Cryolite, chiolite and cryolithionite: optical data redetermined

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The mineral samples for the present study all came from the cryolite mine in Ivigtut, South Greenland, (Bøggild 1953, Pauly 1960).

Cryolite is usually colourless or white. In siderite cryolite, where the mineral occurs together with siderite and sulphides, the crystalline individuals are mostly cm-sized whereas the massive pure cryolite could be found in metre sized individuals. Cryolite from certain radioactive environments is light smoky to nearly black. Crystals of cryolite, which are always secondary, are colourless, vitreous. No other natural colour varieties came from Ivigtut. A purple variety of cryolite has obtained its colour through mechanical deformation connected with blasting in the quarry; the purple hue is thus an artificially introduced colour. Limonite staining on cryolite can easily be removed and is thus not a true colour of cryolite.

All types of cryolite are criss-crossed by numerous twin lamellae. Of the theoretically possible thirteen twin laws (Donnay 1952, Wrinch 1952), four have been found in cryolite crystals and seven in the massive cryolite from Ivigtut (Bøggild 1911). Most twin lamellae are 30 to 50 µm wide. Several of the twin laws result in an interchange of the faces (110) and (001). According to an ongoing study (to be published later) such twin laws cannot be dominating in the massive cryolite. An indication for this is that one can distinguish between parting faces along (110) and (001). This allowed the production of crystallographically oriented sections, which form a basis for the present study.

Chiolite occurred in various intergrowths but also in bladed masses of colourless, vitreous appearance. The basal cleavage is usually observed through the presence of curved shining faces not unlike the cleavage faces often seen on gypsum.

Cryolithionite occurred as cm to dm sized crystals embedded in cryolite. The mineral is colourless, vitreous to white. In two cases a faintly rose to purple variety has been found.

The immersion method

Mixtures of water and glycerole – 2 to 5% of the latter – gave liquids with refractive indices in the vicinity of those reported for cryolite. Their refractive indices were established with the Abbe refractometer, which was checked with pure water i.e. double ion exchanged water. At 27°C it showed 1.3322; this is 0.0001 above the tabulated value in Handbook of Chemistry and Physics (1965). The same correction was found using the calibration glass delivered with the instrument.

Taking into account the coloured fringes of the Becke line it was found that cryolite has refrac-
tive indices between 1.3381 and 1.3392. These results were obtained on powders of cryolite crystals, of massive pure cryolite, and black (smoky) cryolite.

It should especially be noted that cryolite and cryolithionite in a liquid having \( n = 1.3393 \) clearly showed the latter to lie above this liquid whereas the cryolite was partly below the liquid and partly very close to the liquid.

**Preparations for refractometer and Berek compensator determinations**

Krenner (1883) found that the plane of the optical axes in cryolite is perpendicular to (010) and the acute bisectrix or \( \gamma \) makes an angle of 43°54' with the c-axis. These orientations, still accepted, have not been questioned by later authors. Bøggild (1911) and Cesaro & Melon (1936), in fact based their work on these observations.

For the study of the principal birefringences, sections were cut through two blocks of massive cryolite showing well developed parting along (110) and (001). In fact these blocks appeared as cube-like bodies, having edges 6 to 8 cm long. In each of the blocks sections parallel to (010) were cut. The sections, cemented to glass plates, were ground down to a thickness of 250 \( \mu m \). This thickness was chosen because of the extremely low birefringence of the mineral; between crossed polars such sections show grey to white of the first order. Fig. 1 and fig. 2-1 show these sections. About 1/4 of the numerous lamellae show nice bisymmetrical interference figures corresponding to sections perpendicular to the obtuse bisectrix, \( B_2 \). On such lamellae \( \gamma-\beta \) could be determined.

