Absorption Studies in Optical Coatings and Sapphire Crystals

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Lasers and Optics Working Group

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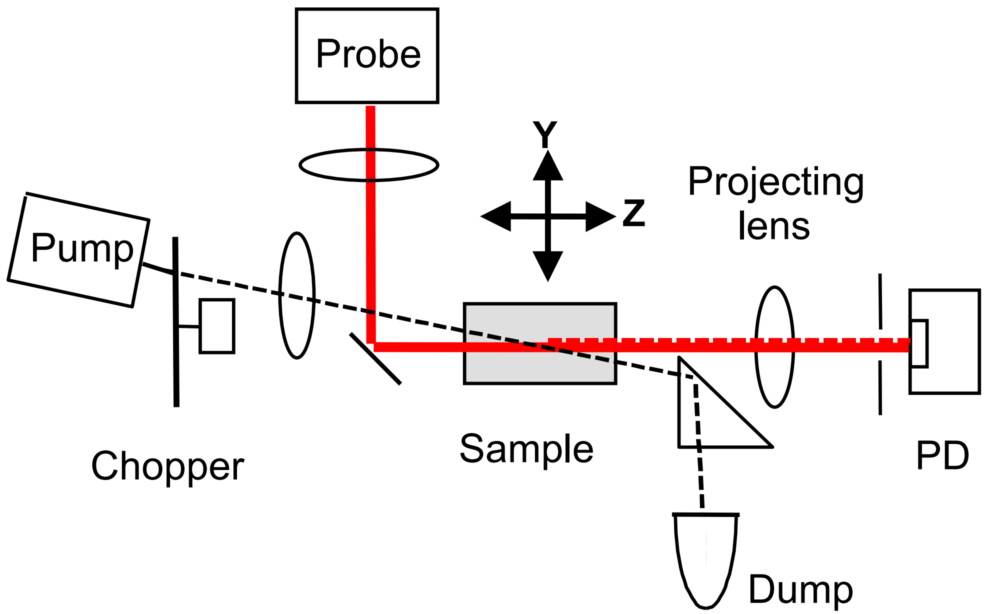
Photothermal Common-Path Interferometry

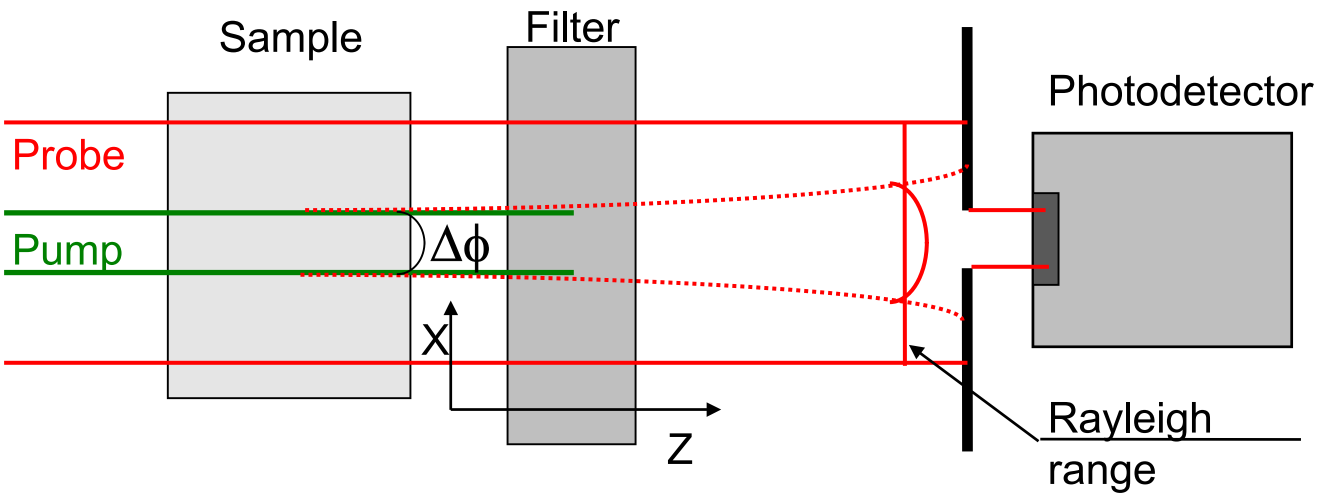
- diffraction regime of cross-beam cw thermal lensing -



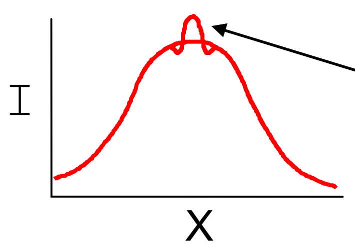
Pump waist	50 μ	Chopping frequency	380 Hz (10Hz- 2 kHz)
Probe waist	120 μ	Crossing angle	1° - 20° (in air)
Pump power	5 W	Probe power	0.5 mW

- **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**

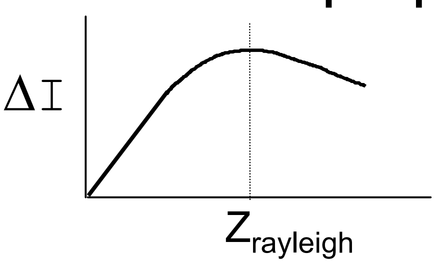
Photothermal Common-Path Interferometry
for optical loss measurements
‘Self-interference’ of probe in the near field



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



$$\Delta I / I = \Delta\phi$$

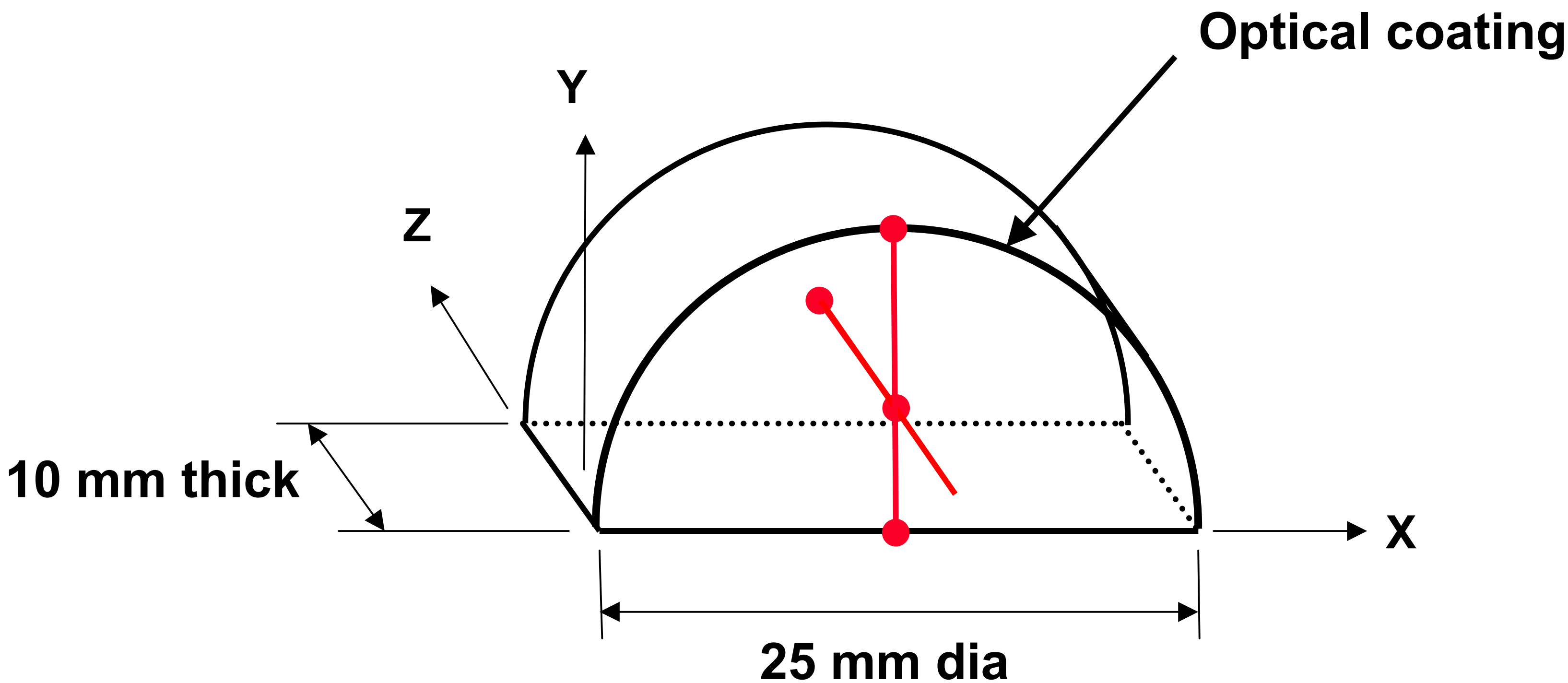


Optical coating loss study

- High reflection multi-layer MLD coatings on General Optics 1” dia fused silica windows annealed at various temperatures. Multiple $\lambda/4$ layers designed for T = 70 ppm (~30-60 layers).
  - Ta_2O_5 / SiO_2 (250 - 500 ^oC)
  - Nb_2O_5 / SiO_2 (300 - 500 ^oC)
  - ZrO_2 / SiO_2 (300 - 400 ^oC)
  - Ta_2O_5 / Al_2O_3 (300 - 400 ^oC)

