NIST High-Accuracy Mid-IR through VUV Refractometry Facility

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Outline

- Motivation and history of NIST refractometry measurements
- Extension of range and accuracy for range VUV – Mid-IR
- Approach and facilities
- Uncertainty analysis
- Example measurements in vis-UV-VUV and
- Recent index measurements in IR
- Project plans

Refractometry

- All light-matter interactions governed by: $\tilde{\epsilon} = \epsilon_r + i\epsilon_i$
  For propagating waves: $\tilde{\mathbf{E}} = \tilde{\mathbf{E}}_0 e^{-i(\omega t - \tilde{\mathbf{k}}\cdot\mathbf{r} - \varphi_E)}$
  Maxwell's Equations $\Rightarrow \tilde{\mathbf{k}} = \tilde{\epsilon}^{1/2}\frac{\omega}{c} = \tilde{n}\frac{\omega}{c}$

$$\tilde{n} = (\epsilon_r + i\epsilon_i)^{1/2} = n + i\kappa$$

  $\Rightarrow$ For a given optical material, all information needed to design optics from calculations or measurements of n and κ.

- Optics industry and scientific community that depends on optics, needs accurate tabulation of $n(\lambda)$ and $\kappa(\lambda)$ for candidate optical materials. Accurate $n(\lambda)$'s are determined by refractometry, especially minimum-deviation-angle refractometry.

- Optical systems are getting more complex, with higher optical specifications. More accurate data are continually needed for important materials and for new materials.

- NMIs good institutions to develop and maintain these data bases.

NIST high-accuracy refractometry vis/UV

NIST (NBS) has long history of high-accuracy measurements of refractive index and other optical properties for industry and science. Examples:

1. Index of water in visible, Tilton and Taylor in 1922-1938.[1]
   - Still most comprehensive measurements.
2. Visible and UV Index of optical materials in 60s (laser applications) by IH. Malitson and MJ Dodge.[2]
   - Series of papers covering most optical materials.
3. Index for optical materials (e.g. CaF_2, BaF_2, fused silica) for DUV lithography, since late 1990s by Burnett, Gupta, Kaplan.[3]
   - Ongoing interaction with lithography industry, e.g., CaF_2, $\sigma \sim 8 \times 10^{-7}$.
4. Immersion lithography ~2004. NIST provided UV measurements of water and other immersion fluids candidates and high-index lens materials.
5. Recently (since 2014) expanded facilities and capabilities to IR materials
   - Near 22 °C, out to 15 μm.

[1]LW Tilton and JK Taylor, "Refractive index and dispersion of distilled water for visible radiation at temperatures 0 to 60° C", J. Res. Natl. Bur. Stand. 20, pp 419-477 (1938).
[2]IH Malitson, "Interspecimen comparison of the refractive index of fused silica", J. Opt. Soc. Am. 55, pp. 1205-1209(1965).
[3]JH Burnett, R. Gupta, and U. Griesmann, "Absolute refractive indices and thermal coefficients of CaF2, SrF2, and LiF near 157 nm", Applied Optics 41, pp 2508-2513 (2002).

Motivation for NIST IR Refractometry Project

- In late 2012 the CEO of SPIE sent a request to NIST Director Patrick Gallagher to inquire whether NIST could address a critical IR materials problem for IR optics manufacturers, designers and users: *Lack of sufficiently accurate index data on key IR materials*.

  Example: standard Refs. for Ge IR index (> 35 years old):
  - *Handbook of Optical Constants of Solids, Edward Palik*
  - *Handbook of Infrared Optical Materials, Paul Klocek*
  - *Materials databases in optical design software Zemax and Code V*

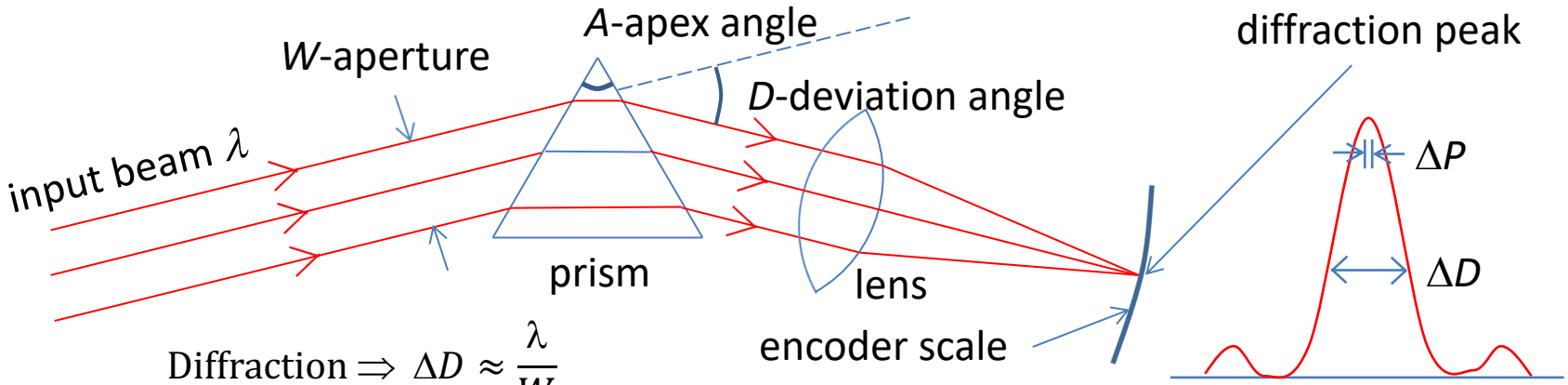
  Index values differ by ~ 1×10^{-3}. Require at least $\Delta n = 1 \times 10^{-4}$.

- The NIST director responded with commitment to address this issue.
  - Modified NIST refractometry facility for higher accuracy $\lambda \leq 15$ μm.

Motivation for NIST IR Refractometry Project

- Have taken on ambitious project to achieve *diffraction-limited* index accuracy of all technologically- and scientifically-important materials in their transmission range 0.12 μm to 15 μm.
- Though NIST have an index measurement service (Special Test 38061S), this project is directed towards generating measurements of the *highest accuracy*, focusing on reliable uncertainties, to update the archival values for the highest-quality material available.
  - To achieve diffraction-limited accuracy for many materials, *requires improvement by ≥ 10*.
  - With all the supportive measurements required, these measurements can take a number months for each material.
- Precision optical communities which benefit include:
  lithography, laser optics, high-energy-physics detectors, astronomy, remote sensing, defense imaging.

Min-Dev-Angle Refractometry - Accuracy



$$\text{Diffraction} \Rightarrow \Delta D \approx \frac{\lambda}{W}$$

- At minimum deviation, index $n(\lambda)$ given by: $n(\lambda) = \sin\left(\frac{A+D(\lambda)}{2}\right) / \sin\left(\frac{A}{2}\right)$
- Deviation angle D spread by diffraction through aperture W of prism: $\Delta D \approx \frac{\lambda}{W}$.

