Absorption Studies in Sapphire

LIGO-G010352-00-Z

A. Alexandrovski, R. K. Route,
M. M. Fejer
E. L. Ginzton Laboratory
Stanford University

route@leland.stanford.edu

Lasers and Optics Working Group

LSC meeting, Hanford WA, Aug. 2001

Why Do We Care?

Imperfect materials $\Rightarrow$ absorption

Absorption $\Rightarrow$ inhomogeneous temperature rise

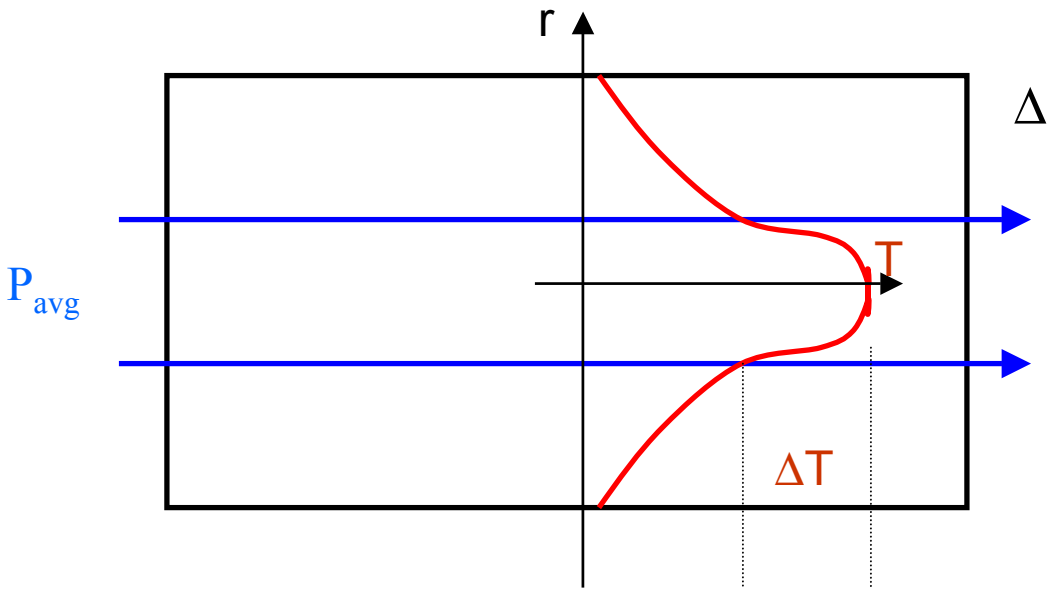
Temperature rise $\Rightarrow$ thermal expansion, change in refractive index

Distorted optic $\Rightarrow$ distorted wavefront

- Implications for IF design
  - limits allowable power on various elements
  - influences cavity stability through power range
- Options
  - transmissive optics
    - low loss materials
    - clever IF design
    - active thermal compensation
  - reflective designs
    - Peter. Beyersdorf's thesis research talk at the March LSC LLO meeting

Temperature Rise in Absorbing Medium

- Absorbed optical power inhomogeneously heats crystal
  - produces radially varying temperature
  - produces optical distortion due to photothermal effects



$$\Delta T = \frac{\alpha P_{avg}}{4\pi k_{th}}$$

- Temperature rise across beam *independent* of spot size
- Leads to radially varying index: $\Delta n = dn/dT \, \Delta T$
- Leads to radially varying phase on optical beam: $\Delta\phi \sim \frac{\alpha \, dn/dT}{2k_{th}\lambda} L P_{avg}$
- Similarly get a bump on surface: $\Delta\phi \sim \frac{\alpha \kappa}{2k_{th}\lambda} L P_{avg}$
  - κ = thermal expansion coeff.

Requirements

- Intrinsic and extrinsic material properties combine to determine distortion
  - transmission FOM: $$FOM \sim \frac{k_{th}}{\alpha \, dn/dT}$$
  - reflection from absorbing substrate: $$FOM \sim \frac{k_{th}}{\alpha \kappa}$$

- For LIGO II
  - ~10 ppm/cm $\Rightarrow$ OK
  - ~40 ppm/cm $\Rightarrow$ with active thermal compensation

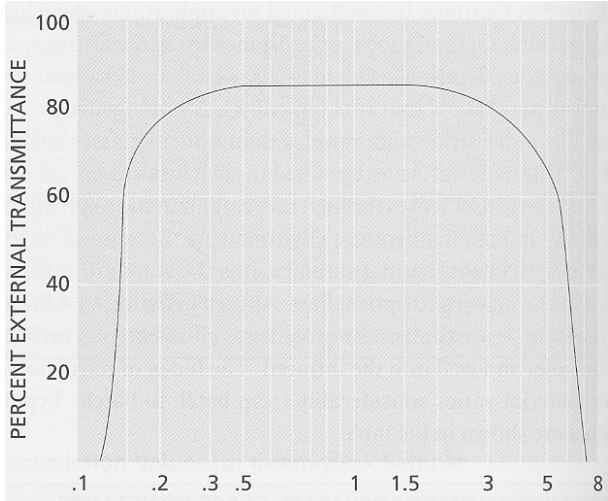
- Currently: 40 ppm/cm in large samples
  - isolated observations at 10 ppm/cm level

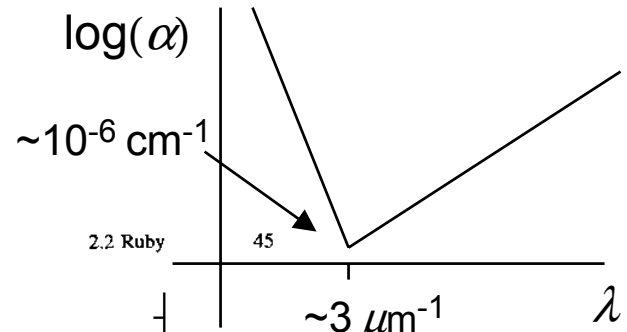
Outline

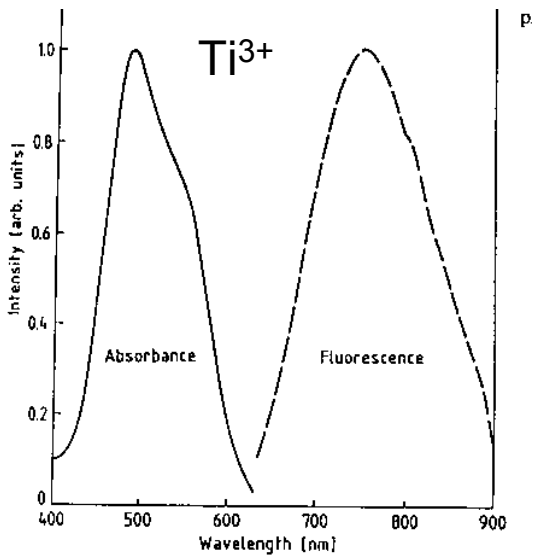
- Absorption characteristics in sapphire
- Absorption measurements
- Crystal growth
- Sample sets
  - growth studies
  - annealing studies
- Observations and trends
- Status and plans

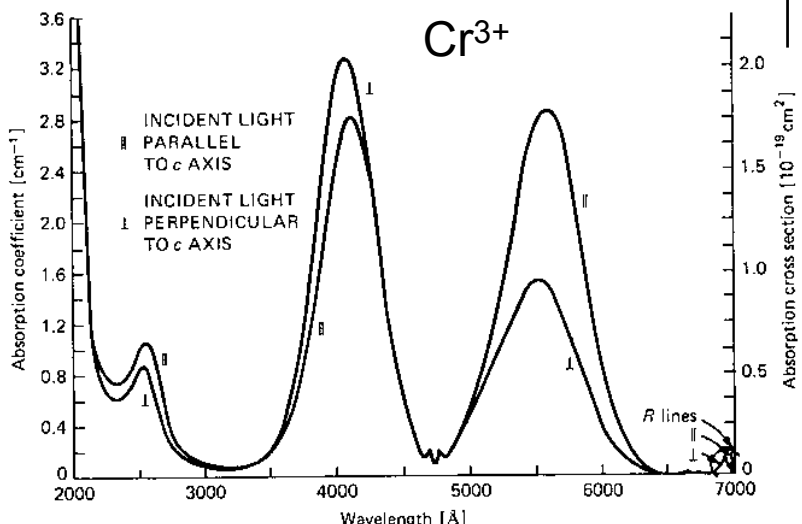
Absorption in Sapphire

- Intrinsic
  - conduction to valence band in UV
  - multiphonon in mid-IR
  - only cure is different material
    expectation and existence proofs indicate this isn't the problem
- Extrinsic
  - native defects
    vacancies, antisites, interstitials,
  - impurities
    e.g. transition metals: Cr, Ti, Fe, …





