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Zirconolite, $CaZr_xTi_{3-x}O_7$; Structure Refinements for Near-End-Member Compositions with $x = 0{\cdot}85$ and $1{\cdot}30$

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Abstract

Zirconolite, nominally $CaZrTi_2O_7$, exhibits a wide variation in its [Ti]/[Zr] ratio as a function of preparation temperature. Single crystals with compositions close to the solid-solution limits, *i.e.* $Ca_{0.993}Zr_{1.304}Ti_{1.700}O_7$, [Ti]/[Zr] = 1·31, and $Ca_{0.961}Zr_{0.850}Ti_{2.169}O_7$, [Ti]/[Zr] = 2·55, have been prepared and their structures refined with data collected on an automatic diffractometer using Mo $K\alpha$ radiation. Cell parameters (space group $C2/c$, $Z = 8$) are: a = 12·445 (4), b = 7·288 (2), c = 11·487 (3) Å, β = 100·39 (1)° and a = 12·444 (2), b = 7·266 (1), c = 11·341 (2) Å, β = 100·59 (1)°, respectively. Atomic positions, anisotropic temperature factors and metal-atom occupancies were refined by full-matrix least squares to yield R = 0·045 and 0·054 (R_w = 0·055 and 0·046) for 2011 and 1126 independent structure factors. The results generally support an earlier powder X-ray diffraction structure determination, but are more precise and reveal new structural features. The structure has (001) sheets of $Ti(Zr)O_6$ octahedra sharing corners in the three- and six-membered-ring arrangement found in {110} planes in pyrochlore. These sheets are interleaved by planes containing Ca and Zr(Ti) atoms ordered into alternating [110]-type rows with Ca and Zr(Ti) eight- and seven-coordinated by O respectively. A Ti atom close to the centre of a six-membered ring of octahedra is not in trigonal-prismatic coordination by O as originally proposed, but instead this atom randomly occupies one of a pair of sites which are ~0·6 Å apart for [Ti]/[Zr] = 1·31 and 0·8 Å apart for [Ti]/[Zr] = 2·55, so as to achieve fivefold trigonal-bipyramidal coordination by O. This unusual behaviour as well as structural aspects associated with the change of [Ti]/[Zr] ratio in zirconolite are discussed.

Introduction

In the $CaO–ZrO_2–TiO_2$ system, the existence of a stable phase with the molar ratio 1:1:2, *i.e.* $CaZrTi_2O_7$, was first established by Coughanour, Roth, Marzullo & Sennet (1955).

From a single-crystal X-ray diffraction study on $CaZrTi_2O_7$, Pyatenko & Pudovkina (1964) proposed that it was an anion-deficient superstructure phase

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derived from the flourite-type structure. They established that the supercell had a *C*-centred monoclinic lattice with a volume eight times that of the fluorite subcell. Recently the structure of $CaZrTi_2O_7$ has been determined by Rossell (1980), using powder X-ray diffraction data.

The naturally occurring analogue of $CaZrTi_2O_7$ is known as zirconolite. The mineral is usually metamict but on heating to 1373–1473 K, the monoclinic phase crystallizes. Occurrences of the mineral are widespread both terrestrially and on the moon (Wark, Reid, Lovering & Goresy, 1973) and considerable variations in its composition have been observed due to substitution of Ca, Zr and Ti by combinations of elements such as rare-earths, Y, Nb, Fe, Th, U and Mg (Wark *et al.*, 1973). The ability of the mineral to accommodate a wide range of elements such as rare-earths and actinides in solid solution has led to the consideration of its use in synthetic mineral assemblages for the immobilization of nuclear wastes (Ringwood, Kesson, Ware, Hibberson & Major, 1979).

Quite large deviations from the composition $CaZrTi_2O_7$ due to variations in the [Ti]/[Zr] ratio are also possible. Wark *et al.* (1973) report that the [Ti]/[Zr] ratio is a sensitive function of the preparation temperature, varying from 1·31 at 1773 K to 2·75 at 1573 K. Single crystals of the monoclinic zirconolite phase have been grown with [Ti]/[Zr] ratios close to these two extremes and structure refinements for the compositions $Ca_{0.993}Zr_{1.304}Ti_{1.700}O_7$ ([Ti]/[Zr] = 1·31) and $Ca_{0.961}Zr_{0.850}Ti_{2.169}O_7$ ([Ti]/[Zr] = 2·55) are reported here. The refinements reveal some interesting new structural details, and allow a comparative study of site occupancies and atomic displacements as a function of the [Ti]/[Zr] ratio.

