

Heat-Treatment and Optical Absorption Studies on Sapphire

LIGO-G040084-00-Z

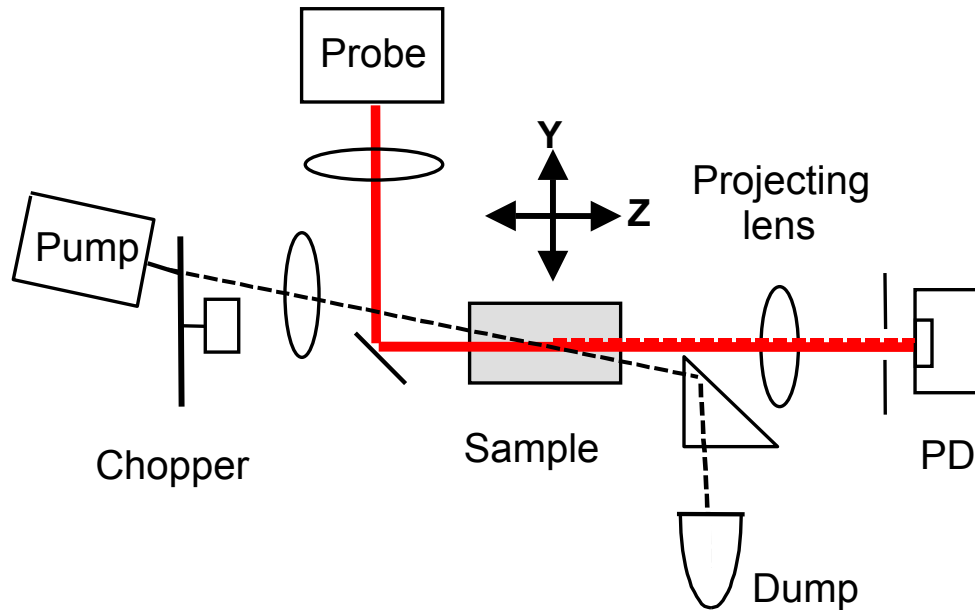
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Lasers and Optics Working Group

LIGO LSC meeting, LLO 3/17/04

Photothermal Common-Path Interferometry

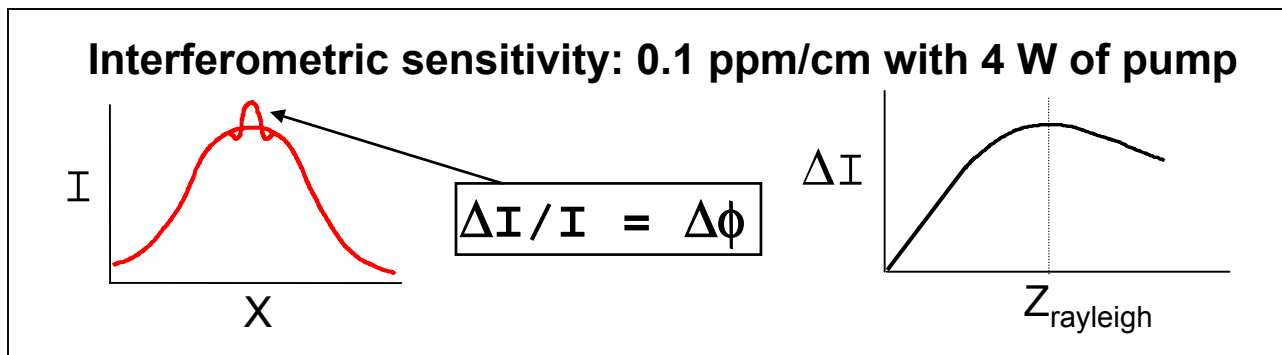
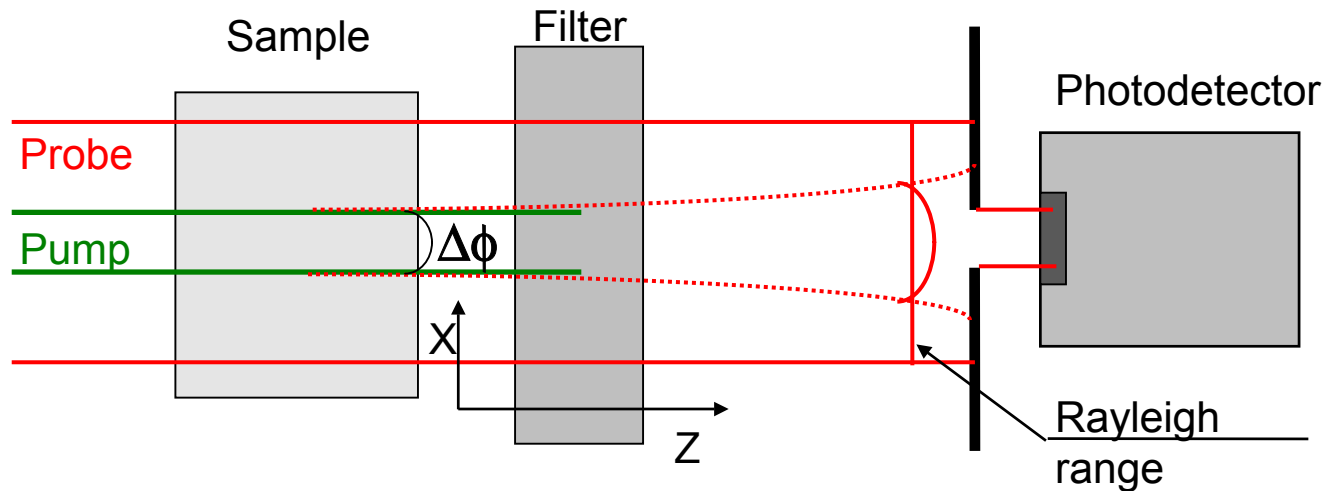
- diffraction regime of cross-beam cw thermal lensing -



Pump waist	50 μ	Chopping frequency	380 Hz (10Hz- 2 kHz)
Probe waist	120 μ	Crossing angle	1° - 20° (in air)
Pump power	5 W	Probe power	0.5 mW

