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The Crystal Structure of $Ca_2Zn_4Ti_{16}O_{38}$

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$Ca_2Zn_4Ti_{16}O_{38}$ crystallizes with rhombohedral symmetry, $R\bar{3}$, with lattice parameters $a = 9.204(3)$ Å, $\alpha = 68.65(2)°$, $z = 1$. The structure was solved using 1013 observed ($F \geq 4\sigma(F)$) symmetry-independent reflections collected using counter methods with Mo$K\alpha$ radiation and refined to a R_w value of 0.039. This synthetic phase is isostructural with the crichtonite-group minerals that have a structure based on a nine-layer (*hhc*) closest-packed anion framework. The unit-cell composition conforms to the general formula for the crichtonite group, $AM_{21}O_{38}$, where the A cation, calcium in this case, occupies a site in the anion framework. The second calcium, together with the zinc and titanium atoms, is ordered into 19 octahedral and 2 tetrahedral sites per unit cell.

Introduction

A new ternary oxide in the CaO–ZnO–TiO_2 system has been characterized recently by chemical and X-ray analysis as $Ca_2Zn_4Ti_{15}O_{36}$ (*1*). It was found to have rhombohedral symmetry, with hexagonal cell dimensions $a_h = 10.371(5)$, $c_h = 20.938(10)$ Å. A close correspondence was noted between the X-ray powder patterns and cell dimensions of the new phase and those of the crichtonite-group minerals senaite (*2*) and davidite (*3*).

We have recently solved the structure of senaite (*4*) and have subsequently refined the structures of a number of isostructural minerals, including crichtonite (*5*), landauite (*6*), loveringite (*7*), and davidite (*8*). These structures are based on a nine-layer closest-packed anion framework (*hhc*) with 39 anions per unit cell and with 1 anion site occupied by a large cation, *A*. The rhombohedral unit-cell compositions for the different minerals were found to conform to the general formula $AM_{21}O_{38}$, where *M* are small cations such as Ti^{4+}, Fe^{3+}, Mg^{2+}, Zr^{4+}, Zn^{2+}, which occupy octahedral and tetrahedral interstices in the closest-packed anion framework. Thus although the new calcium zinc titanate had been reported to be isostructural with the crichtonite-group minerals (*1*) its composition appeared to be different with only 36 oxygen ions and 2 large cations (calcium) per unit cell, cf 38 and 1, respectively. To resolve the apparent differences between the synthetic phase and the minerals, we synthesized single crystals of the titanate and refined its structure; we report here the results of the structure refinement.

Experimental

Single crystals of the ternary oxide were obtained using the procedure described by

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Bartram and Foss (*1*); i.e., a 1 : 2 : 7.5 molar mixture of $CaCO_3$, ZnO, and TiO_2 was calcined at 950°C for 2 hr, then finely ground, pelleted, and sealed in a platinum capsule and heated at 1200°C for 90 hr. A diffractometer trace obtained from part of the finely ground product showed very small amounts of Zn_2TiO_4 and $CaTiO_3$ as the only impurities. The unit-cell parameters were obtained from a least-squares refinement using the 2θ values of 16 powder lines scanned at $1° \min^{-1}$ with Si as internal standard.

Crystal data. $Ca_2Zn_4Ti_{16}O_{38}$, M = 1716.06, a = 9.204(3) Å α = 68.65(2)°, rhombohedral (a_h = 10.381(2), c_h = 20.96(1) Å), U = 651.78 Å^3, d_c = 4.37 g cm^{-3}, $z = 1$. $F(000)$ = 816, $\mu(\text{Mo}K\alpha)$ = 84 cm^{-1}. Mo$K\alpha$ = 0.7107 Å. Space group $R\bar{3}$.

Intensity measurements. The quality of individual crystals from the reaction product was initially checked using oscillation and Weissenberg techniques and the symmetry and unit-cell dimensions obtained by Bartram and Foss (*1*) were confirmed. An approximately spherical-shaped crystal, 0.088 mm in diameter, was transferred to a Philips PW1100 four-circle diffractometer for intensity data collections. Intensities were collected with graphite-monochromated Mo$K\alpha$ radiation. An $\omega - 2\theta$ scan, 2θ limit, 6–60°, was used with a variable scan width given by $\Delta\theta = (1.20 + 0.30 \tan \theta)$ and a scan speed of 0.05° sec^{-1}. Two background measurements, each for half the scan time, were made at the scan limits. The intensities were processed using a program written for the PW1100 diffractometer by Hornstra and Stubbe (*9*). A total of 2546 reflections ($\pm h$, k, l) were measured and reduced to a unique set of 1269 (interscale R factor for equivalent reflections = 0.037), of which 1013 had $F \geq 4\sigma(F)$ and were used in the structure refinement. A spherical absorption correction was applied.