In one of the cryolite blocks were also cut sections parallel with the crystallographical b-axis. Whereas one of these sections formed an angle of 45° above (001) the other was cut at an angle of 45° below (001). These two sections were thus perpendicular to and parallel with the plane of the optical axes respectively. Due to the twinning of the mineral both sections showed lamellae giving interference figures corresponding to sections perpendicular to the acute bisectrix and sections perpendicular to the optical normal or \( \beta \). Also these sections were produced to a thickness of 250 \( \mu m \). Figs 2-2 and 2-3 show these

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*Fig. 1. Thin section of cryolite parallel to (010), \( \times 1.5 \), crossed polars. Vertical twinnlamellae have twin boundaries parallel to (110), inclined lamellae are parallel to (112) and (112). Note: the section between parallel polaroid filters has been used as a photographic negative, yielding a picture as if photographed between crossed polars.*
Fig. 2. Thin sections of cryolite, × 1.5. 2–1 is a section parallel to (010) as if photographed between crossed polars. 2–2 and 2–3 are perpendicular to the section shown in 2–1, making 45° angles with (001). Note: sections between polaroid filters used as photographic negatives. Filters so arranged that the pictures appear as seen between crossed polars and turned 45° from extinction position. Dark areas represent parts of the sections perpendicular to the acute bisectrix.
sections, in which $\gamma-\alpha$ and $\beta-\alpha$ could be determined.
The counterparts to the last two sections were polished so that they could be used in the refractometer examination.

An unoriented piece of black cryolite containing a 2 cm inclusion of cryolithionite was also polished for the refractometer determinations as was a similar sized piece of purple cryolite.

A block of chiolite was cut perpendicular to the cleavage giving a 2 by 6 cm surface which, when polished, allowed the determination of its refractive indices.

Abbe refractometer determinations

It is beforehand clear that the refractive indices determined on the polished sections of cryolite can only be some intermediate values due to the presence of the numerous twin lamellae, see table 1.

Reproducibility of the readings of the instrument seems to lie within plus or minus 0.0001.

Supplementing the determinations of the dispersion coefficient by means of the compensating prism of the instrument, several series were measured using monochromatic light produced by a set of fixed filters. For white cryolite the following values were obtained:

- $n_{488} = 1.3410$ (1.3235)
- $n_{526} = 1.3398$
- $n_{546} = 1.3395$ (1.3335)
- $n_{590} = 1.3388$ (1.3388)
- $n_{644} = 1.3373$
- $n_{656} = 1.3368$ (1.3443)

Similar readings were obtained on the polished sample of purple cryolite. The values given in parentheses are the uncorrected readings of the instrument. Temperature during the measurements was 26°C. Glycerole ($n = 1.4728$) was used for fixing the polished samples on the refractometer.

Birefringences and $2V$ of cryolite

The sections containing the crystallographical b-axis and making 45° angles above and below (001) i.e. section IV$_2$ and V$_2$ (from block 2) and the sections parallel to (010) i.e. section I$_2$ and IV$_1$ (from block 1) were used for determination of the birefringences, see table 2. In the preparation of the sections their thicknesses were kept as close as possible to 250 $\mu$m.

As can be seen in table 2, calculation of $2V$ from the two sets of principal birefringences gave consistent results. The differences in birefringences found on the various sections arise from variations in thickness. On section I$_2$ the thickness was determined through grinding away the cryolite and measuring the thickness of the cementing material. The result indicated a thickness of this section of 250 $\mu$m plus or minus less than 10 $\mu$m. In the other sections the thickness was measured by means of a micrometer screw assuming the cementing material to have the same thickness in all sections. This obviously was not quite correct.

Basing the evaluation of the results on the values obtained on section I$_2$ one arrives at the values underlined in table 2.

| Table 1. Refractive indices of cryolite, cryolithionite and chiolite. |
|---------------------------------|-----------------|-----------------|-----------------|
| Sections of cryolite            | $n_{\text{lowest}}$ | $n_{\text{highest}}$ | $n_F - n_C^*$ |
| $\gamma$ and $\beta$            | 1.3382           | 1.3392           | 0.0036          |
| Black cryolite                  | 1.3386           | 1.3391           | 0.0036          |
| Undetermined orientation        | 1.3384           | 1.3388           | 0.0036          |
| Purple cryolite                 | 1.3395           | 0.0040           |
| Cryolithionite                  | 1.3395           | 0.0040           |
| Chiolite ne                     | 1.3431           | 0.0037           |
| no                              | 1.3497           | 0.0037           |

$^*$Determined from the position of compensating prism of the refractometer.
Table 2: Birefringences and 2V of cryolite.

