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Refractive index of sodium iodide

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The refractive index of sodium iodide, an important scintillator material that is widely used for radiation detection, is based on a single measurement made by Spangenberg at one wavelength using the index-matching liquid immersion method (Z. Kristallogr. **57**, 494 (1923)). In the present paper, we present new results for the refractive index of sodium iodide as measured by the minimum deviation technique at six wavelengths between 436 nm ($n = 1.839 \pm 0.002$) and 633 nm ($n = 1.786 \pm 0.002$). These six measurements can be fit to a Sellmeier model, resulting in a χ^2 of 1.02, indicating a good fit to the data. In addition, we report on ellipsometry measurements, which suggest that the near-surface region of the air sensitive NaI crystal seriously degrades, even in a moisture-free environment, resulting in a significantly lower value of the refractive index near the surface. First-principles theoretical calculations of the NaI refractive index that agree with the measured values within 0.025-0.045 are also presented and discussed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3689746]

I. INTRODUCTION

Although sodium iodide (NaI) is one of the most important scintillator materials used today for a wide range of radiation detection applications, very little is actually known about its optical properties - particularly its refractive index. This lack of data most likely stems from the fact that NaI is extremely hygroscopic and mechanically soft, which makes sample preparation and subsequent optical properties measurements quite difficult.

The only actual reported measurement of the NaI refractive index in the visible region was performed in 1923 by Spangenberg,[1] who measured the refractive index of small flakes of NaI using the index-matching liquid emersion technique. His measurement resulted in a value of $n = 1.7745 \pm 0.0005$ at a wavelength of $\lambda = 589.3$ nm (i.e., at the sodium D line). Using this as the only data point, as well as literature values for the static dielectric constant, the high-frequency dielectric constant, a weighted average of the ultraviolet absorption peaks, and the infrared absorption peak, Li[2] derived a formula for the wavelength dependence of the refractive index, given by

$$n^2 = 1.478 + \frac{1.532\lambda^2}{\lambda^2 - (170)^2} + \frac{4.27\lambda^2}{\lambda^2 - (86210)^2}, \quad (1)$$

where the wavelength is expressed in nanometers. Although Li classified the quality of the data for NaI as "poor" (see Table I of Ref. 2), this formula is considered to be the standard expression of the refractive index of NaI.[3]

There are two additional measurements of the refractive index of NaI, but these measurements were performed in the ultraviolet wavelength region. Miyata[4] performed reflectivity measurements as a function of temperature from 5 to 11.8 eV. His samples were first cleaved while heating them under the illumination of an infrared lamp and then placed immediately in a vacuum. The measured reflection maximum was 5.63 eV, which is close to the band edge of the material. Later, Itoh and Hashimoto[5] measured the NaI reflection and transmission using a thin sample (100-300 nm thickness) of NaI grown from the melt between two quartz plates. Their measurements were made from 205 to 257 nm (6.05 to 4.82 eV) and showed interference fringes from which the refractive index was determined.

Since the quality of the existing refractive index data for NaI is poor and limited to a single wavelength, we have undertaken to measure the refractive index of NaI at multiple wavelengths in the visible part of the spectrum. To ensure that we are measuring the bulk refractive index, we have used the classic minimum deviation technique using prisms fabricated under controlled dry atmospheric conditions from a single crystal of NaI. We have also taken great care to subsequently minimize the water absorption of the crystal during measurements by constructing an appropriate sealed sample chamber. For comparison purposes, we have also performed spectroscopic ellipsometry measurements in a water-free environment using a similarly prepared NaI crystal. First-principles theoretical calculations of the refractive index have also been carried out.

II. SAMPLE PREPARATION AND EXPERIMENT

A large single crystal of sodium iodide was obtained from Harshaw, Inc., from which a prism was fabricated with an apex angle α of 49.9°. The prism was ~2 cm high with a base width of ~3 cm. The two optical faces were then polished, where the final polish was done using a 3-micron aluminum oxide lapping film. Since the NaI is hygroscopic, it was not possible to use a colloidal silica type polish (e.g., Syton or Nalco) to improve the surface quality. Moreover, NaI is quite soft, so it was impossible to totally eliminate all surface scratches. However, the surface was sufficiently

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TABLE I. Refractive indices of NaI as measured by the minimum deviation method.

