Introduction

The production of advanced materials requires fast, accurate, and minimal labor-intensive determinations of material parameters. One of the main parameters required for the application of optical materials, in particular crystals, is refractive index (n).

There are three common methodologies for determining refractive index (1-3):

1) Goniometric method

A goniometer-spectrometer is used to measure transmission at angle, including the angles of minimum deviation of light and n is calculated from Snell's law. This method demands a transparent sample in form of a large prism with precise angles between bottom plane and polished working planes.

2) Ellipsometric method

An ellipsometer is used to directly measure amplitude ratios and phase shifts of reflected light.
This method requires a specific optical model for each material. Standard optical models are included in commercial software packages but an optical model may not be included if you have an unknown or new materials.

3) Spectrophotometric methods
A spectrophotometer, with a sampling accessory, can be used to rotate the sample and the detector to angles that allow absolute specular reflectance data to be collected (or angular transmission data).

Spectrophotometric methods can be further broken down into 3 mostly commonly used methodologies:

3.1) The Fresnel formulas
Measurements of reflectance and transmittance of incident light, of p- and s-polarization, are made and n is calculated from the Fresnel equations. This method requires not only large polished sample surfaces but also software support to solve the Fresnel equations.

3.2) Brewster’s law method
Measurement of reflectance for incident light of p-polarization at the Brewster angle (according Brewster’s law). It is necessary to use samples with large surface area to achieve high accuracy measurements for the large angles.

3.3) Method of reflection at near-normal incidence
This method is based on measurement of the reflection spectrum from one surface at low angle of incidence close to the near normal angle (0 deg to approx. 10 deg). This method permits one to determine the dispersion component of the refractive index from a single polished plane of the sample in a single measurement.

Methods 3.2 and 3.3 do not require significant mathematical post data processing and can be introduced to any laboratory equipped with a Cary UV-Vis-NIR spectrophotometer and the Universal Measurement Accessory (UMA), Figure 1.

The Cary 5000 with the UMA eliminates the need to use multiple consoles, sample replacement and accessory reconfiguration. Thus, it is possible to obtain a full description of the sample, without moving it.

The UMA scheme consists of a fixed light source, 360° rotatable sample holder and an independent detector that can move around sample holder in a horizontal plane in the range of angles from 10 to 350°.

The UMA provides high quality data, measuring all the characteristics from a single consistent area of the sample. An advantage of this accessory is the ability to measure the optical characteristics (absolute reflectance and transmittance) under varying incident light polarization and at different angles of incident light in the same area of the sample within one working sequence according to the scheme presented in Fig. 2.

The Cary 5000 with the UMA is a suitable and unique solution if you need to measure the refractive indices of samples and materials including difficult shaped samples, or when it is impossible to produce a sample in the form of a prism.

This study presents the results of the measurements of the refractive indices for new crystals Gd₃Al₂Ga₃O₁₂:Ce (GGAG) (4) using the Cary 5000 with the UMA by two spectrophotometric methods:

1. by Brewster’s law (Method 3.2);
2. by the spectrum of reflection from one surface at low angle of incidence close to normal (Method 3.3).
Experimental

GGAG belongs to the cubic crystal system and, therefore, is characterized by a single refractive index $n$. We obtained the spectral and angular dependence of reflection coefficients of $p$- and $s$-polarized light in the range of angles (6° – 71°). For example, Figure 3 presents the angular dependence of reflection coefficients of $p$- and $s$-polarized light, $R_p$ and $R_s$, respectively, for $\lambda = 589$ nm. The results have been published previously (4).

results and Discussion

Determination of refractive index according to Brewster’s law (Method 3.2).

According to Brewster’s law (2), if the incident light is polarized in the plane of incidence ($p$-polarization), at some angle of incidence reflectivity is close to zero $R \sim 0$. This angle is called the Brewster’s angle $\theta_B$ and is associated with the refractive index $n$ of the material through equation 1 (2):

$$\Theta_B = \arctan \left( \frac{n}{n_0} \right)$$

where $n_0$ is refractive index air ($n_0=1$).