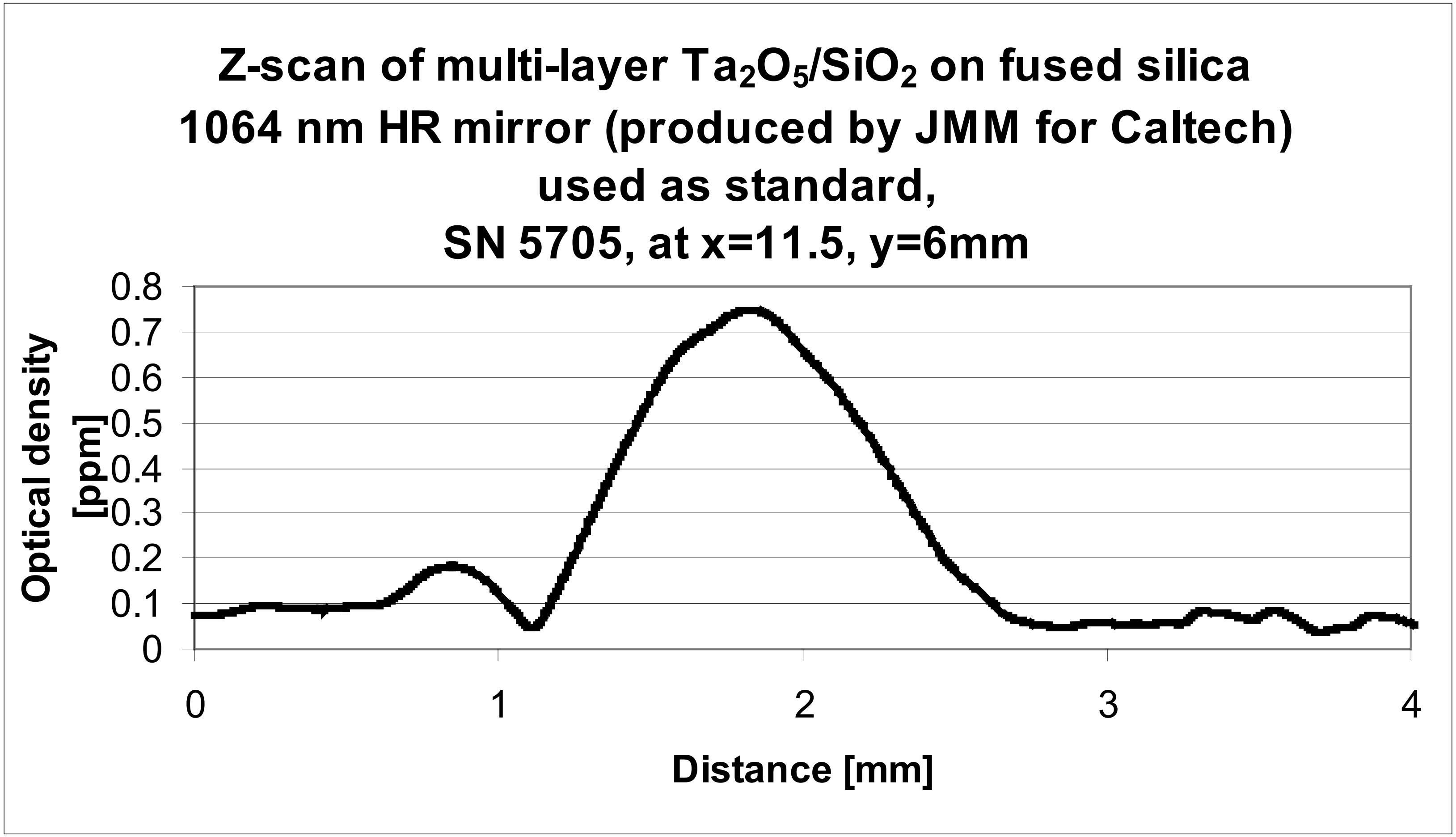
- Specimens from other vendors
  - Newport M/FS 79% ND filter (~19.4 $\pm$0.5% loss) used for calibration (measured by direct insertion loss minus reflection)
  - REO (PL/PL) HR = 0.22 ppm
  - SMA (PL/PL) HR = 0.72 ppm, SMA (Curve) HR =1.1 ppm
  - Wave Precision (PL/PL) HR = 1.7 ppm

Optical loss measurement scheme for optical coatings

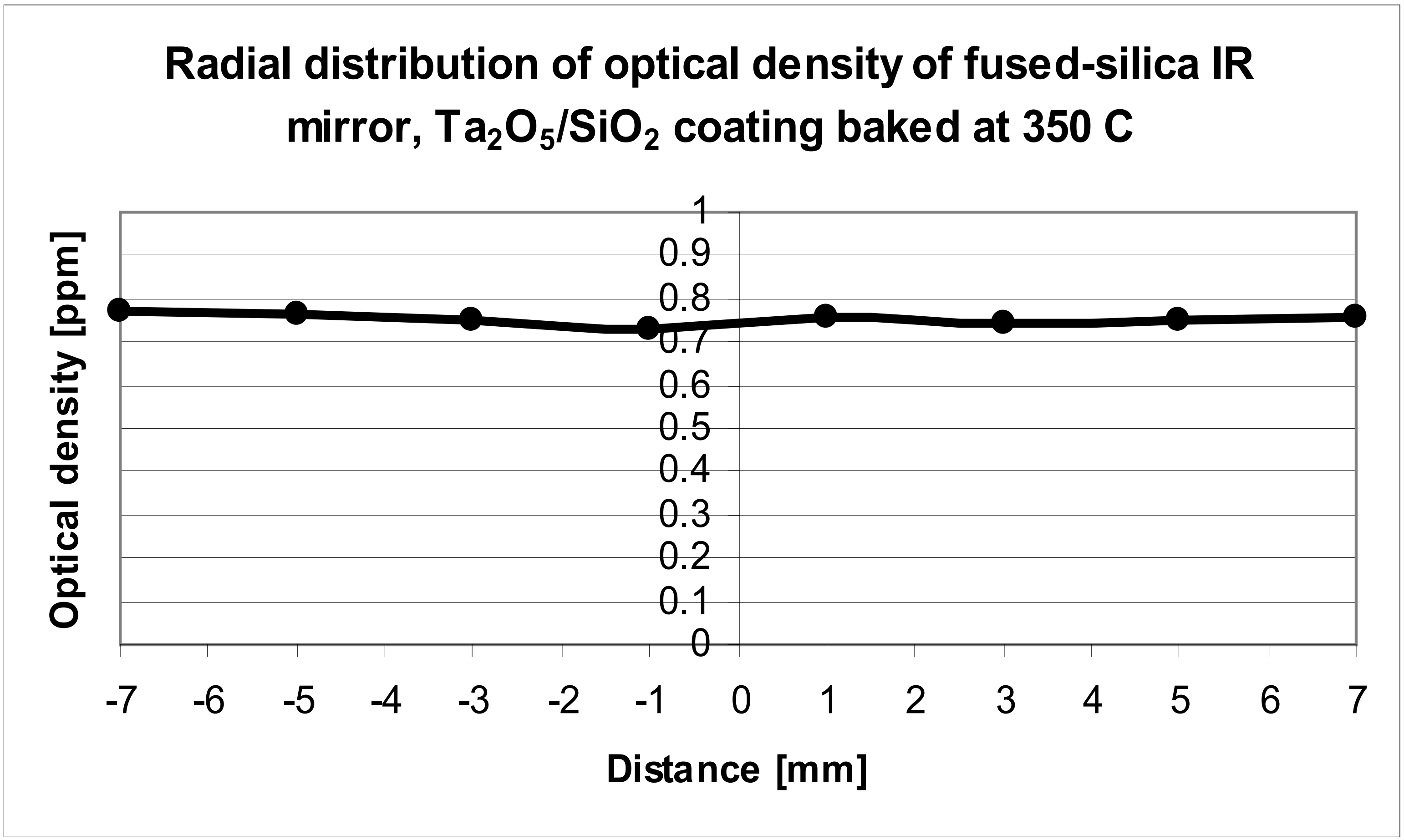


Locus of intersection of pump and probe beam where absorption in a 100 x 25ϕ micron cylinder is measured during Y- and Z-scans

