Refractive index and optical absorption of bariumhexa-aluminate $BaAl_{12}O_{19}$

Recent interest in growing single crystals of hexagonal barium aluminate made it possible to investigate the optical properties of this material. As would be expected, the crystals are completely transparent to the visible spectral region. Absorption and refractive index measurements show a very high band gap ($E_g \approx 6.1$ eV according to $\lambda_g \approx 205$ nm), whereas the refractive index and the dispersion as well are rather low.

Single crystals of barium aluminate of the composition $Ba_{1-x}Al_{12+(2/3)x}O_{19}$ ($x = 0.1 \ldots 0.2$) have been grown by means of the Czochralski technique [1]. The crystals had a diameter of about 25 mm and a length of 90 mm, exhibiting the hexagonal lattice parameters $a = 5.59$ Å and $c = 22.72$ Å. This implies that some bi-refringence is to be expected, the experimental verification of which will be shown later. The crystals were cut into 9.54, 5.80, and 0.11 mm thick slices and polished to optical surface quality.

The optical absorption α and the refractive index n can be computed simultaneously by measuring the optical density $A = \log(I_0/I)$ of two samples of different thicknesses d_1 and d_2, where I_0 and I are the intensity of the light beam before and behind the sample, respectively. For each sample the Lambert–Beer law is valid:

$$T_i = I_i/I_0 = \frac{(1-R)^2 e^{-\alpha d_i}}{1-R^2 e^{-2\alpha d_i}} \quad (i = 1, 2) \qquad (1)$$

where T_i, I_i, and R are the transmission coefficient, the transmitted light intensity, and the reflection coefficient, respectively. With $k = \lambda\alpha/4\pi$ the dimensionless extinction coefficient is then

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \qquad (2)$$

Because of the implicit shape of Equation 1 it is not possible to solve for α and n. Using an iterative method, however, it is possible to get an appropriate choice of n and α which simultaneously satisfy Equation 1 for both samples. The optical density measurements were carried out with the aid of a CARY 17 spectrophotometer.

Fig. 1 shows the results of such computation using two sample pairs having the thickness $d_1 = 9.54$ mm, $d_2 = 5.80$ mm and $d_1 = 5.80$ mm, $d_2 = 0.11$ mm. The two absorption spectra α_1 and α_2 coincide fairly well, whereas the dispersions n_1 and n_2 are considerably different from each other. They merely show generally a normal dispersion behaviour. For comparison Fig. 1 also shows a refractive index spectrum n_B as obtained from reflection measurements as described in [2].

The large deviations of n_1 and n_2 with respect to n_B can be explained by three effects. The first is a possible error of ± 0.01 in reading the optical density as displayed by the CARY 17. This error causes a refractive index error of $\Delta n \approx 0.1$, depending on the sensitivity of n for errors in the optical density $\log(I_0/I)$. The second effect, which can lead to erroneous optical density data, is microcracking within the samples due to the easy cleavability along planes perpendicular to the crystallographic c-axis. These cracks, sometimes visible to the naked eye, are responsible for light scattering which reduces the transmitted

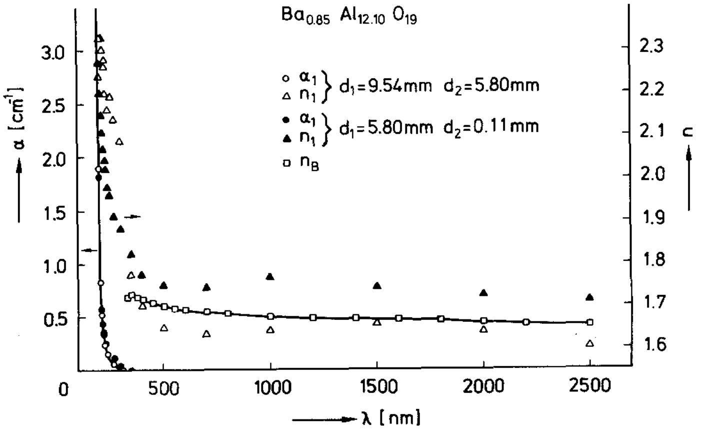

Figure 1 $Ba_{0.85}Al_{12.10}O_{19}$. Optical absorption and dispersion spectra. α_1, n_1: absorption and dispersion as computed from optical density measurements of two samples having thicknesses $d_1 = 9.54$ mm and $d_2 = 5.80$ mm. α_2, n_2: as for α_1, n_1, but with sample thicknesses $d_1 = 5.80$ mm and $d_2 = 0.11$ mm. n_B: refractive index spectrum as obtained from Brewster's angle measurements.

