

*An X-ray investigation of some rare-earth silicates:
cerite, lessingite, beckelite, britholite, and stillwellite.*

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Summary. An X-ray study of a number of rare-earth silicates has been carried out; single-crystal and powder data are presented.

It is found that cerites can contain up to at least 6% CaO without disruption of the structure, which is trigonal with probable space-group $P321$ &c. The cell dimensions are a ca. 10.8 Å., c ca. 37–38 Å., although there is a strong pseudo-cell with a halved c -axis. An ideal formula $(Ca, Ln^\dagger)_3 Si_4(O, OH, F)_6$ is proposed for this series.

Lessingite and beckelite can be regarded chemically as lime-rich members of this cerite series. They do not, however, have the same crystal structure as cerite; their diffraction patterns are very similar to that of britholite, and indicate a structure dimensionally comparable with apatite. For a hexagonal cell, the dimensions are a ca. 9.7 Å., c ca. 7.1 Å., with probable space-group $P6_3$, &c. An ideal formula $(Ca, Ln)_2(Si, Al, P)(O, OH, F)_5$ is proposed for this series. Marked biaxial optical properties suggest that the structure may be truly orthorhombic, with a very close dimensional approximation to a hexagonal cell.

The new mineral, stillwellite, is unrelated to either of these series. It is trigonal with cell dimensions a ca. 6.9 Å., c ca. 6.7 Å., with probable space-group $P3_112$. An ideal formula $(Ca, Ln)(Si, Al, P)B(O, OH, F)_5$ suggested by previous work is confirmed.

THERE are many rare-earth silicates described in the literature. Usually they are of isolated occurrence, and the descriptions by which they are characterized are not very satisfactory. Often the minerals are poorly crystallized, and this, taken with the fact that their refractive indices are usually quite high (1.75 to 1.85), makes an accurate optical definition difficult. This may be the reason why, for some specimens, different investigators have reported different optics, although it is more probable that this is owing to variable optical properties, arising from complex solid solution. Complete separation of the mineral from the rock has not always been possible; together with difficulties in the chemical analysis this leads to uncertainties in the formulae that have been proposed for many of the minerals. Thus, with the properties and constitutions of most of these silicates very imperfectly known, it is difficult to see what, if any, are the relationships between them.

† The symbol Ln is used throughout this paper as an inclusive symbol for the rare-earth elements or lanthanons, Yt, La, Ce, ..., Lu.

The work to be described in this paper was begun with an investigation of a new mineral, stillwellite. Further work on the other minerals was then undertaken in order that they might be compared both with stillwellite and among themselves. The X-ray investigation has been carried out by conventional methods. Single-crystal photographs have been used, in the main, to obtain the cell dimensions and space-group data. These have been used with the chemical analyses to calculate the cell contents and to attempt to derive formulae for the minerals. Where sufficient of the material was available, powder data have been obtained, usually by Geiger-counter diffractometer methods. Other comments upon the methods employed will be made where appropriate.

Cerite.

Cerite occurs as a red-brown mineral usually in the massive form; two of the best known localities are Bastnäs, Sweden, and Jamestown, Colorado, U.S.A. Measurements by Nordenskiöld on a rare well-formed crystal (Hintze, 1897) suggest that the mineral is orthorhombic (pseudo-tetragonal) with $a:b:c::0.9988:1:0.8127$. There appears to be no analysis of the material from which this crystal was taken, although a number of other analyses of cerites from the same locality are given in Hintze. From these a formula $(\text{Ca,Fe})_2\text{Ln}_2\text{Si}_6\text{O}_{26}\text{H}_6$ has been proposed. The optical properties are slightly variable with refractive indices ca. 1.81–1.82 and a low positive birefringence; the mineral also shows a feeble pleochroism.