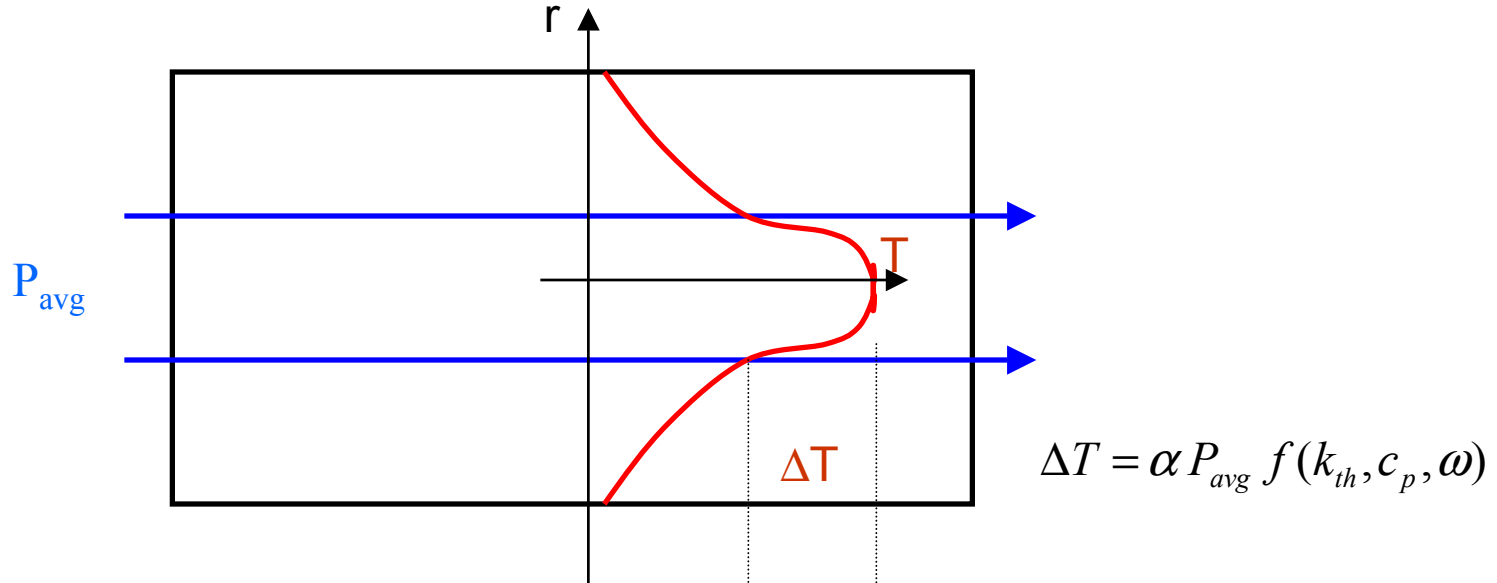
- ac-component of probe distortion is detected by photodiode + lock-in
- absorption coefficient $<10^{-7} \text{ cm}^{-1}$ (~10 ppb coating) can be detected with 5 W pump power
- crossed beams help to avoid false signals from optics and surfaces of the sample

Photothermal Common-Path Interferometry for optical loss measurements 'Self-interference' of probe in the near field



Temperature Rise in Absorbing Medium

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



- Leads to radially varying index:

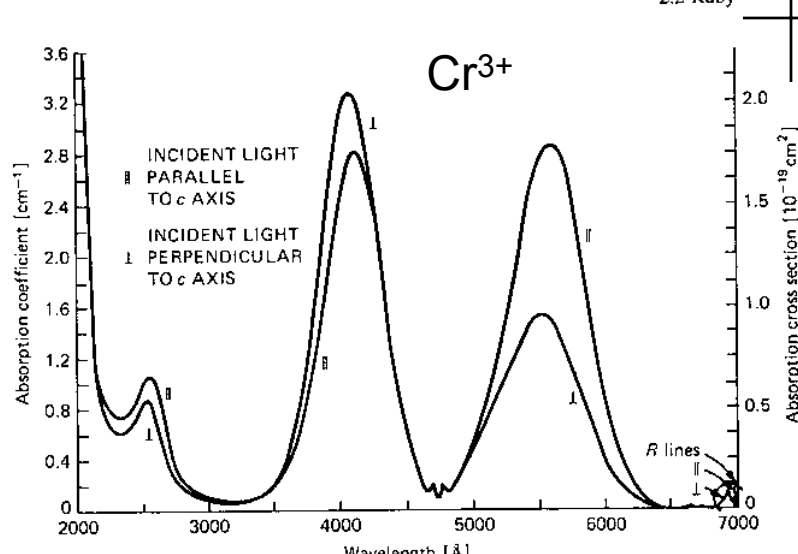
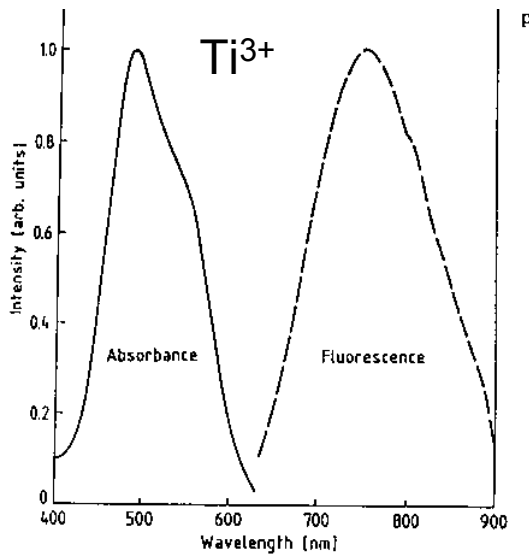
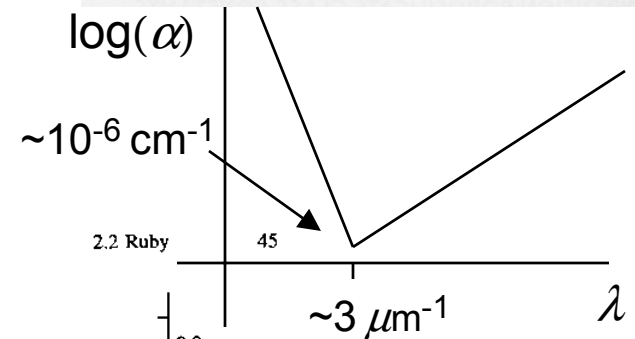
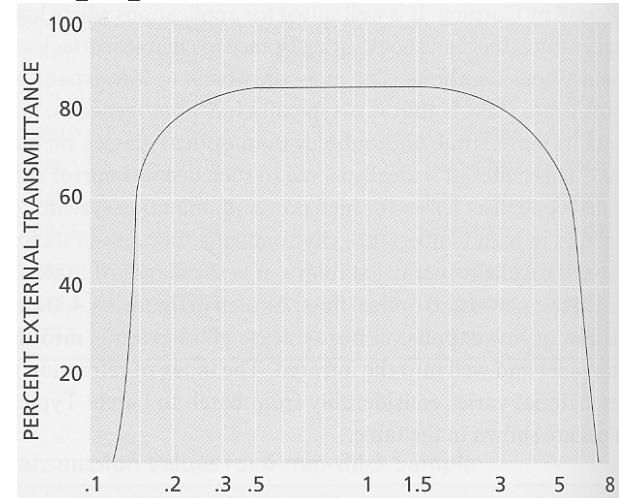
$$\Delta n = \frac{dn}{dT} \Delta T$$

