

# Absorption Studies in Sapphire Crystals and Optical Coatings

LIGO-G030023-00-Z

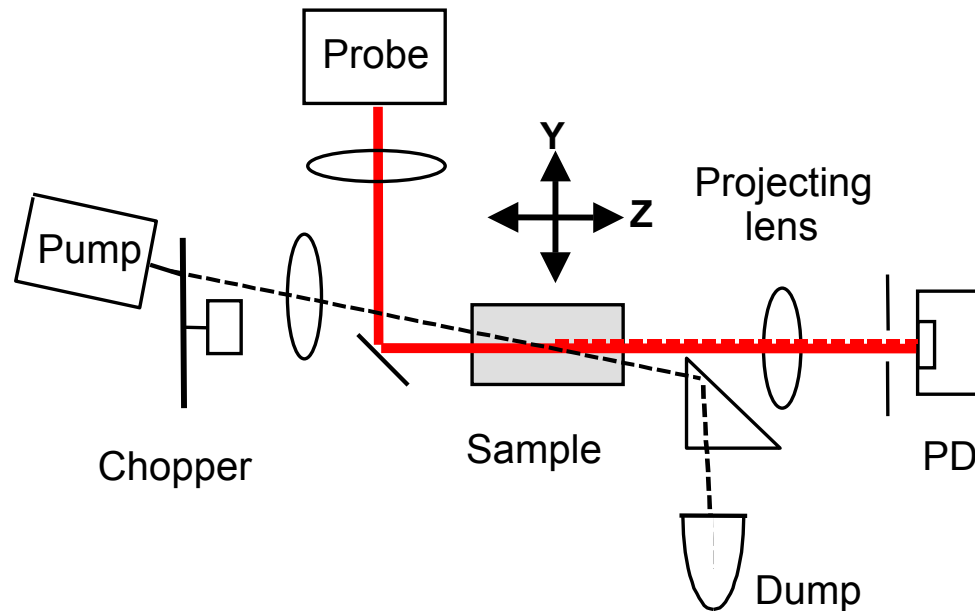
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Lasers and Optics Working Group

LIGO LSC meeting, LLO 3/18/03

# Photothermal Common-Path Interferometry

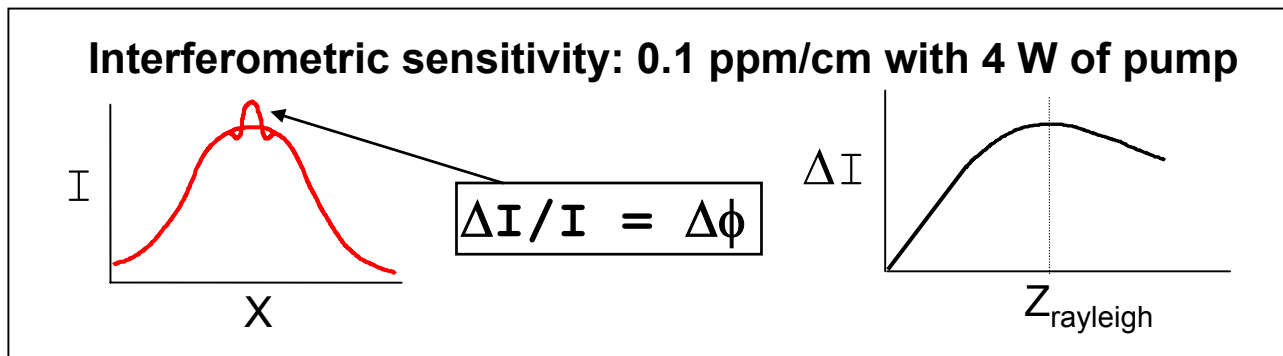
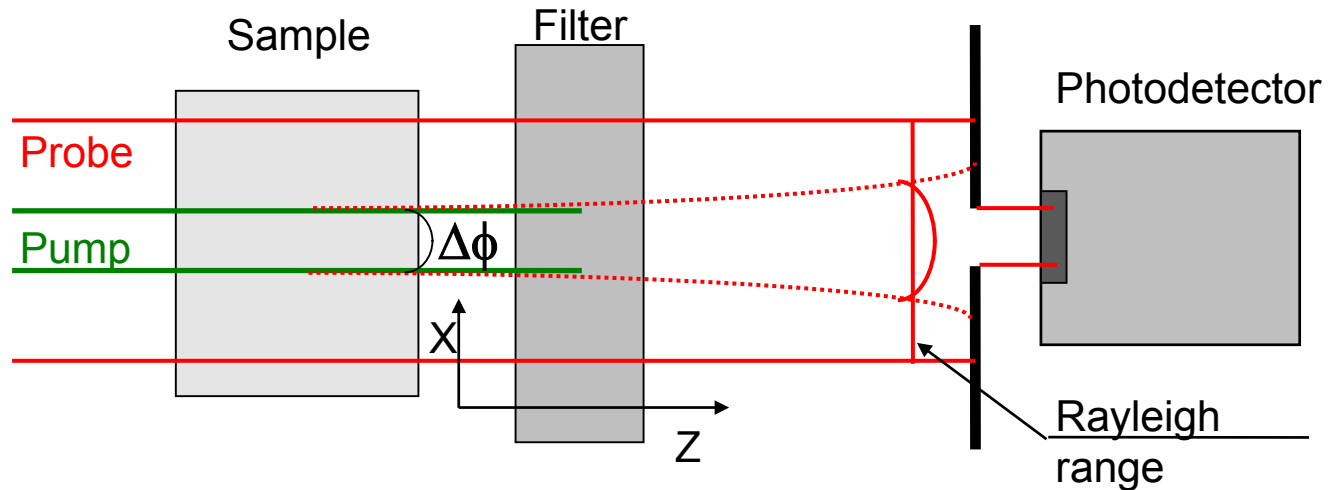
- diffraction regime of cross-beam cw thermal lensing -



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

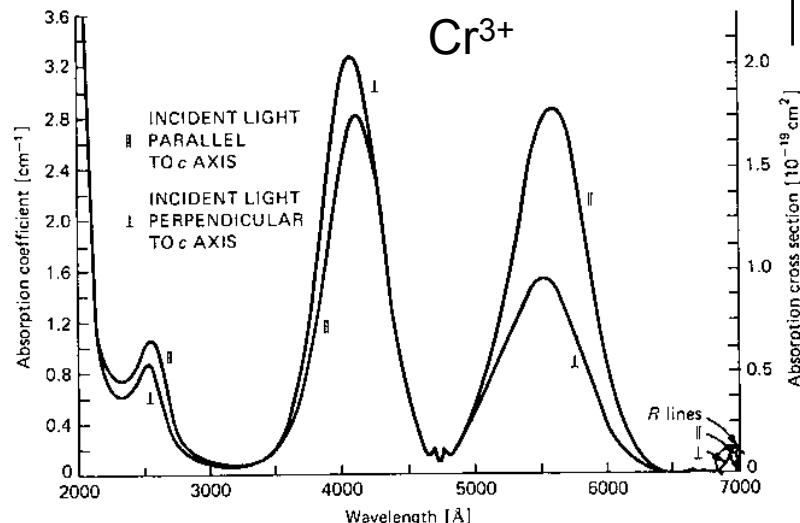
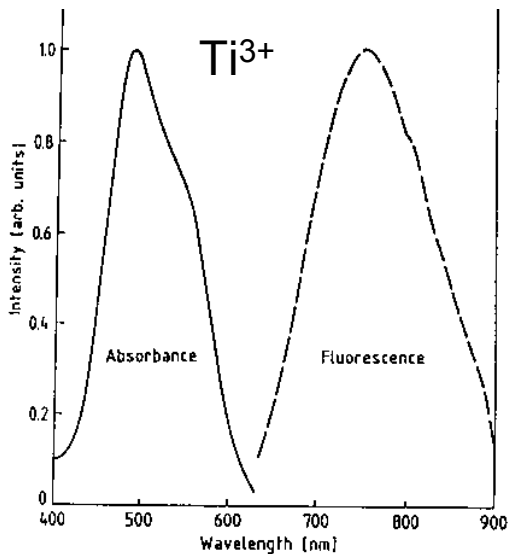
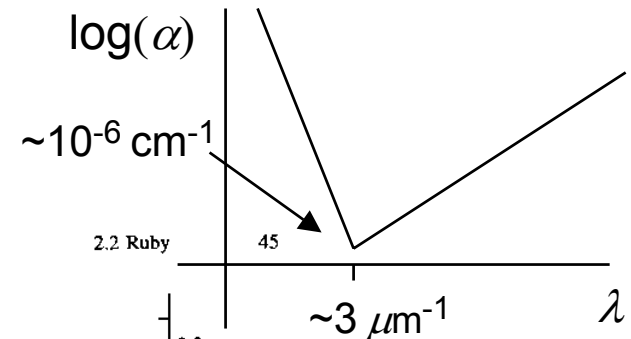
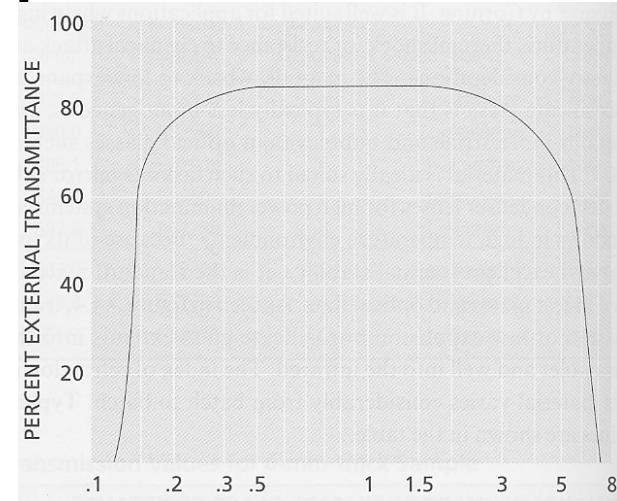
- ac-component of probe distortion is detected by photodiode + lock-in
- absorption coefficient  $<10^{-7} \text{ cm}^{-1}$  (~10 ppb coating) can be detected with 5 W pump power
- crossed beams help to avoid false signals from optics and surfaces of the sample

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



# Study of absorption in sapphire

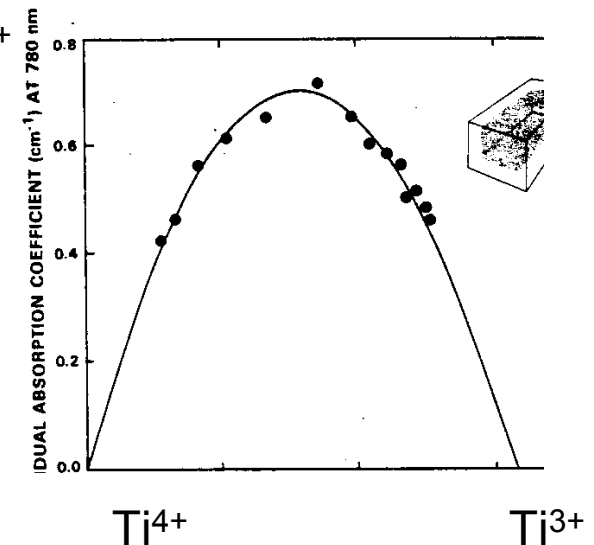
- Intrinsic
  - conduction to valence band in UV
  - multiphonon in mid-IR
  - only cure is different material  
expectation and existence proofs indicate this isn't the problem
- Extrinsic
  - native defects  
vacancies, antisites, interstitials,
  - impurities  
e.g. transition metals: Cr, Ti, Fe,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



