

Measurement of the Refractive Indices of Several Crystals

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An all-reflector spectrometer is used to measure the refractive indices of the cubic crystals ZnS, GaP, SrTiO₃, and Y₃Al₅O₁₂; the tetragonal crystals rutile, CaWO₄, SrMoO₄, CaMoO₄; the hexagonal crystals LiTaO₃, CdSe, ZnO, and AlPO₄; and the monoclinic crystal ZnWO₄. Most of these are measured in the wavelength range 0.4 to 4 μ.

BEYOND measurements for the sodium *D* line there is little published data on the refractive indices of crystals. This is especially true for noncubic crystals in general, and for biaxial crystals in particular. To improve this situation somewhat we have made prisms from available crystals and measured the indices by the method of minimum deviation.

In the method of minimum deviation the prism is placed in a parallel beam of light so that the prism deflects the beam. The prism is then turned about an axis parallel to the prism edge to a position where the deflection *D* is a minimum. The refractive index *n* is then given by the equation:

$$n = \sin[(A+D)/2] / \sin A/2, \quad (1)$$

where *A* is the prism angle. By differentiating Eq. (1) we find that to determine *n* to an accuracy ±δ*n* we must measure *D* to an accuracy

$$\delta D < 2(\delta n/n) \tan(A+D)/2. \quad (2)$$

Hence, if (A+D)/2 is 45° (a reasonable value) and *n* is 2, we need to measure *D* to better than 20'' in order to measure *n* to the fourth decimal. This also means that the prism length, normal to the prism edge, would need to be 40 mm for light of wavelength 4 μ if the diffraction pattern limits the precision. However, one can find the center of a diffraction pattern well enough that a prism of 10 mm length should be adequate.

Examination of Eq. (1) also shows that to determine *n* to an uncertainty δ*n* one needs to know *A* better than to an uncertainty δ*A* where

$$\delta A < 2(\sin^2 A/2 / \sin D/2) \delta n. \quad (3)$$

Hence for *A* = 40°, *D* = 46° (*n* ~ 2) we must know *A* to better than 12'' if we wish to determine *n* to ±10⁻⁴.

We should note one other requirement on *A*. Unless

$$A < 2 \sin^{-1}(1/n),$$

light will not pass through the prism, but will be totally reflected. Hence a 60° prism limits one to measurement of indices below 2, a 40° prism to indices below 2.9.

We also need to know what precision is required in positioning the prism at minimum deviation. Analysis shows that if the prism is turned from its position of minimum deviation, through angle δ*p* about an axis parallel to its edge, an error in *n* of δ*n* is made, where

$$\delta p = \left\{ \frac{\sin A \cos A/2}{\sin D/2 \cos 1/2(A+D)} \delta n \right\}^{\frac{1}{2}}. \quad (4)$$

Hence, to determine *n* = 2 to an accuracy of 10⁻⁴, with *A* = 40° and *D* ≈ 46° requires the prism to be within 0.6° of its minimum deviation position.

Cubic crystals require no special orientation, but noncubic crystals do require special orientation. The prism-bisecting plane of uniaxial crystals must contain the optic axis *c* if Eq. (1) is to apply. In this case at minimum deviation the wave breaks up into two waves traveling at different speeds, both components having wave normals perpendicular to the bisecting plane. One component has an electric-current vector perpendicular to *c* but in the bisecting plane; this is the ordinary wave and the refractive index for this component is called ω. The other component has its electric vector along *c*; the refractive index for this, the extraordinary wave, is called ε. From measurements of *D* for these two observed beams ω and ε can be determined by means of Eq. (1) since this equation applies directly.

If *c* does not lie exactly in the bisecting plane, we do not measure a principle index but an index in a general direction. However, we will misinterpret this as a principal index. Let us assume a coordinate system with *y* in the prism-bisecting plane and perpendicular to the prism edge. We assume *c* along *z* but out of the prism-bisecting plane by amount Δ₁, due to the error in making the prism. The wave normal inside the prism is hence the vector [1, 0, Δ₁]. The current vectors are [0, 1, 0] and [Δ₁, 0, 1]. The index for the current vector *j* is given by

$$n^{-2} = j_{tr} l j, \quad (5)$$

where the matrix *l* for a uniaxial crystal, *z* chosen along *c*, *y* along *b*, is

$$l = \begin{pmatrix} \omega^{-2} & 0 & 0 \\ 0 & \omega^{-2} & 0 \\ 0 & 0 & \epsilon^{-2} \end{pmatrix}, \quad (6)$$