- Leads to radially varying phase on optical beam:

$$\begin{aligned} \Delta \phi &= \frac{2\pi}{\lambda} \frac{dn}{dT} \Delta T L \\ &= \frac{2\pi}{\lambda} \frac{dn}{dT} \alpha P_{avg} L f(k_{th}, c_p, \omega) \end{aligned}$$

Study of absorption in sapphire

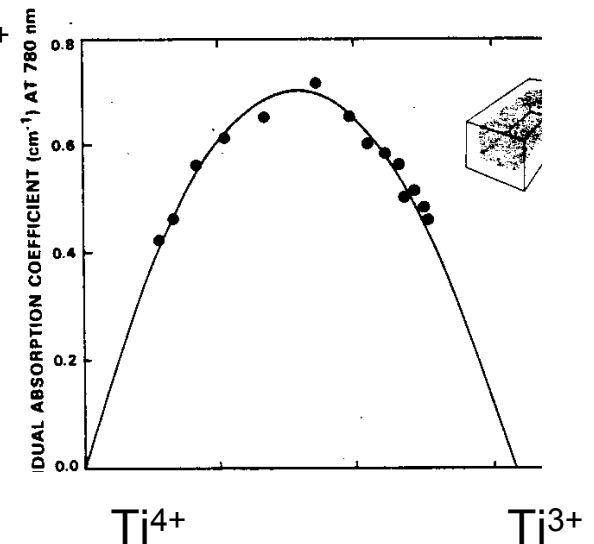
- Intrinsic
 - conduction to valence band in UV
 - multiphonon in mid-IR
 - only cure is different material
expectation and existence proofs indicate this isn't the problem
- Extrinsic
 - native defects
vacancies, antisites, interstitials,
 - impurities
e.g. transition metals: Cr, Ti, Fe, ...



Characteristics of absorbing species

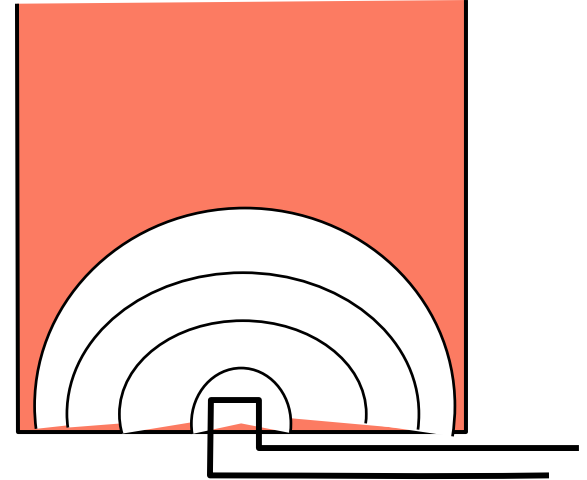
- Allowed transitions
 - large cross sections \Rightarrow ppm concentrations significant
- Broad spectral features
 - identification difficult
 - off “resonant” absorption significant
 - sum of several species can contribute to absorption at given λ
- Redox state important
 - e.g. $\alpha[\text{Ti}^{3+}] \neq \alpha[\text{Ti}^{4+}]$
 - annealing alters absorption without altering impurity concentrations
- Impurities do not necessarily act independently
 - Al : Al : Ti³⁺ : Ti⁴⁺ : Al : Al \neq Al : Ti³⁺ : Al : Al : Ti⁴⁺
 - absorption spectra at high concentrations not always same as low
complicates correlations to known spectra

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



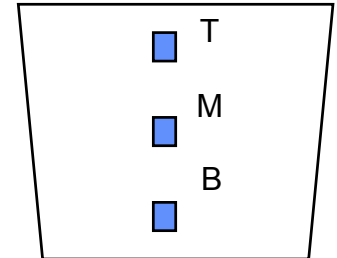
Growth of sapphire at Crystal Systems, Inc. by the HEM process

- 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
- LIGO target - 10 to 20 ppm/cm at 1064 nm
- Typical CSI “Hemex white” 40 to 60 ppm/cm

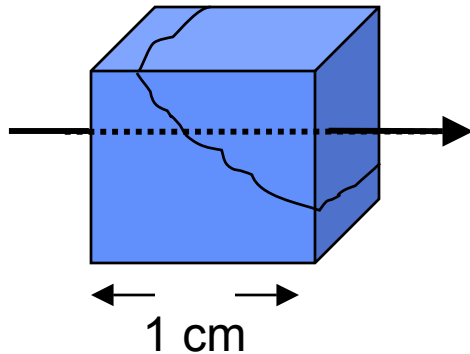


Collaborative studies with CSI

- **Experimental design**
 - anticipated mechanisms: impurity concentration, intrinsic defects, redox state
 - two main control methods: growth and heat treatment
- **Growth Studies**
 - ~ 30 CSI White, 1 cm cubes
 - primarily expected to influence impurity concentration
 - starting materials
 - virgin material from 5 different vendors/purity
 - re-melted boules
 - samples cut from top/middle/bottom of boule
 - explore impurity segregation effects
 - no strong correlation found
- **Heat Treatment Studies**
 - 25 mm dia x 10-12.5 mm thick a-axis CSI Hemex White
 - intermediate temp. annealing: time, temperature, reducing (H_2) or oxidizing (air, O_2) conditions, heating / cooling rates
 - primarily influence redox state of intrinsic defects (e.g. oxygen vacancies) and extrinsic defects
 - high temp. vacuum annealing: time, temp., background pressure, heating / cooling rates
 - may influence extrinsic defect concentrations as well