Experimental

(i) *Preparation and chemical characterization*

The samples were prepared by reacting finely ground and pelleted mixtures of the component oxides, contained in platinum crucibles, in air. Starting materials were Fisher Certified Reagent TiO_2 (anatase), purified Fisher Laboratory Reagent ZrO_2 (hafnium free) and AR grade $CaCO_3$. The TiO_2 and ZrO_2 were dried at 873 K and the $CaCO_3$ was dried at 573 K prior to use.

(*a*) 1773 K preparation. A 1 : 1 : 2 molar mixture of $CaCO_3$, ZrO_2 and TiO_2 was initially fired at 873 K for 4 h, reground and fired at 1473 K overnight. After further grinding the sample was re-pressed into pellets and held at 1773 K for four days. Scanning electron microscopy and powder X-ray diffraction studies showed that the product was predominantly zirconolite, together with rutile and calcium titanate. The zirconolite crystal used for the data collection was analysed with a JXA 50A electron probe using the MK7 version of the computer program *NPL-IC-BM* (Frost, 1977) for data reduction and zirconia (Zr), rutile (Ti), and wollastonite (Ca) as standards: the results are given in Table 1. The composition calculated from this analysis is $Ca_{0.993}Zr_{1.304}Ti_{1.700}O_7$.

Table 1. *Zirconolite microprobe analyses*

Compositions normalized to seven oxygens are $Ca_{0.993}Zr_{1.304}Ti_{1.700}O_7$ (1773 K) and $Ca_{0.961}Zr_{0.850}Ti_{2.169}O_7$ (1573 K).

	Ideal $CaZrTi_2O_7$	Single crystal (1773 K preparation)	Single crystal (1573 K preparation)*
CaO	16·54 wt%	15·45 wt%	15·93 wt%
ZrO_2	36·34	44·57	30·98
TiO_2	47·12	37·66	51·23

* Average of three separate point analyses.

(*b*) 1573 K preparation. A 1:0·8:2·2 molar mixture of $CaCO_3$, ZrO_2 and TiO_2 was pelleted and reacted at 1573 K for two days. The sample was then ground, repelleted and heated for a further two days. The resulting product appeared to be a homogeneous single phase which gave very sharp lines due to zirconolite only in the X-ray powder pattern. The crystals were very much smaller than those formed at 1773 K, with maximum dimensions rarely exceeding 100 μm. The single crystal selected for the X-ray intensity data collection was subjected to a microprobe analysis, the results of which are given in Table 1. The average of three separate point analyses gave a composition $Ca_{0.961}Zr_{0.850}Ti_{2.169}O_7$, with a [Ti]/[Zr] ratio of 2·55.

(ii) *Single-crystal X-ray intensity data*

(*a*) $Ca_{0.993}Zr_{1.304}Ti_{1.700}O_7$. The crystal selected for data collection was a transparent, very pale brown, essentially equidimensional (0·25 mm) fragment with no obvious cleavage or morphological faces. Precession and Weissenberg photographs showed that reflections hkl and $h0l$ were absent for $h + k = 2n + 1$ and $l = 2n + 1$ respectively, which suggested the possible space groups *Cc* or *C*2/*c*: this confirms the observations of Rossell (1980) using electron diffraction patterns.

The crystal was mounted on a Philips PW 1100 four-circle automatic diffractometer in an arbitrary orientation for the intensity-data collection. Lattice parameters were obtained from the average of 25 orientation matrices automatically determined at various stages of the data collection using 24 reflections in the range $2\theta = 22$ to 28°. The resultant cell dimensions, $a = 12{\cdot}445\,(4)$, $b = 7{\cdot}288\,(2)$, $c = 11{\cdot}487\,(3)$ Å and $\beta = 100{\cdot}39\,(1)°$, are in close agreement with those determined by Wark *et al.* (1973)

for a synthetic zirconolite of very similar composition. Intensities were collected with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) monochromated by a flat graphite crystal ($2\theta_m = 12{\cdot}0°$) using a θ–2θ scan technique and a 2θ scan rate of 3° min^{-1}. Backgrounds were determined from stationary counts equal to half the scan time at both ends of each dispersion-corrected scan range (minimum width = 1·5° in 2θ) (Alexander & Smith, 1964). Three non-coplanar reflections measured every 2 h showed no significant variation in either intensity or position. 4673 non-systematically absent reflections were collected from the octants hkl, $h\bar{k}\bar{l}$, $\bar{h}kl$, and $hk\bar{l}$ to a maximum 2θ value of 70° and the resultant data corrected for background, Lorentz and polarization effects using a program written specifically for the PW 1100 diffractometer by Hornstra & Stubbe (1972). Since the plane of reflection of the graphite monochromator was perpendicular to that of the specimen crystal, the Lorentz–polarization correction was of the form $(Lp)^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(\cos^2 2\theta + \cos^2 2\theta_m)$ where θ_m is the Bragg angle of the monochromator. No absorption corrections were applied to the data in view of the moderate value of the linear absorption coefficient (6·08 mm^{-1}) and the equidimensional and irregular external form of the crystal. Multiply measured and symmetry-equivalent reflections consistent with point group $2/m$ were then averaged to yield a set of 2221 unique structure factors, F, each with a standard deviation estimated from $\sigma_F = [\sigma_I^2 + (0{\cdot}03I)^2]^{0{\cdot}5}/2I^{0{\cdot}5}$ where I is the corrected raw intensity and σ_I is derived from counting and averaging statistics.* The overall internal consistency factor between averaged intensities was 0·050 but only those 2011 observations with $F > 3\sigma_F$ were included in the subsequent least-squares analysis.