Wavelength (nm)	Meas. system	Refractive index
435.8	1	1.839 ± 0.002
488.0	2	1.814 ± 0.002
514.5	2	1.804 ± 0.002
546.1	1	1.799 ± 0.002
578.0	2	1.786 ± 0.002
633.0	1	1.778 ± 0.002

polished so that the refracted light beam was only minimally deviated by surface effects (see below). All of the cutting and polishing steps were performed in a dry nitrogen-purged glovebox with water content < 0.5%. As a check on the measurement systems and technique, we also measured a Schott glass SF-10 prism (apex angle 60°). For the ellipsometry experiments, a sample $\sim 2 \times 2 \times 0.2\ \mathrm{cm}^3$ of NaI was polished in a manner similar to that described above.

The sample chamber for the minimum deviation experiments is shown in Fig. 1. The glass side of the chamber was cut from a fused quartz tube 3 in. in diameter. A glass plate was epoxied onto the bottom of the tube, and the top consisted of another glass plate that incorporated a rubber gasket seal. The tube and valve on the top plate are used to evacuate the chamber. A glass tripod was constructed to hold a small petri dish that was filled with P_2O_5 over the prism to absorb any residual water from the atmosphere inside the chamber. The ellipsometry sample was placed in a similar water-free chamber with fused quartz windows that was over-pressured with nitrogen. In both cases, the samples were mounted in the sample chambers in a dry-atmosphere glove box.

Two minimum deviation experiments[6] were performed using two different light sources. The first experiment used a commercial minimum deviation spectrometer originally constructed by American Optical Spencer that is shown schematically in Fig. 2(a). The light source was a mercury calibration lamp (Newport/Oriel Hg(A)) which has three strong lines in the visible: 435.8 nm, 546.1 nm, and 578 nm (an average of two lines). The second minimum deviation spectrometer was constructed on an optical bench and is shown schematically in Fig. 2(b). The light sources for this measurement were a multi-line Ar^+ laser with emission lines of 457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm and a HeNe laser with an emission line at 632.8 nm. The refractive index n is determined from the angle of minimum deviation δ_m, given by

$$n = \frac{\sin\frac{1}{2}(a + \delta_m)}{\sin\left(\frac{a}{2}\right)}. \quad (2)$$

The ellipsometry experiments were performed using the two-modulator generalized ellipsometer (2-MGE) (Ref. 7) from 300 to 750 nm, where the measurements were performed at several times from 15 min to ~22 h after the sample and sample chamber were removed from the dry atmosphere glovebox. The data was modeled using a three-medium approximation: air/surface overlayer/NaI, where the NaI substrate was approximated using the Sellmeier model,[8,9]

$$n^2 = 1 + \frac{A\lambda^2}{\lambda^2 - \lambda_0^2}. \quad (3)$$

The wavelength is given by λ, and the two parameters are A and λ_o. The surface over-layer was approximated using the Bruggemann effective medium approximation,[10] using 50% voids and 50% substrate. Three fitted parameters were used: surface overlayer thickness, Sellmeier A and Sellmeier λ_o resulting in final reduced χ^2 values in the range of 1.45–2.09, indicating a reasonable fit of the data to the model.

III. RESULTS AND DISCUSSION

As a check on the minimum deviation measurement apparatus, we measured the refractive index of a Schott glass

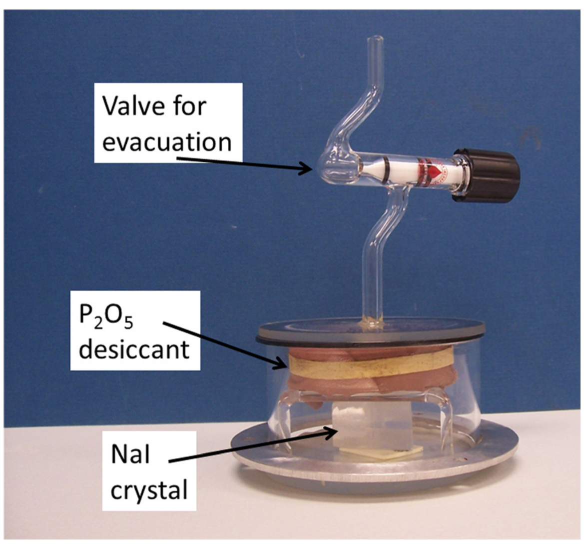

FIG. 1. (Color online) Photograph of the sample chamber used to perform the minimum deviation experiments. The NaI prism is loaded into the chamber inside a controlled atmosphere glovebox with a P_2O_5 desiccant contained in a Petri dish that is supported above the sample. A porous nylon cloth is stretched across the mouth of the Petri dish to prevent dispersal of the desiccant when the chamber is evacuated.

