The Influence of Refractive Index on the Efficacy of Absolute Reflectance References

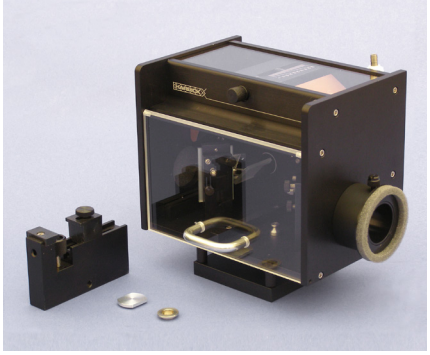

Figure 1. The Seagull™ Variable Angle Reflectance Accessory.

INTRODUCTION

Absolute reflectance measurements are important in the optics industry where they are used for the characterization of materials and coatings. Traditional methods of measuring absolute reflectance are experimentally difficult. However, it has been shown recently that absolute reflectance can be reliably extracted from relative reflectance measurements in the mid-infrared using a specially constructed reference reflector made from a well-characterized and infrared-transparent high refractive index optical material such as Germanium. Since the reflectance reflector is a stand in for a perfect reflector, high reflectivity would seem to be a prerequisite for a good reference. If that were the case, the choice of the optical material for the reference would be restricted to the high refractive index materials.

In this work, we explore the role of the reflectivity of the reference in absolute reflectance measurements. Specifically, the performances of references made from several materials with different well-characterized refractive indices which are non-absorbing in the mid-infrared are explored. The materials investigated include Ge, ZnSe and CaF_2.

THEORETICAL CONSIDERATIONS

Using the relative reflectance method, a specular reflectance accessory is used to collect the spectrum of a sample relative to a known reflectance reference. This gives sample spectrum as the ratio of the sample spectrum at each wavenumber to the reference spectrum at each corresponding wavenumber point. The resulting spectrum is the sample reflectance, R_s, divided by reference reflectance, R_r, as a function of wavenumber k:

$$R(k) = \frac{R_s(k)}{R_r(k)} \qquad (1)$$

To extract the reflectance of the sample from this measurement, the reflectance of the reference must be known at each corresponding wavenumber.

Historically, the materials selected as reflectance references have been highly reflective materials, like aluminum, gold or germanium.

However, there are a number of other materials with lower refractive indices which are optically transparent and for which the optical constants are known to at least four decimal places over the wavenumber ranges of interest.

By selecting materials that are optically transparent, the portion of the refractive index which is responsible for light absorption, known as the absorption index or the imaginary part of refractive index, is negligible and the front surface reflectance can be easily calculated from the Fresnel Equations at any angle of incidence for both polarizations of incident light. For optically transparent materials, reflectance from the back or secondary interface must also be considered. If the reference has two optically polished plane parallel faces, some of the incident radiation transmits through the first interface and partially reflects from the second interface back through the first interface. These additional internally reflected components are difficult to account for theoretically. Thus, the ideal reflectance reference should be designed so radiation reflects solely from the front surface.

With no secondary reflections, the intensity of the first surface reflected component can be described completely by the Fresnel Equations:

$$R_s = \left| \frac{\cos\theta - \sqrt{n^2 - \sin^2\theta}}{\cos\theta + \sqrt{n^2 - \sin^2\theta}} \right|^2 \qquad (2)$$

$$R_p = \left| \frac{n^2\cos\theta - \sqrt{n^2 - \sin^2\theta}}{n^2\cos\theta + \sqrt{n^2 - \sin^2\theta}} \right|^2 \qquad (3)$$

where the subscripts s and p refer to the s and p polarized light respectively, θ is the incident angle and n is the refractive index.

Thus to extract the sample reflectance, R_{s0}, merely take the product of the experimental spectrum, $R(k)$, and the calculated reflectance values of the reflectance reflectance, R_{r0}, at the same wavenumber, polarization and incident angle:

$$R_{s0}(k) = R(k)\, R_{r0}(k) \qquad (4)$$

Note that the sample reflectance, R_{s0}, will only directly follow from the refractive index of the sample through the Fresnel Equations if the sample is also only a front-surface reflector.

