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The crystal structures of cesanite and its synthetic analogue—A comparison

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ABSTRACT

Single crystals of a synthetic apatite-like phase with composition $Na_{6.9}Ca_{3.1}(SO_4)_6(OH)_{1.1}$ were grown under hydrothermal conditions. This compound crystallizes in the hexagonal space group $P\overline{6}$ (a = 9.4434(13) Å, c = 6.8855(14) Å, Z = 1). The structure was solved by direct methods, and subsequently refined using 655 independent reflections ($R1$ = 0.0542). The chemical composition and the unit cell parameters indicated a close structural relationship with the mineral cesanite. A reinvestigation of the mineral showed that the natural and the synthetic phases are isostructural. Small differences result from the incorporation of both H_2O and $(OH)^-$ into the structure of cesanite. Observed systematic absences revealed that the space group $P6_3/m$ allocated to cesanite in earlier studies is incorrect. The crystal structure of a cesanite with composition $Na_{7.0}Ca_{3.0}(SO_4)_6(OH)_{1.0}(H_2O)_{0.8}$ was successfully refined in space group $P\overline{6}$ (a = 9.4630(8) Å, c = 6.9088(5) Å, Z = 1, $R1$ = 0.0468 for 720 independent reflections [$I > 2\sigma(I)$]). The symmetry reduction can be attributed to ordering of the Na and Ca atoms among four symmetrically independent cation sites.

INTRODUCTION

Apatite, $Ca_{10}(PO_4)_6F_2$, shows a great flexibility concerning the substitution of the different cations and anions in the structure without changing the space group symmetry of $P6_3/m$. Several compounds are known with sulfate groups substituted for phosphate groups: $Na_6Pb_4(SO_4)_6Cl_2$ (caracolite; Schneider 1967), $Na_6Ca_4(SO_4)_6(OH)_2$ (cesanite; Tazzoli 1983), $Na_6Cd_4(SO_4)_6Cl_2$, $Na_3Pd_2(SO_4)_3Cl$ (Perret and Bouillet 1975), $Na_6Ca_4(SO_4)_6F_2$, $Na_6Ca_4(SO_4)_6(F_xCl_{1-x})_2$ (Piotrowski et al., unpublished manuscript).

In the course of our own investigations on the crystal chemistry of apatite-like sulfates we tried to synthesize a phase with formal composition $Na_6Ca_4(SO_4)_6(OH)_2$. The natural analogue of such a material would be the mineral cesanite, first described by Cavaretta et al. (1981). Cesanite has been found in core samples of the Cesano-I geothermal well (Cesano area, Latium, Italy). Chemical analysis and the X-ray powder pattern pointed to a close structural relationship with apatite. Therefore, Tazzoli (1983) performed a single crystal structure analysis of cesanite in space group $P6_3/m$. Small differences resulted from the introduction of a split position for the cation site M2 at (x,y,1/4). Furthermore, the structure refinement indicated the incorporation of both hydroxyl groups and water molecules into the crystal structure. The formula resulting from the structure investigation given by Tazzoli (1983) for cesanite was $Na_{7.02}Ca_{2.98}(SO_4)_6(OH)_{0.98}\cdot 0.90H_2O$. Further investigations by Deganello (1983, 1984) and Deganello and Artioli (1982) described the structural behavior of cesanite up to 390 °C. The single crystal structure refinements in these studies were based on the cesanite model proposed by Tazzoli (1983).

EXPERIMENTAL METHODS

Synthetic cesanite

For the synthesis of a compound with formal composition $Na_6Ca_4(SO_4)_6(OH)_2$, mixtures of Na_2SO_4, $CaSO_4$, and $Ca(OH)_2$ in stoichiometric proportions (3:3:1) were heated under hydrothermal conditions. Experiments were performed in externally heated Morey-type autoclaves with a teflon reaction vessel and a reaction volume of 125 mL. Water was used as pressure medium for all experiments. The synthesis experiment which yielded suitable single crystals for structural investigations was carried out at 250 °C for 14 days using 5 g of starting material and 50 mL H_2O saturated with Na_2SO_4 (corresponding to a pressure of about 100 bar). Prismatic single crystals with maximum dimensions of about $10 \times 10 \times 100$ μm^3 were found in a polycrystalline matrix containing Na_2SO_4. For phase analysis, X-ray powder patterns were recorded using a Philips PW 3050 powder diffractometer with Cu$K\alpha_1$ radiation. Data were collected at room temperature with a fixed-slit configuration in the range 10° and 120° 2θ in steps of 0.02° 2θ. For evaluation of the powder patterns the Philips PC-Rietveld plus program package (Fischer et al. 1993) was used.