# Characteristics of absorbing species

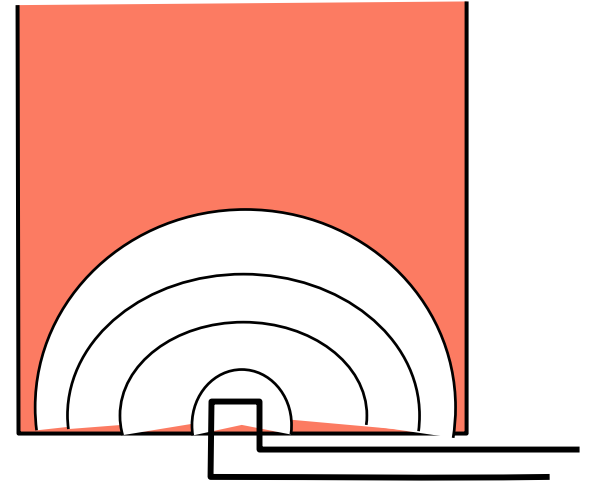
- Allowed transitions
  - large cross sections  $\Rightarrow$  ppm concentrations significant
- Broad spectral features
  - identification difficult
  - off “resonant” absorption significant
  - sum of several species can contribute to absorption at given  $\lambda$
- Redox state important
  - e.g. 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

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



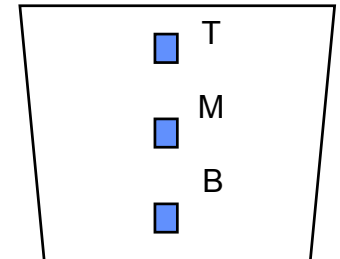
# Growth of sapphire at Crystal Systems, Inc. by the HEM process

- 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

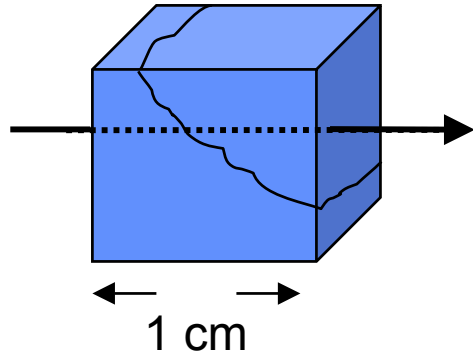
- **Experimental design**
  - anticipated mechanisms: impurity concentration, intrinsic defects, redox state
  - two main control methods: growth and annealing
- **Growth Studies**
  - ~ 30 CSI White, 1 cm cubes
  - primarily expected to influence impurity concentration
  - starting materials
    - virgin 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
- **Annealing Studies**
  - 2.5 cm dia x 1 cm thick a-axis CSI Hemex 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





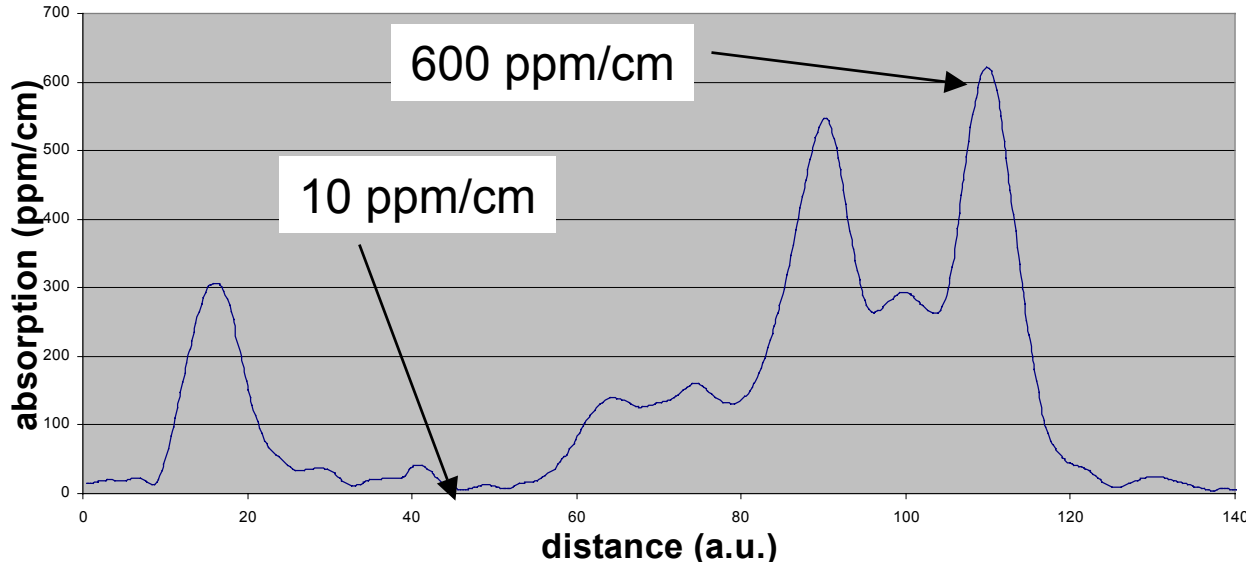


# Low optical loss existence proof (Rosetta sapphire)

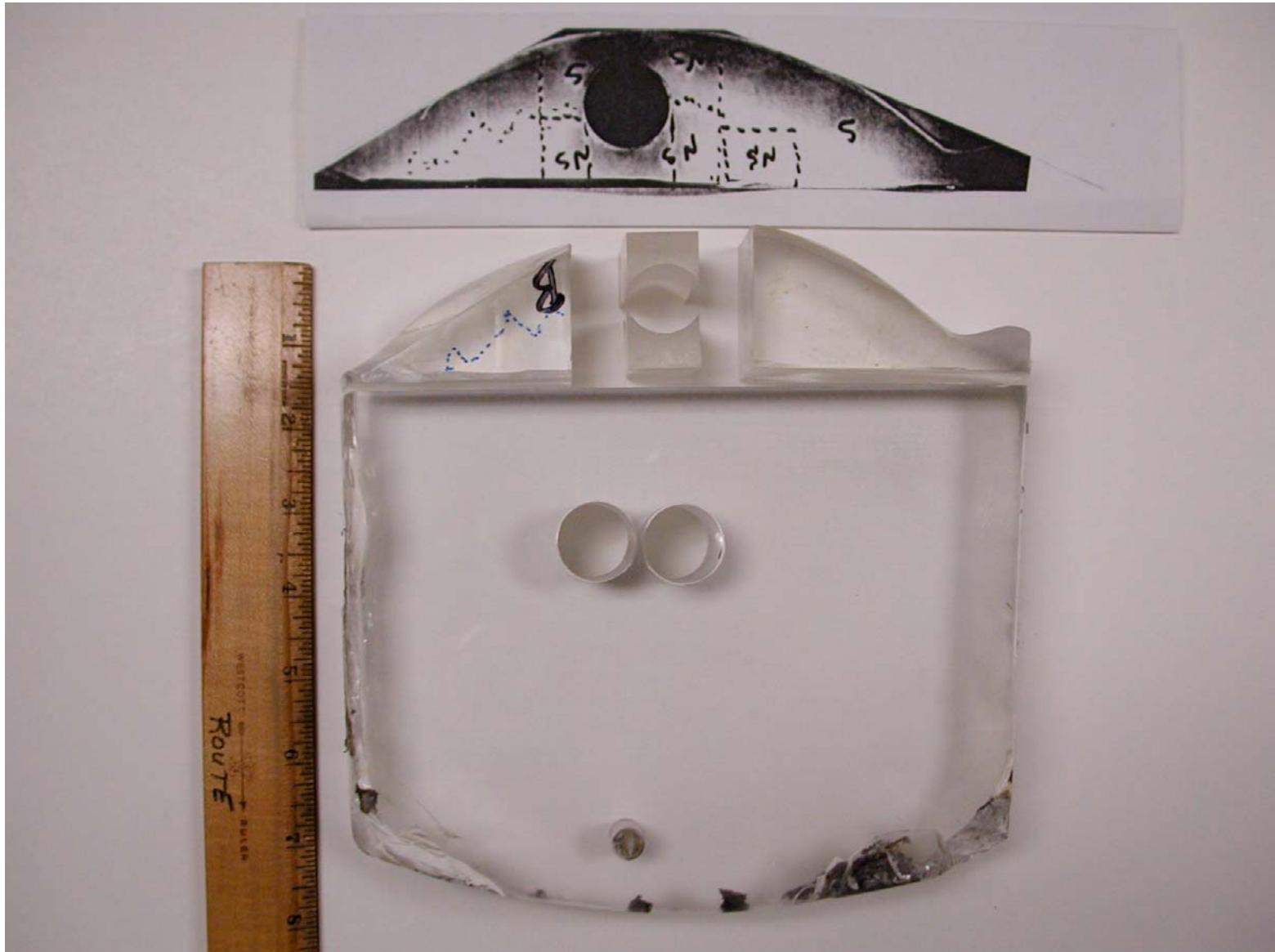


- Single 1 cm sample
  - region with 10 ppm/cm
  - region with 600 ppm/cm
  - abrupt boundary between
- Preparation unexceptional
- Mechanism not yet clear
  - not typical of normal impurity segregation
  - specimen should be useful for “self-normalizing” measurements

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



# Parent slab from which 8-T was taken



# GDMS Studies on HEM Sapphire 8-T

(Measurements by Shiva Technologies, Inc.)

	High Loss ( $\alpha > 50$ ppm/cm)	Low Loss ( $\alpha < 20$ ppm/cm)
Element	Concentration	Concentration
	[ ppm wt ]	[ ppm wt ]
Na	0.25	0.16
Si	0.31	0.13
Cr	< 0.1	< 0.1
Fe	< 1	< 1
Cu	< 1	< 1
Ti	< 0.05	< 0.05
Y	0.15	0.02
Nb	< 5	< 5
Mo	< 1	< 1
Ta	Binder	Binder

# Other Impurity Studies on HEM Sapphire 8-T (Measurements by S. McGuire, Southern Univ.)

## Neutron Activation Analysis of Impurities in CSI Sapphire

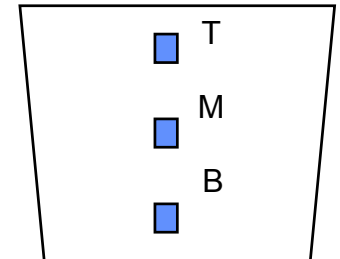
Observed impurity concentrations given in nanogram of impurity per gram of sample.