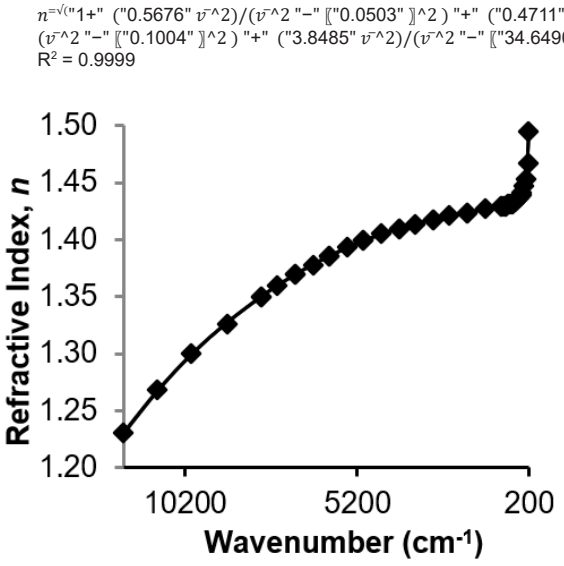

Figure 2. The refractive index, n, of CaF2 as a function of wavenumber.

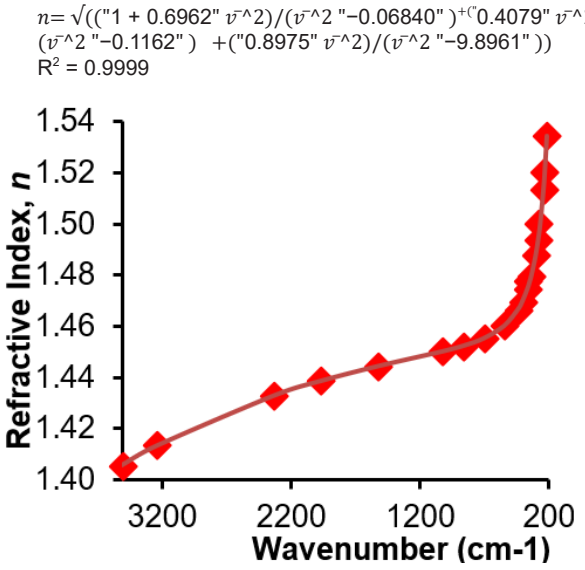

Figure 3. The refractive index, n, of SiO2 as a function of wavenumber.

EXPERIMENTAL

For this work, three candidates were chosen for the reflectance reference: CaF_2, ZnSe and Ge. Ge has been shown previously to work well as a reflectance reference[1] and was included in this study for comparison purposes. All three materials are optically transparent through most of the region and their refractive indices as a function of wavenumber have been extensively investigated[2-10]. The potential reflectance references incorporated a front-surface polished optic and were designed specifically to eliminate second-surface reflectance.

To ascertain the effectiveness of the reference, two samples were examined. Both samples were polished on the front surface and were designed in a similar fashion to the reference to eliminate second surface reflectance. One of the samples, SiO_2, also has a known refractive index over its infrared optically transparent regime and so the results obtained can be compared to theoretical. The other sample investigated was Yittria stabilized ZrO_2 (13 mole% Y_2O_3).

Infrared spectra were collected with Harrick's Seagull variable angle reflection accessory (see Figure 1) installed in a commercial FTIR spectrometer with a DTGS detector. To ensure the best polarization possible, two wire grid polarizers on KRS-5 substrates were installed in the two polarizer mounts supplied with the Seagull.

The incident angle on the Seagull was set for one of the three angles: 30°, 45° or 60°. Then the appropriate reference was installed and the single beam background spectrum was collected. The reference was replaced with one of the two samples and the sample spectrum was measured. All spectra were collected at 8 cm^{-1} resolution and signal-averaged over 32 scans with a reduced aperture. Since these measurements are sensitive to spectrometer stability, the purge gas flow rate and room temperature were stabilized for 12 hours prior to measurements. The experimental data was analyzed as follows. To begin with, the known literature values of the real part of the refractive index as a function of wavenumber were fitted to a curve. Since the literature

