SYNTHETIC BROMELLITE. III. SOME OPTICAL PROPERTIES[1]

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Abstract

The transmittance and refracting properties of BeO were determined in the visible region of the spectrum. Values of the index of refraction for the ordinary ray range from 1.71450 at 0.690 μ to 1.73039 at 0.430 μ, and for the extraordinary ray from 1.73041 at 0.680 μ to 1.74556 at 0.440 μ. The temperature coefficient for the ordinary ray was determined to be $+8.18 \times 10^{-6}/°$ C., and for the extraordinary ray $+13.40 \times 10^{-6}/°$ C. The experimental data were fitted to a two-term Sellmeier equation. Dispersive and resolving properties were calculated permitting the evaluation of BeO as a lens material.

Introduction

This paper describes some optical properties of single crystal synthetic bromellite (BeO) not previously available in the literature and of practical importance in optical design. Measurements were made primarily in the visible region of the spectrum. The following data are reported: transmittance, dependence of refractive index on wavelength, temperature coefficient of refractive index, and the dispersive and resolving properties of the material as a function of wavelength. In addition, a dispersion equation is described for calculating the refractive index at any wavelength within the range of the measured spectral region.

Natural bromellite (Aminoff, 1925) and synthetically grown crystals of BeO belong to the dihexagonal hemimorphic class 6*mm*, and are uniaxially positive with indices of refraction $\omega = 1.719$ and $\epsilon = 1.733$ at $\lambda = 0.589\mu$ (Smith *et al.*, 1964). The habit of the natural crystals is prismatic, with one end terminated by a large pedion and the other end by a hemipyramid modified by a small pedion. The habit of the synthetic crystals grown from molten fluxes is varied and depends on many factors (Austerman, 1963) and (Newkirk and Smith, 1965). Prismatic crystals were selected for refraction angle measurements which had the principal axis (*c*-axis) parallel to the refracting edge. The alternate prism faces approximated a 60° apex angle, had an area of 25 mm² and were flat within $\frac{1}{2}$ wavelength. Table I lists the impurities and their concentrations in a representative batch of flux-grown BeO crystals. Transmittance measurements were made on crystals with well developed {0001} basal planes and bounded by {1010} prismatic faces.

Cation	Concentration, ppm
Aluminum	50
Boron	15
Bismuth	6
Calcium	30
Iron	5
Magnesium	20
Silicon	100
Others	15

TRANSMITTANCE

Durig *et al.* (1962) reported that the transmittance of a 0.1-mm-thick BeO plate was negligible from 1400 cm^{-1} to 300 cm^{-1} and then rapidly increased to 60% in the far infrared from 150 cm^{-1} to 50 cm^{-1}. Three absorption bands at 2350 cm^{-1}, 2050 cm^{-1}, and 1600 cm^{-1} occurred on the high frequency side of the main absorption band. Our measurements show that BeO is transparent throughout the spectral region from 50,000 cm^{-1} to 3,000 cm^{-1}. Figure 1 shows that three absorption bands occur at 2,050 cm^{-1}, 1600 cm^{-1}, and 1400 cm^{-1}. The broad, main absorption peak occurs between 1125 cm^{-1} and 700 cm^{-1} followed by rapidly increasing transmittance to 50% at 500 cm^{-1}. These results show that no anomalous effects in optical properties are to be expected within the measured spectral region of this study.
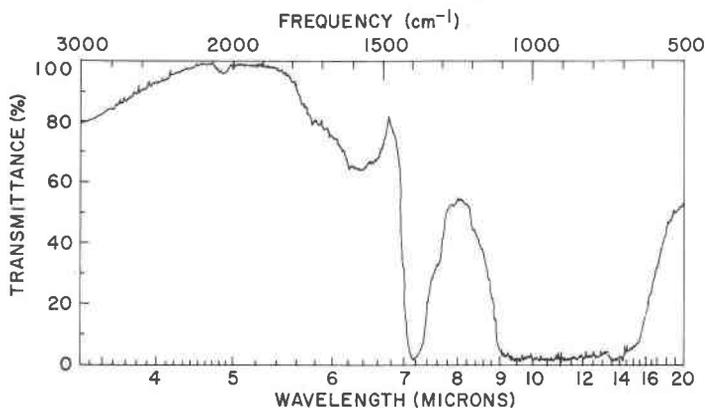

