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Structure Determination of $Ca_3HfSi_2O_9$ and $Ca_3ZrSi_2O_9$ from Powder Diffraction

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The crystal structure of $Ca_3HfSi_2O_9$ has been determined from X-ray powder diffraction data using a recently developed software package in order to find individual intensities from overlapping reflections. The Hf atoms were found from the Patterson map, while Ca atoms were found in a subsequent heavy atom Fourier map. The other atoms were determined by trial and error using the Rietveld method. The atomic parameters for $Ca_3ZrSi_2O_9$ were determined from neutron powder diffraction data with the structure of $Ca_3HfSi_2O_9$ use as the trial model. $Ca_3HfSi_2O_9$, a = 7.3517(4) Å, b = 10.1489(11) Å, c = 10.4319(12) Å, β = 91.084(7)°, $P2_1/c$, and Z = 4; $Ca_3ZrSi_2O_9$, a = 7.3603(1) Å, b = 10.1766(3) Å, c = 10.4514(3) Å, β = 90.875(2)°, $P2_1/c$, and Z = 4. The structure contains ribbons of edge-sharing octahedra parallel to [100]. The structure of these compounds is nearly the same as that of BeY_2O_4, substituting Si_2O groups for 2 Be and doubling the a-axis. The mineral cuspidine ($Ca_4Si_2O_7(F,OH)_2$) has a very similar structure as well.

INTRODUCTION

The calcium zirconium silicates have interesting ceramic properties. Under short wavelength ultraviolet excitation $Ca_3ZrSi_2O_9$ shows a yellow luminescence at room temperature (1). During decalcification of calcia-stabilized zirconia by silica, $Ca_3ZrSi_2O_9$ is formed. Detailed understanding of the properties of this type of compound is important in nuclear safety studies. In a severe nuclear accident, when the reactor core has melted through the reactor vessel, formation of calcium zirconium silicates may occur, due to the abundance of zirconium present in the cladding of the reactor fuel. On meltdown this material reacts with the silicates present in concrete.

The system $CaO–ZrO_2–SiO_2$ has been studied between 1473 K and the melting point (2). Qureshi and Brett (3) and Vetsuki, *et al.* also (4) discussed this system in their respective papers. The compounds $Ca_3ZrSi_2O_9$ and $Ca_2ZrSi_4O_{12}$ have been identified. Recently the structure of the latter phase has been determined from single crystal X-ray diffraction (5). In addition, Roelofsen-Ahl and Peterson (6) have published the structure of the mineral gittinsite with the composition $CaZrSi_2O_7$. This paper deals with the crystal structure of the isomorphous compounds $Ca_3ZrSi_2O_9$ and $Ca_3HfSi_2O_9$.

EXPERIMENTAL

Following Kordyuk and Gulko (2), the compounds were prepared by firing in Pt crucibles, in air, A.R. $CaCO_3$, $ZrO_2(HfO_2)$, and SiO_2 in the proper stoechiometric ratio at 1273 K for 1 day and again at 1673 K for 3 days. In between firings the reaction mixture was ground repeatedly. X-ray powder patterns were obtained using a Philips PW 1050 diffractometer. Monochromatic Cu$K\alpha$ radiation was used. A digital counting system was used to collect the intensities between 10° and 75° 2Θ. The step size was 0.02° and the counting time for each step was 10 sec using a 0.25° slit. Electron diffraction patterns were obtained using a Siemens Emiscop 102, fitted with 40° double tilt and lift cartridge. The operation voltage was 100 kV. Neutron powder diffraction data of the zirconium-based compound were collected in the range of 5° to 155° 2Θ in steps of 0.1°. The source of the neutron radiation was the Petten High Flux reactor of the Netherlands Energy Research Foundation ECN. The neutron data were corrected for absorption in the usual way (μR = 0.12, cylindrical sample (7)). For further details the reader is referred to (8).

