Alkaline-earth–rare-earth silicate and germanate apatites

A. G. Cockbain and G. V. Smith

The Plessey Company Limited, Allen Clark Research Centre,
Caswell, Towcester, Northamptonshire

[Read 8 June 1967]

Summary. A number of new alkaline-earth–rare-earth silicate and germanate compounds with the apatite-type structure have been synthesized including a new calcium lanthanum silicate, $Ca_4La_6(SiO_4)_6(OH)_2$, which has *a* 9·63 Å, *c* 7·12, and *c*/*a* 0·740. This has a random distribution of Ca^{2+} and La^{3+} over the (4f) and (6h) sites in the lattice. X-ray data are given for $Ca_4La_6(SiO_4)_6(OH)_2$ together with cell dimensions for other synthetic silicate and germanate apatites. Silicate apatites with partially occupied or vacant halogen (2a) sites analogous to those of the pyromorphites have been prepared, and a classification for silicate apatites based on synthetic end-members is proposed.

THE large number of naturally occurring and synthetic compounds known that have the apatite-type structure (hexagonal, space group $P6_3/m$) form a group of unique interest and importance. Mineral members occur as common minor constituents of many igenous, metamorphic, and sedimentary rocks, and occasionally form deposits of considerable economic importance. In the biosphere, the calcium phosphate apatites are important constituents of teeth, bones, and urinary calculi, while their synthesis throughout human life during the progressive mineralization of the artery walls affects the lives of us all.

During the course of a study of synthetic compounds for possible use as low-dielectric-loss ceramic dielectrics stable under reducing conditions, a number of new apatite-type compounds were prepared and their electrical properties determined. The extensive ionic substitutions of simple or complex type that may be made without destroying the apatite-type structure, coupled with the ease with which most members may be synthesized, makes the apatites an attractive group in which to seek a range of controlled dielectric properties. In addition, the relationships of some naturally occurring members to each other have been clarified and this has enabled a classification of alkaline-earth–rare-earth silicate apatites based on synthetic end members to be proposed.

The type structure for all members of the apatite group is that of fluorapatite, which has the ideal composition $Ca_{10}(PO_4)_6F_2$, and its structure has been studied by several investigators, e.g. Hentschel (1923), Naray-Szabo (1930), Mehmel (1931), Hendricks *et al.* (1932), and Beevers and McIntyre (1946). All members of the group are hexagonal, and have the space group $P6_3/m$ with a large unit cell (a 9·3 to 10·4 Å c 6·8 to 7·5 Å) containing 42 ion sites, comprising 16 cation sites of three types and two size ranges and 26 anion sites of two types and two size ranges. The structure may be regarded as a series of discrete parallel hexagonal columns, which in the case of fluorapatite consist of a network of calcium and oxygen ions, the columns being linked by more calcium ions and phosphorus-oxygen tetrahedra. The fluorine ions are contained inside the hexagonal columns.

A recent refinement of the structure of hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$ by X-ray and neutron diffraction has been carried out by Kay, Young, and Posner (1964). In the hydroxylapatites the hydroxyl ion fills the anion site occupied by fluorine in fluorapatite, with the O–H axis parallel to the c-axis of the hexagonal columns. It is of interest that Kay *et al.* suggest that 'rocking' of the H about the O may be appreciable (the root mean square thermal vibration amplitude is about 0·18 Å in the c-direction and 0·22 Å perpendicular to c), although small by comparison with the separation between the anion sites inside the columns ($\sim$ 3·5 Å). It is likely that the considerable distance separating the hydroxyl ions along the c-axis coupled with their location in a plane containing three calcium ions is at least partially responsible for the good dielectric properties of some hydroxylapatites, particularly the alkaline-earth–rare-earth silicate apatites.