Single-crystal data were collected at the SUNY X3A1 beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Data were collected by fixing the Bruker SMART 1K CCD detector at 20° 2θ at a

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distance of 3.4 cm from the sample. Normalization of the intensity of the incident beam was based on counts from a beam monitor. Initial cell parameters were determined using sets of reflections with $I > 10\sigma(I)$ from 600 frames measured in ϕ from 0° to 120° in steps of 0.2°. The intensities were integrated and merged using the program SAINT (Bruker 1996). During integration, the cell parameters were refined, and the orientation matrix was optimized every 50 frames. Corrections for background and Lorentz-Polarization effects were made, and absorption corrections were applied using SADABS (Sheldrick 1996). After rejecting satellite outliers from aggregates, an internal residual R_{int} of 0.0555 was obtained for merging the data in Laue group $6/m$. Details of the intensity measurements are given in Table 1.

Natural cesanite

Single crystals of cesanite from the Cesano geothermal field were obtained from the Naturhistorisches Museum Wien. A fragment of cesanite (110 × 110 × 34 μm^3) was used for data collection on a Stoe IPDS single-crystal diffractometer. The data collection was performed with graphite monochromatized Mo$K\alpha$ radiation. The data were corrected for Lorentz and polarization effects. Details of the intensity measurements are given in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

A first indication that the symmetry of the synthetic material was lower than $P6_3/m$ came from the inspection of the powder patterns (cf. Fig. 1). The reflection at 12.86° 2θ, indexed as (001), violates the systematic absences of space group $P6_3/m$ proposed by Tazzoli (1983) for natural cesanite. Possible space groups for this sulfate apatite phase could be $P6$, $P\overline{6}$, or $P6/m$. The assumption of a symmetry reduction was confirmed by single crystal diffraction experiments where the reflections (001) and (003) were unambiguously observed with intensities $I > 5\sigma(I)$ in both synthetic and natural crystals. Since an apatite-like structure arrangement can only be realized in $P\overline{6}$, the structure determination was initiated in this space group by direct methods with the program SIR92 (Altomare et al. 1992). The phase set with the maximum combined figure of merit yielded a structure model with reasonable coordination environments and interatomic distances.

Subsequent refinements were performed with the SHELXL-93 program (Sheldrick 1993). X-ray scattering factors of the cations in their respective valence state and anomalous dispersion corrections were taken from the *International Tables of Crystallography* (Wilson 1995); the values for O^{2-} were taken from Hovestreydt (1983). The refinement of atomic coordinates, anisotropic displacement parameters, and site occupancy factors of the cations converged to $R1 = 0.0542$ and $wR2 = 0.0627$ for the synthetic compound and $R1 = 0.0468$ and $wR2 = 0.0559$ for natural cesanite, respectively. The thermal displacement parameters of the hydroxyl groups were refined only isotropically. Inspection of the Flack-parameter indicated that no inversion twinning was present. For the refinement of site occupancies no constraints were applied and the chemical com-

