National Institute of Standards and Technology
U.S. Department of Commerce

NIST High-Accuracy Index Measurements of IR Materials

John Burnett, Eric Benck, and Simon Kaplan

NIST, Physical Measurement Laboratory, Gaithersburg, MD

CORM 2019 – Ottawa, ON, Canada – 29 October 2019

Outline

- **Motivation for NIST program of IR materials refractometry measurements.**
- **Discussion of apparatus and challenges.**
- **Completed Ge measurements.**
- **ZnSe measurements - preliminary results.**
- **Analysis of data.**
- **Summary and Future Plans for program.**

Refractometry

- **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 *n* and κ.**

- **Flourishing IR optics applications starting in the 1950s, 60s, and 70s resulted in flurry of index measurements of IR materials - accuracy ~10^{-3} – 10^{-4}.**

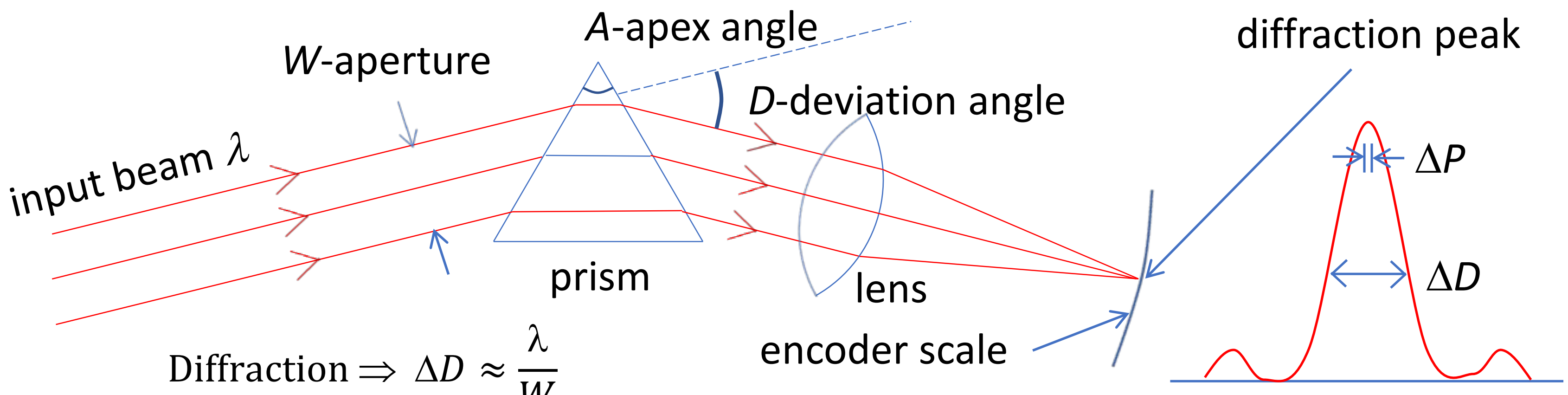
  - Most data used by optical designers in the IR today rely on this data from 1970s or earlier.

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

- **2012 NIST took on mission to update IR index data to higher accuracy – at least ×10 - public database.**

- To achieve this absolute accuracy reliably $\Rightarrow$ Minimum-Deviation Angle Refractometry.

Min-Dev-Angle Refractometry - Accuracy



Diffraction $\Rightarrow \Delta D \approx \dfrac{\lambda}{W}$

- 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:

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

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

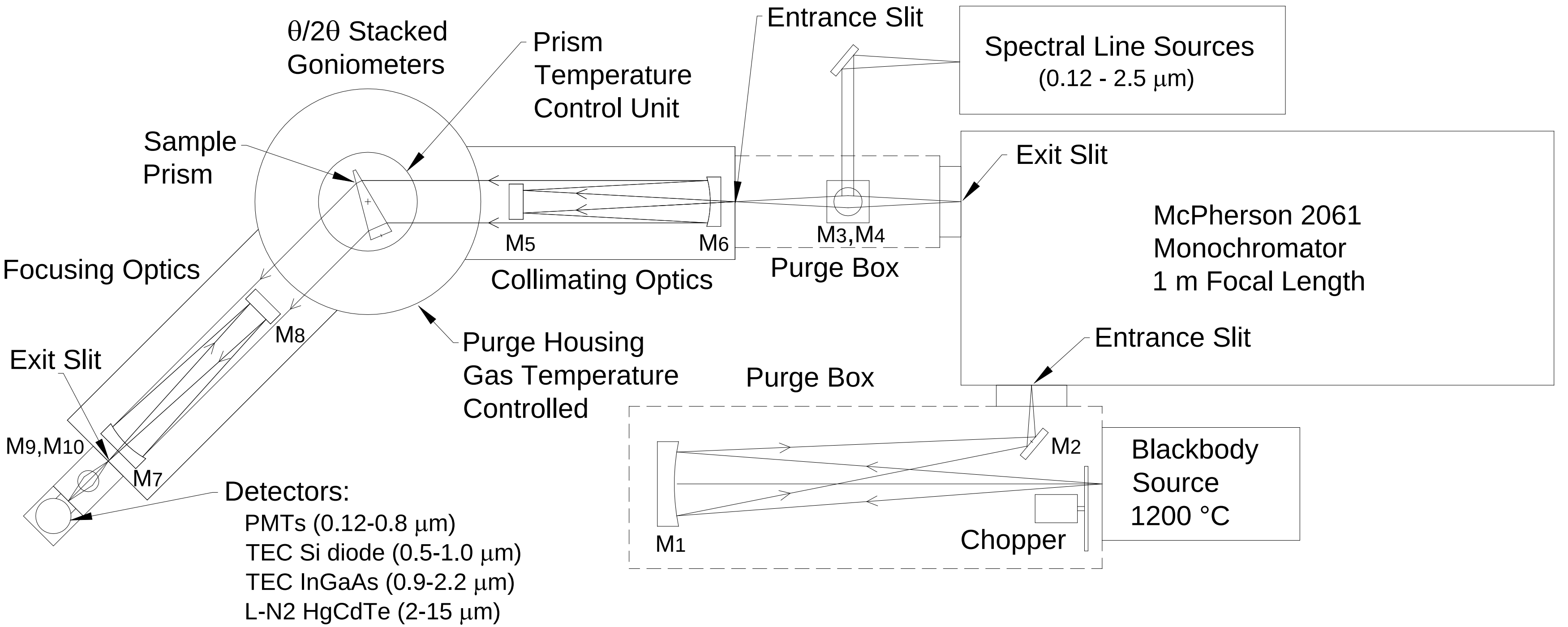
For W=25 mm,
assume *C*=1
f=0.05:

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

NIST Min Dev Angle UV/vis/IR Refractometer

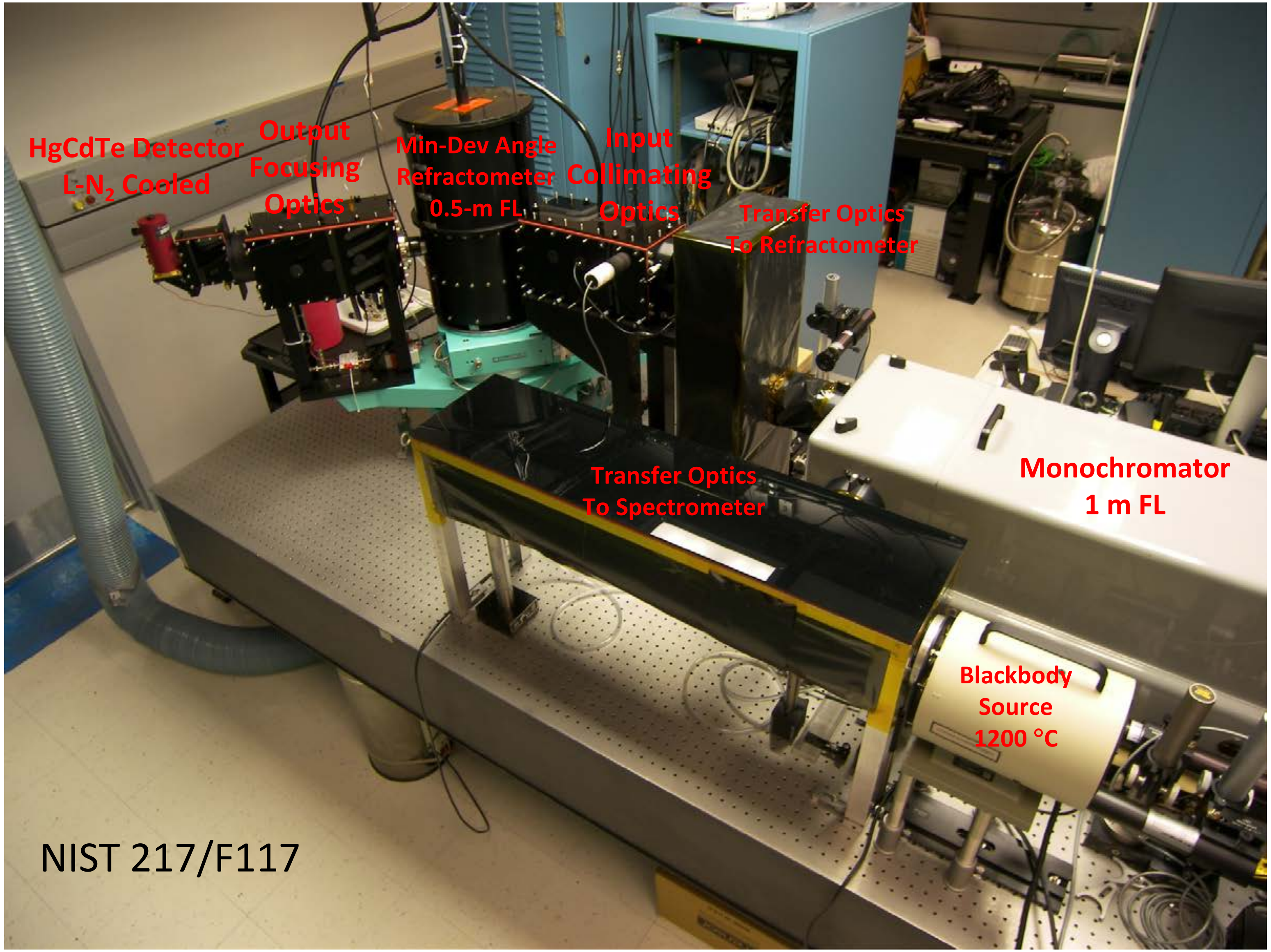
All reflective optics from source to detector. [λ range – λ=0.12-15 μm (T=15-25 °C)]

- VUV-vis-near IR (0.120 – 2 μm) [purged with N_2 gas]
  - Sources: atomic spectral lamps, σ_λ ~ 0.001 nm; Detectors: Si diodes, 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 detection.
- Index accuracy achieves theoretical limit for material, sample geometry, and sample specs.



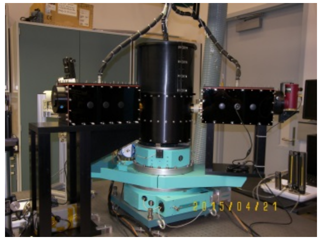
NIST Min Dev Angle UV/vis/IR Refractometer

NIST

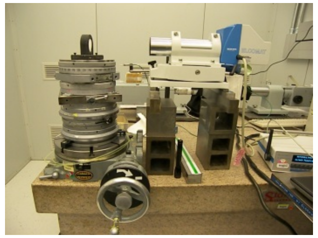


Accuracy Requires Suite of Measurements

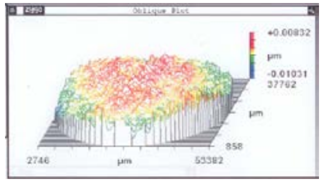
High-Accuracy Index Measurements: Determine index from minimum-deviation-angle. Actually, requires numerous measurements w/ numerous sources of error.



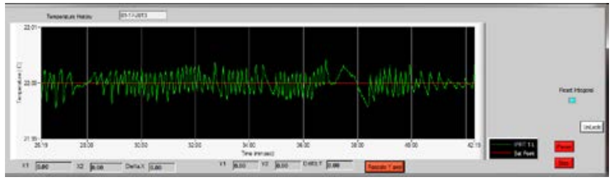
Dev Angle
Goniometer w/
calibrated encoder
Alignment issues
($\Delta\theta \leq$ 0.2 arc-sec)



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

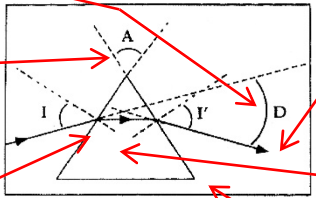


Prism Surface Flatness
Zygo Interferometer
(Wavefront RMS λ/100)



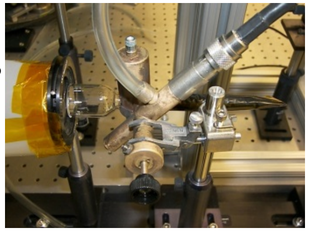
Temp Control – dn/dT
TWP and MPGa calibration
($\Delta T \leq$ 5 milli K)

At Minimum Deviation Angle

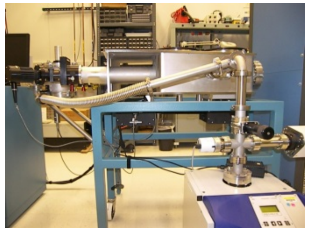


$$n(\lambda) = \frac{\sin\left(\frac{A+D(\lambda)}{2}\right)}{\sin\left(\frac{A}{2}\right)} \cdot n_{gas}(\lambda)$$

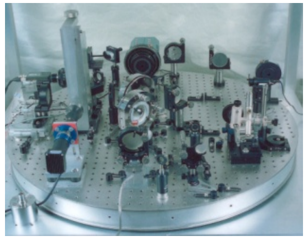
λ Calibrations
Spectral calibration lamps
($\Delta\lambda \leq$ 0.01 nm)
IR - Monochromator
($\Delta\lambda \leq$ 0. 1 nm)



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



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



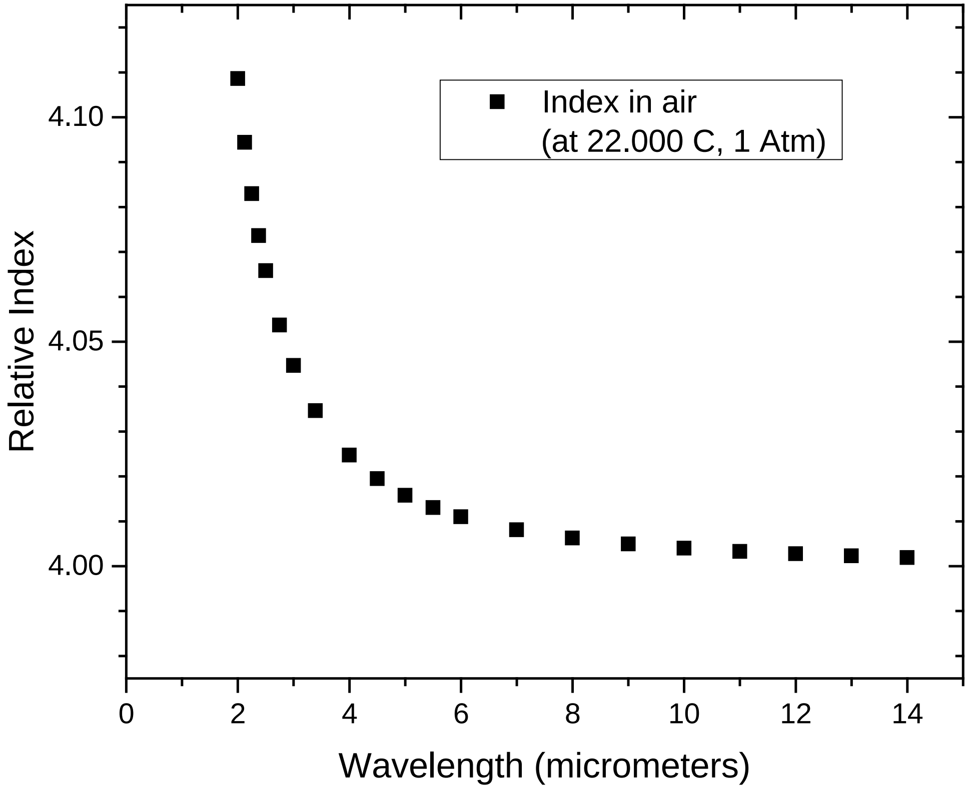
Stress Birefringence
grown-in or external
(stress-optic coeff. - π_{ijkl})
Polarimeter
(1 nm/cm [$\Delta n \leq 1 \times 10^{-7}$])

IR Materials Index Measurement Program

NIST

- First material Ge: order of mag. improvement, diffraction-limited results.
  - Ge is high-quality IR material, but cuts off at 2 μm.
  - Narrow-band semiconductor, w/ E_g 0.67 eV. For visible, need larger E_g.
- ZnSe and ZnS II-VI wide-band-gap semiconductors (2.7, 3.9 eV)
  - visible λ transmitting vis-mid IR: windows, lenses, output couplers
  - Design data used from 1970s (NBS).
- Si, CaF_2, BaF_2, IR fused silica, IRG26, GASIR, BD2.
- Mission:
  1) Update *n* of these materials near RT with new, higher-quality material.
  2) Include thermo-optic coefficients, d*n*/d*T*.
  3) Move to wider temp. dependence – cryogenic temperatures.