and *j*_{tr} is the transpose of vector *j*. Setting *j*_{tr} = [Δ₁, 0, 1], (5) and (6) give us

$$n^{-2} = \epsilon^{-2} + \Delta_1^2 \omega^{-2}. \quad (7)$$

Obviously the error in determining ε⁻² is Δ₁²ω⁻² and *n* = (ε - 1/2ε³ω⁻²Δ₁²). Here 1/2ε³ω⁻²Δ₁² is the error in *n*, i.e., *dn*. To leave an error less than *dn* we must have

$$\Delta_1 < (2\omega^2 \epsilon^{-3} dn)^{\frac{1}{2}}. \quad (8)$$

As an example, in measuring rutile at 0.6 μ, where ω = 2.58, ε = 2.88, we must orient the crystal to better

TABLE I. X-ray data for orienting the nonisometric crystals.

Rutile, TiO ₂	Tetragonal	$a_1=4.58 \text{ \AA}$,	$c_0=2.95 \text{ \AA}$
CaWO ₄	Tetragonal	$a_0=5.23 \text{ \AA}$,	$c_0=11.44 \text{ \AA}$
SrMoO ₄	Tetragonal	$a_0=5.394$,	$c_0=12.020$
CaMoO ₄	Tetragonal	$a_0=5.23 \text{ \AA}$,	$c_0=11.44$
LiTaO ₃	Rhombohedral	$a_0=5.159$	$c_0=14.76$
CdSe	Hexagonal	$a_0=4.299$	$c_0=7.010$
ZnO	Hexagonal	$a_0=3.249$	$c_0=5.205$
AlPO ₄	Trigonal	$a_0=4.942$	$c_0=10.97$
ZnWO ₄	Monoclinic	$a_0=4.9175, b_0=5.73,$ $c_0=4.6806, \beta=90^\circ 36.5'$	

(measurements of A. S. Cooper at B. T. L.)

than 19'. This is easily done by the use of x-rays. If material is plentiful, it is preferable to make c parallel to the prism edge or perpendicular to it; but if material is scarce, a larger prism can be made by allowing c to lie where it will in the prism, bisecting plane. This more general approach complicates the x-ray work.

BIAXIAL CRYSTALS

Orthorhombic, monoclinic, and triclinic crystals are biaxial and the difficulty of determining the refractive indices increases in this order. For an orthorhombic crystal one needs but two prisms, with the prism-bisecting plane of each a coordinate plane (100, 010, or 001) but not the same plane for both. For example, if (100) is one prism-bisecting plane, the other can be (010) or (001). One index is determined twice.

MONOCLINIC CRYSTALS

The standard setting for monoclinic crystals is " b the unique axis (i.e., the binary axis or perpendicular to a plane of symmetry) and $c < a$, β obtuse." With this setting we choose a z axis along c , a y axis along b , the l matrix of Eq. (5) being written:

$$l = \begin{pmatrix} l_{11} & 0 & l_{13} \\ 0 & l_{22} & 0 \\ l_{13} & 0 & l_{33} \end{pmatrix}.$$

A rotation of the coordinate axes counterclockwise of amount ρ diagonalizes the l matrix to:

$$l' = \begin{pmatrix} l_1 & 0 & 0 \\ 0 & l_2 & 0 \\ 0 & 0 & l_3 \end{pmatrix}.$$

l_1, l_2 , and l_3 are considered to be fundamental, l_{11} , etc., derived constants. The axes are now $x', y' (=y)$, and z' . Conversely, a clockwise rotation of amount ρ will re-establish the axes $x, y, z (=c)$ and l will transform as

$$l = a'l'a^{-1}, \quad (9)$$

where

$$a = \begin{pmatrix} \cos\rho & 0 & \sin\rho \\ 0 & 1 & 0 \\ -\sin\rho & 0 & \cos\rho \end{pmatrix}.$$

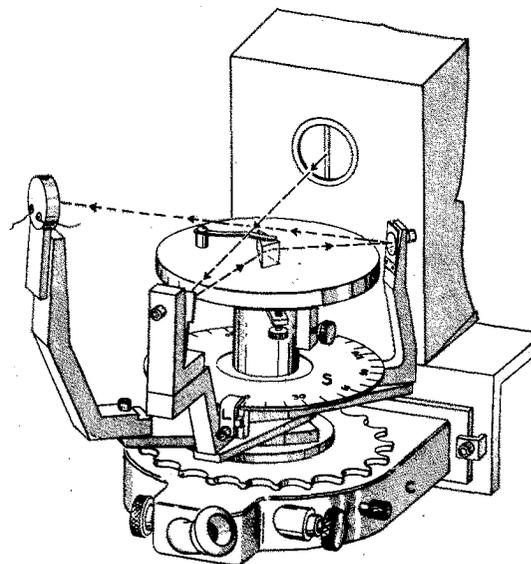


FIG. 1. Reflection spectrometer.

