Heat-Treatment and Optical Absorption Studies on Sapphire

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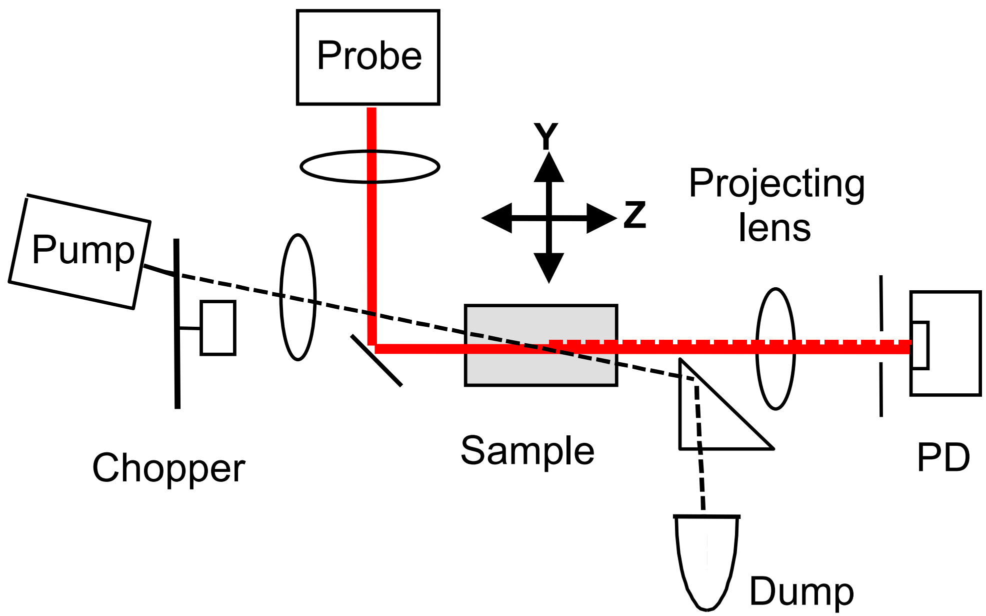
Lasers and Optics Working Group

LIGO LSC meeting, LLO 3/17/04

Photothermal Common-Path Interferometry

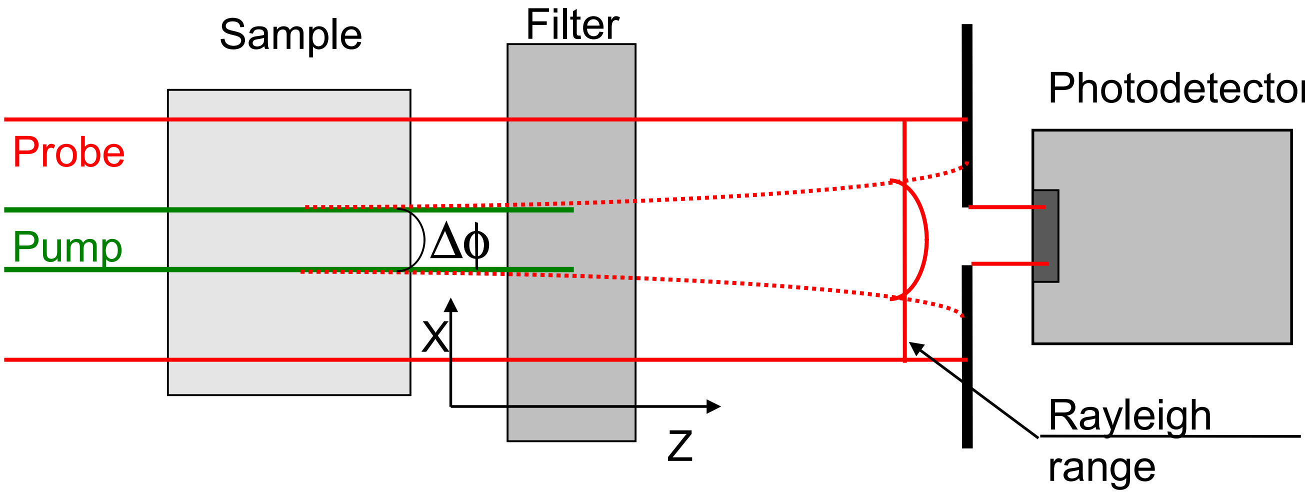
- diffraction regime of cross-beam cw thermal lensing -



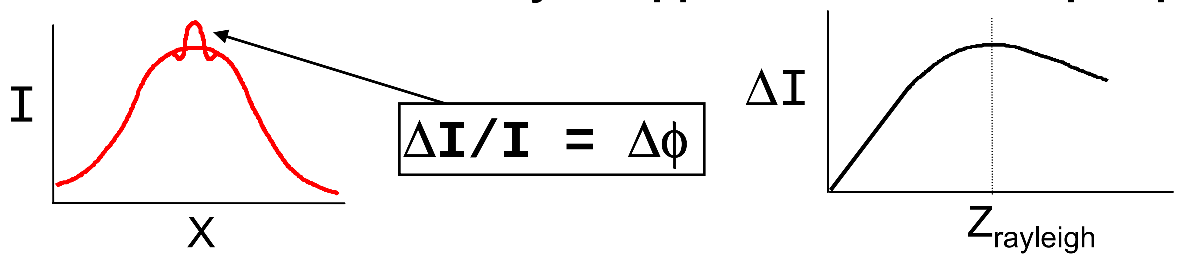
Pump waist	50 μ	Chopping frequency	380 Hz (10Hz- 2 kHz)
Probe waist	120 μ	Crossing angle	1° - 20°(in air)
Pump power	5 W	Probe power	0.5 mW

- **ac-component of probe distortion is detected by photodiode + lock-in**
- **absorption coefficient <10^{-7} 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

