

# Infrared Refractive Index and Thermo-optic Coefficient Measurement at APL

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**D**evelopment of infrared optical systems requires knowledge of the refractive index of the transmissive optical elements. Many Laboratory applications require the knowledge of the refractive index over a wide temperature range. The simplest expression of temperature dependence is the derivative of refractive index with respect to temperature, i.e., the thermo-optic coefficient. A convenient method for determining refractive index in the infrared is measuring interference between surfaces of a thick lamina. Such transmittance measurements, made at several temperatures, provide a comprehensive picture of the temperature-dependent refractive index. (Keywords: Diamond, Infrared materials, KRS-5, Refractive index, Silicon carbide, Thermo-optic coefficient.)

## INTRODUCTION

For many years, APL has measured and modeled the optical properties of materials. Articles on this topic in past issues of the *Technical Digest* include the measurement of scatter,<sup>1</sup> emissivity,<sup>2</sup> reflectance,<sup>3</sup> and the visible thermo-optic coefficient,<sup>4</sup> as well as many of the optical properties of natural diamond<sup>5</sup> and polar materials.<sup>3</sup> In this article, we discuss interferometric measurements to determine refractive index over a broad spectral range in the infrared. Temperature dependence is obtained by taking measurements at several temperatures. Such temperature-dependent data are rarely available in the literature. Results have been applied to several applications, particularly guided missile windows.<sup>6</sup>

## REFRACTIVE INDEX

The refractive index arises from the molecular polarizability  $\alpha$  according to the Lorentz-Lorenz formula:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\rho(T)\alpha(\rho, T)}{3\epsilon_0}, \quad (1)$$

where  $\rho$  is molecular density,  $T$  is temperature, and  $\epsilon_0$  is the permittivity of free space. Differentiating Eq. 1 with respect to temperature gives the temperature dependence of refractive index (or thermo-optic coefficient). Decreasing density with temperature (positive thermal expansion coefficient, the usual case) decreases refractive index, whereas a positive change in polarizability with temperature (the usual case) increases refractive index. Therefore, high thermal expansion materials such as the alkali and thallium halides have negative thermo-optic coefficients, whereas low thermal expansion materials such as diamond and silicon carbide have positive thermo-optic coefficients.

## INTERFEROMETRIC MEASUREMENTS

The highest accuracy refractive index measurement is made with the prism or minimum deviation method,

which requires the material to be made into a prism with a precisely known vertex. Some polycrystalline materials, including those made by chemical vapor deposition, are difficult to make sufficiently thick for accurate index determination using this method. On the other hand, interferometric measurements are easily made on thin plates and provide a convenient way to determine refractive index, especially for experimental materials.

The refractive index  $n$  of a laminar sample with highly parallel surfaces, separated by a distance  $L$ , can be determined by measuring interference between directly transmitted and internally reflected light. Such a sample acts as a solid etalon. Interference produces intensity modulation with maxima occurring when the optical path length difference  $2nL$  between the two paths is exactly an integer number  $m$  of wavelengths  $\lambda$ , hence

$$m\lambda = 2Ln \quad \text{or} \quad m = 2Ln\nu, \quad (2)$$

where  $\nu$  is the wavenumber (reciprocal of the wavelength, usually measured in inverse centimeters). The difference between maxima (or minima) is called the *free spectral range*  $\Delta$  and is related to the refractive index (assuming small  $\Delta$ ) by