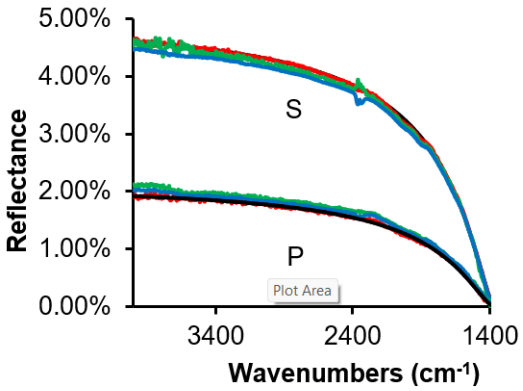

Figure 4. Reflectance of SiO2 extracted from data collected using the CaF_2 (red), Ge (green) and ZnSe (blue) references at 30° for *s*- and *p*-polarizations. Reference values shown in black.

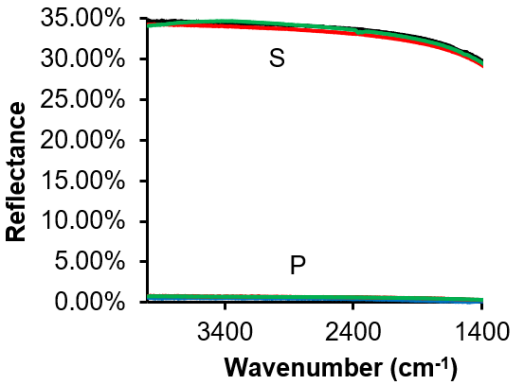

Figure 5. Reflectance of SiO_2 extracted from data collected using the CaF_2 (red), Ge (green) and ZnSe (blue) references at 45° for *s*- and *p*-polarizations. Reference values shown in black.

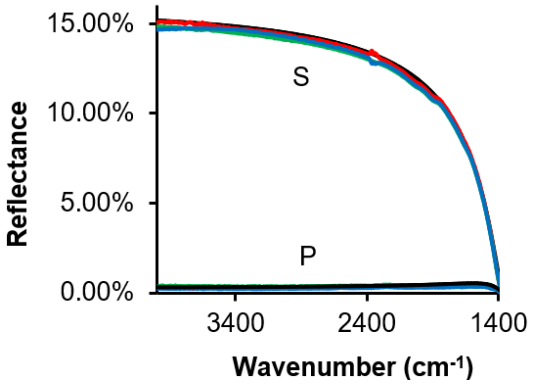

Figure 6. Reflectance of SiO_2 extracted from data collected using the CaF_2 (red), Ge (green) and ZnSe (blue) references at 60° for *s*- and *p*-polarizations. Reference values shown in black.

values of these refractive indices are not known for all wavenumber values of the spectral range, this curve was then used to interpolate the refractive indices for all wavenumbers over which the experimental spectra were collected. Using this refractive index, n(k), the reflectivity of the material, Ge, ZnSe, CaF_2 and SiO_2, was calculated for a given incident angle and polarization in accordance to Eqs. 2 and 3. The extracted theoretical reflectivity of reference was then multiplied by the reflectance measured under the same conditions, per Eq. 4. For SiO_2, the results were compared to the theoretical reflectivity of the sample. For ZrO_2, the results were simply checked for consistency using the three difference references. All data analysis was carried out in Microsoft Excel.

RESULTS AND DISCUSSION

Figures 2 and 3 show the real part of the refractive index, n, as a function of wavenumber for CaF_2 and SiO_2 respectively. The comparable curves for Ge and ZnSe have been published previously[1]. The known literature values are indicated, along with equation for the best fit curve. In both cases, the curves closely fit the data, indicating that a very small error will be introduced due to uncertainties in refractive index values.

Figures 4 through 7 compare the reflectance of SiO_2 extracted from the measured spectra at three angles of incidence using three different references. The theoretical value is also shown for reference. Overall, good agreement and consistency is achieved between the experimental measurements and theoretical values given the experimental constraints detailed below.