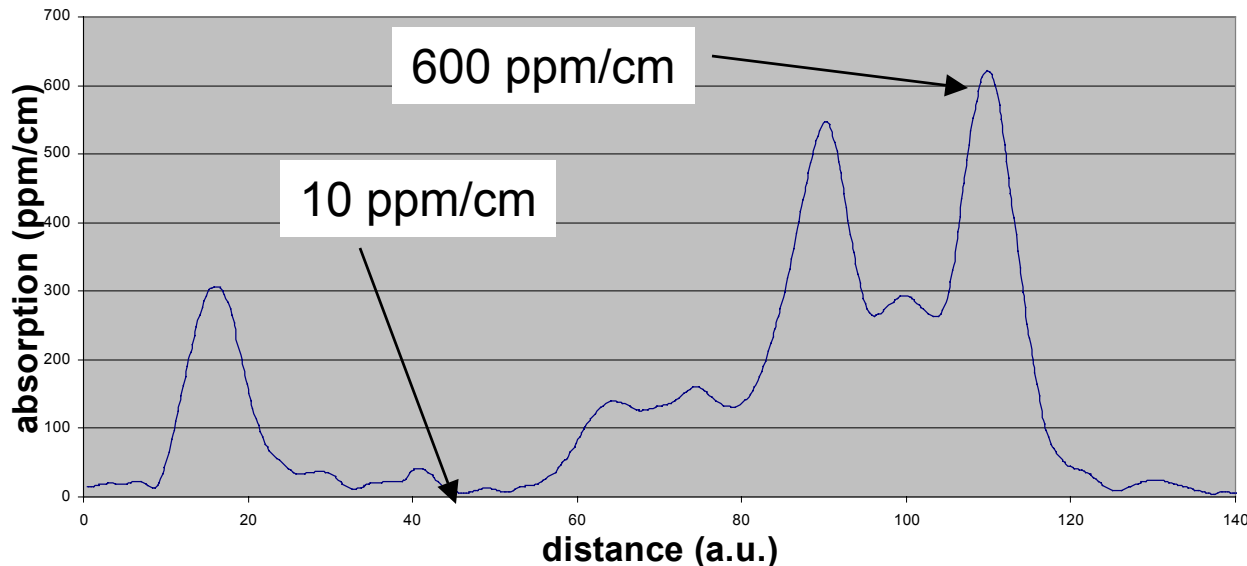


Low optical loss existence proof (Rosetta sapphire)



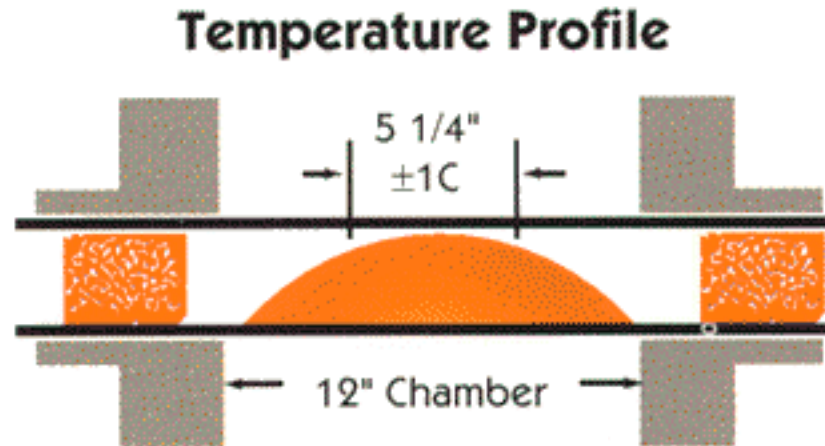
Sapphire cube 8T: IR scan across the scatter boundary
(10 mm-long sample)

- Single 1 cm sample
 - region with 10 ppm/cm
 - region with 600 ppm/cm
 - abrupt boundary between
- Preparation unexceptional
- Mechanism not yet clear
 - not typical of normal impurity segregation
 - specimen should be useful for “self-normalizing” measurements



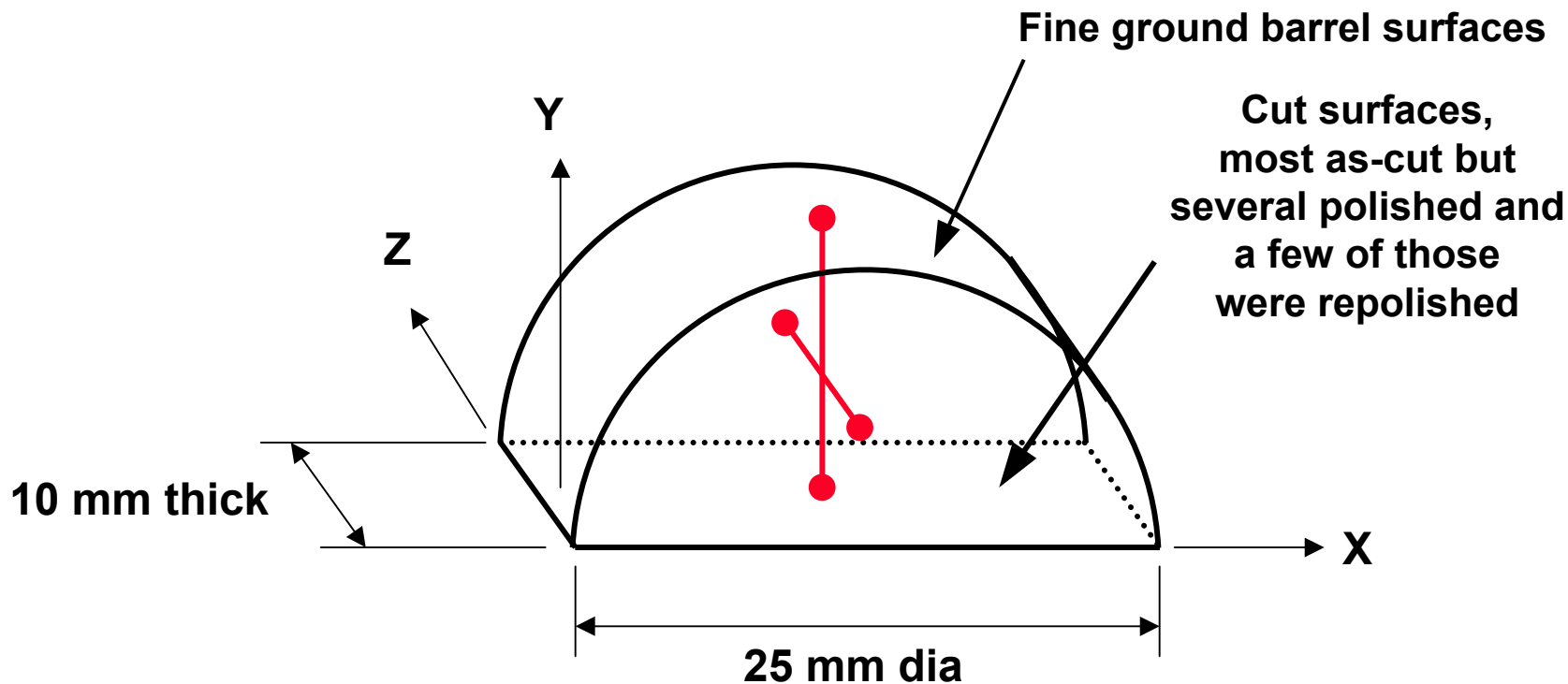
Post-growth heat treatment studies

- Controlled atmosphere processing
 - Oxidizing conditions - air or oxygen
 - Inert/reducing conditions - N₂ w/wo H₂
 - Initial heating / cooling rate studies



MoSi₂ "Super Kanthal" max. temp. to 1700° C
High density 998 alumina process tube, 3" OD
O-ring sealed fittings at both ends for atmosphere control
Vestibules closed with 998 alumina heat shields