$$\frac{1}{2L\Delta(\nu)} = n + \nu \frac{dn}{d\nu}. \quad (3)$$

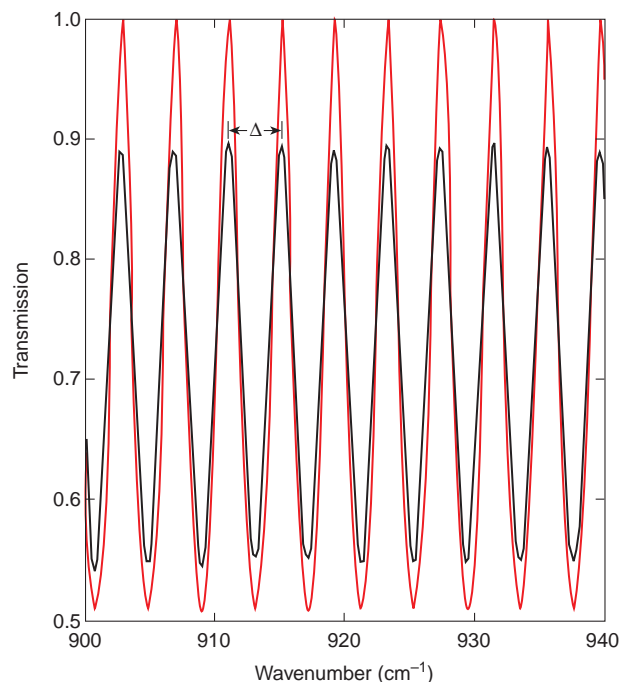
High spectral resolution measurements as in Fig. 1 are used to determine peak locations and hence free spectral range. Also shown in Fig. 1 is an ideal transmission calculation. The smaller range of the transmission modulation is due to effects such as nonparallel surfaces, absorption and scatter, and imperfectly collimated light.

A 0.1-cm-thick sample of refractive index 2 has the nominal free spectral range of  $2.5 \text{ cm}^{-1}$ ; therefore, a spectral resolution of  $0.5 \text{ cm}^{-1}$  or better is needed to accurately determine the free spectral range. We use a Bomem DA3 Fourier transform spectrometer with  $0.04\text{-cm}^{-1}$  resolution to make these measurements.

## EXTRACTING REFRACTIVE INDEX

Equation 3 gives the relationship between refractive index and free spectral range. We have developed two methods to extract  $n(\nu)$  from  $\Delta(\nu)$  data:

1. Use a model for  $n(\nu)$  and fit the free spectral range data to this model. This method was first applied to the material KRS-5<sup>7</sup> and since then to silicon carbide, diamond, and other materials.
2. Integrate Eq. 3 to directly determine  $n(\nu)$ .



**Figure 1.** Detail of the room-temperature infrared transmission of a 0.05142-cm-thick slab of polycrystalline diamond. The modulation of transmission is due to interference between directly transmitted and internally reflected light. The black curve is a measurement and the red curve is a theoretical prediction for a perfect sample. The free spectral range  $\Delta$  is the distance between maxima (or, alternatively, minima).

Although method 1 is often used to model directly measured refractive index data, we believe we are the first to apply this method to determine refractive index from interferometric free spectral range measurements. Method 2 is also believed to be new and is a powerful technique for extending refractive index using interferometric measurements. The two methods complement each other; in particular, method 1 can provide a starting point for method 2.

## Fitting to a Refractive Index Model

Putting  $n(\nu)$  in a suitable analytic form allows us to fit free spectral range data (in the form of  $-1/2L\Delta$ ) using a nonlinear, least-squares routine to derive the model parameters. Long experience has shown the Sellmeier equation to accurately model refractive index in transparent regions:<sup>8</sup>

$$n^2(\nu) = 1 + \sum_i \frac{S_i \nu_i^2}{\nu_i^2 - \nu^2}, \quad (4)$$

where the parameters  $S_i$  and  $\nu_i$  of each term in the summation are the strength and location, respectively, of resonances (absorptions) in the material. Experience has also shown that, at most, three terms are

adequate to model the most precise refractive index data over the entire range of transparency: two representing short-wavelength electronic absorption and one representing the infrared lattice vibration absorption. Often, however, interferometric data do not cover the entire range of transparency and all of the model parameters of Eq. 4 cannot be determined. In such a case, terms of Eq. 4 are approximated by expanding them in a power series and selecting low-order terms that can be determined using the data. Sellmeier model terms representing high-frequency (ultraviolet or electronic) resonances are expanded as<sup>9</sup>

$$\frac{S_i v_i^2}{v_i^2 - v^2} = S_i + \frac{S_i}{v_i^2} v^2 + \frac{S_i}{v_i^4} v^4 + \dots \quad v < v_i, \quad (5a)$$

which is also known as the Cauchy model. The low-frequency (infrared or vibrational) terms are expanded as

$$\frac{S_i v_i^2}{v_i^2 - v^2} = -\frac{S_i v_i^2}{v^2} - \frac{S_i v_i^4}{v^4} - \dots \quad v > v_i. \quad (5b)$$