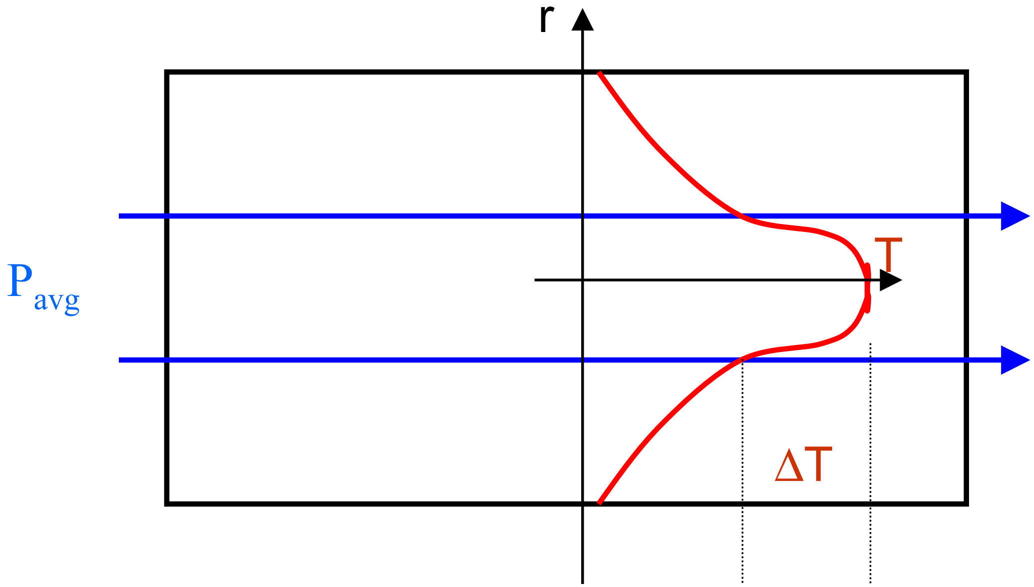


Interferometric sensitivity: 0.1 ppm/cm with 4 W of pump



Temperature Rise in Absorbing Medium

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



$$\Delta T = \alpha P_{avg} f(k_{th}, c_p, \omega)$$

- Leads to radially varying index: $\Delta n = \frac{dn}{dT} \Delta T$

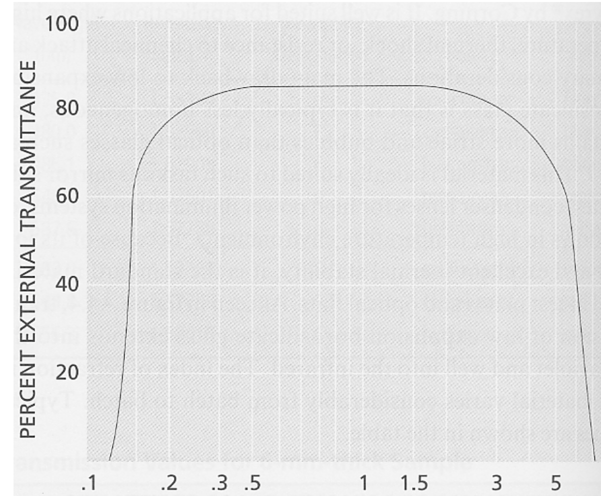
- Leads to radially varying phase on optical beam:

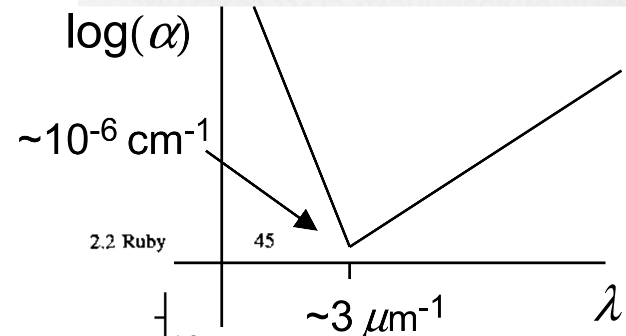
$$\Delta \phi = \frac{2\pi}{\lambda} \frac{dn}{dT} \Delta T\, L$$

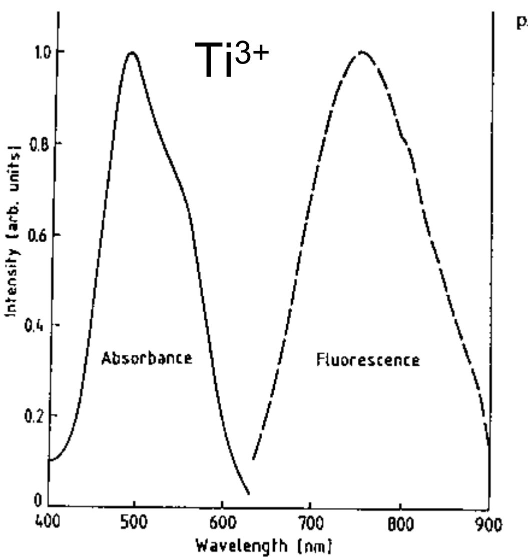
$$= \frac{2\pi}{\lambda} \frac{dn}{dT} \alpha P_{avg} L f(k_{th}, c_p, \omega)$$