TABLE 1. Experimental details for synthetic and natural cesanite

	Natural cesanite	Synthetic cesanite
(A) Cystal data		
a (Å)	9.4630(8)	9.4434(13)
c (Å)	6.9088(5)	6.8855(14)
V (Å^3)	535.80(1)	531.77(5)
Space group	$P\overline{6}$	$P\overline{6}$
Z	1	1
Formula	$Na_{7.0}Ca_{3.0}(SO_4)_6(OH)_{1.0}(H_2O)_{0.8}$	$Na_{6.9}Ca_{3.1}(SO_4)_6(OH)_{1.1}$
D_{calc} (g/cm^3)	2.81	2.83
μ (cm^{-1})	18.5	18.6
(B) Intensity measurements		
Crystal shape	fragment of a crystal	hexagonal prismatic crystal
Diffractometer	Stoe - IPDS	Huber 4-circle diffractometer with Bruker CCD-detector
Monochromator	graphite	Si (111)
Wavelength	0.71073 Å Mo$K\alpha$	0.643 Å
Rotation angle, no. of frames	2.0°, 180	0.2°, 600
Exposure time per frame	2 min	5 s
θ-range	2.85–32.91°	3.0–31.30°
Reflection range	$\lvert h\rvert \leq 14$; $\lvert k\rvert \leq 13$; $l \leq 10$	$\lvert h\rvert \leq 14$; $\lvert k\rvert \leq 13$; $l \leq 10$
No. of measured reflections	14035	2833
No. of observed reflections [$I > 2\sigma(I)$]	10944	1048
No. of uniqure reflections in $6/m$	720	655
R_{int} for $6/m$	0.0466	0.0555
(C) Refinement of the structure		
No. of variable parameters	81	78
$R1$ [$F_o > 4\sigma(F_o)$], $R1$ (all reflections)	0.0468, 0.0559	0.0542, 0.0627
$wR2$ (all reflections)	0.1381	0.1784
Weighting parameters a, b	0.0635, 1.2500	0.0842, 0.0
Goodness of fit	1.146	1.035
Final $\Delta\rho$min (e/Å^3)	–1.29	–0.86
Final $\Delta\rho$max (e/Å^3)	1.02	1.03

Notes: $R1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)]$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [2F_c^2 + \max(F_o^2,0)]/3$.

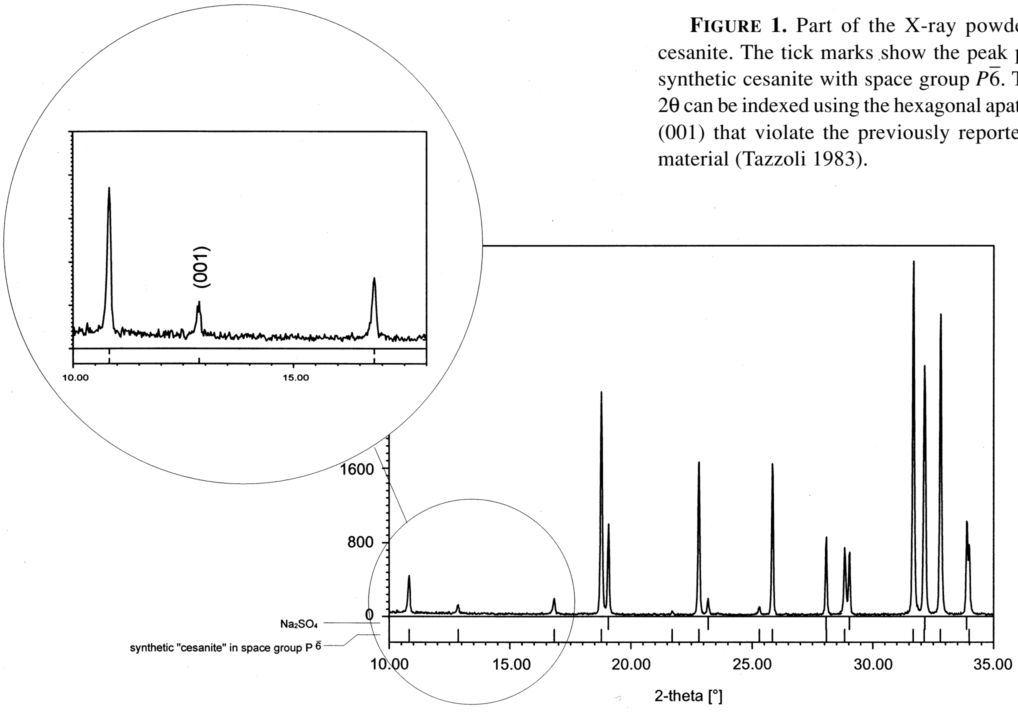

FIGURE 1. Part of the X-ray powder pattern of synthetic cesanite. The tick marks show the peak position of Na_2SO_4 and synthetic cesanite with space group $P\bar{6}$. The reflection at 12.86° 2θ can be indexed using the hexagonal apatite unit cell with indices (001) that violate the previously reported space group for this material (Tazzoli 1983).

