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The Structure of Some Alkaline-Earth Metal Uranates

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The structures of $CaUO_4$, $SrUO_4$ (orthorhombic), $BaUO_4$, Ca_2UO_5, Sr_2UO_5, Ca_3UO_6, and Sr_3UO_6 have been, where necessary, further determined and refined from neutron powder diffraction data. Least-squares parameters were obtained by fitting a calculated profile to the observed data. The standard deviations in the atomic positions varied with the number of independent structure parameters from 0·0007 Å for $CaUO_4$ to 0·029 Å for Sr_3UO_6.

Introduction

The crystal structures of $CaUO_4$ (Zachariasen, 1948) and $BaUO_4$ (Samson & Sillén, 1947) were determined previously with the use of both single-crystal and powder X-ray techniques. $SrUO_4$ (orthorhombic) was found to be isomorphous with $BaUO_4$ (Ippolitova, Simanov, Kovba, Polunina & Bereznikova, 1959). The rhombohedral form of $SrUO_4$ (Zachariasen, 1948) was found to be formed only in the absence of oxygen (Ippolitova *et al.*, 1959; Cordfunke & Loopstra, 1967). This phase is probably oxygen-deficient and has therefore been excluded from the present investigation.

Ca_2UO_5 and isostructural Sr_2UO_5 were solved by X-ray powder methods, but only as regards the metal positions (Sawyer, 1963). Ca_3UO_6 and Sr_3UO_6, which also are isostructural, were determined from X-ray and neutron diffraction powder data (Rietveld, 1966).

The present investigation was undertaken to determine the oxygen positions in Ca_2UO_5 and Sr_2UO_5 and to obtain better oxygen coordinates in the other compounds by using neutron diffraction data and the profile refinement technique (Rietveld, 1967, 1968).

Experimental

All compounds were prepared by heating stoichiometric mixtures of UO_3 and the alkaline earth metal carbonates, or nitrates, at 1000 °C until X-ray powder diagrams showed the product to react no further. The final products contained only a few traces of impurities except Ca_2UO_5 where several per cent of $CaUO_4$ and Ca_3UO_6 were still present even after heating for weeks.

Neutron powder diagrams were obtained under the conditions listed in Table 1. The impurity lines in the diagram of Ca_2UO_5 were corrected for by subtracting properly scaled diagrams of $CaUO_4$ and Ca_3UO_6 obtained under identical conditions.

Table 1. *Experimental details*

α_1 is the angular divergence of the collimator between the reactor and the monochromator, α_3 that of the collimator in front of the BF_3 detector; λ is the wavelength used and $(\sin\theta_m)/\lambda$ the range of observation.

Compound	α_1	α_3	λ	$(\sin\theta_m)/\lambda$
$CaUO_4$	30′	30′	2·576 Å	0·350
$SrUO_4$	10	10	2·566	0·350
$BaUO_4$	10	10	2·562	0·350
Ca_2UO_5	10	10	2·565	0·348
Sr_2UO_5	10	10	2·565	0·333
Ca_3UO_6	10	10	2·565	0·353
Sr_3UO_6	5·5	10	1·103	0·373

X-ray powder intensities were collected on a Philips diffractometer with Cu $K\alpha$ radiation. Unit-cell data for all compounds are shown in Table 2.

Structure determination of Sr_2UO_5 and Ca_2UO_5

From the previous X-ray work (Sawyer, 1963), the metal atoms in Sr_2UO_5 had been found to occupy the positions given in Table 3. Packing considerations led to initial parameters of the oxygen atoms. These were used to construct four structure models which differed from each other only with regard to the sign of the Sr y parameters. The Sr coordinates of all four models were then refined by a least-squares method (Rietveld,

Table 2. *Unit-cell data*

Numbers in parentheses refer to standard deviations in units of the last decimal.