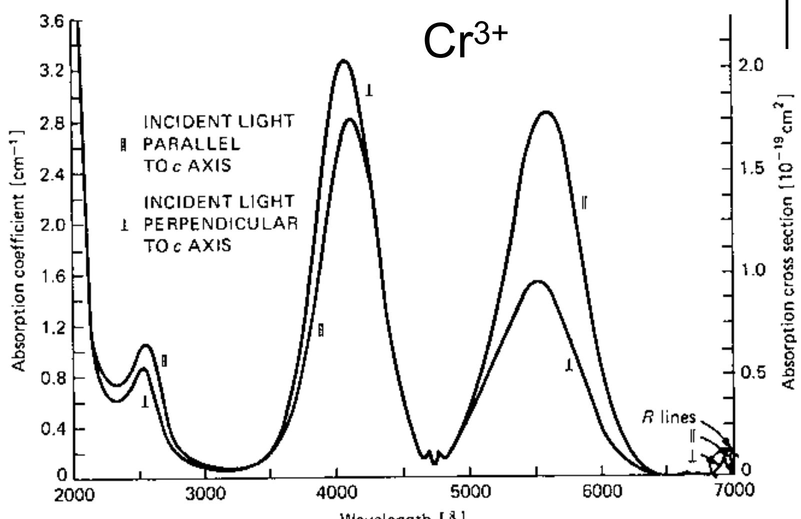
Study of absorption in sapphire

- 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, …







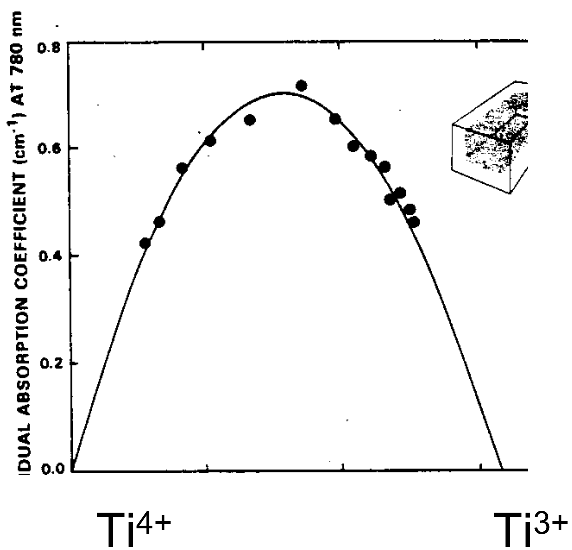


Characteristics of absorbing species

- 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. $\alpha[Ti^{3+}] \neq \alpha[Ti^{4+}]$
  - 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+}
  - absorption spectra at high concentrations not always same as low

    complicates correlations to known spectra

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

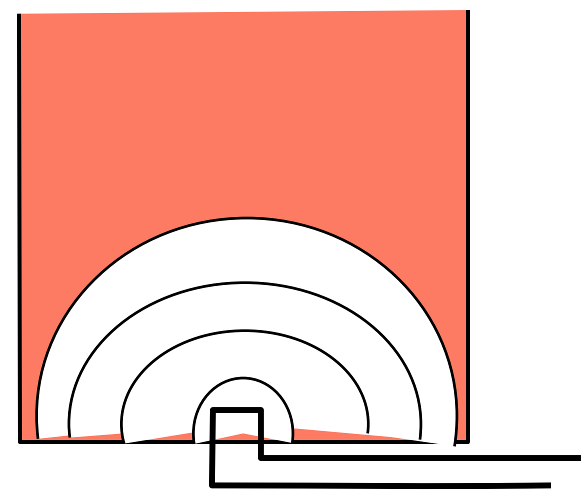


Compositional analysis by GDMS: ppms of everything

	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
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
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
O	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
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
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
Al	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
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
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
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
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
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
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
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
*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
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
*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
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
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
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
Zn	<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
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
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
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
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
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
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
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
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
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
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
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
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
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
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

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

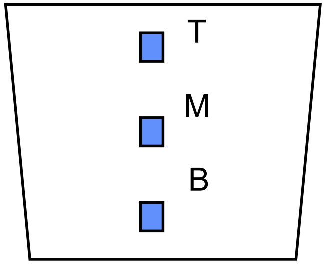
- Heat Exchanger Method
  - He-gas cools bucket of melt
  - solidification outwards from bottom



- 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

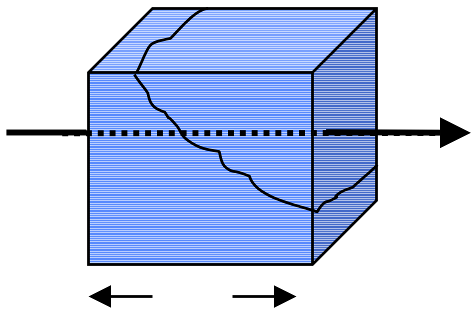
Collaborative studies with CSI

- **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



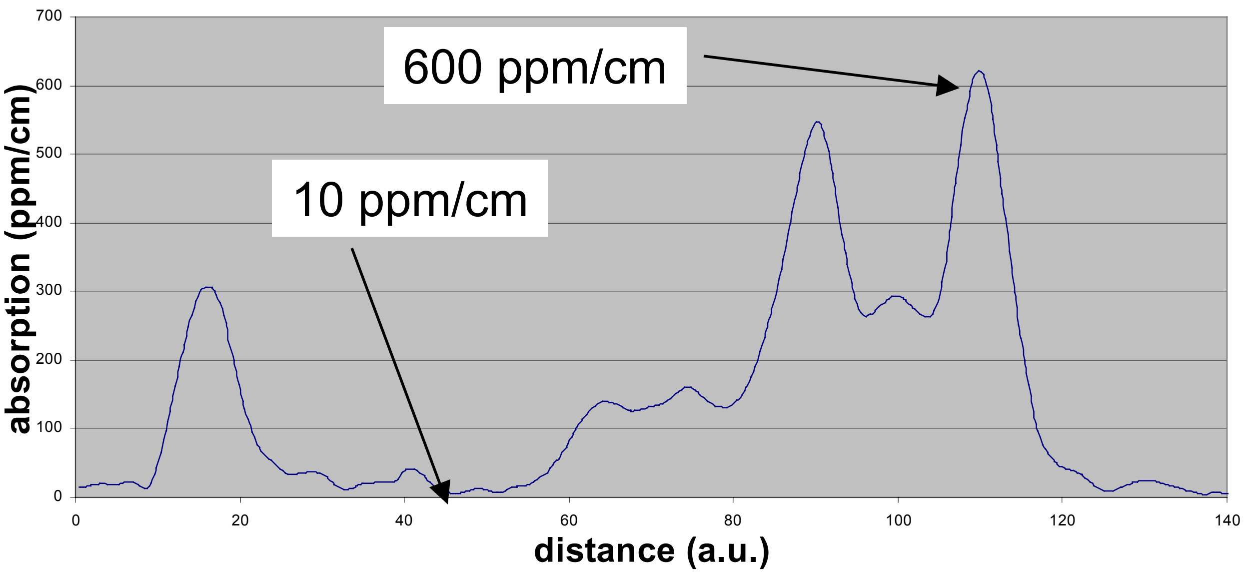
- **Heat Treatment Studies**
  - 25 mm dia x 10-12.5 mm thick a-axis CSI Hemex White
  - intermediate temp. annealing: time, temperature, reducing (H_2) or oxidizing (air, O_2) conditions, heating / cooling rates
    primarily influence redox state of intrinsic defects (e.g. oxygen vacancies)and extrinsic 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)