DETERMINATION OF THE STRUCTURE

From the systematic absences in both the X-ray and electron diffraction patterns obtained, the space group was considered to be $P2_1/c$ for both the zirconium and the hafnium compounds. The $Ca_3ZrSi_2O_9$ pattern was in excellent agreement with the data in the JCPDS file, entry 39-195 (9). Simple density calculations based on the contents of the unit cell, giving Z = 4, and the distribution of the intensities show conclusively that no heavy atoms

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TABLE 1
Survey of the Results for Each Cycle of DOREES

Cycle	N_{strong}	N_{weak}	No. of Single reflections	No. of Overlapping reflections	Weight Patterson criterion
0	—	—	82	314	—
1	10	20	119	277	0.0
2	10	20	155	241	0.0
3	10	20	195	201	0.0
4	10	20	232	164	0.25
5	10	20	269	127	0.75
6	10	20	304	92	1.0
7	10	20	338	58	1.0
8	10	20	374	22	1.0
9	10	20	396	0	1.0

can be present on special positions. Therefore the determination of these structures from powder diffraction alone is not straightforward. It was decided to try to obtain as much accurate intensity data from the powder data as possible, using state of the art software developed by Jansen (10). The data of the hafnium compound were used for the structure determination, because the expectation was that the Hf position would be more easily determined once accurate data were obtained. Moreover, a heavy atom Fourier map based on hafnium was expected to contain more useful information than the corresponding map based on a Zr position. The first approximation of the desired intensities was obtained using the whole powder pattern fitting technique as embodied in the program LSQPROF (Jansen *et al.* (11)). The result of a refinement in $P2_1/c$ was an agreement factor of 4.8%, indicating a successful fit. The cell parameters converged to $a = 7.36$ Å, $b = 10.16$ Å, $c = 10.43$ Å, and $\beta = 91.14°$. The reflections could now be divided into two categories: The well determined, single peaks and the less well-known, overlapping intensities. A reflection is considered to belong to the first group if the distance to its nearest neighbor is more than half the halfwidth parameter of the peak (Jansen *et al.* (11)). The first category contained 82 reflections, while the second category now stood at 314 overlapping reflections. Better intensities for the reflections in the second group were obtained using the computer program DOREES (Jansen *et al.* (12)). DOREES assumes that for each cluster of overlapping reflections the total intensity is correct. However, the individual intensities may differ

TABLE 2
Summary of Crystallographic Data

	$Ca_3HfSi_2O_9$	$Ca_3ZrSi_2O_9$
a (Å)	7.3517(8)	7.3603(1)
b (Å)	10.1489(11)	10.1766(3)
c (Å)	10.4319(12)	10.4514(3)
β (°)	91.084(7)	90.875(2)
V (Å^3)	778.2(2)	784.75(3)
λ (Å)	1.54046/1.54439	2.57168
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
d_{obs} (g cm^{-3})	—	3.46[a]
d_{calc} (g cm^{-3})	4.258	3.493
No. of independent reflections	406	359
Overall B (Å^2)	0.40 (20)	0.71 (5)
No. of parameters refined	55	63
R (%)	9.66	2.14
R_{wp}(%)	13.39	2.85
Goodness of fit	51.52	3.809
Largest shift/error	0.04	<0.005

[a] From Al-Hermezi *et al.* (19).

TABLE 3
Atomic Coordinates for $Ca_3HfSi_2O_9$

	x	y	z
Hf(1)	0.1216(13)	0.0633(6)	0.1165(9)
Ca(1)	0.632(4)	0.8114(19)	0.5933(28)
Ca(2)	0.122(4)	0.8306(21)	0.5828(24)
Ca(3)	0.626(5)	0.4192(20)	0.6144(31)
Si(1)	0.831(6)	0.6215(33)	0.826(4)
Si(2)	0.413(6)	0.636(4)	0.819(4)
O(1)	0.609(11)	0.615(7)	0.777(7)
O(2)	0.069(11)	0.005(6)	0.737(7)
O(3)	0.117(10)	0.394(6)	0.013(7)
O(4)	0.116(11)	0.251(6)	0.747(6)
O(5)	0.332(10)	0.736(7)	0.223(6)
O(6)	0.306(10)	0.505(6)	0.779(6)
O(7)	0.375(9)	0.672(6)	0.959(7)
O(8)	0.122(9)	0.622(6)	0.520(6)
O(9)	0.661(10)	−0.094(7)	−0.022(7)

TABLE 4
Atomic Coordinates for $Ca_3ZrSi_2O_9$

	x	y	z
Zr(1)	0.1245(8)	0.0629(4)	0.1148(5)
Ca(1)	0.6247(8)	0.8070(5)	0.5994(8)
Ca(2)	0.1198(9)	0.8256(5)	0.5884(6)
Ca(3)	0.6301(11)	0.4193(6)	0.6155(6)
Si(1)	0.8340(9)	0.6240(8)	0.8189(7)
Si(2)	0.4000(11)	0.6350(9)	0.8074(7)
O(1)	0.6176(7)	0.6058(5)	0.7757(4)
O(2)	0.0825(9)	−0.0033(6)	0.7541(5)
O(3)	0.1391(8)	0.3794(5)	0.0310(5)
O(4)	0.1069(10)	0.2634(5)	0.7432(5)
O(5)	0.3557(8)	0.7356(5)	0.2253(5)
O(6)	0.3119(6)	0.4990(6)	0.7603(5)
O(7)	0.3791(8)	0.6636(5)	0.9566(5)
O(8)	0.0976(6)	0.6113(5)	0.5056(5)
O(9)	0.6596(7)	−0.1090(6)	−0.0117(5)