  $\Rightarrow$ Size of sample gives ***diffraction limit*** for Min-Dev-Angle measurements.
- Estimate of diffraction limit of n:

$$\Delta n(\lambda) = \frac{dn}{dD} = \frac{\cos\left(\frac{A+D}{2}\right)}{2\sin\left(\frac{A}{2}\right)} \equiv C(A,D) \text{ is on the order 1}$$

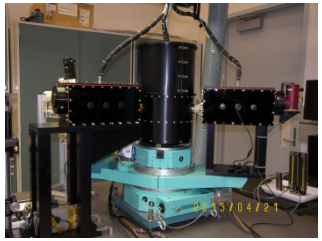
$$\Delta n = \frac{dn}{dD} \times \Delta D \times f = C(A,D) \times \frac{\lambda}{W} \times f, \quad \text{where f} \equiv \frac{\Delta P}{\Delta D} \equiv fraction\ uncertainty\ of\ peak\ (width)$$

For W=25 mm, assume C=1 f=0.05:

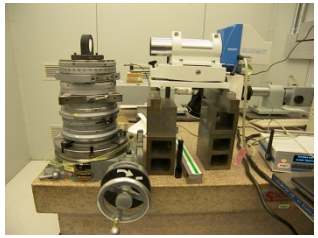
λ (μm)	0.2	.5	1	5	10	15
Δn (x10^{-6})	0.4	1.0	2.0	10	20	30

Minimum Deviation Angle Refractometry

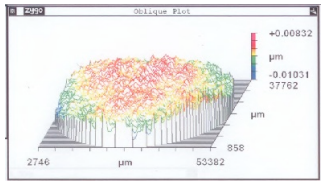
High-Accuracy Index Measurements: Determine index from minimum-deviation-angle. Actually, requires numerous measurements w/ numerous sources of error.



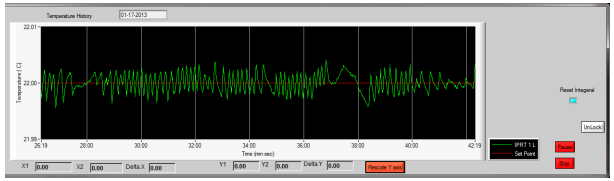
Dev Angle
Goniometer w/ calibrated encoder
Alignment issues
($\Delta\theta \leq 0.2$ arc-sec)



Prism Apex Angle
Auto collimator
+ encoder
($\Delta\theta \leq 0.2$ arc-sec)

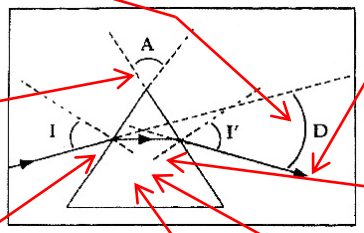


Prism Surface Flatness
Zygo Interferometer
(Wavefront RMS $\lambda/100$)



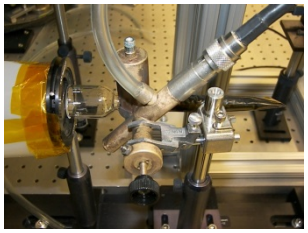
Temp Control – dn/dT
TWP and MPGa calibration
($\Delta T \leq 5$ milli K)

At Minimum Deviation Angle

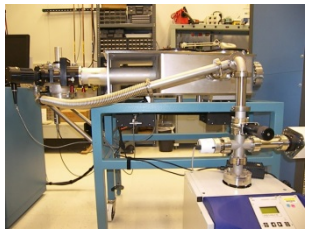


$$n(\lambda) = \frac{\sin\left(\frac{A+D(\lambda)}{2}\right)}{\sin\left(\frac{A}{2}\right)} \cdot n_{gas}(\lambda)$$

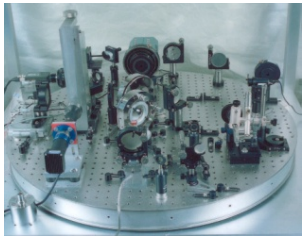
λ Calibrations
Spectral calibration lamps
($\Delta\lambda \leq 0.01$ nm)
IR - Monochromator
($\Delta\lambda \leq 0.05$ nm)



Material Absorb.
Transmission spectrometer
($A_{10} \leq 0.01$/cm)



Index Homogeneity
n variation on ingot $\Rightarrow$
n variation on sample
Vis/UV interferometer
($\Delta n \leq 1 \times 10^{-7}$)



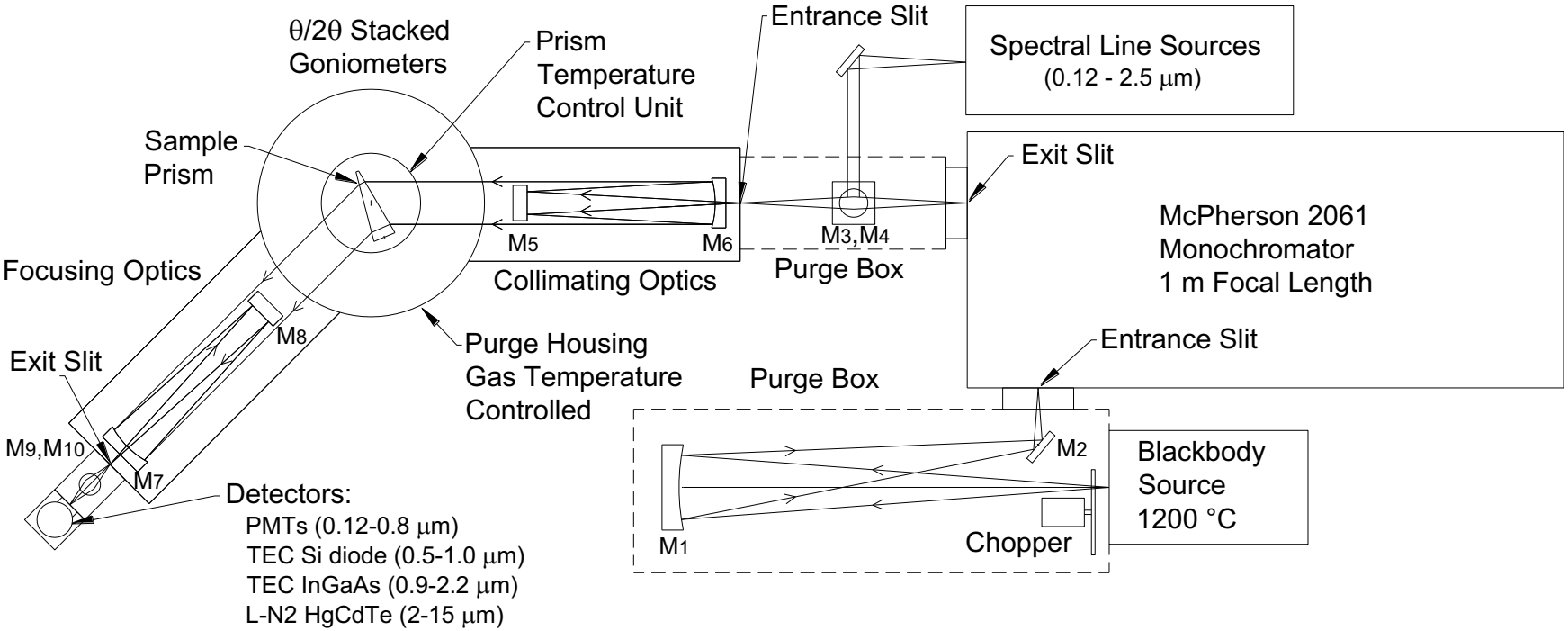
Birefringence-Stress+IBR
grown-in or external
(stress-optic coeff. - π_{ijkl})
Polarimeter
(1 nm/cm [$\Delta n \leq 1 \times 10^{-7}$])

