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Optical properties of synthetic crystals of brushite ($CaHPO_4 \cdot 2H_2O$)

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Abstract

The principal refractive indices of brushite ($CaHPO_4 \cdot 2H_2O$) crystals for sodium light, 589 nm, have been determined by a combination of several methods: microscopic interferometry, retardation measurements with an Ehringhaus 6λ compensator, and determination of the angle $2V$ between optic axes from the measurements of extinction directions using a spindle stage and evaluating the data with the computer program EXCALIBRW. The following values were found: $n_\alpha = 1.54089$, $n_\beta = 1.54620$, $n_\gamma = 1.55191$, and $2V = 88.2^\circ$. The standard deviations of the three indices lie in the range $7–8 \times 10^{-5}$. The results are regarded valuable in connection with studies of crystal growth kinetics in biological mineralization and related fields.

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Keywords: A1. Optical microscopy; B1. Calcium compounds; B1. Phosphates

1. Introduction

In kinetic studies of crystal growth, measurement of retardation, also termed optical path difference, of microscopic birefringent crystals is a convenient method for determination of their dimensions in the direction of sight, i.e. thickness, in particular if they are tabular [1–4]. The relation between retardation Δ and thickness d is [5, p. 273, 6, p. 262]

$$\Delta = (n'_\gamma - n'_\alpha)d, \tag{1}$$

where the factor in parentheses is the birefringence for light polarized perpendicular to the line of sight. Needless to say, the accuracy of the method is directly connected with the precision, at which this quantity is known, and this is frequently the weak point.

Calcium hydrogen phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$, known as the rare mineral brushite, is typically observed as the primary crystalline product, when calcium phosphate is precipitated at low pH and low temperature [7,8]. For a sparingly soluble salt it easily forms large, well-developed crystals well suited for morphological [9] as well as optical studies. Crystallographically it belongs to the crystal class m (monoclinic domatic class), i.e. it has a mirror plane as the sole symmetry element. The space group, according to the revised setting of Heijnen and Hartman [10], is Aa. The usual habit is tabular with {0 1 0} as the dominating form. Its frequent occurrence as a precursor for more basic calcium phosphates, particularly apatite, makes it interesting in connection with biological mineralization.

Optical constants of brushite have been reported for more than 100 years [11,12], often with a precision which is not justified by the method of measurement, if any details of this are given at all [13]. Before the advent of the electronic computer, calculation of uncertainties could be rather tedious and were, for this reason, often left out. Another point is that a sample of pure, well-defined crystals of the compound may not be so easy to obtain. The following information is, however, reliable and well established: birefringence is low. The plane of the optical axes is perpendicular to (0 1 0), and so is the acute bisectrix. The angle between the optical axes, $2V$, is normally

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reported to be close to 90°, and for this reason the optical sign is sometimes reported as positive, sometimes as negative [12,14]. Ranges for the values of refractive indices are: n_α, 1.539–1.5412; n_β, 1.544–1.5458; n_γ, 1.549–1.553. With this scatter, the birefringence seen along [0 1 0] would be uncertain by more than 20%.

The object of the present investigation is to provide more exact, reliable values of the optical constants of brushite crystals for use in studies of crystallization kinetics. The methods used include microscopic interferometry, retardation measurements with tilting compensator, and determination of extinction angle as a function of crystal orientation.

2. Experimental procedure

2.1. Apparatus

Crystals were examined with a Zeiss Jenapol polarizing microscope equipped with the following accessories, also manufactured by Carl Zeiss Jena: spindle stage with matching long-distance condenser and objectives, eyepiece micrometer, and Ehringhaus 6λ tilting compensator. Both of the latter were connected, by means of a transducer, to a Zeiss Retarmet 2 dedicated computer, giving direct readout of length or path difference. Length measurements were calibrated using a glass slide with an engraved scale of 1 mm divided into 100 divisions. As the cells delivered with the spindle stage have a rather large volume and turned out not to be leakproof for all immersion liquids used, a device described in Ref. [5, p. 394] was used instead. It consists of a microscope slide, to which two glass blocks close to each other are cemented. When a cover glass is placed over the blocks, a drop of immersion liquid can be held in place between them by capillarity.