Index Results for Ge 2-14 µm



- Measurements from the absorption edge of Ge (2 µm) to 14 µm.
- Uncertainties (1-σ) below mid-10^{-5} for all wavelengths presented.

Measurements of absolute and relative indices of refraction and total standard uncertainties for one sample of Ge at 22.000 ±0.005 °C.

λ^{vac}(µm)	λ^{air}(µm)	Index^{vac}	Index^{air}	1-σ (10^{-5})
2.00000	1.99947	4.109725	4.108630	1.6
2.12500	2.12443	4.095492	4.094401	1.5
2.25000	2.24940	4.084070	4.082982	1.5
2.37500	2.37437	4.074715	4.073629	1.5
2.50000	2.49933	4.066925	4.065842	1.5
2.75000	2.74927	4.054785	4.053705	1.5
3.00000	2.99920	4.045796	4.044719	1.6
3.39224	3.39133	4.035736	4.034661	1.6
4.00000	3.99894	4.025816	4.024744	1.7
4.50000	4.49880	4.020584	4.019514	1.8
5.00000	4.99867	4.016867	4.015798	1.9
5.50000	5.49854	4.014131	4.013062	2.0
6.00000	5.99840	4.012071	4.011003	2.2
7.00000	6.99814	4.009192	4.008126	2.4
8.00000	7.99787	4.007321	4.006255	2.6
9.00000	8.99761	4.006019	4.004953	2.9
10.00000	9.99734	4.005079	4.004013	3.1
11.00000	10.99707	4.004360	4.003294	3.4
12.00000	11.99681	4.003824	4.002758	3.7
13.00000	12.99654	4.003358	4.002293	4.0
14.00000	13.99627	4.002979	4.001914	4.2

Sellmeier Fit and Residuals for Ge

NIST

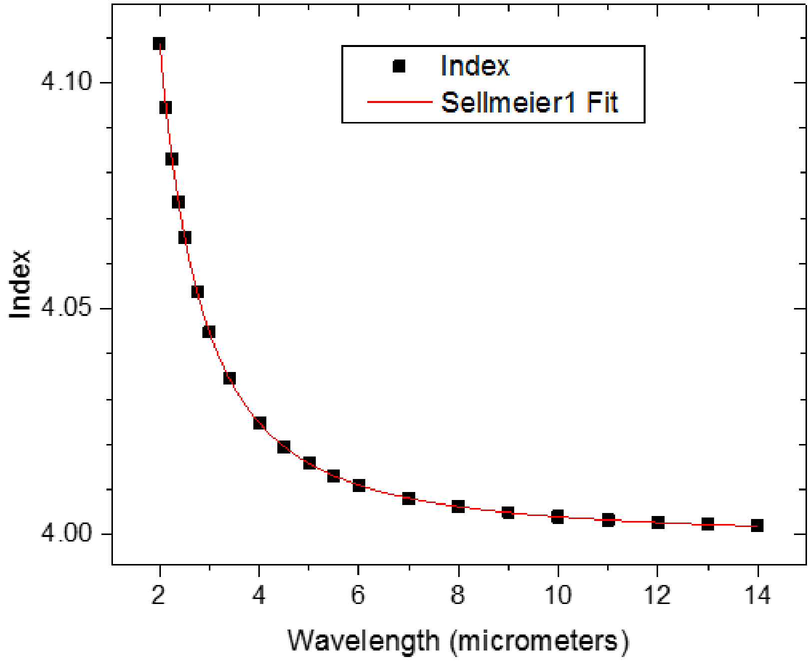
Fit n^{air} data to 3-term Sellmeier1 fitting function: $n^2 - 1 = \frac{K_1\lambda^2}{\lambda^2 - L_1{}^2} + \frac{K_2\lambda^2}{\lambda^2 - L_2{}^2} + \frac{K_3\lambda^2}{\lambda^2 - L_3{}^2}$

(valid: 22.0° C, range: 2.0 μm ≤ λ ≤ 14 μm)

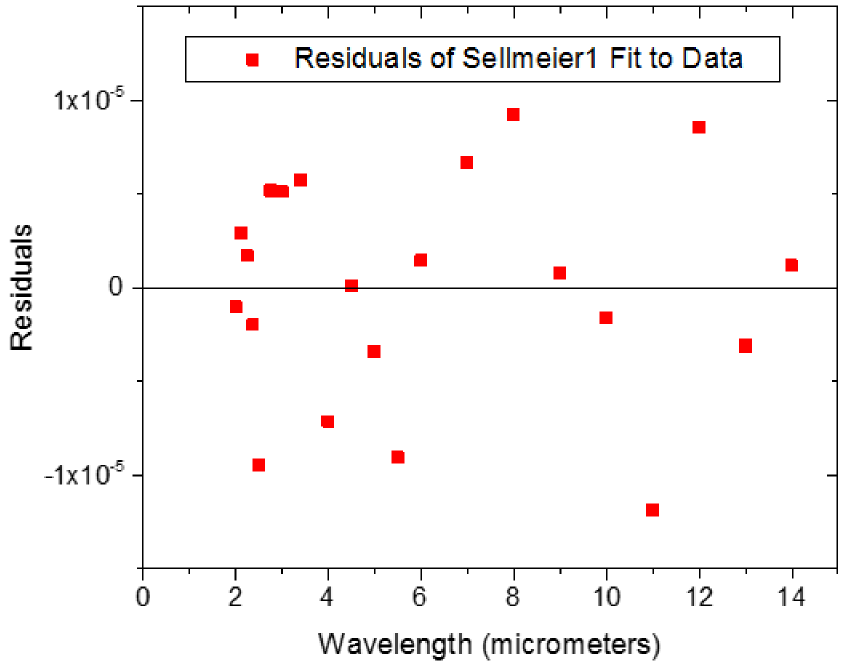
2 poles at shorter λ (band-edge Abs.)
1 pole at longer λ (phonon Abs.)

Sellmeier constants	
K_1	0.362471
K_2	14.640402
K_3	0.008175
L_1	1.243341 μm
L_2	0.412098 μm
L_3	26.5311 μm