NIST Min Dev Angle UV/vis/IR Refractometer

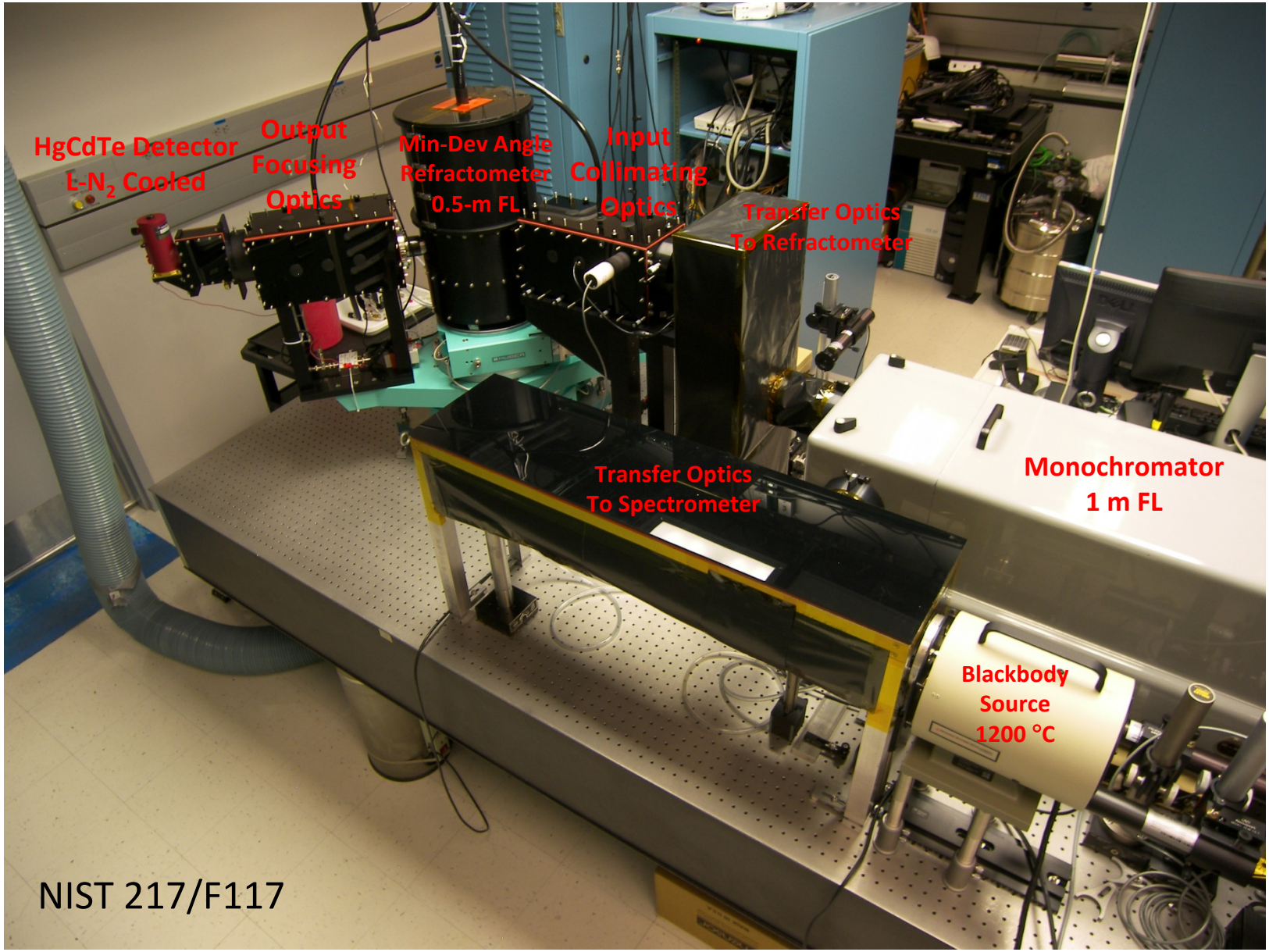
Location: Bldg. 217, Rm. F117

All reflective optics from source to detector. [λ range – λ=0.12-15 μm (T=15-25 °C)]

- VUV-vis-near IR (0.120 – 2 μm) [purged with N_2 gas]
  - Sources: atomic spectral lamps, $\sigma_\lambda \sim 0.001$ nm; Detectors: PMTs.
- Near IR-mid IR (1 – 15 μm) [purged with N_2 gas]
  - Sources: blackbody (1200 °C) (w/ 1 m FL monochromator, Res at λ =5 μm ~ 0.1 nm); IR detectors (TEC Si diode, TEC InGaAs diode, Liquid N_2 cooled MCT), lock-in detect.
- Index accuracy achieves theoretical limit for material, sample geometry, and sample specs.



NIST high-accuracy UV/vis/IR Refractometer



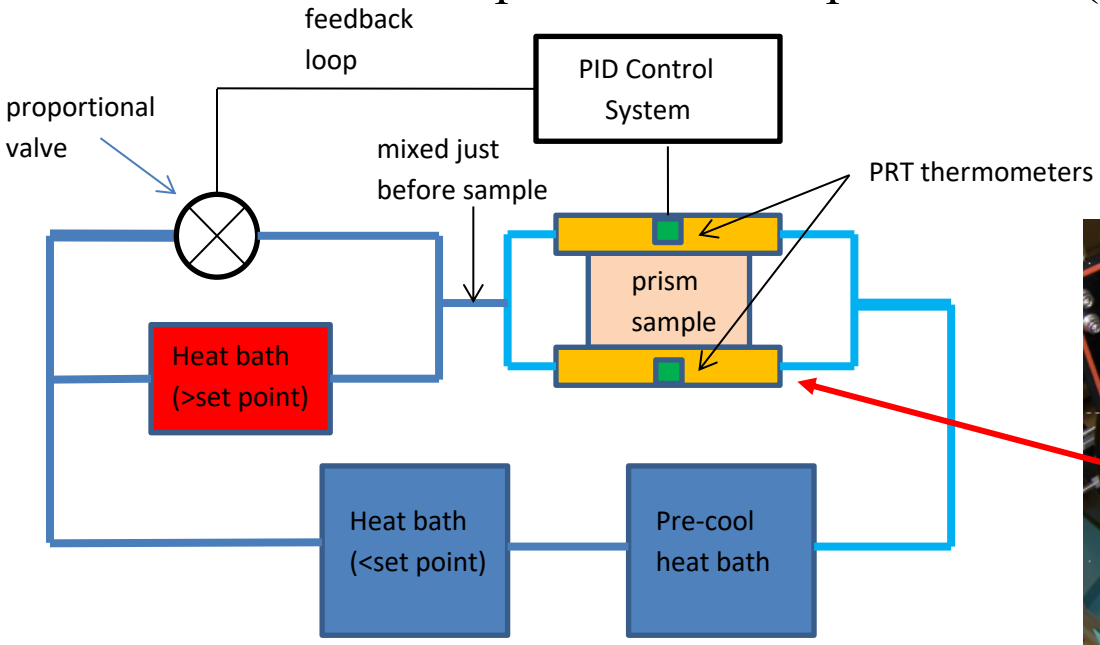
Sources of Uncertainty for UV and IR Index