(*b*) $Ca_{0{\cdot}961}Zr_{0{\cdot}850}Ti_{2{\cdot}169}O_7$. Procedures similar to those in (ii) (*a*) were used. The crystal used for the data collection measured 0·06 × 0·05 × 0·04 mm. The lattice parameters were $a = 12{\cdot}444$ (2), $b = 7{\cdot}266$ (1), $c = 11{\cdot}341$ (2) Å, $\beta = 100{\cdot}59$ (1)°. Because of the smaller crystal volume, the scan rate was reduced to 2° min^{-1}. 4613 reflections were measured to a maximum 2θ value of 70°. These yielded 2119 unique reflections after averaging, of which 1126 with $F > 3\sigma_F$ were used in the refinement.

Crystal structure refinement

(i) $Ca_{0{\cdot}993}Zr_{1{\cdot}304}Ti_{1{\cdot}700}O_7$

Refinement of the structure was initiated in space group $C2/c$ assuming the atomic positions of Rossell (1980) and the stoichiometry $CaZrTi_2O_7$. With the release of coordinates and individual isotropic temperature factors, least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, and $w = 1/\sigma_F^2$, yielded a conventional R value of 0·201 $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{0{\cdot}5} = 0{\cdot}314\}$. The population parameters of all five cations in the asymmetric unit were then added to the list of variables in a crude attempt to account for the fact that the Ti:Zr ratio is not 2·0, but the R value dropped only to 0·182 ($R_w = 0{\cdot}287$). Furthermore, although the thermal parameters of four of the cations were quite reasonable, Ti(2) had a B value of 2·67 Å^2, and the anions had B values in the range −0·1 to 1·34 Å^2. A Fourier difference ($F_o - F_c$) map showed clearly that Ti(2) did not lie on the twofold axis at (0·5,y,0·25), but, in fact, occupied two positions on either side with, as far as could be ascertained, equal probability. The Ti(2) atom was therefore replaced by one with 50% site occupancy at (0·470, 0·049, 0·252) and refinement of this model produced an R value of 0·094 ($R_w = 0{\cdot}122$). With the inclusion of an isotropic extinction parameter as defined by Larson (1967), and the conversion to anisotropic temperature factors,* the refinement converged at $R = 0{\cdot}052$ and $R_w = 0{\cdot}064$.

Table 2. *Fractional atomic coordinates and equivalent isotropic B parameters* (Å^2)

$B_{eq} = \frac{8}{3}\pi^2 \times$ mean square radial displacement.

	Occupancy	x	y	z	B_{eq}
$Ca_{0{\cdot}993}Zr_{1{\cdot}304}Ti_{1{\cdot}700}O_7$					
Ca	0·986 Ca + 0·014 (3) Zr	0·37301 (4)	0·12649 (7)	0·49549 (6)	0·67
Zr	0·983 (4) Zr + 0·017 Ca, Ti	0·12315 (2)	0·12139 (3)	−0·02490 (3)	0·39
Ti(1)	0·812 Ti + 0·188 (3) Zr	0·24932 (5)	0·12667 (7)	0·74574 (6)	0·73
Ti(2)	0·419 Ti + 0·081 (2) Zr	0·47602 (11)	0·05878 (16)	0·25163 (17)	1·11
Ti(3)	0·990 Ti + 0·010 (3) Zr	0·0	0·12607 (9)	0·25	0·47
O(1)		0·3083 (2)	0·1266 (2)	0·2808 (2)	1·81
O(2)		0·4694 (2)	0·1382 (3)	0·0980 (2)	1·03
O(3)		0·2070 (2)	0·0846 (2)	0·5717 (2)	0·59
O(4)		0·3986 (2)	0·1637 (3)	0·7180 (2)	1·24
O(5)		0·7111 (1)	0·1732 (3)	0·5829 (2)	0·59
O(6)		−0·0027 (2)	0·1183 (2)	0·4176 (2)	0·72
O(7)		0·1134 (2)	0·0518 (3)	0·7924 (2)	1·24
$Ca_{0{\cdot}961}Zr_{0{\cdot}850}Ti_{2{\cdot}169}O_7$					
Ca	0·975 Ca + 0·025 (4) Zr	0·3732 (1)	0·1275 (3)	0·4953 (1)	0·68
Zr	0·839 (3) Zr + 0·161 Ti	0·12290 (7)	0·1231 (2)	−0·02483 (7)	0·52
Ti(1)	1·004 (6) Ti	0·2489 (1)	0·1214 (4)	0·7466 (1)	0·82
Ti(2)	0·483 (5) Ti	0·4684 (3)	0·0516 (4)	0·2522 (3)	1·07
Ti(3)	0·993 (8) Ti	0·0	0·1271 (4)	0·25	0·54
O(1)		0·3050 (6)	0·1300 (9)	0·2812 (4)	1·75
O(2)		0·4712 (4)	0·1361 (9)	0·1022 (4)	0·71
O(3)		0·2056 (5)	0·0815 (7)	0·5711 (4)	0·76
O(4)		0·3990 (5)	0·1635 (8)	0·7187 (5)	1·02
O(5)		0·7098 (5)	0·1725 (7)	0·5824 (4)	0·61
O(6)		−0·0033 (4)	0·1231 (9)	0·4183 (4)	1·00
O(7)		0·1126 (5)	0·0523 (9)	0·7931 (5)	1·14

