Cryolite, chiolite and cryolithionite: optical data redetermined

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The optical data for cryolite from Ivigtut, South Greenland, have been determined using the immersion method and the Abbe refractometer to bracket the refractive indices, Tobi's method to establish 2V and the Berek compensator for the determination of the birefringences. The dispersion has been determined with the Abbe refractometer. The refractive indices and the dispersion of chiolite and cryolithionite have also been determined using the Abbe refractometer. The obtained results differ from those to be found in the literature where, moreover, several different values are reported. The extremely low refringence and birefringence of cryolite and its numerous twin lamellae impart difficulties for the determination but it appears that erroneous values have slipped into the literature. As the main sources are more than 50 years old, instrumental inaccuracies may likewise play a role.

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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 refractive 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 γ 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 μm. 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 ¼ of the numerous lamellae show nice bisymmetrical interference figures corresponding to sections perpendicular to the obtuse bisectrix, B_2. On such lamellae γ–β 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 β. Also these sections were produced to a thickness of 250 μm. Figs 2–2 and 2–3 show these

Fig. 1. Thin section of cryolite parallel to (010), × 1.5, crossed polars. Vertical twinlamellae have twin boundaries parallel to (110), inclined lamellae are parallel to $(\bar{1}\bar{1}2)$ 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.

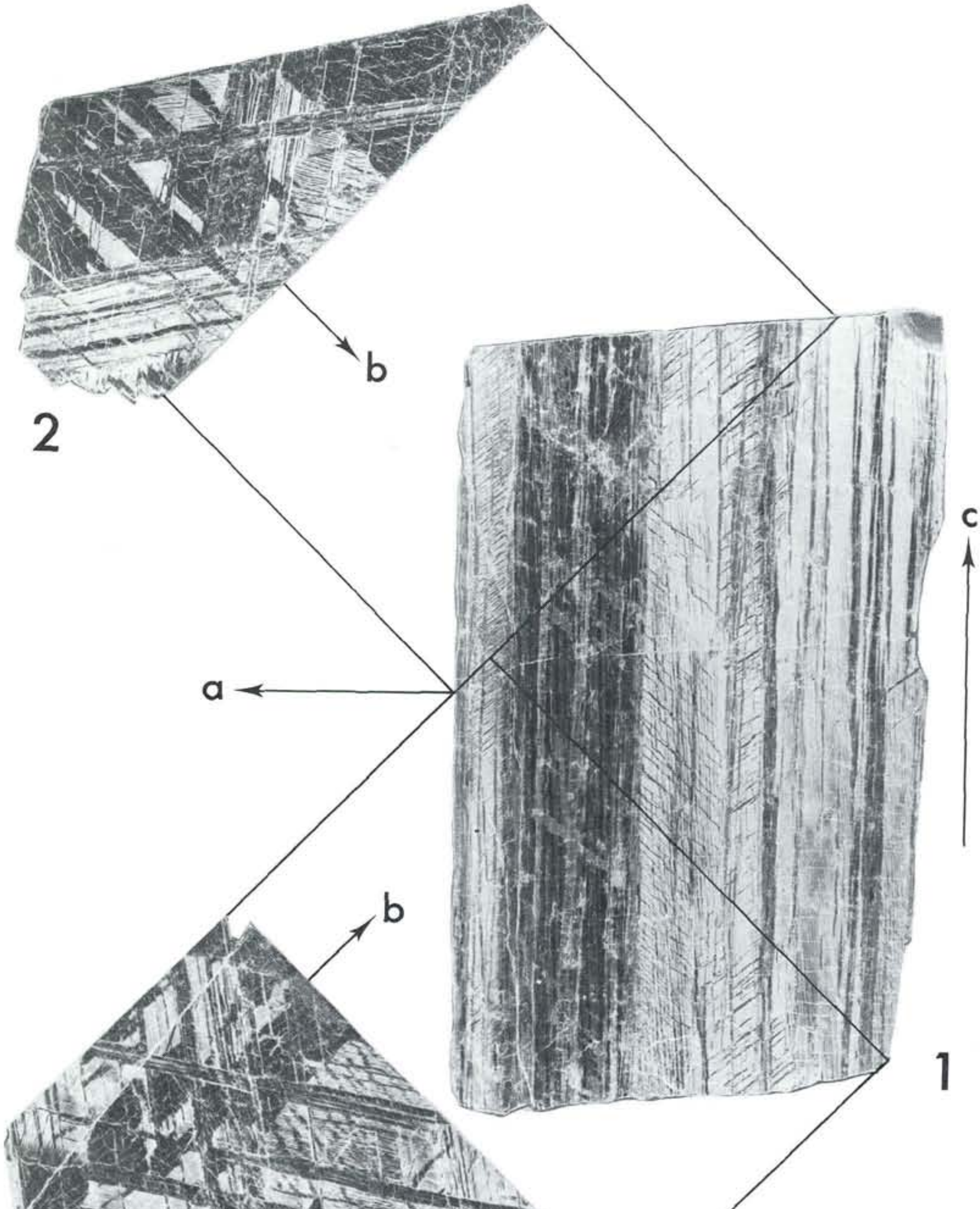

Fig. 2. Thin sections of cryolite, × 1.5. 2–1 is a section parallel to (010) as if photographed between crossed polars. 2–2 and 2–3 are perpendicular to the section shown in 2–1, making 45° angles with (001). Note: sections between polaroid filters used as photographic negatives. Filters so arranged 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 measurings 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 μm.

