Letter

Refractive index of pentaerythritol tetranitrate single crystals at 532 nm

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Abstract

The refractive index of pentaerythritol tetranitrate single crystals (110) was measured at atmospheric pressure using the Duc de Chaulnes method and was for the first time determined to be $n = 1.553 \pm 0.009$ at a wavelength of 532 nm.

Keywords : refractive index, pentaerythritol tetranitrate, single crystals, Duc de Chaulnes method

1. Introduction

Pentaerythiritol tetranitrate (PETN), $C(CH_2ONO_2)_4$, is one of the important energetic materials, because it has been used extensively in composite explosives, detonating fuses and detonators. The initiation sensitivity of PETN is high compared with many other energetic materials. Consequently, PETN is often used to study initiation mechanisms. Recently, we have performed miniature flyer impact experiments to investigate shock initiation of PETN single crystals[1]. The particle velocities of PETN shocked along the [110] axis has been measured using an optically recording velocity interferometer system (ORVIS) with a laser light source at 532 nm. The refractive index at atmospheric pressure is needed to precisely measure the particle velocities of shocked PETN.

Various properties of PETN have been previously investigated. The structure of PETN was studied by X-ray diffraction[2]. The results revealed that PETN forms a body-centered tetragonal structure with space-group symmetry $P\text{-}42_1c$ and has two molecules per unit cell at ambient pressure and room temperature[2]. The theoretical density is 1.778 g cm^{-3} [2),3)]. Dick measured the refractive indices of PETN single crystals at the sodium D line using an Abbe refractometer[4]. He reported that the crystal is birefringent ; the ordinary refractive index along the c axis is 1.5559 ± 0.0006 and the extraordinary index is 1.553 ± 0.001. Other sources reported the ordinary and extraordinary indices of PETN to be 1.556 and 1.551, but the wavelength used for the measurement was not specified[3]. Because there are no refractive index data at other wavelengths, it is impossible to estimate a refractive index at 532 nm by using a dispersion formula such as the Sellmeier equation.

In the present work, we measured the refractive index of PETN single crystals (110) at a wavelength of 532 nm using the Duc de Chaulnes method[5].

2. Experimental

2.1 Review of the duc de chaulnes method

This technique is based on the displacement of an image in an optical microscope[5]. It can measure the refractive index of small transparent grains. The method is illustrated in Figure 1 for an isotropic slab sample within the field of view of a microscope. The transparent sample is placed at the focus of the objective lens. The focal plane A in the absence of the sample is displaced to a new position B. The displacement z is equal to the distance the objective lens is moved to refocus it.

Based on geometrical optics and Snell's law in the form $n \sin\theta_r = \sin\theta_m$, the relationship between the refractive index n of the sample, the displacement z of the focal plane, and the thickness d of the sample is

$$n^2 = (1 - a^2) \cdot \left(\frac{d}{d - z} \right)^2 + a^2 \qquad (1)$$

where $a = \sin\theta_m$ is the numerical aperture defined by the

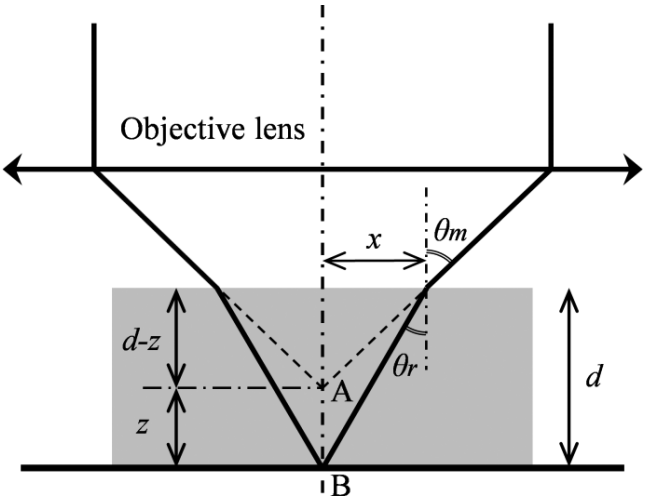

Figure 1 Schematic of the Duc de Chaulnes method.

diameter and focal length of the objective lens. Assuming the field of view is uniformly illuminated, the refractive index can be estimated from Eq. (1) using the known numerical aperture of the lens and the measured parameters d and z.

