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: \( \tilde{\mathbf{E}} = \tilde{\mathbf{E}}_0 e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r} - \varphi_E)} \)

Maxwell’s Equations \( \Rightarrow \mathbf{\tilde{k}} = \tilde{\epsilon}^{1/2} \frac{\omega}{c} = \tilde{n} \frac{\omega}{c} \)

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

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

• 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. CaF₂, BaF₂, fused silica) for DUV lithography, since late 1990s by Burnett, Gupta, Kaplan.³
   - Ongoing interaction with lithography industry, e.g., CaF₂, \( \sigma \approx 8 \times 10^{-7} \).

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.


CORM 2018 – Gaithersburg, MD – 31 July 2018
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 $\sim 1 \times 10^{-3}$. 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 $\lambda \leq 15 \, \mu m$. 
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

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

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

For \( W=25 \text{ mm} \), assume \( C=1 \), \( f=0.05 \):

<table>
<thead>
<tr>
<th>( \lambda ) (( \mu \text{m} ))</th>
<th>0.2</th>
<th>.5</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta n \times 10^{-6} )</td>
<td>0.4</td>
<td>1.0</td>
<td>2.0</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>
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 $\lambda/100$)

$\lambda$ 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. - $\pi_{ijkl}$)
Polarimeter ($1$ nm/cm [$\Delta n \leq 1 \times 10^{-7}$])

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NIST Min Dev Angle UV/vis/IR Refractometer

Location: Bldg. 217, Rm. F117

All reflective optics from source to detector. [\(\lambda\) range – \(\lambda=0.12-15 \mu m\) (T=15-25 °C)]

- VUV-vis-near IR (0.120 – 2 \(\mu m\)) [purged with N\(_2\) gas]
  - Sources: atomic spectral lamps, \(\sigma_{\lambda} \approx 0.001 \text{ nm}\); Detectors: PMTs.
- Near IR-mid IR (1 – 15 \(\mu m\)) [purged with N\(_2\) gas]
  - Sources: blackbody (1200 °C) (w/ 1 m FL monochromator, Res at \(\lambda =5 \mu m \approx 0.1 \text{ nm}\);
    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

HgCdTe Detector L-N₂ Cooled
Output Focusing Optics
Min-Dev Angle Refractometer 0.5-m FL
Input Collimating Optics
Transfer Optics To Spectrometer
Transfer Optics To Refractometer
Monochromator 1 m FL
Blackbody Source 1200 °C

NIST 217/F117
## Sources of Uncertainty for UV and IR Index

<table>
<thead>
<tr>
<th>Sources</th>
<th>Typical mag of uncertainty (1-σ)</th>
<th>UV-VUV uncertainty (1-σ) (λ=185 nm - 254 nm)</th>
<th>IR Index uncertainty (1-σ) (λ=2 μm - 14 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position</td>
<td>1/10th of diffracted peak FWHM Range .1 - 5 sec of arc</td>
<td>0.3 x 10⁻⁶</td>
<td>1.1 - 7.9 x 10⁻⁵</td>
</tr>
<tr>
<td>Prism apex angle</td>
<td>0.13 sec of arc [including λ/30 (633 nm) RMS figure error]</td>
<td>0.4 x 10⁻⁶</td>
<td>1.2 x 10⁻⁵</td>
</tr>
<tr>
<td>Index inhomogeneity and birefringence</td>
<td>0.91 x 10⁻⁵ RMS for IR mat 3.39 nm</td>
<td>&lt; 0.1 x 10⁻⁵</td>
<td>0.91 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>0.1 x 10⁻⁶ RMS for UV materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Encoder angle</td>
<td>0.1 sec of arc</td>
<td>0.5 x 10⁻⁶</td>
<td>0.33 - 0.34 x 10⁻⁵</td>
</tr>
<tr>
<td><strong>Prism temperature</strong></td>
<td>(0.1 K - usual)</td>
<td>&lt; 0.1 x 10⁻⁵</td>
<td>4 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>0.005 K</td>
<td></td>
<td>0.2 x 10⁻⁵</td>
</tr>
<tr>
<td>Wavelength</td>
<td>spectral lines: 0.001 nm</td>
<td>0.1 x 10⁻⁵</td>
<td>2 - 0.02 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>black-body/mono: 0.15 nm</td>
<td></td>
<td>0.5 - 0.005 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>black-body/mono: 0.05 nm - Mod</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alignment</td>
<td>0.05 sec of arc</td>
<td>&lt; 0.2 x 10⁻⁵</td>
<td>0.08 x 10⁻⁵</td>
</tr>
<tr>
<td>N₂ gas temperature</td>
<td>0.02 K</td>
<td>0.02 x 10⁻⁵</td>
<td>0.08 x 10⁻⁵</td>
</tr>
<tr>
<td>N₂ gas pressure</td>
<td>0.02 kPa</td>
<td>0.06 x 10⁻⁵</td>
<td>0.02 x 10⁻⁵</td>
</tr>
<tr>
<td><strong>Total uncertainty:</strong></td>
<td>0.8 x 10⁻⁶ λ=185-254 nm</td>
<td>2 - 8 x 10⁻⁵ λ=2-14 μm</td>
<td></td>
</tr>
</tbody>
</table>
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).