Element	Relative Concentration		Half-life	$\gamma$ - ray energy (keV)	$\gamma$ - ray intensity (%)
	by mass ng/g	Observed radionuclide			
Ti	300± 29	$^{47}_{\text{Sc}}$	3.34 d	159.4	68
Sc	3± 0.20	$^{46}_{\text{Sc}}$	86.6 d	889.1	99.98
Cr	5± 1	$^{51}_{\text{Cr}}$	27.7 d	320.2	9.83
Fe	≤ 1000	$^{59}_{\text{Fe}}$	44.5 d	1099.3	56.5
Mo	1500± 227	$^{99}_{\text{Mo}}$	2.75 d	141.0	90.7
				739.5	12.14
				777.9	4.35

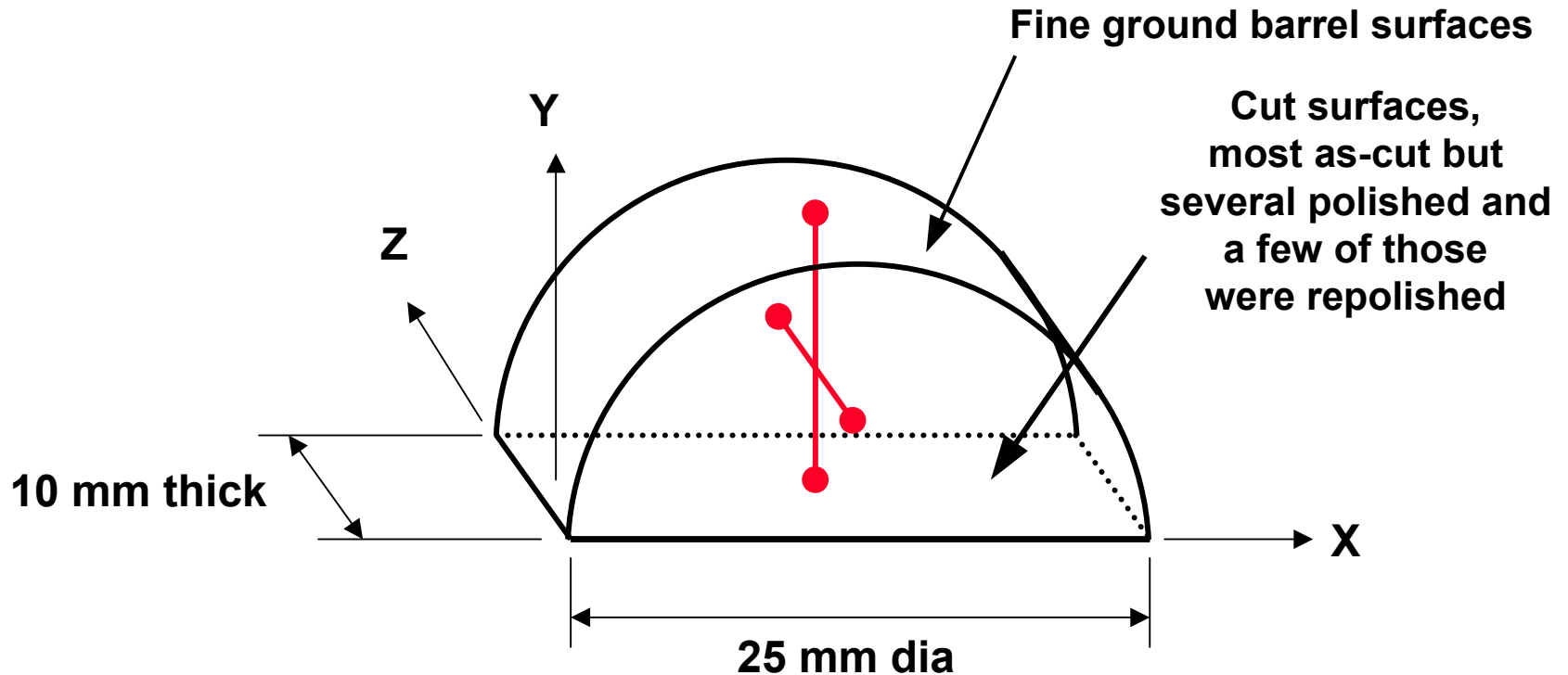
The errors are compounded uncertainties and correspond to one standard deviation.

# Collaborative studies with CSI

- **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
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  - samples cut from top/middle/bottom of boule
    - explore impurity segregation effects
- **Annealing Studies**
  - 2.5 cm dia x 1 cm thick a-axis CSI Hemex white
  - primarily influence redox state, intrinsic defects (e.g. oxygen vacancies)
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  - furnace design
    - accidental introduction of impurities, especially near surface



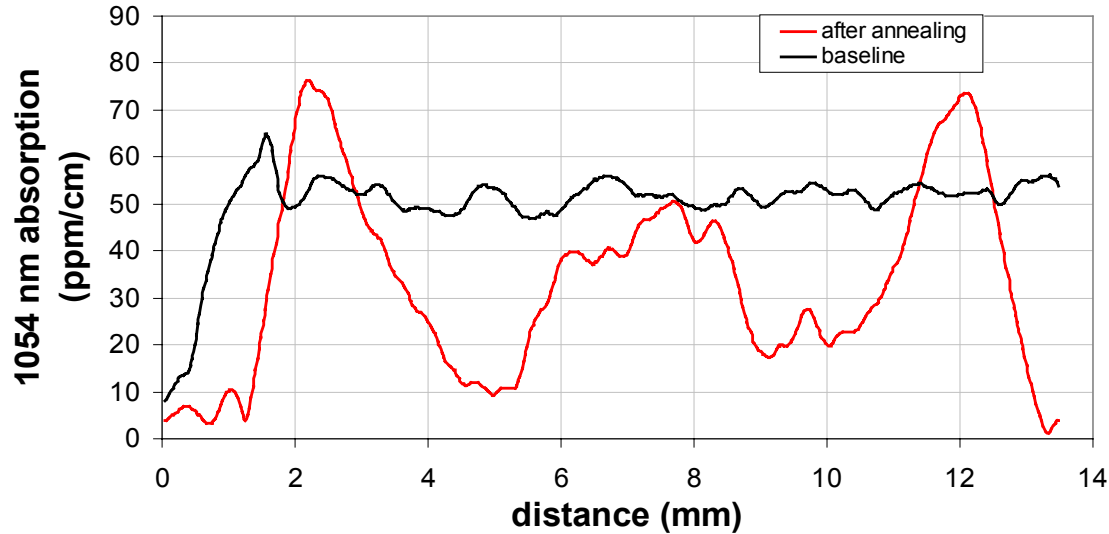
# Optical loss measurement scheme for sapphire windows