X-ray investigation. A number of single-crystal specimens both from Swedish and American localities were used. It was soon established that the symmetry is trigonal, with Laue group $\bar{3}m$. The cell dimensions were found to be a ca. 10.8 Å., c ca. 37–38 Å., though there is a strong pseudo-cell with c ca. 18.5–19 Å. The true unit cell is disclosed by a small number very weak reflections midway between the strong 19 Å. layer-lines on c -axis oscillation photographs; for some specimens, these may be missed if the exposure time is too short. If these weak reflections are ignored the pseudo-cell is rhombohedral with space-group $R32$, $R3m$, or $R\bar{3}m$. If these weak reflections are included it is seen that the true unit cell is hexagonal with space-group probably $P321$, $P3m1$, or $P\bar{3}m1$, &c. The space-groups $P3_112$, &c. cannot be ruled out, for, although a careful examination of the $000l$ reflections has been made, no contradiction of the conditions $000l$ ($l = 3n$) has been found. These absences, however, may well be accidental, for such reflections are all

due to the true cell with the doubled c -axis; the strongest true cell reflection observed is very weak. Piezo-electric tests have provided no positive evidence.

Accurate cell dimensions were obtained for several specimens, using a back-reflection camera (dimensions in Å.):

63425 Bastnäs, Sweden	a	10.81 ± 0.02	c	37.72 ± 0.05	c/a	3.489
53116 „ „		10.82 ± 0.02		37.71 ± 0.05		3.485
63431 Jamestown, Colorado, U.S.A.		10.73 ± 0.02		37.70 ± 0.05		3.514

Specimens from Mountain Pass, California, and Swedish specimens accepted by Nordenskiöld as cerite were also examined. Single crystals from the Californian specimen were of poor quality; although it was possible to confirm that the diffraction pattern was similar to that of other cerites, no dimensional data were obtained. Examination of the Nordenskiöld material showed that it was identical with other Swedish cerites, and no further work was carried out on it.

Besides the small but significant difference in the a cell side in the American cerite, another important difference is in the intensities of the weak true cell reflections. These reflections are about twice as strong for the Jamestown cerite.

It is difficult to obtain satisfactory powder data for cerite. In common with other rare-earth silicates, there is some fluorescence with $\text{Cu-}K\alpha$ radiation; this is presumably due to the L absorption edges of the rare earths, which in the case of lanthanum go up to 2.254 \AA . The quality of the lines on the powder diagrams is poor, probably owing to a partial disruption of the crystal structure towards the metamict state by some radioactive atoms within the crystal. A considerable sharpening of the powder lines may be obtained by heating the specimen for 1 to 2 hours at 800 to 900°C . For cerite in particular the powder pattern is complex, consisting of a large number of relatively weak lines.

Table I presents the results of powder records from a specimen of cerite (53116) heated for 1 hour at 900°C . This table shows a combined spacing list both from diffractometer records (with $\text{Cu-}K\alpha$ radiation and a Si standard) and photographic measurements ($\text{Cr-}K\alpha$ radiation); some of the weaker peaks are lost in the relatively high background of the diffractometer record. The spacings of some planes calculated from the single-crystal cell dimensions are also shown for the first thirteen lines; the indexing refers to the pseudo-cell since no true-cell reflections will be strong enough to be observed on the powder record. The agreement between the calculated and observed spacings is not good but it can be

regarded as satisfactory in the light of the difficulties of measurement. The strongest lines are at 2.93, 2.66, and 1.93 Å.

Chemical analysis. A sample of cerite (53116) was prepared for analysis by crushing and passing through a 90-mesh sieve; after washing with

TABLE I. Powder data for cerite (53116) after heating for 1 hour at 900° C.

$d_{\text{obs.}}$	I	$hkl.$	$d_{\text{calc.}}$	$d_{\text{obs.}}$	I	$d_{\text{obs.}}$	I
8.53*Å.	vw	1 $\bar{1}$ 01	8.39	2.26*	vwv	1.523*	vwv
6.75*	vwv	10 $\bar{1}$ 2	6.65	2.19	vw	1.503*	vwv
6.39*	vwv	0003	6.29	2.13*	vwv	1.470*	vwv
5.32	vw	11 $\bar{2}$ 0	5.41	2.09	vw(b)	1.426*	vwv
4.50	w	20 $\bar{2}$ 1	4.55	2.06	vw(b)	1.414*	vwv
4.20	vw	2 $\bar{2}$ 02	4.20	2.03	vwv	1.374*	vwv
		1 $\bar{1}$ 04	4.21	1.98	vwv	1.357*	vwv
3.50	w	21 $\bar{3}$ 1	3.50	1.96	w	1.336*	vwv
3.45	mw	10 $\bar{1}$ 5	3.48	1.93	mw(b)	1.297*	vwv
3.33	vwv	20 $\bar{2}$ 4	3.32	1.843	vw	1.289*	vwv
3.28	w	21 $\bar{3}$ 2	3.32	1.831	vw	1.265*	vwv
3.10	w	0006	3.14	1.804	vwv	1.256*	vwv
		30 $\bar{3}$ 0	3.12	1.751	vw	1.242*	vwv
2.93	m	2 $\bar{2}$ 05	2.94	1.729	vw	1.224*	vwv
2.80	vw	2 $\bar{3}$ 14	2.83	1.683*	vwv	1.206*	vwv
		3033	2.80	1.658	vwv	1.175*	vwv
2.73	vw	—	—	1.635	vwv	1.166*	vwv
2.66	mw	—	—	1.590*	vwv	—	—
2.55	vw	—	—	1.572	vwv	—	—
2.28*	vwv	—	—	—	—	—	—