Use of an objective lens with a short focal length reduces the error in the calculated refractive index arising from the uncertainty in the position of the lens. Use of a thicker sample also reduces the error in the index, but it is limited by the working distance of the objective lens.

2.2 Sample preparation

Wet powdered PETN was obtained from Asahi Kasei Corp. and was dehydrated using a warm air dryer. It was then recrystallized from acetone (purity above 99.5 %, Wako Pure Chemical Industries, Ltd.). Acetone was saturated with PETN and evaporated under ambient conditions. Many transparent grains resulted but they were mostly stuck together. Individual grains were selected out for use as experimental samples. They were approximately rectangular and had a morphology similar to that of PETN single crystals reported previously[6),7)]. Typical dimensions were 0.5 mm × 0.5 mm × 2 mm starting from 15 mL of acetone. Larger specimens with a face size of several millimeters were obtained by starting from a larger quantity of saturated solution. Single grains containing no cracks, pores, or inclusions as observed under a microscope were used as samples.

2.3 Evaluation of the structural quality of the crystals

The samples were evaluated by X-ray diffraction using a diffractometer from Bruker AXS Inc., model Smart APEX II with Mo $K\alpha$ radiation at a wavelength of 0.71073 Å. A crystal with a size of 0.1 mm × 0.1 mm × 0.3 mm was selected as being appropriate in size for the X-ray diffractometer. The X-ray diffraction measurement was performed at 296 (2) K. The analysis revealed that the crystal was body-centered tetragonal with a space-group symmetry of $P\text{-}42_1c$. Its unit cell dimensions were a = 9.3838 (10) Å, b = 9.3838 (10) Å, and c = 6.7114 (7)Å. The R-factor was 2.49 %. The density was calculated to be 1.777 g cm^{-3} and the orientation of the major face was (110). The diffraction analysis indicated that the [110] axis is perpendicular to the major face of the crystals. These results are in good agreement with previously reported data, confirming that the samples were single crystals.

2.4 Experimental apparatus

The refractive index measurements were performed using surface profilometer VF-7510 from Keyence Co. with a 20× objective lens. The microscope image was displayed on a 15-inch CRT display at 500× magnification. The working distance of the objective lens was 2.9 mm. The VF-7510 was employed as an optical microscope with coaxial epi-illumination. The lens was perpendicular to the surface of sample. The microscope had an adjustment for focusing with a finest scale value of 2 μm. Monochromatic light at a wavelength of 532 nm was selected from a halogen lamp (Mejiro Precision Inc., PHL-150) using a 532-nm bandpass filter having a bandwidth of 10 nm (Opto-Line Inc., 532.0 IF10). This light was transmitted via a fiber bundle to the profilometer to illumine the PETN sample. The sample was placed on optically flat glass. Scale marks were scribed on the surface of the glass and used to determine the focal point.

2.5 Calibration of the microscope

The experimental conditions are likely to be different than the ideal situation for which Eq. (1) was derived. For example, the entire field of view may not be uniformly filled with coaxial epi-illumination. To account for such effects, a in Eq. (1) was calibrated against an actual setup. The relationship between the displacement z and the refractive index n was measured for a standard material whose index at 532 nm is known. Optical-quality BK7and synthetic silica glasses were used as standards, whose refractive indices are 1.519 and 1.461, respectively[8)]. The square of the index n^2 is plotted against $[d/(d-z)]^2$ in Figure 2. The value of a in Eq. (1) derived from a least-squares fit to Figure 2 is a = 0.1850.