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

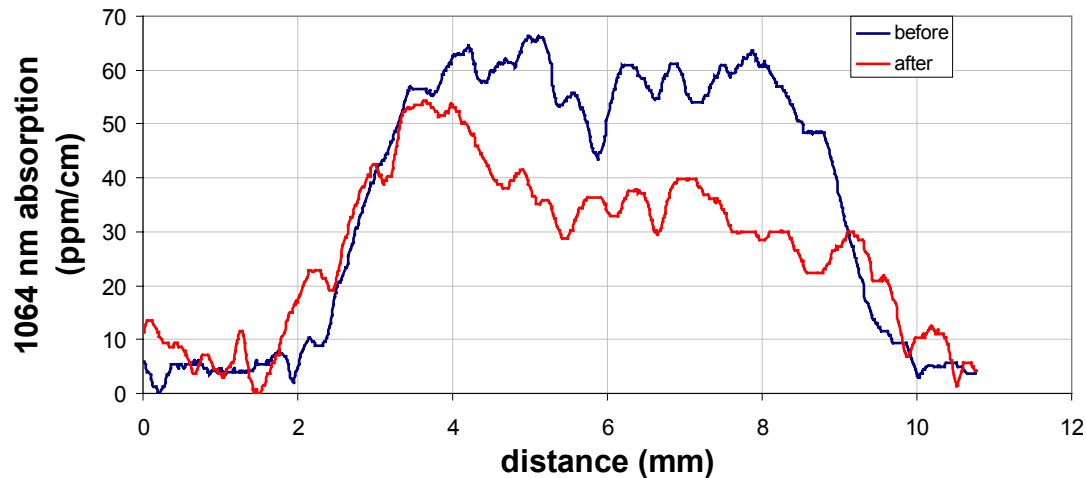
# Apparent furnace effects

**Sapphire L14-1, 10 mm-thick**  
intermediate temperature air annealing



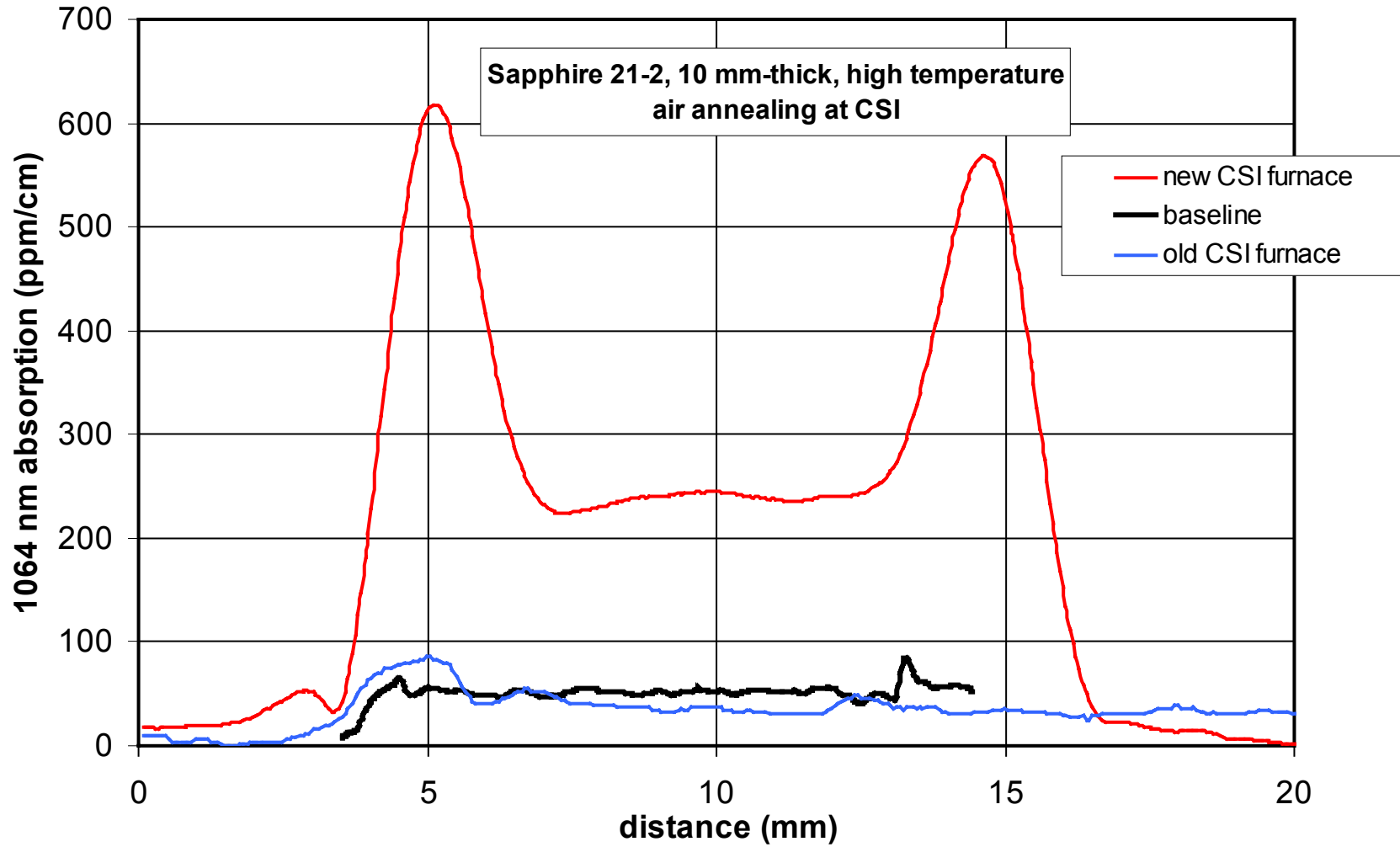
**Annealed at CSI**

**Sapphire B-4, 1/4"-thick**  
intermediate temperature air annealing



**Annealed under similar conditions at Stanford**

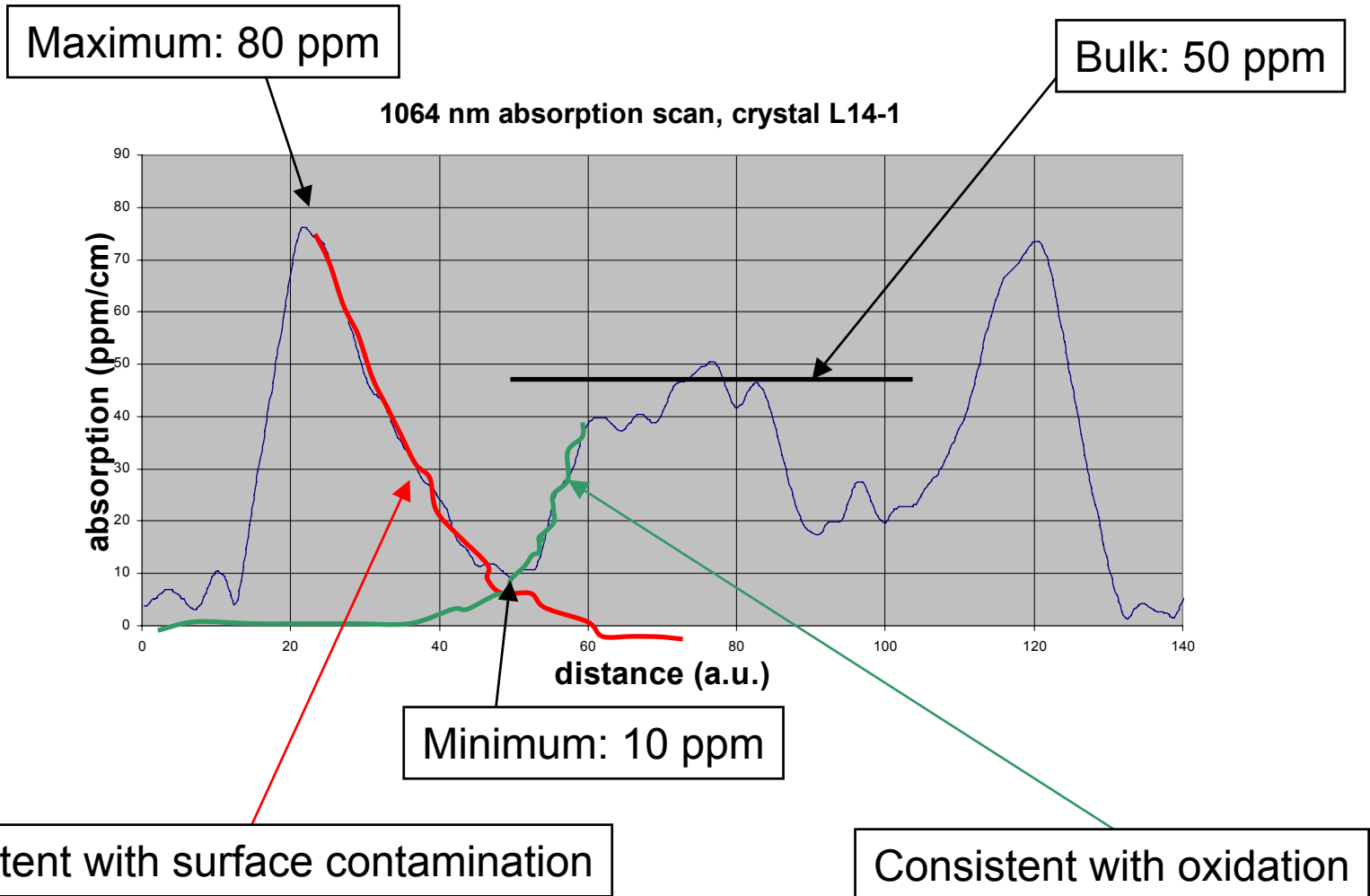
# Apparent furnace effects





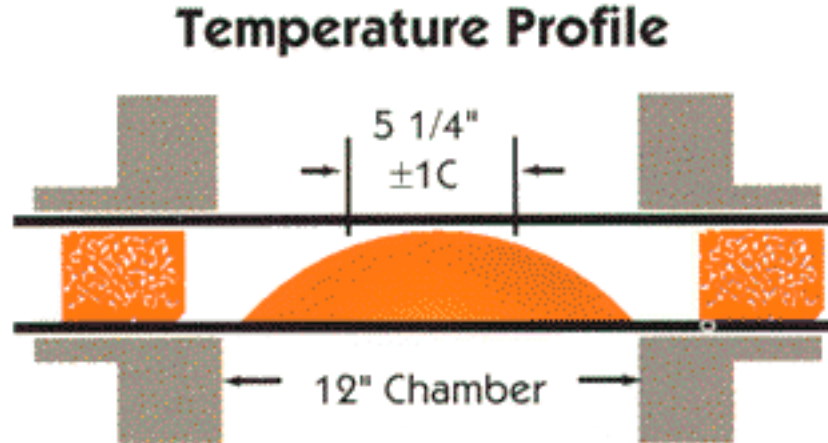
# Complicated air-annealing behavior

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



# Post-growth heat treatment studies at Stanford

- Controlled atmosphere processing
  - Oxidizing conditions - air or oxygen
  - Inert/reducing conditions - N<sub>2</sub> w/wo H<sub>2</sub>



MoSi<sub>2</sub> “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

# Annealing studies under oxidizing conditions

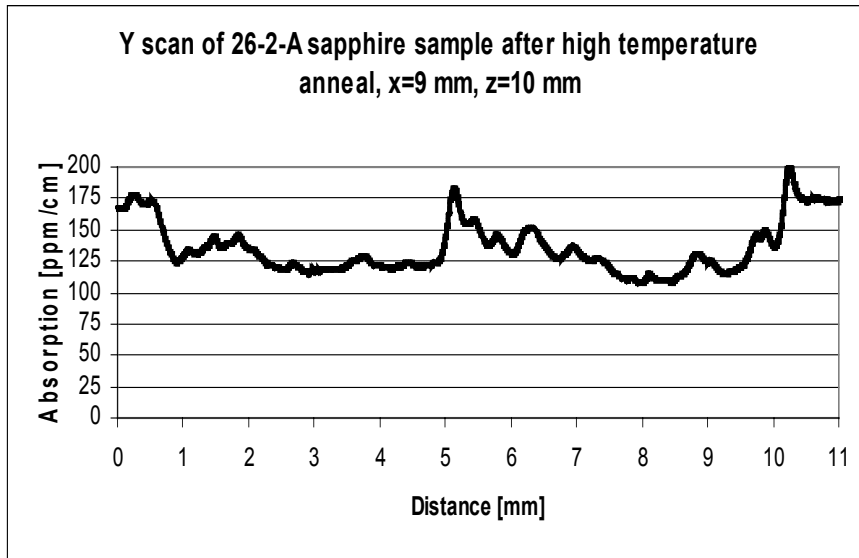
Crystal	Temperature	$\alpha$ (ppm/cm)					
		514 nm			1064 nm		
		bulk	dip	surface	bulk	dip	surface
Annealed at CSI							
LB-1	Control	850-1300	no	no	50-60	no	no
LB-2	Control	1200-1500	no	no	60-70	no	no
L14-1	Intermediate	1350	300	600	50	10-20	75
L14-2	Intermediate	800	300	2200	75	45	4000
L14O-1	Intermediate	1100	250	700	50-60	20	260
L14O-2	Intermediate	700	250	700	45	25	900
L16-1	High	80-170	no	350	25	no	90
L16-2	High	170	no	500	35	no	140
L16O-1	High	120	no	300	80	no	220
L16O-2	High	200	no	375	90	no	300
L1696-1	High	300	no	450	50	no	140
L1696-2	High	230	no	500	32	no	120
22-1	High				4700	no	<<bulk
22-2	High				4800	no	<<bulk
Annealed at Stanford (Cut surfaces unpolished unless specified)							
B-2-B	Control						
B-2-A	Intermediate	NA	NA	NA	NA	NA	NA
B-4-B	Control	1200	no	1200	60	no	60-70
B-4-A	Intermediate	1100	700-800	900-1200	35	<20	20-100
23-1-A	Control				70/80	no	
"	Intermediate				40/50	20	120
24-1-A	Control				70	no	
"	Intermediate				55/60	40	<50
24-2-A	Control				80	no	
"	Intermediate				50	20/30	75/120
26-2-A	Control				50	no	
"	High				130	125	400/700
27-2-B	Control				52	no	
"	Intermediate				45/50	30	<50
31-2-B	Control				35/40	no	
"	Intermediate				30	20	<30
30-2-B	Control				55/65	no	
"	Intermediate				45/55	20/25	<40

# Annealing at high temperatures under oxidizing conditions

## Y-Scan

Fine-Ground

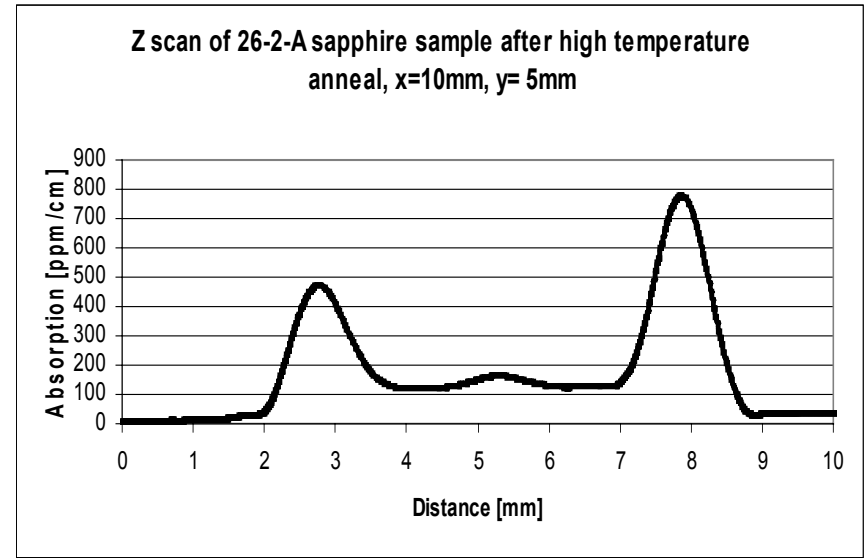
Fine Ground



## Z-Scan

Polished Face

Polished Face



# Consistent trends under oxidizing anneals

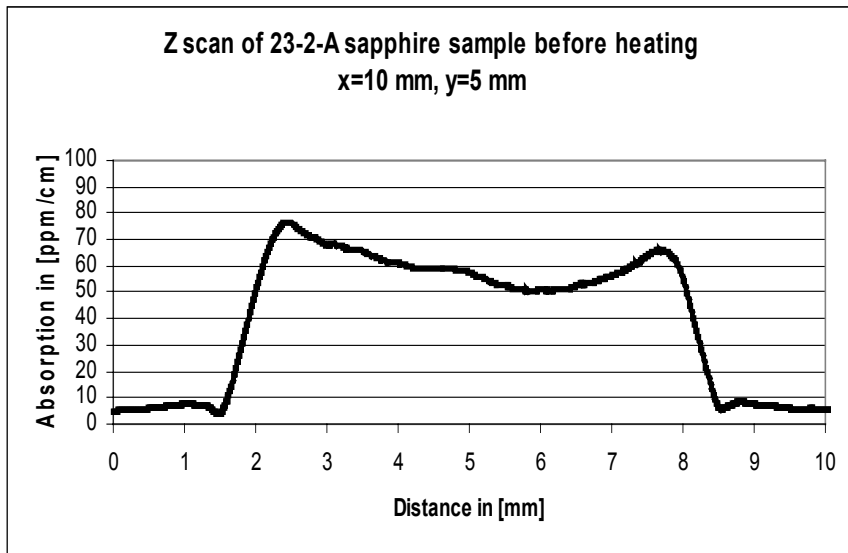
- **As grown**
  - Unclear correlation with starting material or furnace
    - Question of impurities, native defects and process contamination unresolved
  - No strong correlation with position in boule or use of re-melted feedstock
    - “Rosetta” sapphire indicates melt segregation operative during 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  $\text{Ti}^{3+}$ ), 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 be the best route to low loss material**