positions of synthetic and natural cesanite were derived from these structural refinements. However, full occupancy of the two M-sites was assumed. The hydroxyl groups and water molecules are located on the same Wyckoff site 2*g*. However, refinements of the site occupancies indicate that vacancies are also present. The relative amount of the OH-groups was determined from the refined Na/Ca ratio to achieve charge compensation. The final atomic coordinates, equivalent isotropic and anisotropic displacement parameters, as well as selected interatomic distances and angles are given in Tables 2 and 3. The programs ATOMS5.1 (Dowty 2000) and ORTEP-3 (Farrugia 1997) were used for depicting structural details in Figures 2–4.

DESCRIPTION OF THE STRUCTURE

Synthetic and natural cesanite show the typical elements of the apatite structure, as shown in Figure 2. The symmetry reduction from the centrosymmetric space group $P6_3/m$ to the non-centrosymmetric space group $P\bar{6}$ leads to a doubling of the number of the crystallographically independent sites. The origin of the unit cell is shifted by $z + 1/4$ relative to the origin in space group $P6_3/m$. Alternating pairs of isolated tetrahedral anions (here the sulfate-groups) form ribbons running parallel to the **c**-axis. As the sulfur atoms are located on the special Wyckoff positions 3*j* and 3*k* the tetrahedra have the point group symmetry *m*.

The small spread in the S-O distances and O-S-O angles indicates only minor deviations from ideal tetrahedral symmetry. The sub-structure of the array of sulfate tetrahedra shows a distinct pseudo-symmetry, closely mimicking $P6_3/m$. The maximal deviations from $P6_3/m$ symmetry occur at the O4 atom, which is shifted by 0.16 Å (synthetic) and 0.02 Å (natural) from its position in $P6_3/m$.

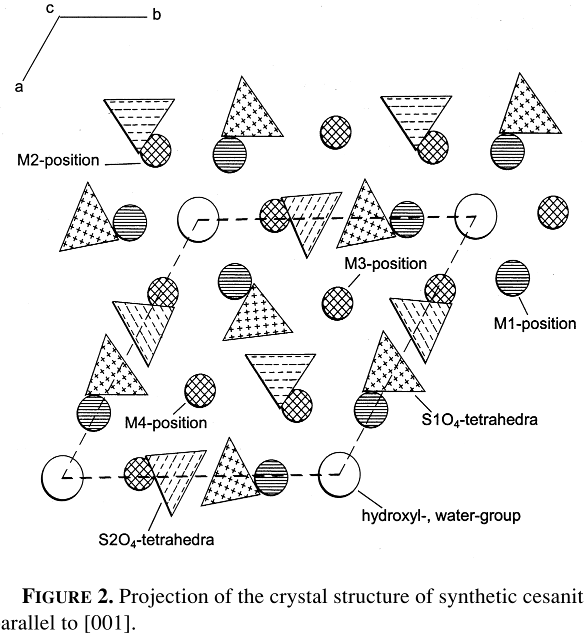

FIGURE 2. Projection of the crystal structure of synthetic cesanite parallel to [001].

The Na and Ca cations are distributed over four independent sites. They are coordinated either by six O atoms and one hydroxyl ion or water molecule (M1, M2) or nine O atoms (M3, M4). A minor difference between the synthetic and the

TABLE 2. Positional parameters in fractional coordinates, equivalent isotropic and anisotropic displacement parameters (Å^2) for synthetic (first line) and natural (second line) cesanite