Hence

$$\begin{aligned} l_{11} &= l_1 \cos^2\rho + l_3 \sin^2\rho, \\ l_{13} &= \frac{1}{2}(l_3 - l_1) \sin^2\rho, \\ l_{22} &= l_2, \\ l_{33} &= l_1 \sin^2\rho + l_3 \cos^2\rho. \end{aligned} \quad (10)$$

A prism in which a plane ($hk0$) makes an acute angle with a plane ($h'k'0$) with (010) as the prism-angle bisector causes the wave normal to be parallel to the

 TABLE II. Results for cubic crystals.^a

$\lambda(\mu)$	ZnS	GaP	SrTiO ₃	Yttrium aluminum garnet (YAG)
0.4				1.8650
0.45	2.4709			1.8532
0.5	2.4208			1.8450
0.6	2.3640	3.4595 (54 μ)	2.537	1.8347
0.7	2.3333	3.2442	2.402	1.8285
0.8	2.3146	2.1830	2.363	1.8245
0.9	2.3026	3.1430	2.340	1.8222
1.0	2.2932	2.1192	2.326	1.8197
1.1		3.0981	2.315	1.8170
1.2	2.2822	3.0844	2.306	1.8170
1.4	2.2762	3.0646	2.299	1.8152
1.6	2.2716	3.0509	2.287	1.8121
1.8	2.2680	3.0439	2.279	1.8093
2.0	2.2653	3.0379	2.270	1.8065
2.2	2.2637	3.0331	2.264	1.8035
2.4	2.2604	3.0296	2.258	1.8004
2.6		3.0271	2.2524	1.7970
2.8		3.0236	2.2490	1.7935
3.0		3.0215	2.2395	1.7896
3.2		3.0197	2.2315	1.7855
3.4		3.0181	2.2236	1.7810
3.6		3.0166	2.2143	1.7764
3.8		3.0159	2.2058	1.7713
4.0		3.0137	2.1951	1.7659
				1.7602

^a The ZnS was from San Antander, Spain and was not transparent beyond 2.4 μ . The other three were synthetic, the GaP being grown by Lincoln Derik of B.T.L., the YAG by L. Van Uitert and J. Rubin of B.T.L., the SrTiO₃ was commercial material from the National Lead Company.

TABLE III. Results for tetragonal crystals.^a

λ	Rutile		CaWO ₄		SrMoO ₄		CaMoO ₄	
	ω	ϵ	ω	ϵ	ω	ϵ		
0.4								
0.45	2.8087	3.1465	1.9497	1.9684	1.9424	1.9497	2.0317	2.0448
0.50	2.4058	2.9990	1.9351	1.9523	1.9263	1.9311	2.0116	2.0239
0.60	2.6034	2.8900	1.9181	1.9343	1.9064	1.9110	1.9884	1.9983
0.70	2.5514	2.8255	1.9089	1.9283	1.8952	1.8993	1.9775	(1.9843)
0.80	2.5213	2.7866	1.9023	1.9173	1.8881	1.8917	1.9683	(1.9761)
0.90	2.4995	2.7612	1.8977	1.9123	1.8834	1.8864	1.9634	1.9705
1.00	2.4880	2.7430	1.8944	1.9089	1.8797	1.8827	1.9597	1.9658
1.10							1.9561	1.9625
1.20	2.4647	2.7193	1.8892	1.9040	1.8747	1.8774	1.9528	1.9588
1.40	2.4514	2.7024	1.8863	1.9004	1.8711	1.8736	1.9492	1.9563
1.60	2.4413	2.6002	1.8835	1.8975	1.8683	1.8708	1.9459	1.9518
1.80	2.4320	2.6793	1.8811	1.9848	1.8660	1.8683	1.9422	1.9483
2.00	2.4238	2.6698	1.8787	1.8924	1.8635	1.8649	1.9393	1.9457
2.20	2.4157	2.6600	1.8760	1.8896	1.8611	1.8634	1.9362	1.9420
2.40	2.4088	2.6501	1.8733	1.8862	1.8590	1.8606	1.9335	1.9390
2.60			1.8706	1.8834			1.9305	1.9360
2.80			1.8679	1.8813			1.9271	1.9327
3.00			1.8648	1.8783			1.9240	1.9294
3.20			1.8615	1.8749			1.9201	1.9255
3.40			1.8579	1.8713			1.9162	1.9215
3.60			1.8542	1.8675			1.9120	1.9174
3.80			1.8502	1.8635			1.9075	1.9130
4.00			1.8457	1.8593				