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* Lists of structure factors, anisotropic thermal parameters, r.m.s. components of thermal displacement and thermal-ellipsoid orientations for both crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35707 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The anisotropic ellipsoids were converted to the following form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Using the population parameters of each cation site as an indication of the identity and quantity of the substituting element (assumed to be only one other species), the refinement was then continued with the total occupancy constrained to be 1·0 [or 0·5 in the case of the Ti(2) site]. Convergence was achieved at $R = 0{\cdot}045$, $R_w = 0{\cdot}055$ (0·050 and 0·056 respectively for all 2221 reflections); the error in an observation of unit weight was 2·99, and the extinction parameter was $7{\cdot}2\,(2) \times 10^{-3}$. Atomic coordinates and equivalent isotropic B parameters, along with their standard deviations estimated from the inverted full matrix, are given in Table 2.*

(ii) $Ca_{0{\cdot}961}Zr_{0{\cdot}850}Ti_{2{\cdot}169}O_7$

With the titanium sites Ti(1), Ti(2) and Ti(3) fully occupied and the deficiency of calcium in site Ca and zirconium in site Zr made up by Zr and Ti respectively, consistent with the microprobe analysis, refinement of the scale, isotropic extinction parameter, coordinates and anisotropic temperature factors for all atoms led to rapid convergence at $R = 0{\cdot}054$, $R_w = 0{\cdot}046$ for the 1126 observed reflections. A further three cycles of refinement of all parameters including the population parameters for all metals did not reduce the R values below these values. It was found necessary to hold the scale fixed during these cycles because of strong correlations with the population parameters. The final weighted R_w for all 2119 reflections was 0·058. The error in an observation of unit weight was 1·364 and the extinction parameter was $1{\cdot}5\,(1) \times 10^{-3}$. The atomic coordinates and equivalent isotropic B parameters are given in Table 2.*

Scattering factors for Ca, Zr, Ti and O (neutral atoms) were obtained from *International Tables for X-ray Crystallography* (1974) and were corrected for both real and imaginary anomalous-dispersion components. Structure refinement and geometry calculations, along with crystal drawings, were all performed with the XRAY 76 system of programs (Stewart, 1976).

It is possible that in minute detail the zirconolite crystal structure may subscribe more closely to the symmetry of space group Cc than to $C2/c$ as described above. Indeed, the presence or absence of the twofold axis is central to the discussion of the electron density at the Ti(2) site. However, several points lead us to conclude that the centrosymmetric structure represents a completely adequate description of the zirconolite atomic arrangement. Firstly, the R_w value dropped from 0·28 to 0·12 upon splitting the site into two half-atoms related by the diad, and the final Fourier difference map was essentially featureless in this region. Secondly, there was no evidence for a doubling of the unit-cell volume which would then allow the Ti(2) half-atoms to occupy fully alternate sites about the 'imaginary' twofold axis in each subcell. Thus, for refinement in space group Cc it was necessary to reproduce the same two half-atoms in order to produce agreement indices as acceptable as those obtained in the $C2/c$ refinement. Finally, the fact that the R value obtained for the centrosymmetric structure was as low as 0·045 means that any deviation from strict $C2/c$ symmetry must of necessity be slight, and of dubious significance.

Discussion of the structure

Zirconolite crystallizes with the topology displayed in Figs. 1 and 2, and the bonding dimensions summarized in Tables 3 and 4. Apart from the splitting of the Ti(2) site, which changes the coordination of this atom from six to five, the structure is essentially as determined from the powder X-ray diffraction study of Rossell (1980).