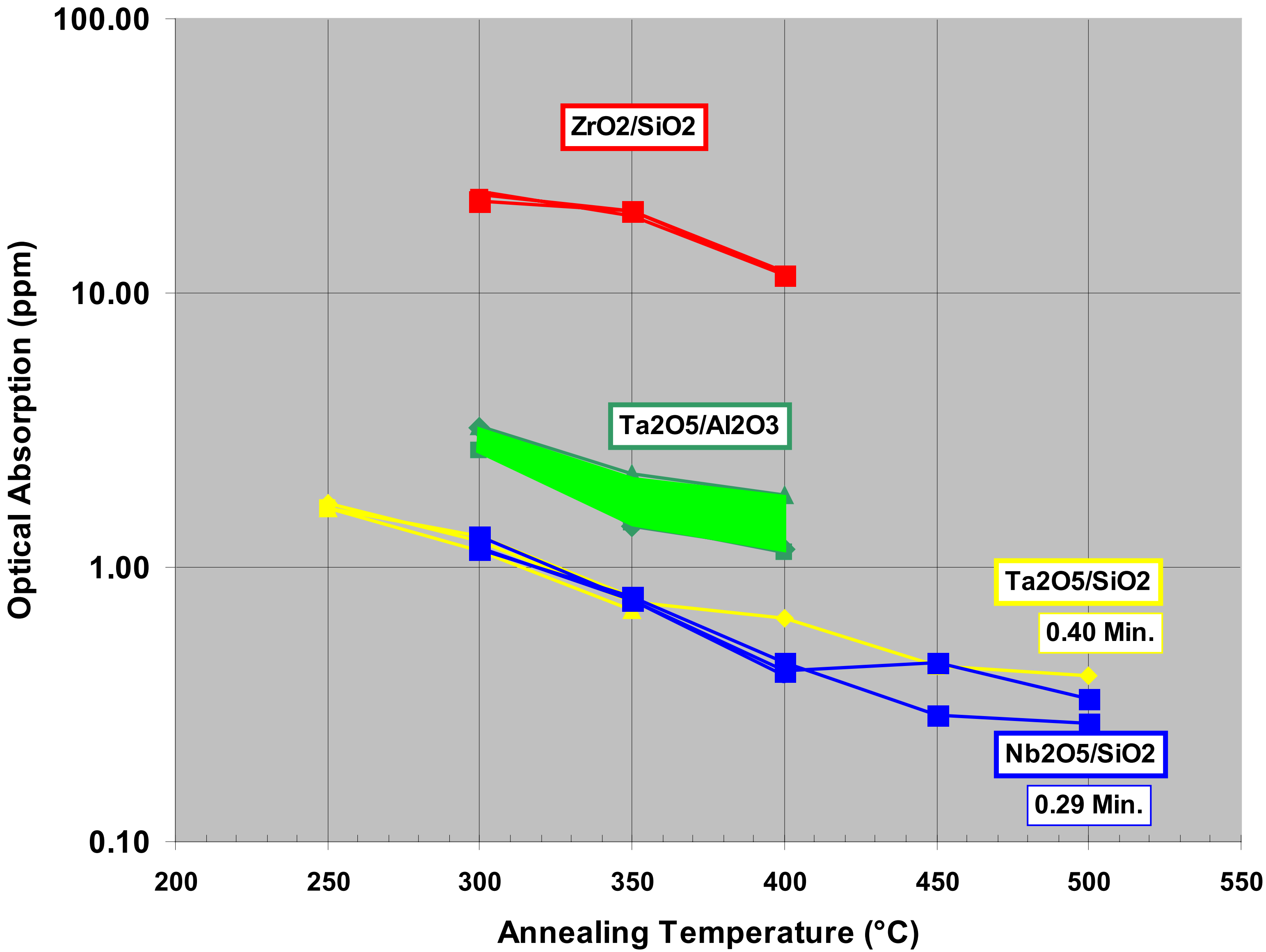
Z-scan to locate optical coating



Y-scan to measure radial uniformity of coating absorption



Optical loss dependence on materials and annealing temperature



Coating loss studies

- Evaluate broader range of annealing

  parameters

- Evaluate different deposition parameters

- Evaluate other material combinations

  e.g. SiO_2/Al_2O_3

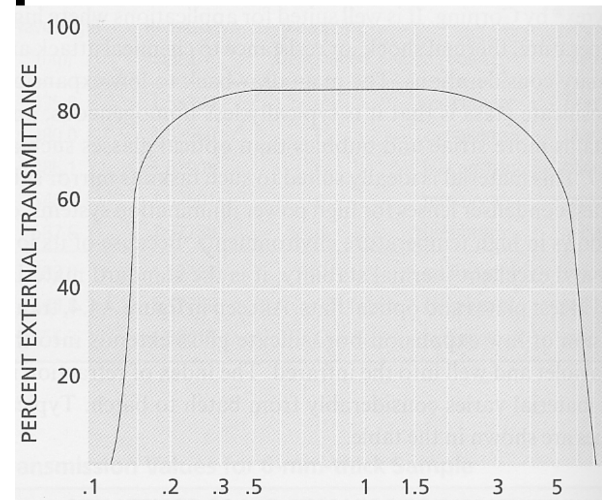
- Develop common calibration standard

  between SMA and Stanford

Study of absorption in sapphire

- Intrinsic
  - conduction to valence band in UV
  - multiphonon in mid-IR
  - only cure is different material

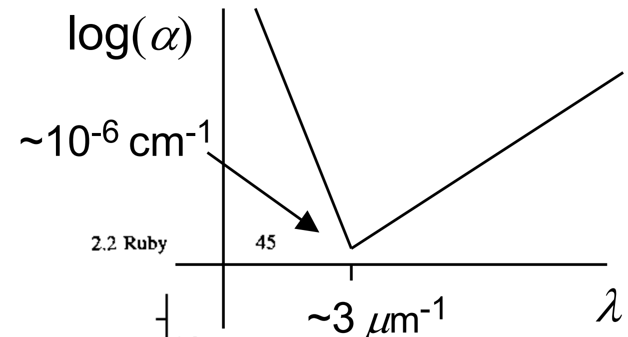
    expectation and existence proofs indicate this isn't the problem

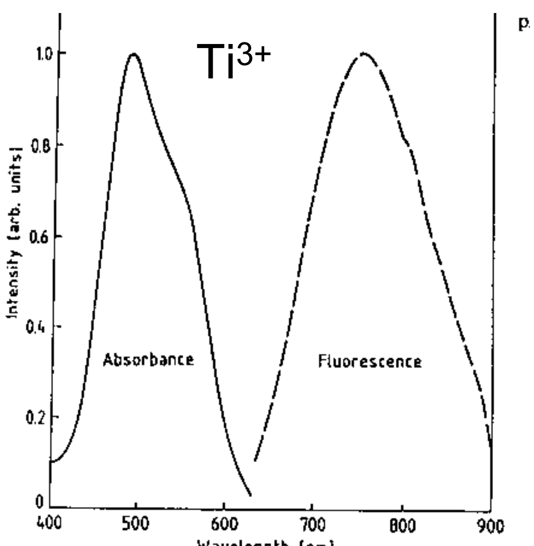


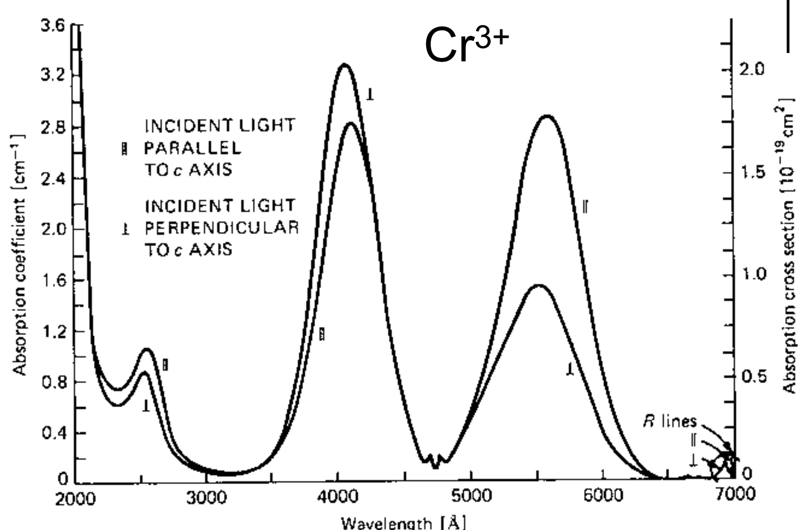
- Extrinsic
  - native defects

    vacancies, antisites, interstitials,
  - impurities

    e.g. transition metals: Cr, Ti, Fe, …



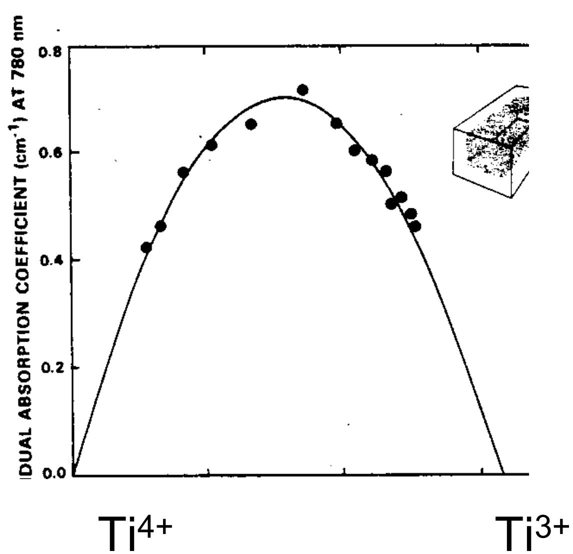




Characteristics of absorbing species

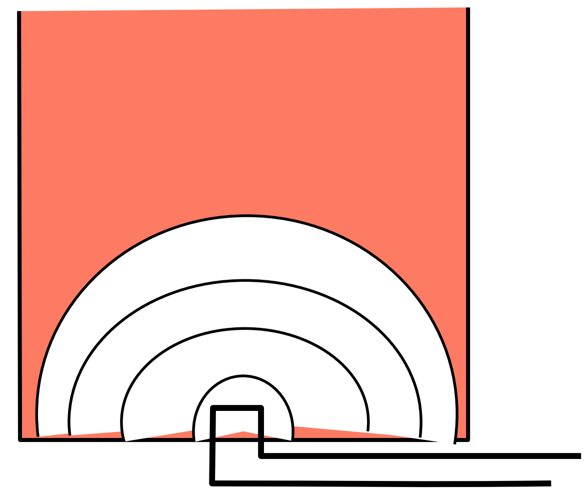
- Allowed transitions
  - large cross sections ⇒ ppm concentrations significant
- Broad spectral features
  - identification difficult
  - off “resonant” absorption significant
  - sum of several species can contribute to absorption at given λ
- Redox state important
  - e.g. $\alpha[Ti^{3+}] \neq \alpha[Ti^{4+}]$
  - 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