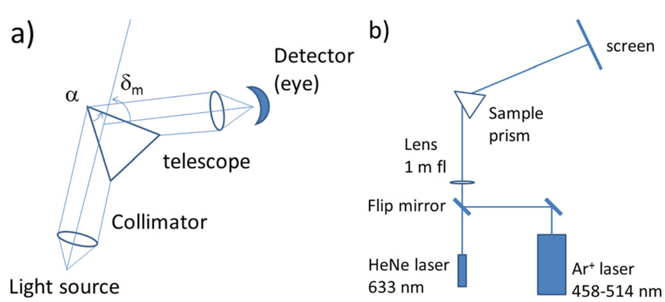

FIG. 2. (Color online) (a) Schematic of a classic minimum deviation spectrometer, where the prism apex angle α and the minimum deviation angle δ_m are clearly shown. (b) Schematic of the minimum deviation system where lasers are used as the light sources. At minimum deviation, the laser light is projected onto a screen ~60 cm from the prism sample. The 1-m focal length lens is placed ~40 cm from the sample, so that the natural divergence of the laser beam is partially corrected.

SF-10 prism with a known refractive index. The glass SF-10 was chosen, since it has a high refractive index [n(633 nm) = 1.723], that is close to the expected value of the refractive index of NaI. When the SF-10 glass prism was inserted into the measurement systems, the resulting optical images at the eye (Fig. 2(a)) or at the screen (Fig. 2(b)) were sharp, and resulted in the determination of the minimum angle of deviation to better than 0.1°. Measurements were taken both with the SF-10 prism inside the chamber shown in Fig. 1 and without the chamber. No significant difference was seen between the measurements. The resulting refractive indices for the SF-10 prism agreed with the published values within 0.001 for all lines measured.

In performing the measurements of refractive index for the NaI crystal, it was found that the images at the eye (system 1) or the screen (system 2) were considerably blurred compared to the measurements using the SF-10 prism, due to the imperfect surface quality of the NaI crystal. While the spots of the 488 and 514 lines at the screen using system 2 were ~1 mm in diameter for the SF-10 prism, the same spots were ~3 mm in diameter when the NaI prism was measured. Because the laser intensity of the 514 and 488 lines from the Ar^+ laser are considerably brighter than the other lines, it was possible to only measure the minimum deviation from the intense laser lines at 488 and 514 nm. The larger NaI spot size resulted primarily in reduced accuracy in the determination of the angle of minimum deviation, and as a result, the refractive index. The measured values of the refractive index of NaI are shown in Table I and in Fig. 3. The line shown in Fig. 3 is a least squares fit to the data using the Sellmeier equation,

$$n^2 = 1 + \frac{1.994\lambda^2}{\lambda^2 - (176)^2}. \tag{4}$$

The reduced χ^2 of the fit is 1.02, indicating a good fit to the data.

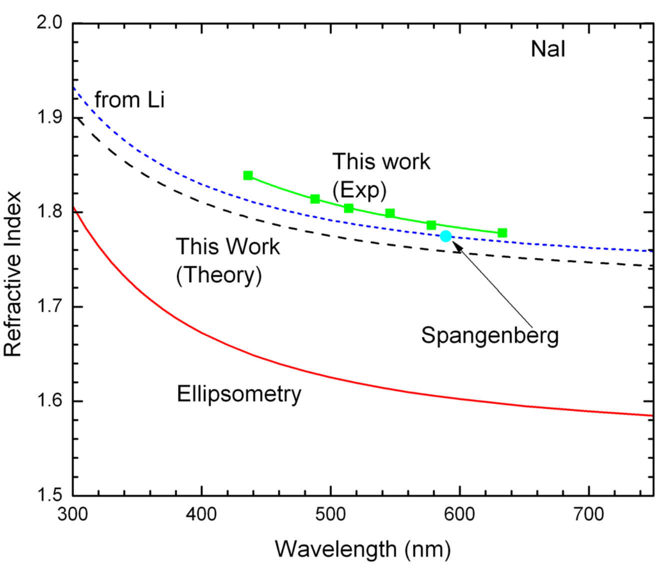

FIG. 3. (Color online) The refractive index of sodium iodide (NaI) as determined by minimum deviation measurements (green, square points) and ellipsometry (red line). The value obtained by Spangenberg (cyan round point, Ref. 1) is also included, as well as the calculated values from Li (blue dashed line, Ref. 2). The theoretical values are also shown (black, long dashed line).