^a The TiO₂ was from the Linde Company, the CaWO₄ and SrMoO₄ were grown by K. Nassau of B.T.L., and the CaMoO₄ by L. G. Van Uitert of B.T.L.

b axis at the position of minimum deviation. On the primed axes x' , y' , z' the possible displacement current vectors are $[100]$ and $[001]$. Applying Eq. (5) we then find two of the fundamental indices:

$$\begin{aligned} n_{x'}^{-2} &= l_1, \\ n_{y'}^{-2} &= l_3. \end{aligned} \quad (11)$$

Fundamental indices are hence measured directly on such a prism.

A prism in which a plane $(hk0)$ makes an acute angle with $(h\bar{k}0)$ with (100) as the prism-bisecting plane causes x to be the wave normal at minimum deviation. The two possible displacement current vectors are $[010]$ and $[001]$. By Eq. (5) $n_y^{-2} = l_2$ so that a third fundamental index is measured directly. Similarly

$$n_z^{-2} = l_{33} = l_1 \sin^2 \rho + l_3 \cos^2 \rho.$$

Consequently, we have

$$\cos^2 \rho = (l_1 - n_z^{-2}) / (l_1 - l_3). \quad (12)$$

For wavelengths at which polarizers are available we should be able to measure ρ directly.

The three indices $n_{x'}$, $n_{z'}$, and n_y are the three fundamental refractive indices α , β , γ , but not, necessarily, respectively. By convention, γ is the largest and α the smallest of the indices. Having sorted these out we are ready to state the "sign" of the crystal and to compute the half angle between axes. If β is nearer in magnitude to α than it is to γ the crystal is biaxial positive while if β is nearer in magnitude to γ it is biaxial negative. For positive crystals the acute bisectrix of the angle between the optic axes is the direction of the displacement current for the highest refractive index.

The angle between the optic axes is $2V$ where

$$\sin^2 V = (l_1 - l_2) / (l_1 - l_3). \quad (13)$$

The measurements were made on an "all-reflection" spectrometer illustrated in Fig. 1. Light from a quartz lamp passes through a grating monochromator, the exit slit of which is the entrance slit of the spectrometer, built firmly onto the monochromator frame. Light from the monochromator exit slit passes over the prism and strikes a concave mirror. This mirror renders the beam parallel and sends it through the prism. The beam, after deflection by the prism strikes another concave mirror which sends the beam back over the prism to a focus at a slit behind which is a photodetector. Four filters were employed to eliminate higher orders of shorter wavelengths.

An annoyance, especially for birefringent crystals, is the rapidity with which the light intensity changes in the two polarization components (vertical and horizontal) as the wavelength is changed. At some wavelengths one component may disappear entirely. This difficulty was overcome by the use of a Soleil compensator. The compensator placed over the monochromator exit slit 45° to the grating line direction is adjusted to take the energy from the strong component and give it to the weak component while this index is being measured. The beam deviations are read on the scale of a Hilger-Watts microptic clinometer which reads to $10''$. The prism position is read from a scale S and positions of minimum deviation are determined by reading two positions near minimum for the same photodetector setting. The prism position is then locked