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



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

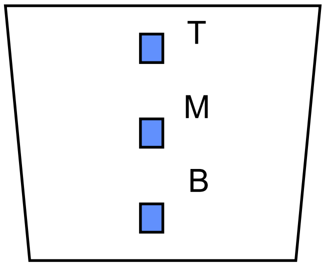
- Heat Exchanger Method
  - He-gas cools bucket of melt
  - solidification outwards from bottom



- Starting materials
  - typically "craquelle" sapphire
  - ppm levels of some transition metals
  - purity ↑ ⇒ $ ↑↑
- 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



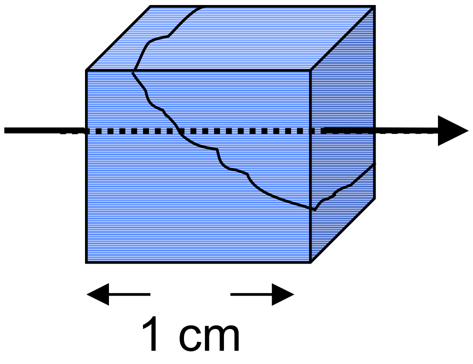
- **Annealing Studies**
  - 2.5 cm dia x 1 cm thick a-axis CSI Hemex White
  - primarily influence redox state, intrinsic defects (e.g. Oxygen vacancies)
  - parameters: time, temperature, reducing (H_2) or oxidizing (air, O_2)
  - furnace design

    accidental introduction of impurities, especially near surface

Compositional analysis by GDMS: ppms of everything

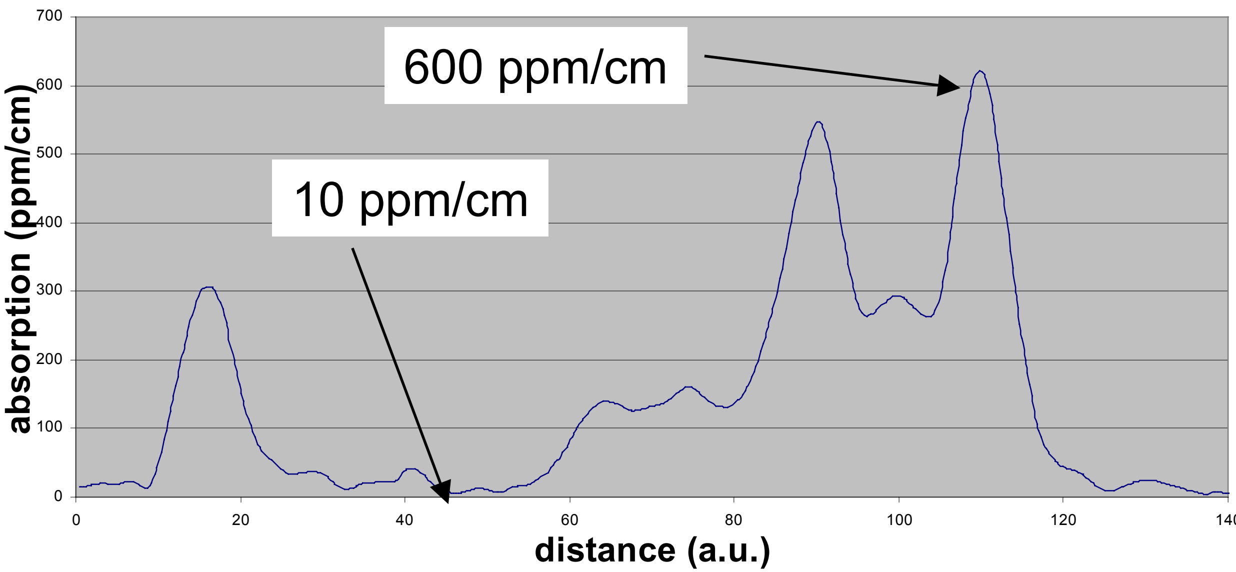
	LIGO #1T Sample #10 ppmw	LIGO #1M Sample #11 ppmw	LIGO #1B Sample #12 ppmw	LIGO #2T Sample #07 ppmw	LIGO #2M Sample #08 ppmw	LIGO #2B Sample #09 ppmw	LIGO #3T Sample #04 ppmw	LIGO #3M Sample #05 ppmw	LIGO #3B Sample #06 ppmw	LIGO #4T Sample #01 ppmw	LIGO #4M Sample #02 ppmw	LIGO #4B Sample #03 ppmw	LIGO #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

Low optical loss existence proof (Rosetta sapphire)

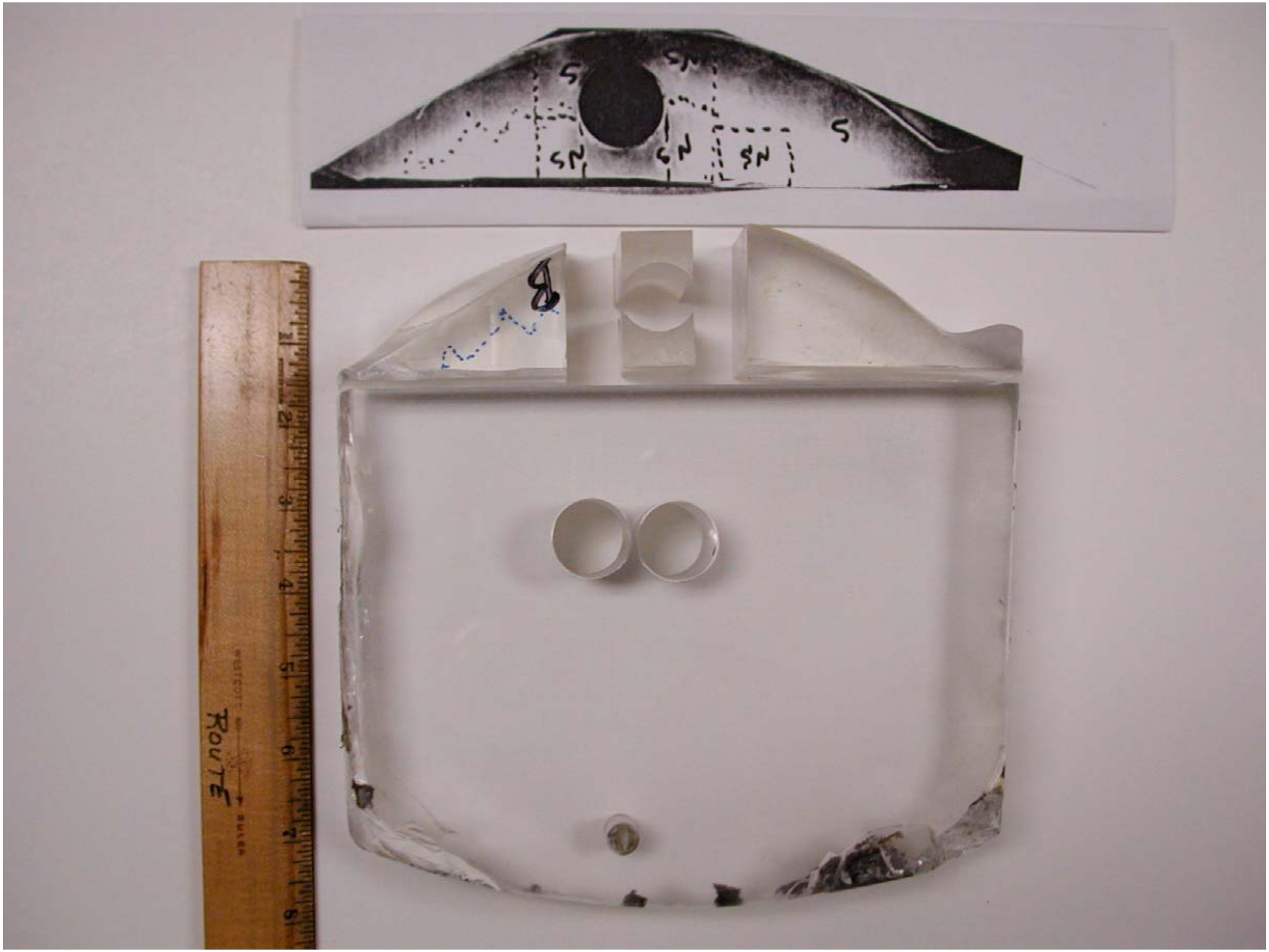


- Single 1 cm sample
  - region with 10 ppm/cm
  - region with 600 ppm/cm
  - abrupt boundary between
- Preparation unexceptional
- Mechanism not yet clear
  - not typical of normal impurity segregation
  - specimen should be useful for “self-normalizing” measurements

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



Parent slab from which 8-T was taken



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

Neutron Activation Analysis of Impurities in CSI Sapphire

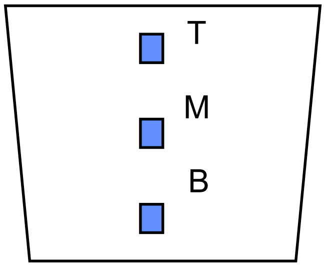
Observed impurity concentrations given in nanogram of impurity per gram of sample.