Atom	Wyckoff site	No. of atoms in unit cell	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}
M1	3*j*	Ca: 2.16(5) Na: 0.84(5)	0.2423(2)	0.2511(2)	0	0.0141(5)	0.0124(9)	0.0108(6)
	3*j*	Ca: 2.14(8) Na: 0.86(8)	0.2512(4)	0.2644(4)	0	0.0401(9)	0.0526(15)	0.0634(17)
M2	3*k*	Ca: 0.70(7) Na: 2.30(7)	0.9856(3)	0.2715(4)	0.5	0.0349(13)	0.0204(14)	0.0435(19)
	3*k*	Ca: 0.50(6) Na: 2.50(6)	0.9913(3)	0.2428(3)	0.5	0.0140(9)	0.0118(11)	0.0185(12)
M3	2*h*	Ca: 0.05(6) Na: 1.95(6)	0.3333	0.6667	0.7500(6)	0.0229(16)	0.0261(18)	0.0261(18)
	2*h*	Ca: 0.34(5) Na: 1.66(5)	0.3333	0.6667	0.7539(5)	0.0296(13)	0.0312(14)	0.0312(14)
M4	2*i*	Ca: 0.19(5) Na: 1.81(5)	0.6667	0.3333	0.2595(5)	0.0237(14)	0.0231(13)	0.0231(13)
	2*i*	Ca: 0.00(5) Na: 2.00(5)	0.6667	0.3333	0.2537(6)	0.0282(11)	0.0323(14)	0.0323(14)
S1	3*j*	3	0.9746(2)	0.3678(2)	0	0.0097(3)	0.0074(5)	0.0114(6)
	3*j*	3	0.9736(2)	0.3645(2)	0	0.0198(4)	0.0203(8)	0.0197(8)
S2	3*k*	3	0.0255(2)	0.6438(2)	0.5	0.0119(3)	0.0063(5)	0.0083(5)
	3*k*	3	0.0260(2)	0.6357(2)	0.5	0.0185(3)	0.0145(7)	0.0217(8)
O1	3*j*	3	0.1538(5)	0.4680(6)	0	0.0187(11)	0.0083(16)	0.0150(18)
	3*j*	3	0.1525(6)	0.4732(7)	0	0.0255(12)	0.0098(19)	0.0157(22)
O2	3*k*	3	0.8488(5)	0.5272(6)	0.5	0.0197(12)	0.0051(17)	0.0137(19)
	3*k*	3	0.8484(8)	0.5291(9)	0.5	0.0305(14)	0.0296(29)	0.0401(33)
O3	3*j*	3	0.9012(7)	0.4701(8)	0	0.0428(19)	0.0258(25)	0.0236(25)
	3*j*	3	0.8928(10)	0.4606(11)	0	0.0535(25)	0.0423(40)	0.0526(44)
O4	3*k*	3	0.1148(6)	0.5568(7)	0.5	0.0424(19)	0.0144(22)	0.0277(26)
	3*k*	3	0.1119(8)	0.5408(10)	0.5	0.0390(16)	0.0254(29)	0.0335(30)
O5	6*l*	6	0.0727(5)	0.7495(6)	0.6712(10)	0.0509(16)	0.0293(20)	0.0407(23)
	6*l*	6	0.0777(6)	0.7427(7)	0.6698(7)	0.0419(14)	0.0390(25)	0.0370(24)
O6	6*l*	6	0.9171(5)	0.2620(6)	0.8294(8)	0.0401(13)	0.0324(21)	0.0340(21)
	6*l*	6	0.9297(6)	0.2587(6)	0.8280(7)	0.0387(13)	0.0324(22)	0.0348(24)
OH7	2*g*	0.29(4)	0	0	0.4203(66)	0.0403(136)		
	2*g*	1.17(7)	0	0	0.4579(15)	0.0345(34)		
OH8	2*g*	0.85(4)	0	0	0.0695(18)	0.0151(30)		
	1*a*	0.59(6)	0	0	0	0.0282(48)		

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} matrix.