FIG. 1. The infrared absorption spectrum parallel to the "*c*" axis for a flux-grown BeO crystal 0.5 mm thick.
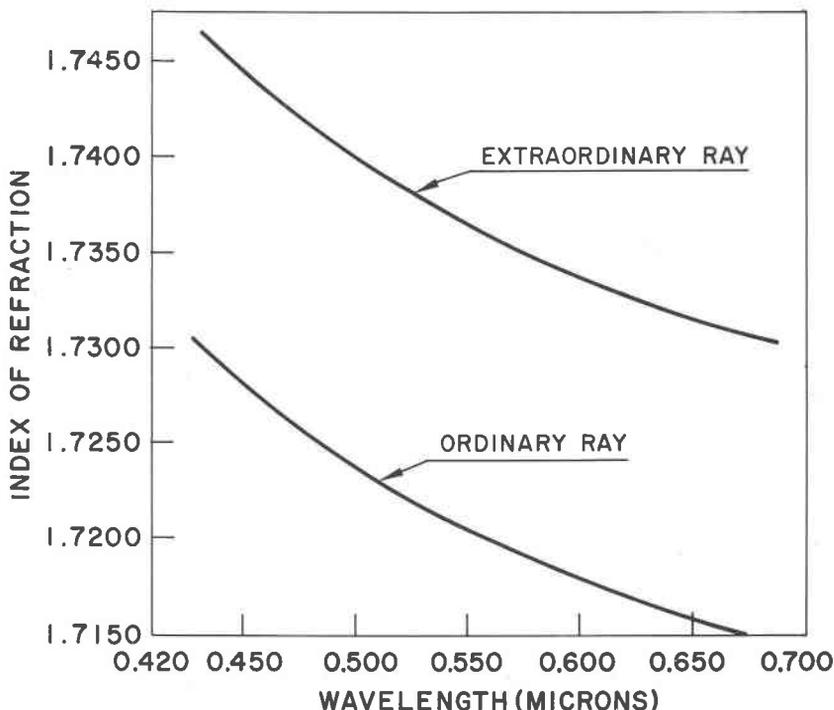
Fig. 2. Dependence of refractive index on wavelength for BeO at 22.40° C.

Refractive Index

Room temperature refraction angle measurements were made with a precision spectrometer by the minimum-deviation method, and the indices were computed in the usual way (Fairbairn, 1952) and (Tilton, 1929, 1931, 1933, 1935). Radiation for dispersion by the BeO prism was obtained from a tungsten ribbon filament lamp and a grating monochromator blazed at 3,000 Å in the first order with a dispersion of 33 Å/mm. The prism was mounted on an inverted goniometer head attached by a bracket to the spectrometer table.

Measurements were made at 27 wavelengths for the ordinary ray and at 25 wavelengths for the extraordinary ray from 0.430μ to 0.690μ. The calculated values are plotted in Fig. 2. These values are greater than those for quartz or calcite (Smakula, 1952), and are comparable to natural sapphire (Malitson, 1962).