Once a suitable model is selected, the accuracy of the derived refractive index is dependent only on accurate sample thickness  $L$  and accurate location of the interferometric maxima (accurate free spectral range). The accuracy of the maxima location is dependent on both the resolution of the measurement and the noise of the measurement.

### Integration Method to Determine Refractive Index

This method integrates Eq. 3 by casting it in the form

$$n(v) + v \frac{dn(v)}{dv} = \frac{d[n(v)v]}{dv} = \frac{1}{2L\Delta}, \quad (6a)$$

and integrating from  $\nu_0$  to  $\nu$  gives ( $\nu > \nu_0$ )

$$n(v) = \frac{1}{v} \left[ \nu_0 n(\nu_0) + \frac{1}{2L} \int_{\nu_0}^{\nu} \frac{dv'}{\Delta} \right]. \quad (6b)$$

The remaining integral in Eq. 6b is solved by noting that it merely counts the number of free spectral ranges

occurring in the frequency range between  $\nu_0$  and  $\nu$ . If the frequency start and end points are chosen to coincide with maxima, the integral is  $\rho(v)$ , the number of free spectral ranges between  $\nu_0$  and  $\nu$ , and Eq. 6b becomes

$$n(v) = \frac{1}{v} \left[ \nu_0 n(\nu_0) + \frac{\rho(v)}{2L} \right]. \quad (6c)$$

Accurate determination of  $n(v)$  requires accurate knowledge of  $L$  and  $n(\nu_0)$ , but the free spectral range data can be “noisy” (i.e., the maxima locations can be somewhat inaccurate).

### Thallium Bromide–Thallium Iodide Mixture (KRS-5)

The first application of the model fitting method was KRS-5, a soft material used for far-infrared applications. Free spectral range data were acquired over the 400–700 and 700–1000  $\text{cm}^{-1}$  spectral regions at room temperature (295–296 K) and also at 482 K for the higher frequency region.<sup>7</sup> Because the spectral coverage of these measurements is far from either electronic or infrared absorption, only a simple refractive index model was used:

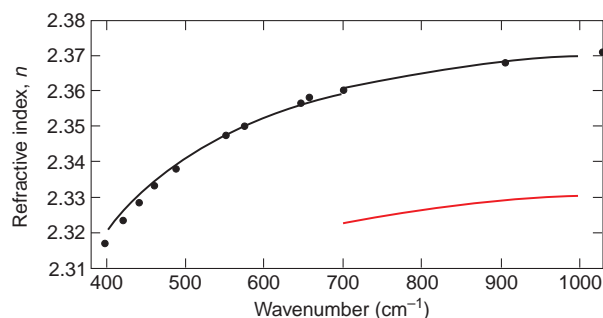
$$n^2 = 1 + S_0 - \frac{S_1 v_1^2}{v^2}, \quad (7)$$

where  $S_0$  represents the electronic contribution, and  $S_1 v_1^2/v^2$  represents the infrared contribution to refractive index (i.e., only the first term from the expansions of Eqs. 5a and 5b is used). The temperature dependence of these terms is given in Table 1.

Figure 2 compares high-precision room-temperature refractive index measurements<sup>10</sup> with values derived from our measurements. Good agreement between measured ( $-224 \times 10^{-6} \text{ K}^{-1}$ ) and literature values<sup>10</sup> of

Table 1. Refractive index model constants (Eq. 7) for KRS-5.