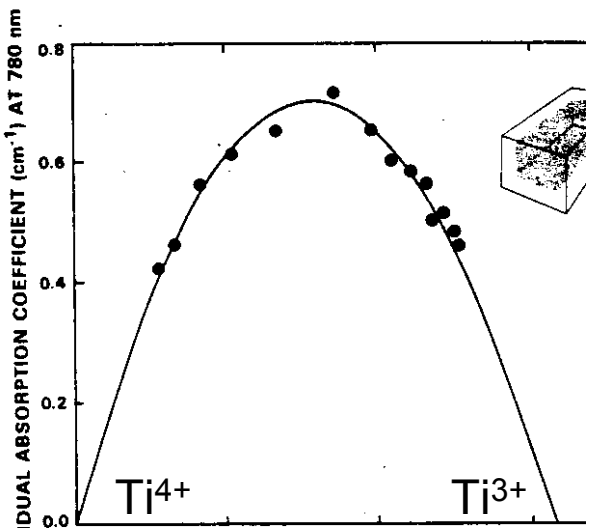




Characteristics of Absorbing Species

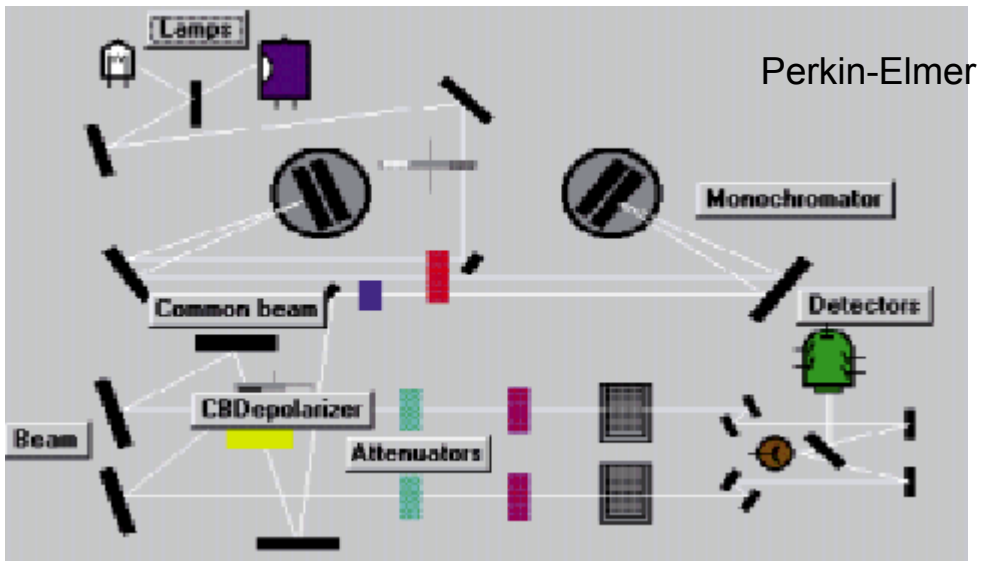
- Allowed transitions
  - large cross sections $\Rightarrow$ ppm concentrations significant
- Broad spectral features
  - identification difficult
  - off "resonant" absorption significant
  - sum of several species can contribute to absorption at given λ
- Redox state important
  - e.g. $\alpha[Ti^{3+}] \neq \alpha[Ti^{4+}]$
  - annealing alters absorption without altering impurity concentrations
- Impurities do not necessarily act independently
  - Al : Al :Ti^{3+} : Ti^{4+} : Al : Al $\neq$ Al : Ti^{3+} : Al : Al : Ti^{4+} : Al
  - absorption spectra at high concentrations
    not always same as low
    complicates correlations to known spectra

$$\Rightarrow \alpha_{IR} \propto [Ti^{3+}][Ti^{4+}]$$



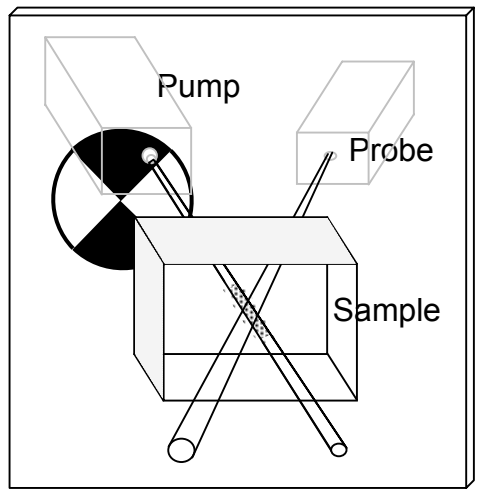
Absorption Measurement

- Spectrophotometer
  - broad continuous wavelength coverage (UV – IR)
  - difficult to resolve below 10^{-3} absorption
    reflections and interference also influence transmission
    especially for broad features
  - no spatial resolution
    gives line-integrated absorption
- Photothermal common-path interferometry (Alexometry)
  - spatially resolved (< 0.5 mm)
  - sensitive (~ 1 ppm/cm absorption)
  - requires laser, so wavelength coverage not continuous
    1.06 μm, 0.532 μm, 0.514 μm, 0.488 μm, …