Dispersion Data with Sellmeier1 Fit



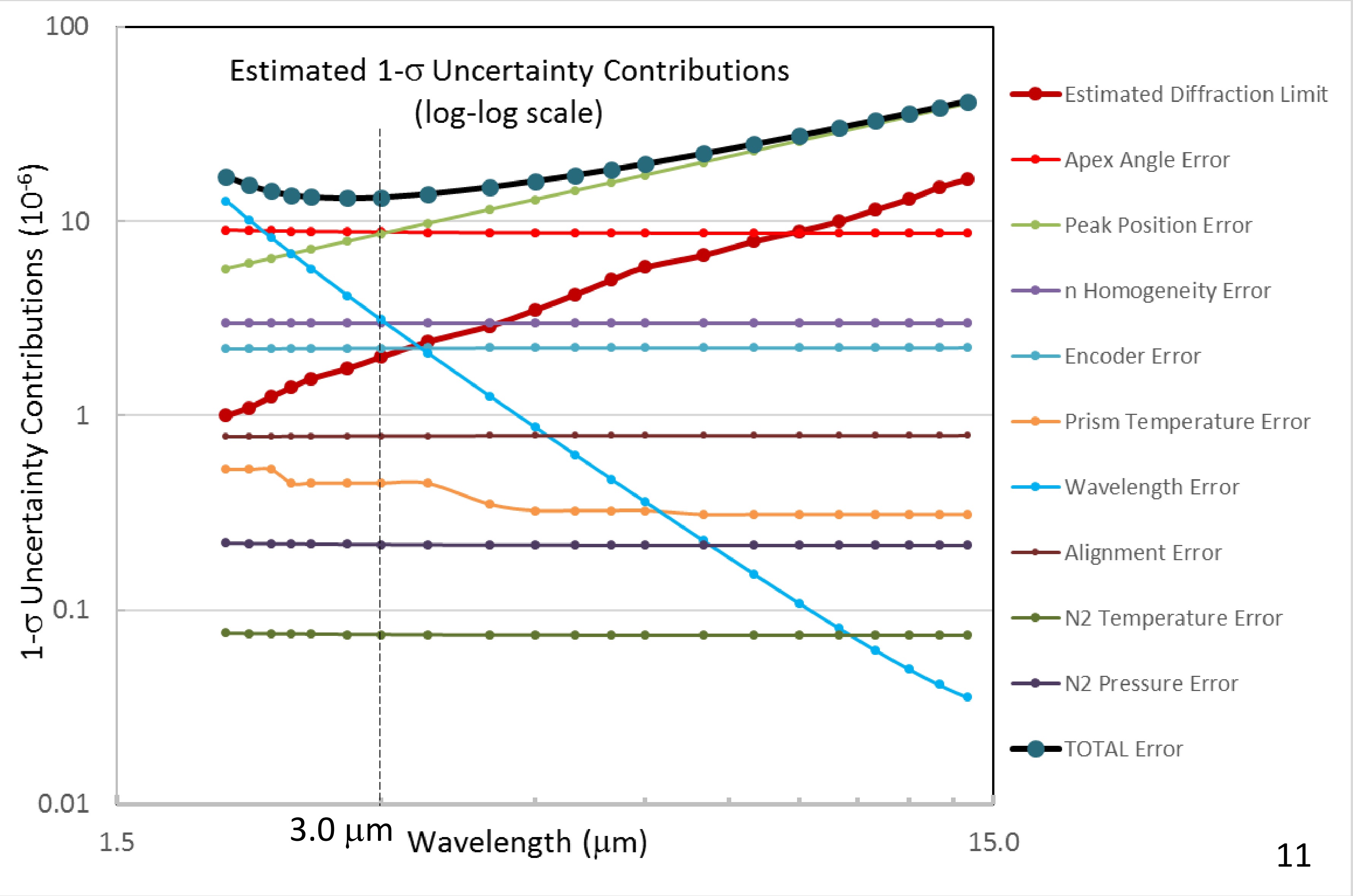
Residuals of Fit of Sellmeier1 Formula to Data



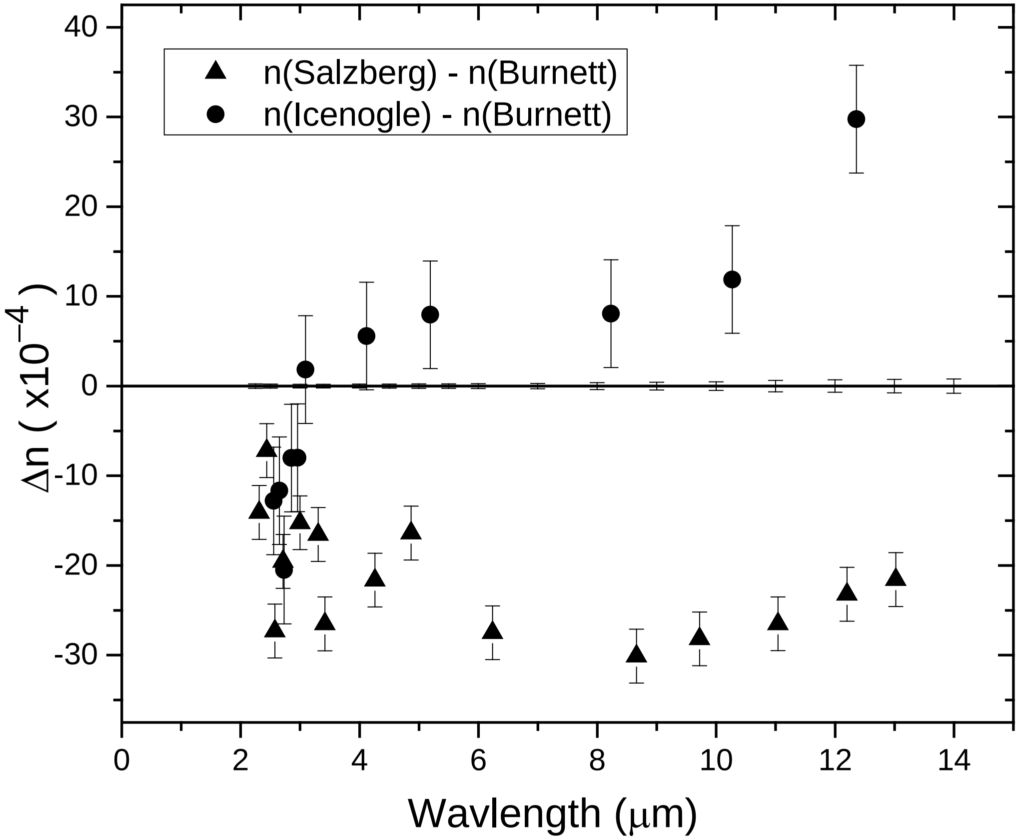
- Residuals of 3-Term Sellmeier Fit are ≤ 1×10^{-5} - well less than stated 1-σ uncertainties for each wavelength.

Uncertainty Contributions for Ge Indices

- **Peak Position Error** drives **Estimated Diffraction Limit**.
- **Apex Angle Error** primarily due to surface flatness error.
- Uncertainties diffraction-limited for $\lambda \geq 3$ µm.
- For $\lambda < 3$ µm, σ's from **Apex Angle** and **Wavelength** start to dominate.



Comparison w/ Extensively-used Ge Data



- 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. The error bars represent standard uncertainties.
- 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).

ZnS and ZnSe – Standard References

SLL 84-U-091

UNCLASSIFIED → Prater

NBS TECHNICAL NOTE 993

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Optical Materials Characterization
Final Technical Report
February 1, 1978-
September 30, 1978

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

19980309 197

PLEASE RETURN TO:
BMD TECHNICAL INFORMATION CENTER
BALLISTIC MISSILE DEFENSE ORGANIZATION
7100 DEFENSE PENTAGON
WASHINGTON D.C. 20301-7100

UNCLASSIFIED

U5160

SLL 84-U-091

SLL 84-U-091

UNCLASSIFIED → Prater

NBS TECHNICAL NOTE 993

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Optical Materials Characterization
Final Technical Report
February 1, 1978-
September 30, 1978

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

19980309 197

PLEASE RETURN TO:
BMD TECHNICAL INFORMATION CENTER
BALLISTIC MISSILE DEFENSE ORGANIZATION
7100 DEFENSE PENTAGON
WASHINGTON D.C. 20301-7100

UNCLASSIFIED

U5160

SLL 84-U-091

NBS ZnSe Data - 1978

Optical Materials Characterization
Final Technical Report
February 1, 1978-September 30, 1978

Albert Feldman, Deane Horowitz,
Roy M. Waxler, and Marilyn J. Dodge

Center for Materials Science
National Measurement Laboratory
National Bureau of Standards
Washington, D.C. 20234

Prepared for

Advanced Research Projects Agency
Arlington, Virginia 22209

U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, Secretary
Jordan J. Baruch, Assistant Secretary for Science and Technology
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Issued February 1979

Table 6.67 Refractive Index of Zinc Selenide

λ (μm)	n	λ (μm)	n
0.42		7.40	2.4201
0.46		7.80	2.4183
0.50		8.20	2.4163
0.54	2.6754	8.60	2.4143
0.58	2.6312	9.00	2.4122
0.62	2.5994	9.40	2.4100
0.66	2.5755	9.80	2.4077
0.70	2.5568	10.20	2.4053
0.74	2.5418	10.60	2.4028
0.78	2.5295	11.00	2.4001
0.82	2.5193	11.40	2.3974
0.86	2.5107	11.80	2.3945
0.90	2.5034	12.20	2.3915
0.94	2.4971	12.60	1.3883
0.98	2.4916	13.00	2.3850
1.00	2.4892	13.40	2.3816
1.40	2.4609	13.80	2.3781
1.80	2.4496	14.20	2.3744
2.20	2.4437	14.60	2.3705