# Previous annealing studies under inert/reducing conditions

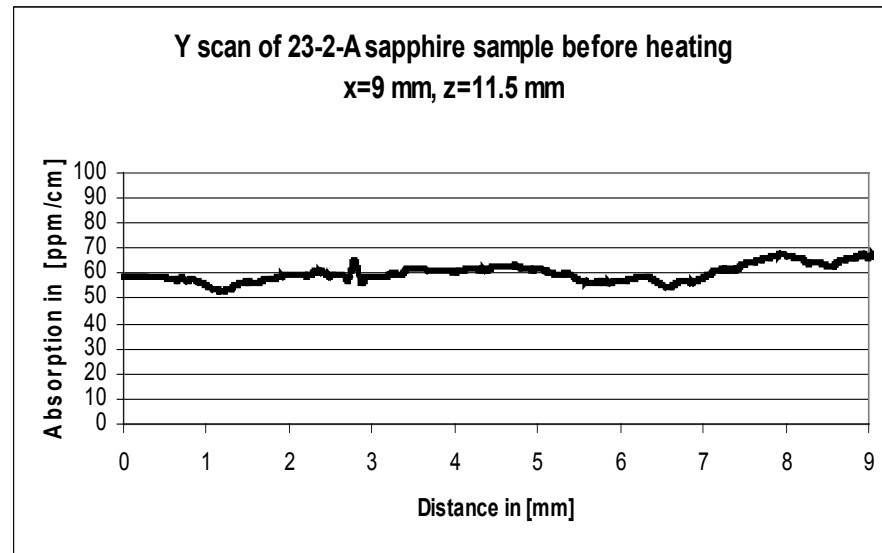
ID	Temperature	Time	Heat/Cool	Gas Flow	Before HT	After HT
-----	-----	-----	-----	-----	-----	-----
23-2-A	Low	Intermediate	200 C/hr	0.4 CFH	50-75	32-40
25-2-A	Low	Intermediate	200 C/hr	0.3 CFH	40-50	Cont.
25-2-A	Low	Long	200 C/hr	0.2 CFH	Cont.	25-35
27-2-A	Low	Long	200 C/hr	0.2 CFH	50	37-40
24-2-B	Low	Short	200 C/hr	0.2 CFH		
24-2-B	Low	Intermediate	200 C/hr	0.2 CFH	80-100	70-95
23-1-B	Low	Intermediate	200/800	0.2 CFH	70-80	30-40
23-2-B	High	Short	200 C/hr	0.2 CFH	60-75	NA
23-2-B	High	Intermediate	200 C/hr	0.2 CFH	NA	40-55
23-2-B	Intermediate	Short	200 C/hr	< 0.2 CFH	40-55	NA
23-2-B	Intermediate	Intermediate	200 C/hr	< 0.2 CFH	NA	50-65
30-1-B	Intermediate	Long	200 C/hr	0.2 CFH	55-65	35-40
27-1-B	Intermediate	Long	200 C/hr	0.2 CFH	50-55	30-35
25-1-A	Intermediate	Short	200 C/hr	0.2 CFH	40	25-30
	Intermediate	Short	200 C/hr	0.2 CFH	25-30	25-30
24-1-A	Intermediate	Short	200 C/hr	0.2 CFH	50-60	50-60
LH12-S-1-A	Low	Short	200 C/hr	0.2 CFH	40-50	28-30
LH12-S-1-A	Low	Short	200 C/hr	0.2 CFH	28-30	28-30
LH12-S-1-A	Intermediate	Short	200 C/hr	0.2 CFH	28-30	25-30
LH12-S-1-B	Low	Short	200 C/hr	0.2 CFH	40-55	32-42

# Annealing at intermediate temperatures under reducing conditions using moderate heating and cooling rates

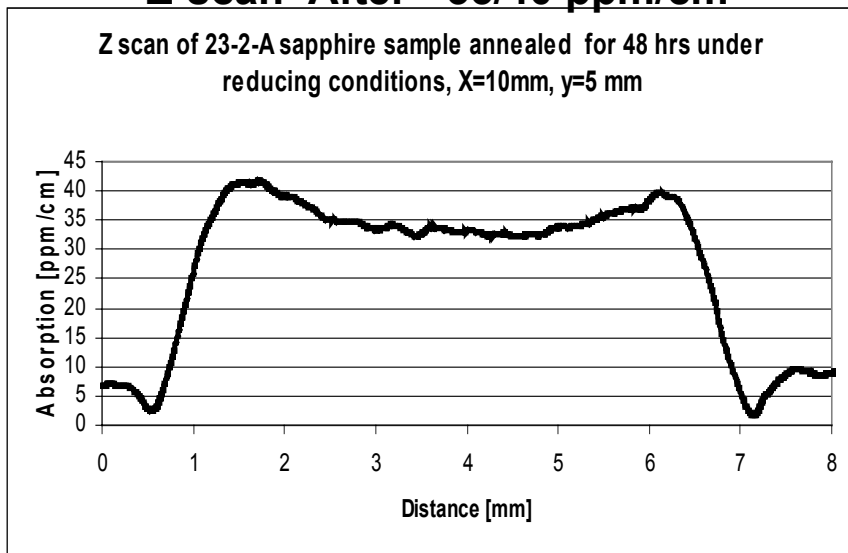
## Z-scan Before - 55/65 ppm/cm



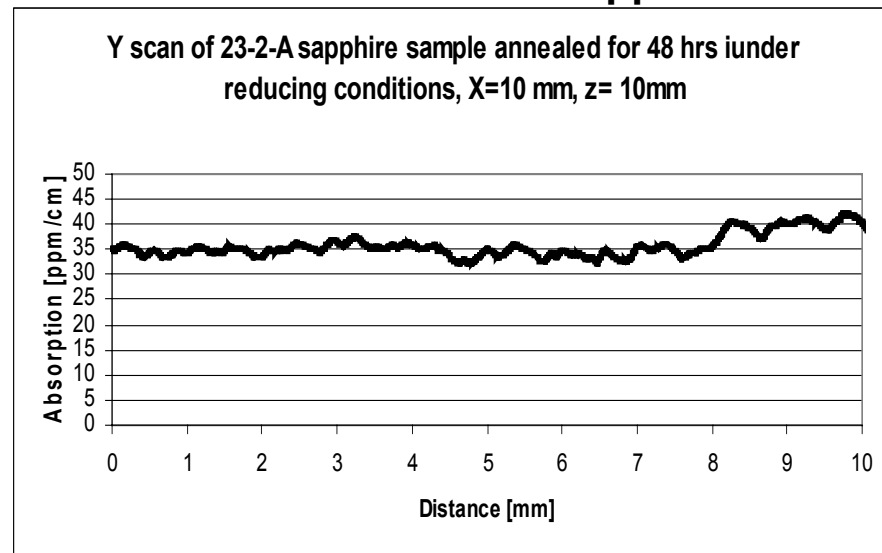
## Y-scan Before - 55/65 ppm/cm



## Z-scan After - 35/40 ppm/cm



## Y-scan After - 35/40 ppm/cm



# Recent annealing studies under inert/reducing conditions

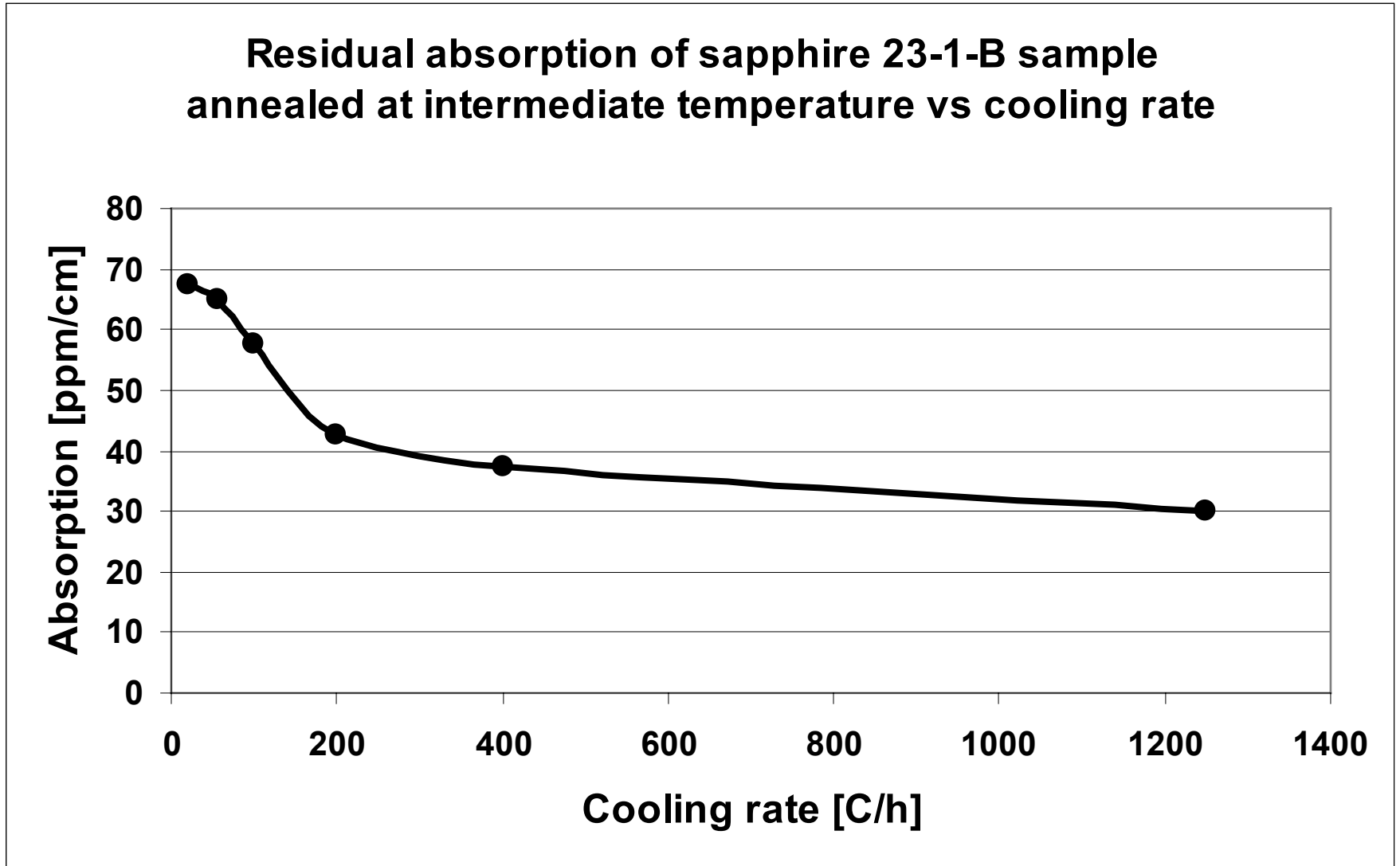
ID	Soak Temp.	Heat/Cool Rate	Absorption Before HT	Absorption After HT	Comments	Gas
27-2-A	Intermediate	200 C/hr	50	37-40		H2/N2
24-2-B	Low	200 C/hr	80-100	70-95		H2/N2
30-1-B	Intermediate	200 C/hr	55-65	35-40		H2/N2
27-1-B	Intermediate	200 C/hr	50-55	30-35		H2/N2
25-1-A	Intermediate	200 C/hr	40	25-30	As-received	H2/N2
24-1-A	Intermediate	200 C/hr	50-60	50-60	Prev. O2 anneal	H2/N2
LH12-S-1-A	Intermediate	200 C/hr	40-50	28-30		H2/N2
LH12-S-1-A	Intermediate	200 C/hr	28-30	28-30		H2/N2
LH12-S-1-A	Intermediate	200 C/hr	28-30	25-28		H2/N2
LH12-S-1-B	Intermediate	200 C/hr	37-45	32-37		N2
LH12-S-1-B	Intermediate	200 C/hr	32-37	32-37		N2
LH12-S-1-B	Intermediate	200 C/hr	32-37	22-27		N2
23-1-B	Intermediate	200/800	70-80	30-40		H2/N2
23-1-B	Intermediate	20 C/hr	30-40	~65	Slow cool	N2
23-1-B	Intermediate	55 C/hr	~65	~65	Slow cool	N2
23-1-B	Intermediate	100 C/hr	~65	55-60		N2
23-1-B	Intermediate	200 C/hr	55-60	40-45		N2
23-1-B	Intermediate	400 C/hr	40-45	35-40		N2
23-1-B	Intermediate	>1250 C/hr	35-40	30	Power-off cool	N2
23-1-B	Intermediate	20 C/hr	30	65-70	Slow cool	H2/N2