<table>
<thead>
<tr>
<th>Section</th>
<th>V2</th>
<th>IV2</th>
<th>IV1</th>
<th>I2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-β : β-α</td>
<td>0.000117</td>
<td>0.000124</td>
<td>0.000803</td>
<td>0.000881</td>
</tr>
<tr>
<td>+β : γ-β</td>
<td>0.000095</td>
<td>0.001059</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2V
40.2° 40.0°

Determination of 2V by Tobi's method

In the sections IV2 and V2 interference figures corresponding to sections perpendicular to the acute bisectrix were present. Measurements of the distances between the arms of the hyperbolae and of the diameter of the field of view (using an objective with N.A. = 0.85) gave a ratio between these distances corresponding to 0.55. From the chart for determination of 2V (or 2E) – after Tobi – in Bloss (1966) one finds 2V = 41°. For this determination n₀ was taken to be 1.338. Taking into account the diffuse character of the arms of the hyperbolae the measurements seem to have a variation corresponding to less than plus or minus 2°.

It should be noted that similar interference figures have been found on grains in the powder mounts examined; none of them, however, were strictly bisymmetrical. In a thin section of a more conventional thickness i.e. 50 μm, it was observed that the hyperbolae show much more diffuse arms. Such sections are not well suited for determination of 2V although they confirm its general magnitude.

The optical data for cryolite

The bracket values for the refractive indices for cryolite obtained by the immersion method and by the refractometer measurements taken together with the values of the principal birefringences are given in table 3.

Table 3: Optical data for cryolite.

<table>
<thead>
<tr>
<th>Data from Krenner:</th>
<th>nα = 1.3382</th>
<th>ng = 1.3383</th>
<th>γ √c = 44°</th>
</tr>
</thead>
<tbody>
<tr>
<td>nβ = 1.3385</td>
<td>nγ = 1.3392</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ny = 1.3389</td>
<td>ny-ňα = 0.0010</td>
<td>+ 2V = 40°</td>
<td></td>
</tr>
<tr>
<td>ny-nC = 0.0036</td>
<td>nF-nC = 0.0036</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Discussion

The optical data for cryolite as they are given in the various handbooks and textbooks originate from four sources: Krenner (1883), Bøggild (1913, 1953), Paduroff (1925) and Cesaro & Melon (1936), see table 4.

Table 4: Optical data for cryolite from literature.

<table>
<thead>
<tr>
<th>Krenner 1883</th>
<th>Bøggild 1953 &amp; 1913*</th>
<th>Paduroff 1925</th>
<th>Cesaro &amp; Melon 1936</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1.364</td>
<td>nα = 1.3385</td>
<td>ng = 1.3383</td>
<td>nα = 1.3376</td>
</tr>
<tr>
<td>nβ = 1.3389</td>
<td>nγ = 1.3396</td>
<td>γ-α = 0.0025</td>
<td>nβ = 1.3377</td>
</tr>
<tr>
<td>ny = 1.3396</td>
<td>ny-ňα = 0.0011</td>
<td>γ-β = 0.0021</td>
<td>ny = 1.3387</td>
</tr>
<tr>
<td>nny = 1.3390*</td>
<td>β-α = 0.0004</td>
<td>2V = 37°30'</td>
<td>ny-ňα = 0.0011</td>
</tr>
<tr>
<td>2Ered = 58°50'</td>
<td>middle = 1.3390*</td>
<td>nγ = 1.3380*</td>
<td>nF = 1.338</td>
</tr>
<tr>
<td>2Eyelowe = 39°24'</td>
<td>2V = 37°30'</td>
<td>2V = 40°</td>
<td>nγ = 1.338</td>
</tr>
<tr>
<td>2Esue = 60°10'</td>
<td>2Vcal = 44°***</td>
<td>2Vcal = 74°</td>
<td>nγ = 1.338</td>
</tr>
<tr>
<td>2Vcaw = 44°***</td>
<td>2Vcal = 47°</td>
<td>2Vcal = 47°</td>
<td>nγ = 1.338</td>
</tr>
</tbody>
</table>

** supposedly misprint for 589.
*** assuming β = 1.338.
Krenner’s value for the refractive index of cryolite is clearly ruled out by Bøggild’s (1913) determination and the determinations in the present work. His 2E determination converted into 2V assuming, $\beta = 1.338$ is close to the value found in the present work. The present birefringence determinations seem, however, rather in favour of the lower value for 2V i.e. 40°.