Composition and nomenclature of the mineral apatites

More than half the naturally occurring elements have been described as significant constituents of natural or synthetic apatites, and while there is some doubt about the occurrence of some ions, e.g. Al^{3+} and I^-, in natural apatites, there is no doubt that very extensive diadochy of either a simple (e.g. Cl^- for F^-) or complex (e.g. $Cr^{3+}+2Cr^{6+}$ for $3P^{5+}$ and $S^{6+}+Si^{4}+$ for $2P^{5+}$) type occurs. However, the extent of solid solution among the various end-members varies from complete to virtually zero, and the division of the mineral members into two sub-groups namely the 'apatites' and the 'pyromorphites' or 'lead apatites' recognizes the extensive solid solution series that exist among the members of each sub-group, and the limited range between the two sub-groups, as well as the striking paragenetic differences between the two sub-groups. (The 'pyromorphites' or lead apatites have the general formula $Pb_{10}(XO_4)_6Z_2$, where X may be phosphorus, arsenic, or vanadium and Z is usually chlorine, but may be other halogens or oxygen or a vacancy.)

The silicate apatites all belong to the 'apatite' sub-group. Ellestadite (McConnell, 1938), and wilkeite (McConnell, 1938) are silicate apatites but do not contain rare earths and will not be considered further. The rare-earth silicate apatites comprise the members of the britholite–abukumalite series where britholite is usually represented as

$$(Ca, Ce)_{10}\{(Si, P)O_4\}_6(OH)_2$$

and abukumalite as

$$(Ca, Yt)_{10}\{(Si, P)O_4\}_6(OH, F)_2.$$

Although these names are well established, there is unfortunately some controversy about the occurrence of pure silicate end members as apatites in nature. Thus while Kupriyanova and Sidorenko (1963) regard lessingite as the pure silicate end member of the britholite series, i.e. $(Ca, Ce)_{10}(SiO_4)_6(OH)_2$, Gay (1957) was led on the basis of optical properties to suggest that the structure of lessingite is probably orthorhombic. Synthetic studies have shown that the pure silicate analogues of britholite and abukumalite exist with apatite-type structures, and there is clearly a need for clarification of the status of lessingite and its close relatives.

It has become customary to refer collectively to the rare-earth group of elements as 'the lanthanons' and the tendency for the rare earths to occur in minerals in two distinct groups is well known. Yttrium, although not strictly a rare earth element, commonly occurs in minerals with the lanthanons and it is suggested that the symbol Cn (for cerons) should be used to include the 'light lanthanon' elements with atomic numbers from 57 to 63 inclusive (i.e. the elements La, Ce, Pr, Nd, Pm, Sm, and Eu) and the symbol Yn (for yttrons) for elements to include yttrium (atomic number 39) and the 'heavy lanthanon' elements with atomic numbers from 64 to 71, i.e. elements Gd, Tb, Ds, Ho, Er, Tm, Yb, and Lu. This symbol system is thus compatible with the proposed Levinson (1966) nomenclature for the rare-earth minerals, and enables pure or nearly pure end members to be identified without automatically introducing new names.

Preparation of synthetic compounds. All the compounds prepared during this work have been made from laboratory-reagent grade

TABLE I. Cell dimensions of synthetic apatite-type compounds and related mineral members of the group

(All mixtures for synthetic compounds were held at the stated temperatures for 1 hour unless otherwise specified)