TABLE 5
Important Bond Lengths (Å) for $Ca_3HfSi_2O_9$

Ca(1)–O(1)	2.77(7)	Ca(2)–O(2)	2.43(7)
Ca(1)–O(3)	2.33(7)	Ca(2)–O(3)	2.10(8)
Ca(1)–O(4)	2.54(8)	Ca(2)–O(3)	2.89(7)
Ca(1)–O(5)	2.65(7)	Ca(2)–O(4)	2.64(8)
Ca(1)–O(6)	2.41(6)	Ca(2)–O(5)	2.21(8)
Ca(1)–O(7)	2.34(7)	Ca(2)–O(7)	2.29(8)
Ca(1)–O(9)	2.53(7)	Ca(2)–O(8)	2.22(6)
Ca(3)–O(1)	2.62(7)	Hf–O(2)	2.21(7)
Ca(3)–O(2)	2.84(10)	Hf–O(4)	2.32(6)
Ca(3)–O(5)	2.34(7)	Hf–O(6)	2.26(7)
Ca(3)–O(6)	3.06(7)	Hf–O(8)	2.34(7)
Ca(3)–O(7)	2.62(7)	Hf–O(8)	2.13(6)
Ca(3)–O(8)	2.38(7)	Hf–O(9)	1.92(7)
Ca(3)–O(9)	2.31(7)		
Ca(3)–O(9)	2.29(7)		
Si(1)–O(1)	1.70(8)	Si(2)–O(1)	1.53(8)
Si(1)–O(2)	1.54(6)	Si(2)–O(5)	1.74(7)
Si(1)–O(3)	1.72(7)	Si(2)–O(6)	1.59(7)
Si(1)–O(4)	1.57(7)	Si(2)–O(7)	1.54(7)

from their present values. Larger differences are expected when peaks in the cluster are closer together. DOREES tries to rearrange the intensities within the cluster by dividing the reflections into three groups: strong, weak, and intermediate reflections. Strong reflections are considered to be estimated too low and will gain intensity from the other groups; weak reflections lose intensity to the other groups. The present version of DOREES uses a combination of five criteria to assign reflections to a particular group: two are based on the triplet relation, two on the quartet relation, and one is based on the Patterson function. After a run of DOREES the reflections of the strong and weak groups are considered to be well determined; they are used in the next cycle of estimation as single reflections. Nine cycles of estimation were performed using the number of strong (N_{strong}) and weak (N_{weak}) reflections to be estimated as given in Table 1. Since the Patterson criterion uses the overlapping reflections (10), this criterion was not taken into account in the first three cycles; it was used with a weight less than 1 in cycles 4 and 5. The weights used are indicated in Table 1.

TABLE 6
Important Bond Lengths (Å) for $Ca_3ZrSi_2O_9$

Ca(1)–O(1)	2.755(9)	Ca(2)–O(2)	2.474(8)
Ca(1)–O(3)	2.345(8)	Ca(2)–O(3)	2.327(10)
Ca(1)–O(4)	2.589(11)	Ca(2)–O(3)	3.064(7)
Ca(1)–O(5)	2.433(8)	Ca(2)–O(4)	2.524(10)
Ca(1)–O(6)	2.483(8)	Ca(2)–O(5)	2.319(9)
Ca(1)–O(7)	2.346(10)	Ca(2)–O(7)	2.373(8)
Ca(1)–O(9)	2.342(9)	Ca(2)–O(8)	2.351(8)
Ca(3)–O(1)	2.534(8)	Zr–O(2)	2.152(8)
Ca(3)–O(2)	2.620(10)	Zr–O(4)	2.224(7)
Ca(3)–O(5)	2.293(7)	Zr–O(6)	2.132(8)
Ca(3)–O(6)	2.923(9)	Zr–O(8)	2.106(6)
Ca(3)–O(7)	2.710(7)	Zr–O(8)	2.116(6)
Ca(3)–O(8)	2.407(9)	Zr–O(9)	1.989(7)
Ca(3)–O(9)	2.395(8)		
Ca(3)–O(9)	2.356(8)		
Si(1)–O(1)	1.659(8)	Si(2)–O(1)	1.667(9)
Si(1)–O(2)	1.629(8)	Si(2)–O(5)	1.602(9)
Si(1)–O(3)	1.578(8)	Si(2)–O(6)	1.603(9)
Si(1)–O(4)	1.623(8)	Si(2)–O(7)	1.596(8)