Scattering factor curves for Ca, Zn, Ti, and O neutral atoms were those of Cromer and Mann (*10*). Anomalous dispersion corrections for all atoms were from Cromer and Liberman (*11*). All computing was carried out on the Monash University Burroughs 6700 and the CSIRO CDC 7600 computers.

Refinement of the structure. The atomic coordinates obtained for loveringite (*7*) in the centrosymmetric space group $R\bar{3}$ were used as starting parameters and a similar ordering of metals into sites $M(0)$ to $M(5)$ (see Fig. 1) on the basis of decreasing size was considered, i.e., Ca in $M(0)$ (in the anion layer), Zn in $M(1)$ and $M(2)$, and Ti in $M(3)$, $M(4)$, and $M(5)$. Least-squares refinement of coordinates and isotropic temperature factors proceeded smoothly to an R value of 0.08. At this stage it was observed that the temperature factor of $M(1)$ was very high and a difference Fourier map displayed a large hole at this site and a large positive peak at site $M(3)$. Bond length calculations were consistent with Ca rather than Zn in $M(1)$ and also indicated that site $M(3)$ contained both Zn and Ti. The temperature factors for all anions were normal and it was apparent at this stage that the unit-cell composition reported by Bartram and Foss (*1*) was not correct. With 39 fully-occupied anion sites per unit cell (38O + 1 Ca), with the second Ca ordered into site $M(1)$, Zn in the tetrahedral site $M(2)$, and Ti in sites $M(4)$ and $M(5)$, the amounts of Ti and Zn in the sixfold site $M(3)$ are fixed by the requirements of electrical neutrality to be 4Ti + 2Zn, giving a unit-cell composition $Ca_2Zn_4Ti_{16}O_{38}$, cf. $Ca_2Zn_4Ti_{15}O_{36}$ (*1*). With the new scattering curves for sites $M(1)$ and $M(3)$ the refinement of all positional and isotropic thermal parameters was continued using unit weights and the R factor was reduced to 0.055. A difference Fourier synthesis showed a small subsidiary peak of 4 e Å^{-2} near $M(0)$ at 0.022, 0.022, 0.022 as the only feature above background. The temperature factor for $M(0)$ was converted to anisotropic and the refinement continued

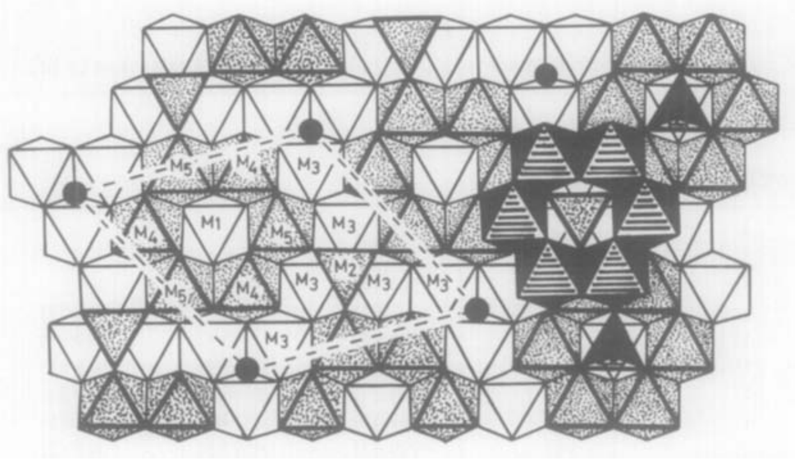

FIG. 1. Representation of three consecutive $(001)_{hex}$ layers of polyhedra in $Ca_2Zn_4Ti_{16}O_{38}$ viewed along $[001]_{hex}$. Only part of the third layer (heavy shading) is shown for clarity. The hexagonal unit cell is outlined. The small solid circles represent Ca in $M(0)$. The labels $M(1)$ to $M(5)$ correspond to those given in Table I.

using a $\frac{1}{\sigma^2(F)}$ weighting scheme. Final convergence was achieved at R and R_w values of 0.046 and 0.039, respectively, for the 1013 observed reflections. The corresponding values for all 1269 reflections were 0.067 and 0.048, respectively. The final atomic coordinates and temperature factors are given in Table I[1] and calculated bond lengths are given in Table II.