![PID Control System Diagram](image)

- Proportional valve
- Feedback loop
- Mixed just before sample
- PID Control System
- PRT thermometers

![T-Controlled Prism Mount](image)
Modifications of Mono to Improve $\lambda$-Accuracy

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

- 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-\(\lambda\) limit, electric-dipole (\(k=0\)) approximation. For short \(\lambda\), the finite \(k\) breaks the light-matter-interaction symmetry (2nd O) in cubic crystals.
  \(\Rightarrow\) cubic crystals, e.g., \(\text{CaF}_2\), \(\text{BaF}_2\), 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.

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

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

Characterization of Absolute vis-UV Index Accuracy

• Considering all sources of uncertainty estimate absolute index accuracy. Sources include: \( \Delta D \) (peak center), \( \Delta D \) (peak center-absorbance apodization), \( \Delta \theta \) (encoder), \( \Delta A \) (apex angle), \( \Delta A \) (surface figure), \( \Delta \lambda \) (source), \( \Delta T \) (prism), \( \Delta T \) (\( N_2 \) gas), \( \Delta P \) (\( N_2 \) gas), \( \Delta n \) (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.

\[
\begin{align*}
\text{fused silica prism} \\
65^\circ & 60^\circ \\
55^\circ & \\
\end{align*}
\]

• Result: for \( \lambda = 185 \text{ nm} - 256 \text{ nm} \), \( n \) for each apex angle equal to within \( 1.0 \times 10^{-6} \).
UV - VUV Index Measurements

• Highest accuracy index needed for DUV lithography, e.g., CaF$_2$ and fused silica.

Typical CaF$_2$ Measurement for Lithography Lens Design

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

$$n^2 - 1 = \frac{K_1 \lambda^2}{\lambda^2 - L_1^2} + \frac{K_2 \lambda^2}{\lambda^2 - L_2^2} + \frac{K_3 \lambda^2}{\lambda^2 - L_3^2} + \frac{K_4 \lambda^2}{\lambda^2 - L_4^2}$$

• 1-$\sigma$ 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 $\lambda = 195 - 256$ $\mu$m) within $1.3 \times 10^{-6}$ 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.

<table>
<thead>
<tr>
<th>Priority</th>
<th>Material</th>
<th>Measurement Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Germanium</td>
<td>15 prisms+flats (Photonic Sense)</td>
</tr>
<tr>
<td>2</td>
<td>ZnSe</td>
<td>6 prisms+flats (II-VI)</td>
</tr>
<tr>
<td>3</td>
<td>ZnS</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Silicon</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CaF2</td>
<td>6 prisms – single crystal</td>
</tr>
<tr>
<td>6</td>
<td>BaF2</td>
<td>6 prisms - single crystal (Hellma), 2 prisms, 6 flats - polycrystalline (ISP)</td>
</tr>
<tr>
<td>7</td>
<td>GASIR 1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>IRG26</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>BD2</td>
<td></td>
</tr>
</tbody>
</table>

- 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

- With linear encoder \( \lambda \)-calibration modification of monochromator system, the \( \lambda \)-uncertainty makes a negligible contribution to the total index uncertainty \( \sigma_{\text{tot}} \).
- \( \lambda \)-uncertainty now has small impact for other materials at shorter \( \lambda \).
## Ge Results

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

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

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

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>0.2</th>
<th>.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta n$ (x10⁻⁵)</td>
<td>0.08</td>
<td>0.2</td>
<td>.4</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>
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.)

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

<table>
<thead>
<tr>
<th>Sellmeier constants</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁</td>
<td>0.4886331</td>
</tr>
<tr>
<td>K₂</td>
<td>14.5142535</td>
</tr>
<tr>
<td>K₃</td>
<td>0.0091224</td>
</tr>
<tr>
<td>L₁</td>
<td>1.1806604 µm</td>
</tr>
<tr>
<td>L₂</td>
<td>0.40328985 µm</td>
</tr>
<tr>
<td>L₃</td>
<td>27.426082 µm</td>
</tr>
</tbody>
</table>

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-\(\sigma\) s. Could be due to differences in material quality.

Comparison With More Recent Measurements

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


Project Plans

- Published preliminary results for 1 sample Ge.
- Completing measurements of $n$ and $dn/dT$ on 5 other Ge samples. Finding index variations between sample near short $\lambda$ 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-$\lambda$ 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