Temperature Coefficient of Refractive Index

Refraction angle measurements above and below room temperature were made using a styrofoam cryostat that surrounded the mounting

TABLE II. ESTIMATES OF THE PARAMETERS A_i, λ_i FROM THE DISPERSION EQUATION:

$$(n^2 - 1) = \frac{A_1\lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2\lambda^2}{\lambda^2 - \lambda_2^2}.$$

	Ordinary Ray of BeO at 22.40° C. n=27	
$\lambda_1 = 0.0852980$	$\lambda_1^2 = 0.00727575$	$A_1 = 1.919087$
$\lambda_2 = 14.11775$	$\lambda_2^2 = 199.31087$	$A_2 = 3.972323$
	Extraordinary ray of BeO at 22.40° C. n=25	
$\lambda_1 = 0.0865196$	$\lambda_1^2 = 0.00748564$	$A_1 = 1.972142$
$\lambda_2 = 27.91937$	$\lambda_2^2 = 779.49122$	$A_2 = 17.57870$

TABLE III. OBSERVED AND COMPUTED REFRACTIVE INDEX FOR THE
ORDINARY RAY OF BeO AT 22.40° C.

Wavelength $\lambda(\mu)$	Refractive Index		Residual $\times 10^5$
	Observed	Computed	
0.690	1.71450	1.71449	+1
0.680	1.71482	1.71483	−1
0.670	1.71517	1.71518	−1
0.660	1.71554	1.71554	0
0.650	1.71589	1.71592	−3
0.640	1.71632	1.71631	+1
0.630	1.71668	1.71671	−3
0.620	1.71710	1.71713	−3
0.610	1.71762	1.71757	+5
0.600	1.71795	1.71802	−7
0.590	1.71856	1.71848	+7
0.580	1.71903	1.71898	+5
0.570	1.71950	1.71950	0
0.560	1.72006	1.72003	+3
0.550	1.72062	1.72060	+2
0.540	1.72121	1.72119	+2
0.530	1.72177	1.72181	−4
0.520	1.72249	1.72246	+3
0.510	1.72308	1.72314	−6
0.500	1.72388	1.72387	+1
0.490	1.72460	1.72464	−4
0.480	1.72542	1.72545	−3
0.470	1.72626	1.72630	−5
0.460	1.72725	1.72722	+3
0.450	1.72820	1.72820	0
0.440	1.72924	1.72924	0
0.430	1.73039	1.73035	+4

apparatus. Three holes in the chamber permitted observation of the deviated and undeviated rays and permitted proper alignment of the prism. Temperatures below ambient were obtained by flowing cooled nitrogen gas through the chamber. Temperatures above ambient were generated by varying the current through a small light bulb attached to

TABLE IV. OBSERVED AND COMPUTED REFRACTIVE INDEX FOR THE
EXTRAORDINARY RAY OF BeO AT 22.40° C.

Wavelength ($\lambda(\mu)$)	Refractive Index		Residual $\times 10^5$
	Observed	Computed	
0.680	1.73041	1.73036	$+5$
0.670	1.73075	1.73074	$+1$
0.660	1.73113	1.73113	0
0.650	1.73156	1.73153	$+2$
0.640	1.73191	1.73198	$+3$
0.630	1.73233	1.73237	-4
0.620	1.73279	1.73281	-2
0.610	1.73322	1.73327	-5
0.600	1.73381	1.73375	$+6$
0.590	1.73423	1.73425	-2
0.580	1.73477	1.73477	0
0.570	1.73530	1.73532	-2
0.560	1.73588	1.73588	0
0.550	1.73644	1.73648	-4
0.540	1.73703	1.73710	-7
0.530	1.73779	1.73776	$+3$
0.520	1.73852	1.73845	$+7$
0.510	1.73918	1.73917	$+1$
0.500	1.74002	1.73994	$+8$
0.490	1.74073	1.74074	-1
0.480	1.74162	1.74160	$+2$
0.470	1.74251	1.74251	0
0.460	1.74348	1.74347	$+1$
0.450	1.74447	1.74450	-3
0.440	1.74556	1.74559	-3

the ceiling of the chamber. The temperature in the chamber was measured with a calibrated thermometer suspended directly over the crystal. Temperatures are believed reliable to $\pm 0.01°$ C. Measurements of refractive angle at room temperature with the styrofoam chamber in place showed that its use introduced no systematic error. Refraction angle measurements were made for the ordinary and extraordinary ray at five different temperatures ranging from $-12.06°$ C. to 44.85° C., and at five different wavelengths ranging from 0.450 μ to 0.670 μ. The temperature

