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REFRACTION, ABSORPTION AND BIABSORPTION IN SYNTHETIC RUBY*

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ABSTRACT

Refractive indices, absorption coefficients, and biabsorption were determined for two synthetic ruby samples, one colored pink by 0.11% Cr_2O_3 and the other colored deep red by 1.40% Cr_2O_3.

The refractive indices of the pink sample vary from $n_\omega = 1.7761$ and $n_\epsilon = 1.7677$ at 480 mμ to $n_\omega = 1.7635$ and $n_\epsilon = 1.7554$ at 700 mμ. For the red sample, n_ω and n_ϵ vary from 1.7821 and 1.7741, respectively, to 1.7696 and 1.7614 for the same spectral region.

The maximum value of the absorption coefficient for the ordinary ray occurs at 560 mμ for both samples, while the maximum value for the extraordinary ray in both samples occurs at 550 mμ. Values of the absorption coefficients at the peak wave lengths are: $k_\omega = 34.9 \times 10^{-6}$, $k_\epsilon = 25.4 \times 10^{-6}$ (for the pink ruby) and $k_\omega = 311.0 \times 10^{-6}$, $k_\epsilon = 138.2 \times 10^{-6}$ (for the red ruby).

The maximum negative ($k_\epsilon < k_\omega$) value of biabsorption for both samples occurs at 570 mμ. These biabsorption values calculated from the absorption coefficients are -10.4×10^{-6} and -184.1×10^{-6} for pink and red ruby, respectively. Those obtained by the visual-matching method are -10.0×10^{-6} and -193.0×10^{-6}.

INTRODUCTION

In a recent paper (Mandarino, 1959), an attempt was made to stimulate interest in the quantitative determination of absorption and biabsorption. This paper continues the study with data on these two properties for synthetic ruby. Refractive index data have also been included for the sake of completeness.

Two samples of synthetic ruby were used: a dark red sample containing 1.40% Cr_2O_3 and a pink sample containing 0.11% Cr_2O_3. The chromium contents were determined by Mr. C. O. Ingamells of the Rock Analysis Laboratory, University of Minnesota.

The writer wishes to thank Dr. R. W. Kebler, of the Linde Air Products Company, Indianapolis, Indiana, for furnishing the samples; Drs. N. Kalenda and A. Emory of the Chemistry Department, University of Michigan, for assisting with the Cary spectrophotometer; and especially, Professor R. M. Denning, of the Mineralogy Department, University of Michigan, who directed the study and contributed many helpful suggestions. The study was supported by the Office of Naval Research.

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TABLE 1. REFRACTIVE INDICES FOR NATURAL AND SYNTHETIC CORUNDUM MEASURED BY VARIOUS INVESTIGATORS

λ(mμ)	Kebler (1955)	Melczer (1902)				Mandarino (1959)			
	Synthetic corundum-colorless	Natural* blue to colorless		Synthetic** ruby		Synthetic ruby pink		Synthetic ruby red	
	n_ω	n_ω	n_ϵ	n_ω	n_ϵ	n_ω	n_ϵ	n_ω	n_ϵ
366.0	1.79354								
434.1	1.78135								
480						1.7761	1.7677	1.7821	1.7741
486.1	1.77551	1.7760	1.7677	1.7803	1.7719				
500						1.7740	1.7658		1.7723
520						1.7724	1.7640		
540						1.7709	1.7626		
560						1.7697	1.7615		
580						1.7684	1.7604		1.7663
589.3	1.76804	1.7686	1.7604	1.7730	1.7647				
600						1.7675	1.7593	1.7732	1.7649
620						1.7664	1.7583	1.7722	1.7641
640						1.7655	1.7575	1.7714	1.7632
656.3	1.76487	1.7653	1.7573	1.7697	1.7612				
660						1.7647	1.7566	1.7704	1.7624
680						1.7640	1.7559	1.7700	1.7619
700						1.7635	1.7554	1.7696	1.7614

* Averages of data from eight crystals.
** Averages of data from five crystals.