For the first thirteen lines the spacing has been calculated from the dimensions of the pseudo-cell determined by single-crystal methods. (*) indicates that the line was observed only on the photograph taken with Cr- $K\alpha$ radiation; all other spacings were observed both on the photographs and the diffractometer records obtained with Cu- $K\alpha$ radiation.

water, a concentrate of cerite was obtained by magnetic separation. The fraction of this concentrate which passed through a 200-mesh sieve was further purified by centrifuging with Clerici solution, the lighter portion being rejected. The separation and analysis were carried out by J. H. Scoon.

The analysis showed 0.30 % CO_2 , presumably owing to bastnäsite (LnFCO_3) that could not be separated from the cerite. The analysis after correction for bastnäsite is shown in table II together with other analyses of cerites.

The present analysis compares quite well with those of Nordström and of Goddard and Glass. As pointed out by Goddard and Glass, the Colorado cerite differs from the Swedish material principally in having a higher CaO content; the 4.35 % CaO in the analysis by Nordström is

higher than the usual lime content in analyses of Swedish material. The fourth analysis, by Hanson and Pearce, is remarkably different from the other three; there are major discrepancies in Al_2O_3 and CaO .

Contents of the unit cell. The density of the analysed sample was 4.89,

TABLE II. Chemical analyses of cerite.

	1.	2.	3.	4.	5.
SiO_2	21.24	21.24	22.79	18.10	17.42
Al_2O_3	nil	nil	1.26	0.32	14.59
Fe_2O_3	0.43	0.43	—	—	—
FeO	0.68	0.68	3.92	1.54	1.40
TiO_2	nil	nil	—	—	—
MnO	nil	nil	—	0.22	0.40
MgO	1.88	1.88	—	0.21	1.68
Ce_2O_3	31.37	30.91	24.06	32.97	21.65
ThO_2	nil	nil	—	—	—
La_2O_3 , &c.	33.37	32.76	} 35.37	35.72	} 27.55
Yt_2O_3 , &c.	5.27	5.18		3.86	
CaO	2.97	2.97	4.35	5.80	15.24
$\text{H}_2\text{O} +$	2.00	2.00	3.44	1.26	0.07
$\text{H}_2\text{O} -$	0.10	0.10	—	—	—
F	1.47	1.36	—	—	—
CO_2	0.30	—	—	—	—
	<u>101.08</u>	<u>99.51</u>			
$\text{O} \equiv \text{F}$	0.62	0.57	—	—	—
Total	<u>100.46</u>	<u>98.94</u>	<u>99.52</u>	<u>100.00</u>	<u>100.00</u>

1. Cerite (53116), Bastnäs, Sweden, this investigation. Material includes some allanite and bastnäsite. Analyst, J. H. Scoon.

2. Analysis of cerite (53116) (col. 1) after correction for bastnäsite, assuming all the CO_2 is present as bastnäsite.

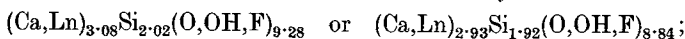
3. Cerite, Sweden. Total includes 4.33 % extraneous material. Analysis by Nordström, quoted in Hintze (1897).

4. Cerite, Jamestown, Colorado, U.S.A. (Goddard and Glass, 1940). Recalculated analysis after correction of cerite rock analysis for 0.86 % uraninite, 5.00 % bastnäsite, 5.00 % quartz, and 11.32 % fluorite. Analyst, J. G. Fairchild.