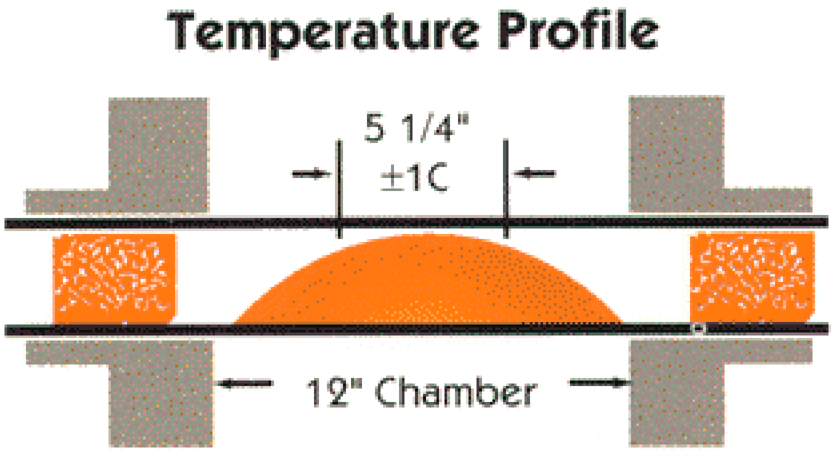
- Single 1 cm sample
  - region with 10 ppm/cm
  - region with 600 ppm/cm
  - abrupt boundary between
- Preparation unexceptional
- Mechanism not yet clear
  - not typical of normal impurity segregation
  - specimen should be useful for "self-normalizing" measurements

