

SHORT STRUCTURAL PAPERS

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Calzirtite – A Fluorite-Related Superstructure

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Abstract. $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$, tetragonal, $I4_1/acd$, $a = 15.2203$ (6), $c = 10.1224$ (5) Å at 300 K, $Z = 8$, $D_m = 4.98$, $D_c = 5.031$ Mg m⁻³; synthetic material. $R = 0.031$ for 112 powder peaks. The unit cell is a $3 \times 3 \times 2$ array of subcells of defect-fluorite (face-centred cubic, MO_{2-x}) type in which anion vacancies and cations are ordered. The Ca, Ti and four-fifths of the Zr cations are eight-, six- and seven-coordinated by O respectively; the remaining Zr occupy randomly one of two sites 0.51 (1) Å apart in a distorted cube of O.

Introduction. Single crystals of natural calzirtite, $\text{Ca}_{1.809}\text{Zr}_{5.159}\text{Ti}_{1.809}\text{Fe}_{0.185}\text{Nb}_{0.008}\text{O}_{16}$, were examined by Pyatenko & Pudovkina (1961): they proposed an anion-deficient fluorite-related superstructure with ideal fluorite-derived atomic coordinates, fully ordered anion vacancies and a cation distribution in accord with the O coordination, but did not refine it. The idealized structure containing the cations Ca, Zr and Ti in a state of complete order would have the composition $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$ (Pyatenko, 1971). Single-phase calzirtite can be synthesized at this composition, and since cation ordering is important in the study of fluorite-related oxides (Rossell & Scott, 1977), it was of interest to refine the structure of this synthetic material.

Pure, powdered CaCO_3 , ZrO_2 and TiO_2 in the molar ratio 2:5:2 were reacted at 1220 K, then ground, compacted and heated in air at 1590 K for 2 weeks. Calzirtite decomposes to form zirconolite ($\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$, $x \approx 1$), perovskite [$\text{Ca}(\text{Zr}, \text{Ti})\text{O}_3$] and ZrO_2 at about 1670 K. Single crystals suitable for X-ray study were not found; however, single-crystal electron diffraction patterns were recorded using a 100 kV electron microscope fitted with a tilting stage. Lattice parameters were determined by least squares from 46 lines on a Guinier powder photograph taken

with Cu $K\alpha_1$ radiation and with ThO_2 ($a = 5.5972$ Å) as an internal standard.

Powder diffraction intensities for $\theta < 47^\circ$ (Ni-filtered Cu $K\alpha$ radiation) were recorded on chart using a powder diffractometer scanned continuously at 0.25° (2θ) min⁻¹. Peak areas were measured with a planimeter. The region of reciprocal space scanned contained 271 non-equivalent reflexions; overlap reduced these to 112 distinct observations of which 53 consisted of a single reflexion. There were 20 unobserved reflexions; these were given intensities of $0.5I_{\min}$, where I_{\min} was the minimum detectable intensity.

The structure was refined from the intensity data using *POWDER*, a full-matrix least-squares program (Rossell & Scott, 1975) that minimizes $\sum w(I_o - I_c)^2$, where $w = 1/(I_o + I_{\min})$. The residual quoted here is $\frac{1}{2}[\sum w(I_o - I_c)^2 / \sum wI_o^2]^{-1/2}$; it is numerically comparable to residuals from refinements based on F . Scattering factors for neutral atoms with corrections for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974) were used.

Systematically absent reflexions in the electron and X-ray diffraction patterns were hkl with $h + k + l \neq 2n$, $hk0$ with $h(k) \neq 2n$, $h0l$ with $l \neq 2n$ and hhl with $2h + l \neq 4n$, so that the space group $I4_1/acd$ determined by Pyatenko & Pudovkina was confirmed. The diffraction patterns were dominated by reflexions corresponding to a subcell derived from the f.c.c. fluorite (MO_2) type. The axes a and c are respectively 3 times and 2 times the formal subcell edges.