0022–2461/80/041066–02$02.20/0

light intensity I in an unpredictable manner. Repetition of the measurements with crystals of higher quality reproduced the deviations of the spectra. More thoroughly performed experiments on taking the optical density spectra, yielded the somewhat astonishing result that the optical density could be shifted upwards and downwards for optical density values of about ± 0.02 by simply rotating the samples around an axis normal to their surfaces. As the above mentioned plane parallelism is to be taken as idealized, a wedge error of some hundredths of degrees of arc is common and can account for a slight aberration of the light beam of the CARY 17. Thus by rotating a wedge-shaped sample the light beam will rotate around the optical axis of the spectrophotometer detector. As the sensitivity is not generally uniform over the entire detector area a change in the optical density reading must occur. This is an effect which is known to other experimentalists who use to take spectra with the CARY 17.

In order to get an idea of the optical properties even below wavelengths of λ = 195 nm or energies above 6.4 eV, a least squares fit was made, fitting the n_B data to a three-term Sellmeier oscillator equation [3]:

$$n_B^2 - 1 = \sum_{i=1}^{3} \frac{F_i}{E_i^2 - E^2} \qquad (3)$$

where F_i and E_i are the oscillator strengths and the position of the ith oscillator with respect to photon energy E, respectively. The results are listed in Table I. The first oscillator represents the total of the lattice vibrations. Its influence on the dispersion data is very weak, so its Sellmeier parameters have a large inherent uncertainty, as indicated by the tilde. The main contribution to the dispersion of barium aluminate stems from the second oscillator located at $E = 10.50$ eV. The influence of the third oscillator, although being of almost equal magnitude to the second, is much weaker, as it is located farther in the ultra-violet (13.00 eV).

TABLE I The Selimeir oscillator parameters as obtained from a least squares fit of the refractive index data n_B

i	F_i (eV^2)	E_i (eV)
1	~ 10^{-7}	~ 0.02
2	123.2	10.50
3	115.5	13.00

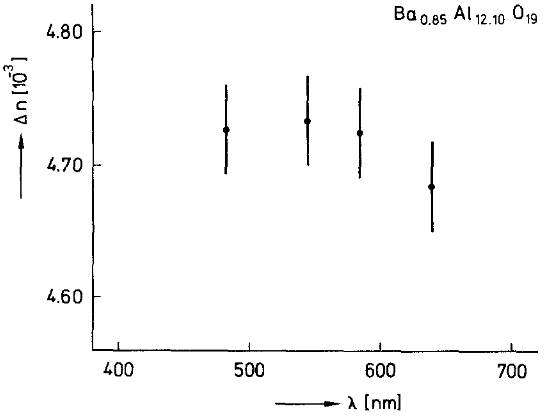

Figure 2 $Ba_{0.85}Al_{12.10}O_{19}$. Bi-refringence for four selected wavelengths.

Bi-refringence measurements were carried out in the visible region with a 100 μm thick sample of $BaAl_{12}O_{19}$ using conventional ellipsometric methods by means of a Leitz microscope. The mean value of about $\Delta n = 0.005$ lies within the precision range of the Brewster's angle measurements [2], so bi-refringence could not be measured with that technique. Fig. 2 shows the results of the measurements taken at four wavelengths selected by interference filters.

Acknowledgement

The authors wish to thank Mr H. Guschigk for evaluating the computer programs HDICKE12 and SELMEIER. The co-operation of Mr H. Laudan in preparing the $BaAl_{12}O_{19}$ crystals is fully acknowledged.

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Received 21 August
and accepted 24 September 1979

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