Name and formula		*a*	*c*	*c/a*	Firing temperature	Atmosphere
Abukumalite	$Ca_4Yt_6(SiO_4)_6(F,OH)_2$*	9·31 Å	6·58 Å	0·707	—	—
	$Ca_4Yn_6(SiO_4)_6(OH)_2$†	9·33	6·78	0·727	1350° C	$N_2+H_2O+H_2$
	$Ca_{10}La_5Ce_5(SiO_4)_{12}(OH)_2$	9·51	7·00	0·736	1350	Air
	$Ca_6Nd_4(SiO_4)_6$	9·52	7·00	0·735	1350	Air
	$Ca_4Nd_6(SiO_4)_6(OH)_2$	9·52	7·00	0·735	1350	Air
	$Ca_6La_2Ce_2(SiO_4)_6$	9·52	7·00	0·735	1300	Air
	$Ca_4La_3Ce_3(SiO_4)_6(OH)_2$	9·52	7·01	0·736	1350	Air
	$Ca_4Nd_6(SiO_4)_6(OH)_2$	9·52	7·02	0·737	1400‡	$N_2+H_2O+H_2$
Ellestadite	$(Ca,C)_4\{(S,Si,P,C)O_4\}_6(Cl,F,O,OH)_2$§	9·53	6·91	0·725	—	—
	$Sr_4Dd_6(SiO_4)_6(OH)_2$‖	9·56	7·06	0·738	1370–1400	$N_2+H_2O+H_2$
Britholite	$(Ca,Ln)_{1\cdot94}(Si,P)_{1\cdot13}(O,OH,F)_{5\cdot12}$¶	9·61	7·03	0·731	—	—
	$Ca_5La_5(SiO_4)_6OH$	9·62	7·12	0·740	1300	$N_2+H_2O+H_2$
	$Ca_5La_5(SiO_4)_6OH$	9·63	7·12	0·739	1300	Air
	$Ca_6La_4(SiO_4)_6$	9·63	7·12	0·739	1300	Air
	$Ca_4La_6(SiO_4)_6(OH)_2$	9·63	7·124	0·740	1300	Air
	$Ca_4La_6(SiO_4)_6(OH)_2$	9·63	7·124	0·740	1350	$N_2+H_2O+H_2$
	$Ca_4La_6(SiO_4)_6F_2$	9·64	7·13	0·740	1375	Cylinder air
Beckelite	$(Ca,Ln)_{1\cdot96}(Si,Al,Zr)_{0\cdot89}(O,OH)_{4\cdot37}$¶	9·66	7·07	0·732	—	—
Lessingite	$(Ca,Ln)_{2\cdot06}(Si,Al,P)_{1\cdot14}(O,OH,F)_{5\cdot37}$¶	9·67	7·08	0·732	—	—
	$Sr_4La_6(SiO_4)_6(OH)_2$ (?)	9·68	7·21	0·745	1300	$N_2+H_2O+H_2$
	$Sr_4La_6(SiO_4)_6(OH)_2$ (?)	9·69	7·23	0·746	1350	Air
	$Tl_2La_8(SiO_4)_6(OH)_2$ (?)	9·69	7·18	0·741	1350	Air
	$La_8(SiO_4)_6$	9·69	7·17	0·740	1300	Air
	$Ba_2La_8(SiO_4)_6O_2$	9·76	7·30	0·748	1300	Air
	$Ca_6La_4(GeO_4)_6$	9·84	7·21	0·733	1350	Air
	$Ca_4La_6(GeO_4)_6(OH)_2$	9·85	7·20	0·731	1350	Air
	$Sr_4La_6(GeO_4)_6(OH)_2$	9·88	7·31	0·740	1350	Air
	$La_8(GeO_4)_6$	9·89	7·26	0·734	1300	Air
	$Ba_2La_8(GeO_4)_6O_2$	9·93	7·37	0·742	1300	Air
	$Ba_3La_7(GeO_4)_6O_{1\cdot5}$	9·99	7·39	0·740	1300	Air

* Trömel and Eitel, 1957.

† 'Yttrium oxide' used for this preparation contained only 56 % Yt_2O_3 the balance being Gd_2O_3 (14 %), Ds_2O_3 (13 %), and other rare earths (17 %).

‡ Fired for 1½ hours. § McConnell, 1938. ‖ Dd_2O_3 = 'Didymium oxide' mixed rare earths. ¶ Gay, 1957.

chemicals apart from rare-earth oxides and metallic germanium. The rare-earth oxides used were a commercially pure lanthanum oxide containing more than 99·9 % La_2O_3, a neodymium oxide containing 98 % Nd_2O_3 and a mixed rare earth oxide 'didymium oxide' containing 52 % Nd_2O_3, 19 % La_2O_3, 14 % Pr_6O_{11}, 8 % Sm_2O_3, and other rare earth oxides about 7 %. Cerous carbonate containing 67 % Ce_2O_3 was used as source of cerium oxide. Germanate compositions were made up using scrap semiconductor-grade germanium metal of at least 99·99 % purity.