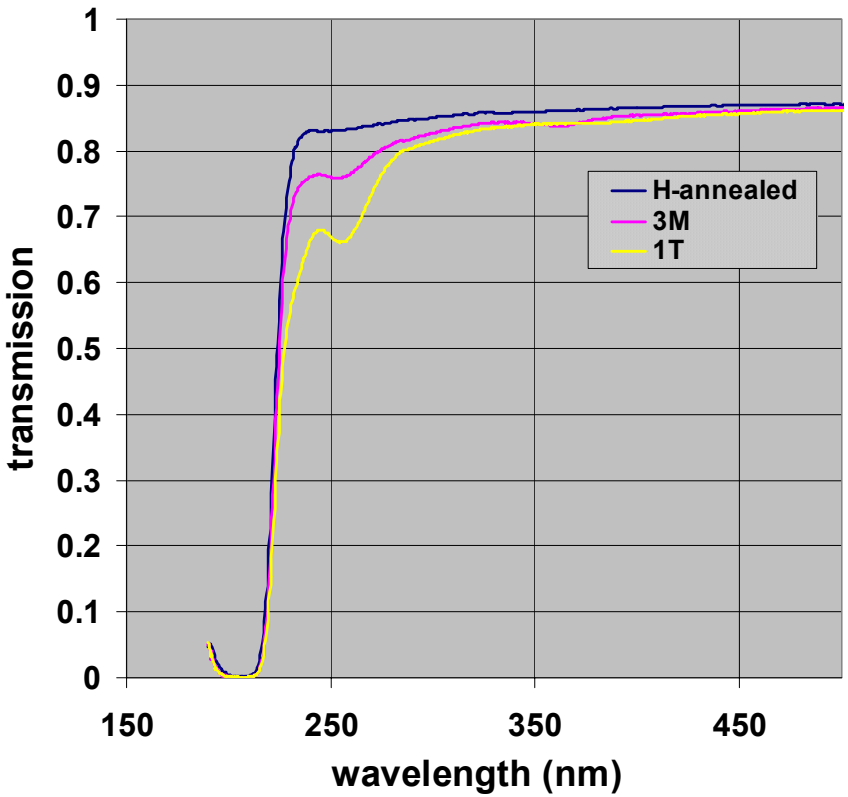
Perkin-Elmer

PCI

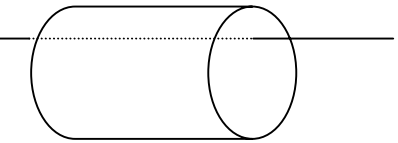


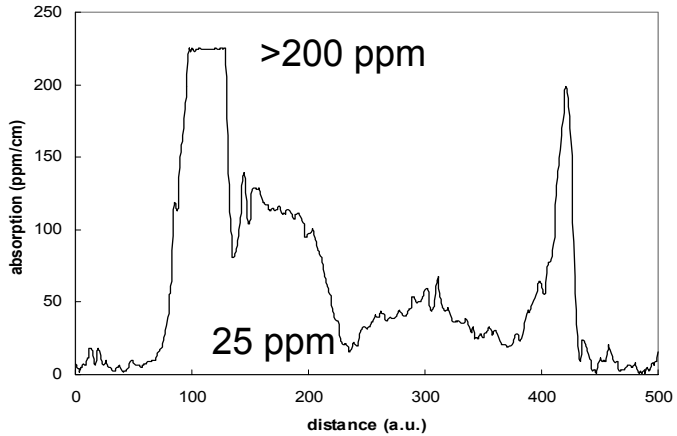
Typical Spectra

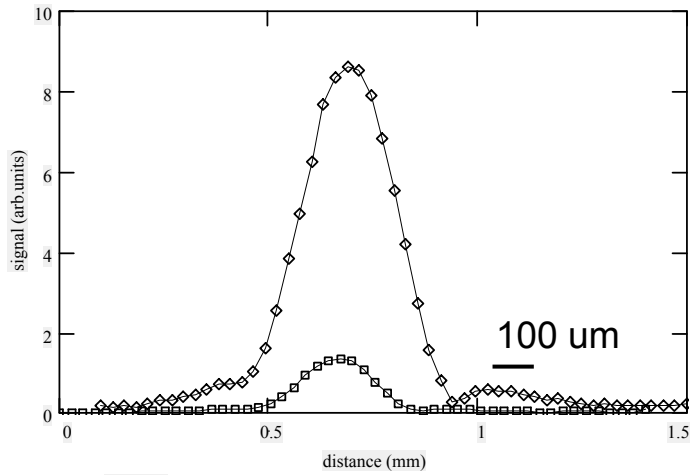
Various Al_2O_3 Samples



longitudinal scan in Al_2O_3





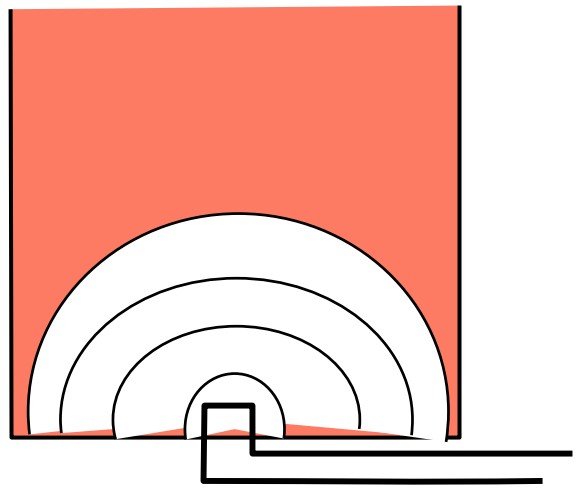


Scan through electroded Al_2O_3

- trace 1: 100A-thick electrode
- trace 2: 1200A-thick electrode

HEM Crystal Growth

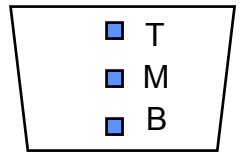
- Heat Exchanger Method
  - He-gas cools bucket of melt
  - solidification outwards from bottom



- Starting materials
  - typically “craquelle” sapphire
  - ppm levels of some transition metals
  - purity $\uparrow \Rightarrow \$ \uparrow\uparrow$
- Segregation
  - impurities rejected ($k < 1$) into melt
  - segregate into outer regions of crystal (last to crystallize)
  - can expect different behavior top/middle/bottom of boule
  - can remelt outer portion to concentrate impurities
    remelt inner portion to reduce impurity concentration
  - opposite argument for $k > 1$ impurities

Collaborative Studies

- Experimental design
  - anticipated mechanisms: impurity concentration, intrinsic defects, redox state
  - two main control methods: growth and annealing
- Growth Studies
  - ~ 30 CSI White, 1 cm cubes
  - primarily expected to influence impurity concentration
  - starting materials
    virgin material from 5 different vendors/purity
    remelted boules
  - samples cut from top/middle/bottom of boule
    explore impurity segregation effects



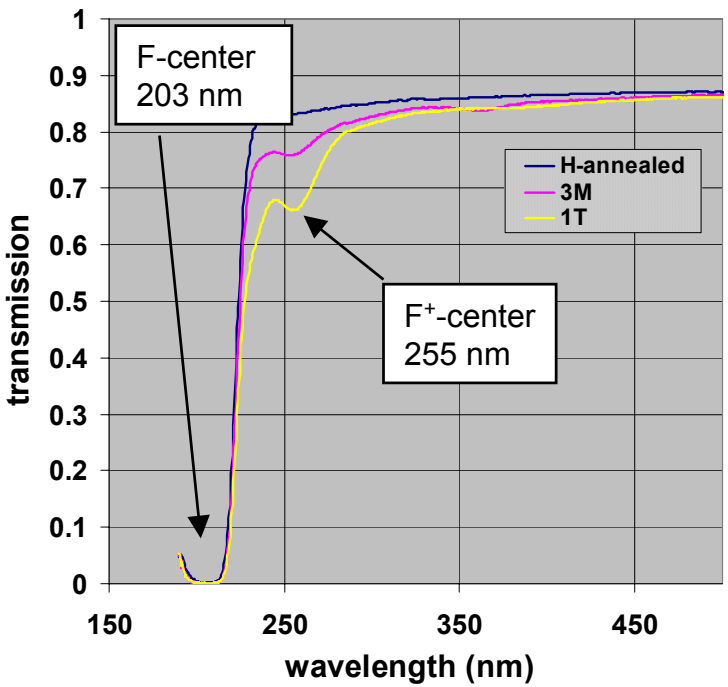
- Annealing Studies
  - 2.5 cm dia x 1 cm thick a-axis Hemex CSI White
  - primarily influence redox state, intrinsic defects (e.g. Oxygen vacancies)
  - parameters: time, temperature, reducing (H_2) or oxidizing (air, O_2)
  - furnace design
    accidental introduction of impurities, especially near surface
- Occasional samples
  - large CSI samples
    from coating or Q tests
  - SIOM crystals

Composition Analysis (GDMS)

	LIGO #1T Sample #10 ppmw	LIGO #1M Sample #11 ppmw	LIGO #1B Sample #12 ppmw	LIGO #2T Sample #07 ppmw	LIGO #2M Sample #08 ppmw	LIGO #2B Sample #09 ppmw	LIGO #3T Sample #04 ppmw	LIGO #3M Sample #05 ppmw	LIGO #3B Sample #06 ppmw	LIGO #4T Sample #01 ppmw	LIGO #4M Sample #02 ppmw	LIGO #4B Sample #03 ppmw	LIGO #5T Sample #13 ppmw	LIGO #5M Sample #14 ppmw	LIGO #5B Sample #15 ppmw	LIGO #6T Sample #16 ppmw
Li	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Be	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
O	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major
F	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Na	0.21	0.42	0.40	0.25	0.75	0.35	0.36	0.44	0.81	0.82	3.2	0.95	0.20	0.26	0.26	0.46
Mg	0.16	0.27	0.30	0.22	0.29	0.18	0.19	0.25	0.25	0.53	0.39	0.20	0.15	0.15	0.10	0.065
Al	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major	Major
Si	12	8.5	10	8.5	7.5	9.5	4.2	5.9	9.5	10	15	8.5	15	7.5	6.9	11
P	0.1	0.053	0.20	0.11	0.11	0.11	0.1	0.15	0.15	0.21	0.19	0.1	0.045	0.045	0.13	0.14
S	1.1	1.5	1.8	0.79	1.2	1.6	1.5	1.5	0.21	1.5	1.8	1.1	0.88	0.60	1.6	1.1
Cl	1.2	5.5	4.2	1.5	2.5	2.5	2.6	2.9	3.1	4.7	6.0	1.0	2.5	1.7	1.5	3.9
K	0.29	0.25	0.39	0.33	0.33	0.35	0.23	0.35	0.33	1.1	1.2	0.40	0.25	0.23	0.21	0.38
Ca	1.1	1.2	1.1	1.1	1.1	1.5	1.2	0.63	0.75	1.7	1.4	0.75	0.80	0.86	1.0	0.82
Ti	0.37	0.11	0.45	0.12	0.36	0.45	0.089	0.39	0.27	0.22	0.14	0.12	0.11	0.19	0.081	0.25
V	0.10	0.037	0.026	0.12	0.23	0.37	0.026	0.021	0.04	0.11	0.086	0.095	0.056	0.072	0.066	0.086
*Cr	2.5	1.1	1.5	1.2	1.1	1.5	1.0	1.4	1.4	1.3	1.0	1.1	1.0	1.0	1.0	1.6
Mn	0.10	0.088	0.065	0.021	0.083	0.15	0.033	0.055	0.068	0.073	0.065	0.03	0.034	0.036	0.017	0.093
*Fe	2.5	2.2	5.5	1.8	1.4	1.5	2.1	1.8	1.8	1.5	1.3	1.5	2.7	3.3	1.8	3.3
Co	0.10	0.018	0.02	0.02	0.01	0.012	0.01	0.018	0.06	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Ni	0.46	0.025	0.23	0.11	0.11	0.067	0.066	0.17	0.28	0.074	0.025	0.060	0.045	0.62	0.045	0.13
Cu	0.23	0.11	0.15	0.31	0.24	0.20	0.38	0.20	0.22	0.096	0.19	0.30	0.10	0.12	0.17	0.29
Zn	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ga	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zr	0.14	0.02	0.15	0.12	0.050	0.22	0.048	0.13	0.15	0.38	0.12	0.14	0.045	0.025	0.025	0.10
Nb	0.027	0.13	0.11	0.047	0.037	0.041	0.065	0.092	0.025	0.019	0.045	0.045	0.021	0.021	0.014	0.019
Mo	0.25	0.24	0.24	0.18	0.37	0.29	0.29	0.29	0.15	0.18	0.26	0.29	0.15	0.25	0.23	0.29
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sn	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Sb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ba	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
La	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ce	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Hf	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Bi	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