Discussion

The new calcium zinc titanate is isostructural with the crichtonite-group minerals having a structure based on a closest-packed anion framework with one large cation per formula unit, calcium, occupying an anion site. The closest-packed anion layers have a nine-layer stacking sequence . . .ABCBCACABA. . ., i.e., (*hhc*. . .). We have previously given a full description of the structure of the crichtonite-group minerals (*4–8*). For ease of discussion we reproduce in Fig. 1 a representation of the structure viewed down the trigonal axis.

The most unusual feature of the structure is the ordering of calcium into two sites with markedly different coordination numbers, 12 in site $M(0)$ and 6 in the octahedral site $M(1)$. Calcium is the largest cation to occupy $M(1)$ and the smallest to occupy site $M(0)$ in the crichtonite-related structures that have been refined (*4–8*). We have previously noted a direct correlation between the unit-cell parameter and the size of the $M(1)$ cation—$Ca_2Zn_4Ti_{16}O_{38}$ fits this pattern in having a larger unit-cell parameter than any of the minerals previously studied (*4–8*). The calculated $M(1)$–O octahedral bond length, 2.36 Å (*12*) is somewhat larger than the observed value, 2.305(5) Å, and there may be partial mixing of zinc with calcium at this site, although the short $M(1)$–O(1) bond may also be explained by undersaturation of O(1) (see Table III).

The calculated bond length for calcium in

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[1] A table of observed and calculated structure factors has been deposited as Document No. NAPS 04000 with the ASIS National Auxiliary Publications Service, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number and by remitting \$5.00 for photocopies or \$3.00 for microfiche. Advance payment is required, make cheque or money order payable to "Microfiche Publications."

TABLE I

$Ca_2Zn_4Ti_{16}O_{38}$: ATOMIC PARAMETERS (×10^4) AND THERMAL PARAMETERS (×10^2)

Atom	Site symmetry	Site occupancy	x	y	z	B (Å^2)
M(0)	$\bar{3}$	Ca	0	0	0	208[a]
M(1)	$\bar{3}$	Ca	½	½	½	22(2)
M(2)	3	2Zn	3092(1)	3092	3092	33(2)
M(3)	1	2Zn + 4Ti	3479(1)	1300(1)	148(1)	53(2)
M(4)	1	6Ti	3034(1)	7205(1)	1495(1)	39(2)
M(5)	1	6Ti	4742(1)	803(1)	6410(1)	36(2)
O(1)	1	6O	2942(5)	6346(5)	3740(5)	62(6)
O(2)	1	6O	1492(5)	2354(5)	9401(5)	71(6)
O(3)	1	6O	9193(5)	4597(5)	3019(5)	58(6)
O(4)	1	6O	1430(5)	5125(5)	9902(5)	66(6)
O(5)	1	6O	3897(5)	4864(5)	1355(5)	43(6)
O(6)	1	6O	7135(4)	2397(5)	693(5)	39(6)
O(7)	3	2O	2125(3)	2125	2125	37(12)

[a] Anisotropic temperature coefficients for M(0): $B_{11} = B_{22} = B_{33} = 208(8)$; $B_{12} = B_{23} = B_{13} = -13(6)$.

12-fold coordination is 2.71 Å (*12*). This is much smaller than the observed mean M(0)–O bond length of 2.777 Å. The results of the refinement indicate that the small calcium ion does not occupy the center of this site but is displaced along the threefold axis by about 0.5 Å, resulting in a nine-fold coordination. This displacement is probably dynamic in origin with the calcium oscillating within the cuboctahedral cavity. The temperature factor for this site is an order of magnitude greater than for the other cation sites, as observed for other crichtonite-related structures (*4–8*).