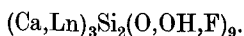
5. Cerite, Jamestown, Colorado, U.S.A. (Hanson and Pearce, 1941). Analysis recalculated from cerite rock analysis.

in good agreement with previous density determinations. On the basis of this and the X-ray data, the cell contents may be calculated as: $(\text{Ca}, \text{Ln}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})$ 61.52, Si 40.36, total anions 185.62.

Z may then be taken as either 20 or 21, which yield a formula



thus the ideal formula of this cerite must be regarded as



The large cell dimensions make it difficult to determine Z unambiguously.

Discussion. From the above results it is established that the North American and Swedish cerites are structurally similar and that they have trigonal symmetry.¹ It seems probable, therefore, that the early goniometrical measurements were carried out on some other mineral. A chemical formula for the Bastnäs cerite has been established; this is very similar to that previously proposed, which is usually written in the form $(\text{Ca}, \text{Fe})\text{O} : 1\frac{1}{2}\text{Ln}_2\text{O}_3 : 3\text{SiO}_2 : 1\frac{1}{2}\text{H}_2\text{O}$. On the basis of their work, Goddard and Glass proposed a series with increasing CaO content of the cerite, from a hypothetical CaO-free cerite, $2\text{Ln}_2\text{O}_3 : 3\text{SiO}_2 : \text{H}_2\text{O}$, through the intermediate cerite from Colorado, $\text{CaO} : 2\text{Ln}_2\text{O}_3 : 3\text{SiO}_2 : \text{H}_2\text{O}$, to a CaO-rich variety described as lessingite, $2\text{CaO} : 2\text{Ln}_2\text{O}_3 : 3\text{SiO}_2 : \text{H}_2\text{O}$.

Swedish cerites may be regarded as intermediate in this series between the CaO-free and Colorado cerites. The chemical constitution proposed by Hanson and Pearce for the Colorado cerite does not fit into this series, and is unrelated to that of the Swedish varieties; the inclusion of water in the formula is also disputed by these authors. The present work supports the suggestion that a series of cerites with variable lime content exists. The close structural similarity between the Swedish and American varieties, and the agreement between the present analysis and that of Goddard and Glass, show that the work of Hanson and Pearce must be rejected.

It is noteworthy that the ratio of the CaO contents in the Jamestown and Bastnäs materials is roughly the same as the ratio of the intensities of the weak true cell reflections. Thus it is thought that the hypothetical CaO-free cerite will be truly rhombohedral; the addition of lime forms a hexagonal superstructure, which becomes more pronounced with increasing lime content. To what extent this CaO content can be increased before the cerite structure is disrupted will become clear after the descriptions of the examinations of lessingite and beckelite ($3\text{CaO} \cdot 2\text{Ln}_2\text{O}_3 \cdot 3\text{SiO}_2$).

Lessingite, beckelite, and britholite.

It is convenient to discuss these three minerals together since they are very similar.

Lessingite was described by Zilbermintz (1929) from the Kyshtym district of the Urals, Russia. It is a red-brown mineral with refractive

¹ In a recent note (Glass, Evans, Carron, and Rose, 1956) cerite from Mountain Pass, California, was incorrectly described as monoclinic. The relationship of this 'monoclinic cell' to the trigonal cell has been discussed in detail elsewhere (Gay, 1957).

indices ca. 1.78–1.79 and low negative birefringence (0.006); it is biaxial with $2V_\alpha$ ca. 44° . The density was 4.69, and a formula $\text{Ca}_2\text{Ln}_4\text{Si}_3\text{O}_{15}\text{H}_2$ was suggested on the basis of a chemical analysis. It could therefore be considered a calcic member of the cerite series.

Beckelite was described by Morozewicz (1905, 1930) as large crystals occurring in mariupolite from the Sea of Azov, Russia. The yellow-brown material was thought to be cubic, although large crystals show weak birefringence; the refractive index is ca. 1.81. The density was 4.15, and chemical analysis suggests a formula $\text{Ca}_3\text{Ln}_4\text{Si}_3\text{O}_{15}$. It has been regarded as a member of the pyrochlore family, but it seems more likely that it is to be regarded as a lime-rich member of the cerite family.