# Recent annealing studies under inert/reducing conditions

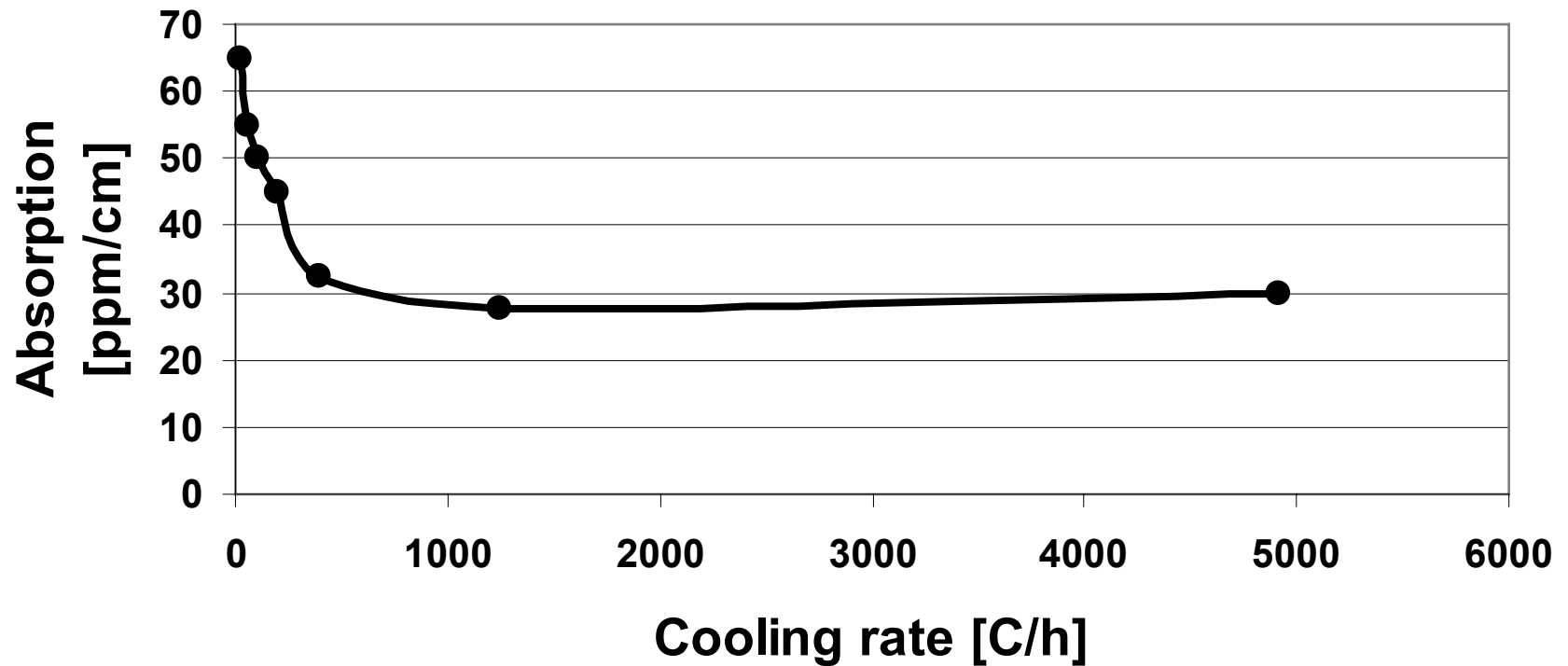
ID	Soak Temp.	Heat/Cool Rate	Absorption Before HT	Absorption After HT	Comments	Gas
24-1-B	Low	200 C/hr	~60	~45		N2
24-1-B	Intermediate	200 C/hr	~45	~45		N2
24-1-B	Intermediate	20 C/hr	~45	~65	Slow cool	N2
24-1-B	Intermediate	55 C/hr	~65	~55	Slow cool	N2
24-1-B	Intermediate	100 C/hr	~55	50		N2
24-1-B	Intermediate	200 C/hr	50	40-45		N2
24-1-B	Intermediate	400 C/hr	40-45	30-35		N2
24-1-B	Intermediate	>1250 C/hr	30-35	25-30	Power-off cool	N2
24-1-B	Intermediate	20 C/hr	25-30	55	Slow cool	H2/N2
24-1-B	Intermediate	4920 C/hr	55	30	Forced cool	H2/N2
30-2-A	Low	1250 C/hr	50-55	50-55	Power-off cool	H2/N2
30-2-A	High	2700 C/hr	53	26	Power-off cool	H2/N2
30-1-A	Low	880 C/hr	42-45	42-45	Power-off cool	H2/N2
30-1-A	High	2700 C/hr	42-45	20-25	Power-off cool	H2/N2
30-1-A	Intermediate	5100 C/hr	20-25	21	Forced cool	H2/N2
30-1-A	Intermediate	4920 C/hr	21	18-20	Forced cool	H2/N2
31-1-A	Low	780 C/hr	85	85	Power-off cool	H2/N2
31-1-A	High	2700 C/hr	85	30-40	Power-off cool	H2/N2
31-2-A	Intermediate	2000 C/hr	35	22-24	Power-off cool	H2/N2

# Observed trends under inert/reducing conditions

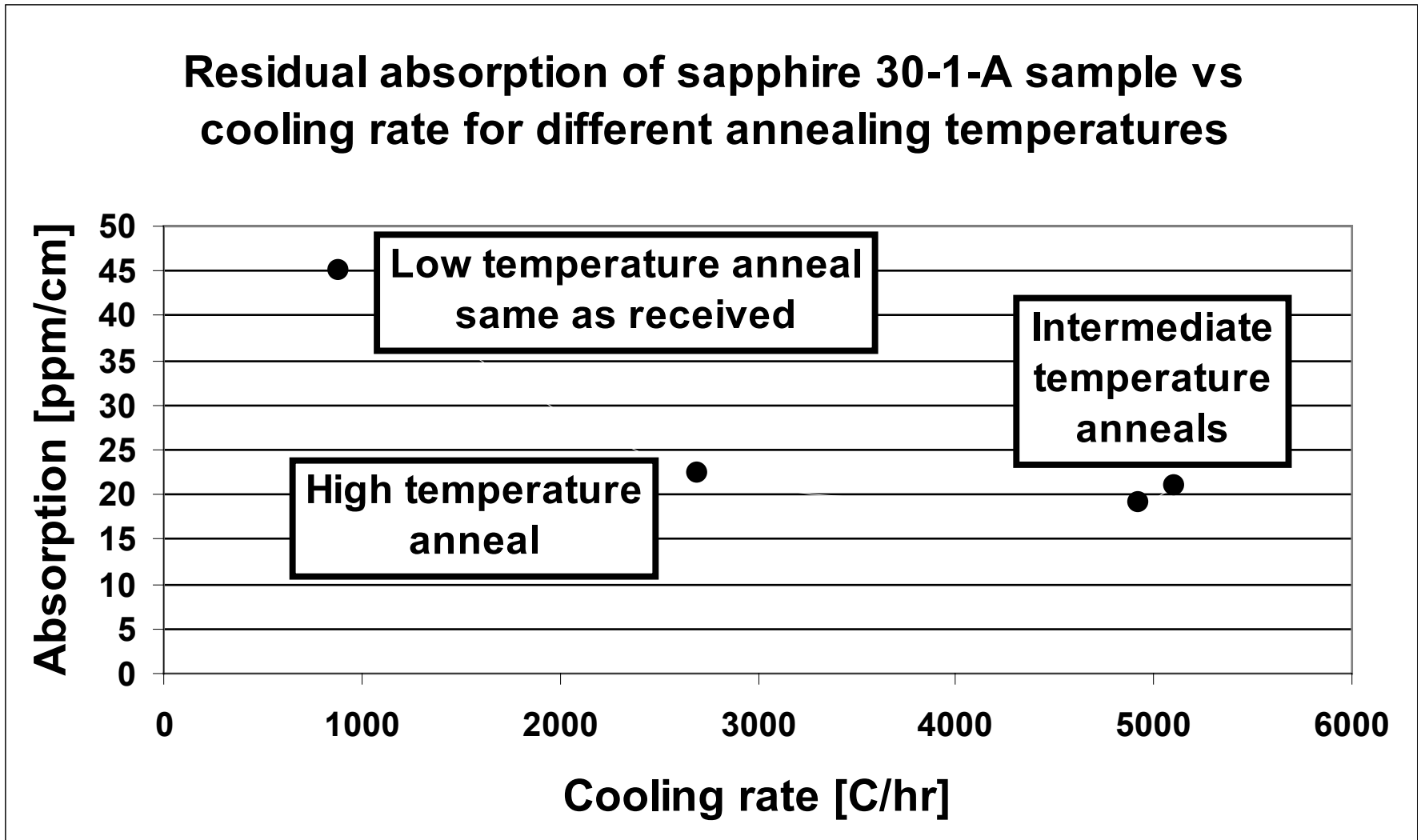


# Observed trends under inert/reducing conditions

Residual absorption of sapphire 24-1-B sample annealed at intermediate temperature vs cooling rate