Substance	*a*	*b*	*c*	*α*	*β*	*γ*	Space group	*Z*
$CaUO_4$	6·2683 (6) Å	6·2683 (6) Å	6·2683 (6) Å	36·040 (2)°	36·040 (2)°	36·040 (2)°	$R\bar{3}m$	1
$SrUO_4$	5·4896 (7)	7·9770 (9)	8·1297 (12)	90	90	90	$Pbcm$	4
$BaUO_4$	5·7553 (10)	8·1411 (21)	8·2335 (11)	90	90	90	$Pbcm$	4
Ca_2UO_5	7·9137 (13)	5·4409 (7)	11·4482 (19)	90	108·803 (7)	90	$P2_1/c$	4
Sr_2UO_5	8·1043 (13)	5·6614 (8)	11·9185 (18)	90	108·985 (10)	90	$P2_1/c$	4
Ca_3UO_6	5·7275 (12)	5·9564 (8)	8·2982 (13)	90	90·568 (9)	90	$P2_1$	2
Sr_3UO_6	5·9588 (22)	6·1795 (22)	8·5535 (38)	90	90·192 (41)	90	$P2_1$	2

1966) using the X-ray powder intensities. They were found to converge quickly to only two different models, of which one was clearly favoured by lower values of the agreement factor and the minimum function. This model refined smoothly on subsequent alternate X-ray and neutron data refinements until the X-ray data refinements no longer produced any significant shifts in the parameters. The final refinement was based on the neutron data and is described below.

Table 3. *Metal positions in* Sr_2UO_5 *according to Sawyer* (1963)

	Point position	*x/a*	*y/b*	*z/c*
U(1)	2 (*a*)	0	0	0
U(2)	2 (*b*)	0·5	0	0
Sr(1)	4 (*e*)	0·157	0·028	0·328
Sr(2)	4 (*e*)	0·343	0·023	0·640

Because Ca_2UO_5 is isostructural with Sr_2UO_5, the final Sr_2UO_5 parameters were used as initial Ca_2UO_5 parameters.

Structure refinement

In neutron powder diffraction, it is customary to use as least-squares data the integrated values of the diffraction peaks, even when these consist of more than one Bragg reflexion. The loss of information inherent in this technique can, however, be eliminated by using the complete observed powder pattern in a direct manner (Rietveld, 1967). This method determines the estimates of the structure parameters by finding a least-squares fit between the observed and calculated profile intensities. The contribution of each Bragg reflexion to the profile at position $2\theta_i$ is given as

$$2\sqrt{\ln 2}\,cjF^2\exp\{-4\ln 2(2\theta_i-2\theta_0)^2/b^2\}/(\sqrt{\pi}b\sin 2\theta_0\sin\theta_0)$$

where j is the multiplicity, F the structure factor, and $2\theta_0$ the position of the Bragg reflexion; b is the half-width of the Bragg peak at position $2\theta_0$ and c an overall scale factor. The quantities b and $2\theta_0$ in this expression have to be determined from an inspection of the powder pattern and from the known values of the unit-cell parameters and the wavelength.

In the present investigation, the above quantities were also refined. To this end, the following expression for the half-width was assumed:

$$b^2=P\tan^2\theta_0+Q\tan\theta_0+R\,.$$

The peak position was expressed in the usual manner as

$$2\theta_0=2\arcsin(\sqrt{Ah^2+Bk^2+Cl^2+Dkl+Ehl+Fhk})-z\,,$$

where z is the zero-point position of the counter and $A=4a^{*2}/\lambda^2$, $D=8b^*c^*\cos\alpha^*/\lambda^2$, . . ., all symbols having the normal meaning. During the refinement, proper constraints were introduced between the parameters A, B, . . ., F to account for the crystal symmetry. The validity of the use of a quadratic function to describe the variation of the half-width is clearly demonstrated by the observed and calculated profile of $CaUO_4$ [Fig. 1(*a*)]. This pattern consists almost completely of single peaks and therefore serves well to show the agreement obtainable with this type of function. In addition, it can be seen that the peak shape is almost exactly Gaussian.

Obviously, this well resolved pattern could equally well have been reduced to integrated intensities, yielding in this way probably the same structure parameters. The only advantage, here, of the profile method lies in the more reliable estimates of the standard deviations due to the larger number of statistically independent data. However, the real potential of the profile method can best be shown in patterns exhibiting severe overlap, *e.g.* the powder pattern of Sr_2UO_5 [Fig. 1(*b*)]. The good agreement between the calculated and the observed profile, even in regions with severe overlap, shows the extent to which the method uses the available information.