TABLE II. *d*-spacings and intensities from $Ca_4La_6(SiO_4)_6(OH)_2$

(Guinier type camera using monochromatic Cu–$K\alpha$ radiation)

hkil	$d_{meas.}$	$d_{calc.}$	$(I/I_1)_{meas.}$	$(I/I_1)_{calc.}$
$10\bar{1}0$	8·4	8·35	2	4
$11\bar{2}0$	4·8	4·82	1	3
$20\bar{2}0$	4·18	4·17	29	30
$11\bar{2}1$	3·99	3·99	27	19
0002	3·56	3·56	23	17
$10\bar{1}2$	3·28	2·28	32	34
$21\bar{3}0$	3·155	3·154	38	31
$21\bar{3}1$	2·88	2·88	100	100
$11\bar{2}2$	2·86	2·86	52	71
$30\bar{3}0$	2·78	2·78	36	54
$20\bar{2}2$	2·71	2·71	3	7
$21\bar{3}2$	2·36	2·36	2	2
$31\bar{4}0$	2·31	2·31	11	8
$10\bar{1}3$ $22\bar{4}1$	2·28	2·28	4	1
$30\bar{3}2$	2·200	2·20	2	3
$31\bar{4}1$	2·195	2·192	3	1
$11\bar{2}3$	2·13	2·13	11	12
$40\bar{4}0$	2·085	2·085	6	4
$20\bar{2}3$	2·06	2·064	1	2
$22\bar{4}2$	1·995	1·995	25	33
$31\bar{4}2$	1·94	1·940	16	22
$32\bar{5}0$	1·913	1·913	5	7
$21\bar{3}3$	1·898	1·897	31	30
$32\bar{5}1$	1·848	1·848	20	22
$41\bar{5}0$	1·820	1·820	20	19
$40\bar{4}2$	1·800	1·799	25	27
0004	1·781	1·781	9	14
$20\bar{2}4$	1·639	1·638	2	2
$41\bar{5}2$	1·620	1·621	2	2
$42\bar{6}0$	1·577	1·576	6	5
$33\bar{6}1$	1·567	1·566	5	5
$21\bar{3}4$	1·551	1·551	6	8
$50\bar{5}2$	1·512	1·511	10	8
$30\bar{3}4$ $51\bar{6}0$	1·499	1·500	7	13
$32\bar{5}3$	1·490	1·490	8	8
$51\bar{6}1$ $33\bar{6}2$	1·465	1·466	9	14

The usual ceramic procedures of milling, prefiring, mixing with an organic binder, and pressing to form small discs for firing were used to make samples for X-ray analysis. Most mixes were fired in ordinary atmospheric air, at temperatures in the range 1000° to 1400° C, others were made in 'dry' air (i.e. with the partial water-vapour pressure of ice at liquid air temperatures), and some in an atmosphere of nitrogen 91 %, steam 7 %, and hydrogen 2 %.

Table I gives the compositions and lattice parameters of the synthesized compounds, while table II gives the observed and calculated *d*-spacings and intensities for the composition $Ca_4La_6(SiO_4)_6(OH)_2$.

Since there was some doubt about how the four calcium and six lanthanum ions were distributed among the (4f) and (6h) sites, a computer programme was used to calculate the intensities of the lines for various arrangements of the ions in these sites. The effect on the calculated intensities for certain lines is striking, and for comparison the actual measured intensities are:

hkil	*I* (obs)	*I* (calc) Random	*I* (calc) Ordered (1)	*I* (calc) Ordered (2)
0002	23	17	33	2·7
$10\bar{1}2$	32	32	15	39
$21\bar{3}1$	100	100	100	63
$11\bar{2}2$	52	71	22	100
$R = \frac{\Sigma\lvert\lvert F_0\rvert - F_c\rvert}{\Sigma\lvert F_0\rvert} =$		0·13	0·28	0·42

The arrangements of ions for ordered (1) was $4Ca^{2+}$ on (4f) sites and $6La^{3+}$ on (6h) sites and for ordered (2) was $4La^{3+}$ on (4f) sites and $4Ca^{2+}$ and $2La^{3+}$ randomly distributed over the (6h) sites. Particularly noteworthy are the reversal in intensities of lines 0002 and $10\bar{1}2$ for the random and ordered (1) arrangements and the reversal in intensities of $21\bar{3}1$ and $11\bar{2}2$ for either the random or ordered (1) arrangements and ordered (2).

The agreement of intensities observed and calculated using the same atomic parameters as in fluorapatite and an isotropic temperature factor $B = 2$ for a random distribution of Ca^{2+} and La^{3+} ions shown by the residual 0·13 is considered good. It is therefore concluded that a random distribution of Ca^{2+} and La^{3+} ions exists on the (4f) and (6h) sites in the lattice.