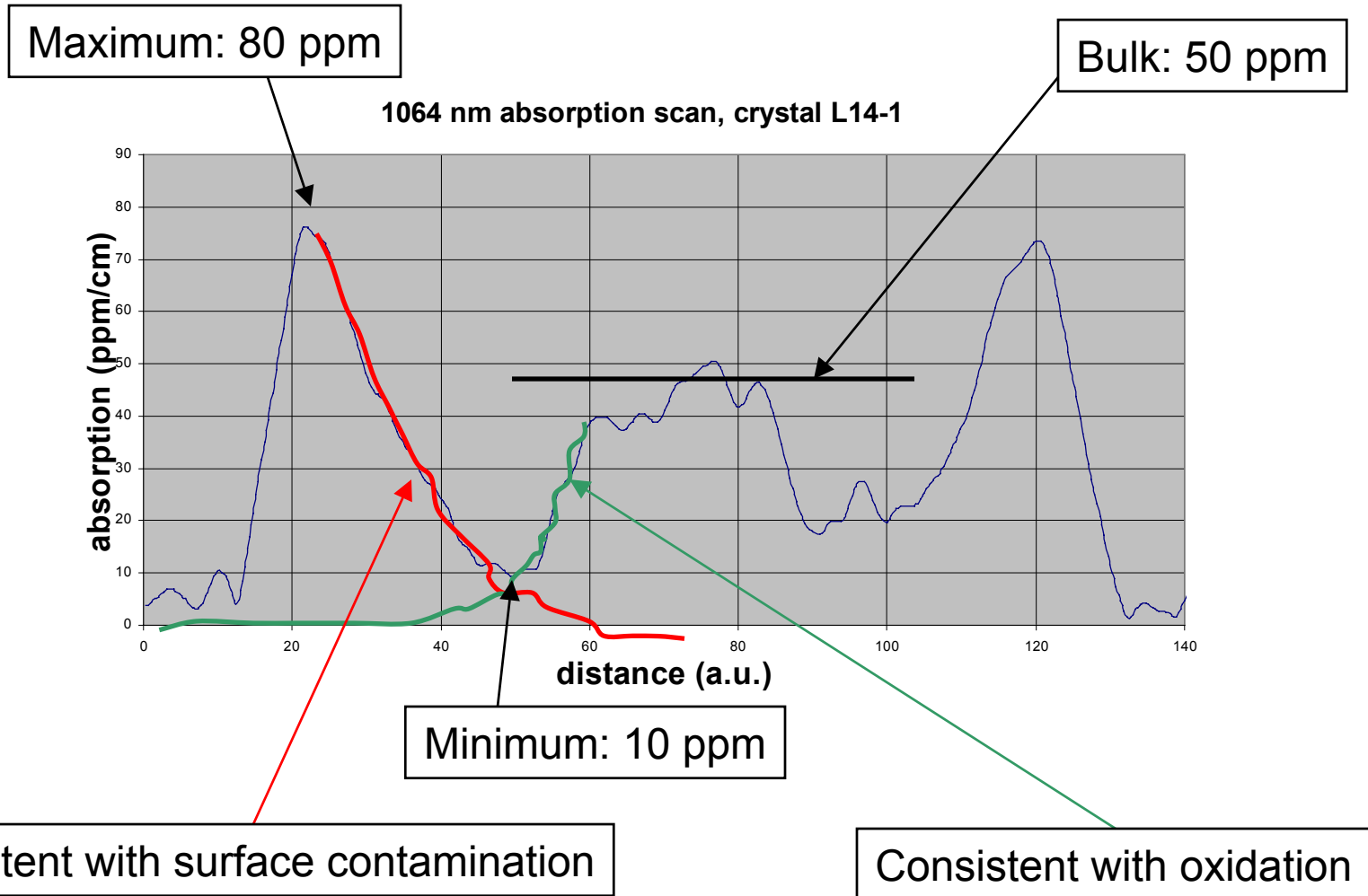
Optical loss measurement scheme for sapphire windows



● — ● Locus of intersection of pump and probe beam where absorption in a 100 micron long x 25 ϕ micron cylinder is measured during Y- and Z-scans

Complicated air-annealing behavior

(1064 nm absorption through cross-section of a window)