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



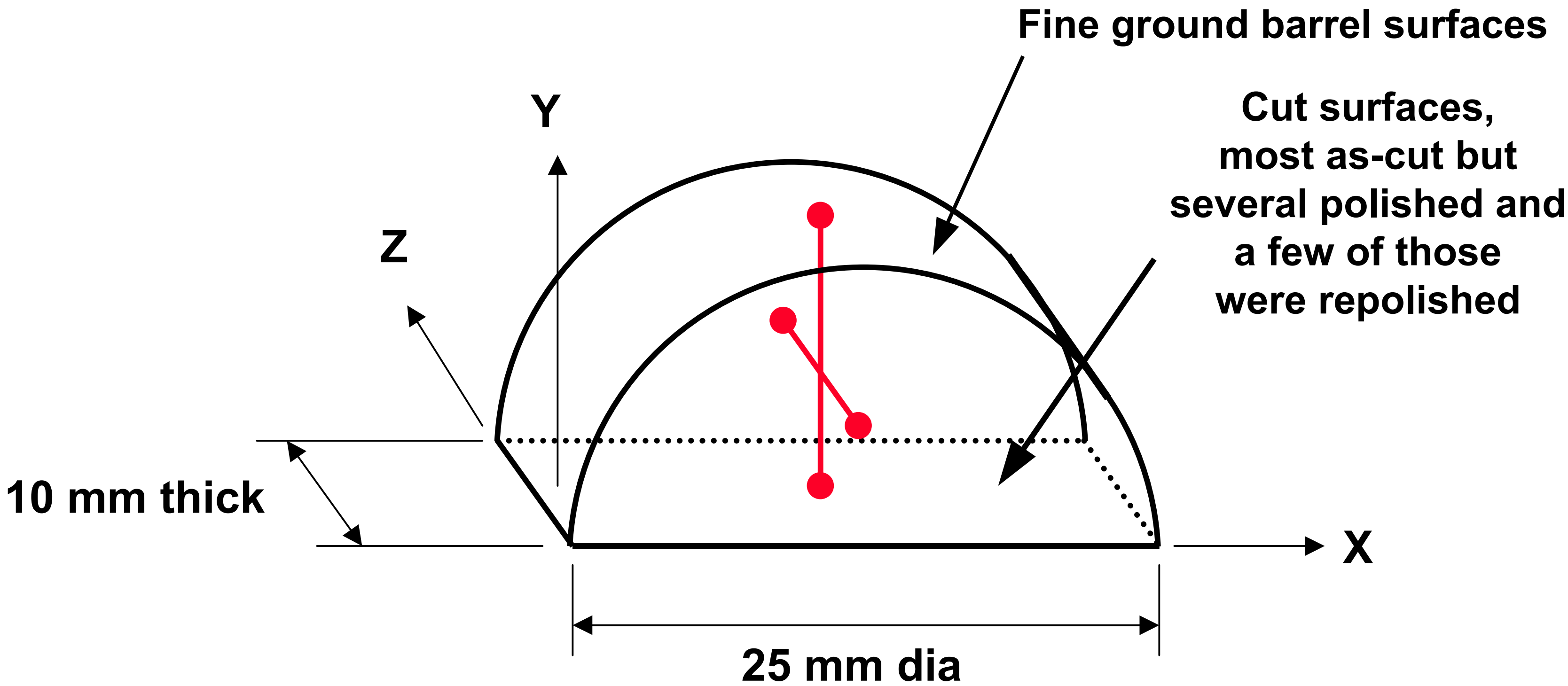
Post-growth heat treatment studies

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



$MoSi_2$ “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

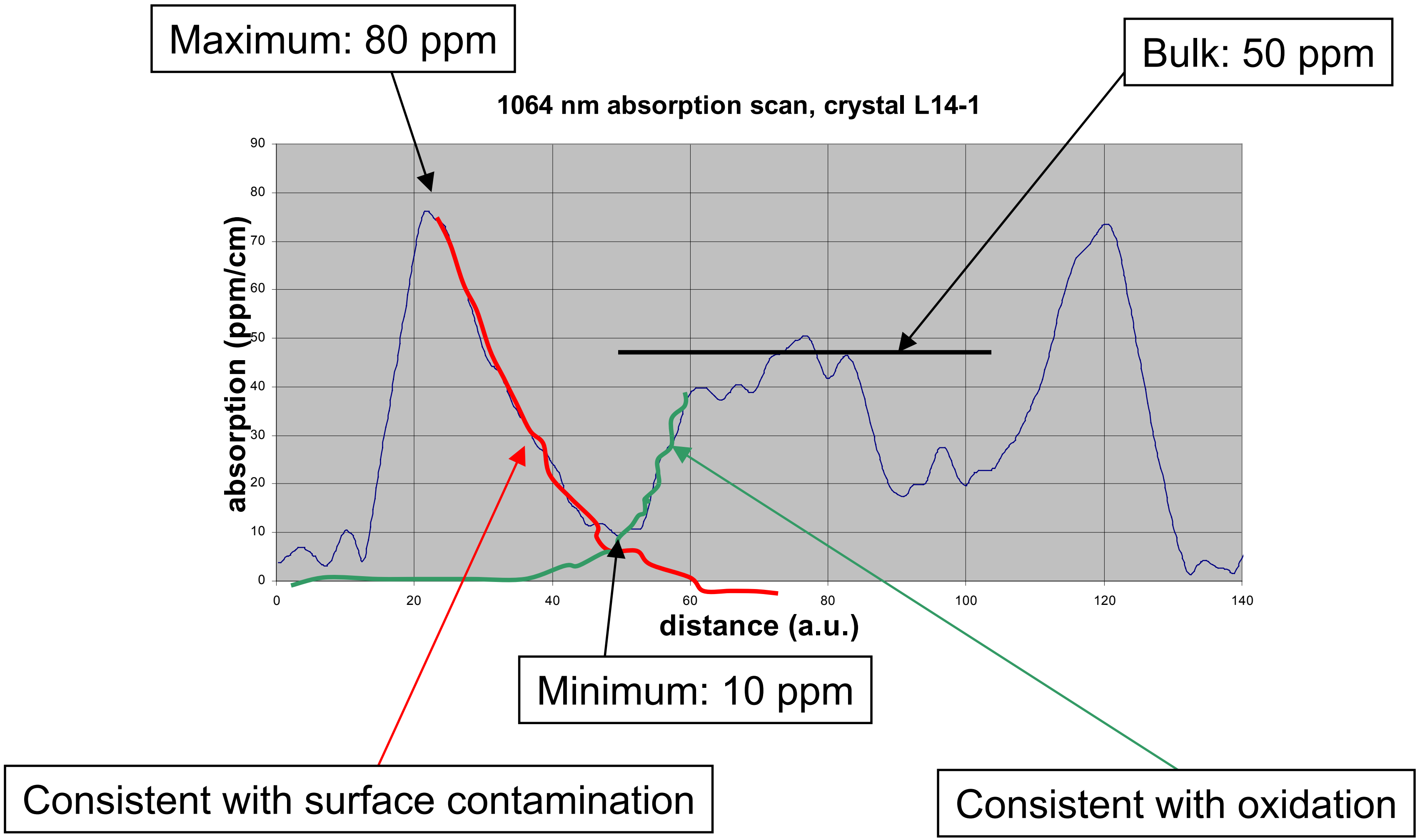
Optical loss measurement scheme for sapphire windows



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

Complicated air-annealing behavior

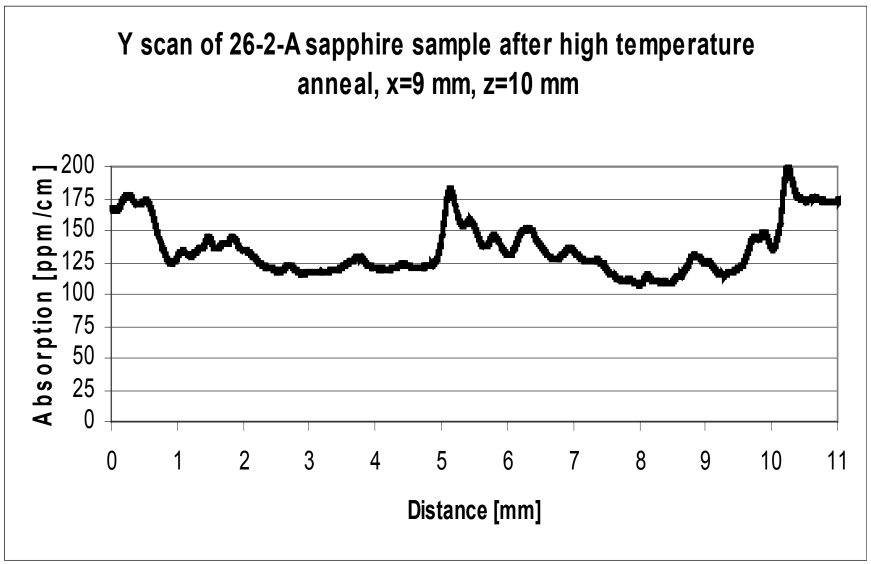
(1064 nm absorption through cross-section of a window)