Based on the results of this refinement procedure a Patterson function was calculated. From this map the Hf position was readily determined. Based on the position of this very heavy atom the usual F_{obs} Fourier was calculated. From this map the three highest peaks were interpreted as Ca positions. Attempts to find the other atoms from consecutive F_{obs} Fourier maps failed. Obviously the quality of the intensity data obtained from the estimation procedures did not allow us to find the light atoms in the usual way.

The Hf and Ca positions were entered in the GSAS program version 6.1 (13) and refined. It was obvious now from the Hf–Hf distance, that if HfO_6 octahedra were to occur, they had to be edge-shared, which is unusual for Hf atoms. The next step was to enter a silicon atom at the most likely position, which was obtained by taking the next highest peak of the F_{obs} Fourier map and to refine the model again. This led to a lower R-value, and thus to the belief that the Si position was a true one. However, when the second silicon atom was added to the model in a similar environment as the first, the GSAS program shifted the second silicon to a totally different position. After close examination of some projections of the current model, the conclusion was that the second Si position was the most likely one. Therefore the first silicon atom was replaced by oxygen and another silicon atom entered at a position in a similar environment as the second Si atom. This led to an large decrease of the R-value.

The other oxygen atoms were found by adding them one by one to the model at chemically sensible positions and refining the positions of the atoms.When this led to a lower R-value the new oxygen position was accepted. The most likely positions of the oxygen atoms to be added were found by examining projections of the model, taking into account the coordination of the cations. The complete model refined to an R_{wp}-value of 13.39% (Table 2).

The positional parameters obtained were used for the refinement of the neutron diffraction data of $Ca_3ZrSi_2O_9$.

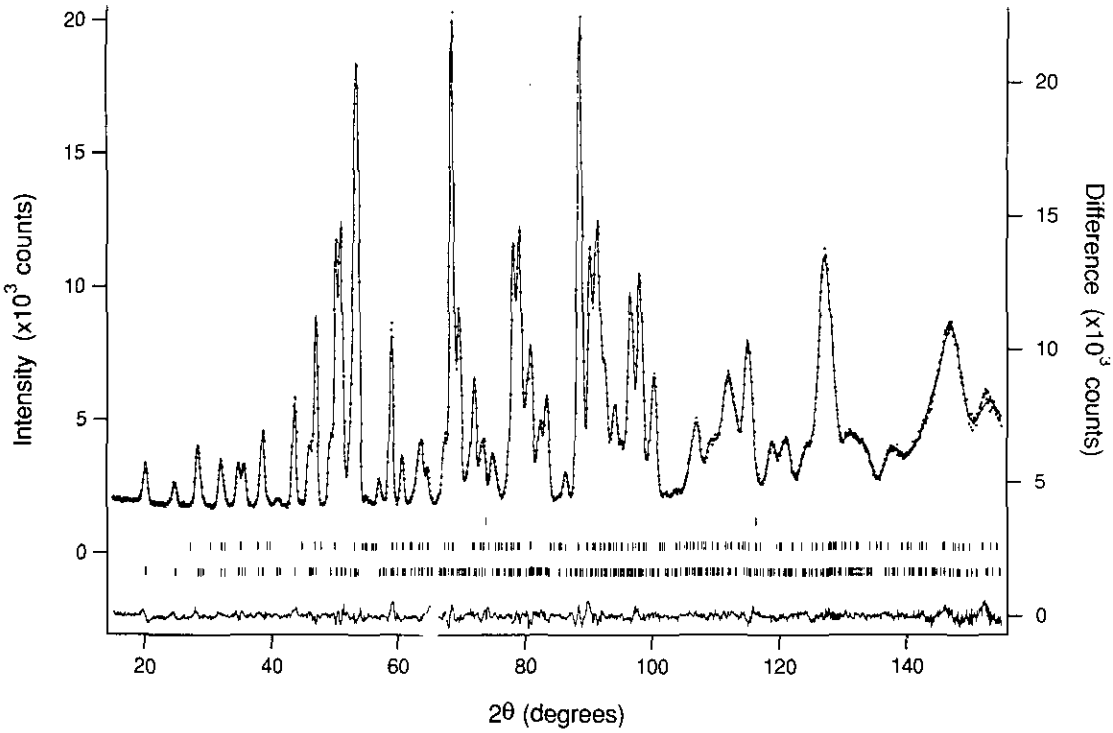

FIG. 1. Observed (dotted line) and calculated (full line) neutron diffraction pattern of $Ca_3ZrSi_2O_9$; the difference ($I_{obs} - I_{calc}$) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections of V, β-Ca_2SiO_4, and $Ca_3ZrSi_2O_9$, respectively.