ppm’s of everything

Example of As-Grown Sample Data and Inference



Observations

255 nm absorption correlates with 1064 nm
- extrapolates to limit of 40 ppm
- weaker correlation at high concentration

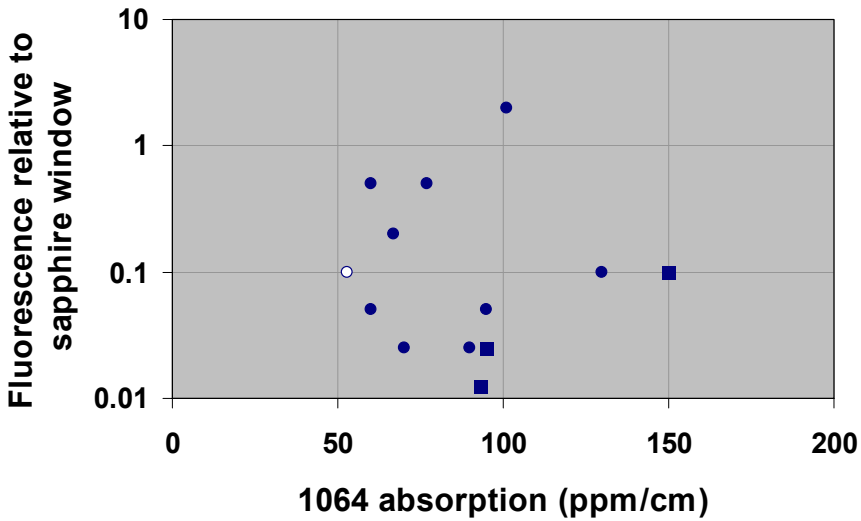
No correlation of 1064 nm absorption and Ti fluor.

Tentative Conclusions

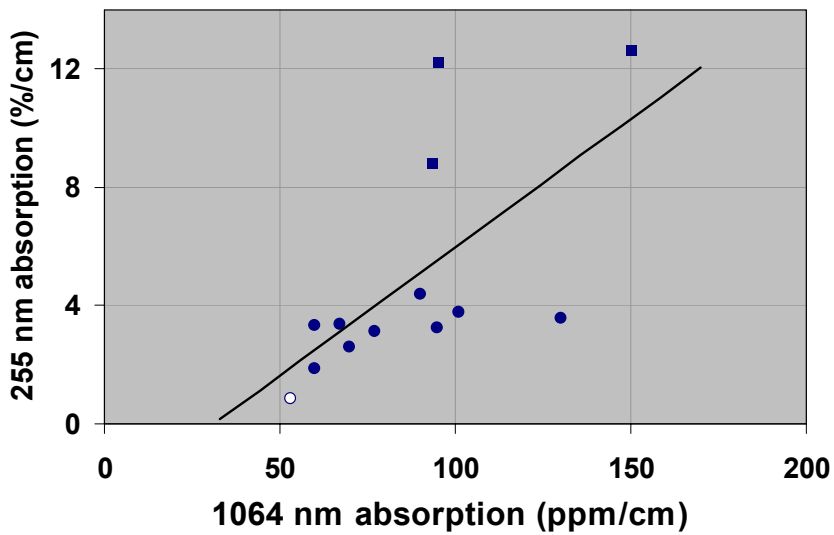
F-center (or correlated defect) contributes to 1064 abs.
- can drive this defect to negligible level
- remaining 40 ppm from another defect

Ti not related to these defects

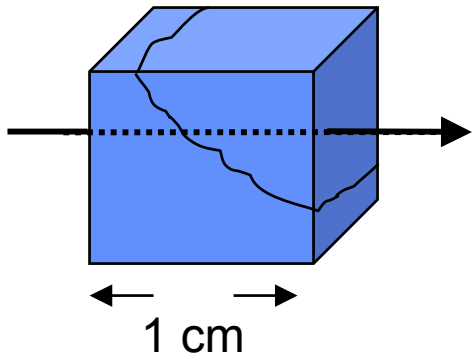
Typical of process for other observed correlations



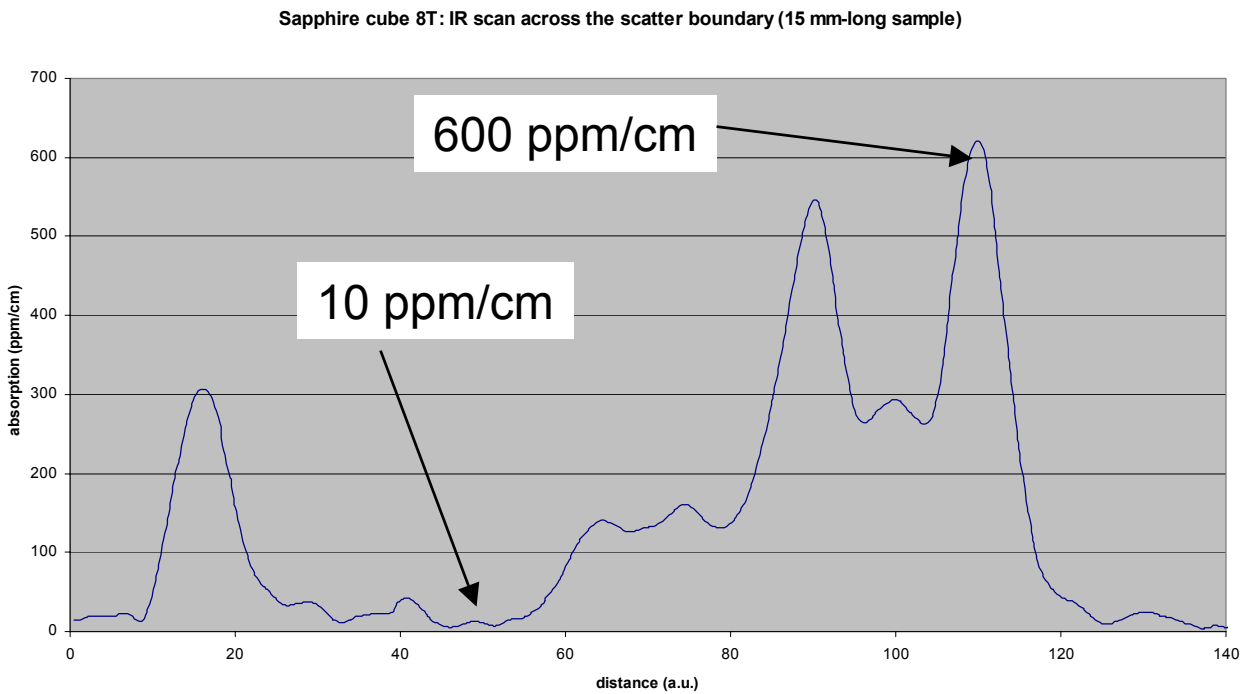
Correlation of absorption in 255 nm band and at 1064 nm



