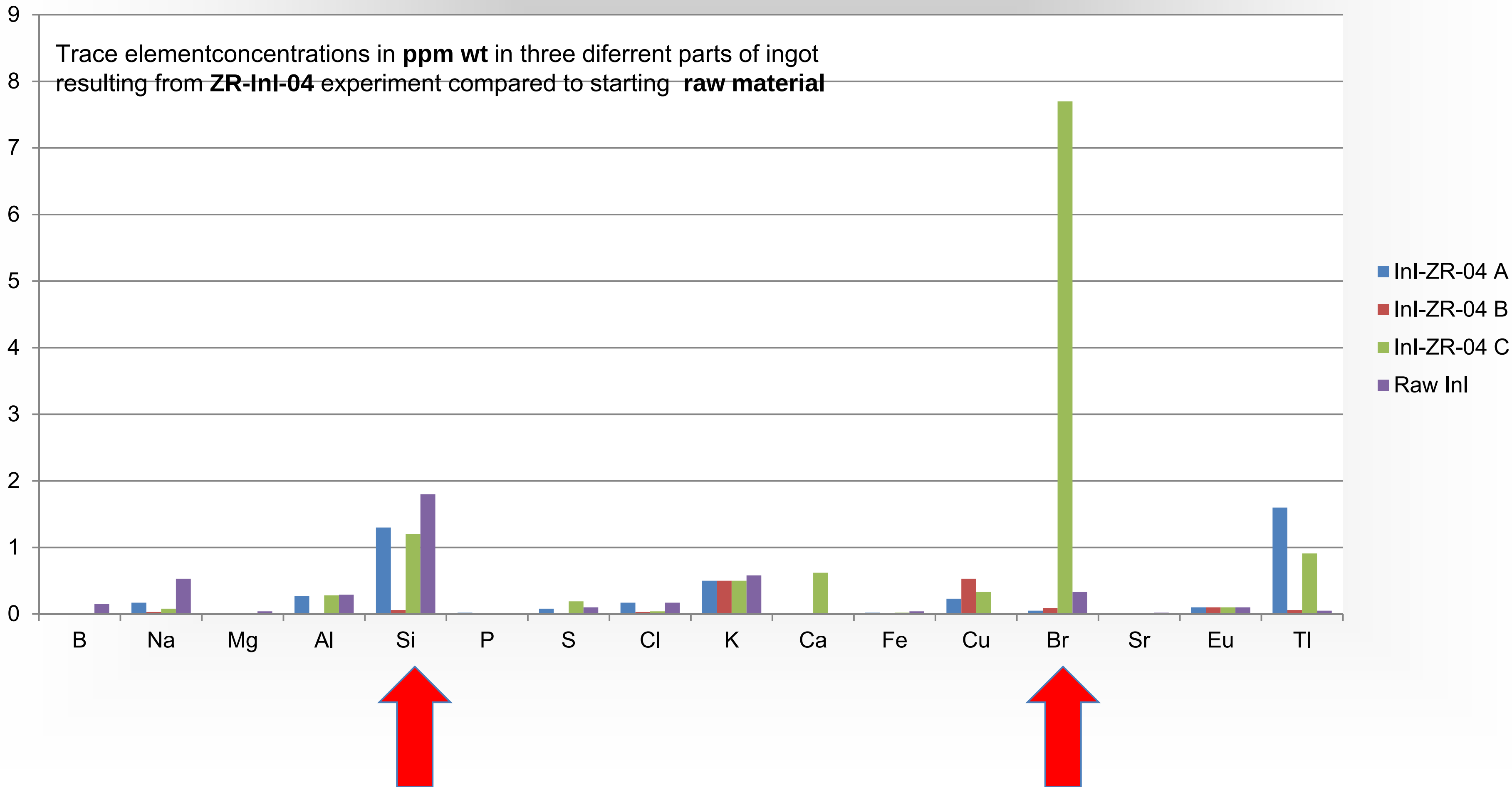
RMD 2015

- Zone Refining (ZR)
- Bubbling Ar+5% H_2 through the melt



RMD 2015: Zone Refining (ZR)

Charge: InI (Sigma Aldrich, 99.999 %)



InI *Sample ID:* :