Annealing at high temperatures under oxidizing conditions

Y-Scan

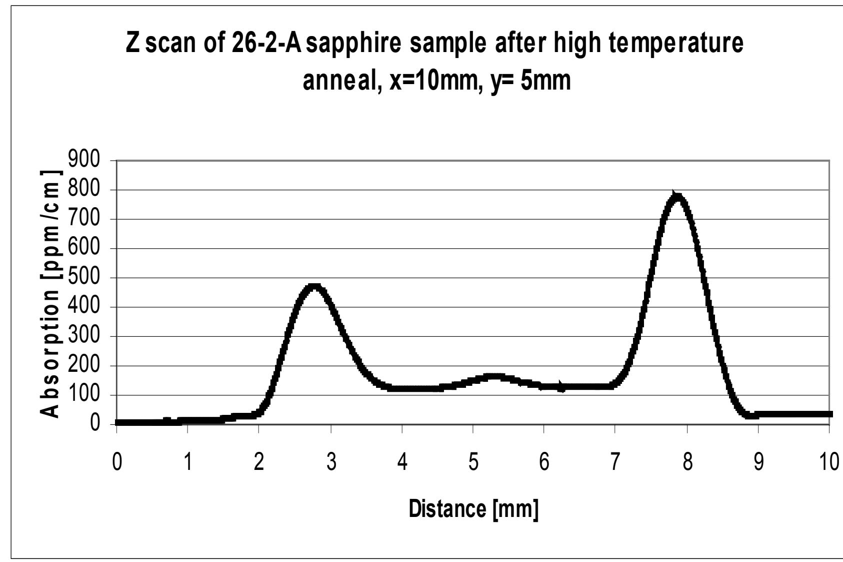
Fine-Ground **Fine Ground**



Initial absorption - 50 ppm/cm

Z-Scan

Polished Face **Polished Face**



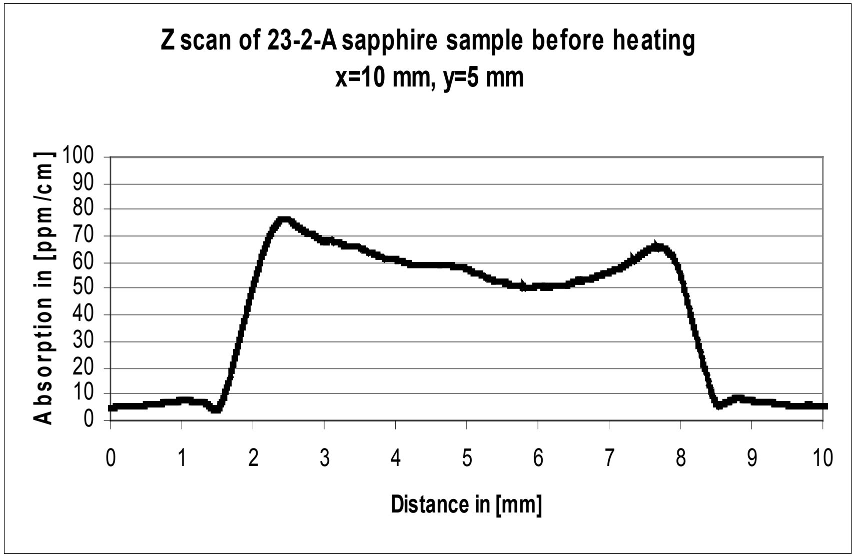
Initial absorption - 50 ppm/cm

Consistent trends under oxidizing anneals

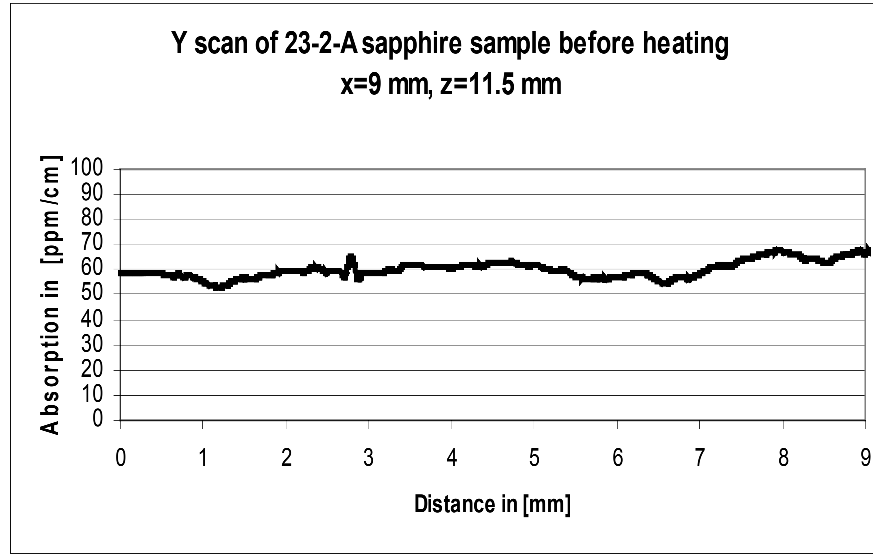
- **As grown**
  - Unclear correlation with starting material or furnace
    - Question of impurities, native defects and process contamination unresolved
  - No strong correlation with position in boule or use of re-melted feedstock
    - “Rosetta” sapphire indicates melt segregation operative during 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**

Reducing anneals at intermediate temperatures using moderate 200° C/hr heating and cooling rates