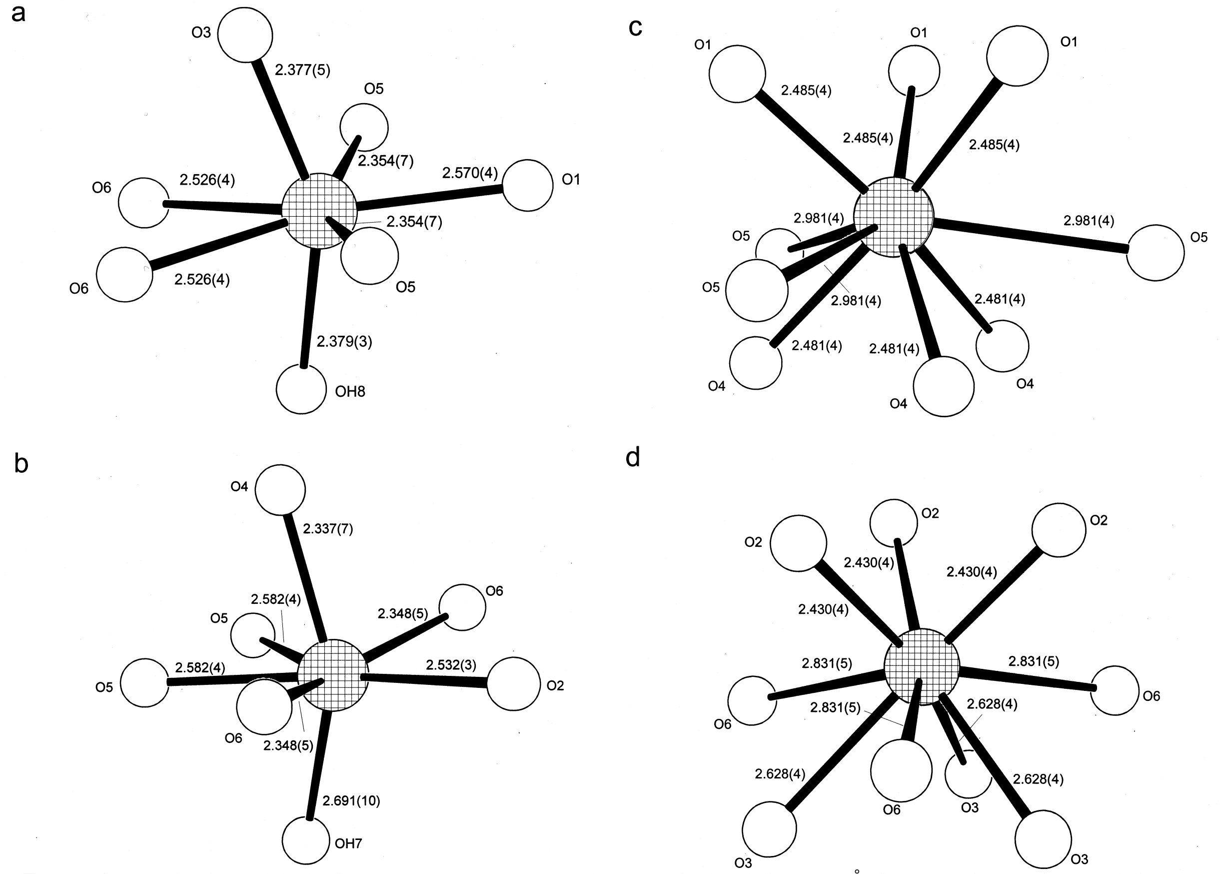

FIGURE 3. Coordination polyhedra for M1(**a**), M2(**b**), M3(**c**), and M4(**d**) with bond distances [Å] for synthetic cesanite. Bond distances to hydroxyl groups occupying split positions have been drawn only once.

TABLE 2.—*extended*

U_{33}	U_{23}	U_{13}	U_{12}
0.0215(10)	0	0	0.0078(5)
0.0258(13)	0	0	0.0442(13)
0.0250(21)	0	0	0.0041(11)
0.0142(13)	0	0	0.0095(9)
0.0166(26)	0	0	0.0131(9)
0.0263(28)	0	0	0.0156(7)
0.0249(28)	0	0	0.0115(7)
0.0201(29)	0	0	0.0162(7)
0.0145(9)	0	0	0.0028(5)
0.0181(8)	0	0	0.0092(5)
0.0122(9)	0	0	0.0020(4)
0.0158(7)	0	0	0.0065(6)
0.0288(35)	0	0	0.0028(15)
0.0357(33)	0	0	–0.0050(16)
0.0315(36)	0	0	–0.0018(15)
0.0238(30)	0	0	0.0190(27)
0.0867(59)	0	0	0.0182(22)
0.0845(71)	0	0	0.0378(38)
0.0910(63)	0	0	0.0150(20)
0.0559(43)	0	0	0.0130(24)
0.0402(32)	–0.0308(21)	0.0187(21)	–0.0145(16)
0.0244(20)	–0.0098(19)	0.0058(22)	0.0000(20)
0.0191(27)	–0.0157(18)	0.0104(18)	–0.0096(16)
0.0266(22)	–0.0097(19)	0.0077(22)	0.0000(17)