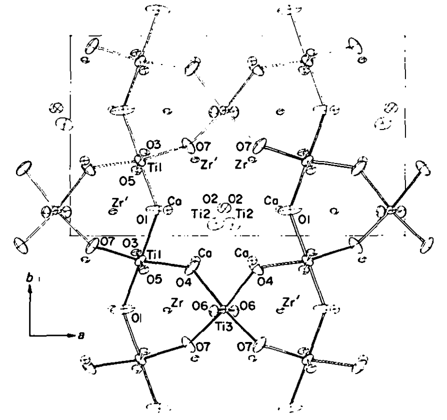

Fig. 1. Diagram of the sheet of TiO_6 octahedra at $z = 0{\cdot}25$ in the zirconolite unit cell. Thermal ellipsoids for all atoms represent 75% probability surfaces. One each of the $Ti(1)O_6$ and $Ti(3)O_6$ octahedra have been indicated by filled conical bonds but no bonds have been drawn to the two Ti(2) half-atoms or to the Ca and Zr atoms above and below the sheet. Zr atoms below the plane are indicated by primes.

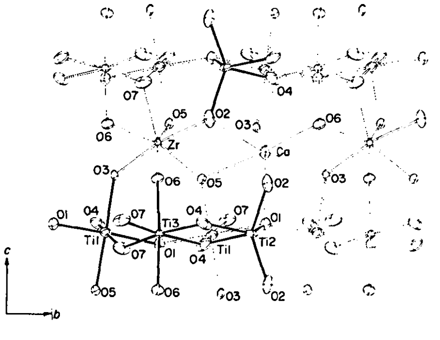

Fig. 2. 'Edge-on' view of two sheets of TiO_6 octahedra and a Ca/Zr layer at $x = 0{\cdot}125$ in the zirconolite unit cell. One each of the unique TiO_6 octahedra, together with one set of Ti(2) half-atoms, have been indicated by filled conical bonds.

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* See deposition footnote.

Table 3. *Metal–oxygen distances* (Å) *for* $Ca_{0\cdot993}$-$Zr_{1\cdot304}Ti_{1\cdot700}O_7$ (Zr-*rich*) *and* $Ca_{0\cdot961}Zr_{0\cdot850}Ti_{2\cdot169}O_7$ (Ti-*rich*)

	Zr-rich	Ti-rich		Zr-rich	Ti-rich
Ti(1)–O(1)	1·940 (2)	1·933 (7)	Ca–O(3)	2·396 (2)	2·393 (6)
O(7)	1·942 (2)	1·933 (7)	O(2)	2·401 (3)	2·400 (6)
O(4)	1·959 (2)	1·975 (7)	O(3)′	2·404 (2)	2·420 (6)
O(5)	1·971 (2)	1·948 (5)	O(1)	2·452 (3)	2·420 (5)
O(3)	1·997 (2)	1·986 (5)	O(2)′	2·457 (2)	2·467 (6)
O(1)′	2·000 (2)	1·969 (7)	O(5)	2·517 (2)	2·502 (6)
Mean	1·968	1·957	O(4)	2·533 (3)	2·508 (5)
			O(6)	2·546 (2)	2·507 (6)
Ti(2)–O(2)	1·832 (3)	1·792 (5)	Mean	2·463	2·452
O(2)′	1·845 (3)	1·815 (6)			
O(4)	1·890 (3)	1·792 (7)	Zr–O(3)	2·039 (2)	2·011 (5)
O(1)	2·228 (3)	2·194 (8)	O(6)	2·105 (3)	2·082 (5)
O(4)′	2·234 (3)	2·253 (7)	O(5)	2·117 (2)	2·091 (5)
Mean	2·006	1·969	O(7)	2·142 (2)	2·109 (6)
			O(2)	2·181 (2)	2·196 (6)
Ti(3)–O(7) × 2	1·913 (2)	1·910 (6)	O(5)′	2·310 (2)	2·321 (6)
O(6) × 2	1·933 (2)	1·916 (5)	O(6)′	2·360 (2)	2·390 (6)
O(4) × 2	1·977 (2)	1·964 (6)	Mean	2·179	2·171
Mean	1·941	1·930			

Table 4. *Oxygen–oxygen distances and associated* O–*M*–O *angles for* Ti(1), Ti(2) *and* Ti(3) *in* $Ca_{0\cdot993}$-$Zr_{1\cdot304}Ti_{1\cdot700}O_7$ (Zr-*rich*) *and* $Ca_{0\cdot961}Zr_{0\cdot850}Ti_{2\cdot169}O_7$ (Ti-*rich*)