The measure of agreement can be expressed as

$$R_1=100\sqrt{\Sigma\, w(I_{\rm obs}-I_{\rm calc})^2/\Sigma\, wI^2_{\rm obs}}\,,$$

where $I_{\rm calc}$ and $I_{\rm obs}$ are the calculated and observed intensities at each counter position and w is the corresponding statistical weight. The sums are taken only over those regions of the pattern where Bragg peaks can be expected. An estimate of the more conventional agreement index

$$R_2=100\Sigma\,|F^2_{\rm obs}-F^2_{\rm calc}|/\Sigma\,F^2_{\rm obs}$$

can be obtained by splitting the compound peaks into the constituent $F^2_{\rm obs}$ values according to their $F^2_{\rm calc}$ values. This method will produce a lower R value, the more overlap there is in the pattern. However, it still may serve to enable a comparison between the results of the present method and those using integrated powder intensities.

The final values of the structure parameters have been listed in Table 4.

Discussion of results

An inspection of Table 5 shows the mean standard deviation of the coordinates to increase with an increase in the number of parameters, while the number of statistically independent I_{obs} values remains practically constant, except for $CaUO_4$. To some extent, this effect could have been expected from the corresponding decrease in the number of degrees of freedom. However, its magnitude is many times too large. A possible explanation is based on the fact that, together with the increase in the number of parameters, there is also an increase in the number of independent Bragg reflexions which results in a larger amount of overlap. As a consequence, the available information is reduced.

Two of the three scattering lengths of Sr and Ca in Table 4 agree well within the limits set by their standard deviations. Averaging these values gives $b_{\mathrm{Ca}}=0{\cdot}474\,(3)\times10^{-12}$ cm and $b_{\mathrm{Sr}}=0{\cdot}683\,(7)\times10^{-12}$ cm. These determinations, however, are only relative to the scattering lengths of O and U, which were taken to be 0·577 and $0{\cdot}85\times10^{-12}$ cm respectively. Comparing these scattering lengths, and also the scattering length $b_{\mathrm{Ba}}=0{\cdot}531\,(8)\times10^{-12}$ cm, with the tabulated values (*International Tables for X-ray Crystallography*, 1962) of $b_{\mathrm{Ca}}=0{\cdot}49$, $b_{\mathrm{Sr}}=0{\cdot}57$, and $b_{\mathrm{Ba}}=0{\cdot}52$ (all in units of 10^{-12} cm), shows a very large discrepancy for b_{Sr} while the other two do not differ significantly. The same discrepancy has been observed by Willis (1967) for SrF_2.