Comments on Data

- **Major accomplishment – first comprehensive measurements.**
- **All optical designs w/ this material based on this work.**
- **The NBS values commonly used in IR Refs.: Handbook of Optics II (Boreman), *Handbook of Optical Constants of Solids* (Palik), and *Handbook of Infrared Optical Materials* (Klocek), and in commercial optics software, e.g., ZEMAX and Code V.**
- **4 decimal places shown through range 0.54 – 18.2 μm. But:**

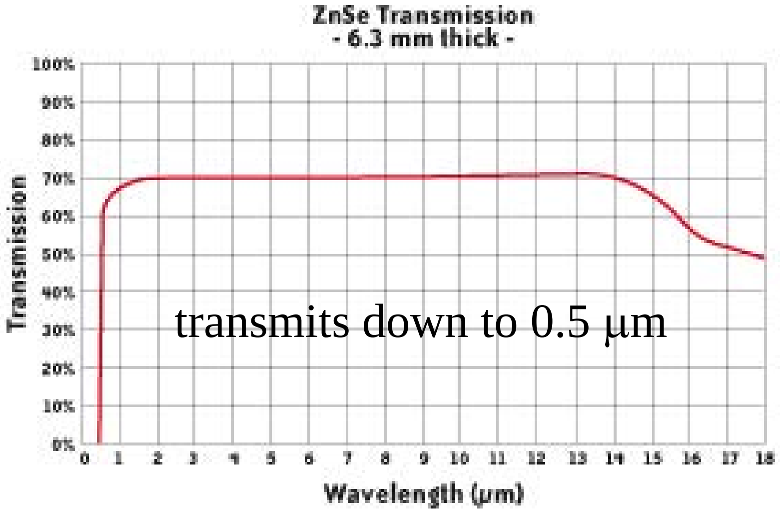
  1) Limited analysis given in this or original NBS report.

  2) Temp not controlled. Lab temperature ~0.5 °C.

  3) Early material.

ZnSe

- **Crystalline structure: cubic (zencblende) or hexagonal (wurtzite).**
  Commercial ZnSe grown in plates by CVD – polycrystalline.
  - CVD Raytran ZnSe (Raytheon) [Used in NBS report.]
  - Prism grade ZnSe (II-VI Infrared) – used for high-quality optics.

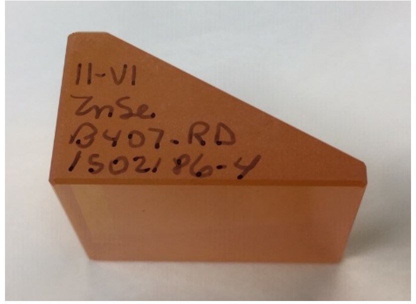


From: II-VI Infrared technical brochure.

ZnSe

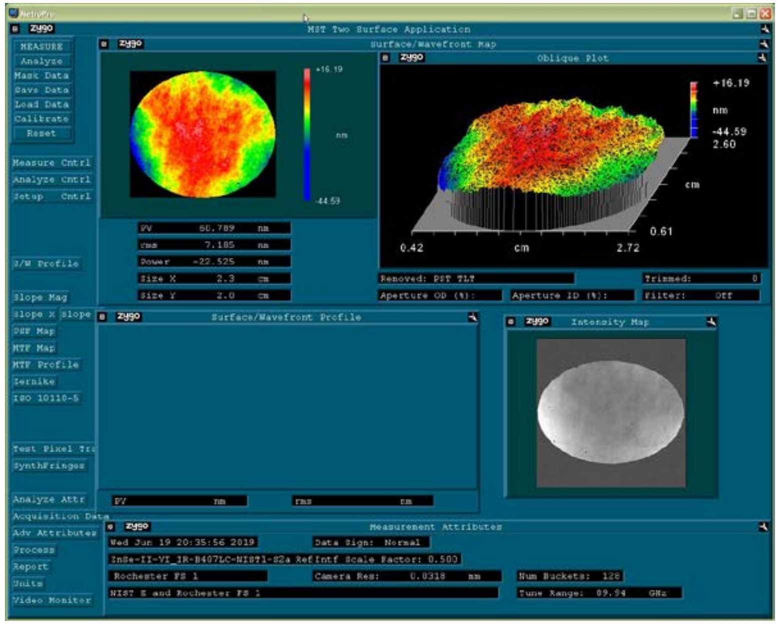
- 6 prism samples from various parts of the growth plate to investigate sample location.

ZnSe prism sample



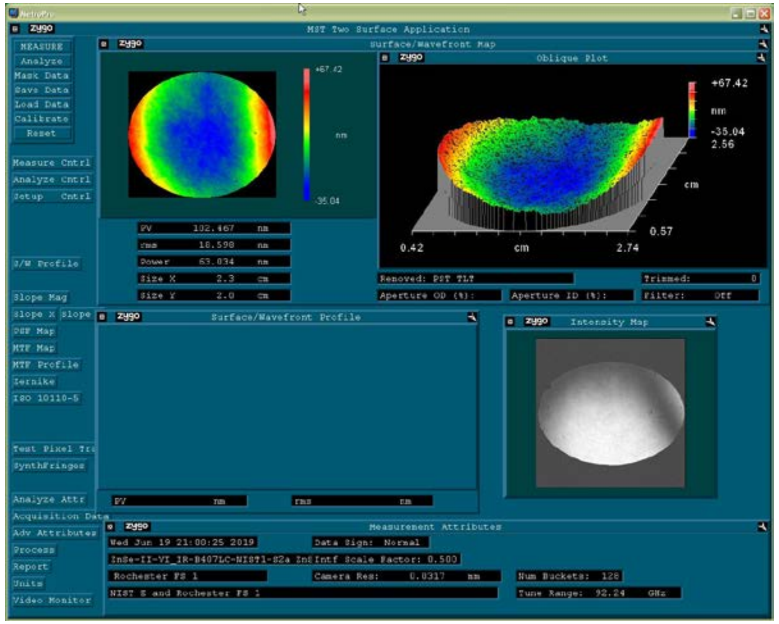
ZnSe prism samples meet all our high specifications, e.g., surface flatness.

ZnSe-NIST1 Surface Flatness – SIDE A



PV: 60.8 nm **(λ/10.4)**, rms: 7.2 nm (λ/87.9)

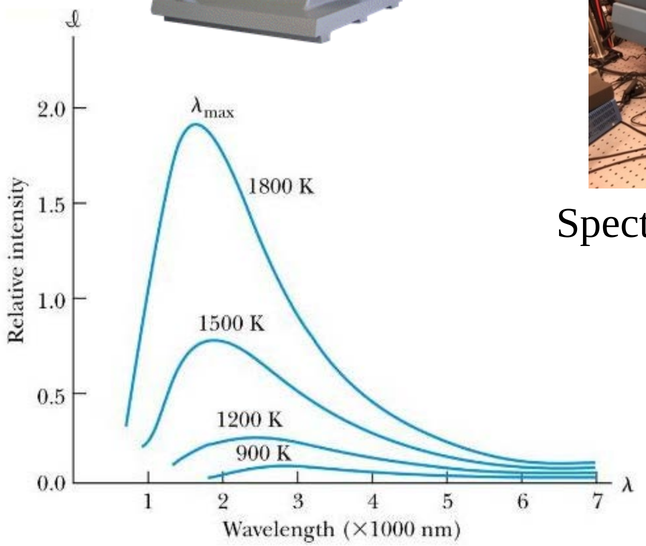
ZnSe-NIST1 Surface Flatness – SIDE B



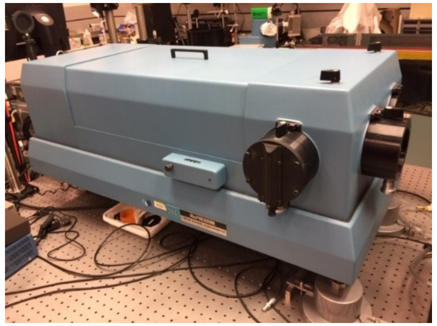
PV: 102.5 nm **(λ/6.2)**, rms: 18.6 nm (λ/34.0)

Near/Mid IR Region 2-14 μm

Blackbody Radiation Source 1200 °C
(Infrared Systems IR-564/301)