Measurements of individual refractive indices were carried out using a Zeiss Jenapol Interphako microscope equipped with a 589 nm interference filter with a bandwidth (FWHM) of 7.5 nm and a Zeiss Velomet photometer for precise location of interference fringes in the image. The measuring compensator was connected via a built-in transducer to the Retarmet 2 computer mentioned above. Refractive indices of immersion liquids were measured with a Zeiss refractometer of the Pulfrich type with thermostated prism with $n_D = 1.62098$ at 18 °C and a temperature coefficient of $-3.5 \times 10^{-6}\,K^{-1}$ [15] and using a sodium lamp as light source. The temperature of the specimen for microscopic interferometry was measured with a small thermistor fixed to the microscope slide with adhesive tape and connected to a Normameter MP 11 in the resistance mode. This instrument gives readings of resistance to four significant digits, and the setup was calibrated against the digital thermometer of the thermostat used with the refractometer to ensure self-consistent results.

2.2. Materials

Brushite crystals for determination of refractive indices were prepared by one of the two methods: (1) brushite powder synthesized from analytical reagent grade chemicals according to Tovborg Jensen and Rathlev [16] was dissolved in dilute acetic acid. After partial evaporation of the solvent, crystals 2–3 mm long and about 1 mm broad were found at the bottom of the vessel. They were filtered off, washed with ethanol and allowed to dry in air. (2) Suitable crystals were collected from precipitation experiments with calcium chloride and potassium phosphate solutions at 40 °C under such conditions that the primary precipitate was amorphous and later crystallized to regular brushite crystals [17].

For refractive index measurements five different immersion liquids were used (literature values for n_D at 20 °C in parentheses [11,18, p. 212]): chlorobenzene (1.52459), nitrobenzene (1.55257), bromobenzene (1.5600), clove oil (1.544), and aniseed oil (1.55). The three pure liquids were purified by fractional distillation, whereas the oils were used as delivered. The refractive indices of all five liquids were measured at different temperatures in the relevant range of 20–30 °C. Values found for the distilled liquids agreed well with literature values. The immersion liquids used with the spindle stage were two oil mixtures with refractive indices 1.5397 and 1.5485.

2.3. Procedures

Two of the principal refractive indices of brushite crystals, n_α and n_β, were measured by dualbeam interferometry, using the shearing method, with total image splitting, of the Interphako microscope [18, p. 188]. The third principal index corresponds to polarization perpendicular to the large (0 1 0) face of the tabular crystals and cannot be measured with this method. The temperature of the specimen was measured several times during each interferometric measurement with thermistor as described above. If the thickness of a crystal had been known with adequate accuracy, measurements in a single immersion liquid of path differences between the crystal and liquid with the two privileged directions of polarization would have been sufficient for determination of the two indices. With two different crystals, one in either of two different liquids, four different path differences are found, and then the two unknown thicknesses may be eliminated from the equations. Using a total of five liquids yields a system with three degrees of freedom, and thus reasonably precise values of the indices may be found by regression analysis. A precision better than ± 1 nm (90% confidence interval) was readily attained on individual path differences. This precision was ensured by repetitive measurements, typically 10.

Another determination of birefringence $n_\beta - n_\alpha$ was carried out on a regular, well-developed crystal from a precipitation experiment. The retardation was measured

with the Ehringhaus compensator, and then the widths of the projections of the lateral dome faces on the (0 1 0) plane were measured with the eyepiece micrometer. Knowing the crystal axes and the Miller indices of the lateral faces [9], the thickness of the crystal may be calculated. The birefringence is then found from Eq. (1) by inserting the mean of the values of thickness found from individual domes. On the same crystal was measured the angle between the fast direction of polarization α- and the c-axis, which is parallel to the longest edge of the crystal, formed by the {1 2 0} dome.

The third principal refractive index, n_γ, was determined by two methods with the aid of the spindle stage. In both methods, which were used simultaneously, a crystal of suitable optical quality was glued to the needle of the spindle in a random orientation, so as to ensure that the spindle axis was not coincident with any of the principal axes of the indicatrix. It was placed in one of the two index-matching liquids mentioned above. Readings were taken for a whole 360° rotation of the spindle in increments of 10°. For each tilting angle S, read on the spindle scale, one of the corresponding extinction directions E_S was determined by visual observation by turning the rotating stage. Then the stage was turned 45° to a subtraction orientation with respect to the Ehringhaus compensator and the retardation measured, still by visual observation. One series of measurements was made with monochromatic light, using the 589 nm interference filter, two others with white light. Before or after a series of measurements the spindle was rotated to bring the crystal into vertical position, and its thickness was then measured with the eyepiece micrometer. In the same position the angle E_0 between the spindle axis and the normal to the (0 1 0) face was measured by turning the stage so as to align first the spindle and then the crystal with the crosshair.