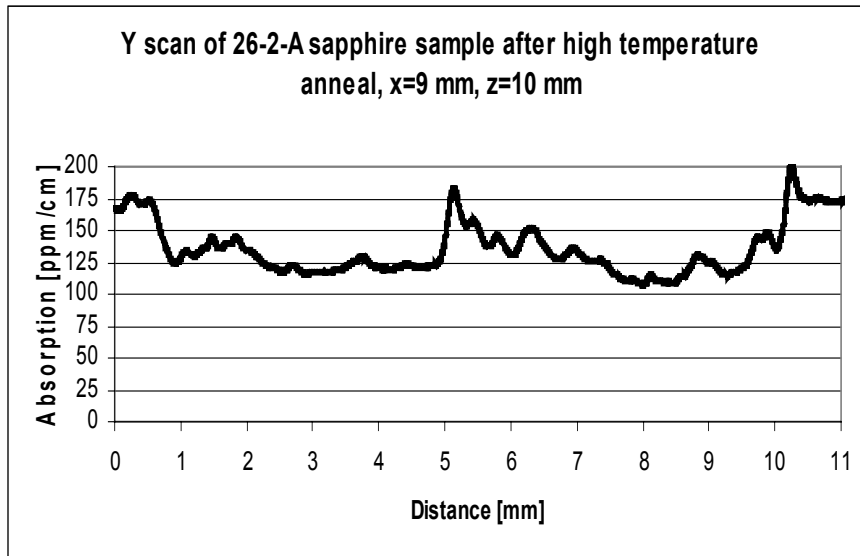


Annealing at high temperatures under oxidizing conditions

Y-Scan

Fine-Ground

Fine Ground

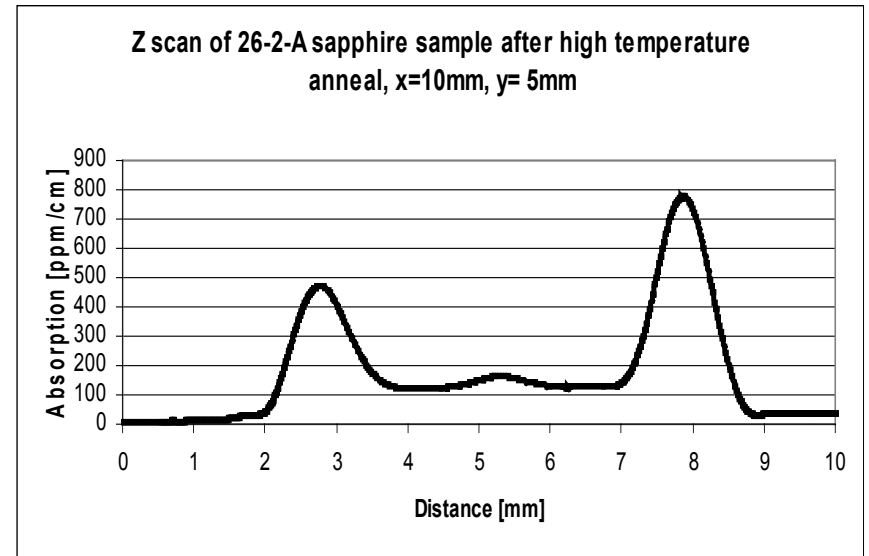


Initial absorption - 50 ppm/cm

Z-Scan

Polished Face

Polished Face



Initial absorption - 50 ppm/cm

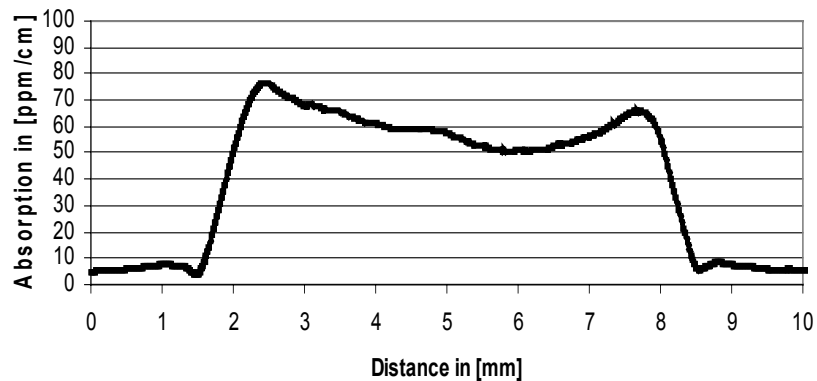
Consistent trends under oxidizing anneals

- **As grown**
 - **Unclear correlation with starting material or furnace**
 - Question of impurities, native defects and process contamination unresolved
 - **No strong correlation with position in boule or use of re-melted feedstock**
 - “Rosetta” sapphire indicates melt segregation operative during growth
 - Difficult to understand as simple impurity segregation
- **After oxidizing anneals**
 - **Intermediate temperature annealing reduces bulk absorption at 1064 nm and reduces fluorescence (due to Ti^{3+}), but increases scatter**
 - **High temperature annealing increases bulk absorption and increases scatter**
 - **Surface kinetics and/or surface contamination influences outcome**
 - Two diffusion “waves”: one reduces loss, one increases it
 - Rough surfaces enhance effect
- **Oxidizing anneals do not appear to offer a feasible route to low loss material**

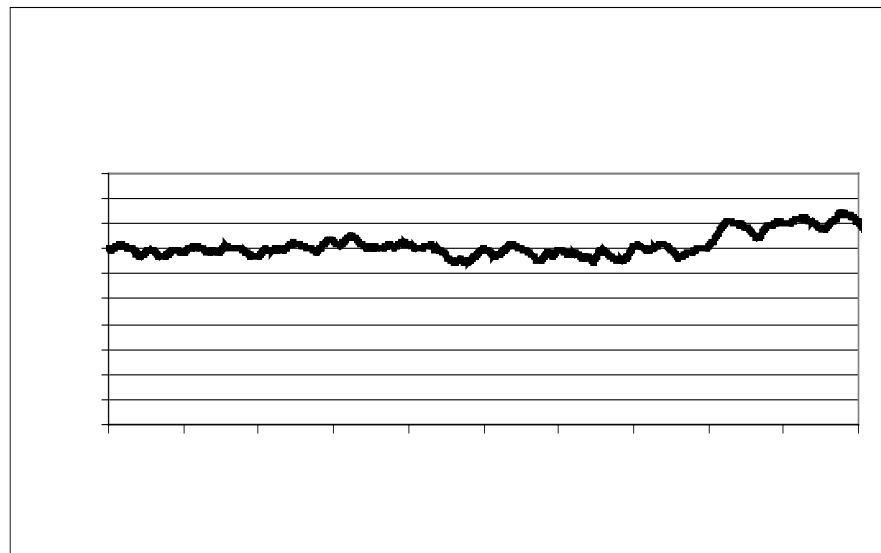
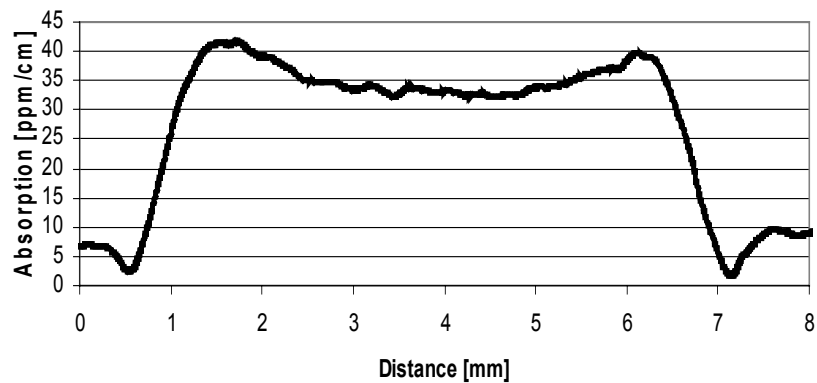
z