Element	Relative Concentration by mass ng/g	Observed radionuclide	Half-life	γ - ray energy (keV)	γ - ray intensity (%)
Ti	300 ± 29	^{47}Sc	3.34 d	159.4	68
Sc	3 ± 0.20	^{46}Sc	86.6 d	889.1	99.98
Cr	5 ± 1	^{51}Cr	27.7 d	320.2	9.83
Fe	≤ 1000	^{59}Fe	44.5 d	1099.3	56.5
Mo	1500 ± 227	^{99}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
    - re-melted 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 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

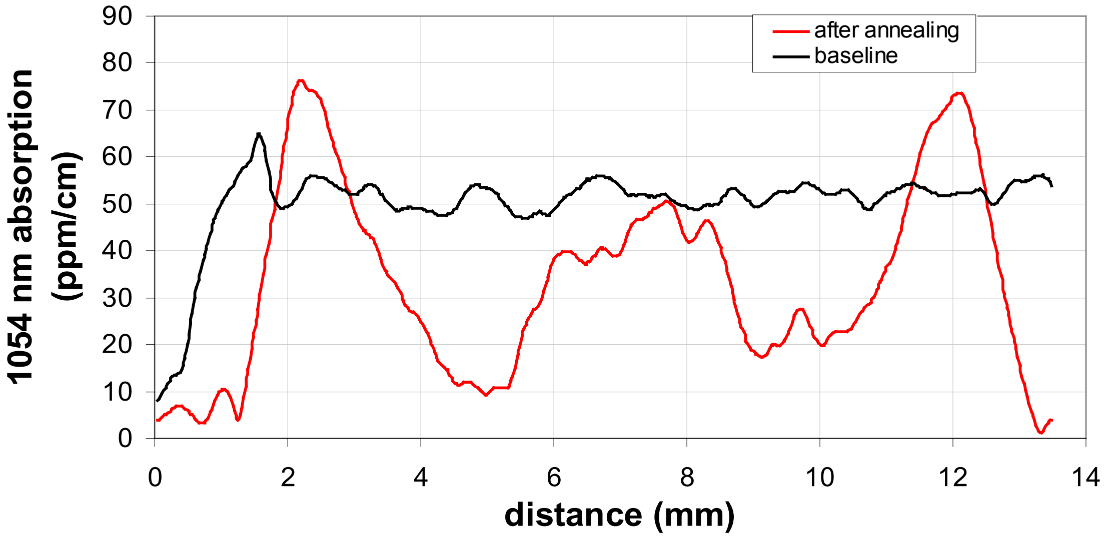
    accidental introduction of impurities, especially near surface

Annealing Experiments at CSI Showed Variety of Outcomes

Crystal	α (ppm/cm)						Scattering	Fluor.^
	514 nm			1064 nm				
	bulk	dip	surface	bulk	dip	surface		
LB-1	850-1300	no	no	50-60	no	no	no	1/2
LB-2	1200-1500	no	no	60-70	no	no	no	1/2
L14-1	1350	300	600	50	10-20	75	Near surfaces*	2^^
L14-2	800	300	2200	75	45	4000	Near surfaces*	1/2^^
L14O-1	1100	250	700	50-60	20	260	Near surfaces*	1/2^^
L14O-2	700	250	700	45	25	900	Near surfaces*	1/2^^
L16-1	80-170	no	350	25	no	90	Maximum in the bulk**	1/200
L16-2	170	no	500	35	no	140	Maximum in the bulk**	1/200
L16O-1	120	no	300	80	no	220	Maximum in the bulk**	1/200
L16O-2	200	no	375	90	no	300	Maximum in the bulk**	1/200
LH17-a	600-1700	no	25000	60-170	no	37000	no	1/2^^^
LH17-b	1700	no	5000	125	no	250	no	1/2^^^
L1696-1	300	no	450	50	no	140	Maximum in the bulk**	1/400
L1696-2	230	no	500	32	no	120	Maximum in the bulk**	1/300
L17H1696-1	300	no	1300	100	no	500	Maximum in the bulk**	1/400
L17H1696-2	230	no	900	35	no	250	Maximum in the bulk**	1/400
LN16-1	400	no	450	50	no	80	Maximum in the bulk**	<1/100
LN16-2	300	no	350	40	no	600	Maximum in the bulk**	<1/100
L169-1	3500	no	4000	550	no	1200	Weak in the bulk	<1/100
L169-2	700	no	800	150	no	165	Maximum in the bulk**	<1/100
LH14-1	650-800		1200-1300	40		70	no	
LH14-2	1750		2000	60		80	no	