coefficients of refractive index (dn/dT) were determined graphically for each wavelength. No significant variation of dn/dT with wavelength was noted. Therefore, these values were averaged over the wavelength range studied for the ordinary and extraordinary ray. The refractive indices increased with increasing temperature for both rays in a manner similar to that reported for calcite and quartz (Smakula, 1952) and sapphire (Malitson, 1962). The coefficient for the ordinary ray was determined to be $+8.18 \times 10^{-6}/°$ C., and $+13.40 \times 10^{-6}/°$ C. for the extraordinary ray.

DISPERSION EQUATION

To relate index of refraction to wavelength, the room temperature experimental values of refractive index were fitted to a two-term Sellmeier equation of the form

TABLE V. COMPUTED REFRACTIVE INDICES AND DISPERSION FOR THE ORDINARY RAY OF BeO AT 22.40° C.

Wavelength $\lambda(\mu)$	Computed Refractive Index (n)	Dispersion $-dn/d\lambda$	Wavelength $\lambda(\mu)$	Computed Rrefractive Index (n)	Dispersion $-dn/d\lambda$
0.699	1.71446	0.0336	0.555	1.72028	0.0563
0.685	1.71463	0.0341	0.550	1.72057	0.0576
0.680	1.71480	0.0347	0.545	1.72086	0.0590
0.675	1.71497	0.0352	0.540	1.72116	0.0605
0.670	1.71515	0.0353	0.535	1.72146	0.0620
0.665	1.71533	0.0364	0.530	1.72178	0.0636
0.660	1.71551	0.0370	0.525	1.72210	0.0652
0.655	1.71570	0.0376	0.520	1.72243	0.0669
0.650	1.71589	0.0383	0.515	1.72277	0.0687
0.645	1.71608	0.0389	0.510	1.72311	0.0706
0.640	1.71628	0.0396	0.505	1.72347	0.0725
0.635	1.71648	0.0404	0.500	1.72384	0.0745
0.630	1.71668	0.0411	0.495	1.72422	0.0767
0.625	1.71689	0.0419	0.490	1.72461	0.0789
0.620	1.71710	0.0427	0.485	1.72501	0.0812
0.615	1.71732	0.0435	0.480	1.72542	0.0836
0.610	1.71754	0.0444	0.475	1.72584	0.0861
0.605	1.71776	0.0453	0.470	1.72628	0.0887
0.600	1.71799	0.0462	0.465	1.72673	0.0915
0.595	1.71822	0.0471	0.460	1.72719	0.0944
0.590	1.71846	0.0481	0.455	1.72767	0.0974
0.585	1.71870	0.0492	0.450	1.72817	0.1006
0.580	1.71895	0.0502	0.445	1.72868	0.1039
0.575	1.71921	0.0514	0.440	1.72921	0.1074
0.570	1.71947	0.0525	0.435	1.72976	0.1111
0.565	1.71973	0.0537	0.430	1.73032	0.1149
0.560	1.72000	0.0550			

$$(n^2 - 1) = \frac{A_1\lambda^2}{\lambda^2 - \lambda_1{}^2} + \frac{A_2\lambda^2}{\lambda^2 - \lambda_2{}^2} .$$

Here n is the measured refractive index, λ is the wavelength, and A_i and λ_i are unknown parameters related to the strengths of the absorption bands and the absorption wavelengths, respectively. These parameters were estimated using the method of least squares (Olsen and Browne, 1964 and IBM Share Prog. No. 3094 Rev.) (Table II). A comparison of the measured indices of refraction with those predicted from the Sellmeier equation at constant wavelength is made in Tables III and IV. A test for the degree of fit between the last two decimal positions of these data was performed using the chi square (χ^2) test (Hald, 1952). If there were no significant differences in the last two decimals between the measured refractive index data and the predicted refractive index data, one would expect, 95% of the time, $\chi^2 \leq 36.42$ and $\chi^2 \leq 38.89$ for the extraordinary

TABLE VI. COMPUTED REFRACTIVE INDICES AND DISPERSION FOR THE EXTRAORDINARY RAY OF BeO AT 22.40° C.