3. Results

Fig. 1 shows an example of an interference image of a brushite crystal with partial image splitting. The two black squares mark positions of the diaphragm of the Velomet photometer. By measuring at identical points in the two images of the brushite crystal, phase shift and thus sensitivity is doubled compared with measurements on the crystal and in the surroundings. Results of these measurements are given in Table 1. For a given immersion liquid, measurements in the α and β directions are made on the same crystal. We have for each path difference g between a crystal of thickness d and the surrounding liquid with refractive index n

$$g = d(n_c - n), \tag{2}$$

where n_c is the refractive index of the crystal corresponding to the given direction of polarization; d is eliminated by division of the two path differences for the same crystal

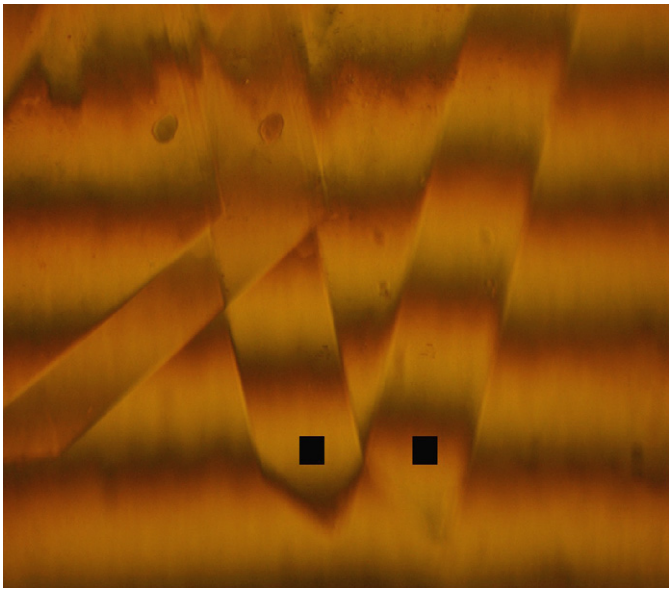

Fig. 1. Interference image of brushite crystal with partial image splitting. Black squares mark identical points in the two images, where fringe displacement is measured.

Table 1
Results from interferometry on brushite crystals

Liquid	Pol. direction	T (°C)	n_l at 589 nm	g (nm)
Chlorobenzene	α	26.28	1.52120	1019.6
	β	26.62	1.52102	1301.6
Nitrobenzene	α	26.47	1.54945	−1027.8
	β	26.30	1.54953	−399.2
Bromobenzene	α	26.38	1.55665	−337.6
	β	26.38	1.55665	−223.7
Clove oil	α	25.52	1.53278	488.5
	β	25.48	1.53280	804.0
Aniseed oil	α	25.45	1.55668	−1097.0
	β	25.97	1.55642	−721.0

and the same liquid:

$$x = \frac{g_\beta}{g_\alpha} = \frac{n_\beta - n_2}{n_\alpha - n_1}, \tag{3}$$

where the refractive index of the liquid equals n_1 or n_2, because the temperature may have changed between the two measurements of path differences. From Eq. (3) we have

$$n_1 x - n_2 = n_\alpha x - n_\beta. \tag{4}$$

Hence, if the left side is plotted versus x, a straight line is obtained with slope n_α and intercept n_β. The plot turns out to be perfectly linear with regression coefficient R^2 deviating from 1 by less than 10^{-8}. The following values were found:

$$n_\alpha = 1.54091 \pm 0.00007, \quad n_\beta = 1.54617 \pm 0.00008,$$
$$n_\beta - n_\alpha = 0.00526 \pm 0.00011.$$