TABLE IV. Results for hexagonal crystals.^a

λ	LiTaO ₃		CdSe		ZnO		AlPO ₄	
	ω	ϵ	ω	ϵ	ω	ϵ	ω	ϵ
0.40							1.5369	1.5465
0.45	2.2420	2.2468			2.1058	2.1231		
0.50	2.2160	2.2205			2.0511	2.0681	1.5287	1.5385
0.60	2.1834	2.1878			1.9985	2.0147	1.5243	1.5334
0.70	2.1652	2.1696			1.9735	1.9897	1.5215	1.5301
0.80	2.1538	2.1578	2.6448	2.6607	1.9597	1.9752	1.5192	1.5281
0.90	2.1454	2.1493	2.5826	2.6027	1.9493	1.9654		
1.00	2.1391	2.1432	2.5502	2.5696	1.9435	1.9589	1.5161	1.5245
1.20	2.1305	2.1341	2.5132	2.5331	1.9354	1.9500	1.5136	1.5223
1.40	2.1236	2.1273	2.4929	2.5133	1.9298	1.9429	1.5112	1.5198
1.60	2.1174	2.1213	2.4818	2.5008	1.9257	1.9402	1.5088	1.5174
1.80	2.1120	2.1170	2.4732	2.4930	1.9226	1.9370	1.5062	1.5145
2.00	2.1066	2.1115	2.4682	2.4873	1.9197	1.9330	1.5034	1.5116
2.20	2.1009	2.1053	2.4642	2.4840	1.9173	1.9313	1.5001	1.5083
2.40	2.0951	2.0993	2.4612	2.4798	1.9152	1.9297	1.4969	1.5048
2.60	2.0891	2.0936	2.4590	2.4784	1.9128	1.9265	1.4928	1.5006
2.80	2.0825	2.0871	2.4562	2.4757	1.9100	1.9251		
3.00	2.0755	2.0799	2.4522	2.4741	1.9075	1.9214		
3.20	2.0680	2.0727	2.4532	2.4726	1.9049	1.9186		
3.40	2.0601	2.0649	2.4518	2.4714	1.9022	1.9160		
3.60	2.0513	2.0561	2.4509	2.4702	1.8994	1.9127		
3.80	2.0424	2.0473	2.4498	2.4694	1.8964	1.9101		
4.00	2.0335	2.0377	2.4491	2.4685	1.8891	1.9068		

^a The LiNbO₃ and LiTaO₃ were grown by A. Ballman of B.T.L., CdSe was from Harshaw, the ZnO was grown from the vapor phase by the Minnesota Mining and Mfg. Company. The AlPO₄ was grown by J. M. Stanley of the Signal Corps, Ft. Monmouth, New Jersey.

TABLE V. Results for the monoclinic crystal ZnWO₄.^a

λ	α	β	γ	ρ	V
0.42	2.2587	2.2788	2.4497		
0.45	2.2344	2.2555	2.4191	85.6°	20.8°
0.50	2.2059	2.2253	2.3802	86.1	20.5
0.55	2.1870	2.2051	2.3547	84.8	20.1
0.60	2.1728	2.1905	2.3362	85.1	20.1
0.65	2.1626	2.1795	2.3224	82.6	21.7
0.70	2.1545	2.1701	2.3118	83.0	19.2
0.80	2.1434	2.1590	2.2970	80.3	19.4
0.90	2.1356	2.1508	2.2865	82.3	19.4
1.00	2.1299	2.1447	2.2790	82.4	19.2
1.10	2.1255	2.1400	2.2731	82.4	19.2
1.20	2.1220	2.1363	2.2684	82.3	19.1
1.40	2.1165	2.1305	2.2612	82.1	18.9
1.60	2.1121	2.1260	2.2554	82.1	19.8
1.80	2.1083	2.1220	2.2503	81.9	18.9
2.00	2.1047	2.1182	2.2455	82.0	18.8
2.20	2.1011	2.1145	2.2406	81.5	18.8
2.40	2.0968	2.1108	2.2359	80.8	19.3
2.60	2.0931		2.2309		
2.80	2.0893	2.1027	2.2254	81.8	19.1
3.00	2.0852	2.0984	2.2199	81.6	19.1
3.20	2.0807	2.0939	2.2140	81.4	19.1
3.40	2.0752	2.0892	2.2079	81.6	19.7
3.60	2.0711	2.0841	2.2013	81.6	18.1
3.80	2.0658				
4.00	2.0603				

^a This material was grown by J. Rubin and L. Van Uitert of B.T.L. Since this work was done a report by C. Spengler and S. O'Hara was published [Appl. Opt. B, 1084 (1964)], covering the visible spectrum.

by means of the clamp L while the minimum deviation is read on the main scale.

The light from a GE6.6A/T4Q/200W quartz lamp was chopped at 390 cps before it fell on the entrance slit of the Bausch & Lomb grating monochromator. An Eastman Kodak photoconductor was used as a detector. A General Radio battery-operated transistor-tuned amplifier, type 1232A, was tuned to the chopping frequency. This made an adequate detecting unit for the photodetector. Beyond 2.5 μ we used a lead sulfide detector cooled by liquid nitrogen to take us to 4 μ . The minimum deviations were determined by reading the main circle at 70% max deflection of meter needle on each side and averaging the two angles. The x-ray data used for orienting the nonisometric crystals are as shown in Table I.

RESULTS

Tables II-V give the results for cubic crystals, tetragonal crystals, hexagonal crystals, and the monoclinic crystal, respectively.

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