Y

Z scan of 23-2-A sapphire sample before heating
x=10 mm, y=5 mm

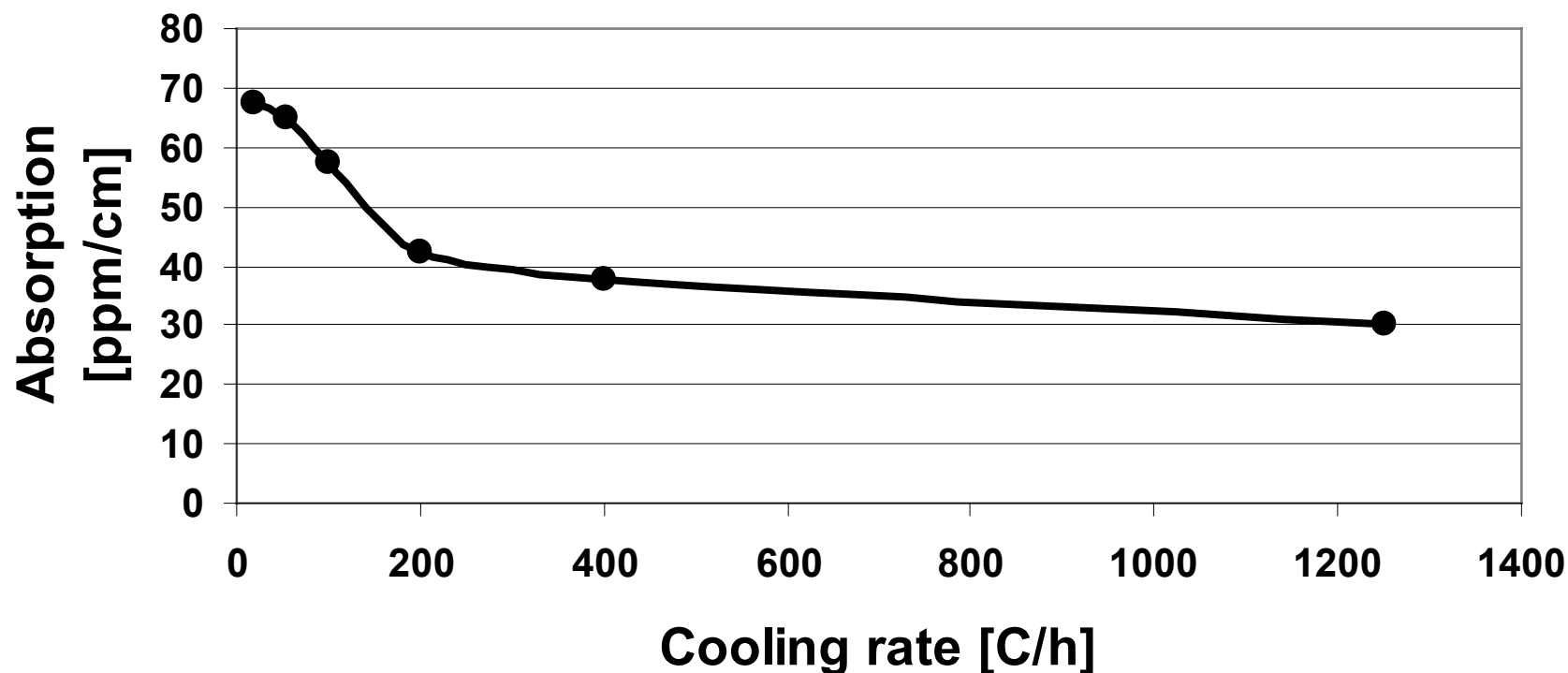


Z scan of 23-2-A sapphire sample annealed for 48 hrs under
reducing conditions, X=10mm, y=5 mm



Observed trends under inert/reducing conditions

Residual absorption of sapphire 23-1-B sample
annealed at intermediate temperatures vs cooling
rate

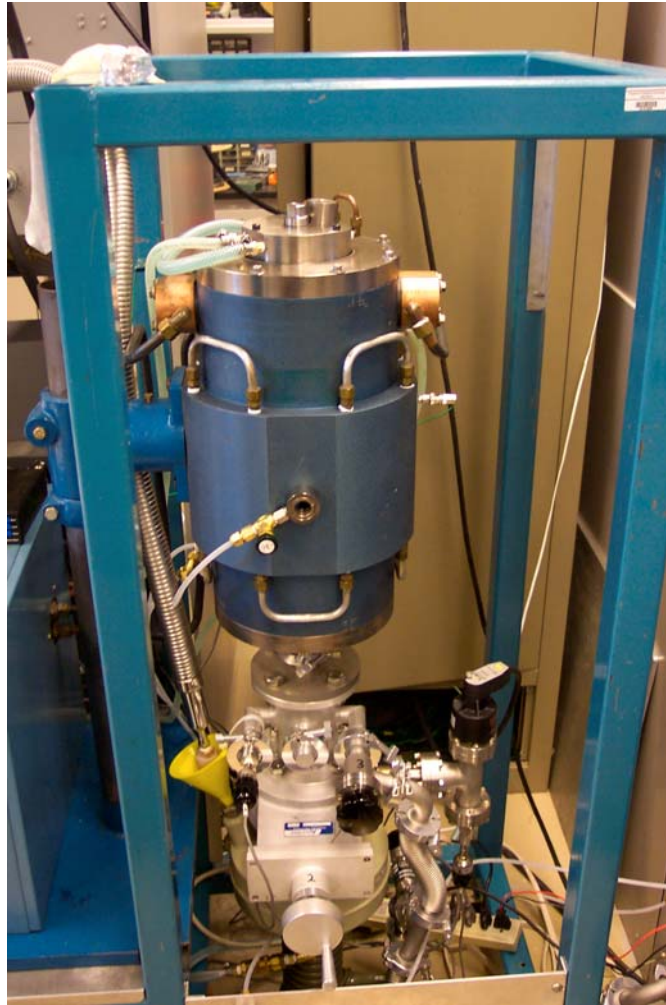


Thermal Stability of Rapidly Cooled Sapphire Windows

ID	Ambient	Temp.	Time	Cooling Rate	Gas Flow	Before HT	After HT	Comments
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Half CSI windows, 25.4 mm dia by 10 mm thick								
24-1-B	H2/N2	Intermediate	18 hrs	4900 C/hr	0.2 CFH	55	22-24	Fan cool
24-1-B	H2/N2	500 C	13 hrs	100 C/hr	0.2 CFH	22-24	22-24	Low T stability
30-2-A	H2/N2	low-intermediate	18 hrs	1250 C/hr	0.2 CFH	50-55	50-55	Crash cool
30-2-A	H2/N2	high	18 hrs	2700 C/hr	0.2 CFH	53	26	Crash cool
30-2-A	H2/N2	500 C	13 hrs	100 C/hr	0.2 CFH	25-30	25-30	Low T stability
30-2-A	H2/N2	600 C	13 hrs	100 C/hr	0.2 CFH	25-30	25-30	Low T stability
31-1-A	H2/N2	low	18 hrs	780 C/hr	0.2 CFH	85	85	Crash cool
31-1-A	H2/N2	high	18 hrs	2700 C/hr	0.2 CFH	85	30-40	Crash cool
31-2-A	H2/N2	intermediate	18 hrs	2000 C/hr	0.2 CFH	35	22-24	Crash cool
31-2-A	H2/N2	600 C	13 hrs	100 C/hr	0.2 CFH	22-24	22-24	Low T stability