Discussion. The ready synthesis of members of the hydroxylapatite family in inorganic systems at moderate temperatures (below 1000° C) is well known, and, for example, Schleede, Schmidt, and Kindt (1932) observed the formation of hydroxylapatite both by the action of water on calcium phosphates and during the slow cooling of calcium phosphate melts in the presence of moisture. They also noted that the water in hydroxylapatite is only driven off at 1400° C. More recent references to the formation of hydroxylapatites by heating mixtures in atmospheric air include Chaudron and Wallaeys (1949) and Johnson (1960).

Attempts to synthesize rare-earth apatites free from hydroxyl ions, or to see if the apatite structure fails to form in dry air have been unsuccessful, and this is considered to be due to the affinity of La_2O_3 (and to a lesser extent the other rare earth oxides) for water vapour, coupled with the tenacity with which it seems to retain at least part of it. Although we have not found evidence for LaO(OH) in the prefired mixtures, LaOF was found in prefires during the preparation of the fluor analogue of the calcium lanthanum silicate apatite, and it seems reasonable to suppose that, since this is derived from the calcium fluoride added to the mixture of oxides to make the fluor silicate apatite, LaO(OH) is present in the prefires used for the hydroxylapatite. Attempts to confirm the presence of the hydroxyl ion in the calcium lanthanum silicate apatite by infra-red absorption spectroscopy have so far been unsuccessful, and an oxyapatite formula $Ca_4La_6(SiO_4)_6O$ such as has been suggested for voelckerite and oxy-pyromorphite could be proposed instead of $Ca_4La_6(SiO_4)_6(OH)_2$. However, since hydroxylapatites are readily synthesized in air, retain their structural water up to high temperatures, and the compound forms easily at high temperatures in the presence of steam (i.e. in an atmosphere nominally of 2 % hydrogen, 7 % H_2O, and 91 % N_2), it is considered that the most likely formula is $Ca_4La_6(SiO_4)_6(OH)_2$.

Although many investigators, e.g. Rankin and Wright (1915), Muan and Osborn (1951), have studied the join $CaO–SiO_2$ either as a binary system or as part of ternary systems, and the existence of four calcium silicates with several polymorphs is well known, few studies have been made either of the join $La_2O_3–SiO_2$ or the ternary system $CaO–La_2O_3–SiO_2$. Keler, Godina, and Savchenko (1961) have described three lanthanum silicates, $La_2O_3.SiO_2$, $2La_2O_3.3SiO_2$, and $La_2O_3.2SiO_2$, and the corresponding neodymium and gadolinium compounds. A limited study of the join $2CaO.SiO_2–2La_2O_3.3SiO_2$ has been carried out by Toropov and Fedorov (1965) who found only a simple eutectic and little or no solid solution between either $2La_2O_3.3SiO_2$ or $2Nd_2O_3.3SiO_2$ and α-$2CaO.SiO_2$. Eitel *et al.* (1930) described a hexagonal compound $CaO.La_2O_3.2SiO_2$ with *a* 11·01 Å, *c* 8·98 Å, *c*/*a* 0·8156 and in a later publication Trömel and Eitel (1957) suggested a formula

$$Ca_2La_3(SiO_4)_3N = Ca_4La_6(SiO_4)_6N_2$$

where N = OH, F, or Cl for this compound. Unfortunately, neither the original data for the flux-grown crystals nor the later data *a* 9·65 Å, *c* 6·84 Å, *c*/*a* 0·711 correspond with the data for the apatite type phase $Ca_4La_6(SiO_4)_6(OH)_2$ prepared during this investigation which has *a* 9·63 Å, *c* $7{\cdot}12_4$ Å, and *c*/*a* 0·740, although this compound was first synthesized in mixtures with the bulk composition $CaO.La_2O_3.2SiO_2$. The flux used in the early work by Eitel *et al.* (1930) was sodium tungstate or sodium vanadate: incorporation of either sodium or vanadium ions into the lattice could be expected to cause an increase in the cell size, although it is very large indeed even for vanadium apatites, and it is probably not an apatite at all. Although the use of a flux or a phosphate is not described in the later work, the small *c* parameter of 6·84 Å is much closer to that of the phosphate apatites (6·78–7·29) than for the silicate apatites (7·0–7·30), and the incorporation of phosphorus from the flux in these later crystals seems likely.