Curious observation (Rosetta Sapphire)



- Single 1 cm sample
  - region with 10 ppm/cm
  - region with 600 ppm/cm
  - abrupt boundary between
- Preparation unexceptional
- Tantalizing existence proof
- Mechanism not yet clear
  - suggests “self-normalizing” measurements

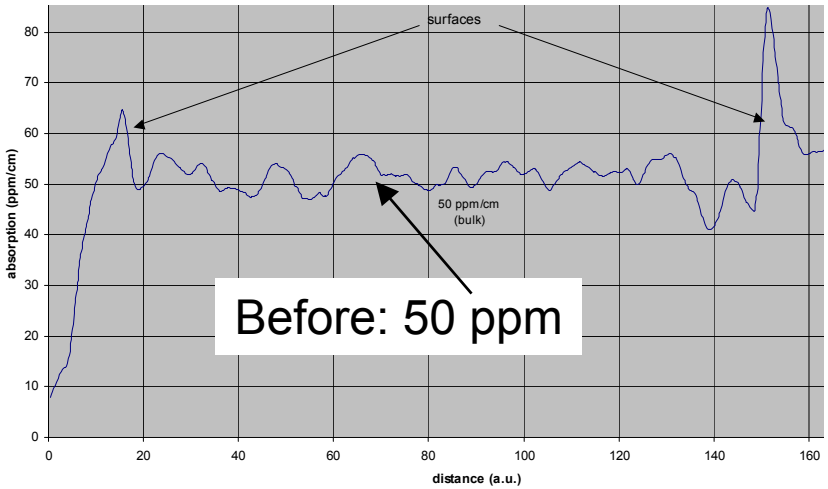


Annealed Samples Show Variety of Outcomes

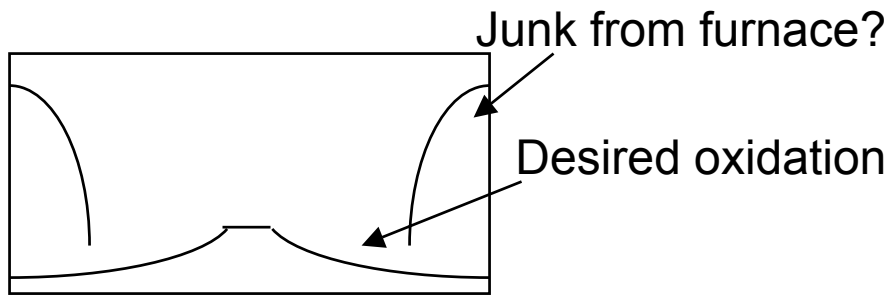
Anneal #	Crystal	Anneal	bulk	dip	surface	bulk	dip	surface	Scattering	Fluor.^
1	LB-1	No	850-1300	no	no	50-60	no	no	no	1/2
1	LB-2	No	1200-1500	no	no	60-70	no	no	no	1/2
2	L14-1	1450C,48 hrs, air	1350	300	600	50	10-20	75	Near surfaces*	2^^
2	L14-2	1450C,48 hrs, air	800	300	2200	75	45	4000	Near surfaces*	1/2^^
3	L14O-1	1450C,48 hrs, air w /O2 assist	1100	250	700	50-60	20	260	Near surfaces*	1/2^^
3	L14O-2	1450C,48 hrs, air w /O2 assist	700	250	700	45	25	900	Near surfaces*	1/2^^
4	L16-1	1600C, 48 hrs, air	80-170	no	350	25	no	90	Maximum in the bulk**	1/200
4	L16-2	1600C, 48 hrs, air	170	no	500	35	no	140	Maximum in the bulk**	1/200
5	L16O-1	1600C,48 hrs, air w /O2 assist	120	no	300	80	no	220	Maximum in the bulk**	1/200
5	L16O-2	1600C,48 hrs, air w /O2 assist	200	no	375	90	no	300	Maximum in the bulk**	1/200
6	LH17-a	1750C, 24 hrs, H2	600-1700	no	25000	60-170	no	37000	no	1/2^^^
6	LH17-b	1750C, 24 hrs, H2	1700	no	5000	125	no	250	no	1/2^^^
7	L1696-1	1600C, 96 hrs, air	300	no	450	50	no	140	Maximum in the bulk**	1/400
7	L1696-2	1600C, 96 hrs, air	230	no	500	32	no	120	Maximum in the bulk**	1/300
8	L17H1696-1	1750C, 24 hrs, H2+1600C,96hrs,air	300	no	1300	100	no	500	Maximum in the bulk**	1/400
8	L17H1696-2	1750C, 24 hrs, H2+1600C,96hrs,air	230	no	900	35	no	250	Maximum in the bulk**	1/400
9	LN16-1	1600C, 48 hrs, nitrogen	400	no	450	50	no	80	Maximum in the bulk**	<1/100
9	LN16-2	1600C, 48 hrs, nitrogen	300	no	350	40	no	600	Maximum in the bulk**	<1/100
10	L169-1	1600C,48 hrs, air - 900C hold 48 hrs during CD	3500	no	4000	550	no	1200	Weak in the bulk	<1/100
10	L169-2	1600C,48 hrs, air - 900C hold 48 hrs during CD	700	no	800	150	no	165	Maximum in the bulk**	<1/100
11	LH14-1	1450C,48 hrs, hydrogen	650-800		1200-1300	40		70	no	
11	LH14-2	1450C,48 hrs, hydrogen	1750		2000	60		80	no	
	^Relative to the reference 3 mm-thick w indow									