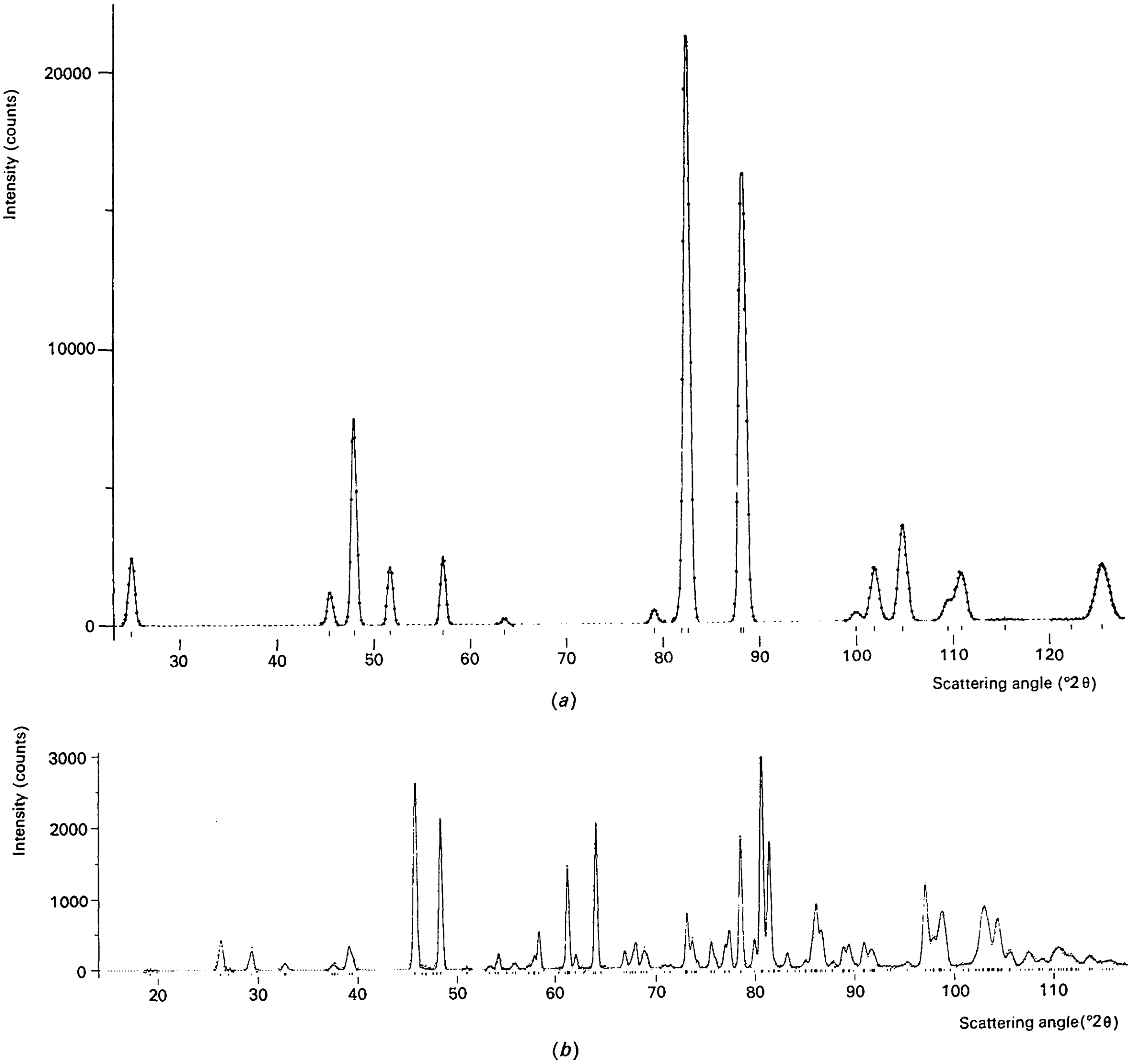

Fig. 1. Observed and calculated neutron powder diffraction patterns measured at $\lambda=2{\cdot}57$ Å for (*a*) $CaUO_4$ and (*b*) Sr_2UO_5. Dots: observed data, corrected for background. Full curve: calculated pattern.

Table 4. *Final least-squares parameters*

Numbers in parentheses refer to standard deviations in units of the last decimal.