The compound $Ca_4La_6(SiO_4)_6(OH)_2$ and its fluor analogue $Ca_4La_6(SiO_4)_6F_2$ are related to fluor- and hydroxylapatite by the substitution of La^{3+} and Si^{4+} for $Ca^{2+}+P^{5+}$. It has been found possible to produce apatite type compounds which are deficient in the (2a) or so-called *Z* or F halogen site, and the calcium lanthanum compound has the formula $Ca_6La_4(SiO_4)_6$, i.e. the substitution now is $4La^{3+}+6Si^{4+} \rightleftharpoons 4Ca^{2+}+6P^{5+}+2(OH)^-$.

Unlike the fluor and hydroxylapatites, where the hydroxyl can only be accommodated with a slight expansion of the lattice, particularly perpendicular to *c*, the lattice parameters of $Ca_4La_6(SiO_4)_6(OH)_2$ and $Ca_6La_4(SiO_4)_6$ are virtually identical, since the substitution of La^{3+} for part of the Ca^{2+} has expanded the lattice sufficiently for $(OH)^-$ or F^- or a vacancy to be accommodated without strain. The composition halfway between these two end members, i.e. $Ca_5La_5(SiO_4)_6OH$ has also been synthesized.

A corresponding series with half the La^{3+} ions replaced by Ce^{3+} has been prepared and may be summarized thus:

$$\begin{tikzcd}
\textit{La Series} & \textit{La Ce Series} \\
Ca_6\,La_4(SiO_4)_6 \arrow[d] & Ca_{12}La_4Ce_4(SiO_4)_{12} \\
 & \text{i.e. } Ca_6La_2Ce_2(SiO_4)_6 \arrow[d] \\
Ca_5La_5(SiO_4)_6(OH) \arrow[d] & Ca_{10}La_5Ce_5(SiO_4)_{12}(OH)_2 \arrow[d] \\
Ca_4La_6(SiO_4)_6(OH)_2 & Ca_8La_6Ce_6(SiO_4)_{12}(OH)_4 \\
 & \text{i.e. } Ca_4La_3Ce_3(SiO_4)_6(OH)_2
\end{tikzcd}$$

The relations of these to the three minerals beckelite, lessingite, and britholite and the synthetic slag compound *cefluosil* may now be discussed.

Gay (1957) has given X-ray data for beckelite, lessingite, and britholite, showing their close affinity to each other, and he suggested that they may be orthorhombic, not hexagonal, with an ideal formula of $(Ca, Ln)_2(Si, P, Al)(O, OH, F)_5$. However, as he points out, the chemical analyses used are old and possibly inaccurate.

The synthetic studies carried out in these laboratories suggest that beckelite and lessingite may be members of the silicate apatite group. The beckelite analysis quoted by Gay recalculated on a molar basis yields a ratio of Ca:Ln:Si of 2·8:2:2·8, reasonably close to the ratio for $Ca_6La_4(SiO_4)_6$ and $Ca_{12}La_4Ce_4(SiO_4)_{12}$. It is suggested that the pure beckelite end-member is in fact completely deficient in ions in the OH or F site and has a La:Ce ratio of 1:1.

The lessingite analysis also quoted by Gay yields a Ca:Ln:Si ratio of 5:5:8 and it is suggested that lessingite corresponds ideally to the composition $Ca_{10}La_5Ce_5(SiO_4)_{12}(OH)_2$, where the Ca:Ln:Si ratio is 5:5:6, but with only half the OH or F sites filled and a La:Ce ratio of 1:1. A mineral corresponding to $Ca_4La_3Ce_3(SiO_4)_6(OH)_2$ is as yet unknown. (In nature, it is to be expected that mineral representatives will be fluor analogues rather than hydroxyl apatites.)