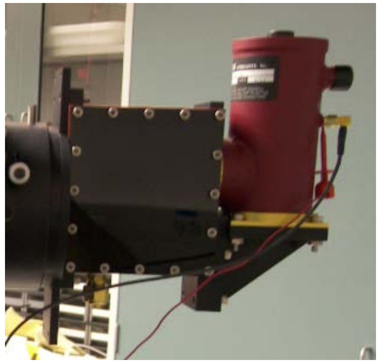


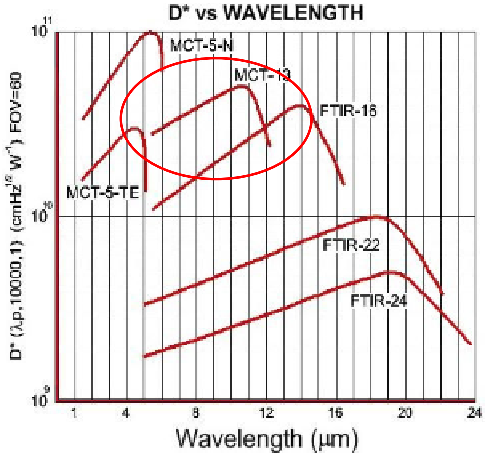
McPherson 2061 spectrometer



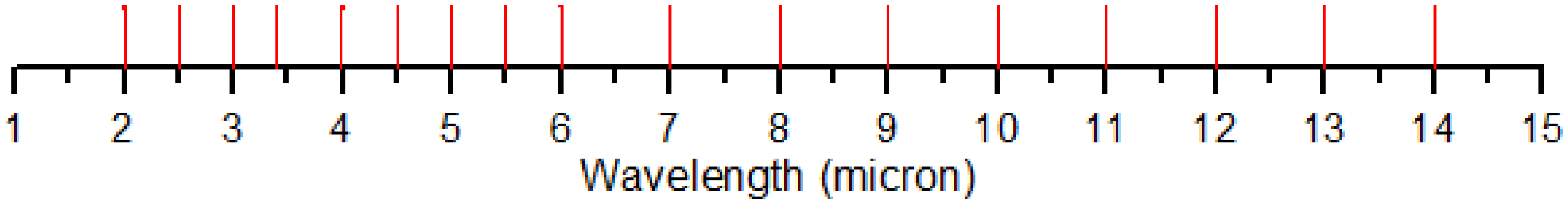
Spectral uncertainty: 0.1 nm

IR Detector
(IR Associates MCT-13)





SPECTRAL BANDS



Near IR Region 0.8-1.2 μm

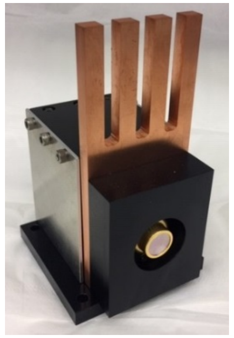
SOURCES

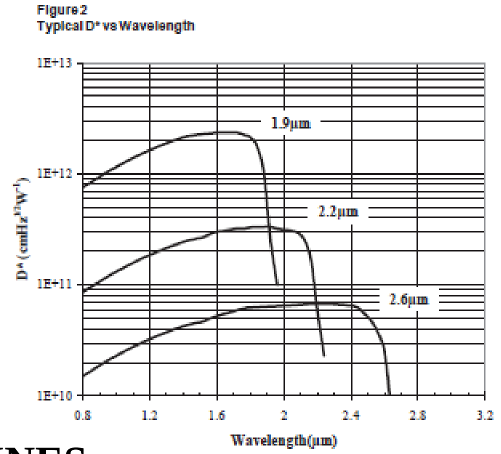
Spectral lamps: Hg
Blackbody
Source/Monochromator

Spectral uncertainty:
1×10^{-4} nm – 0.1 nm

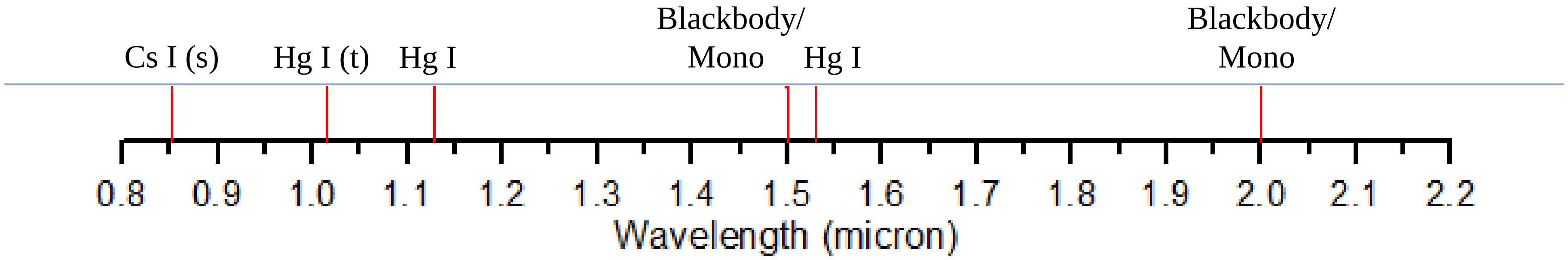
DETECTORS

Extended
InGaAs
Photodiode
Range:
0.8 – 2.2 μm





SPECTRAL LINES



Visible/Near IR Region 0.5-1.1 µm

NIST

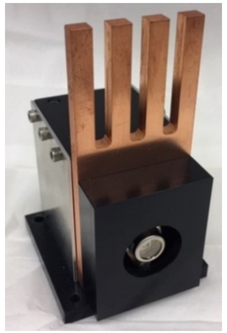
SOURCES

Spectral lamps: Hg, He, Cd, Cs

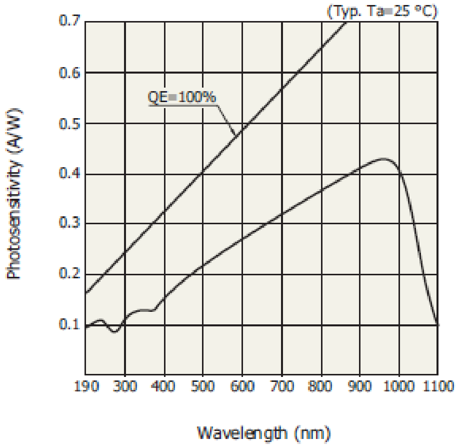
Spectral uncertainty: 1×10^{-4} nm

DETECTORS

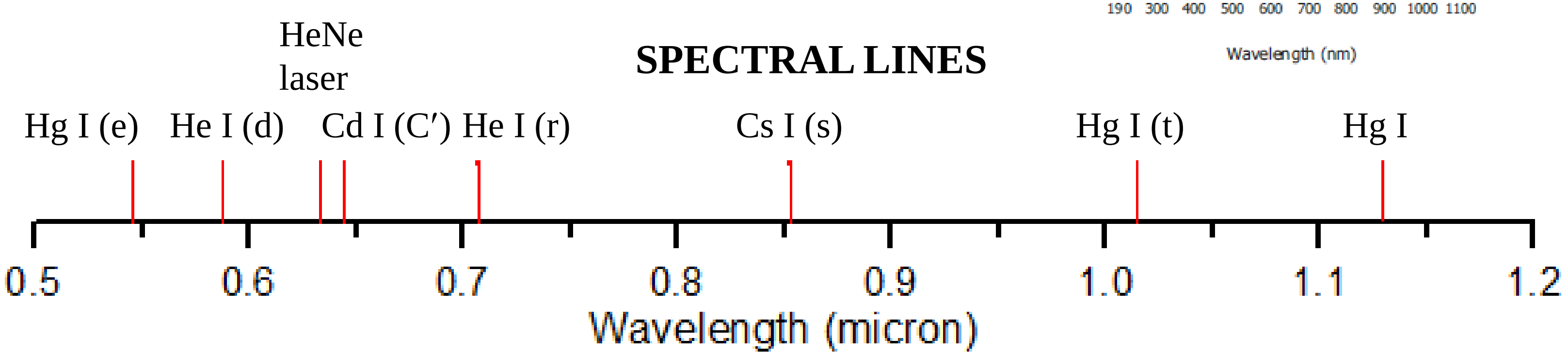
TE-Cooled
Si Photodiode



Spectral response (Hamamatsu S3477-03)