Sources	Typical mag of uncertainty (1-σ)	UV-VUV uncertainty (1-σ) **(λ=185 nm - 254 nm)**	IR Index uncertainty (1-σ) **(λ=2 µm - 14 µm)**
Peak position	1/10th of diffracted peak FWHM Range .1 - 5 sec of arc	0.3×10^{-6}	$1.1 - 7.9 \times 10^{-5}$
Prism apex angle	0.13 sec of arc [including λ/30 (633 nm) RMS figure error]	0.4×10^{-6}	1.2×10^{-5}
Index inhomogeneity and **birefringence**	0.91×10^{-5} RMS for IR mat 3.39 nm 0.1×10^{-6} RMS for UV materials	$< 0.1 \times 10^{-6}$	0.91×10^{-5}
Encoder angle	0.1 sec of arc	0.5×10^{-6}	$0.33 - 0.34 \times 10^{-5}$
Prism temperature	**(0.1 K - usual)** **0.005 K**	$< 0.1 \times 10^{-6}$	**4×10^{-5}** **0.2×10^{-5}**
Wavelength	spectral lines: 0.001 nn **black-body/mono: 0.15 nm** **black-body/mono: 0.05 nm - Mod**	0.1×10^{-6}	**2 - 0.02 x 10-5** **0.5 - 0.005 x 10-5**
Alignment	0.05 sec of arc	$< 0.2 \times 10^{-6}$	0.08×10^{-5}
N_2 gas temperature	0.02 K	0.02×10^{-6}	0.08×10^{-5}
N_2 gas pressure	0.02 kPa	0.06×10^{-6}	0.02×10^{-5}
	Total uncertainty:	**0.8×10^{-6} λ=185-254 nm**	**$2 - 8 \times 10^{-5}$ λ=2-14 µm**

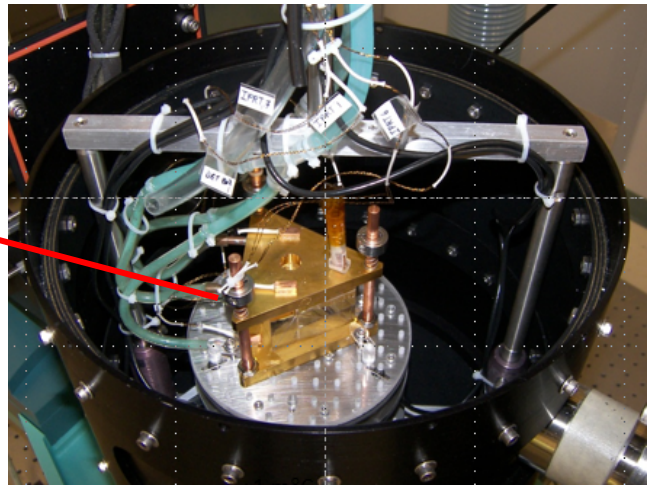
Temperature Control

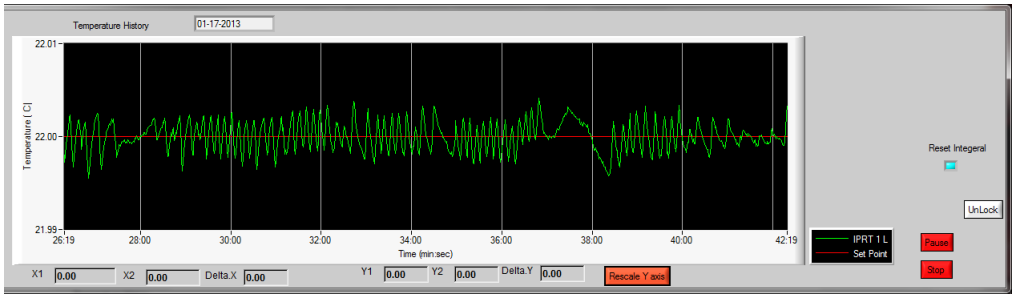
Sample- and gas-temperature control by PID feedback control loop.

- PRT thermometers calibrated at triple-point water and melting-point of Ga.
- PID control loop using mixing of hot and cold baths.
- Controls absolute temperature of sample < 5 mK (<2 mK RMS).



T-Controlled Prism Mount

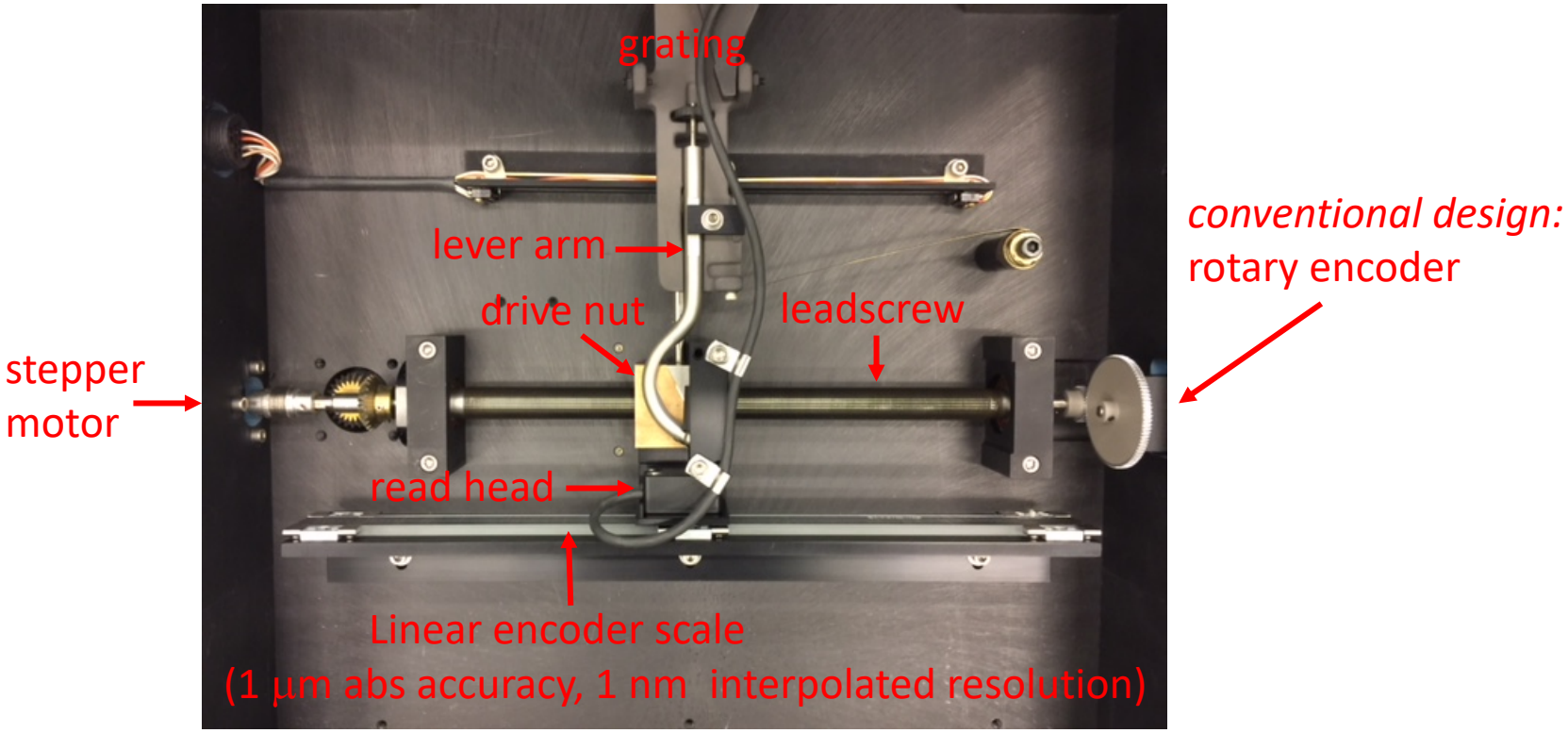




Modifications of Mono to Improve λ-Accuracy

- Replace rotary-encoder λ-calibration w/ linear-encoder on drive nut.
  - More directly connects encoder to grating – no gears.