These suggested relationships are shown as follows:

Synthetic *La Series*	Synthetic *La Ce Series*	? Natural *La Ce Series*
$Ca_6La_4(SiO_4)_6$	$Ca_{12}La_4Ce_4(SiO_4)_{12}$	$Ca_{12}La_4Ce_4(SiO_4)_{12}$ (beckelite)
a = 9·63 Å	a = 9·52 Å	a = 9·66 Å
c = 7·12 Å	c = 7·00 Å	c = 7·07 Å
c/a = 0·739	c/a = 0·735	c/a = 0·73
↓	↓	↓
$Ca_5La_5(SiO_4)_6(OH)$	$Ca_{10}La_5Ce_5(SiO_4)_{12}$ $(OH)_2$	$Ca_{10}La_5Ce_5(SiO_4)_{12}$ $(OH)_2$ (lessingite)
a = 9·62 Å	a = 9·51 Å	a = 9·67 Å
c = 7·12 Å	c = 7·00 Å	c = 7·08 Å
c/a = 0·740	c/a = 0·736	c/a = 0·732
↓	↓	↓
$Ca_4La_6(SiO_4)_6(OH)_2$	$Ca_8La_6Ce_6(SiO_4)_{12}$ $(OH)_4$	$Ca_8La_6Ce_6(SiO_4)_{12}$ $(OH)_4$
a = 9·63 Å	a = 9·52 Å	Not known
c = 7·12 Å	c = 7·01 Å	
c/a = 0·740	c/a = 0·736	

Rudneva, Nikitin, and Belov (1962) recently described a calcium rare earth silicate apatite cefluosil (сефтосил), found in a blast furnace slag, with a CaO content of 15·6 %, rare earths 57·5 % (CeO_2 28·0 %, Nd_2O_3 14·5 %, La_2O_3 11·0 %, Pr_2O_3 6·0 %), and SiO_2 19·04 % and a similar compound was synthesized in a CO atmosphere by Leonov (1963). It resembles the composition of beckelite although it contains rather more silica and fluorine is a major constituent. It is a synthetic compound with *a* 9·54, *c* 7·01, *c*/*a* 0·735 and would appear to lie between beckelite and lessingite, and thus hardly justifies a special name. However, in its ready synthesis under reducing conditions, it closely resembles the conditions under which $Ca_4La_6(SiO_4)_6(OH)_2$ was first synthesized (nitrogen, steam, and hydrogen in the proportions 91:7:2).

The relationship of britholite to this group is considered on the basis of Gay's quoted compositions, lattice parameters, and calculated cell contents to be that of an apatite containing a ratio of approximately one (phosphate) apatite molecule to two beckelite molecules, i.e. ideally $Ca_{7\cdot33}La_{1\cdot33}Ce_{1\cdot33}(SiO_4)_4(PO_4)_2(OH)_{1\cdot66}$. Assuming the sum of the cations to be 16, this formula yields a total of 25·66 anions and suggests that approximately $\frac{1}{6}$ of the (2a) sites may be vacant.

Wondratschek (1963) has described a series of lead apatites (or pyromorphites), which range from those in which the (2a) or *Z* site is fully occupied, e.g. with F or (OH), to those where this site is wholly vacant. The calcium lanthanum and calcium lanthanum cerium silicate apatites resemble these lead apatites in tolerating a variation in site occupancy in the (2a) position.

Several other alkaline-earth–rare-earth silicate apatites have been prepared and include the barium and strontium analogues of $Ca_4La_6(SiO_4)_6(OH)_2$. These show the expected increase in lattice parameters with increasing cation size. Neodymium may be substituted for lanthanum in $Ca_4La_6(SiO_4)_6(OH_2)$ resulting in a decrease in lattice parameter.

Germanate analogues of many of the silicate apatites have been prepared, and apart from the increased lattice parameters, closely resemble the corresponding silicates. Both the $BaO–La_2O_3–SiO_2$ and $BaO–La_2O_3–GeO_2$ systems are more complicated than the corresponding calcium oxide systems and contain several apatite-type compounds, e.g. $Ba_2La_6(SiO_4)_6O_2$ and $Ba_3La_7(GeO_4)_6O_{1\cdot5}$. Strunz *et al.* (1960) have reported a germanate apatite with the composition $Ca_2Ce_3(GeO_4)_3Cl = Ca_4Ce_6(GeO_4)_6Cl_2$ with *a* 9·467, *c* 6·999, *c*/*a* 0·7392, and although a synthesis of the corresponding oxy or hydroxyl compound has not yet been attempted, there seems little reason to doubt that such compounds would synthesize easily, particularly in view of the ready formation of $Ca_4La_6(GeO_4)_6(OH)_2$ with *a* 9·85, *c* 7·20, *c*/*a* 0·733.