TABLE 3. Selected interatomic distances (Å) and bond angles (°) for synthetic (first line) and natural (second line) cesanite

S1-O3	1.443(5) 1.452(6)	S2-O4	1.442(4) 1.482(5)
S1-O6	1.460(5) × 2 1.473(5) × 2	S2-O5	1.463(6) × 2 1.465(5) × 2
S1-O1	1.469(3) 1.477(4)	S2-O2	1.470(4) 1.465(5)
Mean	1.458 1.469	Mean	1.460 1.469
M1-O5	2.354(7) × 2 2.370(5) × 2	M3-O4	2.481(4) × 3 2.528(6) × 3
M1-O3	2.377(5) 2.372(7)	M3-O1	2.485(4) × 3 2.457(4) × 3
M1-OH8	2.379(3) 2.442(3)	M3-O5	2.981(4) × 3 2.906(5) × 3
M1-O6	2.526(4) × 2 2.585(5) × 2		
M1-O1	2.570(4) 2.573(5)		
Mean	2.441 2.471	Mean	2.649 2.630
M2-O4	2.337(7) 2.457(9)	M4-O2	2.430(4) × 3 2.470(4) × 3
M2-O6	2.348(5) × 2 2.363(5) × 2	M4-O3	2.628(4) × 3 2.554(5) × 3
M2-O2	2.532(3) 2.617(4)	M4-O6	2.831(5) × 3 2.962(3) × 3
M2-O5	2.582(4) × 2 2.505(4) × 2		
M2-OH7	2.691(10) 2.358(3)		
Mean	2.489 2.453	Mean	2.630 2.662
O1-S1-O3	110.7(3) 110.1(4)	O2-S2-O4	110.0(3) 111.8(4)
O1-S1-O6	110.8(2) 108.0(2)	O2-S2-O5	110.8(2) 110.3(2)
O1-S1-O6	110.8(2) 108.0(2)	O2-S2-O5	110.8(2) 110.3(2)
O6-S1-O3	108.6(2) 111.6(2)	O5-S2-O4	108.9(3) 108.9(2)
O6-S1-O6	107.2(3) 107.5(3)	O5-S2-O5	107.4(3) 106.4(3)
O6-S1-O3	108.6(2) 111.6(2)	O5-S2-O4	108.9(3) 108.9(2)
Mean	109.5 109.5	Mean	109.5 109.4

Note: Bond distances to the hydroxyl groups OH7 and OH8 occupying twofold split positions are only listed only once.

natural sample results from the location of the hydroxyl groups OH8 in the coordination sphere of M1. This group in the natural sample is located at Wyckoff-site 1*a* in (0 0 0), whereas the corresponding group in the synthetic compound occupies a split position [Wyckoff site 2*g*, (0 0 *z*)]. Both hydroxyl positions are only partially occupied. Figures 3a–d show coordination spheres of the M positions for synthetic cesanite (similar coordination polyhedra are observed in the natural sample). The polyhedra around M1 and M2 can be approximated as distorted pentagonal bipyramids. The $M3O_9$ and $M4O_9$ polyhedra can be described as tricapped trigonal prisms. Adjacent $M3O_9$ and $M4O_9$ prisms share common faces (located at $z = 0$ and 1/2) and form columns parallel to [001].

The results of the site occupancy refinements show a distinct preference of Na for the cation positions M3 and M4 (cf., Table 2) in both structures. The M2 site is also enriched in sodium but the site preference for Na is less pronounced compared with M3 and M4. Calcium prefers the remaining M1 site. A similar concentration of sodium at the M3 and M4 sites has been found in Na-Ca-sulfate apatites (Piotrowski et al., unpublished manuscript).