As noted by Pyatenko & Pudovkina, there are two distinct ways to fit a fluorite structure into the supercell, characterized by cations at one or the other of the special positions 222 or $\bar{4}$. Trial structures for each alternative and for all possible ordered arrangements of cations (with atoms in ideal fluorite-derived positions and no vacancies) were examined. After refinement of

Table 1. Fractional atomic coordinates

Standard deviations of the last digits are in parentheses. The origin is at $\bar{1}$ in $I4_1/acd$ (Pyatenko & Pudovkina chose 4 as origin, at $0, \frac{1}{4}, \frac{1}{8}$ from $\bar{1}$).

Point set	Occupancy	x	y	z
M(1)	16(f) $\frac{1}{2}[0.86(3)\text{Zr} + 0.14\text{Ti}]$	0.0120 (7)	0.2620	0.125
M(2)	16(f) 0.93Ti + 0.07Zr	0.1688 (3)	0.4188	0.125
Ca	16(f)	0.3325 (4)	0.5825	0.125
Zr	32(g)	-0.0178 (2)	0.5884 (2)	0.1104 (3)
O(1)	32(g)	0.0784 (18)	-0.0079 (16)	-0.0445 (22)
O(2)	32(g)	0.0651 (16)	0.1694 (16)	-0.0044 (22)
O(3)	32(g)	0.1114 (13)	0.3323 (16)	0.0013 (25)
O(4)	16(e)	0.25	-0.0362 (22)	0.0
O(5)	16(e)	0.25	0.1831 (24)	0.0
X(6)	16(e) Formal O vacancy	0.25	0.3333	0.0

scale and cation coordinates, one structure with $R = 0.13$ was clearly superior to the others, which had $R > 0.22$.

The formal anion vacancies of this trial structure were identified by refinement of O occupancies, when the value for one O at a 16-fold site fell to zero. Refinement of anion coordinates and adjustment of the cation distribution through refinement of occupancies and application of the stoichiometry restraint produced $R = 0.054$. An electron density difference synthesis constructed from the low-angle single-reflexion observations indicated that the cation placed initially at 222 ($0, \frac{1}{4}, \frac{1}{8}$) in fact occupied two closely spaced positions on either side with apparently equal probability. Refinement of this model produced $R = 0.031$, with mean parameter shift less than $10^{-3} \sigma$ on the final cycle. An overall isotropic temperature factor was used; however, the refined value, $0.35(7) \text{ \AA}^2$, will be influenced by effects such as non-ideality of specimen surface. The structure was chemically reasonable and the bond-strength sums calculated from the parameters of Brown & Wu (1976) were all within 5% of the nominal valences. The atomic coordinates are given in Table 1.*

Discussion. The calzirtite structure is derived from the fluorite arrangement of edge-sharing MO_8 cubes by the ordering of vacancies as pairs across the body diagonals of some cubes, to produce MO_6 octahedra adjacent to MO_7 polyhedra and cubes (Fig. 1). The octahedra are corner-linked into helical chains about the 4₁ axes. The cations (ignoring for convenience the