Britholite was first described by Winther (1901) as phenocrysts in pegmatite from Naujakasik, Greenland. The brown mineral is said to be orthorhombic (pseudo-hexagonal by twinning on {110}) with $a:b:c :: 0.620:1:0.423$; large crystals sometimes show a sectored development. The mineral has a low negative birefringence and small $2V_\alpha$; according to Barth and Berman (1930) its refractive index is about 1.77–1.78. The density was 4.45, and the formula $(\text{Ca},\text{Ln})_5(\text{Si},\text{P})_3(\text{O},\text{OH},\text{F})_{13}$ has been suggested. Bøggild (1912) disputed the orthorhombic character of the mineral and regarded it as uniaxial with optical anomalies. X-ray measurements by Hägele and Machatschki (1939) showed a hexagonal cell with a 9.61, c 7.02 Å.; these authors also suggested that britholite belonged to the apatite group.

X-ray investigation. Single crystals of the three minerals were obtained from rock specimens from the type localities. For lessingite and britholite there was no difficulty in identifying the minerals. The beckelite crystals, however, were only obtained after a number of sections of mariupolite had been examined; in these, large crystals that seemed to conform to the earlier incomplete description of the mineral were located; the material for the X-ray work was then obtained from the large phenocrysts in the rock specimens that matched the grains located in the corresponding section. Probably this material is identical with beckelite as defined by Morozewicz.

The three minerals give very similar diffraction patterns. Laue photographs established an apparent hexagonal symmetry, with probable Laue group $6/mmm$. Single-crystal studies, however, revealed intensity discrepancies between corresponding reflections. For these minerals a reliable comparison of intensities is difficult owing to the relatively high absorption and fluorescence with $\text{Cu-K}\alpha$ radiation. If allowance is made for these effects, it seems probable that the true

Laue symmetry is $6/m$, although the possibility that the crystals are only dimensionally hexagonal cannot be completely discounted (see later). Taking the symmetry to be hexagonal, $000l$ reflections are present only when $l = 2n$, suggesting a probable space-group $P6_3$ or $P6_3/m$. Piezo-electric tests provided no positive evidence.

TABLE III. Powder data for lessingite.

$d_{\text{obs.}}$	I	hkl	$d_{\text{calc.}}$	$d_{\text{obs.}}$	I	hkl	$d_{\text{calc.}}$
4.72 Å.	vw	11 $\bar{2}$ 0	4.83	2.019	vwv	40 $\bar{4}$ 1	2.007
4.19	vw	20 $\bar{2}$ 0	4.19	1.995	w	22 $\bar{4}$ 2	1.996
3.99	w	11 $\bar{2}$ 1	3.99	1.941	vw	31 $\bar{4}$ 2	1.941
3.58	w	20 $\bar{2}$ 1	3.60	1.894	w	33 $\bar{6}$ 1	1.901
3.54	w	0002	3.54	1.890	w	21 $\bar{3}$ 3	1.891
3.34*	vw	—	—	1.855	vw	32 $\bar{5}$ 1	1.854
3.26	w	10 $\bar{1}$ 2	3.26	1.827	vw	41 $\bar{5}$ 0	1.827
3.16	mw	21 $\bar{3}$ 0	3.16	1.802	w	40 $\bar{4}$ 2	1.802
2.89	s	21 $\bar{3}$ 1	2.89			30 $\bar{3}$ 3	1.801
2.86	m	11 $\bar{2}$ 2	2.86			0004	1.770
2.79	mw	30 $\bar{3}$ 0	2.79	1.769	vwv	41 $\bar{5}$ 1	1.769
2.32	vwv	31 $\bar{4}$ 0	2.32	1.577	vwv	—	—
2.25	vwv	10 $\bar{1}$ 3	2.27	1.547	vwv	—	—
2.12	vw	11 $\bar{2}$ 3	2.19	1.516	vwv	—	—
2.10	vwv	40 $\bar{4}$ 0	2.09	1.495	vwv	—	—
2.05	vwv	20 $\bar{2}$ 3	2.05	1.470	vwv	—	—
				1.271	vwv	—	—
				1.255	vwv	—	—

* This reflection could not be indexed on the basis of the single-crystal cell dimensions, and is probably due to impurity.

The following cell dimensions were found using single-crystal back-reflection methods:

Lessingite	a	9.67 ± 0.02 Å.	c	7.08 ± 0.02 Å.	c/a	0.732
Beckelite		9.66 ± 0.02		7.07 ± 0.02		0.732
Britholite		9.61 ± 0.02		7.03 ± 0.02		0.731

There are only very slight differences between the three minerals.