REFRACTIVE INDICES

The ordinary and extraordinary indices of refraction for both pink and red synthetic ruby were determined by the method of minimum deviation. A prism was cut from each boule so that the prism edge was parallel to the crystallographic *c*-axis. This enabled both n_ω and n_ϵ to be measured directly.

Table 1 contains the values of n_ω and n_ϵ for both crystals. Also included in the table are data from Kebler (1955), for n_ω in colorless synthetic corundum measured by the American Optical Company; and Melczer (1902), from whom the data in *Dana's System of Mineralogy* by

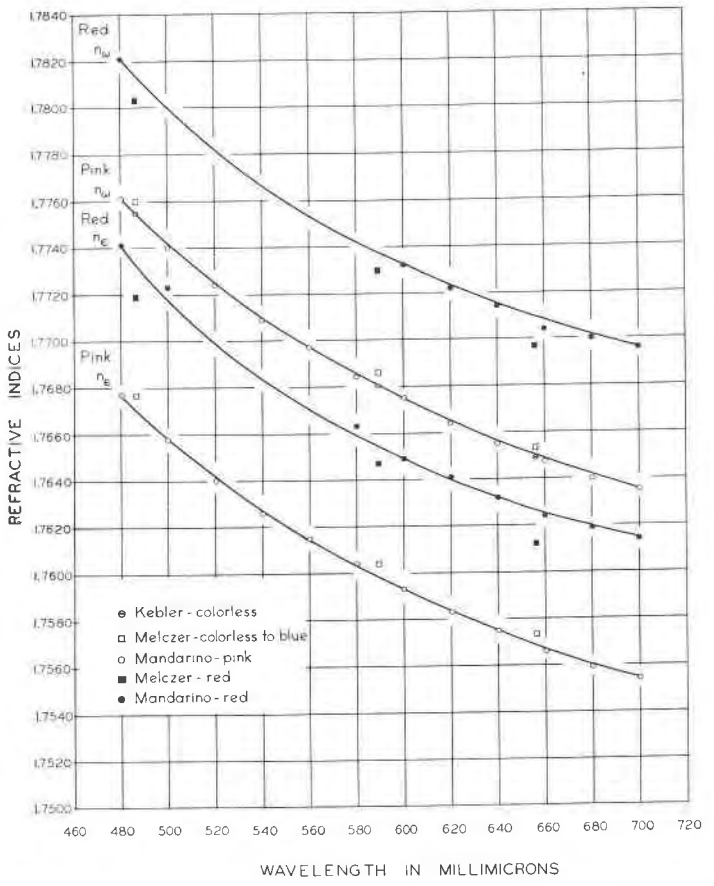


FIG. 1. Refractive indices of natural and synthetic corundum of various colors.

Palache et al. (1944) were taken. It should be pointed out that Melczer's data for blue and colorless corundum are averages of the data from eight natural crystals. Melczer's slightly higher values, also mentioned by Palache et al. (page 526, footnote 18), are for synthetic ruby.

The data from Table 1 are presented graphically in Fig. 1. It can be seen that the refractive indices for colorless, blue, and pink corundum (both natural and synthetic) are almost equal. The deeper red varieties, however, have distinctly higher refractive indices.

The measured values of the refractive indices of pink and red synthetic ruby are considered accurate to within ± 0.0002 for the spectral region 700 mμ to 600 mμ, and ± 0.0005 for wave lengths below 600 mμ. In red synthetic ruby the values of n_ω for the spectral region 500 mμ through 580 mμ could not be measured because of the high absorption of the

TABLE 2. HARTMANN CONSTANTS FOR PINK AND RED SYNTHETIC RUBY

Hartmann Constants	Pink Synthetic Ruby		Red Synthetic Ruby	
	n_ω	n_ϵ	n_ω	n_ϵ
n_o	1.7475	1.7399	1.7578	1.7507
c	79.57	76.88	50.40	43.18
λ_o	202.1	203.2	272.5	295.2

ordinary ray in this region. Likewise, n_ϵ could not be measured between 520 mμ and 560 mμ.