Top View of McPherson 2061 Monochromator w/ Linear Encoder



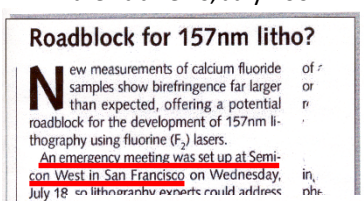
- Improves *long-term reproducibility* from 0.05 nm to: 0.001 nm (50×)
  Improves *long-term calibrated accuracy* from 0.1 to: 0.01 nm (>10×)

Spatial-Dispersion-Induced Birefringence in Crystals

- Common knowledge in optics: cubic crystals can not be anisotropic and birefringent, due to symmetry.
- Actually, just true in long-λ limit, electric-dipole (k=0) approximation. For short λ, the finite k breaks the light-matter-interaction symmetry (2nd O) in cubic crystals.

  $\Rightarrow$ cubic crystals, e.g., CaF_2, BaF_2, Si, Ge, etc., have anisotropic, birefringent n.
- This "curiosity" was a known, but unrecognized as having consequences for optics.
- NIST alerted the lithography industry in 2001*, w/ substantial impact on Litho.

WaferfabNews, July 2001

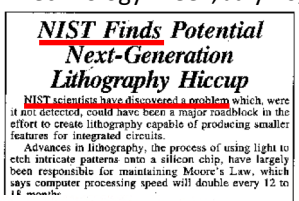


Roadblock for 157nm litho?

New measurements of calcium fluoride samples show birefringence far larger than expected, offering a potential roadblock for the development of 157nm lithography using fluorine (F_2) lasers.

An emergency meeting was set up at Semicon West in San Francisco on Wednesday, July 18 so lithography experts could address

New Technology Week, July 16, 2001

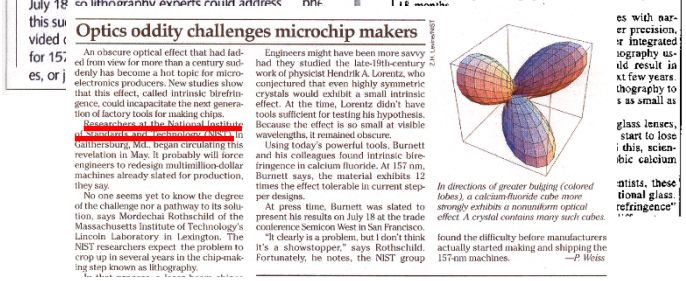


NIST Finds Potential Next-Generation Lithography Hiccup

NIST scientists have discovered a problem which, were it not detected, could have been a major roadblock in the effort to create lithography capable of producing smaller features for integrated circuits.

Advances in lithography, the process of using light to etch intricate patterns into a silicon chip, have largely been responsible for maintaining Moore's Law, which says computer processing speed will double every 12 to

Science News, July 21, 2001



Optics oddity challenges microchip makers

An obscure optical effect that had faded from view for more than a century suddenly has become a hot topic for microelectronics producers. New studies show that this effect, called intrinsic birefringence, could incapacitate the next generation of factory tools for making chips.

Researchers at the National Institute of Standards and Technology (NIST), in Gaithersburg, Md., began circulating this revelation in May. It probably will force engineers to redesign multimillion-dollar machines already slated for production, they say.

No one seems yet to know the degree of the challenge nor a pathway to its solution, says Mordechai Rothschild of the Massachusetts Institute of Technology's Lincoln Laboratory in Lexington. The NIST researchers expect the problem to crop up in several years in the chip-making step known as lithography.

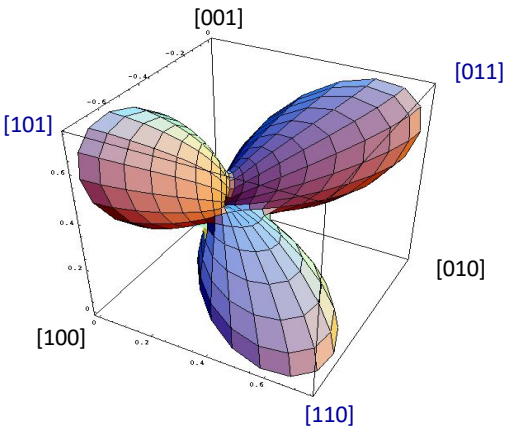
Engineers might have been more savvy had they studied the late-19th-century work of physicist Hendrik A. Lorentz, who conjectured that even highly symmetric crystals would exhibit a small intrinsic effect. At the time, Lorentz didn't have tools sufficient for testing his hypothesis. Because the effect is so small at visible wavelengths, it remained obscure.

Using today's powerful tools, Burnett and his colleagues found intrinsic birefringence in calcium fluoride. At 157 nm, Burnett says, the material exhibits 12 times the effect tolerable in current stepper designs.

At press time, Burnett was slated to present his results on July 18 at the trade conference Semicon West in San Francisco.

"It clearly is a problem, but I don't think it's a showstopper," says Rothschild. Fortunately, he notes, the NIST group found the difficulty before manufacturers actually started making and shipping the 157-nm machines. —P. Weiss

In directions of greater bulging (colored lobes), a calcium-fluoride cube more strongly exhibits a nonuniform optical effect. A crystal contains many such cubes.



$$\Delta n(\mathbf{q}[l_1,l_2,l_3]) = -n(0)^3(\beta_{11}-\beta_{12}-2\beta_{44})q^2\left[\left(l_1^2l_2^2+l_2^2l_3^2+l_3^2l_1^2\right)^2-3l_1^2l_2^2l_3^2\right]^{1/2}$$

- Consequence for index data: 1) characterize IBR parameter vs λ for every cubic-crystal material, 2) must measure n at a certain crystallographic direction/polarization.

*J.H. Burnett, Z.H. Levine, E.L. Shirley, Phys. Rev. B **64**, 241102 (2001)

Characterization of Absolute vis-UV Index Accuracy

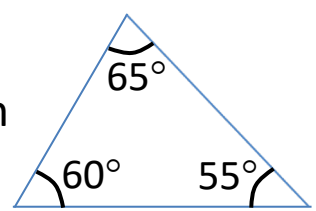
- Considering all sources of uncertainty estimate absolute index accuracy.

  Sources include: ΔD (peak center), ΔD (peak center-absorbance apodization), $\Delta\theta$ (encoder), ΔA (apex angle), ΔA (surface figure), $\Delta\lambda$ (source), ΔT (prism), ΔT (N_2 gas), ΔP (N_2 gas), Δn (alignment errors) – summed in quadrature.

- Nevertheless experience says: most serious errors are unknown systematic errors. Minimum deviation method is most robust against these because:
  1) Simple analysis (no modeling - only depends on Snell's law)
  2) Min dev is extremum condition – insensitive alignment errors a lowest order.

- Test: SiO_2 Prism with 3 different apex angles. Meas. $n(\lambda)$ using each apex angle.