A powder pattern was obtained for lessingite; suitable material was not available for the other two minerals. The diffractometer record with $\text{Cu-K}\alpha$ radiation is of the same quality as those for the other rare-earth silicates examined. Measurements of line spacings are listed in table III, together with the calculated spacings of certain planes obtained from the single-crystal data; there is satisfactory agreement between the observed and calculated spacings. It is reasonable to assume that the powder patterns of beckelite and britholite will be very similar to that of lessingite, with some small changes in line positions and intensities. For lessingite the strongest lines are at 2.89, 2.86, and 2.79 and 3.16 Å.

Chemical analyses. In view of the limited amount of the minerals available, it was not possible to undertake any new chemical analyses. Since, however, there are close similarities in the structural arrangements, it is of interest to compare the three published analyses; these are given in table IV. They show a correlation that is particularly marked for lessingite and britholite if allowance is made for the replacement of Si by P.

TABLE IV. Chemical analyses of lessingite, beckelite, and britholite.

	1.	2.	3.
SiO ₂	19.85	17.13	16.77
P ₂ O ₅	1.13	—	6.48
Al ₂ O ₃	0.26	0.30	—
ZrO ₂	—	2.50	—
Fe ₂ O ₃	0.65	—	0.43
Mn ₂ O ₃	—	0.07	—
Ce ₂ O ₃ , &c.	22.48	28.10	} 60.54
La ₂ O ₃ , &c.	36.65	31.60	
Yt ₂ O ₃ , &c.	3.42	2.86	
MnO	0.88	—	—
MgO	0.17	—	0.13
CaO	11.71	15.46	11.28
K ₂ O	} 0.08	0.39	—
Na ₂ O		0.78	1.85
H ₂ O	1.56	0.99	1.27
H ₂ O ⁻	0.38	—	—
F	0.54	—	1.33
CO ₂	0.35	—	—
	<u>100.11</u>	<u>100.18</u>	<u>100.08</u>

1. Lessingite, Kyshtym district, Urals, Russia (Zilbermintz, 1929).
2. Beckelite, Mariupol, Sea of Azov, Russia (Morozewicz, 1905).
3. Britholite, Naujakasik, Julianehaab, Greenland (Winther, 1901).

Contents of the unit cell. By using the analyses and densities quoted above, together with the determined cell dimensions, the contents of the unit cells may be calculated:

Ca, Ln, Fe, &c.:	Lessingite 10.32	Beckelite 9.78	Britholite 9.67
Si, Al, P, &c.	5.72	4.44	5.63
Total anions:	26.87	21.84	25.61

If $Z = 5$ the formulae are: Lessingite $(Ca, Ln)_{2.06}(Si, Al, P)_{1.14}(O, OH, F)_{5.37}$; beckelite $(Ca, Ln)_{1.96}(Si, Al, Zr)_{0.89}(O, OH)_{4.37}$; britholite $(Ca, Ln)_{1.94}(Si, P)_{1.13}(O, OH, F)_{5.12}$.

It is to be expected that the cell contents would be approximately the same for all three minerals. It is probable that the lessingite should be

corrected for a small amount of bastnäsite impurity (0.35% CO_2); when this is done, there is good agreement between lessingite and britholite. As expected, the beckelite cell-contents are not satisfactory; in the absence of new data, it is not possible to say whether this is owing to errors in the analysis or density (which is rather low for these minerals). If Z is chosen as 5, the best structural formulae given in the table are obtained; the idealized structural formula for this series appears to be $(\text{Ca}, \text{Ln})_2(\text{Si}, \text{Al}, \text{P})(\text{O}, \text{OH}, \text{F})_5$.

Discussion. From the evidence given above, it must be concluded that lessingite, beckelite, and britholite are very similar. They are based upon the same crystal structure, which appears to be dimensionally similar to apatite. Complex replacement can occur within the structure, leading to the differences in optical properties by which the minerals have been distinguished. The basic structure is different from that of the cerite series, showing that the cerite structure is disrupted by too large a proportion of Ca ions.