Wavelength $\lambda(\mu)$	Computed Refractive Index (n)	Dispersion $-dn/d\lambda$	Wavelength $\lambda(\mu)$	Computed Refractive Index (n)	Dispersion $-dn/d\lambda$
0.680	1.73036	0.0369	0.555	1.73618	0.0595
0.675	1.73055	0.0375	0.550	1.73648	0.0609
0.670	1.73074	0.0381	0.545	1.73679	0.0623
0.665	1.73093	0.0387	0.540	1.73710	0.0639
0.660	1.73113	0.0393	0.535	1.73743	0.0655
0.655	1.73132	0.0400	0.530	1.73776	0.0671
0.650	1.73153	0.0407	0.525	1.73810	0.0688
0.645	1.73173	0.0414	0.520	1.73845	0.0706
0.640	1.73194	0.0421	0.515	1.73880	0.0725
0.635	1.73215	0.0428	0.510	1.73917	0.0745
0.630	1.73237	0.0436	0.505	1.73955	0.0765
0.625	1.73259	0.0444	0.500	1.73994	0.0786
0.620	1.73281	0.0453	0.495	1.74033	0.0808
0.615	1.73304	0.0461	0.490	1.74074	0.0832
0.610	1.73327	0.0470	0.485	1.74117	0.0856
0.605	1.73351	0.0480	0.480	1.74160	0.0881
0.600	1.73375	0.0489	0.475	1.74205	0.0907
0.595	1.73400	0.0499	0.470	1.74251	0.0935
0.590	1.73425	0.0510	0.465	1.74298	0.0964
0.585	1.73451	0.0520	0.460	1.74347	0.0994
0.580	1.73477	0.0532	0.455	1.74398	0.1026
0.575	1.73504	0.0543	0.450	1.74450	0.1060
0.570	1.73532	0.0555	0.445	1.74504	0.1094
0.565	1.73560	0.0568	0.440	1.74559	0.1131
0.560	1.73588	0.0581			

and ordinary ray data, respectively. The calculated values were 10.65 and 11.66. One concludes there is no significant difference between the actually measured data and the data predicted from the Sellmeier equation.

DISPERSIVE AND RESOLVING PROPERTIES

The two Sellmeier equations were differentiated with respect to λ using the estimates of the parameters obtained by least squares (Table II).
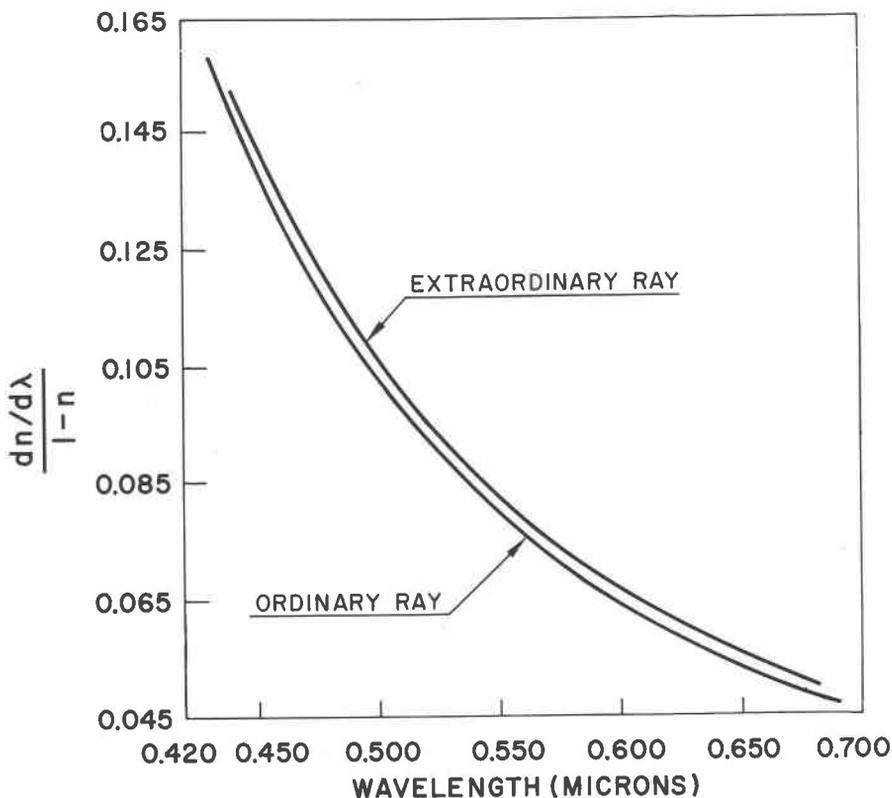