#4 InI-ZR-05 A

Element	Concentration [ppm wt]	Element	Concentration [ppm wt]
Li	< 0.01	Ag	< 0.05
Be	< 0.01	Cd	< 1
B	< 0.01	In	Matrix
F	< 0.5	Sn	< 0.5
Na	0.02	Sb	< 0.1
Mg	0.04	Te	< 0.5
Al	1.1	I	Matrix
Si	1.8	Cs	< 1
P	< 0.01	Ba	< 0.1
S	0.24	La	< 0.05
Cl	0.02	Ce	< 0.05
K	< 0.5	Pr	< 0.05
Ca	< 0.01	Nd	< 0.01
Sc	< 0.01	Sm	< 0.01
Ti	< 0.01	Eu	0.16
V	< 0.01	Gd	< 0.01
Cr	< 0.01	Tb	< 0.01
Mn	< 0.01	Dy	< 0.01
Fe	0.03	Ho	< 0.01
Co	< 0.01	Er	< 0.01
Ni	< 0.01	Tm	< 0.01
Cu	< 0.01	Yb	< 0.01
Zn	< 0.01	Lu	< 0.05
Ga	< 0.05	Hf	< 0.01
Ge	< 0.05	Ta	Source
As	< 0.05	W	< 0.01
Se	< 0.1	Re	< 0.01
Br	1.3	Os	< 0.01
Rb	< 0.01	Ir	< 0.05
Sr	< 0.01	Pt	< 0.1
Y	< 0.01	Au	< 0.1
Zr	< 0.01	Hg	< 0.05
Nb	< 0.01	Tl	0.91
Mo	< 0.01	Pb	< 0.05
Ru	< 0.01	Bi	< 0.05
Rh	< 0.01	Th	< 0.01
Pd	< 0.05	U	< 0.01

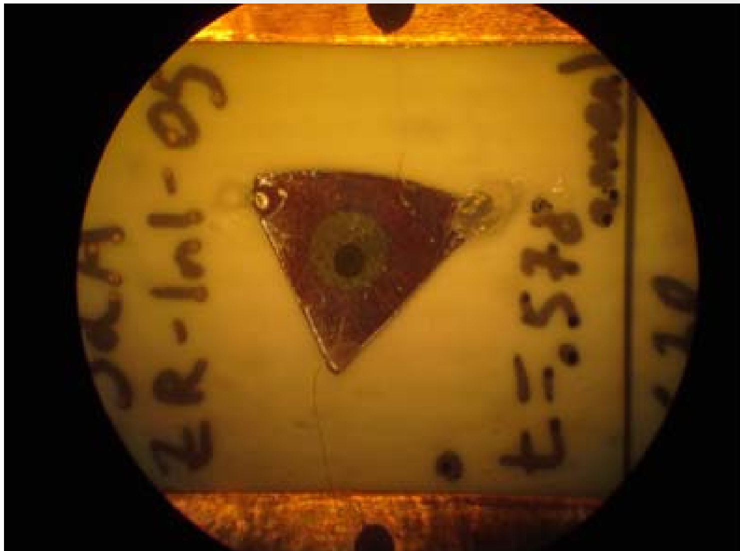
20-Jul-15 *Job #* :

InI *Sample ID:* :