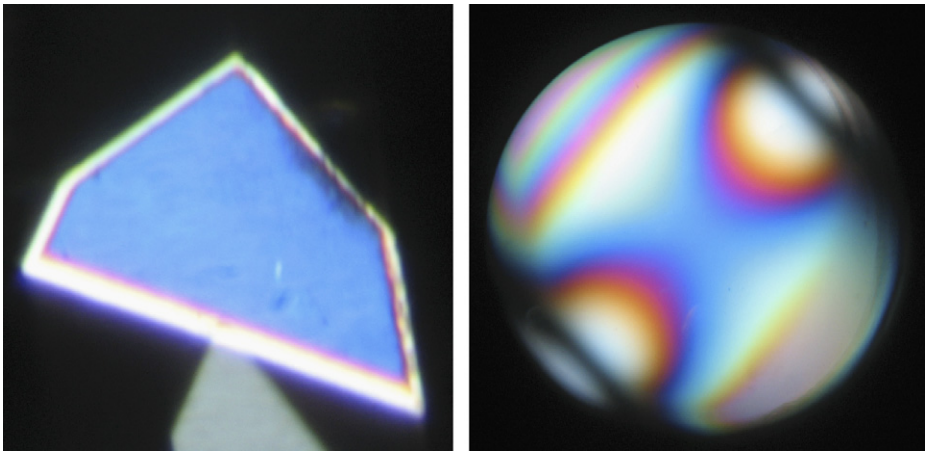

Fig. 2. Left: brushite crystal used for determination of birefringence. The long edge is 0.56 mm. Right: interference figure of crystal at left at numerical aperture 1.30.

The regular crystal showed interference color of second-order blue and is shown together with its interference figure in convergent light (conoscopic observation) in Fig. 2. Its retardation as measured with the Ehringhaus compensator was

$$\Delta = 606.5 \pm 1.8\,\text{nm}.$$

Table 2 shows the other values found for this crystal; b is the width of the projection of a lateral dome face on the (0 1 0) plane (contour of light color in Fig. 2), v is the angle between such a face and (0 1 0), and the thickness d is found as

$$d = 2b \tan v, \tag{5}$$

assuming that the lateral dome forms are symmetric. The weighted mean of the thickness, also given in Table 2, together with Δ yields the birefringence

$$n_\beta - n_\alpha = 0.00534 \pm 0.00008.$$

Finally, the weighted mean birefringence from the results of the two methods, which are not significantly different, is

$$n_\beta - n_\alpha = 0.00531 \pm 0.00007.$$

Fig. 4 shows a drawing of a regular brushite crystal and its stereographic projection. The angle between the α direction and the c-axis equals 15.2°.

The data from measurements of corresponding tilting and extinction angles, (S, E_S), were analyzed as indicated by Bloss [6, Chapter 6], using the computer program EXCALIBRW [19], a Windows version of the original EXCALIBR [6,20]. The program adjusts the orientation of the indicatrix, as well as the angle $2V$ between the optic axes, until the best fit is obtained, between the calculated and observed values of E_S, for the given values of S. Fig. 3 shows the stereographic plots, generated by the program, of results for the two crystals studied, indicating the measured angles (S, E_S) as well as directions of optic axis, bisectrices, and optic normal. The spindle axis is horizontal in the plots. Numerical values are given in Table 3.

Table 2
Measurements on regular brushite crystal

Face	b (μm)	v (deg)	d (μm)
(1 2 0)	37.2±1.3	56.07	111±4
(1 2 2)	22.7±0.7	67.33	109±3
(1 1 1)	17.6±0.9	71.07	103±5
(1 1 1)	13.7±0.5	78.45	134±5
(0 1 1)	21.2±0.6	69.79	115±3
Mean			114±2

Assuming that refraction at the interface between crystal and immersion liquid is negligible as a result of nearly perfect index matching, we may calculate for each value of S the distance d' travelled in the crystal by a light ray parallel to the microscope axis from

$$d' = \frac{d}{\sin E^0 \sin(S - S^0)}, \tag{6}$$

where S^0 is the angle read on the spindle scale, when the crystal is in the vertical position. The birefringence for this orientation, $n'_\gamma - n'_\alpha$, is found by division of the measured retardation by d'. The angle θ between an optic axis of the crystal and the microscope axis is calculated from Ref. [6, p. 275]:

$$\cos\theta = \sin E_{\text{OA}} \cos[S_{\text{OA}} - (S + 90°)], \tag{7}$$

where the values of E_{OA} and S_{OA} for each optic axis are given in the output from EXCALIBRW. Given the two values of θ, θ_1 and θ_2, we have [5, p. 303ff, 6, p. 276ff]

$$\frac{1}{n'^2_\alpha} - \frac{1}{n'^2_\gamma} = \left(\frac{1}{n^2_\alpha} - \frac{1}{n^2_\beta}\right) \sin\theta_1 \sin\theta_2. \tag{8}$$

As the two individual refractive indices on the left side of this equation are not known from measurement with the tilting compensator, which yields only their difference, we