	Zr-rich	Ti-rich	Zr-rich	Ti-rich
Ti(1) octahedron				
O(1)–O(7)	2·729 (3) Å	2·722 (9) Å	89·32 (11)°	89·5 (3)°
–O(4)	2·997 (4)	2·950 (9)	100·45 (12)	98·0 (3)
–O(5)	2·788 (3)	2·751 (7)	90·94 (10)	90·3 (2)
O(3)	2·730 (3)	2·702 (8)	87·80 (10)	87·1 (2)
O(7)–O(5)	2·545 (3)	2·548 (8)	81·14 (9)	82·1 (3)
–O(3)	2·984 (3)	2·966 (8)	98·47 (9)	98·4 (2)
–O(1)′	2·776 (4)	2·762 (9)	89·52 (11)	90·1 (3)
O(4)–O(5)	2·869 (3)	2·837 (8)	93·76 (9)	92·6 (2)
O(3)	2·719 (3)	2·733 (8)	86·84 (9)	87·3 (2)
O(1)′*S**	2·559 (3)	2·593 (9)	80·53 (11)	82·2 (3)
O(5)–O(1)′	2·724 (3)	2·713 (8)	86·61 (10)	87·7 (2)
O(3)–O(1)′	2·939 (3)	2·914 (7)	94·65 (9)	94·9 (2)
Ti(2) trigonal bipyramid				
O(2)–O(2)′	3·437 (6)	3·297 (6)	138·41 (14)	132·1 (3)
–O(4)	3·279 (3)	3·204 (8)	123·52 (14)	126·7 (3)
–O(1)	2·865 (4)	2·855 (8)	89·21 (12)	90·0 (3)
O(4)′	2·820 (3)	2·780 (8)	87·26 (10)	86·0 (3)
O(2)′–O(4)	2·820 (3)	2·780 (8)	98·06 (12)	100·8 (3)
O(1)	3·155 (4)	3·154 (9)	101·13 (11)	103·3 (3)
O(4)′	3·279 (3)	3·204 (8)	106·64 (12)	103·4 (3)
O(4)–O(1) *S*	2·559 (3)	2·593 (9)	76·35 (10)	80·5 (3)
–O(4) *S*	2·499 (4)	2·483 (7)	74·07 (13)	74·8 (3)
O(1)–O(4)′	4·215 (4)	4·256 (8)	141·67 (11)	146·3 (3)
Ti(3) octahedron				
O(7)–O(7)′	2·814 (4)	2·793 (8)	94·69 (13)	94·0 (3)
–O(6) × 2	2·838 (3)	2·833 (7)	95·10 (9)	95·5 (3)
–O(6)′ × 2	2·539 (3)	2·544 (9)	82·62 (9)	83·3 (3)
O(4) × 2	2·834 (3)	2·831 (9)	93·50 (9)	93·9 (3)
O(6)–O(4) × 2	2·713 (3)	2·691 (9)	87·86 (9)	87·8 (3)
–O(4)′ × 2	2·877 (3)	2·828 (7)	94·74 (9)	93·5 (3)
O(4)–O(4)′ *S*	2·499 (4)	2·483 (9)	78·38 (13)	78·4 (3)

* *S* signifies a shared edge.

As described by Rossell (1980), zirconolite is an anion-deficient superstructure related to fluorite. Planes of metal atoms parallel to (001) in zirconolite are derived from fluorite (111) metal-only planes, and alternatively contain Ti only, or a mixture of Ca and Zr. As in other anion-deficient fluorite superstructures, the oxygen sites formally vacant compared to the parent substructure occur in pairs separated by lattice vectors of the type $\frac{1}{2}[111]_{\mathrm{fl}}$.

The (001) sheets of Ti atoms are similar to the sheets of octahedra parallel to {110} in the pyrochlore structure (Yagi & Roth, 1978). The Ti(1) and Ti(3) atoms in these layers are each coordinated by six O atoms at the corners of irregular octahedra, sharing vertices to form three- and six-membered rings (Fig. 1 and Table 3). The primary reason for the irregularity of these octahedra appears to be the steric constraints imposed by the formation of the three-membered rings, causing the internal valence angles of the kind O(7)–Ti(3)–O(4) to be, on average, about 12° wider than the external ones such as O(4)–Ti(3)–O(4). The Ti-only (001) layers of zirconolite contain a third Ti atom near the centre of the six-membered ring of Ti(1) and Ti(3) octahedra. Were this atom to occupy the geometric centre of the ring it would be coordinated by six O atoms at distances of 2·47 to 2·67 Å and by two O(2) atoms at 1·72 Å. Moreover, the two O(7) atoms on one side of the cavity would then be overbonded, and the two O(4) atoms on the other side would be significantly underbonded. A more favourable site is therefore one which is displaced towards the O(4) side of the six-membered ring, as observed by Rossell (1980). If the Ti(2) atom is then constrained to lie on the twofold axis it is coordinated by six O atoms at the corners of an approximate trigonal prism. However, the single-crystal refinements outlined above indicate quite clearly that the Ti(2) atom in fact occupies two equivalent positions 0·3–0·4 Å on either side of the twofold axis (Fig. 1). Each of these half-atoms is then more appropriately described as occurring in trigonal-bipyramidal coordination: the three 'equatorial' bonds are approximately equal in length and are significantly shorter (by about 0·4 Å) than the two 'axial' bonds.

