Refractive Indices of Thallium Bromide-Iodide Crystals for Visible and Infrared Radiant Energy [1] -

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The refractive indices of two specimens of thallium bromide-iodide (KRS_5) were measured at a constant room temperature of 27° C from 0.577 to 39 microns by use of a minimum-deviation spectrometer and a Perkin-Elmer infrared spectrometer equipped with a calibrated screw for operation of the Littrow mirror. In order to cover the entire region over which the prisms are transparent, many known wavelengths were used, including lines of mercury, sodium, hydrogen, and helium for the visible region. A cadmium-mercury lamp was the source from 1 to 2 microns. From 2 to 39 μ various absorption bands of carbondioxide, water, methylcyclohexane, polystyrene, and polyethylene were used, with a Globar as source, for the identification of wavelengths.

Mixed crystalline thallium bromide-iodide, a material known as KRS-5, has a very high refractive index, 2.63 for sodium light, and also a high density. It is opaque to wavelengths shorter than about 0.5 μ but very transparent in the infrared to about 40 μ. The material is a solid solution of thallium bromide and thallium iodide. That is, it is truly a mixed crystal of the cubic system and therefore not double refracting when free from strain. Interferometer photographs indicate that some of the material is produced in a reasonably homogeneous state, although certainly not as uniform as good optical glass.

For growing these crystals, commercially obtainable chemicals of reagent quality are further purified by crystallization, and then proper mixtures are melted and well stirred. The Germans report that a crystal nucleus is introduced at the top and that the whole is cooled from the upper surface, but it is also successfully grown from the bottom in this country. Crystalline KRS-5 was of great importance to the Germans in the design of optical systems transmitting infrared energy. Incidentally, thallium bromide and iodide have been more or less known to petrographers for 15 or 20 yr as powders that could be mixed and

melted for producing a series of solid immersion media having sodium-lines indices ranging from about 2.40 to 2.65 accordingly as the proportion of thallium iodide is varied from 0 to 75 percent. Solid solutions with more than 75 percent of the iodide component are not stable in the cubic system but invert into a birefringent orthorhombic modification.[2]

Crystals of KRS-5 have been grown by a number of investigators in the United States and are now grown by the Harshaw Chemical Co. of Cleveland. The measurements of refractive index herein reported were made on a 25° prism with faces about 6 by 6.2 cm, from a crystal grown by Harshaw, and on a 12° prism with faces about 4 by 6.5 cm, from a crystal grown by Francis P. Phelps at this Bureau. These prisms were made in the Bureau's Optical Shop, and the surfaces were flat within a few wavelengths over about 80 percent of their apertures. Both these prisms were designed to contain approximately 58 percent of thallium iodide. The Phelps prism was analyzed by Howard B. Knowles of this Bureau and found to contain 58.3 percent of thallium iodide

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[1] The work described in this paper was carried out in 1947 in part under contract S & A 28658 between the Bureau of Ships and the National Bureau of Standards, in order to confirm and extend our knowledge of the optical properties of this medium.

[2] Tom. Barth, Am. Mineral. **14**, 358 (1929). The curves of refractive index for the visible region versus composition by weight, figure 2 of Barth's paper, seem too low in the neighborhood of 60% thallium iodide by about 0.03 in index, as judged by the data of this paper on the Phelps prism which, by analysis, contains 58.3% thallium iodide. Similarly, Barth's curves would seem too low by 0.05 if judged by the Hettner and Leisegang data on a prism said to contain 56% thallium iodide. (See footnote 4.)

and 41.7 percent of thallium bromide. The Harshaw prism has not been analysed, because it is in almost constant use on a long program of investigations in the infrared. Moreover, since this material is very susceptible to deformation by stress or shock, it seems unwise to jeopardize the homogeneity of this uniquely valuable optical component by the mechanical operations necessary in removing a sample for analysis. Later it is hoped that an analysis can be made in order to confirm the reasonable inference that this prism is about 0.5 percent higher in thallium iodide content than is the Phelps prism, which has refractive indices only 0.002 lower than those of the Harshaw prism.