To determine the values of the refractive index, we measured the spectral dependencies of the reflection coefficient at different angles of incidence of $p$-polarized light. Figure 3 presents the scheme of determination of the Brewster angle, for example, of the angular dependence of the reflection coefficient $p$-polarized light at the wavelength of 589 nm, where the angle of incidence was varied from 60° to 65° in 1° increments (area 1). As a result, it was found that the Brewster angle is around 60°. For accurate determination of the minimum angle (the Brewster angle) we used the method of iterations by changing the pitch angle of the incident light from 1° to 0.04° steps. Then using equation (1) we determined $n$.

The same procedure can be applied to other wavelengths. In our case we measured the angular dependence of the $p$-polarized light reflection coefficient at: 400 nm, 425 nm, 589 nm, 650 nm, 700 nm, and 800 nm. For approximation of the refractive index experimental values we calculated the dispersion dependences of refractive index (Figure 4).

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + ...$$

Figure 3. Angular dependence of the reflection of $p$- and $s$-polarized light at $\lambda = 589$ nm (4): 1 – the Brewster angle area, 2 – the area for the method of reflection from one surface at normal incidence of light.

Figure 4. Gd$_3$Al$_2$Ga$_3$O$_{12}$:Ce refractive indices (4). Dotes – measured values, line – the Cauchy dispersion.

Hence, to determine the refractive index, the sequence of actions is as follows:

1) to measure the spectral dependence of the reflectance depending on the angle of incidence of $p$-polarized light beam for wavelength you need (Figure 3);
2) to find the area of angles corresponding the area of minimum value of reflectance;
3) using the method of iterations by changing the pitch angle of the incident light of 1° to 0.04° to measure the angular spectral dependence of the reflectance depending on the determined in step 2 area of angles of incidence of $p$-polarized light beam for wavelength you need;
4) to determine the Brewster angle: it's the angle when the reflectance value is minimum;
5) using equation (1) to obtain the refractive index for this wavelength;
6) repeat steps 1 to 5 for another wavelengths;
7) approximate the refractive indices if necessary.

**Determination of refractive index using the spectrum of reflection from one surface at low angle of incidence close to normal (Method 3.3).**

The scheme for determination of the refractive index according to this method corresponds to the area 2 in Figure 3. According to Figure 3 at low angle of incidence close to normal (up to 10º) intensities of reflection of p- and s- polarized light become close. In this case, the reflection coefficient of light from one surface can be represented as (2):

\[ R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \]

where \( \kappa(\lambda) \) is the extinction coefficient.

According to the formula (3) in order to estimate the refractive index it is necessary to know not only the value of the reflection coefficient \( R \) but also the values of the extinction coefficient \( \kappa \). However, for single crystal Gd3Al2Ga3O12:Ce the values of the extinction coefficient \( \kappa \) is negligibly small even in the absorption bands.

We can transform the formula (3) excluding the extinction coefficient \( \kappa \), and measure the reflection coefficient \( R \) at an angle of incidence close to the normal in the wavelength range of (200 – 720) nm with a step of 1 nm. This way we can calculate the refractive indices \( n \) and construct dispersion curves (Fig. 5) according to the foregoing formula:

\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \]

To avoid the reflection from the second face (the inner surface of the sample) it is better to use sample with a grinding finish surface on the opposite side or a sample with non-planar faces.

Values of \( n \) for GGAG obtained by these two methods are close. So both methods may be introduced in the practice of laboratories. Choice depends on the form of the sample.

To establish the confidence interval of this method we carried out metrological measurements on a reference sample of
fused quartz. We measured the reflection coefficients at the angle of light incidence close to normal, and then calculated the metrological characteristics of the method. For the reference sample, the accuracy was $\pm 0.4\%$. This value falls in the confidence interval of the method.

**Conclusion**

1. A study of the use of the Cary 5000 spectrophotometer with Universal Measurement Accessory was conducted to refractive indices of different types of materials, especially single crystal optical materials, by two spectrophotometric methods
   - Brewster's law method;
   - reflection from one surface at low angles of incidence close to normal.

2. Refractive indices obtained by the two methods were close enough. A laboratory equipped with the Cary 5000 and UMA may choose any method. The best choice depends on the form of the sample.

3. The accuracy of the spectrophotometry method is less than 0.4%.

**References**