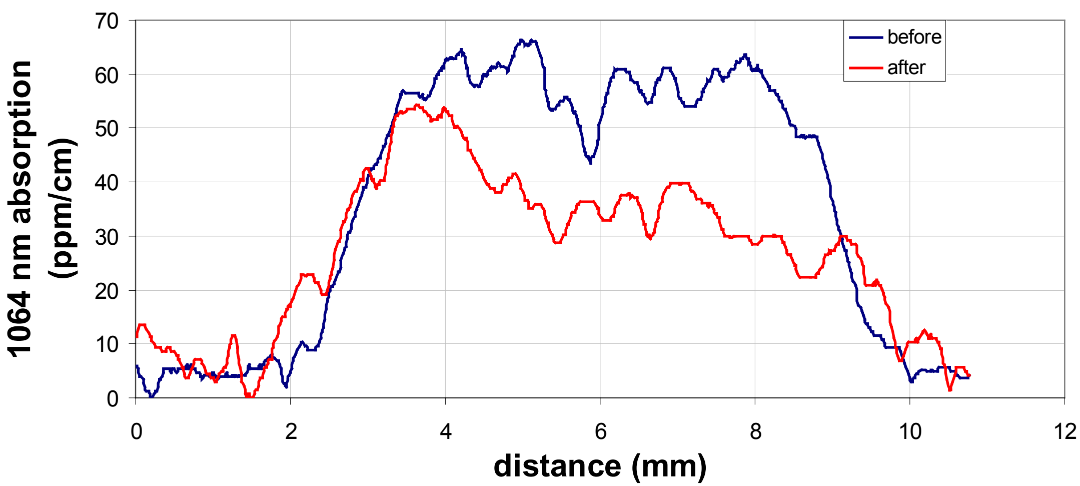
Apparent furnace effects

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



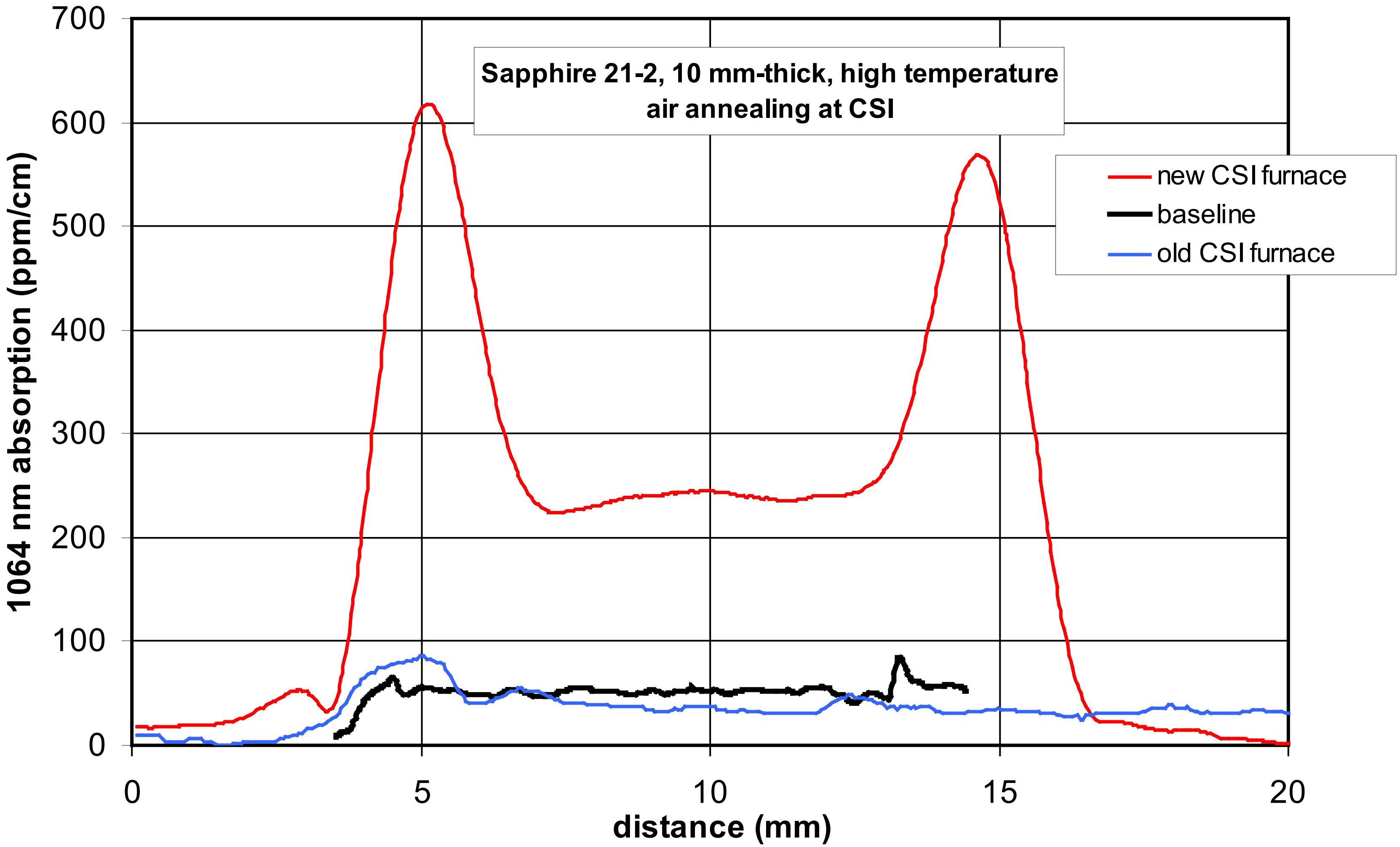
Annealed at CSI

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



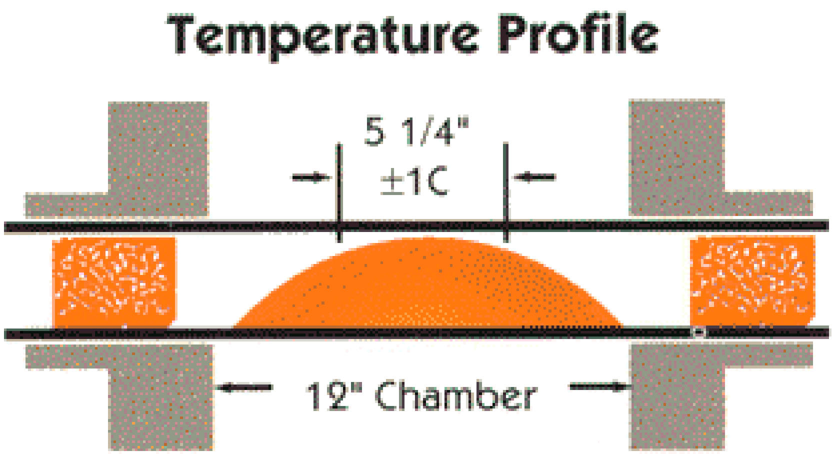
Annealed under similar conditions at Stanford

Apparent furnace effects



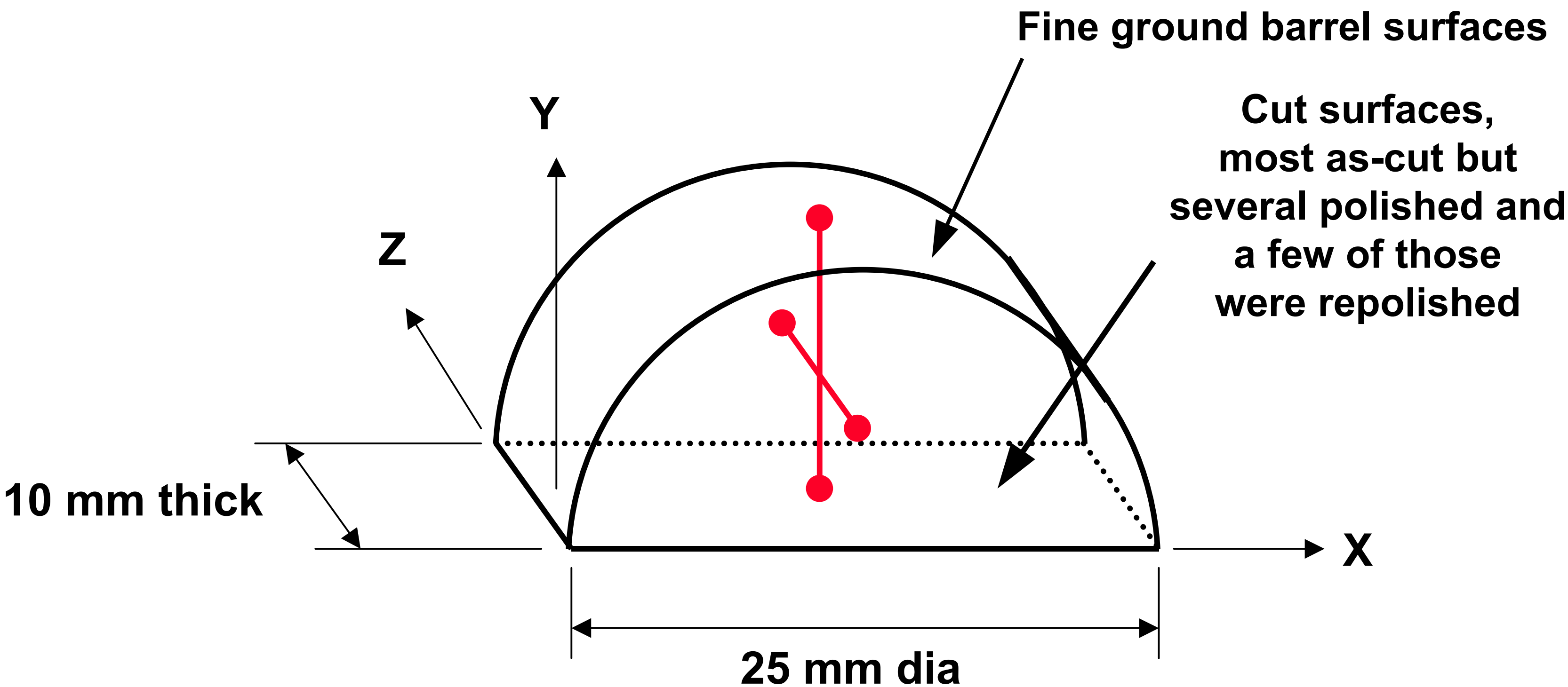
Post-growth heat treatment studies at Stanford

- Controlled atmosphere processing
  - Oxidizing conditions - air or oxygen
  - Inert/reducing conditions - N2 w/wo H2



$MoSi_2$ “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

Annealing studies under oxidizing conditions

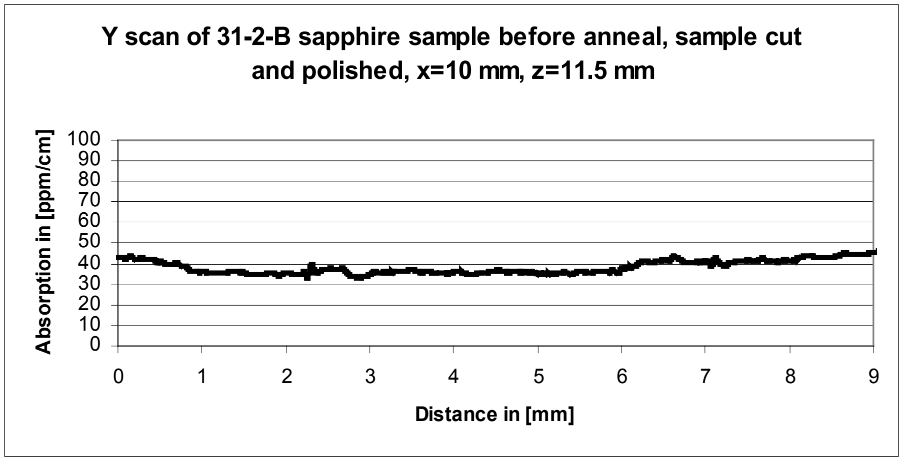
Crystal	Temperature	α (ppm/cm)					
		514 nm			1064 nm		
		bulk	dip	surface	bulk	dip	surface
Annealed at CSI							
LB-1	Control	850-1300	no	no	50-60	no	no
LB-2	Control	1200-1500	no	no	60-70	no	no
L14-1	Intermediate	1350	300	600	50	10-20	75
L14-2	Intermediate	800	300	2200	75	45	4000
L14O-1	Intermediate	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

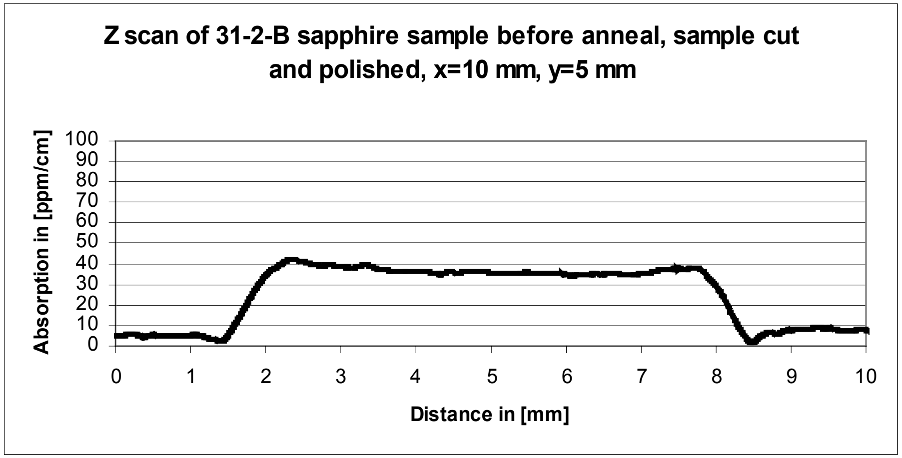
Annealing at intermediate temperatures under oxidizing conditions