The refractive indices of these prisms were first measured in the visible region for eight wavelengths in the yellow and red. This was done by use of a minimum-deviation spectrometer, chiefly at room temperatures near 23° C. The results for each prism were expressed by a Ketteler-Helmholtz dispersion formula of the form

$$n^2 = a^2 - k\lambda^2 + \frac{m}{\lambda^2 - \lambda_v^2}, \qquad (1)$$

in which the parameters a^2, k, m, and λ_v^2 were adjusted by the method of averages. The average residual of 7×10^{-5}, somewhat larger than anticipated, may be ascribed in part to somewhat imperfect surfaces and some inhomogeneity, but also it is due in large part to lack of careful temperature control and observation for these preliminary data with visible energy. Also, since this material is practically opaque to visible radiation shorter than about 5,000 A, the indices measured in the yellow region are affected to some extent by the fact that the yellow light is more predominantly transmitted near the apex and perhaps not at all through the thicker portions of the prism near its base. Therefore, the effective apertures for yellow and for red light do not exactly coincide. The resulting error in index measurement is probably appreciable in the yellow region but of little importance in the red and beyond.

Subsequent measurements for $\lambda = 5,876$ and $\lambda = 6,678$ at 30° C were much lower than those near 23°, and a temperature coefficient of -16×10^{-5}/deg C was found for light of approximately 6,000 A. This optical sensitivity to temperature is over four times that of rock salt.

The method to be described for the index measurements in the infrared is not self-sufficient. For each prism the adjusted index (computed by eq 1) for the cadmium red line, $\lambda = 6,438$, is taken as the basis with respect to which the infrared indices are to be computed. The use of eq 1 for adjusting the data in the visible region probably compensates in large part for the inadequate knowledge of temperatures of the KRS-5 during individual observations. These basic indices for cadmium red at an average temperature of 23° were then reduced to 27° C, the temperature of the room in which the infrared observations were made.

In the infrared region use was made of a Perkin-Elmer infrared spectrometer equipped with a calibrated screw for operation of the Littrow mirror, M of figure 1. The concave collimating mirror, C, focal length 27.5 cm, approximately 18° off axis, has an aperture of about 7.5 cm but was stopped down to a rectangular aperture of about 5×5 cm to reduce stray energy. The angular separation of the entrance and exit slits is 1.9636° at the face of the Littrow mirror. The angular equivalent of the screw was found to be 27.05' or 1623'' per turn, averaged over almost its total length. This was done by means of 64 successive steps with two mirrors that were set at an angle of 5' of arc. A collimator and telescope were used for precision in making the steps. Evidence was found that seemed to indicate that the periodic errors of a single turn may be ± 10 sec, and that progressive corrections to the average equivalent of the screw may sometimes exceed 30 sec, but it is possible that this was merely evidence of distortion of the Littrow mirror, introduced by clamping.
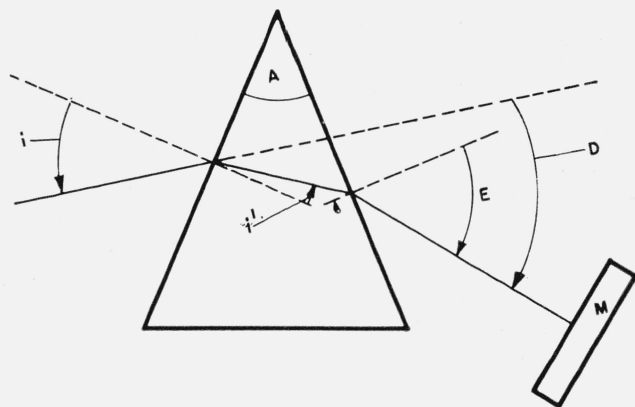

FIGURE 1. *Prism installed on infrared spectrometer.*

The detector was of the Golay type with a KRS–5 window, the incident beam being interrupted about 10 times per sec. Slit widths as wide as 0.35 to 0.43 mm were necessary for visible radiation and for the region where the water vapor absorption was utilized. Widths of from 0.03 to 0.20-mm were sufficient in the intermediate region. A measure of the energy received by the detector is automatically recorded on a Leeds & Northrup Speedomax recording potentiometer.

This spectrometer was used, not because it is particularly favorable for this work, but because it was available and index values were required. An objection is the return passage of energy through the prism, which causes additional losses by reflection and absorption. This is particularly disadvantageous in that the energy does not exactly retrace its path because of the angular separation of entrance and exit slits.