Compound	Atom	*x*	*y*	*z*	*B* (Å^2)	Scattering length (10^{-12} cm)
$CaUO_4$	U	0·0000 (–)	0·0000 (–)	0·0000 (–)	0·29 (7)	—
	Ca	0·5000 (–)	0·5000 (–)	0·5000 (–)	0·54 (19)	0·471 (4)
	O(1)	0·1118 (1)	0·1118 (1)	0·1118 (1)	0·42 (7)	—
	O(2)	0·3627 (1)	0·3627 (1)	0·3627 (1)	0·42 (7)	—
$SrUO_4$	U	0·0000 (–)	0·0000 (–)	0·0000 (–)	0·12 (9)	—
	Sr	0·4710 (8)	0·2013 (4)	0·2500 (–)	0·00 (20)	0·693 (7)
	O(1)	0·2998 (7)	0·9193 (4)	0·0810 (4)	0·01 (10)	—
	O(2)	0·1726 (9)	0·2500 (–)	0·0000 (–)	0·01 (10)	—
	O(3)	0·8602 (8)	0·0300 (6)	0·2500 (–)	0·01 (10)	—
$BaUO_4$	U	0·0000 (–)	0·0000 (–)	0·0000 (–)	0·00 (11)	—
	Ba	0·4749 (14)	0·2008 (8)	0·2500 (–)	1·01 (31)	0·531 (8)
	O(1)	0·2939 (8)	0·9246 (5)	0·0690 (5)	0·87 (12)	—
	O(2)	0·1515 (12)	0·2500 (–)	0·0000 (–)	0·87 (12)	—
	O(3)	0·8775 (12)	0·0276 (8)	0·2500 (–)	0·87 (12)	—
Ca_2UO_5	U(1)	0·0000 (–)	0·0000 (–)	0·0000 (–)	0·62 (13)	—
	U(2)	0·5000 (–)	0·0000 (–)	0·0000 (–)	0·62 (13)	—
	Ca(1)	0·1592 (13)	0·0621 (16)	0·3200 (10)	0·55 (25)	0·447 (6)
	Ca(2)	0·3462 (12)	0·9985 (19)	0·6414 (8)	0·55 (25)	0·447 (6)
	O(1)	0·4447 (11)	0·3202 (15)	0·3267 (7)	1·16 (12)	—
	O(2)	0·8802 (9)	0·2831 (14)	0·3532 (7)	1·16 (12)	—
	O(3)	0·6197 (10)	0·3043 (14)	0·0720 (8)	1·16 (12)	—
	O(4)	0·0163 (9)	0·2610 (13)	0·1295 (7)	1·16 (12)	—
	O(5)	0·2507 (14)	0·1873 (15)	0·9953 (9)	1·16 (12)	—
Sr_2UO_5	U(1)	0·0000 (–)	0·0000 (–)	0·0000 (–)	0·23 (16)	—
	U(2)	0·5000 (–)	0·0000 (–)	0·0000 (–)	0·23 (16)	—
	Sr(1)	0·1571 (13)	0·0747 (13)	0·3181 (7)	0·78 (21)	0·738 (9)
	Sr(2)	0·3359 (10)	0·9926 (14)	0·6379 (6)	0·78 (21)	0·738 (9)
	O(1)	0·4501 (13)	0·3215 (18)	0·3354 (8)	0·17 (15)	—
	O(2)	0·8912 (12)	0·2959 (16)	0·3579 (8)	0·17 (15)	—
	O(3)	0·6017 (12)	0·2978 (17)	0·0731 (8)	0·17 (15)	—
	O(4)	0·0153 (12)	0·2573 (17)	0·1176 (8)	0·17 (15)	—
	O(5)	0·2499 (15)	0·1552 (13)	0·9956 (10)	0·17 (15)	—
Ca_3UO_6	U	0·2459 (28)	0·0000 (–)	0·2519 (20)	0·30 (15)	—
	Ca(1)	0·2621 (52)	0·9975 (83)	0·7488 (37)	1·06 (20)	0·476 (5)
	Ca(2)	0·2723 (28)	0·4223 (48)	0·0123 (15)	1·06 (20)	0·476 (5)
	Ca(3)	0·7532 (29)	0·0288 (54)	0·4761 (15)	1·06 (20)	0·476 (5)
	O(1)	0·6319 (37)	0·4100 (52)	0·5173 (24)	1·33 (9)	—
	O(2)	0·5605 (32)	0·1618 (39)	0·1938 (25)	1·33 (9)	—
	O(3)	0·0747 (39)	0·2744 (54)	0·3323 (32)	1·33 (9)	—
	O(4)	0·1165 (33)	0·0484 (55)	0·0152 (23)	1·33 (9)	—
	O(5)	0·0327 (32)	0·3053 (38)	0·6942 (24)	1·33 (9)	—
	O(6)	0·5740 (38)	0·1963 (55)	0·8252 (32)	1·33 (9)	—
Sr_3UO_6	U	0·2478 (48)	0·0000 (–)	0·2472 (29)	2·50 (31)	—
	Sr(1)	0·2391 (51)	0·0126 (68)	0·7546 (30)	0·12 (17)	0·674 (7)
	Sr(2)	0·2671 (34)	0·4975 (52)	0·0066 (18)	0·12 (17)	0·674 (7)
	Sr(3)	0·7527 (36)	0·0859 (46)	0·4803 (20)	0·12 (17)	0·674 (7)
	O(1)	0·6308 (35)	0·4511 (48)	0·5243 (32)	1·67 (19)	—
	O(2)	0·5048 (35)	0·1892 (55)	0·1971 (37)	1·67 (19)	—
	O(3)	0·0893 (50)	0·2948 (72)	0·3244 (34)	1·67 (19)	—
	O(4)	0·1505 (39)	0·0682 (56)	0·0173 (33)	1·67 (19)	—
	O(5)	0·0545 (34)	0·3444 (56)	0·7087 (41)	1·67 (19)	—
	O(6)	0·5713 (49)	0·2381 (66)	0·8271 (35)	1·67 (19)	

Table 5. *Available information, number of parameters, and accuracy of least-squares results*