As can be seen from Fig. 1, the dispersion of n_ω and n_ϵ with respect to wave length is normal for both pink and red synthetic ruby. The dispersion for all four sets of data can be expressed by the Hartmann dispersion equation (Hardy and Perrin, 1932):

$$n_\lambda = n_0 + \frac{c}{\lambda - \lambda_o} \tag{1}$$

Table 2 lists the Hartmann constants n_o, c, and λ_o for all four indices. Table 3 compares the measured values of n_ω and n_ϵ for both crystals with the values calculated from Equation 1 and the constants of Table 2. In general, the measured and calculated values are compatible, within the probable error of the measurements.

The reciprocal dispersion ν (Hardy and Perrin, 1932) was calculated from:

$$\nu = \frac{n_D - 1}{n_F - n_C} \tag{2}$$

For the pink ruby, $\nu_\omega = 72.5$ and $\nu_\epsilon = 74.5$. The values of ν_ω and ν_ϵ for the red ruby are, respectively, 69.7 and 69.6. Kebler (1955) found $\nu_\omega = 72.2$ in colorless synthetic corundum.

ABSORPTION COEFFICIENTS

The values of the ordinary and extraordinary absorption coefficients for pink and red synthetic ruby were calculated from measurements made with a Cary spectrophotometer. A complete description of the Cary spectrophotometer can be found in a paper by Tarrant (1953). Briefly, the instrument is a recording spectrophotometer employing photoelectric tubes to measure optical density ($D = \log_{10} I_o/I$). The instrument is a comparison-type spectrophotometer; i.e., two optical paths are used, one containing the sample and the other acting as a reference path. A "balancing" circuit makes it possible to trace a curve of constant optical density for a given spectral region before the sample is inserted.

TABLE 3. MEASURED AND CALCULATED REFRACTIVE INDICES OF PINK AND RED SYNTHETIC RUBY

$\lambda(m\mu)$	Pink				Red			
	n_ω		n_ϵ		n_ω		n_ϵ	
	meas.	calc.	meas.	calc.	meas.	calc.	meas.	calc.
480	1.7761	1.7761	1.7677	1.7677	1.7821	1.7821	1.7741	1.7741
500	1.7740	1.7742	1.7658	1.7658		1.7800	1.7723	1.7718
520	1.7724	1.7725	1.7640	1.7642		1.7782		1.7699
540	1.7709	1.7710	1.7626	1.7627		1.7766		1.7683
560	1.7697	1.7697	1.7615	1.7614		1.7753		1.7670
580	1.7684	1.7686	1.7604	1.7603		1.7742	1.7663	1.7659
600	1.7675	1.7675	1.7593	1.7593	1.7732	1.7732	1.7649	1.7649
620	1.7664	1.7665	1.7583	1.7583	1.7722	1.7723	1.7641	1.7640
640	1.7655	1.7656	1.7575	1.7575	1.7714	1.7715	1.7632	1.7632
660	1.7647	1.7649	1.7566	1.7567	1.7704	1.7708	1.7624	1.7625
680	1.7640	1.7641	1.7559	1.7560	1.7700	1.7702	1.7619	1.7619
700	1.7635	1.7635	1.7554	1.7554	1.7696	1.7696	1.7614	1.7614

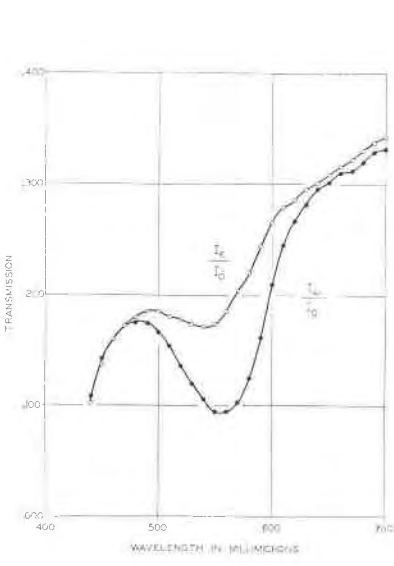
To confine each measurement to a particular vibration direction, a polar must be placed in the sample path. A sheet of Polaroid was used for this purpose. The polished ruby plates (cut parallel to the c-axis) were mounted in rotatable holders so that each vibration direction of the plates could be made parallel to the vibration direction of the polar.