Since on the infrared spectrometer the prism is stationary, and only the rotation of the Littrow mirror may be observed, it is necessary to use the method of known incidence angle for refractive-index measurements with a spectrometer of this type. This method of known incidence was used by Rydberg [3] over a century ago, and Martens [4] found it useful in measuring indices in the ultraviolet. Martens recommended the computation of indices by the equations

$$\tan\left(i'-\frac{A}{2}\right)=\tan\frac{A}{2}\cot\frac{A+D}{2}\tan\left(i-\frac{A+D}{2}\right),\quad(2)$$

and

$$n=\frac{\sin i}{\sin i'}$$

especially when logarithms are used. For use with computing machines it is preferable to use the equivalent forms

$$\cot i'=\cot A+\frac{\sin E}{\sin A\sin i},\quad(3)$$

and

$$n=\sin i\ (1+\cot^2 i')^{1/2},$$

where the symbols have the meanings designated in figure 2.

[3] F. Rydberg, Poggendorf's Annalen **14**, 45 (1828).
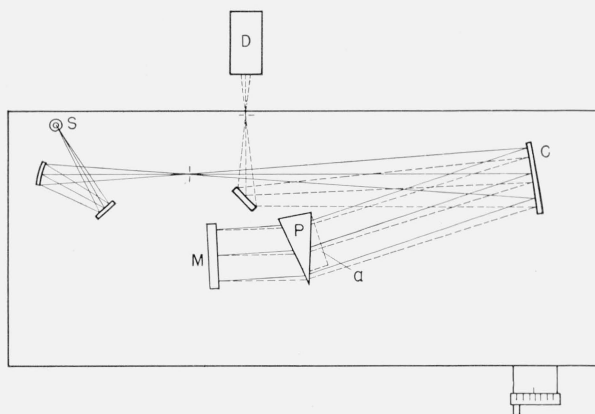[4] F. F. Martens, Verhandl. deut. physik. Ges. **3**, 10 (1901).

FIGURE 2. *Simplified relation of Littrow mirror to deviation produced by prism.*

In order to install each prism of KRS–5 with suitable known incidence angle, i, on an infrared spectrometer of this type, small auxiliary prisms of glass were made with angle, A_x, approximately equal, in each case, to $(A+D)/2$ for the minimum-deviation condition and some wavelength of visible radiant energy traversing the KRS–5 prism. Although there is nothing very precise about the selection of a favorable incidence angle, i, it is necessary to know the i that is actually used. Consequently, the angles of the auxiliary glass prisms are carefully measured, and they are used in the installation of the corresponding prisms of KRS–5 on the spectrometer as shown at A in figure 1. With any intense visible radiation focused on the entrance slit, the prism pair is so oriented that light reflected from the outer polished face of the auxiliary prism is returned to the entrance slit. After removal of the auxiliary prism, any energy from the entrance slit will be incident on the unknown sample prism at an angle $i=A_x$, where A_x is the measured refracting angle of the auxiliary glass prism.

For any prism, starting with the refracting angle, A, the index, n, as adjusted for $\lambda_0=6,438$, $t=27°$, and incidental angle, i, it is possible to trace rays through the prism, as indicated in figure 2, and find E_0, angle of emergence for these basic or initial conditions. If the Littrow mirror were normal to the emergent ray (zero angle between entrance and emergence slits), or even if the incidence angle of $\delta E/2$ on the Littrow mirror remained constant for the different wavelengths to be used, then the observable angular increments for the Littrow mirror, as determined from the

drum readings of the screw, would be the exact increments applicable to E_0 to give E_λ.

Fortunately, $\delta E/2$, the incidence angle on the Littrow mirror, varies rather slowly as n changes, and it is not difficult to trace a series of pairs of rays (for i and for $i-1.9636°$) for arbitrarily selected evenly spaced values of n, as 2.60, 2.50, 2.40, 2.30, and form an interpolation table of $\delta E/2$ as a function of n. Then when computing n by means of eq 1, it is found that correct pre-estimation of n within 1 or 2×10^{-3} will enable one to select a satisfactory value for the small correction to the observed angular increment in E, for use in computing n correctly within ±1 or 2×10^{-5}.

In order to cover the entire infrared region over which these prisms are transparent, many wavelengths were used, including those for various absorption bands of carbondioxide, water, methylcyclohexane, polystyrene, and polyethylene, with a Globar as source. The ordinarily sharp zero branches of the absorption curves for various vapors could not be used, because the recorded contours of these branches are not sharp at the center when the dispersion is low as is the case for these prisms from 3.4 to 14.3 μ. Here, however, the recordings of the ordinarily broad bands of absorption of polystyrene, polyethylene, and methylcyclohexane become usefully narrow.