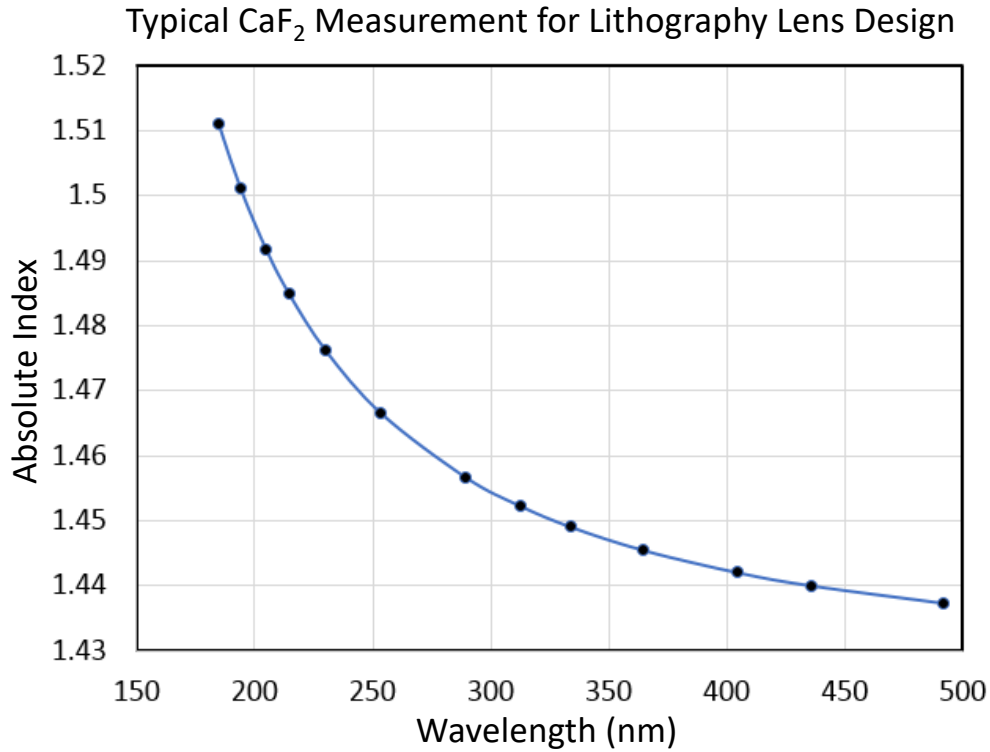
fused silica prism



- Result: for λ = 185 nm – 256 nm, n for each apex angle equal to within 1.0×10^{-6}.

UV - VUV Index Measurements

- Highest accuracy index needed for DUV lithography, e.g., CaF_2 and fused silica.



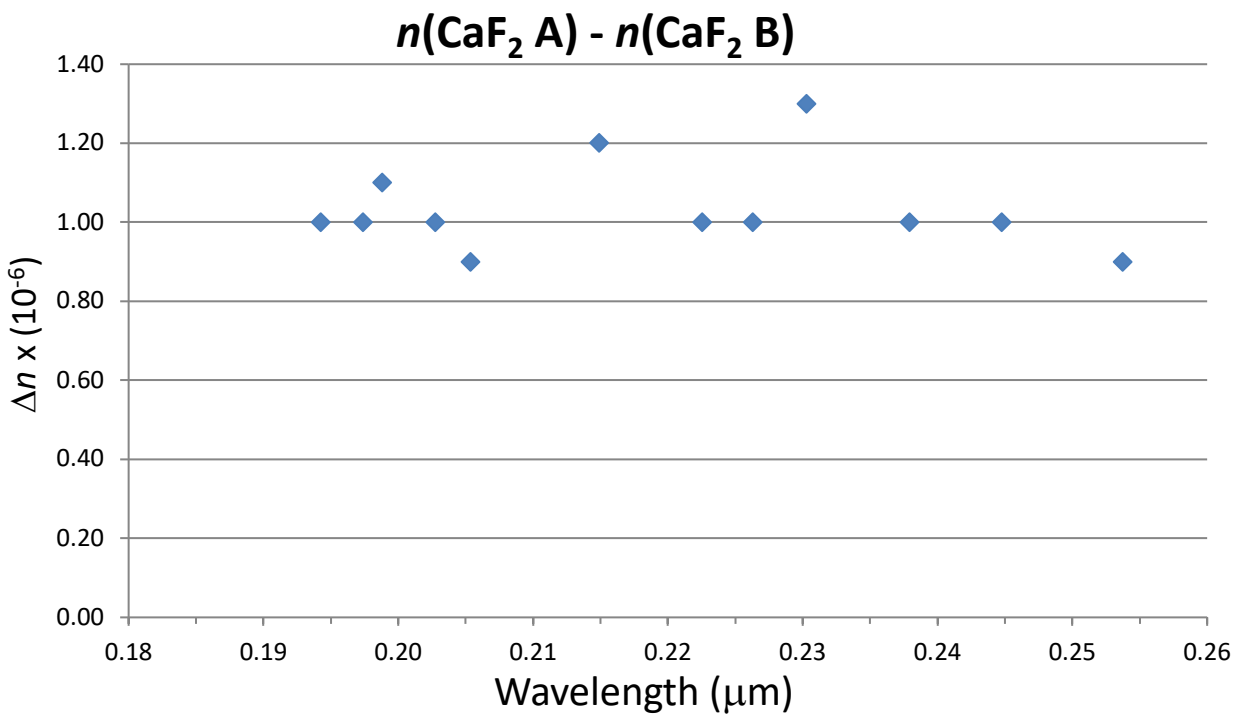
- Fit data to 3-term or 4-term Sellmeier fitting function.

$$n^2 - 1 = \frac{K_1\lambda^2}{\lambda^2 - {L_1}^2} + \frac{K_2\lambda^2}{\lambda^2 - {L_2}^2} + \frac{K_3\lambda^2}{\lambda^2 - {L_3}^2} + \frac{K_4\lambda^2}{\lambda^2 - 4^2}$$

- 1-σ uncertainties: $1.1 - 0.8 \times 10^{-6}$, for $\lambda = 490 - 185$ nm (fit residuals: $<5 \times 10^{-7}$)
  Results within diffraction limit for sample size.

Measuring Index Difference Between Samples

- Measured indices of 2 different CaF_2 samples. $\Delta n(\lambda) = 0.8 \times 10^{-6}$.



- Found: all n (for λ = 195 - 256 μm) within 1.3×10^{-6} of each other. n(sample A) systematically higher. Could be systematic difference, but difference marginally within combined uncertainties.
- Demonstrates potential for distinguishing small index differences between samples.

IR Materials

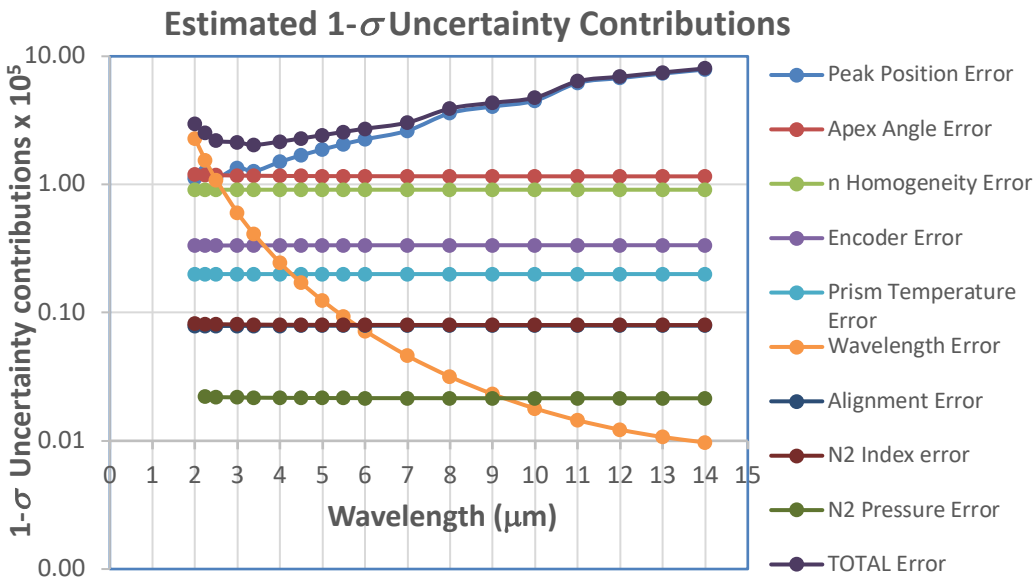
- Working with SPIE IRMWG, developed priority list based on industry survey.