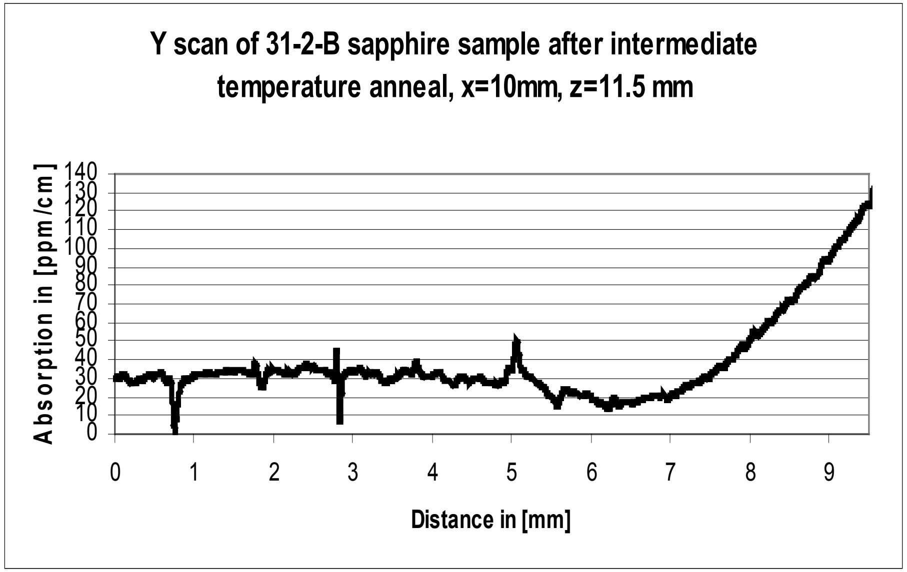
Y-Scan

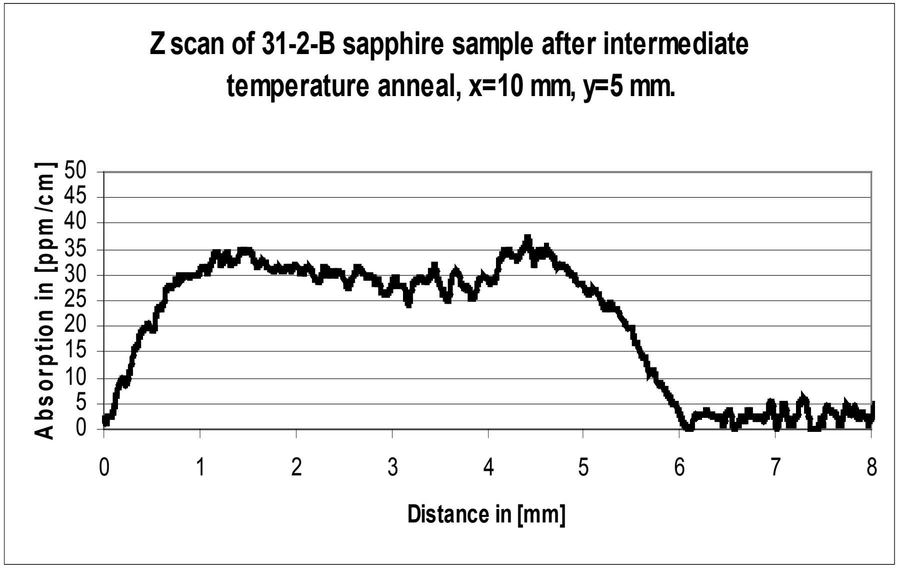
Z-Scan

Polished Flat **Fine-Ground Barrel** **Polished Face** **Polished Face**





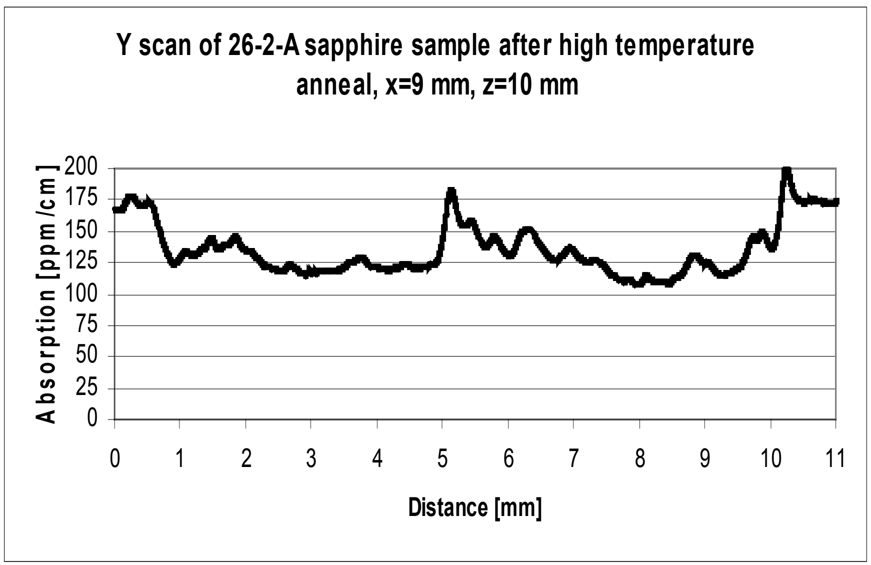




Annealing at high temperatures under oxidizing conditions

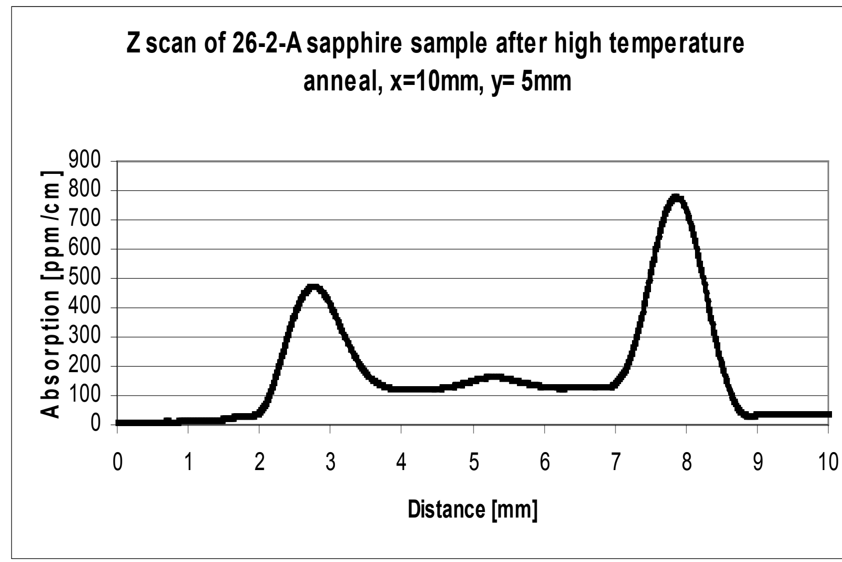
Y-Scan

Fine-Ground **Fine Ground**



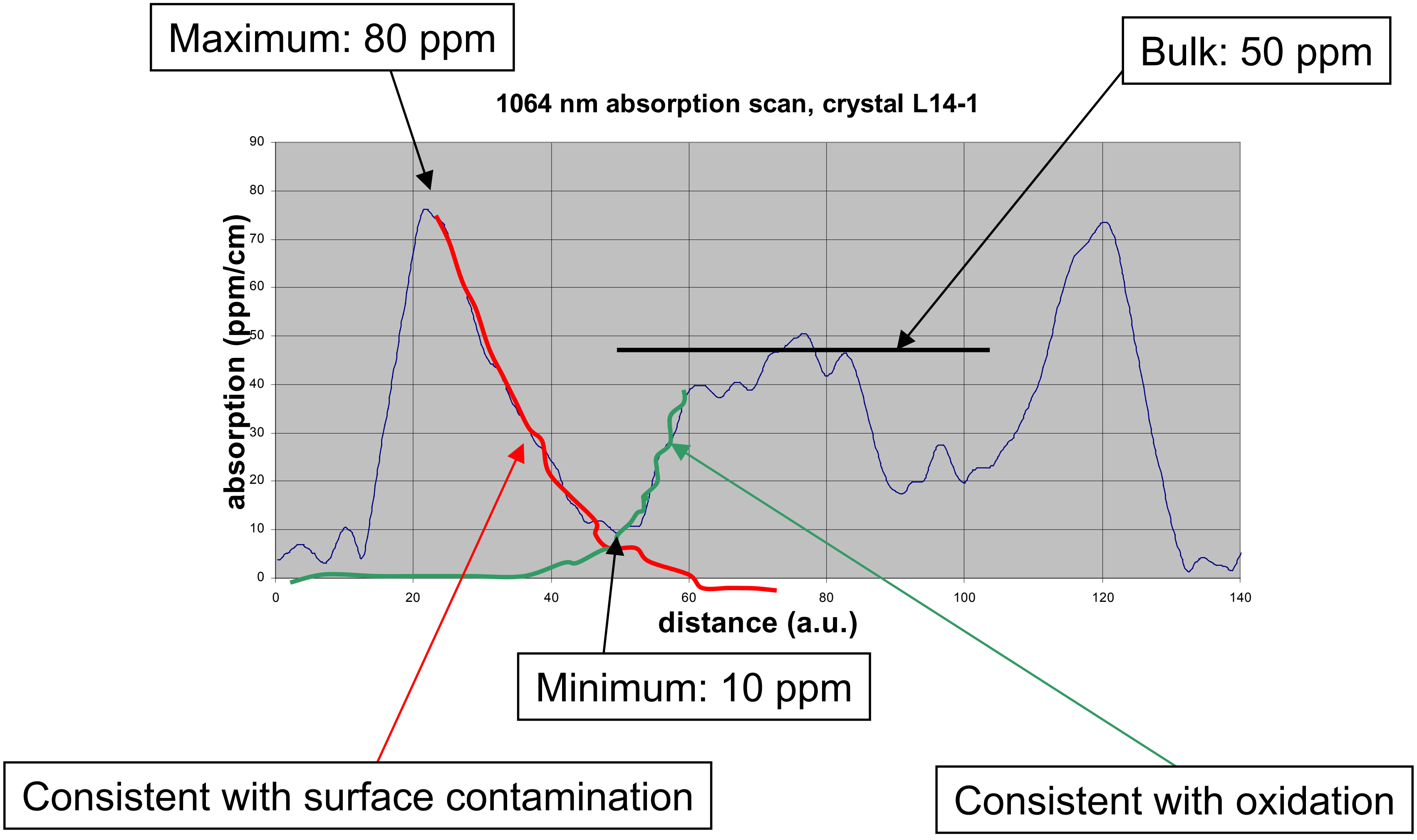
Z-Scan

Polished Face **Polished Face**



Complicated air-annealing behavior

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

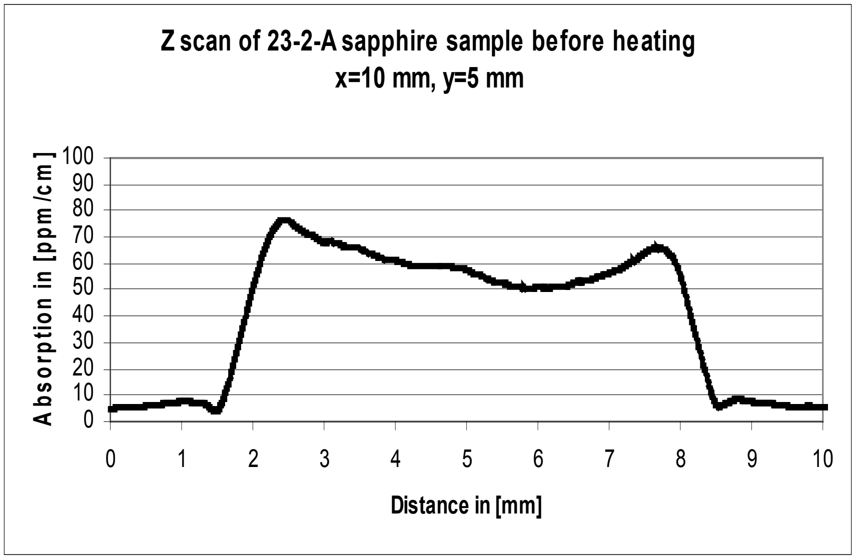


Consistent trends under oxidizing anneals

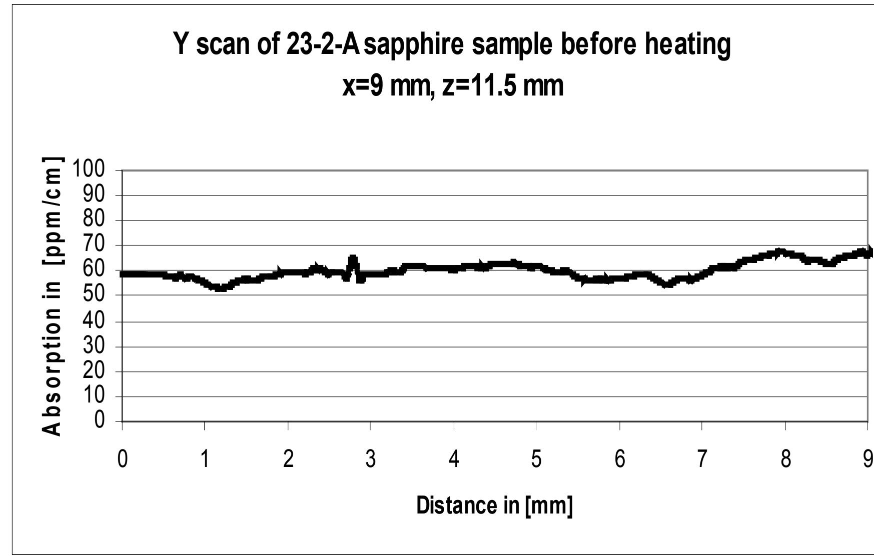
- As grown
  - Unclear correlation with starting material or furnace
    - Question of impurities, native defects and process contamination unresolved
  - No strong correlation with position in boule or use of re-melted feedstock
    - "Rosetta" sapphire indicates melt segregation operative during growth
    - 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 be the best route to low loss material

Annealing at intermediate temperatures under reducing conditions

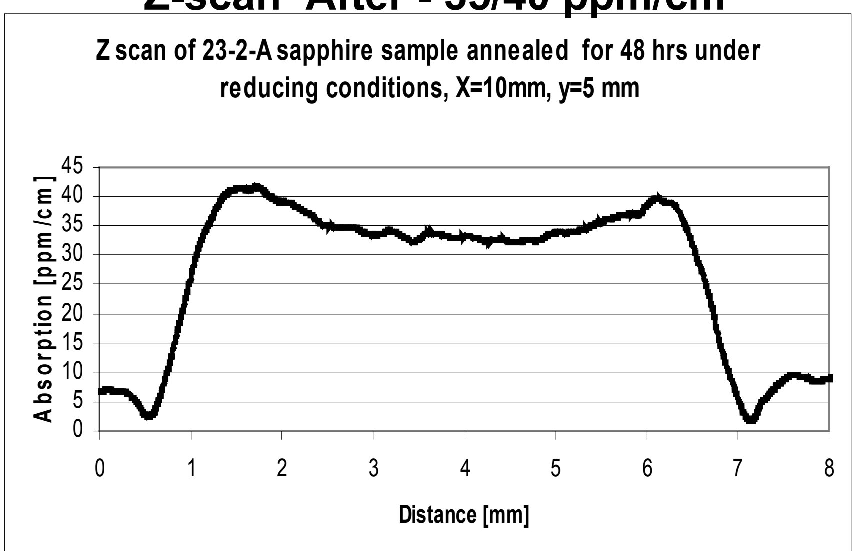
Z-scan Before - 55/65 ppm/cm



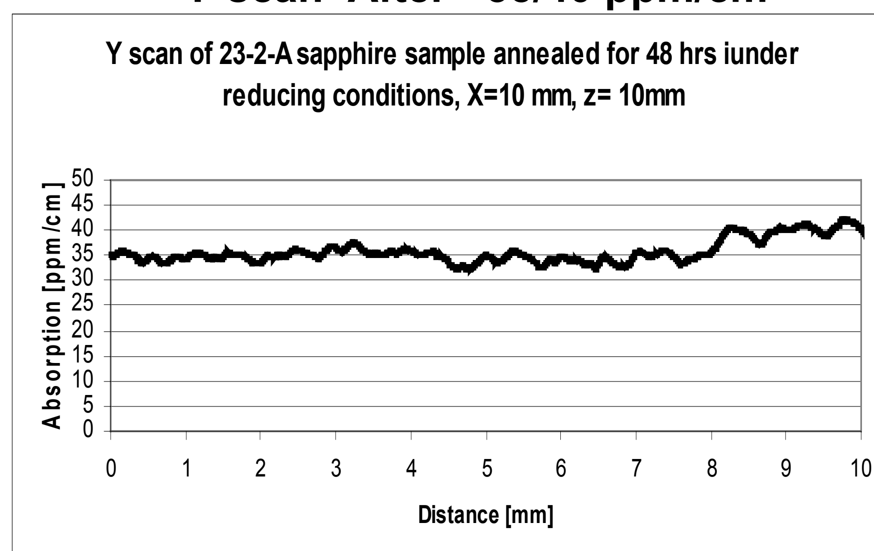
Y-scan Before - 55/65 ppm/cm



Z-scan After - 35/40 ppm/cm



Y-scan After - 35/40 ppm/cm



Recent annealing studies under inert/reducing conditions

ID	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

Observed trends under inert/reducing conditions