With only the polar in the sample path, the instrument was balanced for an arbitrary optical density reading of 1.00 ($I/I_o=0.100$). After balancing, an optical density curve was obtained for the polar alone. The curve covered the spectral region 440 mμ to 700 mμ. Values from this curve were converted to values of I_o and were found to deviate very little from a value of 0.100. Next, the pink ruby plate was placed in the sample path, and an optical density curve was obtained for the ordinary vibration direction. The ruby plate was then rotated 90° in its own plane, and an optical density curve for the extraordinary vibration direction was obtained. Similarly, curves were recorded for the ordinary and extraordi-

TABLE 4. VALUES OF I_ω/I_o AND I_ϵ/I_o FOR THE SPECTRAL REGION 440 mμ–700 mμ

λ(mμ)	Pink Ruby (t=0.302 cm.)		Red Ruby (t=0.073 cm.)	
	I_ω/I_o	I_ϵ/I_o	I_ω/I_o	I_ϵ/I_o
440	.108	.102	.053	.047
450	.142	.138	.139	.130
460	.160	.159	.219	.229
466	—	—	.252	.275
469	—	—	.240	.257
470	.172	.171	—	—
473	—	—	.260	.309
476	—	—	.235	.269
480	.175	.180	.248	.309
490	.174	.185	.209	.291
500	.166	.185	.148	.251
510	.153	.180	.092	.200
520	.135	.177	.047	.155
530	.119	.173	.022	.120
540	.105	.171	.012	.102
550	.094	.173	.007	.100
560	.094	.185	.006	.116
570	.102	.204	.008	.155
580	.125	.220	.015	.214
590	.162	.243	.042	.288
600	.209	.265	.109	.350
610	.245	.278	.205	.398
620	.267	.285	.288	.427
630	.282	.294	.335	.437
640	.295	.301	.356	.446
650	.302	.308	.368	.452
660	.309	.315	.365	.452
670	.312	.322	.360	.452
680	.319	.330	.372	.457
690	.328	.337	.356	.457
693	—	—	.332	.452
700	.331	.342	.372	.463

nary vibration directions of the red ruby. The optical density values from these curves were converted (at selected wave lengths) to values of I'. Division of I' values by the predetermined value of I_o (0.100) resulted in values of I'/I_o (the transmittance values uncorrected for reflection losses).



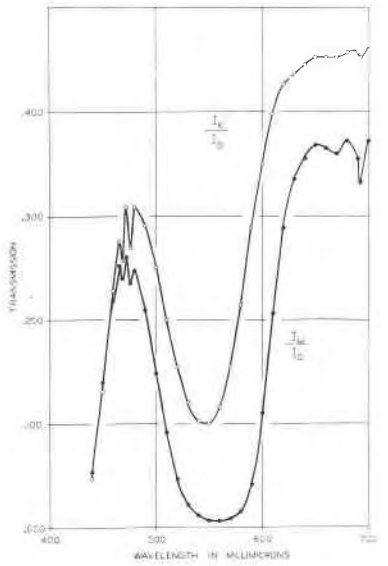


FIG. 2 (*left*). Transmittance of pink synthetic ruby corrected for reflection losses. Sample thickness = 0.302 cm.

FIG. 3 (*right*). Transmittance of red synthetic ruby corrected for reflection losses. Sample thickness = 0.073 cm.

The corrected transmittance values (I/I_o) for the ordinary and extraordinary vibration directions of both crystals were determined from the values of I'/I_o and n, according to the well-known Fresnel equation for reflection losses. The values of I_ω/I_o and I_ϵ/I_o for pink and red ruby are given in Table 4. These data are also presented graphically in Fig. 2 (pink ruby) and Fig. 3 (red ruby). For certain wave lengths, the red ruby seems to be more transparent than the pink ruby. This can be explained by the difference in thickness of the two samples. The pink ruby was 0.302 cm. thick while the red ruby was only 0.073 cm. thick. Transmittances of media having different chromophore concentrations should not be compared if the media have different thicknesses. Comparison of absorption coefficients of such media is permissible, however, because absorption coefficients are independent of thickness.