Spectral interval ( $\text{cm}^{-1}$ )	Temperature (K)	$1+S_0$	$S_1 v_1^2$ ( $\text{cm}^{-2}$ )
700–1000	295	5.66285	$4.373 \times 10^4$
700–1000	482	5.46864	$3.580 \times 10^4$
400–700	296	5.65541	$4.363 \times 10^4$



**Figure 2.** Room-temperature (295 K) infrared refractive index of KRS-5 derived from model fits to free spectral range data (black curves, see Eq. 7 and Table 1) compared with values found in the literature (circles, see Ref. 10). The red curve shows 482 K interferometric measurements.

$dn/dT$  is achieved in the measured spectral region between 700 and 1000  $\text{cm}^{-1}$ .

## Diamond

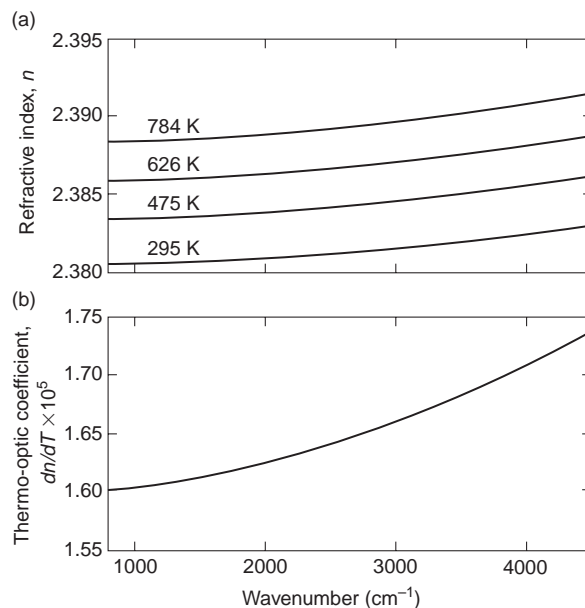
Optical properties of natural diamond are found in an earlier *Technical Digest* article.<sup>5</sup> We also made optical measurements on samples of polycrystalline diamond prepared by the chemical vapor deposition method, including determination of  $dn/dT$  from the free spectral range.<sup>11</sup> These temperature-dependent data (295–784 K) were recently reanalyzed by fitting the data to a refractive index model. Since diamond has no infrared-active modes (to first order), and the free spectral range data came from low-absorption infrared (800–1500 and 4000–4500  $\text{cm}^{-1}$ ) regions, the refractive index is nearly constant. The selected refractive index model has a Cauchy form:

$$n^2 = 1 + S_0 + \frac{S_1}{\nu_1^2} \nu^2. \quad (8)$$

Fitting this model to the temperature-dependent free spectral range data gives a temperature dependence to both the  $S_0$  and  $S_1/\nu_1^2$  terms as given in Table 2 (temperature in K). Figure 3 shows the modeled refractive index and  $dn/dT$  values for diamond in the infrared.

Table 2. Temperature-dependent refractive index model constants (Eq. 8) for diamond (295–784 K).

Term	Temperature dependence
$1 + S_0$	$5.64380 + 7.605 \times 10^{-5} T$
$S_1/\nu_1^2$	$5.13865 \times 10^{-10} + 3.364 \times 10^{-13} T \text{ cm}^2$



**Figure 3.** (a) Infrared refractive index of polycrystalline diamond at several temperatures as derived from model fits (see Eq. 8 and Table 2) and (b) the resulting room-temperature value of the thermo-optic coefficient.