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 μm plus or minus less than 10μm. 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.

	n_{lowest}	$n_{highest}$	n_F-n_C*
Sections of cryolite			
⊥ and // O.A.P.	1.3382	1.3392	0.0036
Black cryolite			
undetermined orientation	1.3386	1.3391	0.0036
Purple cryolite			
undetermined orientation	1.3384	1.3388	0.0036
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.

Section	V_2	IV_2	IV_1	I_2
$\perp B_1 : \beta - \alpha$	0.000117	0.000124		
$\perp B_2 : \gamma - \beta$			0.000803	0.000881
$\perp \beta : \gamma - \alpha$	0.000995	0.001059		
2V	40.2°	40.0°		

Determination of 2V by Tobi's method

In the sections IV_2 and V_2 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 n_β 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.

		Data from Krenner:	
$n\alpha$	=1.3382	O.A.P.	$\perp$(010)
$n\beta$	=1.3383	$\gamma \wedge c$	44°
$n\gamma$	=1.3392		
$n\gamma - n\alpha$	=0.0010		
+ 2 V	=40°		
nF–nC	=0.0036		

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.

Krenner *1883*	Bøggild *1953 & 1913**	Paduroff *1925*	Cesaro & Melon *1936*
	$n\alpha$ = 1.3385		$n\alpha$ = 1.3376
n = 1.364	$n\beta$ = 1.3389		$n\beta$ = 1.3377
	$n\gamma$ = 1.3396	$\gamma - \alpha$ = 0.0025	$n\gamma$ = 1.3387
	$n\gamma - n\alpha$ = 0.0011	$\gamma - \beta$ = 0.0021	$n\gamma - n\alpha$ = 0.0011
	^{n}middle = 1.3390*	$\beta - \alpha$ = 0.0004	^{n}middle = 1.338
$2E_{red}$ = 58°50'		2V = 37°30'	n_{477} = 1.319
$2E_{yellow}$ = 59°24'			n_{541} = 1.331
$2E_{blue}$ = 60°10'			n_{598}** = 1.338
2Vcal = 44°***	2Vcal = 74°	2Vcal = 47°	n_{662} = 1.343
$\gamma \wedge$43°54'			
α // b			

** 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, β = 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_β is clearly wrong if one accepts – as he himself did – Krenner's value for the axial angle. His n_α is of course not far from the value obtained in the present work. The real difficulty emerges from his n^γ 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.

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:

$$n_{477} = 1.319$$
$$n_{541} = 1.331$$
$$n_{598} = 1.338$$
$$n_{662} = 1.343$$

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:

$$n_{477} = 1.340$$
$$n_{541} = 1.3395$$
$$n_{589} = 1.338$$
$$n_{662} = 1.334$$

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:

$$n_\gamma - n_\alpha = 0.001135$$
$$n_\gamma - n_\beta = 0.000979$$
$$n_\beta - n_\alpha = 0.000156$$

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-á-dire que l'on ait

$$n_g + n_m + n_p = 4.014$$

en tenant compte des biréfringences mesurées, on arrive á

n_g = 1.3387, n_m = 1.3377 and n_p = 1.3376"

That this was an unfortunate basis on which to establish the indices of refraction of cryolite is rather obvious.

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Dansk sammendrag

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 tvillingdannelse 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 hjælp af immersionsmetoden fandtes lysbrydningen for kryolit at ligge mellem 1.3381 og 1.3392. Det viste sig iøvrigt at gælde for såvel sort kryolit som for hvid kryolit. Tilsvarende værdier opnåedes ved totalreflexionsmålinger på polerede stykker af kryolit, såvel hvid som sort og violet kryolit. Der udførtes tillige målinger på polerede stykker af kryolithionit og kiolit. På kryolithionit fandtes samme lysbrydning som Ussing (1904) fandt ved måling på et prisme fremstillet af mineralet. Ved disse målinger bestemtes tillige dispersionen for de pågældende mineraler; resultaterne ses i tabel 1.

Den rene hvide kryolit kløves ofte i kasseformede stykker, spaltekryolit kalder man denne type. Brudfladerne er plane, men er som Bøggild påpeger resultatet af afsondring i forbindelse med tvillingdannelser. De flader, der fremkommer i afsondringsstykkerne, er dels (110) flader og dels (001). Denne sidste er dog sjældent særlig pænt udviklet. Ved hjælp af sådanne kryolitstykker fremstilledes tyndsnit blandt andet orienteret parallelt med de optiske axers plan samt snit parallelle med planet vinkelret herpå indeholdende den optiske normal og anden bisektrix. Disse tyndsnit blev kun slebet ned til 0,25 mms tykkelse, idet mineralets ringe dobbeltbrydning så medførte, at snittene viste hvidt til lysegråt af første orden mellem krydsede nicoler. Blandt de talrige tvillinglameller i disse snit fandtes sådanne, der viste tosymmetriske B_1- og B_2-snit. På disse bestemtes med Berek kompensatoren de tilsvarende dobbeltbrydninger, se tabel 2. Endelig bestemtes, efter Tobis metode, axevinklens størrelse i snit, der var vinkelret på B_1; 2V fandtes at være 41°. Axevinklen beregnet udfra dobbeltbrydningsbestemmelserne viste sig at blive 40°.

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

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