The absorption coefficients for the four sets of data were calculated from the following equation:

$$k = -\frac{\lambda \, ln(I/I_o)}{4\pi t} \qquad \text{Mandarino (1959) (3)}$$

Values of k_ω and k_ϵ for both samples are listed in Table 5, and these data are presented graphically in Fig. 4.

TABLE 5. VALUES OF k_ω AND k_ϵ FOR THE SPECTRAL REGION 440 mμ–700 mμ

λ(mμ)	Pink Ruby		Red Ruby	
	k_ω	k_ϵ	k_ω	k_ϵ
440	25.8×10^{-6}	26.5×10^{-6}	140.9×10^{-6}	146.8×10^{-6}
450	23.2	23.5	96.7	100.0
460	22.2	22.3	76.2	73.9
466	—	—	70.1	65.6
469	—	—	72.8	69.4
470	21.8	21.9	—	—
473	—	—	69.1	60.4
476	—	—	75.0	68.2
480	22.1	21.7	73.0	61.5
490	22.6	21.8	83.5	65.9
500	23.6	22.2	104.0	75.0
510	25.2	23.0	132.6	89.1
520	27.4	23.7	173.2	105.4
530	29.7	24.5	220.0	122.2
540	32.0	25.1	260.0	134.4
550	34.2	25.4	297.0	138.2
560	34.9	24.9	311.0	131.4
570	34.3	23.9	300.0	115.9
580	31.7	23.1	265.0	97.3
590	28.3	22.0	203.6	79.8
600	24.7	21.0	144.6	68.7
610	22.6	20.5	105.3	61.1
620	21.5	20.5	83.8	57.6
630	21.0	20.3	75.2	56.6
640	20.6	20.3	72.0	56.5
650	20.5	20.2	70.8	56.4
660	20.5	20.1	72.6	57.3
670	20.6	20.0	74.6	58.0
680	20.4	19.8	73.3	57.9
690	20.2	19.8	77.6	58.7
693	—	—	83.4	60.2
700	20.4	19.8	75.4	58.8

Several interesting points are illustrated in Fig. 4 and Table 5. In both samples, the absorption peaks for the ordinary ray occur at 560 mμ, while the peaks for the extraordinary ray occur at 550 mμ. (When Vogel (1934) investigated absorption in synthetic and natural ruby, he did not present absorption curves for both the ordinary and extraordinary rays. He did

obtain a composite curve, however, with a peak at 555 mμ.) In general, the absorption curves for both rays in the pink ruby are quite simple. The curves show only one rather poorly-defined absorption band. The absorption curves for both the ordinary and extraordinary rays in red ruby, however, are much more complex. The major absorption band is very sharp and well defined. There are four subordinate absorption bands at 469 mμ, 476 mμ, 670 mμ, and 693 mμ. The band at 670 mμ is poorly defined. In addition, the 693 mμ band is sharper for the ordinary ray than

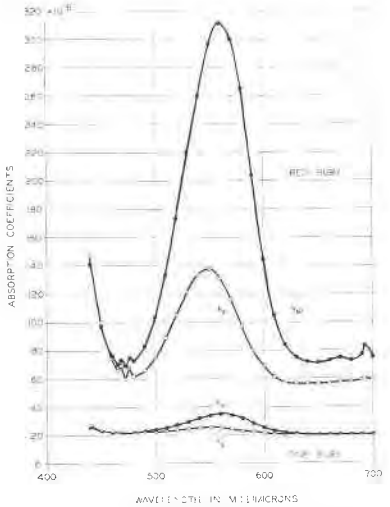


Fig. 4—Absorption coefficients for pink and red synthetic ruby.

for the extraordinary ray; while for the 469 mμ and 476 mμ bands, the reverse holds true.

Probably the most striking feature of the curves in Fig. 4 is the extreme difference in pleochroism, or biabsorption (k_ϵ-k_ω), of the two samples.

An analysis of the probable sources of error indicates that the average total error in the calculated absorption coefficients is about three per cent.