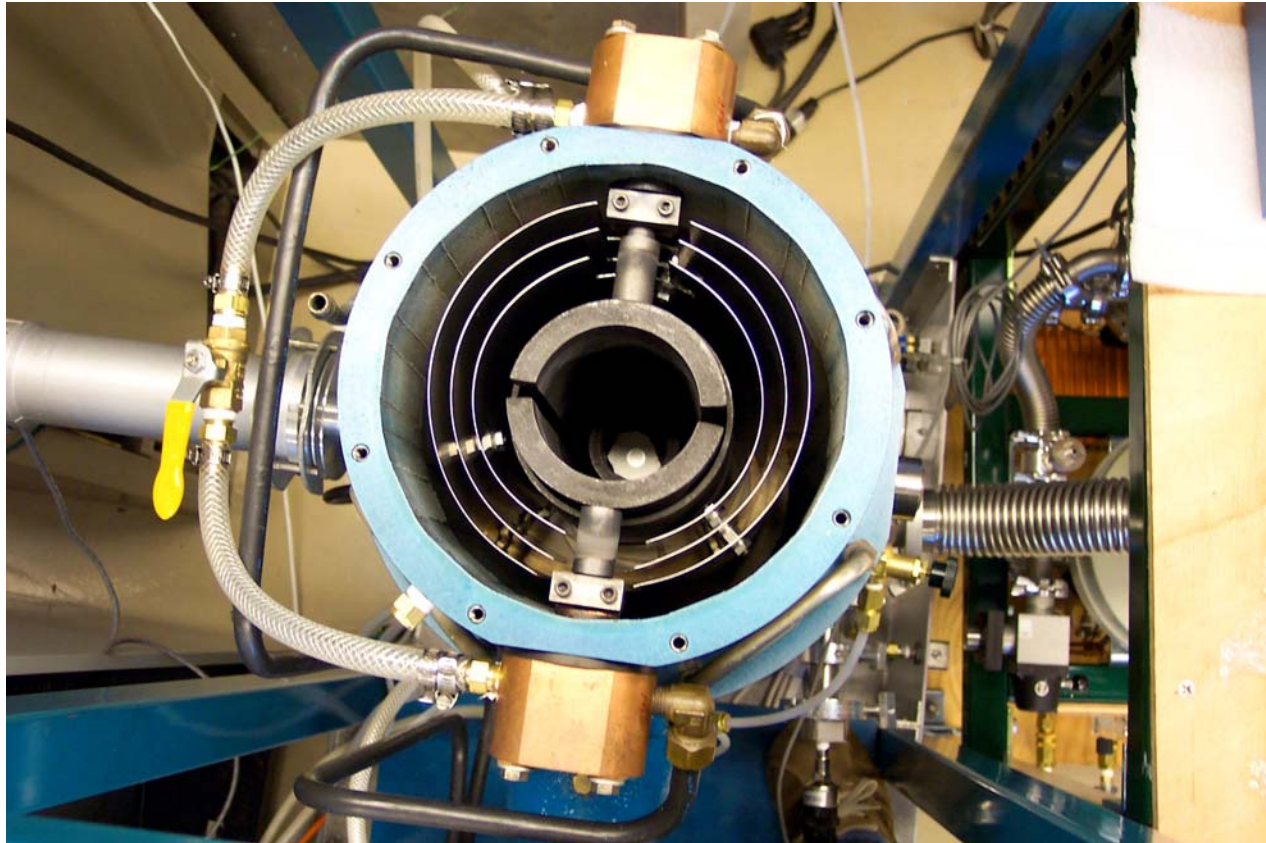
Post-growth heat treatment studies

- High vacuum furnace
 - $T \geq 1800^{\circ}\text{C}$, pressures to $\leq 10^{-5}$ Torr



Post-growth heat treatment studies

- High vacuum furnace - interior view
 - Four concentric molybdenum heat-shields
 - Graphite “picket fence” resistance heater, 3” ID
 - Carbon pedestal with molybdenum or tungsten hearth



Recent Hi-Temp. Vacuum Annealing Results

ID	Ambient	Temp.	Time	Hearth	Cooling Rate	Before HT	After HT	Comments
-----	-----	-----	-----	-----	-----	-----	-----	-----
Half CSI windows, 25.4 mm dia by 10 mm thick								
29-1-B	H2/N2	intermediate	15 hrs	Sapphire	3000 C/hr	70-80	30	
29-1-B	H2/N2	intermediate	13 hrs	Sapphire	200 C/hr	30	50	
29-1-B	Hi-Vac.	very high	~50 hrs	W	Furnace Failure	50	25	Repolished
Half CSI windows, 25.4 mm dia by 12.5 mm thick								
103-A	H2/N2	intermediate	12 hrs	Sapphire	310 C/hr	30	20-25	
103-A	Hi-Vac.	very high	13 hrs	Mo	800 C/hr	20-25	18	
103-B	Wet H2/N2	intermediate	16 hrs	Sapphire	310 C/hr	27-30	20	
103-B	Hi-Vac.	very high	24 hrs	Mo	800 C/hr	20	12-15	
103-B	Hi-Vac.	very high	42 hrs	Mo	20 C/hr	12-15	12	Repolish req'd
107	Hi-Vac.	very high	TBD	W	20 C/hr	80	TBD	

Absorption Loss Measurement Calibration

Date	Description	Average optical absorption (ppm/cm)		Variance
		SU	SMA / LMA - VIRGO	
4-03	CSI sapphire, No. AJ5 L46, optical grade, 314 mm dia x 131 mm	-	30-130	
1-04	CSI sapphire, 250 mm dia x 120 mm thick	-	(Corrected) 40 - 60	
1-04	CSI sapphire, mech. grade, "pink", 314 mm dia x 131 mm thick	-	(Corrected) 29 - 31	
3-04	CSI sapphire window, #111, 25 mm dia x 12.7 mm thick	90	68	24%
3-04	CSI sapphire window, #110, 25 mm dia x 12.7	45	34	24%
3-04	CSI cube, 6M, 1.0 cm all sides	120 - 140	Not reported	
3-04	GO-FS100-1, S/N5976, fused silica window, 6.2 mm thick	16	12.6	21%

Sapphire Summary

- **Status:**
 - 40-60 ppm/cm at 1064 nm in large volumes from CSI
 - Oxidizing anneals irreversibly increase bulk absorption and scatter
 - Reducing anneals at intermediate temperatures reversibly lower absorption
 - Annealing at $> 1100^{\circ}\text{C}$ in H_2/N_2 yields reductions greater than 50%
 - 25-30 ppm/cm achieved with passive cooling at rates of $>200^{\circ}\text{C/hr}$
 - 20 ppm/cm achieved with forced cooling at rates of $>400^{\circ}\text{C/hr}$
 - Cooling kinetics of the annealing process are controlling variables
 - High temperature vacuum annealing reduces absorption by equal or greater amounts without having to cool rapidly
- **Current thinking:**
 - Point defect equilibrium important factor in current CSI material
 - At least two extrinsic defect species (eg. $\text{Ti}^{3+}:\text{Ti}^{4+}$ complex plus other(s))
 - Extrinsic defects appear to be mobile at high temperature ($>1800^{\circ}\text{C}$)
- **Next steps:**
 - Determine limiting mechanism(s) in the vacuum annealing process
 - Continue study of vacuum annealing in larger size samples
 - Determine the kinetics and activation energies of the process
 - Continue spectroscopic and chemical analysis of high-loss specimens to identify extrinsic species associated with $1.06\ \mu\text{m}$ absorption