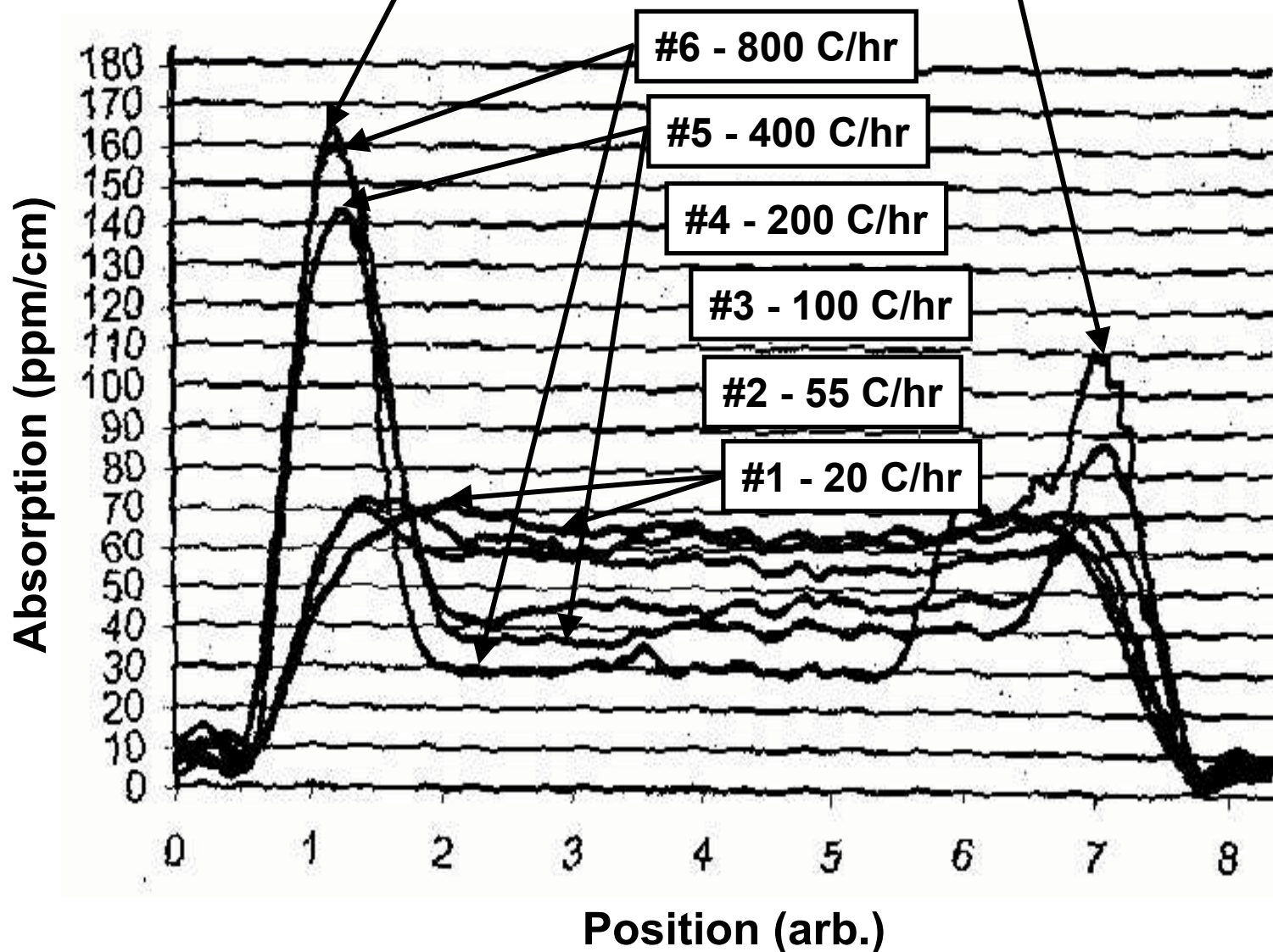


# Observed trends under inert/reducing conditions



# Sequential z-scans of 23-1-B heated to intermediate temperatures in N<sub>2</sub> and cooled at rates shown

Increasing surface degradation from oxygen impurity in N<sub>2</sub>



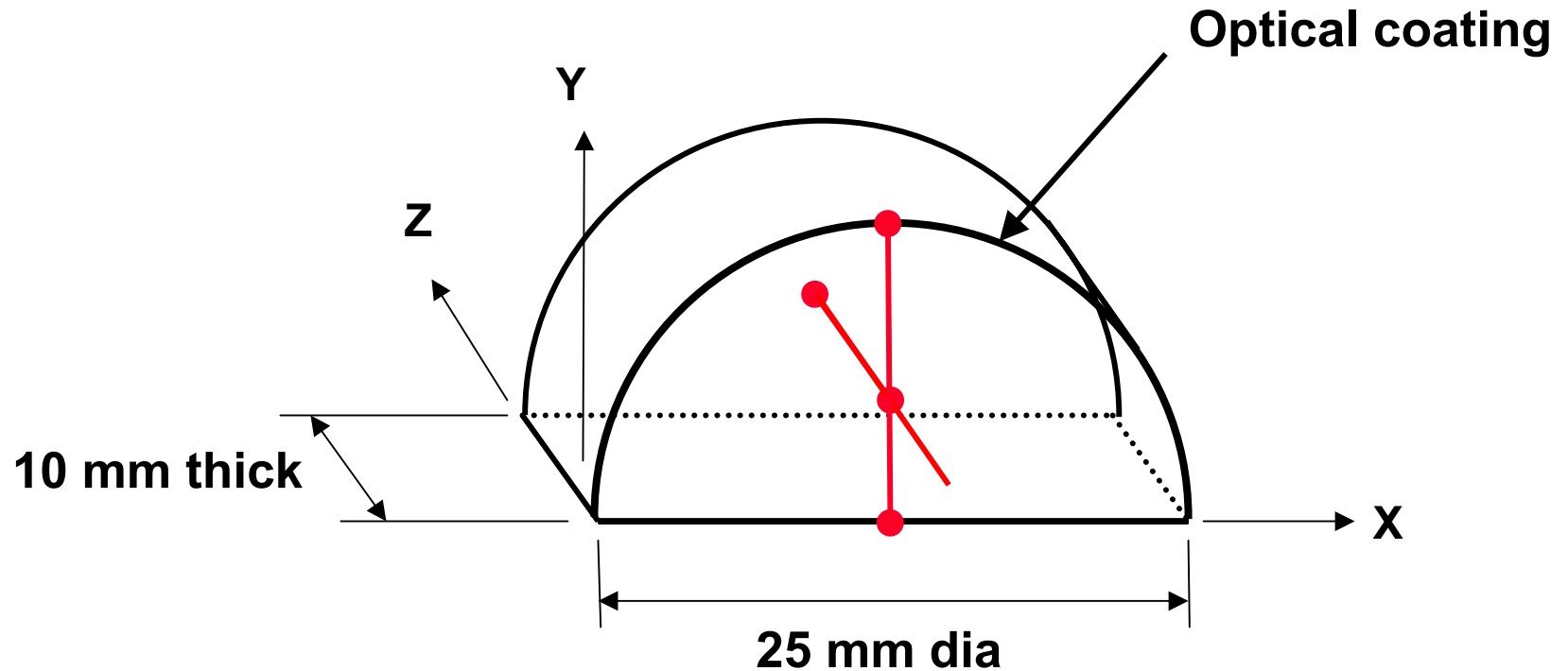
# Sapphire Summary

- **Status:**
  - 40-60 ppm/cm at 1064 nm in large volumes from CSI
  - Heat treatment (annealing) can strongly influence optical losses
  - Oxidizing anneals irreversibly increase bulk absorption and scatter
  - Reducing anneals reversibly lower absorption without causing scatter
    - Annealing at intermediate temperatures in H<sub>2</sub>/N<sub>2</sub> yields >50% reductions
      - 25-30 ppm/cm achieved with passive cooling at rates of >200° C/hr
      - 20 ppm/cm achieved with forced cooling at rates of >400° C/hr
  - Cooling kinetics of the annealing process are controlling variables
- **Current thinking:**
  - At least two extrinsic defect species (eg. Ti<sup>3+</sup>:Ti<sup>4+</sup> complex plus other(s))
  - Point defect equilibrium most important factor in current CSI material
    - Metastable state resulting from rapid cooling from high temp is beneficial
  - Low loss 8-T “Rosetta” at 10 ppm/cm suggests extrinsic defects still present and responsible for the 20 ppm/cm floor in optical absorption
- **Next steps:**
  - Continue study of processing kinetics in larger size samples
    - How fast can large sapphire windows be cooled?
  - Complete chemical analysis of low-loss regions of 8-T and both matrix phase and scattering centers in high loss regions
  - Refine list of “suspects” and design purposeful doping studies to evaluate

# Optical coating loss study

- High reflecting MLD coatings on 1" dia GO fused silica. Multiple  $\lambda/4$  layers designed for T = 70 ppm (~30-60 layers).
  - Ta<sub>2</sub>O<sub>5</sub> / SiO<sub>2</sub> (Annealed from 250 - 500 °C)
  - Nb<sub>2</sub>O<sub>5</sub> / SiO<sub>2</sub> (Annealed from 300 - 500 °C)
  - ZrO<sub>2</sub> / SiO<sub>2</sub> (Annealed from 300 - 400 °C)
  - Ta<sub>2</sub>O<sub>5</sub> / Al<sub>2</sub>O<sub>3</sub> (Annealed from 300 - 400 °C)
- Partially reflecting MLD coatings on 1" dia fused silica. (30  $\lambda/4$  layers).
  - SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Annealed, R = 60 to 80%)
- Specimens from other vendors
  - Newport M/FS 79% ND filter (~19.4 ±0.5% loss) used for calibration (measured by direct insertion loss minus reflection)
  - REO (PL/PL) HR = 0.22 ppm
  - SMA (PL/PL) HR = 0.72 ppm, SMA (Curve) HR = 1.1 ppm
  - Wave Precision (PL/PL) HR = 1.7 ppm

# Optical loss measurement scheme for optical coatings

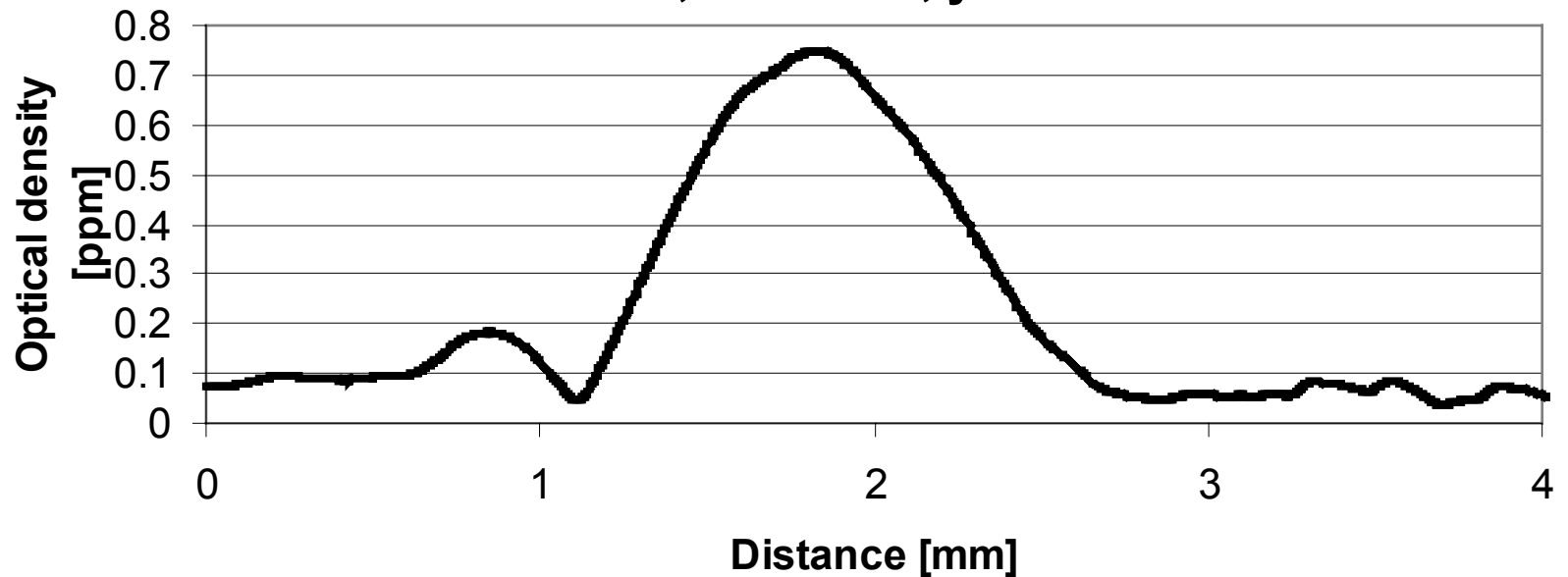


● — ● Locus of intersection of pump and probe beam where absorption in a 100 x 25 $\phi$  micron cylinder is measured during Y- and Z-scans