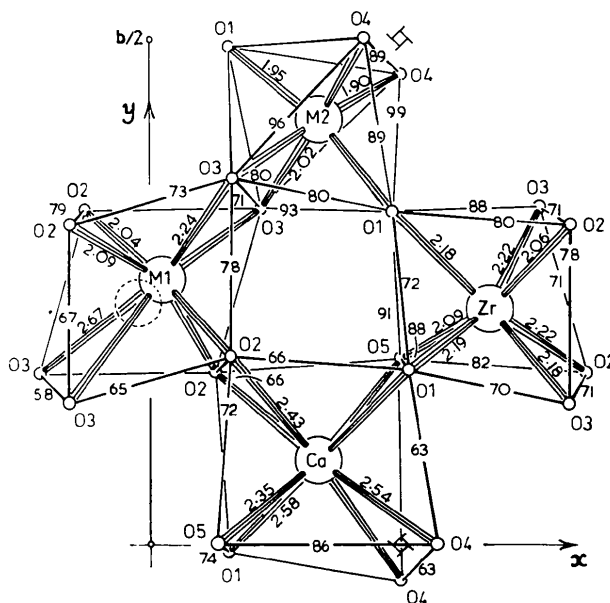


Fig. 1. Portion of the structure projected down c , showing the four distinct MO_n polyhedra. Anions are at $z \sim 0$ and $z \sim \frac{1}{4}$, cations at $z \sim \frac{1}{8}$. $M-O$ distances (\AA) have e.s.d.'s $\sim 0.025 \text{ \AA}$; $O-M-O$ angles ($^\circ$), marked near the corresponding $O-O$ edges, have e.s.d.'s $\sim 1^\circ$. The two $M(1)$ positions are $0.51(1) \text{ \AA}$ apart. The majority of $O-O$ distances lie in the range $2.6-2.9 \text{ \AA}$, with e.s.d.'s $\sim 0.035 \text{ \AA}$. The extremes are $3.34(4) \text{ \AA}$ for $O(4)-O(5)$ in the CaO_8 polyhedron and $2.52(3) \text{ \AA}$ for an $O(1)-O(3)$ in $M(2)O_6$.

small exchange of Ti and Zr) are ordered so that the smallest, Ti (radius 0.605 \AA , Shannon, 1976), occupy the octahedra, while most of the Zr (0.78 \AA) are seven-coordinated by O, and the Ca (1.12 \AA) are eight-coordinated. The anions have relaxed from their ideal fluorite positions to produce nearly regular MO_6 octahedra.

The fully ordered arrangement of formal anion vacancies found here confirms the choice made by Pyatenko & Pudovkina. However, the cation distribution determined here differs from theirs: in particular, the eight-coordinated 222 site ($0, \frac{1}{4}, \frac{1}{8}$) which they postulated to contain Ca was found to contain instead $0.9 \text{ Zr} + 0.1 \text{ Ti}$ distributed at two positions close to it. The atomic nature is confirmed by the bond-strength sum, which is 3.8 valence units no matter whether Ca or Zr is assumed to be at ($0, \frac{1}{4}, \frac{1}{8}$).

The random occupation of one of two closely spaced sites by a cation is unusual in fluorite-related oxides, although similar behaviour of a (Zr, Ti) cation has been found in zirconolite (Gatehouse, Grey, Hill & Rossell, 1981). There was no evidence in the electron diffraction patterns for doubling of any cell axes, as might occur if the occupancy of these sites was ordered. It can be seen from the figure that a cation at either

* A list of calculated and observed powder intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36333 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

position could be described as adopting triangular-prismatic coordination by O. However, the bond-strength sums show that such a cation is significantly underbonded (3.5 valence units), so that the two more remote O(3), which contribute 0.15 v.u. each, belong to the coordination figure. Bond-strength sums calculated for the structure with this cation at $(0, \frac{1}{4}, \frac{1}{8})$ differ significantly from those of the determined structure only for the atom O(3), whose bonding improves from 1.79 in the former case, to 1.96 v.u. Therefore, this study has allowed little insight into the unusual cation behaviour: the more precise results that could be expected from a single-crystal study may be of benefit in this regard.

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Structure d'un Trimétaphosphate–Tellurate de Rubidium Monohydraté: $\text{Te}(\text{OH})_6 \cdot \text{Rb}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$

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Abstract. $\text{Te}(\text{OH})_6 \cdot \text{Rb}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$, monoclinic, $P2_1/a$, $a = 15.56$ (1), $b = 8.358$ (3), $c = 13.72$ (1) Å, $\beta = 113.27$ (5)°, $Z = 4$. The structure has been solved by direct methods. The final R value is 0.04 for 1833 reflexions. As already described for trimetaphosphates–tellurates of sodium and potassium, P_3O_9 and TeO_6 anions are independent.