Bøggild’s refractive indices were not published before 1953 when he published the revised edition of his Greenland mineralogy (1953). In 1913, however, he gave the mean refractive index which can be seen to be the mean also of the 1953 values. His $n_p$ is clearly wrong if one accepts – as he himself did – Krenner’s value for the axial angle. His $n_\alpha$ is of course not far from the value obtained in the present work. The real difficulty emerges from his $n_\nu$ value which is higher than the value he quotes – from Ussing (1904) – for cryolithionite from Ivigtut, Bøggild (1913). In that work it is seen that Bøggild used the total refractometer for his refractive index determinations. Ussing stated in his 1904 paper that he made his measurements of the refractive index of cryolithionite on a carefully cut and polished prism of the mineral. Little wonder therefore that his value seemingly stands. The comparison of the two minerals in a liquid having an index of refraction $= 1.3393$ rather clearly showed cryolithionite to be higher than the liquid and the cryolite to be lower, although in some positions cryolite was very close to the refractive index of the liquid. So there can hardly be any doubt about Bøggild’s values being a little too high. As this might be caused by an instrumental error his refractive indices of chiolite were checked, but the resulting values were 7 to 11 higher in the fourth decimal, as can be seen in table 1.

The optical data given by Paduroff are difficult to accept as they so clearly deviate from the main trend reported in the other papers and the results obtained in the present work.

Cesaro & Melon’s cryolite data deserve attention because these data have been incorporated in Dana’s System of Mineralogy (1951). They published their note on the optics of cryolite because as they say there was a lack of information as to the birefringence of this mineral. They stated that Krenner’s orientation and his angular values for cryolite form the basis for their work.

Pauli: Cryolite, chiolite and cryolithionite

Cesaro & Melon carried out determinations of the refractive index using an Abbe-Pulfrich refractometer measuring on a (001) face of a crystal in monocromatic light using filters. They reported the following values:

$$
\begin{align*}
n_{477} &= 1.319 \\
n_{541} &= 1.331 \\
n_{598} &= 1.338 \\
n_{662} &= 1.343
\end{align*}
$$

Due to a regretable error these values were, however, the uncorrected readings of the instrument. According to professor Melon (personal communication kindly offered 1976) the corrected values should be as follows:

$$
\begin{align*}
n_{477} &= 1.340 \\
n_{541} &= 1.3395 \\
n_{598} &= 1.338 \\
n_{662} &= 1.334
\end{align*}
$$

which compares fairly well with the results obtained in this study, see above.

The next step in their determinations consisted in establishing the retardation on (110) and (001) faces of several mm-sized crystals. From these values and taking into account Krenner’s determinations the principal birefringences of the mineral were calculated. Their results are:

$$
\begin{align*}
n_\eta - n_\sigma &= 0.001135 \\
n_\nu - n_\alpha &= 0.000979 \\
n_\beta - n_\alpha &= 0.000156
\end{align*}
$$

These values compare rather well with those found through direct measurement on oriented sections in the present study.

Finally it should be noted that on the last page of their paper Cesaro & Melon have the following assumption for the values of the refractive indices of cryolite: "En supposant que l’indice mesuré, 1.338, soit l’indice médian, c’est-à-dire que l’on ait

$$n_\eta + n_\alpha + n_\rho = 4.014$$

en tenant compte des biréfringences mesurées, on arrive à

$$n_\eta = 1.3387, n_\alpha = 1.3377 \text{ and } n_\rho = 1.3376"
That this was an unfortunate basis on which to establish the indices of refraction of cryolite is rather obvious.

Acknowledgement. I owe sincere thanks to Mr. Ib H. Nielsen, Mineralogical Institute, Technical University of Denmark, for the production of both the magnificent large thin sections and the polished sections.

Dansk sammentrag

Kryolits optiske data, d.v.s. lysbrydningen, dispersionen, dobbeltbrydningen og axevinklen, synes der at være nogen uenighed om i litteraturen, se tabel 4.

Lysbrydningsbestemmelsen vanskeliggøres af mineralets intensive opdeling i ganske tynde lameller på grund af tvillindannelsen efter op til 7 forskellige tvillinglove. I den foreliggende undersøgelse er det forsøgt at gennemføre bestemmelserne af de optiske konstanter ved at kombinere resultaterne fra flere forskellige metoder.


Ved at kombinere resultaterne fra de forskellige bestemmelser kommer man frem til de i tabel 3 anførte værdier for kryolits optiske data.

References