## $\beta$ -Silicon Carbide

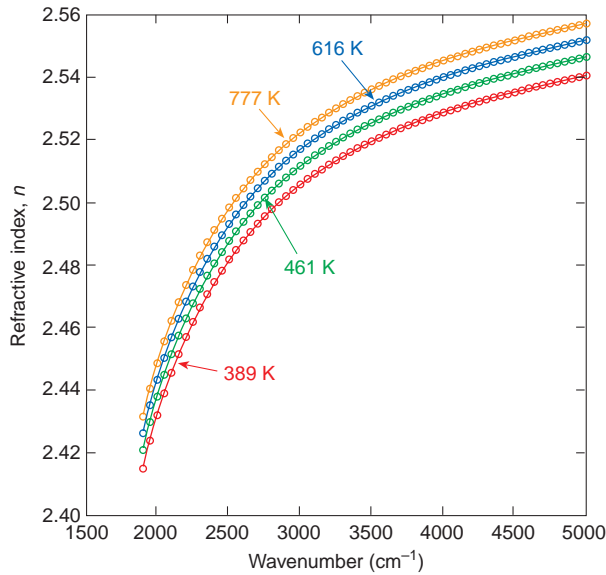
Infrared free spectral range measurements<sup>12</sup> were also made on a sample of optical-quality polycrystalline cubic-phase (or “ $\beta$ ”) silicon carbide produced by Morton<sup>13</sup> using the chemical vapor deposition method. This material, like diamond, has high hardness and thermal shock resistance.

Previous infrared free spectral range measurements were reanalyzed using both the model fitting and index integration methods. These temperature-dependent measurements cover the 1900–5000  $\text{cm}^{-1}$  spectral range spanning the region from the edge of infrared transparency to a low-dispersion region. In this case, the refractive index model includes a complete Sellmeier infrared term:

$$n^2 = 1 + S_0 + \frac{S_1}{\nu_1^2} \nu^2 + \frac{S_2 \nu_2^2}{\nu_2^2 - \nu^2}. \quad (9)$$

The  $S_1/\nu_1^2$  term could not be determined accurately and is set to a constant value based on room-temperature refractive index measurements.<sup>14</sup>

The starting value of refractive index needed in the integration method is the value at 5000  $\text{cm}^{-1}$  derived from the model fit. Figure 4 compares the two methods, which give virtually identical refractive indices. Table 3 gives the model constants derived from the model fitting method. The infrared thermo-optic coefficient derived from both methods is nearly constant



**Figure 4.** Infrared refractive index of polycrystalline  $\beta$ -silicon carbide at several temperatures. Circles are values derived from model fits (see Eq. 9 and Table 3). Curves were determined using the integration method (see Eq. 6).

at  $34 \times 10^{-6}/\text{K}$  from 1900 to  $5000 \text{ cm}^{-1}$ , slightly below the value given in Ref. 12.

Room-temperature infrared refractive index results were combined with visible index data from the literature<sup>14</sup> to form a Sellmeier model that covers the complete range of transparency:

$$n^2 = 1 + \frac{5.58245\lambda^2}{\lambda^2 - (0.1625394)^2} + \frac{2.468516\lambda^2}{\lambda^2 - (11.35656)^2} \cdot (10) \quad (10)$$

## CONCLUSION

Interferometric measurements of optical samples provide valuable information regarding the infrared refractive index (typical accuracy of  $\pm 0.001$ ) and especially the thermo-optic coefficient. New analytical methods were described and, to our knowledge, were applied for the first time. They were used on previously

Table 3. Temperature-dependent refractive index model constants (Eq. 9) for  $\beta$ -silicon carbide (289–777 K).

Parameter	Equation ( $T$ in K)
$1 + S_0$	$6.44669 + 1.76331 \times 10^{-4} T$
$S_1/v_1^2$	$1.45 \times 10^{-9} \text{ cm}^2$
$S_2v_2^2$	$1.88536 \times 10^6 + 51.3412 T \text{ cm}^{-2}$
$v_2^2$	$8.07274 \times 10^5 - 56.65 T \text{ cm}^{-2}$

measured interferometric results for polycrystalline diamond and silicon carbide, giving new results for infrared refractive index and its temperature dependence. Additional materials will be measured and analyzed in the near future.

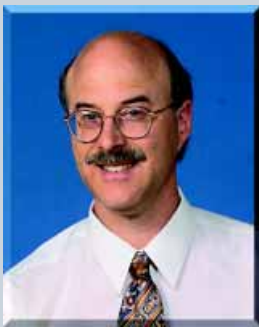
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