FIG. 3. The dispersive power of a BeO prism at wavelength λ. Dispersion tends to minimize in the near infrared.

Values of λ differing by a small constant amount were introduced into $dn/d\lambda$ and the appropriate dispersion coefficients were obtained. These data, together with computed refractive index values are listed in Tables V and VI. The programmed data (Olsen and Browne, 1964) provided graphical aids for estimating the dispersive and resolving properties of BeO as a function of wavelength, namely

$$\frac{\mathrm{d}n/\mathrm{d}\lambda}{1-n}, \qquad \frac{1-n}{\mathrm{d}n/\mathrm{d}\lambda}, \quad \text{and} \quad \left| \left(\frac{\lambda \mathrm{d}n}{\mathrm{d}\lambda} \right) \right|^{-\lambda}.$$

A plot of the function

$$\frac{\mathrm{d}n/\mathrm{d}\lambda}{1-n}$$

versus wavelength is shown in Fig. 3. This defines the dispersive power of a BeO prism at wavelength λ. The relative dispersion decreases with
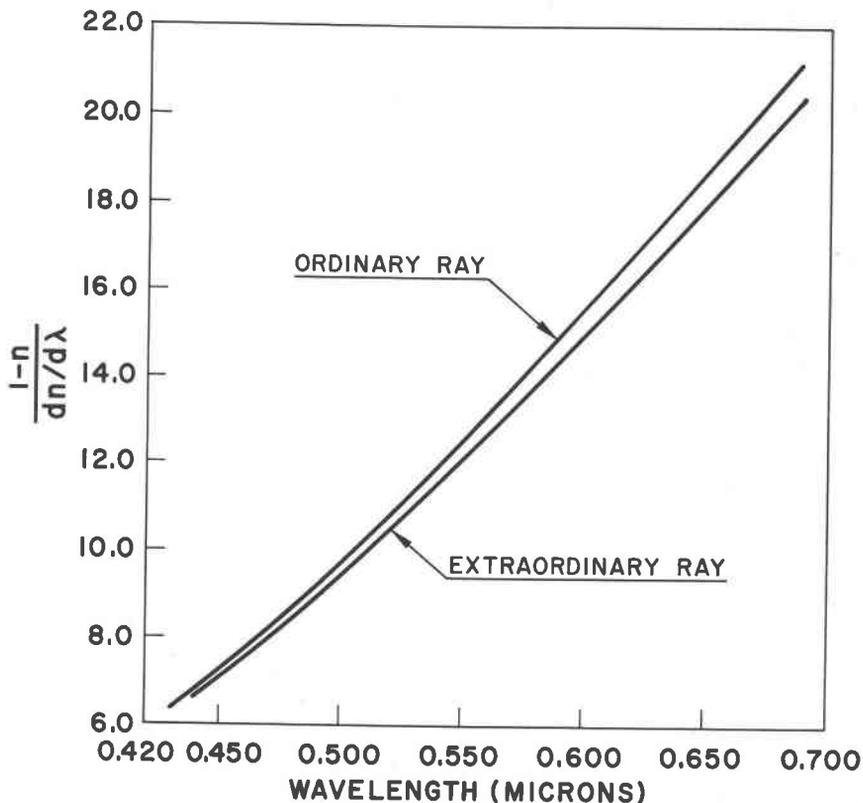