- 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 reducing/inert anneals**
  - **Intermediate temperature annealing under reducing conditions reduces absorption at 1064 nm without introducing scatter or influencing Ti^{3+} fluorescence**
  - **Currently under investigation:**
    - **Are temperatures above 1200 C necessary to optimum results?**
    - **Does hydrogen play an important role as a reducing agent or is an inert gas equally effective?**
    - **Is cooling rate an important variable?**

Sapphire - Status / Plans

- **Currently**:
  - 25 ppm/cm reproducible in macroscopic volumes
  - 10 ppm/cm in isolated regions
  - Annealing at intermediate temperatures under oxidizing conditions reduces bulk absorption but increases scatter
  - Annealing at high temperatures under oxidizing conditions greatly increases bulk absorption and scatter
  - Annealing at intermediate temperatures under reducing conditions reduces absorption, does not appear to cause scatter, and appears to have favorable kinetics

    (Recent results suggest absorption < 25 ppm in macroscopic volumes)

- **Straw Man**
  - Two defect species (eg. Ti^{3+}:Ti^{4+} complex plus another species)
  - One of which is reduced to negligible levels by reduction

- **Next steps**:
  - Continue study of annealing process (controlled atmosphere and processing kinetics)
  - Revisit spectroscopic analysis given reproducible annealing plus “Rosetta”
  - Chemical analysis of scattering centers as well as 8-T
  - Revisit impurity correlations after annealing is reproducible and optimized