Biabsorption

In the preceding section on absorption, the values of the absorption coefficients k_ω and k_ϵ for pink and red synthetic ruby were presented for the spectral region 440 mμ to 700 mμ. Biabsorption values (k_ϵ-k_ω) can be calculated from the values of k_ω and k_ϵ. However, biabsorption can also be measured directly with very little equipment. Biabsorption values for

TABLE 6. VALUES OF BIABSORPTION FOR PINK AND RED SYNTHETIC RUBY DETERMINED VISUALLY AND PHOTOELECTRICALLY

λ (mμ)	Pink Ruby			Red Ruby	
	Visual Photometric Determination		Calculated from k_ϵ and k_ω	Visual Photometric Determination	Calculated from k_ϵ and k_ω
	t=0.341 cm.	t=0.477 cm.	t=0.302 cm.	t=0.073 cm.	t=0.073 cm.
440	—	—	$+ 0.8\times10^{-6}$	—	$+ 5.9\times10^{-6}$
450	—	—	+ 0.3	—	+ 3.3
460	—	—	+ 0.1	—	− 2.3
470	—	—	+ 0.1	—	—
480	$- 0.8\times10^{-6}$	—	− 0.4	—	− 11.5
490	− 0.8	—	− 0.4	$- 13.5\times10^{-6}$	− 17.6
500	− 2.3	—	− 1.4	− 29.5	− 29.0
510	− 2.3	-2.7×10^{-6}	− 2.2	− 52.4	− 43.5
520	− 3.5	−3.7	− 3.7	− 73.3	− 67.8
530	− 4.9	−5.5	− 5.2	− 95.4	− 97.8
540	− 7.3	−7.1	− 6.9	−127.3	−125.6
550	− 9.1	−8.5	− 8.8	−165.1	−158.8
560	−10.1	−9.3	−10.0	−194.5	−179.6
570	− 9.9	−9.2	−10.4	−193.0	−184.1
580	− 8.8	−7.9	− 8.6	−164.1	−167.7
590	− 4.7	−5.4	− 6.3	−113.0	−123.8
600	− 2.3	−3.3	− 3.7	− 63.9	− 75.9
610	− 1.6	−1.8	− 2.1	− 30.4	− 44.2
620	− 0.5	−1.4	− 1.0	− 24.7	− 26.2
630	− 0.7	−1.0	− 0.7	− 21.0	− 18.6
640	− 0.5	−1.2	− 0.3	− 18.8	− 15.5
650	− 0.3	−1.1	− 0.3	− 13.7	− 14.4
660	—	—	− 0.4	− 7.2	− 15.3
670	—	—	− 0.6	—	− 16.6
680	—	—	− 0.6	—	− 15.4
690	—	—	− 0.4	—	− 18.9
700	—	—	− 0.6	—	− 16.6

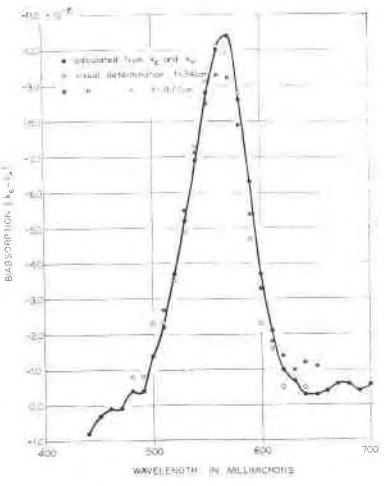
both types of ruby were calculated from the values of I_ω/I_ϵ. These ratios were measured by the double-image method described previously (Denning and Mandarino, 1955; Mandarino, 1959).

Biabsorption measurements were carried out for two specimens: a pink ruby parallelopiped and a red ruby plate. The pink ruby sample provided two dissimilar thicknesses for investigation (0.341 cm. and 0.477 cm.), while the red sample had a single thickness of 0.073 cm.