For this purpose the GSAS program version 6.1 (13) was used and 61 parameters were used for this refinement: a scale factor; three half-widths parameters, defining the Gaussian-like shape of the reflections; an assymmetry parameter; six background parameters; the unit cell parameters; the atomic positional parameters; and an overall isotropic thermal parameter. In the refinement 359 reflections were used. At the end of the refinement, traces of β-Ca_2SiO_4 (14) and V of the sample holder were detected. Refinement of scale factors for these phases led to the final result.

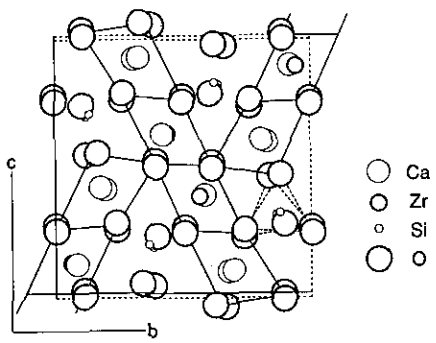

FIG. 2. Projection of the structure of $Ca_3ZrSi_2O_9$ along the a-axis.

DISCUSSION

The results of the final refinements are shown in Tables 2, 3, and 4 and some selected distances in Tables 5 and 6. The agreement between the observed and calculated profiles of the neutron diffraction data are shown in Fig. 1. The structure of $Ca_3ZrSi_2O_9$ contains ribbons of edge-sharing CaO_6 and ZrO_6 octahedra. The long direction of the ribbons is parallel to [100] and the width spans four octahedra. The ZrO_6 octahedra are in the middle of the ribbons and alternate with CaO_6 octahedra parallel to [100]. The ZrO_6 octahedra have a common edge almost parallel to (010) and are related by an inversion center (Fig. 2).

A given ribbon touches (and shares oxygen with) two other ribbons at either end of its width; the touching ribbons diverge at an angle of approximately 48° leaving narrow channels along [100]. In this channel trigonal prisms can be observed. Inserting in the prisms a nonlinear Si_2O group, a pyrosilicate group, Si_2O_7, with a trigonal prism outline is formed. Of course only alternate prisms can be occupied. The Si–O bond lengths range from 1.578(8) to 1.667(9) Å and O–Si–O angles from 98.7(5)° to 117.8(6)°. The Si–O1–Si angle is 147.9(4)°. These results are in good agreement with existing silicates (15). Nearly the same structure is found

for BeY_2O_4 with lattice parameters a = 3.5315(5) Å, b = 9.8989(10) Å, and c = 10.4000(10) Å (16), where YO_6 octahedra form the same ribbons with Be in a planar three-coordination at the top and bottom of the trigonal prisms. The space group $Pmcn$ for BeY_2O_4 reduces to $P2_1/c$ for $Ca_3ZrSi_2O_9$ through the substitutions, with a doubling of the a-axis as well. The structure resulting from the completed refinement clearly showed a close relation to that of the minerals cuspidine, $Ca_4Si_2O_7(F,OH)_2$ (17), and lavenite (18). However, while the space group is the same and the axes are very similar, the monoclinic angle β differs from that of the current structure by approximately 20°. Furthermore, the ZrO_6 octahedra in lavenite do not share edges. Al-Hermezi *et al.* (19) have reported the existence of the mineral baghdadite of the general composition $Ca_3(Zr_{0.87}Ti_{0.11})(Si_{0.98}Fe_{0.01})O_9$, with a similar structure.

In general the atomic parameters of $Ca_3HfSi_2O_9$ are in good agreement with the atomic parameters of $Ca_3ZrSi_2O_9$. Considering the almost identical ionic radii of Zr^{4+} and Hf^{4+} this is not unexpected.

Clearly, the state of the art software used to find the individual intensities is a very powerful tool; its use was essential for the successful crystal structure determination of the compounds discussed in this paper.

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