Acknowledgements. The authors wish to thank the directors of the Plessey Company for permission to publish this paper.

References

Beevers (C. A.) and McIntyre (D. B.), 1946. Min. Mag., vol. 27, p. 254.

Chaudron (G.) and Wallaeys (R.), 1949. Bull. Soc. Chim. Franç. p. 132.

Eitel (W.), Herbinger (E.), and Trömel (G.), 1930. Ver. Kais. Wil. Inst. Silik., vol. 3, p. 103.

Gay (P.), 1957. Min. Mag., vol. 31, p. 455.

Hendricks (S. B.), Jefferson (M. E.), and Mosley (V. M.), 1932. Zeits. Krist., vol. 81, p. 352.

Hentschel (H.), 1923. Centr. Min. Geol., p. 609.

Johnson (W.), 1960. Min. Mag., vol. 32, p. 408.

Kay (M. I.), Young (R. A.), and Posner (A. S.), 1964. Nature, vol. 204, p. 1050,

[Keler (E. K.), Godina (N. A.), and Savchenko (E. P.)] 1961. Келер (Е. К.), Година (Н. А.), и Савченко (Е. П.), [Изв. Акад. наук СССР, Отд. хим. наук (Bull. Sci., Acad. Sci. URSS, Cl. Sci. Chim., p. 1728], abst. Chem. Abstr., 1963, vol. 58, no. 4150.

[Kupriyanova (I. I.) and Sidorenko (G. A.)] Куприянова (И. И.) и Сидоренко (Г. А.), 1963. [Докл. Акад. наук СССР (Compt. Rend. Acad. Sci. URSS), vol. 148, p. 912], abstr. Chem. Abstr., 1963, vol. 59, no. 3651.

[Leonov (A. I.)] Леонов (А. И.), 1963. [Изв. Акад. наук СССР, Сер. хим. (Bull. Sci., Acad. Sci. URSS, sér. chim.), vol. 12, p. 2084]; abstr. Chem. Abstr., 1964, vol. 60, no. 10, 189.

Levinson (A. A.), 1966. Amer. Min., vol. 51, p. 152.

McConnell (D.), 1938. *Ibid.*, vol. 23, p. 1.

Mehmel (M.), 1931. Zeits. physikal. Chem., vol. 15B, p. 223.

Muan (A.) and Osborne, 1951. Paper at Iron and Steel Institute, New York, 23–24 May.

Naray-Szabo (S.), 1930. Zeits. Krist., vol. 75, p. 387.

Rankin (G. A.) and Wright (F. E.), 1915. Amer. Journ. Sci., ser. 4, vol. 39, p. 5.

[Rudneva (A. V.), Nikitin (A. V.), and Belov (N. V.)], Руднева (А. В.), Никитин (А. В.), и Белов (Н. В.), 1962. [Докл. Акад. наук СССР (Compt. Rend. Acad. Sci. URSS), vol. 146, p. 1182] abstr. in Chem. Abstr., 1963, vol. 58, no. 3207.

Schleede (A.), Schmidt (W.), and Kindt (H.), 1932. Zeits. Electrochem., vol. 38, no. 8*a*, p. 633.

Strunz (H.), Freigang (H.), and Contag (B.), 1960. Neues Jahrb. Min., Monats. p. 47.

[Toropov (N. A.) and Fedorov (N. F.)] Торопов (Н. А.) и Федоров (Н. Ф.), 1965. [Изв. Акад. наук СССР, Неорг. матер. (Bull. sci., Acad. Sci. URSS, Mat. inorg.), vol. 1, p. 126]; abstr. in Chem. Abstr., 1965, vol. 62, no. 15 482.

Trömel (G.) and Eitel (W.), 1957. Zeits. Krist., vol. 109, p. 231.

Wondratschek (H.), 1963. Neues Jahrb. Min., Abh., vol. 99, p. 113.

[*Manuscript received 6 November 1966*]