It is well-known that infrared spectroscopy is susceptible to problems with thermal stability. For many spectroscopic applications, a high degree of temperature stability is desirable but not essential; instabilities primarily affect the baseline and the baselines are corrected as needed. However, for absolute reflection measurements such as these, the essential information is contained in the baseline,

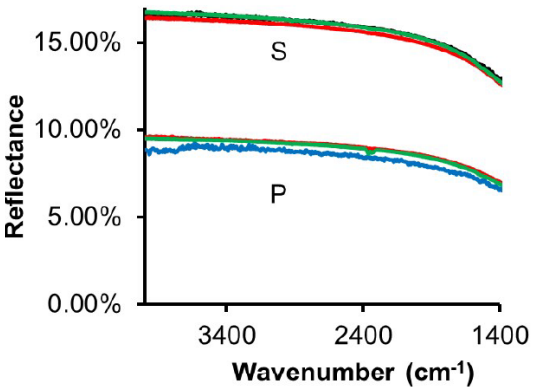

Figure 7. Reflectance of ZrO_2 extracted from data collected using CaF_2 (red), Ge (green) and ZnSe (blue) references at 30° for *s*- and *p*-polarizations.

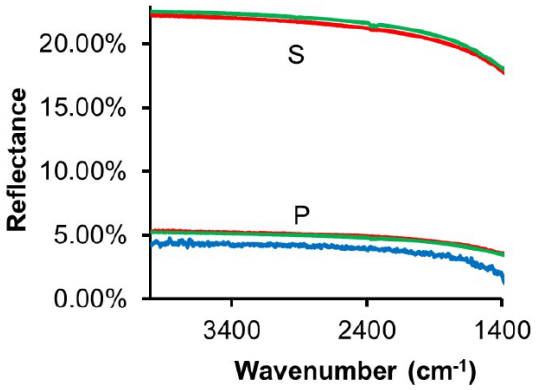

Figure 8. Reflectance of ZrO_2 extracted from data collected using CaF_2 (red), Ge (green) and ZnSe (blue) references at 45° for *s*- and *p*-polarizations.

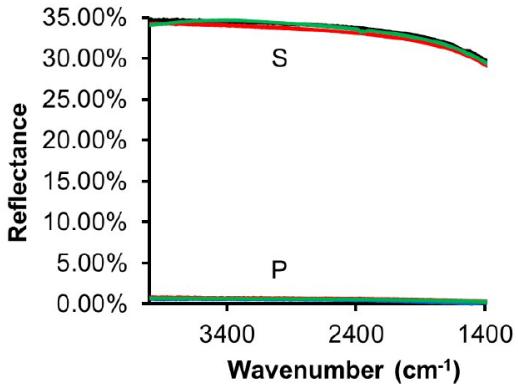

Figure 9. Reflectance of ZrO_2 extracted from data collected using CaF_2 (red), Ge (green) and ZnSe (blue) references at 60° for *s*- and *p*-polarizations.

so thermal stability is critical. While we did our best to minimize the experimental error by stabilizing the ambient conditions, we were not able to sufficiently thermally stabilize the laboratory such that temperature variations would not be reflected in the data. The discrepancies between the measured and theoretical values observed in this work were consistent with thermal drift.

Figures 7 through 9 show the extracted reflectance of Yittria stabilized ZrO_2. Again the results obtained using references of different refractive indices are consistent. Note that the refractive index of Yittria stabilized ZrO_2 has been extensively studied[7,11-13] and no direct comparison is drawn here to the literature values. There are significant inconsistences in the literature which we were unable to resolve and we believe that they are due to inhomogeneities in the crystal structure of the Yittria stabilized material. The reflectance method demonstrated here could be used to extract the refractive indices for a particular lot of material should it be required.

CONCLUSIONS

In this work, the absolute reflectance of SiO_2 was extracted using several reflectance references with different reflectivities. The reflectance of SiO_2 was measured relative to specially designed CaF_2, Ge and ZnSe reflectance reference at 30º, 45º and 60º. The absolute reflectance of SiO_2 was extracted from this measurement using known reflectivity data. The resulting reflectivities were consistent and in good agreement with the theory.

These results demonstrate that relative reflectance measurements can be effectively used to extract absolute reflectivity in the infrared regardless of the reflectivity of the reflectance reference. For best results, the ambient conditions and polarization must be tightly controlled.

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