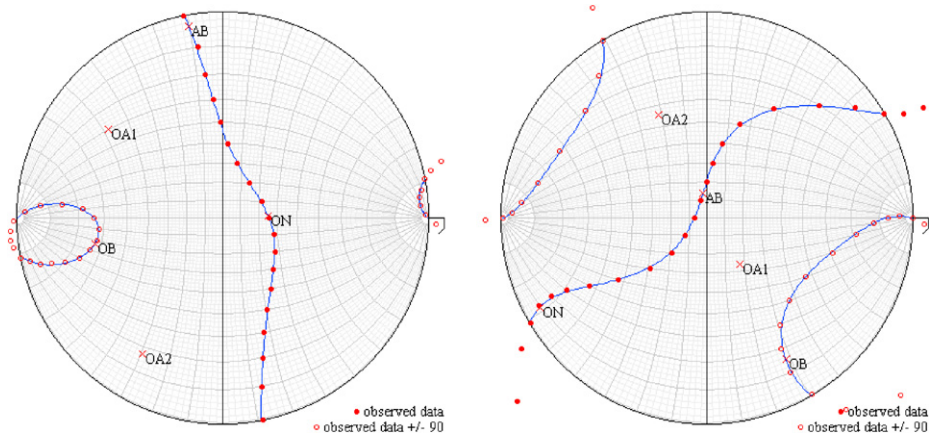

Fig. 3. Stereographic plots of results from measurements with spindle stage on two brushite crystals. OA1 and OA2: optic axes. AB: acute bisectrix. OB: obtuse bisectrix. ON: optic normal.

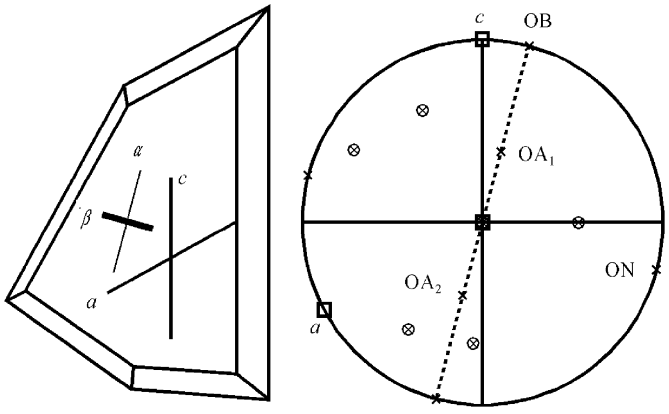

Fig. 4. Drawing of brushite crystal and its stereographic projection, indicating structural axes a and c, polarization directions α and β, optic axes OA_1 and OA_2, obtuse bisectrix OB, and optic normal ON.

must use an approximation, valid for low birefringence as in the present case. Eq. (8) may be rewritten

$$\frac{n'_\gamma + n'_\alpha}{n'^2_\gamma n'^2_\alpha}(n'_\gamma - n'_\alpha) = \frac{n_\gamma + n_\alpha}{n^2_\gamma n^2_\alpha}(n_\gamma - n_\alpha)\sin\theta_1 \sin\theta_2. \quad (9)$$

As the various refractive indices are not widely different, the values of the two fractions in front of the parentheses on either side are very nearly identical. We thus end up with the simplified equation

$$n'_\gamma - n'_\alpha = (n_\gamma - n_\alpha)\sin\theta_1 \sin\theta_2, \quad (10)$$

from which the total birefringence $n_\gamma - n_\alpha$ maybe obtained. With certain orientations of the crystal the retardation exceeds 6λ, which is the limit for the Ehringhaus compensator used. Thus, for crystal no. 1 we have 26 readings and for no. 2, 32 readings instead of the maximum of 36. The means of total birefringence for each series of measurements are given in the last column of Table 3 together with the overall mean.

Table 3
Results from measurements with spindle stage

Crystal no.	Light	$2V$ (deg)	d (μm)	$n_\gamma - n_\alpha$
1	589 nm	88.8±1.3	102.4±0.5	0.01115±0.00008
1	White	88.4±0.6	103.1±0.4	0.01105±0.00005
2	White	89.2±0.4	106.6±0.5	0.01088±0.00012
Mean		88.9±0.3		0.01105±0.00004