The results given above have been calculated upon the hypothesis that the crystals have hexagonal symmetry. Within the limits of the experimental accuracy, the minerals are dimensionally hexagonal; the orthorhombic axial ratios given by Winther (1901) for britholite would certainly have been detected. Nevertheless, some doubts as to the true symmetry are raised by the optical properties; both britholite and lessingite have been described as biaxial, and an examination of beckelite shows some biaxial character. Some optical work upon the present specimens has been carried out by Drs. I. D. Muir and J. D. C. McConnell. They have shown that beckelite and britholite are similar in that they have substantially the same refractive indices, with a small optic axial angle. Such discrepancies might well be attributed to anomalous uniaxial behaviour; but the examination of lessingite confirmed that the optic axial angle was large ($2V_\alpha$ ca. 35°) and it seems unlikely that this can be explained as an anomalous property.

To resolve these doubts and establish the true symmetry of these minerals would require the accurate measurement of the intensities of reflections from planes of related indices. As has been pointed out earlier, this is very difficult to carry out, for the minerals have high absorption and fluoresce with $\text{Cu-K}\alpha$ radiation. The problem of the absorption could be overcome by the use of $\text{Mo-K}\alpha$ radiation but unfortunately this still causes some fluorescence. No further work has been carried out on this point at the moment.

Stillwellite.

Stillwellite, a new mineral from the Mary Kathleen lease, N.W. Queensland, has been described by McAndrew and Scott (1955). In a preliminary report they describe the mineral as trigonal with a 6.85 Å., c 6.64 Å., and space-group¹ $P3m$, $P\bar{3}m$, or $P3_n2$. The density was 4.57; on the basis of this and a preliminary analysis, an ideal formula (Ln,Ca) $B(Si,P)(O,OH,F)_5$ with $Z = 3$ was suggested. The mineral, which is colourless in thin section, shows slightly variable optics with moderate birefringence, the refractive indices being about 1.78.

An examination of the mineral from the same locality had been commenced before the preliminary report described above was published. The more detailed X-ray and chemical examination will be described below.

X-ray investigation. The Laue group was established as $\bar{3}m$. Single-crystal oscillation and Weissenberg photographs showed that the lattice is hexagonal, and 000 l reflections are present only if $l = 3n$, suggesting a space-group of the type $P3_112$, &c. In view of the ambiguities in the space-groups reported above, a further investigation was made to seek the absent reflections using both Cu- $K\alpha$ radiation and Mo- $K\alpha$ radiation, but none was found. For this material it seems unlikely that all orders could be fortuitously absent, and thus it must be concluded that the probable space-group is $P3_112$, &c. Piezo-electric tests provide no positive evidence.

Cell dimensions determined from single-crystal back-reflection photographs are a 6.89 ± 0.03 Å., c 6.70 ± 0.02 Å., c/a 0.972. These agree with those determined by McAndrew and Scott.

Powder data for stillwellite have been obtained from powder diffractometer records using Cu- $K\alpha$ radiation. Difficulties similar to those described earlier for cerite had to be overcome before a satisfactory pattern could be obtained. The spacings are listed in table V, together with the spacings of a number of planes calculated from the single-crystal cell dimensions; the agreement is satisfactory. There are a few weak lines that cannot be indexed, which are probably due to apatite inclusions (see later). The strongest lines are at 2.96 Å., 3.43 Å., and 2.91 Å.

Chemical analysis. A sample of stillwellite (77991) for analysis was prepared in the manner described earlier for cerite. A small amount of apatite and uraninite could not be removed; a correction for the

¹ The symbol $P3_n2$ was used to imply the space-groups $P32$ and $P3_112$, &c.

apatite was applied by carrying out a partial analysis of a sample from which the apatite had been removed by cold nitric acid. The separation and analyses were carried out by J. H. Scoon and the results are shown in table VI. When compared with the preliminary analysis of McAndrew and Scott, it is seen that there is good agreement if allowance for apatite is made in the earlier work.

TABLE V. Powder data for stillwellite (77991) after heating for 2 hours at 900° C.