Introduction. Le sel de rubidium $\text{Te}(\text{OH})_6 \cdot \text{Rb}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$ est le troisième exemple de phosphate–tellurate renfermant un anion cyclique P_3O_9 . Son étude structurale montre que, conformément aux résultats des travaux antérieurs sur les sels de sodium: $\text{Te}(\text{OH})_6 \cdot 2\text{Na}_3\text{P}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ (Boudjada, Averbuch-Pouchot & Durif, 1981a) et de potassium: $\text{Te}(\text{OH})_6 \cdot \text{K}_3\text{P}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ (Boudjada, Averbuch-Pouchot & Durif, 1981b), les groupements TeO_6 sont indépendants des cycles trimetaphosphates P_3O_9 . Cette absence d'anions mixtes condensés phosphotellurates dans les sels cités ci-dessus se retrouve dans les monophosphates–tellurates précédemment étudiés: $\text{Te}(\text{OH})_6 \cdot \text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ et $\text{Te}(\text{OH})_6 \cdot 2(\text{NH}_4)_2\text{HPO}_4$ (Durif, Averbuch-Pouchot & Guitel, 1979), $\text{Te}(\text{OH})_6 \cdot \text{Rb}_2\text{HPO}_4 \cdot \text{RbH}_2\text{PO}_4$ (Averbuch-Pouchot, Durif & Guitel, 1979), $\text{Te}(\text{OH})_6 \cdot 2\text{Ag}_2\text{HPO}_4$ (Durif & Averbuch-Pouchot, 1981), $\text{Te}(\text{OH})_6 \cdot$

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- BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
 GATEHOUSE, B. M., GREY, I. E., HILL, R. J. & ROSSELL, H. J. (1981). *Acta Cryst.* **B37**, 306–312.
International Tables for X-ray Crystallography (1974). Vol. IV. Tables 2.2A and 2.3.1. Birmingham: Kynoch Press.
 PYATENKO, YU. A. (1971). *Izv. Akad. Nauk SSSR Neorg. Mater.* **7**, 630–633.
 PYATENKO, YU. A. & PUDOVKINA, Z. V. (1961). *Kristallografiya*, **6**, 196–199.
 ROSSELL, H. J. & SCOTT, H. G. (1975). *J. Solid State Chem.* **13**, 345–350.
 ROSSELL, H. J. & SCOTT, H. G. (1977). *J. Phys. (Paris)*, **38**, (Suppl. to No. 12), C7-28–C7-31.
 SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.

$2\text{TiH}_2\text{PO}_4 \cdot \text{Ti}_2\text{HPO}_4$ et $\text{Te}(\text{OH})_6 \cdot 2\text{TiH}_2\text{PO}_4$ (Averbuch-Pouchot & Durif, 1981) qui présentent la même caractéristique: les tétraèdres PO_4 et les groupements TeO_6 forment des entités séparées. Notons que cette particularité se retrouve dans les monoarséniates–tellurates isotopes des monophosphates–tellurates cités plus haut: $\text{Te}(\text{OH})_6 \cdot \text{Na}_2\text{HAsO}_4 \cdot \text{H}_2\text{O}$, $\text{Te}(\text{OH})_6 \cdot 2(\text{NH}_4)_2\text{HAsO}_4$ et $\text{Te}(\text{OH})_6 \cdot \text{Rb}_2\text{HAsO}_4 \cdot \text{H}_2\text{RbAsO}_4$ (Averbuch-Pouchot & Durif, 1979).

Les cristaux de $\text{Rb}_3\text{P}_3\text{O}_9 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$ sont des prismes monocliniques incolores; leur longueur peut atteindre 15 mm. Le cristal choisi pour recueillir les données de diffraction était un fragment de prisme, taillé approximativement sous la forme d'un cube d'arête $\approx 15/100$ mm. A l'aide d'un diffractomètre Philips PW 1100 utilisant la longueur d'onde $K\alpha$ de l'argent (0.5608 Å) monochromatisée par une lame de graphite, 2612 réflexions ont été mesurées parmi lesquelles 1833 indépendantes. Ces mesures ont été effectuées sur un domaine angulaire s'étendant de 3 à 20°(θ). Chaque raie était explorée en balayage ω à la vitesse de 0,02° s⁻¹ dans un zone angulaire de 1,20°; le fond continu était mesuré durant 10 s de part et d'autre de cette zone. Les deux réflexions de référence 218 et 218 n'ont subi aucune variation d'intensité durant la