Knowing $2V$, we may calculate n_γ from the equation [6, p. 92]

$$\tan^2 V = \frac{(1/n^2_\alpha) - (1/n^2_\beta)}{(1/n^2_\beta) - (1/n^2_\gamma)}, \quad (11)$$

using the two other principal refractive indices found by interferometry. The result is

$$n_\gamma = 1.55169 \pm 0.00019.$$

On the other hand, the retardation measurements yield

$$n_\gamma = 1.55196 \pm 0.00008.$$

The weighted mean from the two methods is

$$n_\gamma = 1.55191 \pm 0.00008.$$

4. Discussion

One of the relations used above to obtain optical parameters from experimental data, Eq. (9), is an approximation. This approximation was necessary, because not all the information necessary for using the exact equation (8) was available. We should now check the validity of the approximation. This will be done by calculating the result for three special settings of the crystal: (1) viewed along the acute bisectrix, (2) viewed along the optic normal, and (3) viewed along the obtuse bisectrix.

In the first case we have

$$\theta_1 = \theta_2 = V, \quad n'_\alpha = n_\alpha, \quad n'_\gamma = n_\beta.$$

In the calculation we should not use the value of $2V$ in Table 3, but the one calculated from Eq. (11) with the values of the three refractive indices found above, i.e. $2V = 87.8^\circ$, to ensure consistency. Insertion in Eq. (10) and solving for $n_\gamma - n_\alpha$ yields

$$n_\gamma - n_\alpha = 0.01094.$$

This gives a systematic error of -0.00006. In the second case it is easily seen that the error is 0. Finally, in the third case we have

$$\theta_1 = \theta_2 = 90^\circ - V, \quad n'_\alpha = n_\beta, \quad n'_\gamma = n_\gamma,$$

which yields

$$n_\gamma - n_\alpha = 0.01106,$$

i.e. a systematic error of 0.00006. The systematic errors in the extreme cases thus lie within the standard deviation, and positive and negative errors tend to be equally frequent. Hence there is no need for further refinement. There are, however, two inconsistencies in the above results: (1) the value adopted for the birefringence $n_\beta - n_\alpha$ is not exactly equal to the difference between the individual refractive indices found from interferometry, and (2) the value of $2V$ issuing from Eq. (11) is not the same as that found from (S, E_S) data using EXCALIBRW. The first inconsistency may be removed by decreasing n_α by 0.00002 and increasing n_β by 0.00003 (the standard deviation of the latter is slightly higher than that of the former). This adjustment gives us two new values of n_γ:

$$\text{From } 2V, \qquad n_\gamma = 1.55178,$$
$$\text{From retardation}, \quad n_\gamma = 1.55194.$$

The difference thus decreases from 0.00027 to 0.00016, but the weighted mean does not change. The new refractive indices yield

$$2V = 88.2^\circ.$$

In conclusion, we regard the following values for the refractive indices as the most reliable results of the present investigation:

$$n_\alpha = 1.54089, \quad n_\beta = 1.54620, \quad n_\gamma = 1.55191.$$

The standard deviations of the three values lie in the range $7\text{–}8 \times 10^{-5}$.

With the present results it is possible to determine the thickness of regular brushite crystals, and hence the crystal growth rate, with a precision of about $\pm 1.3\%$, provided that a good measuring compensator of the Ehringhaus, Berek, or Senarmont type is available. Knowledge of n_γ makes it possible to estimate and correct for the effect of misalignment of the crystal. Of course, only regular crystals can be measured with this precision. Irregular crystals and crystals with elongated and more or less pronounced parallelogram habit often appear rather thin as judged from their interference color, typically first-order gray. The extinction angle, measured from one of the long parallel edges, often deviates by several degrees of arc from the value found above for the regular crystal. Further, in conoscopic observation with an objective with numerical aperture 0.95, both melatopes are often seen in the field in 45° position; this indicates a value of $2V < 66^\circ$. For such a crystal we cannot count on the birefringence found in the present study. Thus, irregular growth is connected with structural disorder such as, e.g. multiple twinning, causing optical anomalies.

The results have been obtained with equipment which, for the major part, is no longer manufactured by Zeiss. In particular, the Pulfrich refractometer is a very old instrument. It is, however, significantly more precise than the conventional Abbe refractometer, where the smallest division corresponds to 0.001 in the refractive index. Still, it requires a relatively small amount of liquid as compared to most interferometers, the alternative for precise measurements. An exception to this is the microinterferometric devices delivered with the Interphako microscope. They consist of microscope slides, in which a small groove with precisely known depth is made in the glass, the refractive index of which is also known precisely. These have not been used in the present investigation, but would probably be a useful alternative to the Pulfrich refractometer in future work.

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