TABLE II

$Ca_2Zn_4Ti_{16}O_{38}$: M–O BOND LENGTHS (Å)

M(0) calcium cuboctahedron		M(1) calcium octahedron	
M(0)–O(2) × 6	2.762(5)	M(1)–O(1) × 6	2.305(5)
–O(6) × 6	2.792(5)		
Mean	2.777		
M(2) zinc tetrahedron		**M(3) titanium + zinc octahedron**	
M(2)–O(5) × 3	1.971(4)	M(3)–O(4)	1.939(4)
		–O(3)	1.962(5)
–O(7)	2.026(4)	–O(2)	1.974(5)
		–O(7)	2.026(3)
Mean	1.985	–O(4)′	2.030(5)
		–O(2)′	2.114(5)
		Mean	2.007
M(4) titanium octahedron		**M(5) titanium octahedron**	
M(4)–O(2)	1.885(5)	M(5)–O(1)	1.834(4)
–O(1)	1.906(4)	–O(4)	1.889(5)
–O(6)	1.965(5)	–O(3)	1.928(4)
–O(3)	1.990(5)	–O(5)	1.991(5)
–O(6)′	2.024(5)	–O(6)	2.043(5)
–O(5)	2.042(5)	–O(5)′	2.149(5)
Mean	1.969	Mean	1.972

The observed mean M–O bond lengths for the small cations M(2) to M(5) in Table II agree well with the calculated values based on the site occupancies given in Table I, i.e., 1.98, 2.02, and 1.975 Å, respectively (*12*), for Zn^{2+} tetrahedral ($0.33Zn^{2+} + 0.67Ti^{4+}$) and octahedral and Ti^{4+} octahedral.

The ordered occupation of the M(4) and M(5) sites by tetravelent titanium is an invariant compositional feature that is common to all crichtonite-related structures studied. For the six compounds whose structures have been refined, the mean M(4)–O and M(5)–O values differ by no more than 0.007 Å from the grand average

TABLE III

$Ca_2Zn_4Ti_{16}O_{38}$: ELECTROSTATIC VALENCE SUMS

Anion site	Bonding cations	$\Sigma s_i{}^a$	$\Sigma s_i{}^b$
O(1)	$M(1) + M(4) + M(5)$	1.67	2.05
O(2)	$M(0) + 2M(3) + M(4)$	1.94	2.02
O(3)	$M(3) + M(4) + M(5)$	1.89	2.01
O(4)	$2M(3) + M(5)$	1.78	1.92
O(5)	$M(2) + M(4) + 2M(5)$	2.50	2.01
O(6)	$M(0) + 2M(4) + M(5)$	2.17	1.86
O(7)	$M(2) + 3M(3)$	2.17	1.91

[a] s_i = Valence of M/coordination of M.

[b] s_i calculated using empirical bond length–bond strength parameters of Brown and Wu (*13*).

value of 1.971 Å, although individual $M(4)$, $M(5)$–O bond lengths vary over a wide range from 1.83 to 2.18 Å (*4–8*).

Electrostatic valence sums for the oxygen ions O(1) to O(7) are given in Table III. It is seen that there are large local charge imbalances. In particular, O(5) is severely oversaturated with $\Sigma s_i = 2.50$ and O(1) is highly undersaturated with $\Sigma s_i = 1.67$. These local charge variations are reflected in lengthening and shortening, respectively, of the individual M–O(5) and M–O(1) bonds. A calculation of Σs_i, allowing for bond-length variations, using the empirical parameters of Brown and Wu (*13*), gives values close to theoretical (see Table III).

The struture refinement for the calcium zinc titanate unambiguously confirms that the closest-packed anion framework comprises 38 oxygens and 1 calcium, and that 19 octahedral and 2 tetrahedral sites per unit cell are occupied, giving a unit-cell composition $AM_{21}O_{38}$, consistent with that for the other crichtonite-related compounds (*4–8*). The unit-cell composition based on 36 oxygens reported by Bartram and Foss (*1*), i.e., $Ca_2Zn_4Ti_{15}O_{36}$, is therefore incorrect. The observed small, approximately equal amounts of $CaTiO_3$ and Zn_2TiO_4 impurities in our preparations based on 1:2:7.5 molar ratios of CaO:ZnO:TiO_2 are consistent with the composition determined from the structure analysis according to the reaction

$$2CaO + 4ZnO + 15TiO_2 \rightarrow 0.92Ca_2Zn_4Ti_{16}O_{38} + 0.16CaTiO_3 + 0.16Zn_2TiO_4.$$

Pabst (*3*) had also reported a unit-cell composition normalized to 36 oxygens for the crichtonite-group mineral davidite. He suggested that such a possibility could arise if all anion sites on the trigonal axis (i.e., the one-fold site $M(0)$ and the two-fold site O(7)) were occupied by large cations. We find no evidence of this in either davidite (*8*) or the calcium zinc titanate. However, we are presently refining the structure of a new crichtonite-group mineral mathiasite (A = K dominant) in which partial occupation of O(7) by large cations does occur (*14*).

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