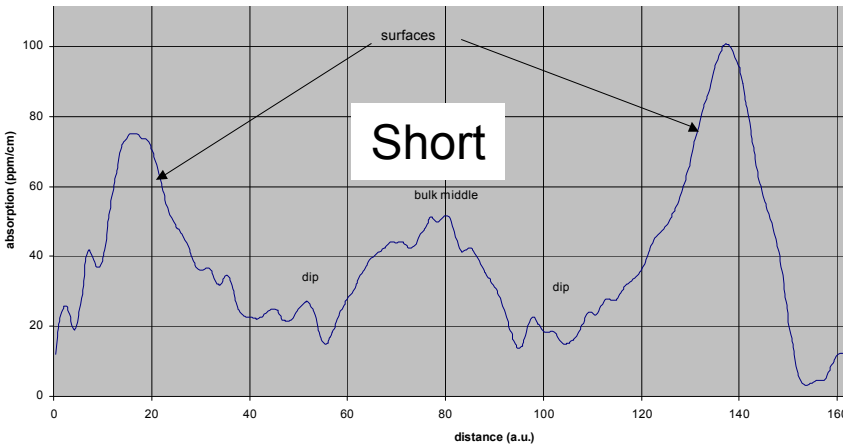
similar table exists for as-grown cubes

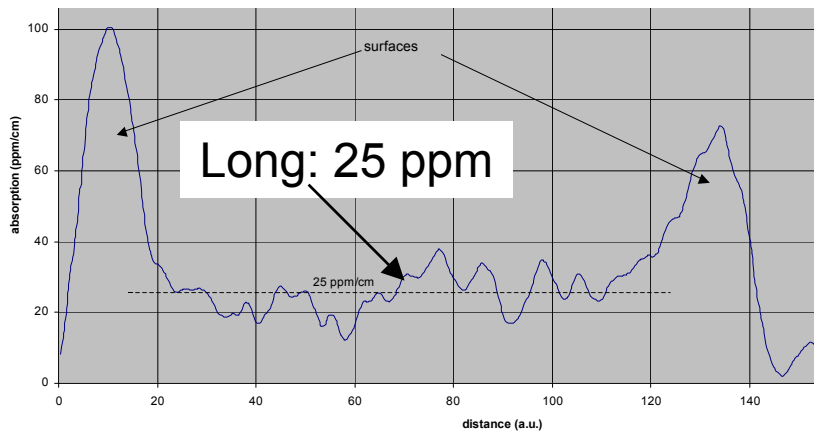
Typical Annealing results



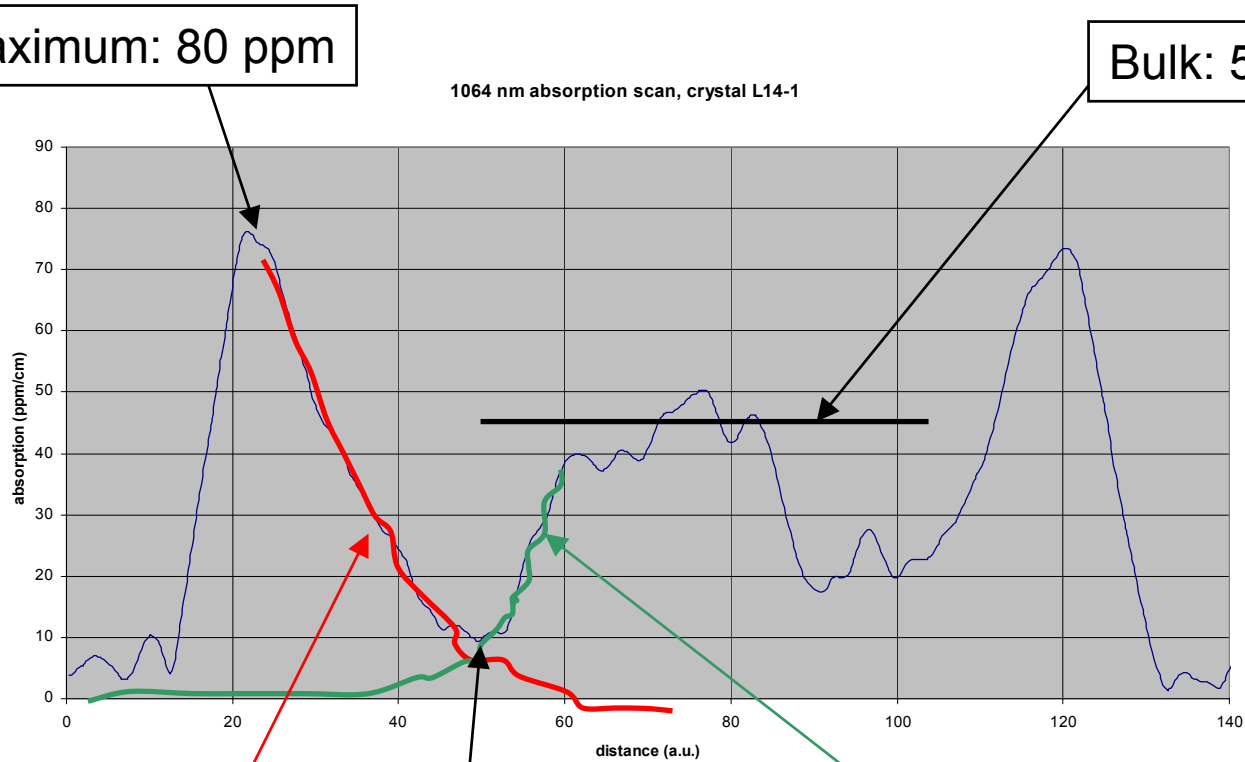
- 1 cm thick window
- Two diffusion waves?





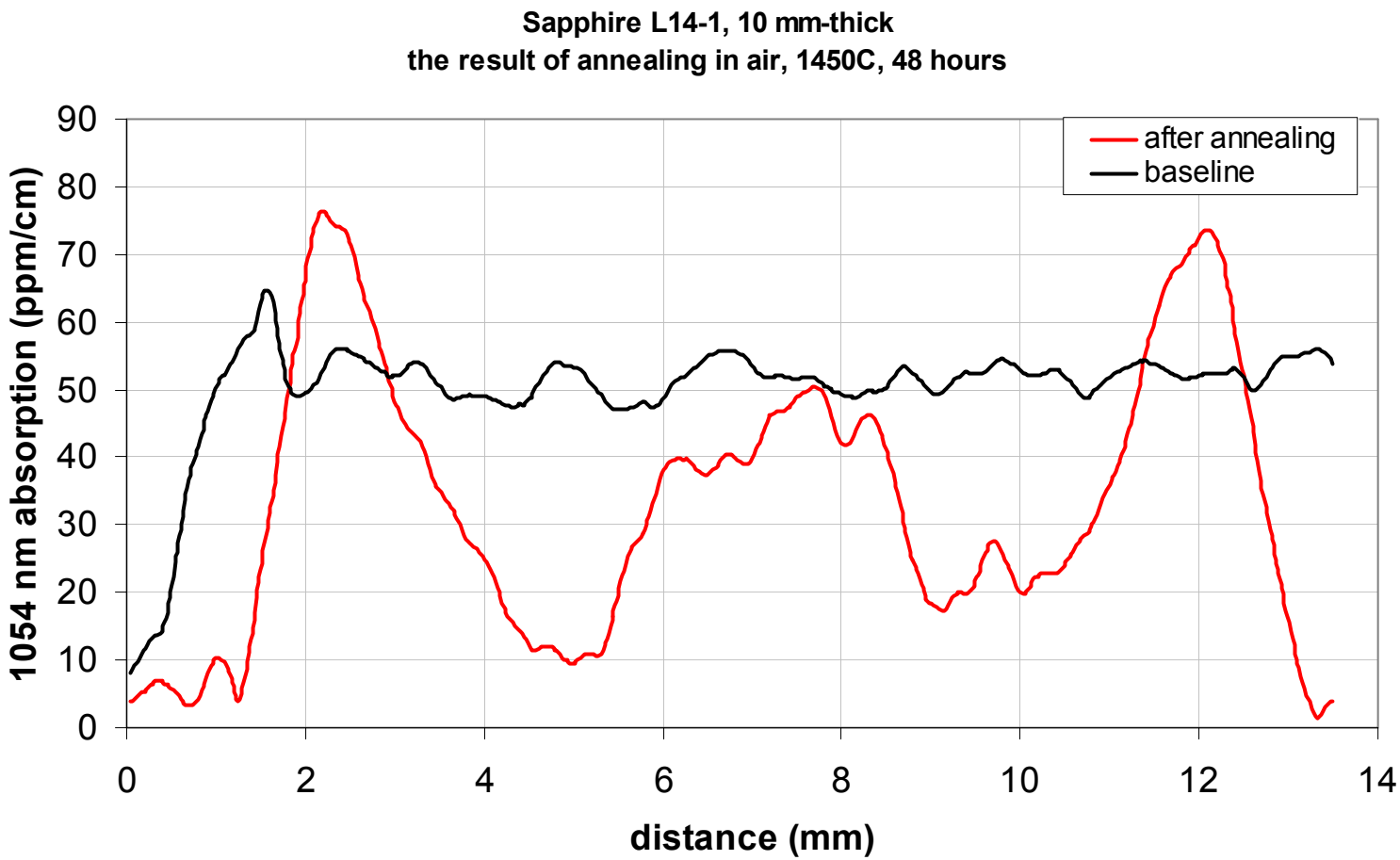


Complicated Annealing Phenomena



1064 nm absorption through cross-section of a cube

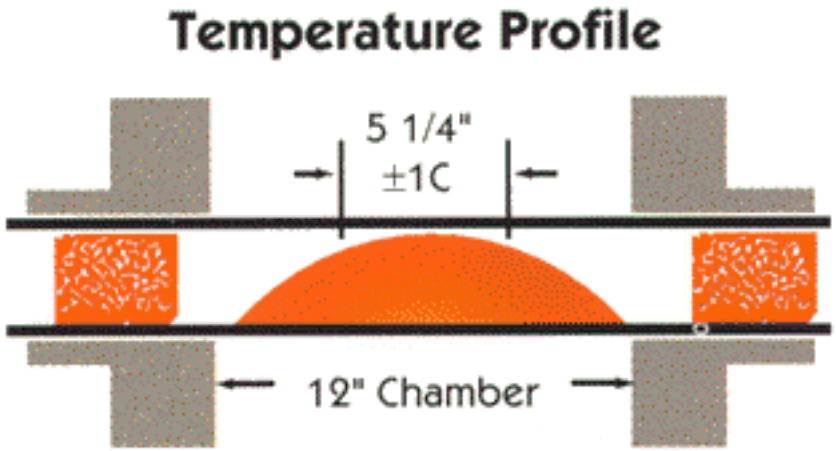
Annealing Reduces Absorption, Inhomogeneously