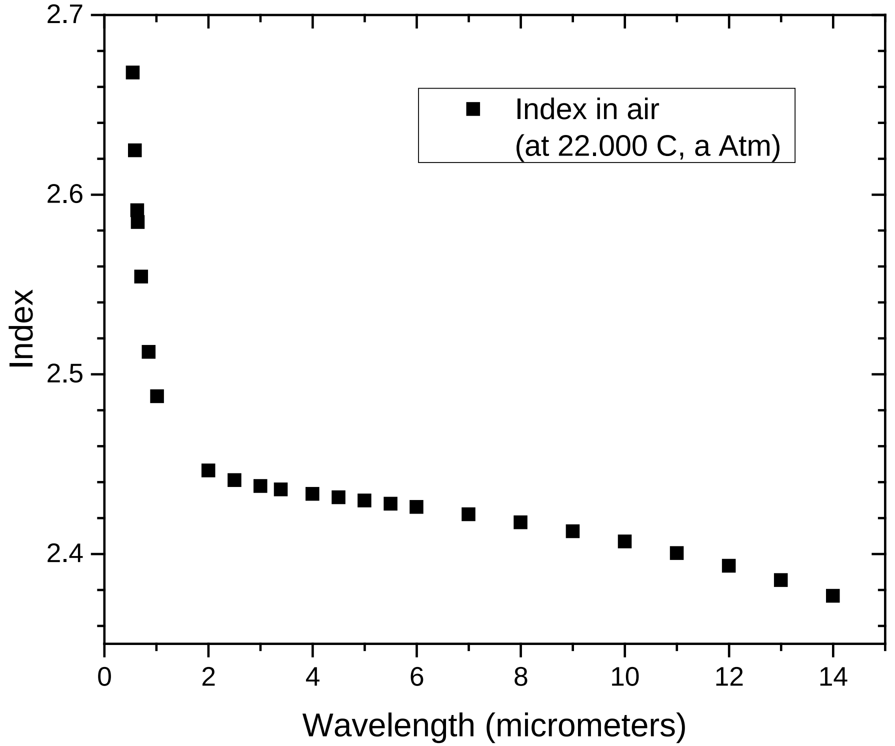


SPECTRAL LINES



Preliminary Index Results ZnSe 0.5-14 µm

NIST



- Measurements from the absorption edge of ZnSe (0.55 µm) to 14 µm.
- Uncertainties (1-σ) below mid-10^{-5} for all wavelengths presented.
- Approximate diffraction limit right column.

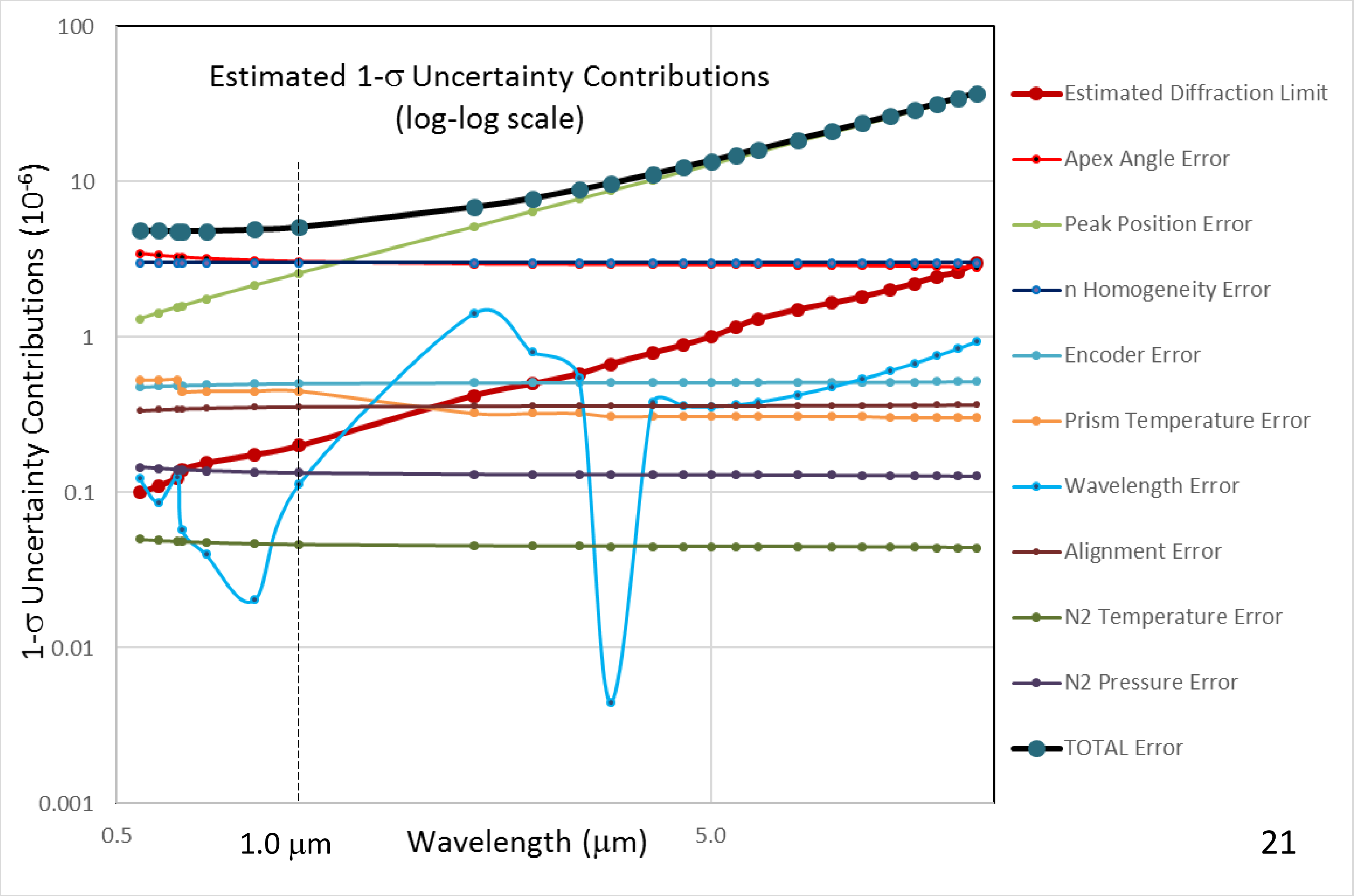
Measurements of absolute and relative indices of refraction and total standard uncertainties for one sample of ZnSe at 22.000 ±0.005 °C.

spectral lines

λ^{vac}(µm)	λ^{air}(mm)	Index^{vac}	Index^{air}	σ (x10^{-5})	Est Diff Limit
0.5462268	0.5460786	2.6686980	2.6679741	0.49	0.10
0.5877249	0.5875659	2.6253130	2.6246028	0.48	0.11
0.6329914	0.6328206	2.5919944	2.5912948	0.48	0.13
0.6440249	0.6438512	2.5853800	2.5846825	0.48	0.14
0.7067138	0.7065236	2.5550714	2.5543838	0.48	0.16
0.8523453	0.8521167	2.5130930	2.5124191	0.49	0.18
1.0142530	1.0139816	2.4883898	2.4877241	0.51	0.20
2.0000000	1.9994671	2.4471359	2.4464839	0.7	0.4
2.5000000	2.4993342	2.4417697	2.4411194	0.8	0.5
3.0000000	2.9992012	2.4384647	2.4378155	0.9	0.6
3.3922350	3.3913319	2.4365275	2.4358789	1.0	0.7
4.0000000	3.9989353	2.4340406	2.4333928	1.1	0.8
4.5000000	4.4988023	2.4322018	2.4315544	1.2	0.9
5.0000000	4.9986693	2.4304182	2.4297714	1.4	1.0
5.5000000	5.4985363	2.4286115	2.4279652	1.5	1.2
6.0000000	5.9984032	2.4267584	2.4261125	1.6	1.3
7.0000000	6.9981372	2.4227542	2.4221095	1.9	1.5
8.0000000	7.9978711	2.4182663	2.4176228	2.1	1.7
9.0000000	8.9976051	2.4132131	2.4125710	2.4	1.8
10.0000000	9.9973390	2.4075333	2.4068927	2.6	2.0
11.0000000	10.9970729	2.4011272	2.4004882	2.9	2.2
12.0000000	11.9968068	2.3940368	2.3933998	3.2	2.4
13.0000000	12.9965408	2.3861136	2.3854786	3.4	2.6
14.0000000	13.9962747	2.3773138	2.3766812	3.7	3.0

Uncertainty Contributions for ZnSe Indices

- **Peak Position Error** drives **Estimated Diffraction Limit**.
- Contributions from **Wavelength Error** negligible at short λ due to use of spectral lines.
- **Apex Angle Error** primarily due to surface flatness error.
- Uncertainties diffraction-limited for $\lambda \geq 1$ μm.
- For $\lambda < 1$ μm, σ's from **Apex Angle** and **Homogeneity** start to dominate.