$d_{\text{obs.}} \text{ \AA.}$	I	hkl	$d_{\text{calc.}}$	$d_{\text{obs.}} \text{ \AA.}$	I	hkl	d_{calc}
5.96	vwv	10 $\bar{1}$ 0	5.97	1.785	vw	20 $\bar{2}$ 3	1.788
4.44	m	10 $\bar{1}$ 1	4.46	1.704	w(b)	22 $\bar{4}$ 0	1.723
3.43	s	11 $\bar{2}$ 0	3.44			30 $\bar{3}$ 2	1.710
3.13*	w	—	—	1.646	mw(b)	22 $\bar{4}$ 1	1.668
3.05	w	11 $\bar{2}$ 1	3.06			31 $\bar{4}$ 0	1.655
2.96	s	20 $\bar{2}$ 0	2.98	1.612	vw	10 $\bar{1}$ 4	1.612
2.79*	vw	—	—			31 $\bar{4}$ 1	1.606
2.71	mw	20 $\bar{2}$ 1	2.73	1.526	vw(b)	—	—
2.40	w	11 $\bar{2}$ 2	2.40	1.476	vwv	—	—
2.24	mw	21 $\bar{3}$ 0	2.25	1.458	vwv	—	—
2.23	mw	{ 0003	2.23	1.448	vwv	—	—
		{ 20 $\bar{2}$ 2	2.23	1.357	vw	—	—
2.13	ms	21 $\bar{3}$ 1	2.14	1.341	vw	—	—
2.09	vwv	10 $\bar{1}$ 3	2.09	1.335	w	—	—
1.979	vw	30 $\bar{3}$ 0	1.989	1.324	vwv(b)	—	—
1.935*	w	—	—	1.259	vw	—	—
1.896	w	30 $\bar{3}$ 1	1.906	1.205	vw	—	—
1.864	m	{ 11 $\bar{2}$ 3	1.874	1.185	vwv	—	—
		{ 21 $\bar{3}$ 2	1.871	1.118	vwv	—	—

* These reflections could not be indexed on the basis of the single-crystal cell dimensions, and are probably due to apatite inclusions that could not be separated from the stillwellite. Fluorapatite has relatively strong reflections for spacings of 2.78 Å. and 1.933 Å.; there is also a weak line at 3.16 Å., which may account for that observed at 3.13 Å.

Contents of the unit cell. The density of the analysed sample was 4.58. On the basis of this and the X-ray data the cell contents are: Ca, Ln, &c., 3.04; Si, Al, P, 2.98; B, 2.66; total anions 14.88.

If Z is taken as 3, the formula becomes $(\text{Ca,Ln})_{1.01}(\text{Si,Al,P})_{0.99}\text{B}_{0.89}(\text{O,OH,F})_{4.96}$; thus the ideal formula must be regarded as $(\text{Ca,Ln})(\text{Si,Al,P})\text{B}(\text{O,OH,F})_5$.

Discussion. Stillwellite shows no simple relationship to cerite and related minerals. It may be distinguished from them both by optical and X-ray methods. It may be compared with another boron-bearing rare-earth silicate, melanocerite, of which, unfortunately, no specimen was available for investigation.

TABLE VI. Chemical analyses of stillwellite.

	1.	1a.	2.	3.
SiO ₂	21.46	22.30	22.40	20.1
P ₂ O ₅	1.93	0.64	0.67	2.58
Al ₂ O ₃	0.40	—	0.42	—
Fe ₂ O ₃	0.17	—	0.18	—
MgO	0.06	—	0.06	—
CaO	2.65	0.91	0.95	3.96
Ce ₂ O ₃	31.87	} 61.50	33.15	} 58.4
La ₂ O ₃ , &c.	26.80		27.95	
Y ₂ O ₃ , &c.	0.71		0.74	
B ₂ O ₃	11.73	—	12.23	11.5
H ₂ O ⁺	0.81	—	0.85	—
H ₂ O ⁻	0.10	—	0.10	—
F	0.40	—	0.30	—
U ₃ O ₈	0.67	—	—	—
ThO ₂	0.06	—	—	—
	99.82			
O ≡ F	0.17			
Total	99.65		100.00	

1. Stillwellite (77991) in stillwellite-garnet-allanite skarn, Mary Kathleen leases, Mt. Isa district, Queensland, Australia. The material contains apatite and uraninite inclusions. Analyst, J. H. Scoon.

1a. Partial analysis of stillwellite with apatite removed by HNO₃ extraction. The figure for the rare earth oxides is wt. % with cerium as CeO₂.

2. Analysis in column 1 recalculated to 100 after removal of uraninite and enough CaO, P₂O₅, and F to reduce the values of CaO and P₂O₅ to these shown in column 1a for the apatite-free material.

3. Results of preliminary analysis published by McAndrew and Scott (1955).

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