Priority	Material		Measurment Status
1	Germanium	15 prisms+flats (Photonic Sense)	6 underway, 1 completed
2	ZnSe	6 prisms+flats (II-VI)	Have characterized samples
3	ZnS		
4	Silicon		
5	CaF2	6 prisms – single crystal	
6	BaF2	6 prisms - single crystal (Hellma), 2 prisms, 6 flats - polycrystalline (ISP)	
7	GASIR 1		
8	IRG26		
9	BD2		

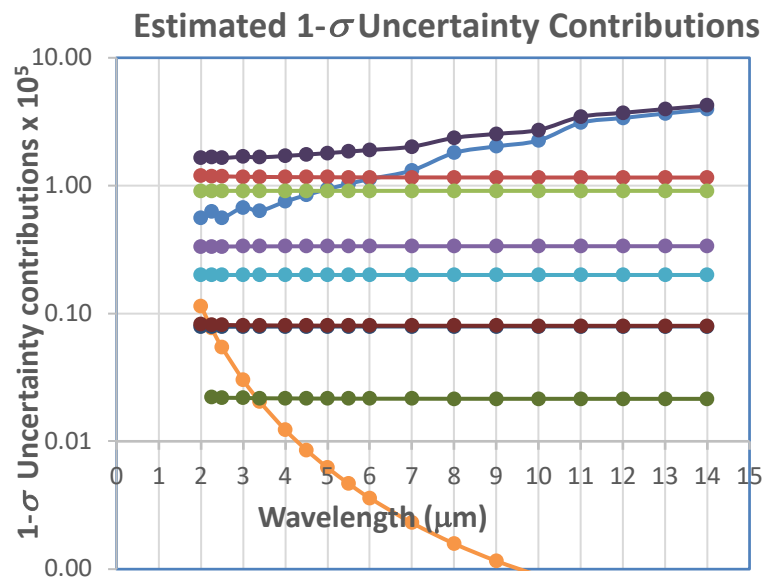
- Ge, ZnSe, BaF_2, CaF_2 samples received.
- Completed/published measurements on Ge.
- Project Goals:
  - establish generic $n(\lambda)$ values for all important IR materials
  - establish supplier variations and sample variations within boule
  - provide accurate standard values of artifact materials for calibration at metrology labs

Sources of Uncertainty

Original System



Upgraded System



- With linear encoder λ-calibration modification of monochromator system, the λ-uncertainty makes a negligible contribution to the total index uncertainty σ_{tot}.
  - λ-uncertainty now has *small* impact for other materials at shorter λ.

Ge Results

Table 1. Measured relative and absolute indices of refraction, and total standard uncertainties.

λ^{vac}(μm)[a]	λ^{air}(μm)[b]	Index^{vac}	Index^{air}	σ(x10^{-5})
2.2500	2.2494	4.084061	4.082973	2.5
2.5000	2.4993	4.066938	4.065855	2.2
3.0000	2.9992	4.045788	4.044711	2.1
3.3922	3.3913	4.035707	4.034633	2.0
4.0000	3.9989	4.025809	4.024738	2.2
4.5000	4.4988	4.020564	4.019494	2.3
5.0000	4.9987	4.016859	4.015790	2.4
5.5000	5.4985	4.014126	4.013058	2.6
6.0000	5.9984	4.012056	4.010988	2.7
7.0000	6.9981	4.009179	4.008112	3.0
8.0000	7.9979	4.007305	4.006238	3.9
9.0000	8.9976	4.006008	4.004942	4.3
10.0000	9.9973	4.005056	4.003990	4.8
11.0000	10.9971	4.004362	4.003296	6.4
12.0000	11.9968	4.003801	4.002736	6.9
13.0000	12.9965	4.003375	4.002310	7.5
14.0000	13.9963	4.002958	4.001893	8.0

- Index uncertainty target: roughly 50×10^{-5}. Exceeded by factor ~10.
- Uncertainties approximately the diffraction limit for sample size .

λ (μm)	0.2	.5	1	2	5	10	15
Δn (x10^{-5})	0.08	0.2	.4	1	2	4	6

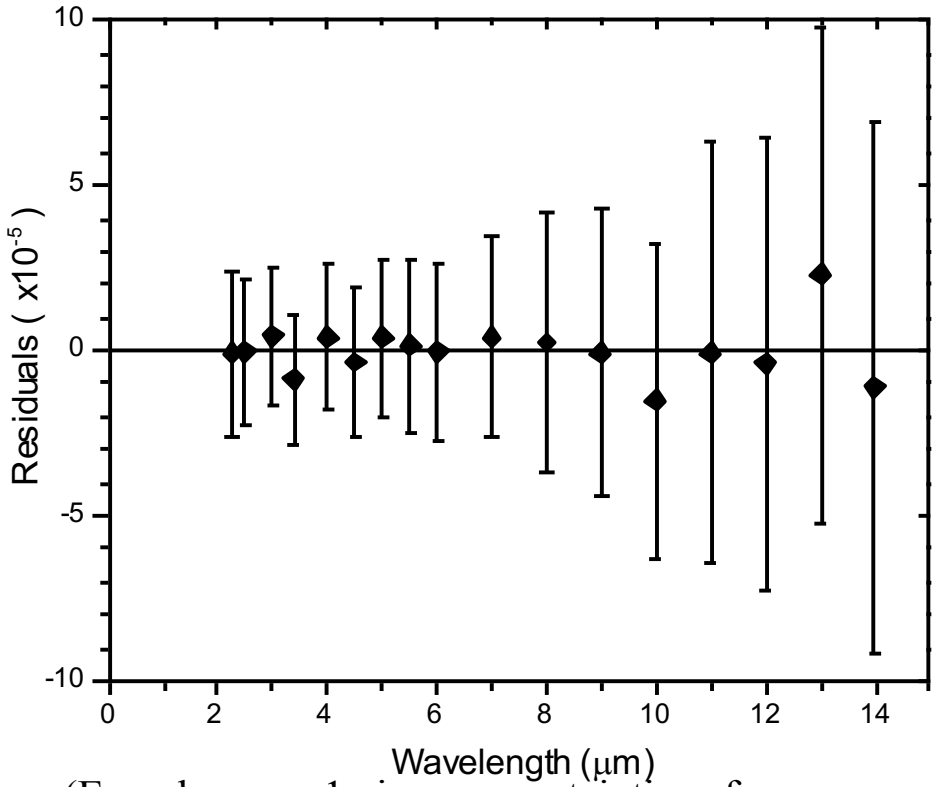
Sellmeier Fit and Residuals

Fit data to 3-term Sellmeier fitting function.
(valid in the range: 2.25 μm < λ < 14 μm)
2 poles at shorter l (band-edge Abs.)
1 pole at longer l (phonon Abs.)

$$n^2 - 1 = \frac{K_1\lambda^2}{\lambda^2 - {L_1}^2} + \frac{K_2\lambda^2}{\lambda^2 - {L_2}^2} + \frac{K_3\lambda^2}{\lambda^2 - {L_3}^2}$$