Compound	Number of I_{obs} values	Number of independent Bragg reflexions	Number of parameters	R_1 index	R_2 index	Mean deviation of coordinates
$CaUO_4$	300	19	13	4·8	1·5	0·0007 Å
$SrUO_4$	913	71	20	11·3	5·8	0·0040
$BaUO_4$	905	76	20	13·1	5·1	0·0052
Ca_2UO_5	1114	160	34	12·6	7·6	0·0084
Sr_2UO_5	1044	160	34	9·6	3·7	0·0074
Ca_3UO_6	1079	115	42	10·8	7·2	0·0238
Sr_3UO_6	869	159	42	12·1	9·0	0·0286

Table 6. *Coordination of* U *atoms*

Compound	Atom(1)–atom(2)	Distance	Number of equivalent distances
$CaUO_4$	U–O(1)	1·963 (2) Å	2
	U–O(2)	2·298 (1)	6
$SrUO_4$	U–O(1)	1·886 (4)	2
	U–O(2)	2·208 (2)	2
	U–O(3)	2·186 (2)	2
$BaUO_4$	U–O(1)	1·887 (5)	2
	U–O(2)	2·214 (3)	2
	U–O(3)	2·187 (2)	2
Ca_2UO_5	U(1)–O(2)	2·022 (7)	2
	U(1)–O(4)	2·027 (7)	2
	U(1)–O(5)	2·247 (9)	2
	U(2)–O(1)	2·128 (8)	2
	U(2)–O(3)	1·953 (8)	2
	U(2)–O(5)	2·206 (9)	2
Sr_2UO_5	U(1)–O(2)	2·005 (7)	2
	U(1)–O(4)	2·012 (8)	2
	U(1)–O(5)	2·217 (9)	2
	U(2)–O(1)	2·118 (7)	2
	U(2)–O(3)	1·968 (8)	2
	U(2)–O(5)	2·189 (8)	2
Ca_3UO_6	U–O(1)	2·102 (30)	1
	U–O(2)	2·034 (27)	1
	U–O(3)	2·023 (32)	1
	U–O(4)	2·112 (28)	1
	U–O(5)	2·026 (28)	1
	U–O(6)	2·181 (33)	1
Sr_3UO_6	U–O(1)	2·104 (34)	1
	U–O(2)	1·975 (39)	1
	U–O(3)	2·157 (46)	1
	U–O(4)	2·091 (37)	1
	U–O(5)	2·077 (38)	1
	U–O(6)	2·047 (42)	1

A list of U–O distances appears in Table 6. The U atoms in all compounds are 6-coordinated except in $CaUO_4$. In this compound the U-atom coordination is eight. The alkaline-earth metals are in most cases 7-coordinated, except in $CaUO_4$, where the Ca atom is 5-coordinated, and in Sr_3UO_6 and Ca_3UO_6, where two of the three alkaline-earth-metal atoms are 6-coordinated.

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Crystal Structure of $Y_2SiBe_2O_7$

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Diyttrium silicon beryllate, $Y_2SiBe_2O_7$, is tetragonal with $a=7\cdot283\pm0\cdot002$, $c=4\cdot755\pm0\cdot001$ Å, $Z=2$. Refinement of its crystal structure in space group $P\bar{4}2_1m$ by full-matrix least-squares calculations gave $R=0\cdot096$. Yttrium atoms lie within distorted square oxygen antiprisms and silicon atoms in isolated SiO_4 tetrahedra. Beryllium atoms occupy distorted tetrahedra linked at one corner to form double Be_2O_7 pyramids oriented upward or downward relative to the c axis. $Y_2SiBe_2O_7$ is isostructural with silicate minerals of the melilite family, such as $Ca_2SiAl_2O_7$ and $Ca_2MgSi_2O_7$. The M_2O_7 group is capable of accepting various small ions of different valence, giving this structural arrangement a remarkable versatility.

Introduction

A new complex oxide of Y, Si, and Be was first observed during studies on the $BeO–Y_2O_3$ binary phase diagram. Its composition was determined by crystallographic analysis and by analogy with isostructural minerals to be $Y_2SiBe_2O_7$. It often coexisted with Y_2BeO_4 whose crystal structure has recently been determined by Harris & Yakel (1967).

Melilite is a complex silicate mineral which varies in composition from åkermanite, $Ca_2MgSi_2O_7$, to gehlenite, $Ca_2SiAl_2O_7$. Its crystal structure was first eluci-