The ellipsometry measurements resulted in a consistent value of the refractive index at all times after the removal of the sample and sample chamber from the dry atmosphere glovebox. The measurements also showed that there was a very small surface over-layer thickness that increased with time. The initial measurement, 14 min after removal, showed that the surface over-layer was 2.6 ± 0.1 nm, increased to 3.3 ± 0.1 nm after 100 min, to 5.3 ± 0.1 nm after 400 min, and to 5.9 ± 0.1 nm after 22 h. The resulting refractive indices were considerably lower than the data determined using minimum deviation, as shown in Fig. 3. At 633 nm, the ellipsometric value of n was 1.597, compared to the minimum deviation value of 1.786 (from Table I).

One possible explanation for this discrepancy is that the refractive index near the surface decreases from the bulk value to a different, lower value at the sample surface. If this decrease is gradual enough, then the ellipsometric measurement will measure the surface refractive index and not the bulk refractive index.[9,11] If the dielectric function profile is linear from the bulk of the material ($\varepsilon_2 = n_2^2$) to the surface of the material ($\varepsilon_1 = n_1^2$), then the criterion for this to be true is[9]

$$\frac{(\varepsilon_1 - \varepsilon_2)^2}{\varepsilon_{ave}^3}\left(\frac{\lambda}{2\pi d}\right)^2 \ll 1, \tag{5}$$

where ε_{ave} is the average of ε_1 and ε_2 and d is the thickness. Therefore, at 633 nm, $\varepsilon_1 = 2.550$, $\varepsilon_2 = 3.120$, and the criterion is $d \gg 13$ nm. That is, if the refractive index decreases from the bulk to the surface over a distance much greater than 13 nm, then the ellipsometric measurement will see only the surface refractive index. The ellipsometry result is in contrast to the minimum deviation method, where the measured refractive index is that of the bulk. This may also explain the smaller difference between the Spangenberg measurement[1] and the minimum deviation results of this paper, since the emersion technique will also exhibit sensitivity to the surface refractive index.

For comparison purposes, we performed calculations of the optical properties of pure NaI. These were done using a recently developed potential functional due to Tran and Blaha,[12] denoted TB-mBJ. This potential greatly improves the bandgap values of simple semiconductors and insulators,[12–15] which is essential for first principles calculations of the optical properties. The calculations were carried out as described in our previous work on the optical properties of other halide scintillators.[16,17] We used the general potential linearized augmented plane wave (LAPW) method, as implemented in the WIEN2k code.[18] We used well-converged basis sets, with LAPW sphere radii of 2.6 bohr for Na and 2.8 bohr for I. The calculations were performed relativistically, including spin-orbit interactions at the experimental lattice parameter $a = 6.47$ Å. The calculated bandgap is direct and has a value of 5.3 eV, which is in much better accord with the experimental value of 5.63 eV (Ref. 4) than the value of 3.3 eV, which we obtained using the standard generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE). We used the TB-mBJ electronic structure with no scissors operator or other adjustment to calculate the optical properties using the optical package of the WIEN2k code. The results of the theoretical calculations of the refractive index are also shown in Fig. 3. As can be seen, the theoretical values are reasonably close to the measured values - being lower by 0.045 at 436 nm and 0.025 at 633 nm.

IV. CONCLUSIONS

The refractive index of NaI has been measured using the classic minimum deviation technique, resulting in values that are accurate to 0.002 over a range of wavelengths in the visible part of the spectrum. The resulting values are slightly higher than the original single measurement by Spangenberg[1] and the subsequent associated calculated values from Li.[2] Ellipsometric measurements of the refractive index were also made, but the resulting values of the refractive index indicate that the refractive index of the surface is considerably less than the refractive index of the bulk. First-principles theoretical calculations were also performed, resulting in refractive indices that are close to the measured values.

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