DISCUSSION

The results of this study confirm the close structural relationship between synthetic and natural cesanite (both $P\overline{6}$) on the one hand and calcium phosphate apatite ($P6_3/m$) on the other (cf., Fig. 4). The symmetry reduction principally results from partial ordering of Na and Ca at the Ca1 position in apatite. The crystallographic description of cesanite given by Tazzoli (1983) in space group $P6_3/m$ is now shown to be incorrect.

Most natural and synthetic apatite compounds crystallize in space group $P6_3/m$. An exception to this observation is $Ca_{10}(PO_4)_6Cl_2$, which adopts space group $P2_1/b$ (Hughes et al. 1990). The reduction from hexagonal symmetry is induced by a displacement of the Cl-atoms from the **c**-axis and is coupled with a doubling of the *a* dimension relative to the hexagonal

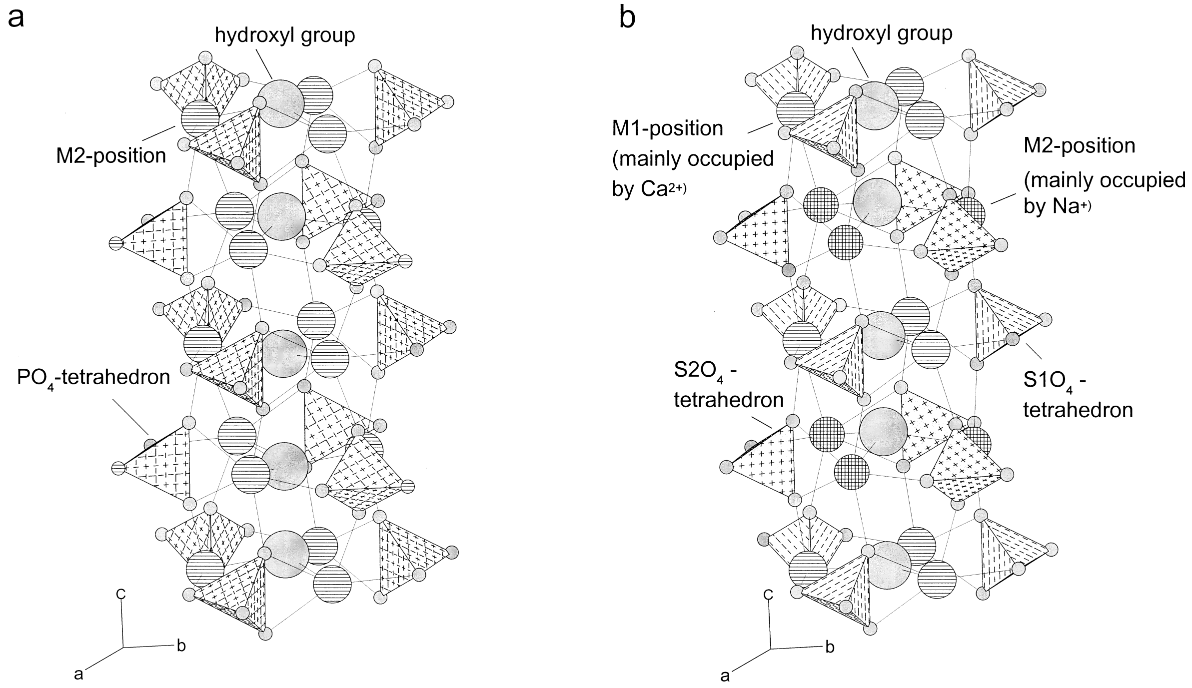

FIGURE 4. Arrangement of the cations and sulfate tetrahedra about the 6_3 and the $\bar{6}$ axes, respectively. (**a**) phosphate apatite (Sudarsanan 1980), (**b**) synthetic cesanite, this work.

cell. Another apatite-like phase crystallizing in space group $P\bar{6}$ is $Ba_6La_2Na_2(PO_4)_6F_2$ (Mathew et al. 1979). Consistent with our results for cesanite, the symmetry lowering in this phase results from a partial ordering of Ba, La, and Na at the M1 and M2 sites.

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