FIG. 4. The influence of dispersion upon chromatic aberration for a BeO prism. Chromatism is a minimum in the near infrared.

increasing wavelength, tending to minimize in the near infrared. The reciprocal of this function is shown in Fig. 4. This function may be used to qualitatively assess the degree of chromatic aberration in BeO. Since

$$\frac{1-n}{\mathrm{d}n/\mathrm{d}\lambda}$$
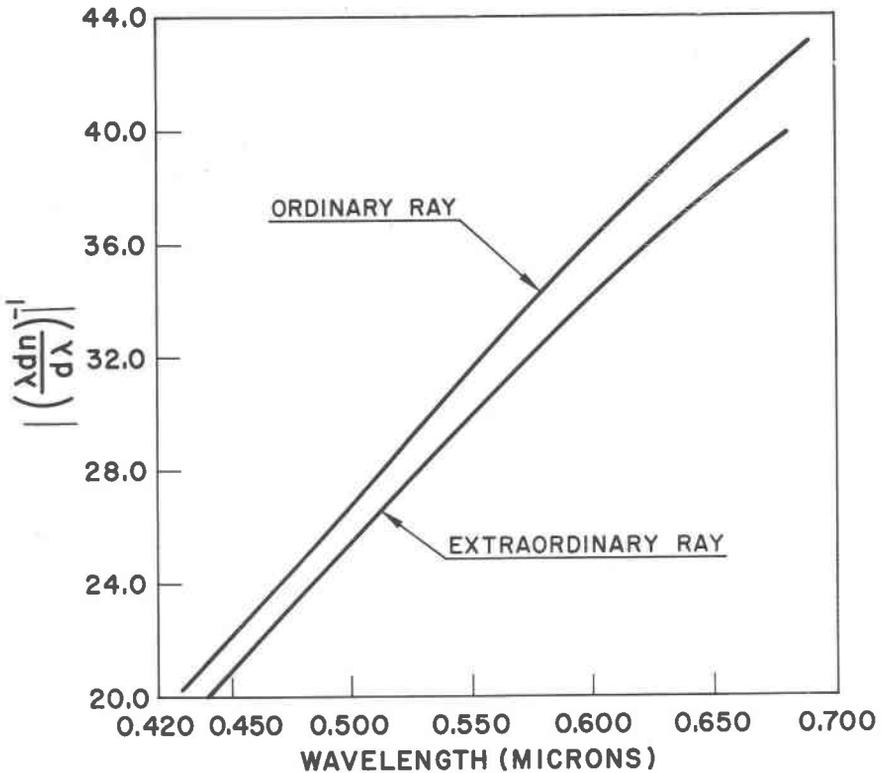
Fɪɢ. 5. Dependence of resolution at a chosen wavelength upon the dispersion of BeO. Resolution will maximize at wavelengths shorter than 0.4 micron and in the infrared.

is inversely proportional to the chromatic aberration, the shape of this curve indicates that chromatism is decreasing and will reach a minimum in the near infrared, for a single element BeO lens. Finally, Fig. 5 shows the variation with wavelength of the quantity

$$\left| \left(\frac{\lambda dn}{d\lambda} \right)^{-1} \right|.$$

This provides an estimation of the spectral limit of resolution that can be obtained, since it is inversely proportional to the resolution. For BeO, high resolution should occur at wavelengths shorter than 0.4 micron and for wavelengths in the infrared.

In general, the dispersive and resolving properties of BeO are those to be expected of a material with a high degree of ionic character to the bonding, and are similar to those of crystalline quartz, calcite and sapphire.

ACKNOWLEDGMENTS

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