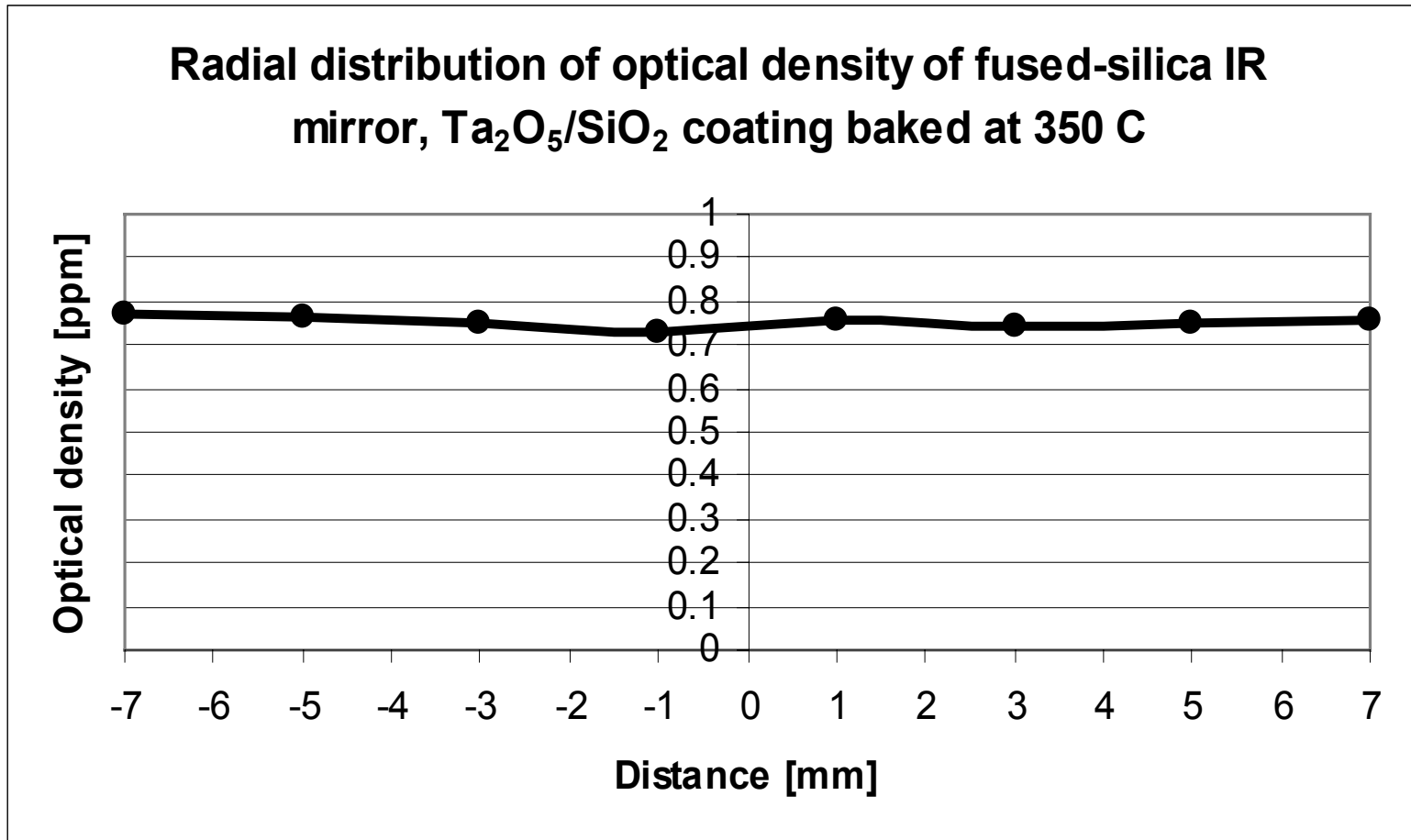


# Z-scan to locate optical coating

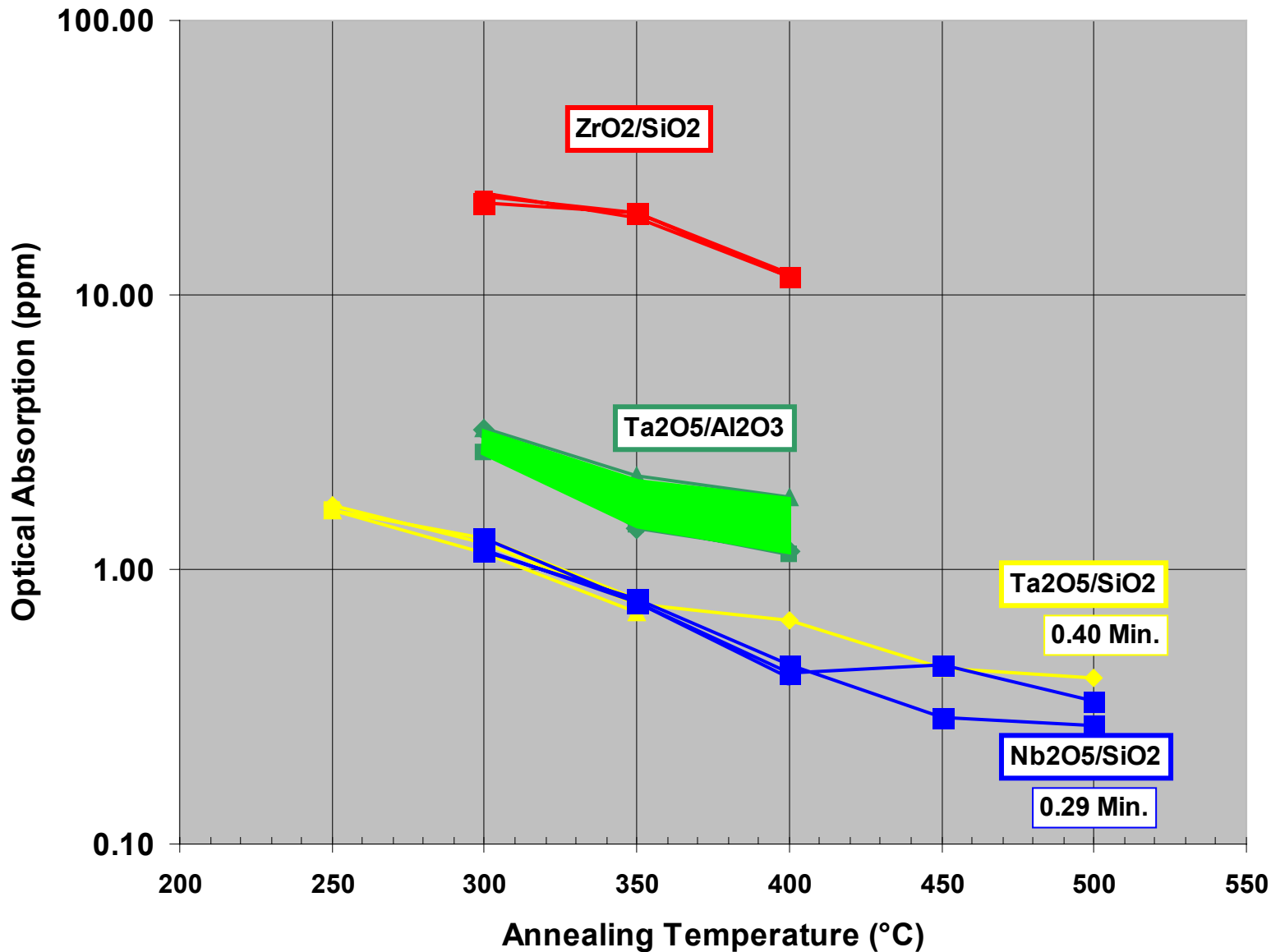
**Z-scan of multi-layer Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> on fused silica  
1064 nm HR mirror (produced by JMM for Caltech)  
used as standard,  
SN 5705, at x=11.5, y=6mm**



# Y-scan to measure radial uniformity of coating absorption

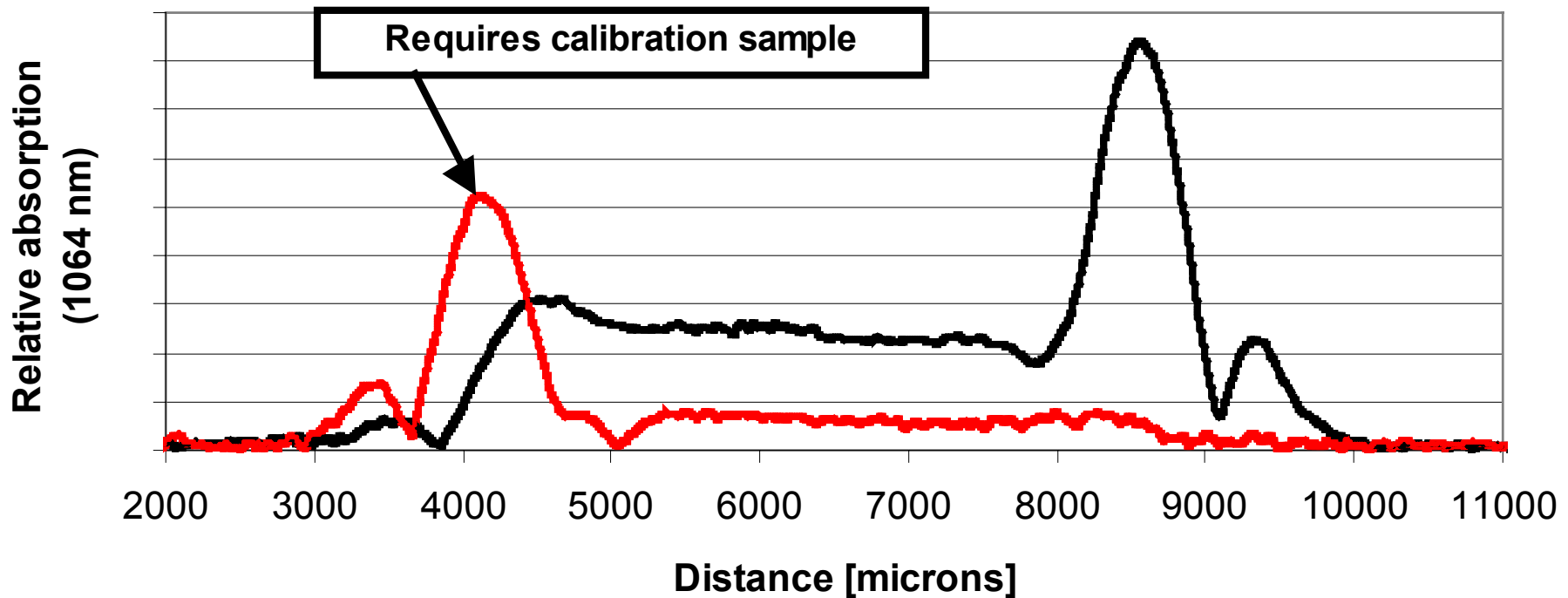


# Dependence on materials and annealing temperature of optical loss in high reflectivity multilayer coatings



# Coating loss studies on partially reflecting films

Z scans of FSIRM S/N8137 (30 layers of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>),  
for regular (**front surface**) and reverse (rear surface)  
geometry



# Current coating loss estimates based on Newport metal-coated neutral density filter\*

Partially-reflecting multilayers of SiO <sub>2</sub> and Al <sub>2</sub> O <sub>3</sub>					(3/12/03)
COATINGS BY MLD					
Serial No.	Substrate	Coating Design	Configuration	PCI Loss (PPM)	Notes
8132	PL/PL	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Front Illuminated	1.75 - 2.0	R = 0.70 to 0.77 (30 layers)
8137	PL/PL	(Partial Reflectors)	Front Illuminated	1.8 - 2.2	R = 0.68 to 0.75 (30 layers)
8178	PL/PL	"	Front Illuminated	1.7 - 1.8	R = 0.77 to 0.80 (30 layers)
8211	PL/PL	"	Front Illuminated	1.8 - 2.0	R = 0.62 to 0.79 (30 layers)
MISC. COATINGS BY OTHER VENDORS					
REO (HR+AR)	PL/PL	Ta <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> *	Front Illuminated	HR = 0.22	
			Front Illuminated	AR = ~3.6	Requires standard for calibration
SMA (HR Ref. 01044/11)	Curve	Ta <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> *	Front Illuminated	HR = 1.1	0.95 by SMA
Wave Precision (GO 5703)	PL/PL	Ta <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub> *	Front Illuminated	HR = 1.7	
HR/AR - Ref. E000718/7			Front Illuminated	AR = ~2.4	Requires standard for calibration
Newport M/FS ND filter	FSQ-ND01 (79%)	Metal Coated FS PL/PL	Front Illuminated	18% **	Used as Primary Standard
SMA (HR Ref. 01045/12, GO)	PL/PL	Ta <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> *	Front Illuminated	HR = 0.72	1.2 by SMA, used as Secondary Standard
				* Structure of coating unknown	** Loss determined by photometric methods

\* Newly-designed coating reference standard will have only half the front surface coated to allow self-referencing between adjacent coated and non-coated surfaces