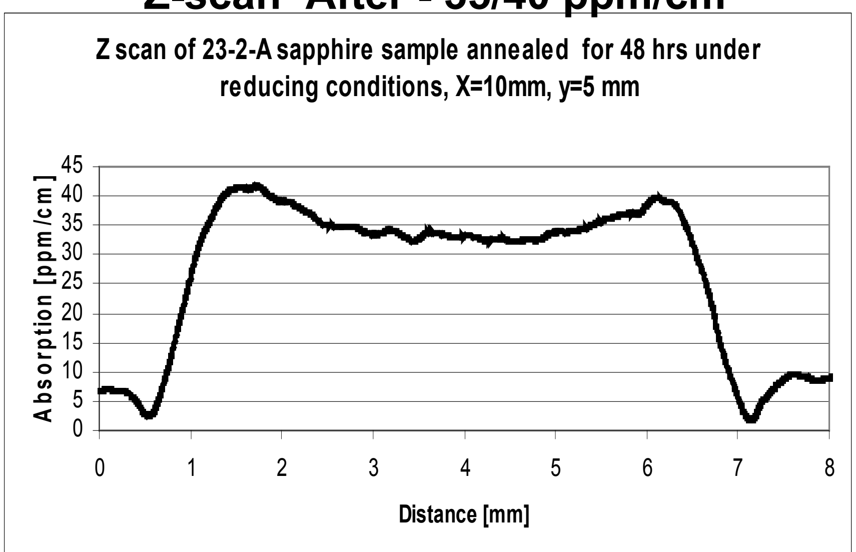
Z-scan Before - 55/65 ppm/cm



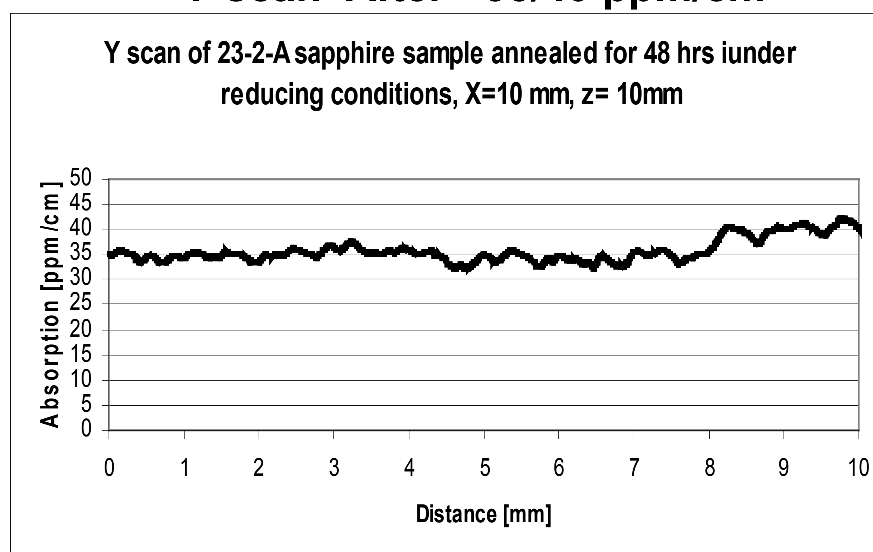
Y-scan Before - 55/65 ppm/cm



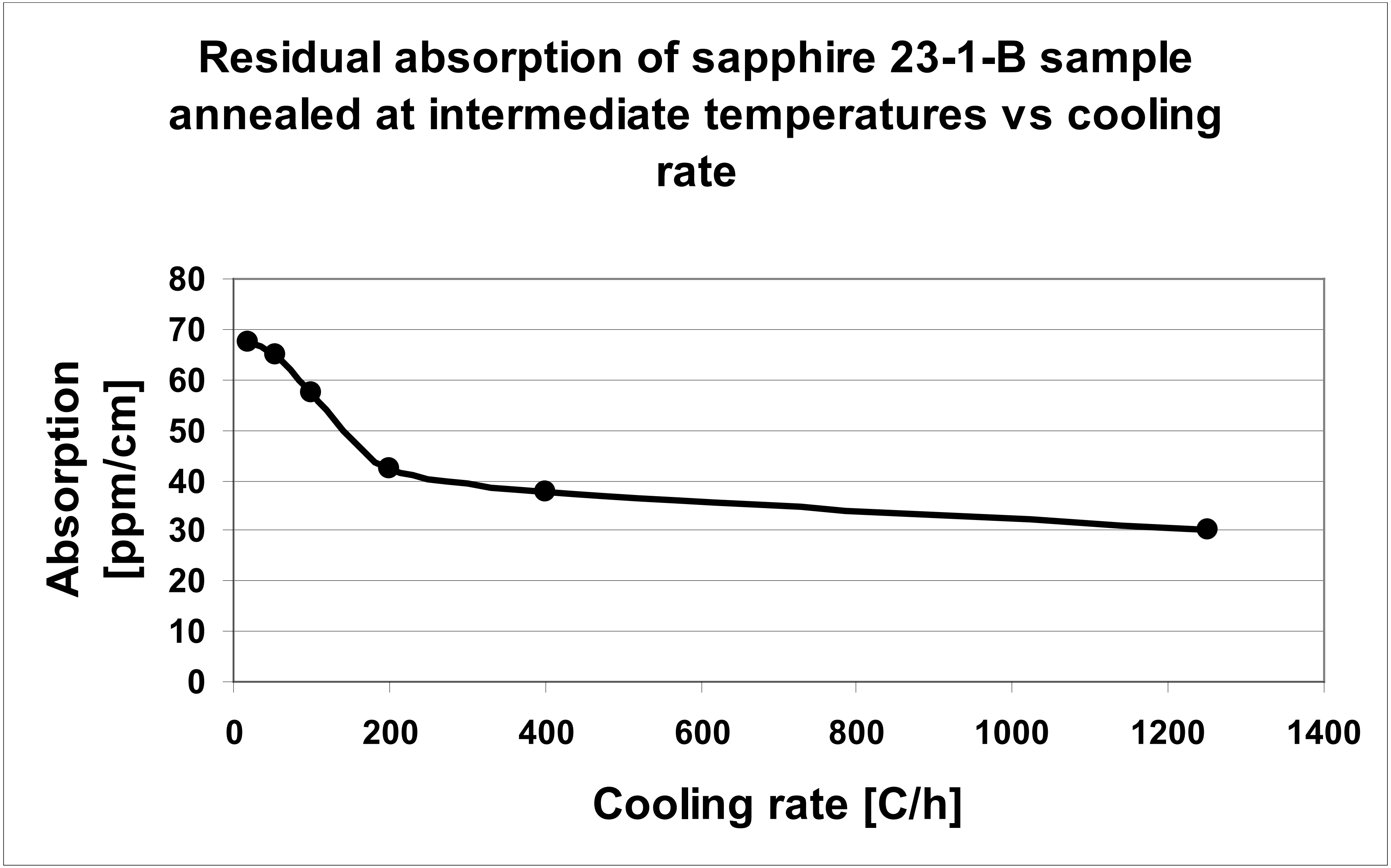
Z-scan After - 35/40 ppm/cm



Y-scan After - 35/40 ppm/cm



Observed trends under inert/reducing conditions

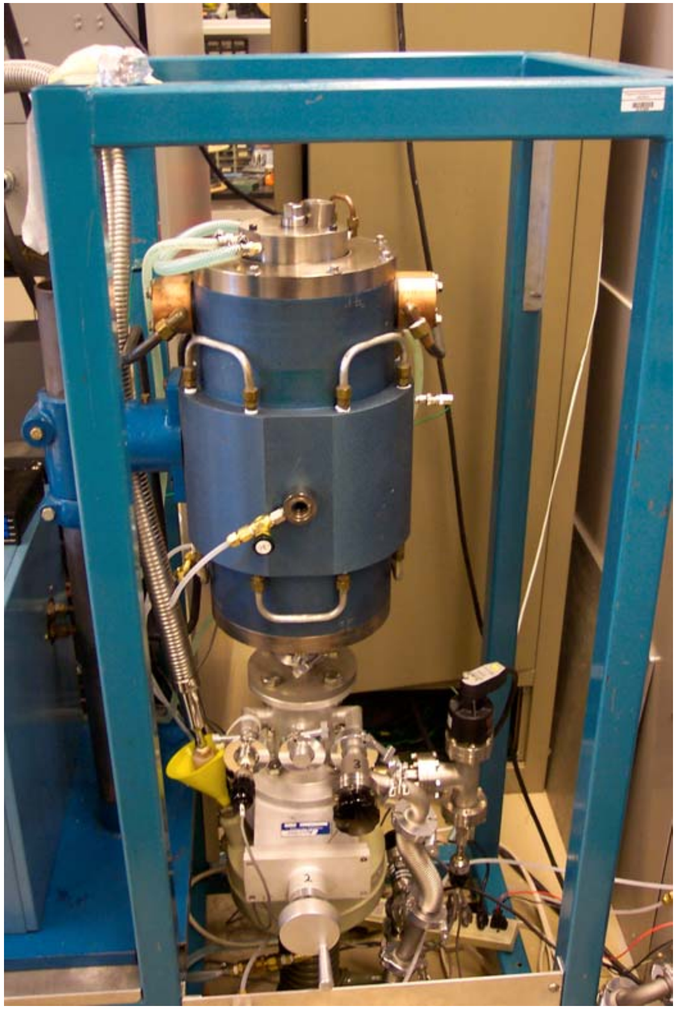


Thermal Stability of Rapidly Cooled Sapphire Windows

	ID	Ambient	Temp.	Time	Cooling Rate	Gas Flow	Before HT	After HT	Comments
	---------	---------	---------	---------	---------	---------	---------	---------	---------
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