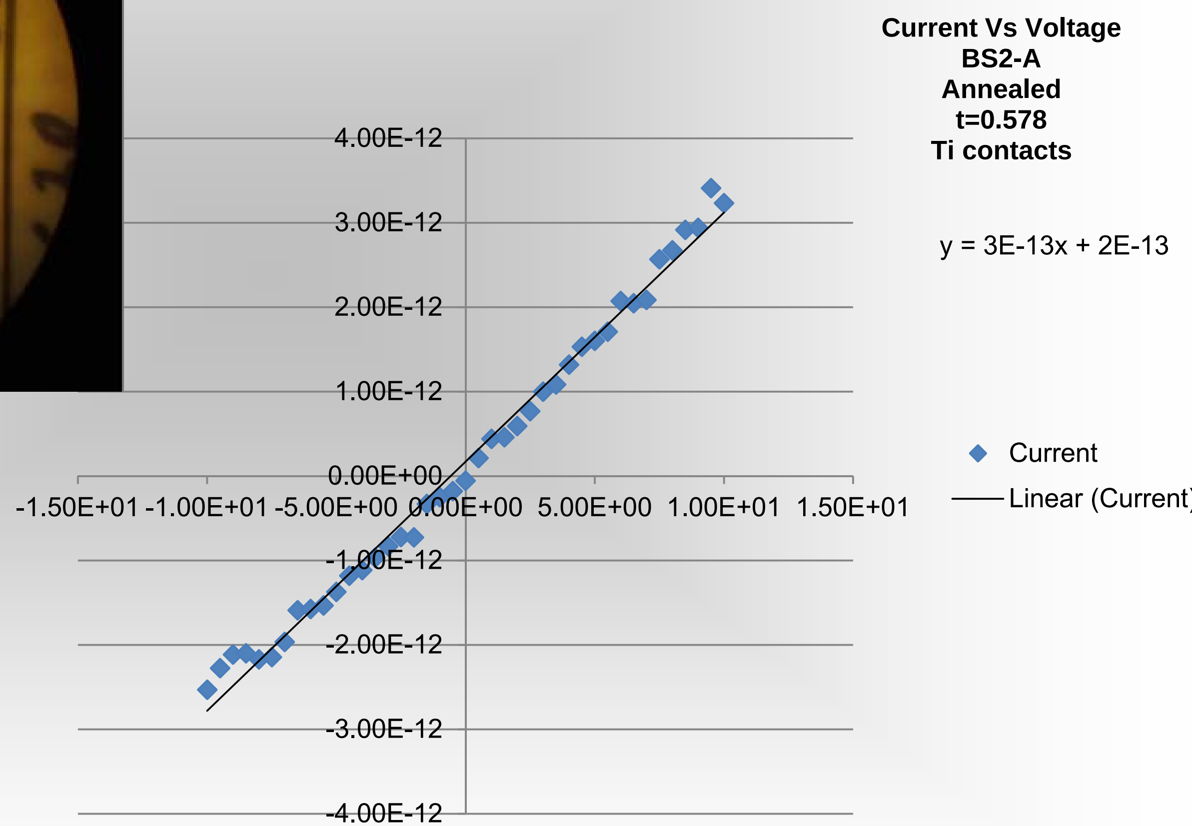
#2 InI-ZR-04 B

Element	Concentration [ppm wt]	Element	Concentration [ppm wt]
Li	< 0.01	Ag	< 0.05
Be	< 0.01	Cd	< 1
B	< 0.01	In	Matrix
F	< 0.5	Sn	< 0.5
Na	0.03	Sb	< 0.1
Mg	< 0.01	Te	< 0.5
Al	< 0.01	I	Matrix
Si	0.06	Cs	< 1
P	< 0.01	Ba	< 0.1
S	< 0.01	La	< 0.05
Cl	0.03	Ce	< 0.05
K	< 0.5	Pr	< 0.05
Ca	< 0.01	Nd	< 0.01
Sc	< 0.01	Sm	< 0.01
Ti	< 0.01	Eu	< 0.1
V	< 0.01	Gd	< 0.01
Cr	< 0.01	Tb	< 0.01
Mn	< 0.01	Dy	< 0.01
Fe	< 0.01	Ho	< 0.01
Co	< 0.01	Er	< 0.01
Ni	< 0.01	Tm	< 0.01
Cu	0.53	Yb	< 0.01
Zn	< 0.01	Lu	< 0.05
Ga	< 0.05	Hf	< 0.01
Ge	< 0.05	Ta	Source
As	< 0.05	W	< 0.01
Se	< 0.1	Re	< 0.01
Br	0.09	Os	< 0.01
Rb	< 0.01	Ir	< 0.05
Sr	< 0.01	Pt	< 0.1
Y	< 0.01	Au	< 0.1
Zr	< 0.01	Hg	< 0.05
Nb	< 0.01	Tl	0.06
Mo	< 0.01	Pb	< 0.05
Ru	< 0.01	Bi	< 0.05
Rh	< 0.01	Th	< 0.01
Pd	< 0.05	U	< 0.01

I-V curve of detector *BS2-A_(annealed)*:



$d_{contact}$=3mm



$\rho_{BS2\text{-}A}$=4.07 x 10^{12} Ω cm

Material	$Cd_{0.9}Zn_{0.1}Te$ (CZT)	HgI_2	InI
Average atomic number, Z	49.1	62	51
Density, g/cm^3	5.78	6.4	5.31
Band gap, eV	1.55	2.14	2.0
Melting point, ^oC	~1100	259	351
Structure	Zincblende	Tetrahedral-layered	Orthorhombic
Knoop Hardness, kg/mm^2	92	10	27
Molecule Disassoc. Energy eV Herzberg's tables [19]	1.2	0.35	3.43
Electrical Resistivity, Ohm-cm	3×10^{10}	10^{13} to 10^{14}	1×10^{11}

$$\rho \approx 4 \times 10^{12}$$

CASIS/NASA, 2015: "Detached Melt and Vapor Growth of InI in SUBSA Hardware"

(a) Detached directional solidification: 3 crystals

Improve crystalline perfection

Observe the dewetting process in microgravity

(b) ***Physical vapor transport growth***: ***3*** crystals.