Equation 1 was found definitely inadequate for accurately representing the index of refraction, even to four decimal places, over so long a spectral range as that covered in this investigation. Also, the four-constant Sellmeier formula with two terms, namely,

$$n^2=1+\frac{M'\lambda^2}{\lambda^2-\lambda_r^2}+\frac{m'\lambda^2}{\lambda^2-\lambda_v^2},\qquad(4)$$

exactly equivalent to one form of the Kettler-Helmholtz formula (as strictly limited to two resonance frequencies), namely,

$$n^2=a^2-\frac{M}{\lambda_r^2-\lambda^2}+\frac{m}{\lambda^2-\lambda_r^2},\qquad(5)$$
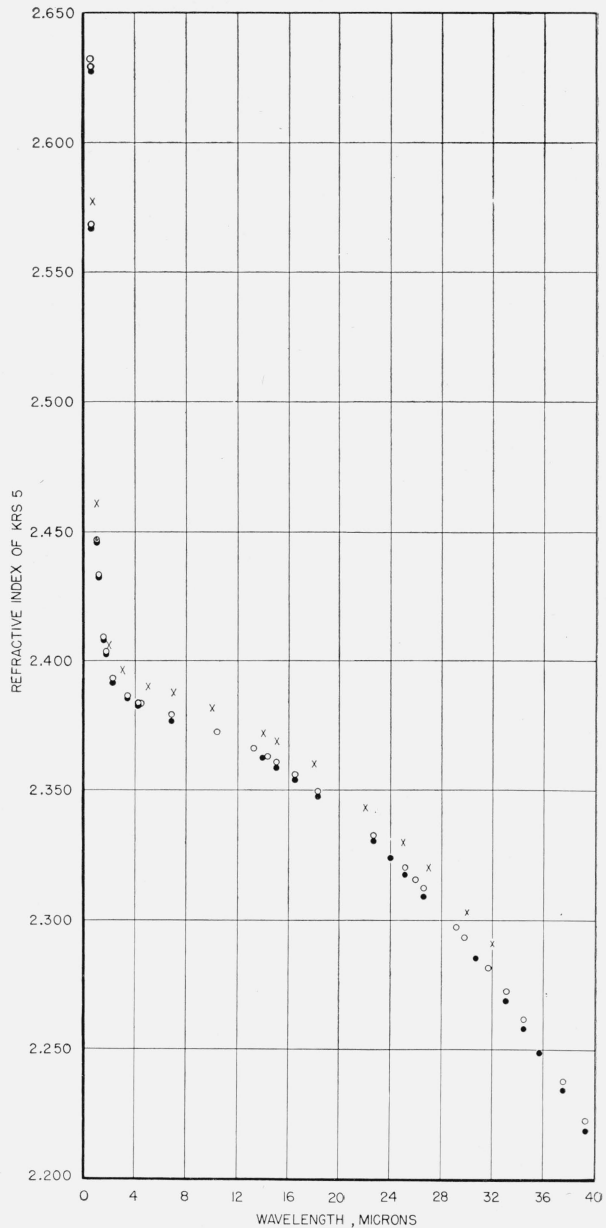

FIGURE 3. *Index of refraction of* KRS–5.

The raw observed values for the Harshaw and the Phelps prisms are used here, this graph being identical with that shown at the New York meeting of the Optical Society of America, March 1948.

where

$$a^2 = 1 + \frac{M}{\lambda_r^2} + \frac{m}{\lambda_v^2} = 1 + M' + m',$$

was found to be considerably worse than eq 1, which is merely a partially expanded, and therefore an approximate, form of eq 4 or 5. Equation 4 or 5 can, however, account for the effect of only one absorption band in the infrared and one in the ultraviolet, whereas their expanded forms can, with the same number of constants, approximate the effects of multiple bands, and these prisms of KRS–5 are known to have two prominent infrared bands, one each for the bromide and iodide constituents. By retaining in the expansion a term in $-\lambda^4$, however, and adjusting the five parameters by least squares, the equation

$$n^2 = 5.676\,927 - 0.000\,452\,226\,4\lambda^2 -$$
$$0.000\,000\,018\,019\,7\lambda^4 +$$
$$\frac{0.287\,301\,7}{\lambda^2 - 0.102\,773\,4}, \quad (6)$$

was found to represent the indices of the 25° Harshaw prism.

The same equation with $a^2 = 5.667\,927$ serves so well (see residuals in table 1) for the 12° Phelps prism that a betterment by least squares is unnecessary.