Fivefold coordination of Ti by O has been documented in the minerals fresnoite, lamprophyllite and innelite, and in the synthetic compounds Y_2TiO_5 and $K_2Ti_2O_5$ (Tillmanns, 1972). In the first four of these compounds the coordination is square pyramidal with the apical bond significantly shorter than the four basal bonds. However, in $K_2Ti_2O_5$ the polyhedron is a somewhat distorted trigonal bipyramid with three equatorial bonds of average length 1·75 Å and two axial bonds of length 2·00 Å. Even allowing for the presence of some Zr in the Ti(2) sites the corresponding trigonal-bipyramidal bonds in zirconolite are considerably longer than those in $K_2Ti_2O_5$, with the result that the Ti atom is underbonded by about 0·7 valence units (using the bond-strength parameters of Brown & Wu, 1976). However, the next-nearest anion is more than 2·8 Å away and contributes less than 0·1 valence units to the bond-strength sum. The apparently random occupation of the two Ti(2) half-atom sites probably accounts for the relatively elongate ellipsoids of thermal vibration of the equatorial O atoms O(1,4,7) (Fig. 1) as the octahedra rotate about [001] in response to different ordering schemes on the unit-cell scale.

The displacement of the Ti(2) atom from the twofold axis is the major difference between the results of the powder and single-crystal refinements. Its detection was a consequence of the availability of Fourier methods and the much larger number of high-angle reflections in the latter studies. Subsequent refinement of the split-atom model using the powder data produced $R = 0{\cdot}040$, a significant improvement on the $R = 0{\cdot}054$ of the original powder refinement (Rossell, 1980).

The Ca and Zr atoms within alternate (001) sheets are themselves ordered into rows running parallel to [110] or $[1\bar{1}0]$ in every second layer of this kind (Fig. 1). The Ca atoms are coordinated by eight anions at the corners of a distorted cube (Fig. 2) and contain about 3% of substituted Zr. Two of the vertices of this cube, O(1) and O(4), extend into the centre of the Ti-only layers in the [001] direction but the remaining six vertices are shared with adjacent Ca or Zr polyhedra in the same sheet (Fig. 2). The polyhedron of anions about Zr has a similar arrangement of vertices in the Ca/Zr sheet, but has only one vertex, O(7), which penetrates the adjacent Ti-only layers, and is therefore seven-coordinated: the missing cube vertex represents the 'vacant' anion site from the fluorite structure. In both cases the bond lengths are close to the values expected for ions in the appropriate coordination (Shannon, 1976).

Effect of [Ti]/[Zr] *variation*

Atomic coordinates and site occupancies for the structures corresponding to Ti-rich, [Ti]/[Zr] = 2·55, and Zr-rich, [Ti]/[Zr] = 1·31, compositions (Table 2) show that the major atomic displacements that accompany the change in [Ti]/[Zr] ratio are associated with the site Ti(2). For the Ti-rich phase, this site is occupied solely by Ti whereas for the Zr-rich phase, about 16 at.% of Ti is replaced by Zr. The *M*—O and O—O distances associated with the Ti(2) site are compared in Tables 3 and 4. The increase in [Ti]/[Zr] ratio results in a displacement of Ti(2) by 0·10 Å towards the equatorial oxygen O(4), together with a shortening of the O(2)—O(2) edge between the two other equatorial oxygens by 0·14 Å. The combined effect is to decrease the mean equatorial bond length by 0·06 Å. The corresponding reduction in the mean axial bond length is less than 0·01 Å and the difference in the average Ti(2)—O bond length for the trigonal-bipyramidal sites is 0·04 Å. The separation between the 'split' Ti(2) atoms decreases from 0·80 to 0·60 Å as the Zr content of the site is increased from 0 to 16 at.%. However, with increasing Zr content of site Ti(2), the point where the 'split' atoms merge and a single atom occupies the special site on the twofold axis with six O neighbours in approximately trigonal-prismatic coordination does not occur. In fact the Zr-rich crystal studied here has a composition corresponding to the maximum reported Zr content of zirconolite, [Ti]/[Zr] = 1·31 (Wark *et al.*, 1973), and so other factors, such as local charge balance, at oxygen sites, must prevent the formation of the ordered phase, ideally $CaZr_{1\cdot5}Ti_{1\cdot5}O_7$, [Ti]/[Zr] = 1·0.