Sellmeier Fit and Residuals

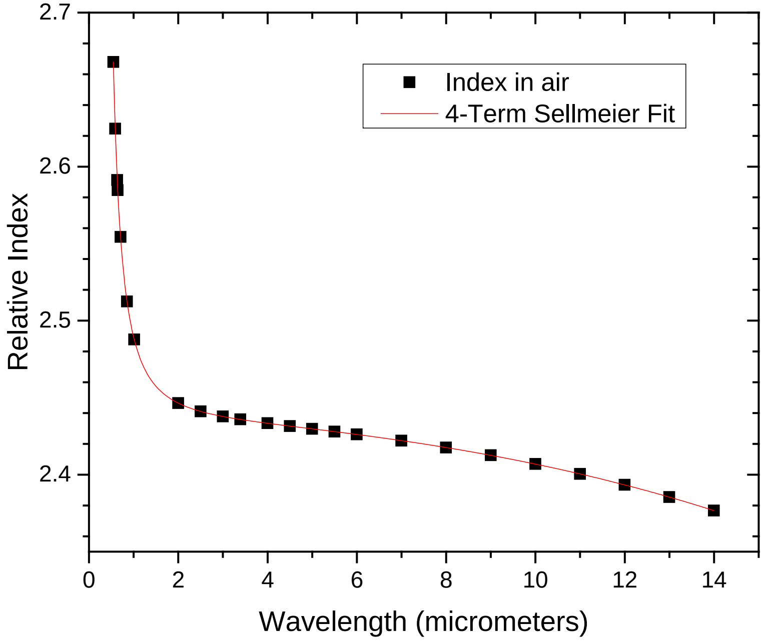
Fit n^{air} data to 4-term Sellmeier1 fitting function: $$n^2 - 1 = \frac{K_1\lambda^2}{\lambda^2 - {L_1}^2} + \frac{K_2\lambda^2}{\lambda^2 - {L_2}^2} + \frac{K_3\lambda^2}{\lambda^2 - {L_3}^2} + \frac{K_4\lambda^2}{\lambda^2 - {L_4}^2}$$

(valid: 22.0° C, range: 0.546 μm ≤ λ ≤ 14 μm)

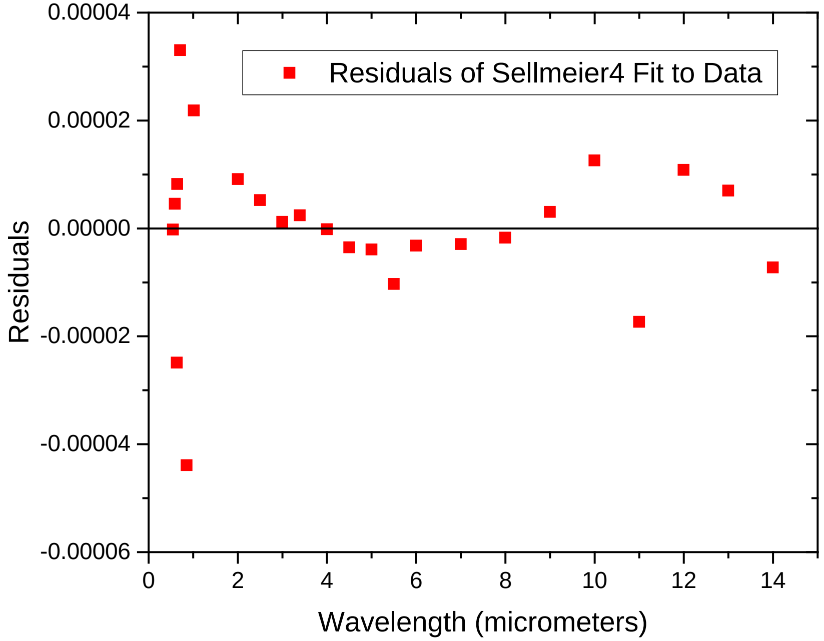
3 poles at shorter λ (band-edge Abs.)
1 pole at longer λ (phonon Abs.)

Sellmeier constants	
K_1	4.1926080
K_2	0.7309307
K_3	0.0030734
K_4	2.8967481
L_1	0.1902586
L_2	0.3658392
L_3	0.50348836
L_4	47.2021

Dispersion Data with Sellmeier1 Fit

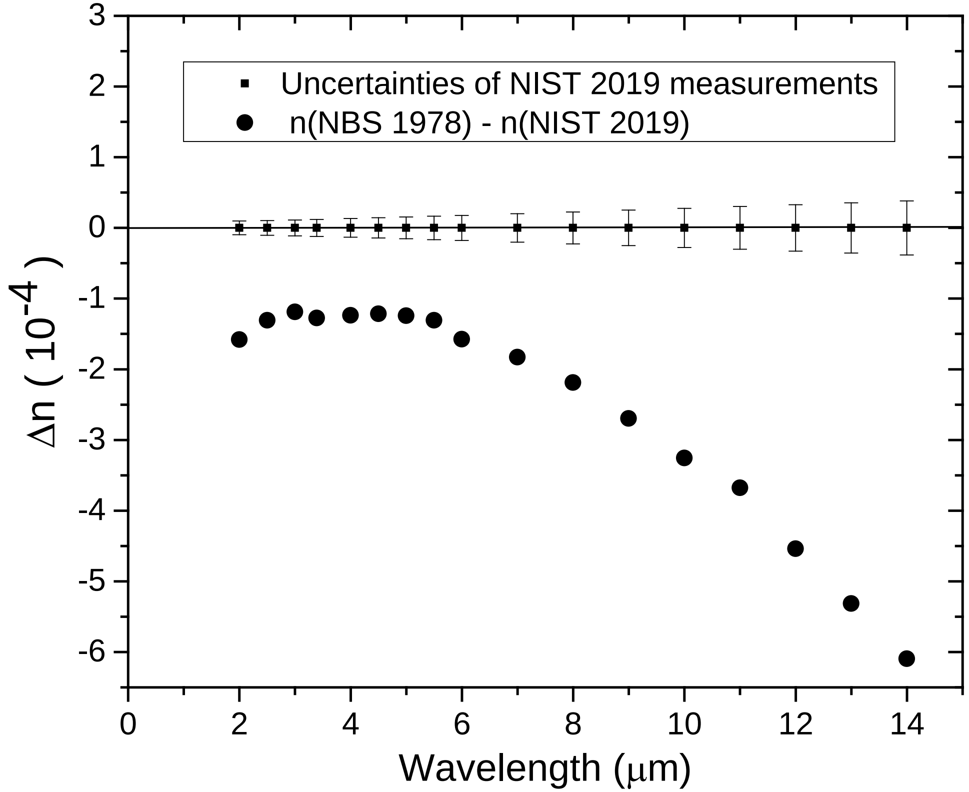


Residuals of Fit of Sellmeier1 Formula to Data



- Residuals of 4-Term Sellmeier Fit are ≤ 2×10^{-5} down to 2 μm, ≤ 4×10^{-5} below 2 μm.

Comparison with NBS 1978 Measurements



- Differences between the Sellmeier values from the 1987 NBS measurements, and of this work.
  - The NBS values are commonly used in IR Refs.: Handbook of Optics II (Boreman), *Handbook of Optical Constants of Solids* (Palik), and *Handbook of Infrared Optical Materials* (Klocek), and in commercial optics design software, e.g., ZEMAX and CodeV.
- Values differ well outside 1-σs. Could be due to differences in material quality.

Summary and Future Directions

Summary:

- Demonstrated can make state-of-art index measurements of IR materials - Ge, ZnSe.
  - Improved uncertainties in literature by an order of magnitude.
- Can achieve diffraction limit for sample size, except if errors dominated by materials issues, e.g., index homogeneity.

Future Directions of Program:

- Make measurements of multiple samples - establish variations w/ ingot position and supplier.
- Continue with important IR materials: ZnS, Si, CaF_2, BaF_2, IR fused silica …
- Include d*n*/d*T* for all materials.
- Develop publicly accessible index database.
- Modify apparatus with sample cryostat for low-temperature measurements.