Equation 5 with five constants, that is one in which

$$a^2 = 1 + \frac{M}{\lambda_r^2} + \frac{m}{\lambda_v^2} + \ldots,$$

was not tried because if five constants are to be used, it appears much better to try the expanded form as in eq 6, where not only the constant, but certain other additional terms relating to any other pertinent absorption bands are automatically taken into account.

Table 1 gives, according to eq 6 and 7, the indices and the residuals, observed minus computed, for each of these prisms for the wavelengths that were used. The agreement between observed and computed indices for each prism is entirely satisfactory, and the computed indices for these prisms are probably typical for this material. The differences in index from wavelength to wavelength, easily obtainable from table 2, are probably accurate to a few units in the fifth decimal. The

TABLE 1. *Observed and computed data on index or refraction of KRS–5 (27° C)*

Wave-length	Source or absorbing media	Computed index Harshaw prism	$(o=c) \times 10^4$	Computed index Phelps prism	$(o=c) \times 10^4$
μ					
0.5770	Hg yellow _ _ _ _ _ _ _ _ _	2.6316	+1	_ _ _ _	_ _ _ _ _ _
.5780	Mean Hg yellow _ _ _ _	_ _ _ _	_ _ _ _ _ _	2.6286	−14
.5791	Hg yellow _ _ _ _ _ _ _ _	2.6291	+1	_ _ _ _	_ _ _ _ _ _
.6438	Cd red _ _ _ _ _ _ _ _ _	2.5687	−6	2.5670	−6
1.0142	Hg _ _ _ _ _ _ _ _ _ _ _ _	2.4468	+3	2.4450	+13
1.1289	Hg _ _ _ _ _ _ _ _ _ _ _ _	2.4334	+2	2.4316	+11
1.5298	Hg _ _ _ _ _ _ _ _ _ _ _ _	2.4092	+3	2.4073	+12
1.700	Hg _ _ _ _ _ _ _ _ _ _ _ _	2.4039	+2	2.4020	+11
2.26	Polyethylene abs _ _ _ _	2.3942	−5	2.3923	−5
3.42	Polystyrene abs _ _ _ _	2.3867	+2	2.3848	+10
4.24	CO_2 abs. in air _ _ _ _ _ _	2.3843	−1	2.3824	+8
4.4	CO_2 flame emission _ _	2.3839	−4	_ _ _ _	_ _ _ _ _ _
6.86	Methylcyclohexane abs.	2.3794	+1	2.3775	−4
10.34	_ _ _ _ _ do _ _ _ _ _ _ _ _ _ _	2.3730	+0	_ _ _ _	_ _ _ _ _ _
13.23	Polystyrene abs _ _ _ _	2.3662	+3	_ _ _ _	_ _ _ _ _ _
13.90	Polyethylene abs _ _ _ _	_ _ _ _	_ _ _ _ _ _	2.3625	+6
14.32	Polystyrene abs _ _ _ _	2.3632	+1	_ _ _ _	_ _ _ _ _ _
14.98	CO_2 abs. in air _ _ _ _ _ _	2.3613	−1	2.3594	−2
16.48	Methylcyclohexane abs.	2.3567	−2	2.3547	−1
18.29	_ _ _ _ _ do _ _ _ _ _ _ _ _ _ _	2.3504	−4	2.3485	−3
22.60	_ _ _ _ _ do _ _ _ _ _ _ _ _ _ _	2.3328	+1	2.3308	+3
23.92	Water vapor abs.[a]	2.3265	+3	2.3246	+1
25.16	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.3203	+0	2.3184	−4
25.97	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2,3160	−1	_ _ _ _	_ _ _ _ _ _
26.60	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.3127	−3	2.3107	−7
28.33	_ _ _ do.[a] _ _ _ _ _ _ _ _	_ _ _ _	_ _ _ _ _ _	2.3008	−2
29.15	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2978	−6	_ _ _ _	_ _ _ _ _ _
29.81	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2937	−1	_ _ _ _	_ _ _ _ _ _
30.69	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	_ _ _ _	_ _ _ _ _ _	2.2861	+2
31.70	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2814	−0	_ _ _ _	_ _ _ _ _ _
33.11	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2715	+10	2.2695	0
34.48	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2614	+1	2.2594	−7
35.7	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	_ _ _ _	_ _ _ _ _ _	2.2500	−7
37.45	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2377	−3	2.2357	−6
39.22	_ _ _ _ _ do.[a] _ _ _ _ _ _ _	2.2224	−1	2.2204	−6