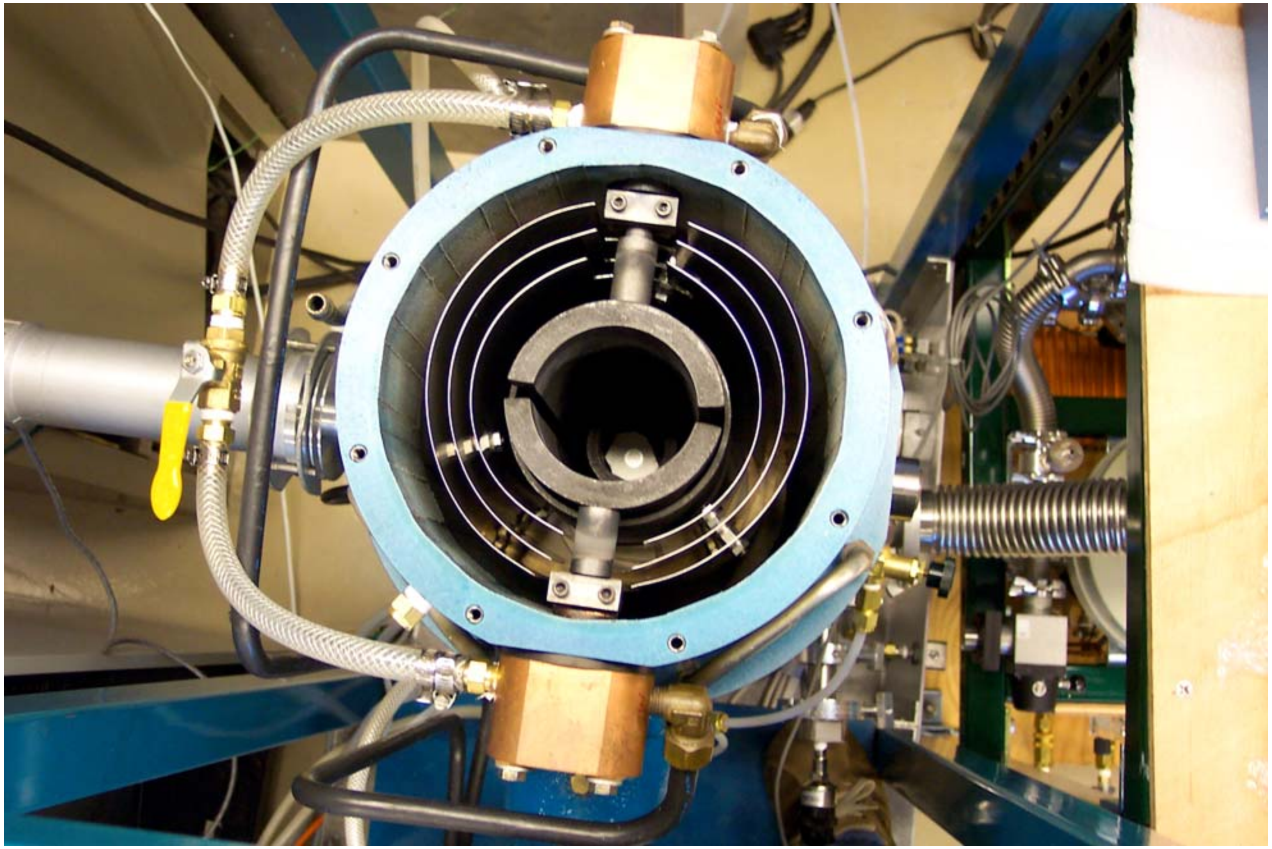
Post-growth heat treatment studies

- High vacuum furnace
  - $T \geq 1800°$ 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 º C in H2/N2 yields reductions greater than 50%**
      - **25-30 pm/cm achieved with passive cooling at rates of >200º C/hr**
      - **20 ppm/cm achieved with forced cooling at rates of >400º 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. Ti^{3+}:Ti^{4+} complex plus other(s))**
  - **Extrinsic defects appear to be mobile at high temperature (>1800º 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 μm absorption**