- Annealing by CSI in air at 1450°C lowers absorption to 10 ppm
- “Wings” suggested surface contamination in CSI furnace
- CSI acquire new (uncontaminated) 1700° C furnace
- Stanford carry out parallel studies for comparison purposes

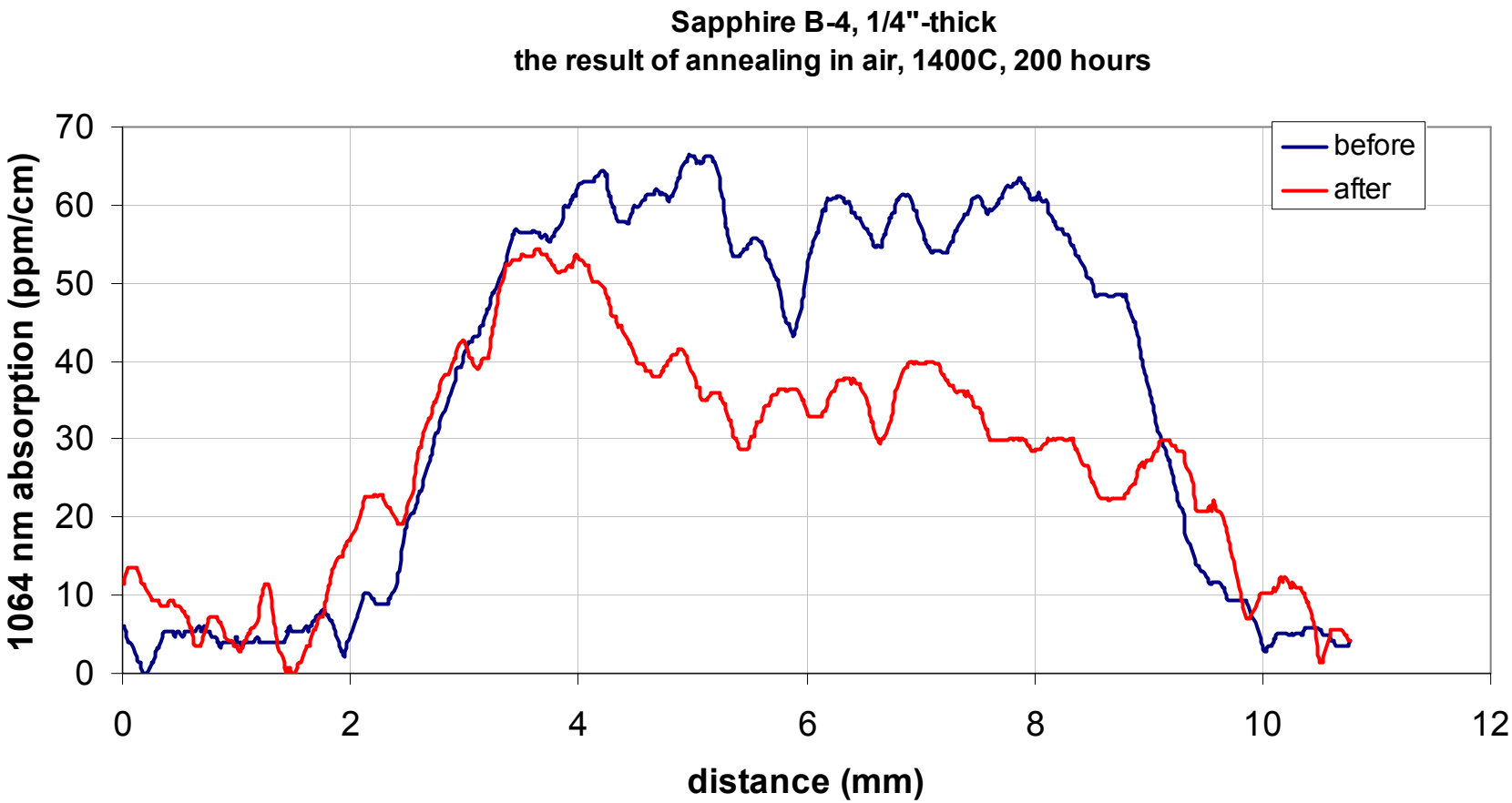
Post-Growth Heat Treatment Studies

- Controlled Atmosphere Processing at Stanford
  - Oxidizing conditions - air or oxygen
  - Reducing conditions - 5% H2 : 95% N2



SiC "glowbar" heated, 1400° C maximum
2" dia, high density 998 alumina process tube
O-ring sealed Ultratorr fittings at both ends for atmosphere control
Vestibules packed with firebrick

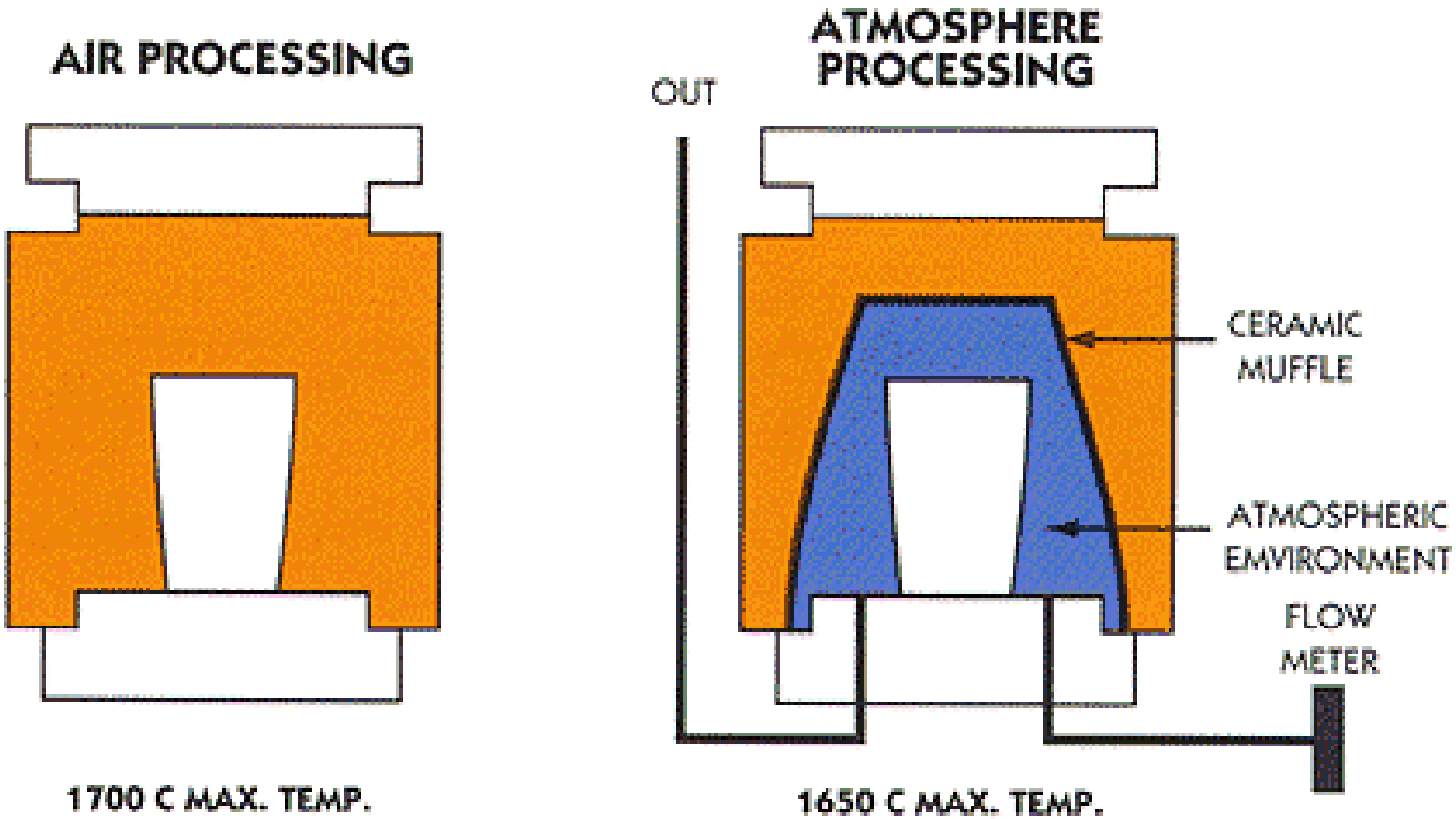
Test contamination by comparison with SU furnace