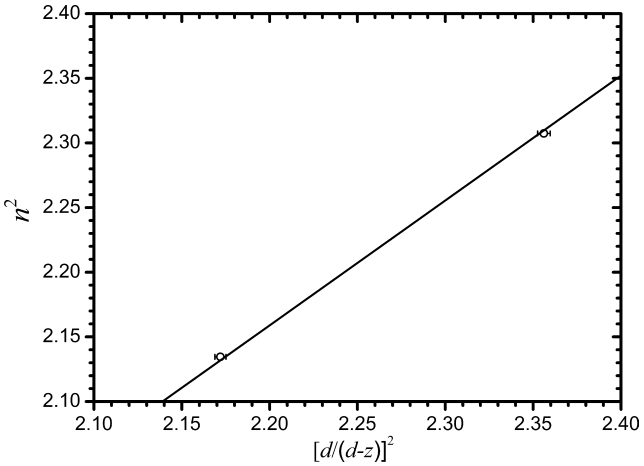

Figure 2 Relationship between n^2 and $[d/(d-z)]^2$ used to calibrate the microscope at a wavelength of 532 nm. Measured data points for the SiO_2 and BK7 glass samples are indicated. The error bars are due to the uncertainty in the displacement of the image.

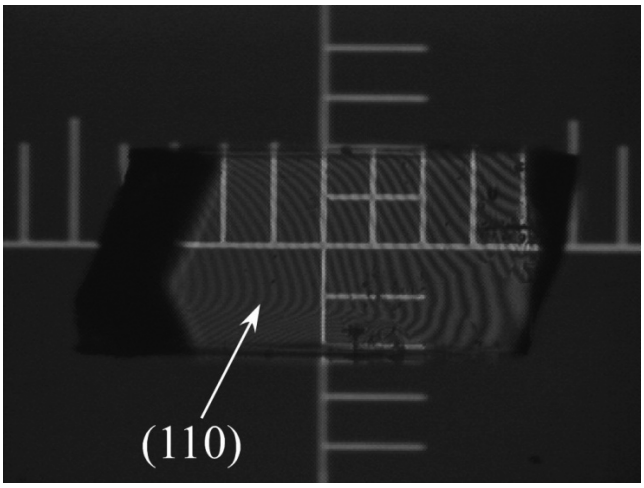

Figure 3 Micrograph of a PETN single crystal (110) illuminated at 532 nm using a 10× objective lens. The smallest increment on the scale is 100 μm.

Table 1 Experimental conditions and results.

Sample	RT[a)] [℃]	AP[b)] [hPa]	d [μm]	z [μm]	n
1	20.8	1018	1837	669	1.557
2	19.9	1008	1714	617	1.547
3	19.9	1008	2598	940	1.551
4	20.7	1008	2688	980	1.558
5	20.7	1008	2157	780	1.550

a) Room temperature, b) Atmospheric pressure.

3. Results

The (110) surface of a PETN single crystal was illuminated at 532 nm. Figure 3 shows a micrograph taken by the VF-7510. Interference fringes are observed at the interface between the glass substrate and the PETN sample, indicating that the sample has a flat surface. Values of $[d/(d-z)]^2$ were measured for five samples with thicknesses ranging from 1.714 to 2.688 mm. Using Eq. (1) with $a = 0.1850$, the refractive index of each sample was computed. The results are summarized in Table 1. The arithmetic mean of the refractive index of PETN (110) at 532 nm is $n = 1.553 \pm 0.009$, where the error bar corresponds to two standard deviations ($\pm 2\sigma$). This result is consistent with the index measured at the sodium D line. PETN single crystal has two refractive indices due to ordinary and extraordinary rays along the plane perpendicular to the [110] axis. Published data[4)] indicate that the difference between the indices for the ordinary and extraordinary ray is 0.0029 at the sodium D line. The present experimental error is larger than this difference and therefore the two indices cannot be separately measured.

4. Conclusion

The refractive index of PETN single crystals (110) was measured at 532 nm using the Duc de Chaulnes method and was found to be $n = 1.553 \pm 0.009$. The apparatus is currently being improved to measure the birefringence and to reduce the experimental error. It is desirable to measure the refractive index at other wavelengths such as 488 and 514.5 nm relevant to an argon-ion laser and 632.8 nm applicable to a He-Ne laser. For such applications, we plan to determine the dispersion formula of PETN single crystals.

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波長532nmに対するペンスリット単結晶の屈折率

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大気圧下におけるペンスリット単結晶（110）面の屈折率をDuc de Chaulnes（デュクドショルヌ）法によって測定した。その結果，波長532 nmに対する屈折率は $n = 1.553 \pm 0.009$であることが分かった。

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