Other significant changes resulting from an increase in the [Ti]/[Zr] ratio from 1·31 to 2·55 are an increase in the Ti content at the Zr site from 0 to about 15 at.% and a decrease in the Zr content of Ti site Ti(1) from 19 to 0 at.%. These substitutions are accompanied by small decreases in the mean Zr—O and Ti(1)—O bond lengths of about 0·01 Å. The incorporation of Ti into the Zr site results in a significant increase in the range of *M*—O bond lengths, from 0·32 to 0·38 Å. The Ti(3) site is relatively unaffected by changing the [Ti]/[Zr] ratio. At the Zr-rich end, the refined Zr occupancy of this site is only three times the e.s.d., 0·010 (3). Similarly, the contents of the Ca site are not significantly different, with about 3 at.% of Zr replacing Ca. Thus, to summarize, the variation in [Ti]/[Zr] ratios in zirconolites in the pseudo-ternary system $CaO–ZrO_2–TiO_2$ is accommodated by substitution of excess Ti in the seven-coordinated Zr site and substitution of excess Zr in both the five-coordinated Ti(2) site and the six-coordinated Ti(1) site.

Much of the current interest in zirconolite stems from the consideration of its use in synthetic mineral assemblages, SYNROC, for the immobilization of nuclear wastes (Ringwood *et al.*, 1979). On the basis of the present study it is not possible to predict with any certainty how the radwaste elements would be accommodated in the structure. They are larger than either Ti^{4+} or Zr^{4+} and it is therefore unlikely that they would move directly into the five- or six-coordinated Ti sites. Their sizes are more compatible with substitution in the seven-coordinated Zr site (perhaps then displacing Zr into the Ti sites), or the even larger eight-coordinated Ca site. Although the Ca contents of zirconolites synthesized in the present study are essentially constant at one atom per formula unit, in the terrestrial and lunar zirconolites analysed by Wark *et al.* (1973) the values are variable and significantly reduced from unity, suggesting that Ca also plays a very important role in the crystal chemistry of this phase. Structural studies of zirconolites containing significant concentrations of appropriate radwaste elements are currently underway, using both powder and single-crystal data, in an attempt to ascertain the limits and effects of various elemental concentrations on the integrity of the atomic arrangement.

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The Structure of $K_3(K_{0\cdot333},H_2O_{0\cdot667})_6Na_2(Na_{0\cdot38},H_3O^+_{0\cdot12},H_2O_{0\cdot50})_6Fe^{3+}_6O_2(SO_4)_{12}.6H_2O$ and Its Relationship with the Parent Compound*

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Abstract

The spontaneous solid-state transformation of a hydrated iron sulphate related to metavoltine and α-Maus's salt is studied here ($R\bar{3}$, $a = 18{\cdot}225$ Å, $\alpha = 30{\cdot}515°$, $Z = 1$; $R = 0{\cdot}079$ for 1607 reflexions). This transformation is a topotactic reaction in which the solid product is formed by a translation of adjacent sandwich sheets, $[Na_2K_2Fe^{3+}_6O_2(SO_4)_{12}(H_2O)_6]^{6-}$, by $\frac{1}{3}$ in the **a** + **b** crystallographically equivalent orientation relative to the parent crystal. Thus, the reaction product has similar *a* and *b* parameters and *c* is three times that of the reactant lattice. The mechanism mainly involves a resettlement of Na atoms, reducing their coordination number, and the partial removal of water molecules.

Introduction

Recently the crystal structure of a synthetic compound with chemical formula $K_2(K_{0\cdot41},H_2O_{0\cdot59})_6Na_{3\cdot98}$-$H_3O^+_{0\cdot78}X^+_{0\cdot68}(Fe^{2+}_{0\cdot05},\square_{0\cdot95})Fe^{3+}_6O_2(SO_4)_{12}$. $11{\cdot}91H_2O$ has been solved (Scordari, 1980*a*). This compound, 'salt *X*', has been obtained from a solution containing K_2SO_4 (0·6g), $Na_2SO_4.10H_2O$ (3·4g) and $Fe_2(SO_4)_3.nH_2O$ (4·3g), at about 353 K. These crystals are not stable under standard conditions and gradually change into other crystals, which are related to the parent crystals in symmetry and lattice parameters. The solid-state reaction has been revealed accidentally by two successive X-ray powder patterns, which were carried out with a two month interval.

This study was undertaken to discover what initiates the transformation process and what happens in the crystal structure of salt *X* when the reaction occurs.

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