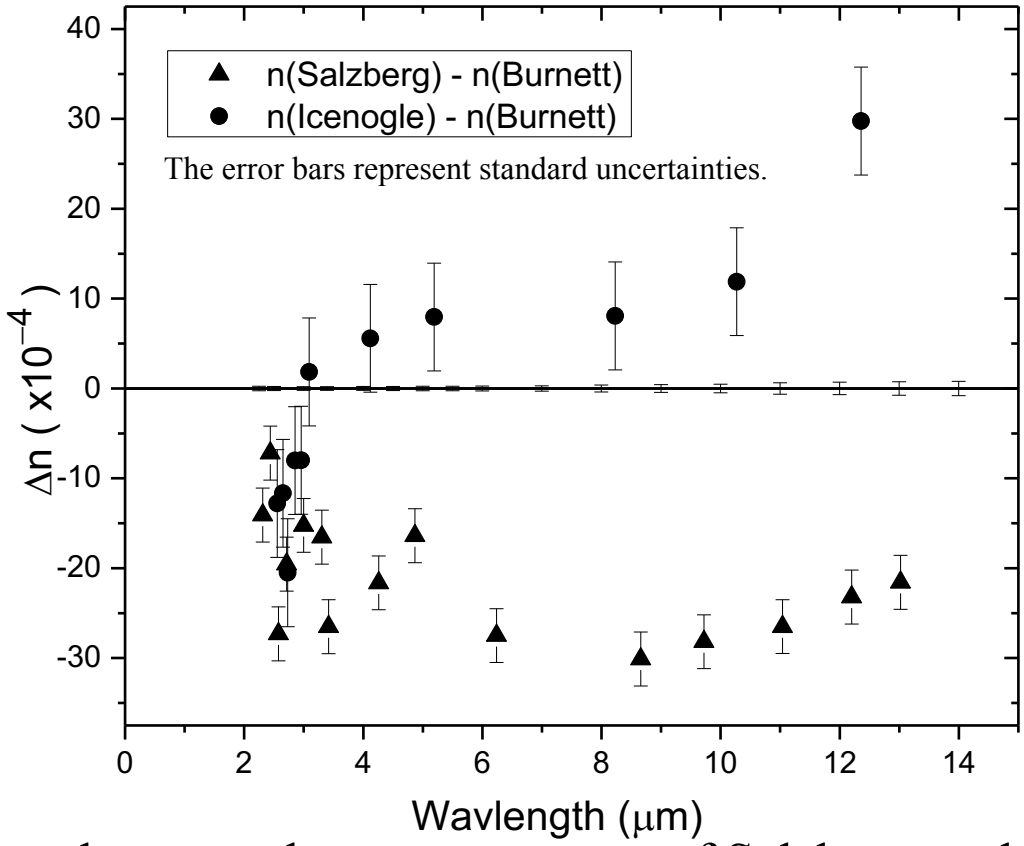
Sellmeier constants	
K_1	0.4886331
K_2	14.5142535
K_3	0.0091224
L_1	1.1806604 μm
L_2	0.40328985 μm
L_3	27.426082 μm

Plot of residuals of fit to data of Sellmeier formula



(Error bars are 1-sigma uncertainties of measurements.)

Comparison With Extensively Used Measurements

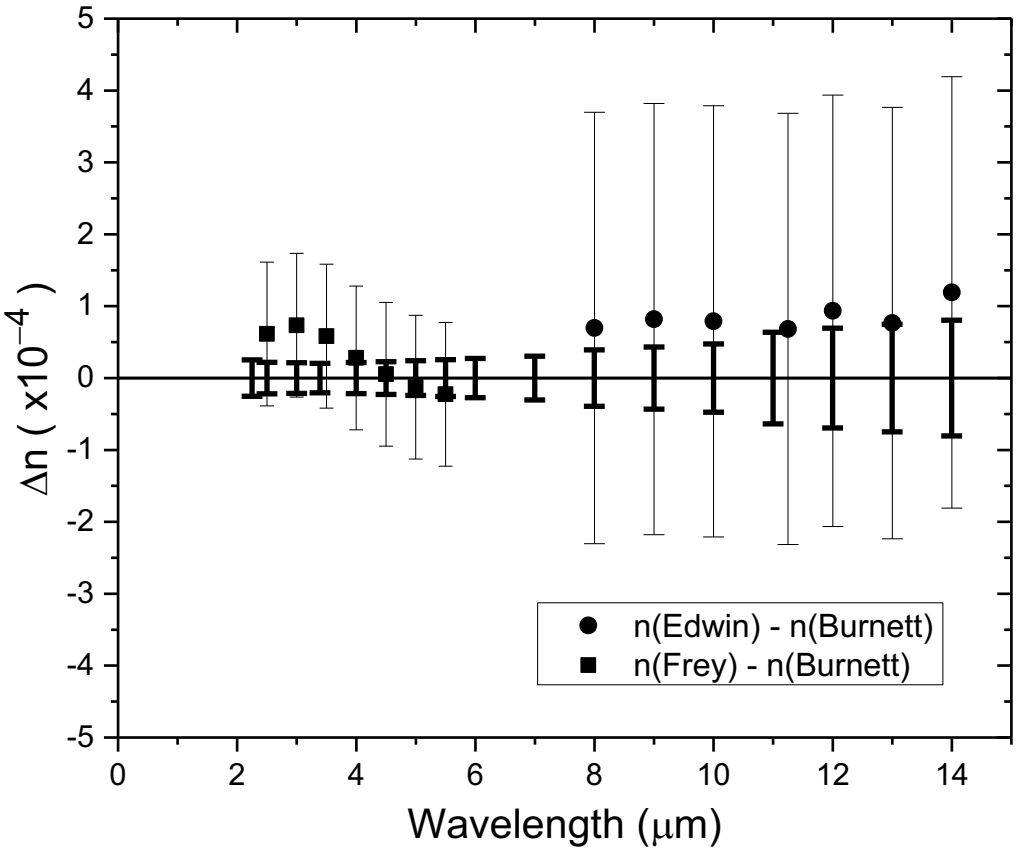


- Plot of differences between the measurements of Salzberg et al.[1] and of Icenogle et al.,[2] and values of the Sellmeier formula of this work.
  - Results used in IR Refs.: *Handbook of Optical Constants of Solids* (Palik) and *Handbook of Infrared Optical Materials* (Klocek) and in commonly used commercial optics design software.
- Values differ well outside 1-σs. Could be due to differences in material quality.

[1]Salzberg, C. D. and Villa, J. J., "Index of Refraction of Germanium," J. Opt. Soc. Am. 48, 579 (1958).

[2]Icenogle, H. W., Platt, B. C., and Wolfe, W. L., "Refractive indexes and temperature coefficients of germanium and silicon," Appl. Opt. 15(10), 2348-2351 (1976)

Comparison With More Recent Measurements



- Plot of. differences between the measurements of Edwin et al.[3] and Frey et al.,[4] and values of the Sellmeier formula of this work. The error bars represent standard uncertainties.

[3]Edwin, R. P., Dudermel, M. T., and Lamare, M., "Refractive index measurements of a germanium sample," Appl. Opt. 17(7), 1066-1068 (1978).
[4]Frey, B. J., Leviton, D. B., Madison, T. J., "Temperature-dependent refractive index of silicon and germanium," Proc. SPIE 6273, 62732J (2006).

Project Plans

- Published preliminary results for 1 sample Ge.
- Completing measurements of n an dn/dT on 5 other Ge samples. Finding index variations between sample near short λ end.
  - Disseminate (publish) generic Ge index dispersion (Sellmeier formulas) with range of variations. Use in Code V opt software.
- Repeat measurement approach with other priority IR materials, e.g., ZnSe, ZnS, Si, CaF_2, BaF_2, etc.
  - Make n measurements to short-λ end of transmission
- Build up index data base (on website) for optical materials (VUV-IR) in order of priority determined by industry consensus and scientific interest and need. Will be incorporated into commercial optical design software.
- Upgrade facilities make high-accuracy measurements at temperatures from cryogenic to high temperatures of interest