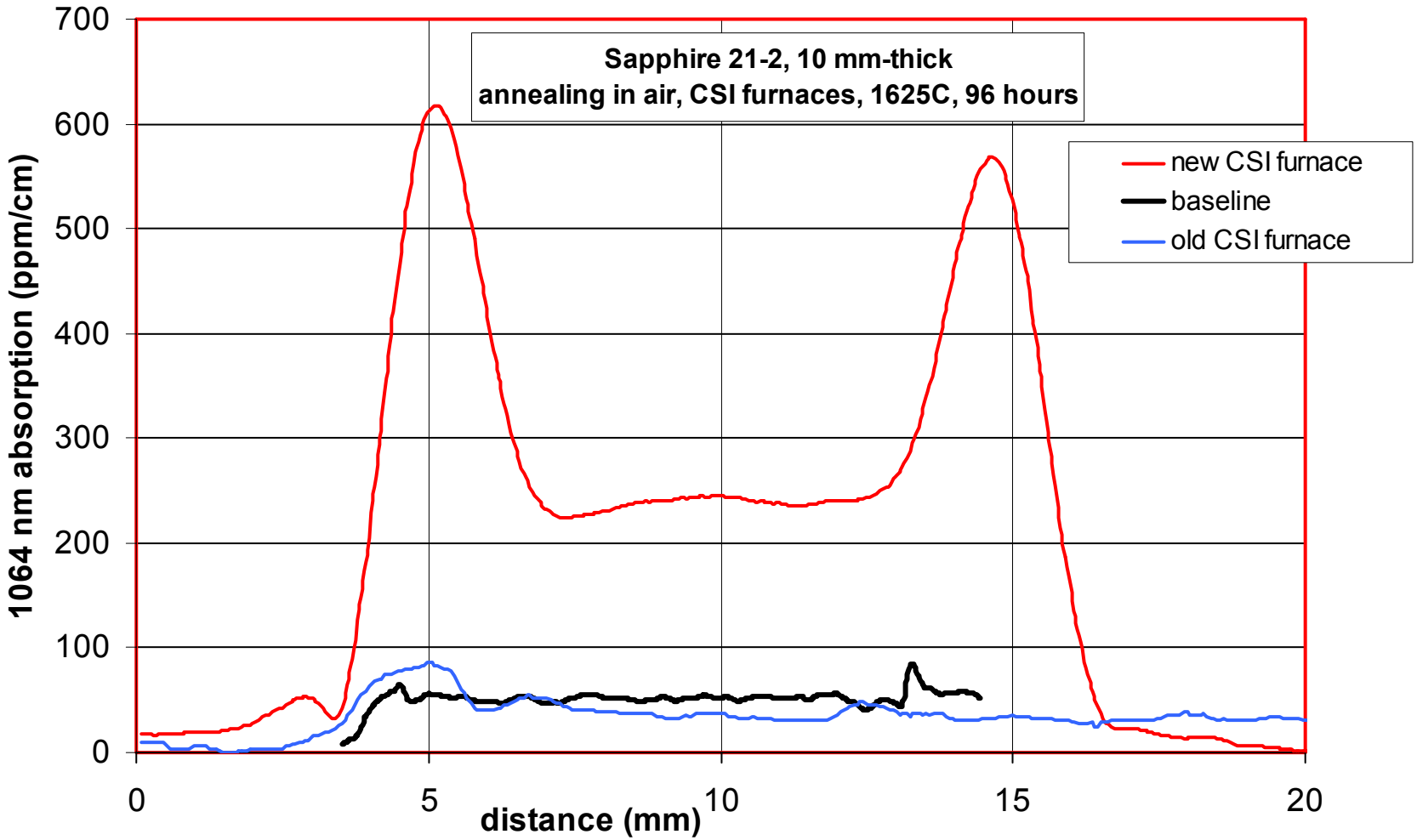
- Annealing in air at 1400°C lowers absorption compared to ref
- No evidence of surface contamination in SU furnace

Post-Growth Heat Treatment Studies

- High Temperature Processing at Crystal Systems
  - Purge gas conditions – air, oxygen or forming gas (5% H2 in N2)



Annealing in New CSI Furnace in Air



- New furnace appears to have more serious contamination than old

Highlights of Annealing Experiments in Air

Crystal	Anneal	α (ppm/cm)						Scattering	Fluor.^
		514 nm			1064 nm				
		bulk	dip	surface	bulk	dip	surface		
annealed in CSI									
L14-1	1450C,48 hrs, air	1350	300	600	50	10-20	75	Near surfaces*	2^^
L1696-2	1600C, 96 hrs, air	230	no	500	32	no	120	Max. in bulk**	1/300
21-2	1625C, 96 hrs, air				240	no	600		
annealed in Stanford									
B-4-B	Control	1200	no	1200	60	no	60-70		
B-4-A	1400C, 200 hrs, air, tube #2	1100	700-800	900-1200	35	<20	20-100		

^Relative to the reference 3 mm-thick window

*Moderate, increases from surface to the bulk, drops to zero in the central part

**Strong, increases from surface to the bulk

^^Fluorescence in the central part of the crystal; drops by orders of magnitude closer to surfaces

- Highlights chosen from a total of 36 separate annealing experiments
- New furnace appears to have more serious contamination than old

Observed Trends

- Annealing
  - oxygen annealing appears to reduce bulk absorption
  - surface contamination appears to limit final outcome
    two diffusion “waves”: one reduces loss, one increases it
- No strong correlation with starting material
  - native defect?
  - furnace contamination ✓
- No strong correlation with position in boule or use of re-melted feedstock
  - native defect?
  - furnace contamination ✓
  - multiple impurities?

Highlights of Annealing Experiments in Hydrogen

Crystal	Anneal	α (ppm/cm)						Scattering	Fluor.^
		514 nm			1064 nm				
		bulk	dip	surface	bulk	dip	surface		
annealed in CSI									
LB-1	No	850-1300	no	no	50-60	no	no	no	1/2
LB-2	No	1200-1500	no	no	60-70	no	no	no	1/2
LH17-a	1750C, 24 hrs, H2	600-1700	no	25000	60-170	no	37000	no	1/2^^^
LH17-b	1750C, 24 hrs, H2	1700	no	5000	125	no	250	no	1/2^^^
LH14-1	1450C,48 hrs, hydrogen	650-800	no	1200-1300	40	no	70	no	
LH14-2	1450C,48 hrs, hydrogen	1750	no	2000	60	no	80	no	
LH12-1	1200C, 48 hrs, hydrogen				30-40	no	60	no	
LH12-2	1200C, 48 hrs, hydrogen				20-30	no	30	no	
annealed in Stanford									
LH12S-1	As-grown				40-50	no	40-50	no	
A-1	Control				1200-1500	?	?		
A-1	1200C, 24 hrs, 5%H2/N2, tube #1				1000-1200	?	?		
B-1-B	Control								
B-1-A	1400C, 48 hrs, 5%H2/N2, tube #1				30-35	no	<=bulk		
B-3-B	Control				45-80	no	50-110		
B-3-A	1400C, 200 hrs, 5%H2/N2, tube #2	900-1200	no	900-1000	25-50	no	<=bulk		
^Relative to the reference 3 mm-thick w indow									

- Highlights chosen from a total of 36 separate annealing experiments
- Low temperature hydrogen annealing promising
- High temperature hydrogen annealing in clean system needs study

Status / Plans

- Currently:
  - ~ 40 ppm/cm ~reproducible
  - 25 ppm/cm observed in macroscopic volumes
  - 10 ppm/cm in isolated regions
  - tested and verified existence of surface contamination in CSI process
    comparison using low temperature annealing furnace at SU
    probably confounded comparisons of source material and location in boule
- Next steps:
  - elimination of surface effects is essential for reproducible studies
    modification to CSI annealing furnace / process is clearly needed
    installation of 1700 C tube furnace at SU for parallel studies
    use of larger sample sets
    more careful surface prep and absorption measurement prior to annealing
  - repeat best annealing conditions w/o surface contamination “wave”
  - revisit impurity correlations after reproducible annealing
  - neutron activation with Southern U. (McGuire)
  - multi-wavelength PCI

  - “solid-state electrolysis” from General Physics Institute (Y, Danileiko)?