Values of biabsorption were calculated by substituting the measured values of I_ω/I_ϵ and the appropriate constants in the following equation:

$$k_\epsilon - k_\omega = \frac{\lambda \ln(I_\omega/I_\epsilon)}{4\pi t} \tag{4}$$

These biabsorption values are listed in Table 6 for two thicknesses of pink ruby and one thickness of red ruby. Table 6 also includes the values of biabsorption calculated from the values of k_ϵ and k_ω. Biabsorption



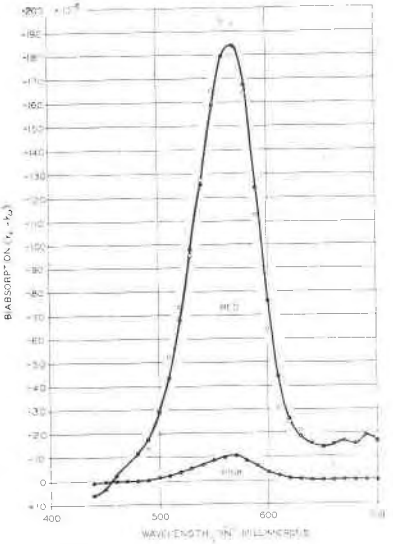


FIG. 5 (*left*). Biabsorption values for pink synthetic ruby.

FIG. 6 (*right*). Biabsorption values for red synthetic ruby. Data for pink synthetic ruby from Figure 5 replotted for comparison. Open circles from visual matching method; solid circles from values of k_ϵ and k_ω.

values for pink ruby are plotted in Fig. 5 and those for red ruby are plotted in Fig. 6. Biabsorption values for the pink ruby (calculated from the absorption coefficients) are also included in Fig. 6 for comparison.

It can be seen that the biabsorption reaches a maximum negative value between 560 mμ and 570 mμ for both pink and red ruby. There is a striking difference in the values of biabsorption for the two types of ruby, particularly at the peak wave length.

The visually determined values of biabsorption agree quite well with those calculated from the photoelectrically determined values of k_ϵ and k_ω. In the visual determination of biabsorption the greatest source of error occurs in matching the intensities of the images formed by the ordinary and extraordinary rays. Because the errors in the visual match-

TABLE 7. PERCENTAGE ERRORS OF BIABSORPTION VALUES FOR PINK AND RED SYNTHETIC RUBY

λ(mμ)	Pink Ruby		Red Ruby
	t=0.341 cm.	t=0.477 cm.	t=0.073 cm.
480	40 %	—	—
490	40 %	—	12 %
500	15 %	—	5½%
510	15 %	9 %	3½%
520	10 %	7 %	2½%
530	7½%	4½%	2 %
540	5 %	4 %	2 %
550	4 %	3½%	2 %
560	4 %	3 %	2 %
570	4 %	3 %	2 %
580	4½%	3½%	2 %
590	8½%	5½%	2 %
600	17 %	9 %	3 %
610	25 %	16 %	6½%
620	60 %	21 %	8 %
630	60 %	27 %	10 %
640	60 %	27 %	11 %
650	60 %	27 %	15½%
660	—	—	26 %

ing process are largely psychological, it is difficult to derive equations for them. However, the reproducibility of the measurements can be determined. Over a period of several weeks, seventy-five I_ω/I_ϵ values were determined for each sample at each wave length. A statistical analysis of the resulting data yielded the average values and standard deviations of the measurements. The effect of the error (standard deviation) in I_ω/I_ϵ on biabsorption was then calculated for the samples at each wave length. The resulting errors in biabsorption are listed in Table 7. In the region of maximum biabsorption (530 mμ to 590 mμ) the errors in biabsorption are generally well below 5% and do not exceed 10%.

COMMENTS

The next step in this study might be a correlation of the optical properties with the chromium content. But a correlation based on only two or three* samples would be highly questionable. It should be pointed out, however, that the absorption and biabsorption data for the limited

* The third sample could be considered as pure Al_2O_3 with the absorption coefficients and biabsorption being equal to zero.

range of chromium content presented here do follow Bouguer-Beer's law.

According to Stillwell (1926), corundum takes on a green color when the chromium content becomes high (around 30–45% Cr_2O_3). To the writer's knowledge, no quantitative work has been done through this range. It is hoped that corundum samples with higher chromium contents will become available and thus enable this study to be extended over a wider range of chromophore concentration.

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