[a] For the wavelengths of the absorption bands of water vapor, see H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, Phys Rev. **52**, 160 (1937).

index residuals for the Phelps prism are larger, because the effects on index of accidental errors in deviation measurement are fully twice as large for the prism of 12° angle. Moreover, since the resolution is much lower, the angular errors themselves are larger. The average difference in raw observed index between the two prisms varies from 13×10^{-4} in the visible region to 28×10^{-4} at 39 μ, figure 3, whereas the corresponding differences are 17 to 20×10^{-4} in the computed indices. In other

TABLE 2. *Refractivity of KRS–5 at 27° C for use in computing partial dispersions*

This table is an average for two samples of KRS–5 grown independently in different laboratories in the United States in efforts to produce solid solutions of minimum melting point. One, by analysis, contains 58.3 percent thallium iodide and the other, by inference from its indices, contains 58.8 percent thallium iodide. The measurements were made at 35 wavelengths well distributed over the range of 40 μ. The table is computed by means of equation 6, except that a^2 has the value 5.672427. It is estimated that differences taken from this table are reliable to $\pm 2 \times 10^{-5}$.

Wavelength	Tenths of microns									
	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
	Values of $(n-2) \times 10^5$									
μ										
0	-----	-----	-----	-----	-----	-----	60561	53262	49137	46542
1	44789	43544	42623	41923	41376	40940	40586	40296	40053	39848
2	39673	39523	39393	39279	39178	39089	39009	38937	38873	38814
3	38760	38711	38666	38623	38584	38548	38514	38482	38452	38423

Wave-length	$(n-2) \times 10^5$	Wave-length	$(n-2) \times 10^5$	Wave-length	$(n-2) \times 10^5$	Wave-length	$(n-2) \times 10^5$
μ		μ		μ		μ	
1	44789	11	37062	21	33883	31	28506
1.5	40940	11.5	36949	21.5	33670	31.5	28172
2	39673	12	36832	22	33451	32	27832
2.5	39089	12.5	36710	22.5	33226	32.5	27485
3	38760	13	36584	23	32996	33	27131
3.5	38548	13.5	36453	23.5	32760	33.5	26770
4	38396	14	36317	24	32518	34	26403
4.5	38276	14.5	36176	24.5	32271	34.5	26028
5	38173	15	36030	25	32017	35	25647
5.5	38081	15.5	35880	25.5	31758	35.5	25258
6	37994	16	35724	26	31493	36	24862
6.5	37910	16.5	35564	26.5	31222	36.5	24459
7	37826	17	35398	27	30945	37	24048
7.5	37740	17.5	35227	27.5	30662	37.5	23630
8	37653	18	35051	28	30373	38	23205
8.5	37563	18.5	34870	28.5	30078	38.5	22772
9	37471	19	34683	29	29776	39	22331
9.5	37374	19.5	34491	29.5	29468	39.5	21882
10	37274	20	34294	30	29154	--------	-----------
10.5	37170	20.5	34092	30.5	28833	--------	-----------

words, there is little if any difference in dispersion between these two prisms. The corresponding difference, if any, in the proportions in which the bromide and the iodide are present would be about 0.5 percent, the Harshaw prism to have the slightly higher iodide content.

Figure 3 shows by open circles the (observed) indices of the 25° prism grown by Harshaw and by black dots the indices of the 12° prism grown by Phelps. Some indices of a sample of KRS–5 according to "Hettner",[5] as read from a curve ob- tained from Germany, are entered on this figure as crosses. They extend, however, only to 32 μ. At the long wavelengths that sample of KRS–5 aver- aged fully 100×10^{-4} higher in index than the Phelps prism even allowing for a possible difference of 10 deg C. This indicates, according to the index curves published by Barth, that the Hettner sample contained about 2.5 percent *more* thallium iodide than the Phelps prism.[6]

[5] Possibly based on the data published later by G. Hettner and Gertrud Leisegang, Optik **3**, 305 (1948).

[6] The Hettner and Leisegang prism (footnote 4) is said, however, to contain 56% of thallium iodide, which is about 2.3% *less* than that in the Phelps prism. With reference to index stability, it may be added that check measurements for λ=6438 were made on the Phelps prism after a 15-month interval, using a different spectrometer, and no change was found in the fourth decimal place.