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Structure refinement of calzirtite from Jacupiranga, Brazil

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ABSTRACT

The crystal structure of calzirtite, $Ca_2Zr_5(Ti_{1.5}Nb_{0.29}Fe_{0.18})O_{16}$, $a = 15.094(2)$, $c = 10.043(2)$ Å, space group $I4_1/acd$, Z = 8 has been refined by the method of least-squares using 1327 reflections to an R index of 0.040 ($R_w = 0.047$). The data were collected on a four-circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation. The cations occupy fluorite-type positions in the tetragonal cell. They are ordered into planes parallel to (010) and form two layers containing Ti, Ca, and Zr sandwiched between layers of 7- and 8-coordinated Zr. At the 8-coordinate site, Zr shows a statistical displacement off special position 8(b). Corner-linked TiO_6 octahedra form chains that zig-zag parallel to c. The results are in agreement with those obtained from a powder refinement of synthetic calzirtite by Rossell (1982, *Acta Crystallographica,* B38, 593–595).

INTRODUCTION

Calzirtite, $Ca_2Zr_5Ti_2O_{16}$, occurs in several localities in association with zirconolite ($CaZrTi_2O_7$), a key compound in the nuclear waste ceramic SYNROC (Ringwood et al., 1979a, 1979b). The first occurrence of calzirtite was reported by Zdorik et al. (1961) in metasomatic calcite-forsterite-magnetite rocks from an alkaline-ultrabasic massif in Eastern Siberia. Pyatenko and Pudovkina (1961) showed the structure to be an anion-deficient superstructure phase closely related to fluorite arrangement. A recent refinement of synthetic calzirtite (Rossell, 1982) using powder diffraction data resulted in a change in the O2 oxygen position and significant cation ordering at the cation positions. The results of Rossell were not available to us at the start of this work.

CRYSTAL-STRUCTURE ANALYSIS

Chemical analyses of calzirtite from Jacupiranga, Brazil (Melcher, 1966), and Kaiserstuhl, Germany, were done using an energy-dispersive electron-microprobe operating at 15 kV, 3-nA current, and count time of 100 s. Data reduction was done by the method outlined by Ware (1981). The samples from Kaiserstuhl carbonatite contain more Nb than the Jacupiranga samples.

Single-crystal Weissenberg and precession photographs of samples from Brazil showed a tetragonal cell with Laue symmetry $4/mmm$; the systematic absences hkl, $h + k + l = 2n$; for $hk0$, $h = 2n$; for $h0l$, $l = 2n$; and for hhl, $2h + l = 4n$ define the space group uniquely as $I4_1/acd$.

The crystal used for data collection was a transparent, pale-orange cube. The crystal was mounted on an automatic Picker FACS-1 four-circle diffractometer, with the c-axis approximately parallel to the ϕ axis of the machine. Unit-cell dimensions and crystal orientation matrix were obtained by least-squares refinement of the setting angles of twelve centered reflections having 2θ values close to 50°. Crystal data are given in Table 1.

Intensity data were measured by the θ–2θ continuous-scan technique with a scan speed of 2° min^{-1} (2θ) and range from 0.8° below the $K\alpha_1$ to 0.8° above the $K\alpha_2$ peak for the reflection concerned. Stationary 10-s background counts were made at each end of the scan range and were assumed to vary linearly between these extremes. Three standard reflections, 600, 060, 004 did not show any significant variations in intensity throughout the course of the experiment. Intensities were collected for 4017 reflections having 2θ values between 3 and 80° for all positive hkl except those that were absent from the I-centering condition. The data were corrected for absorption (De Meulenaer and Tompa, 1965), sorted and averaged and reduced to structure amplitudes in the usual way. Reflections for which $I/\sigma(I) < 3.0$ were classed as unobserved. A total of 1327 unique observed reflections were available for subsequent structural analysis. The statistical discrepancy value for this data set R_s ($= \Sigma\,\sigma/\Sigma|F_o|$, where σ is

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Table 1. Analytical and crystal data for calzirtite

	1	2	Crystal Data
Nb_2O_5	8.5	4.4	a 15.094(2)Å
TiO_2	10.5	13.3	c 10.043(2)
ZrO_2	67.0	68.2	V 2288(1)Å^3
*FeO	1.6	1.5	D_c 5.24 gcm^{-3}
CaO	11.5	12.4	Z 8
Σ	99.1	99.8	μ 6.79 mm^{-1}
Nb	0.59	0.29	Rad/Mon. Mo/Gr.
Ti^{4+}	1.20	1.50	Crystal
Fe^{2+}	0.18	0.18	Size 0.075mm
Σ	1.97	1.97	Space
Zr^{4+}	5.03	5.03	Group $I4_1/acd$
Ca^{2+}	1.93	2.00	R(final) 0.040
O^{2-}	16	16	R_w(final) 0.049

+ 1: Kaiserstuhl, Germany; 2: Jacupiranga, Brazil; all crystal data for Jacupiranga sample. * Iron as FeO assumed.

Table 3. Interatomic distances (Å) and O–M–O angles (°) of Jacupiranga calzirtite

M1	-O5	2.034(3)	2x
	O5	2.073(3)	2x
	O4	2.247(3)	2x
	O4	2.704(3)	2x
Mean		2.265	
M1	-M1	0.539(1)	
M2	-O1	1.888(2)	2x
	O3	1.952(3)	2x
	O4	1.988(3)	2x
Mean		1.943	
M3	-O2	2.303(3)	2x
	O5	2.415(3)	2x
	O1	2.532(3)	2x
	O3	2.557(3)	2x
Mean		2.452	
M4	-O5	2.056(3)	
	O2	2.086(2)	
	O3	2.142(3)	
	O4	2.170(3)	
	O4	2.178(3)	
	O3	2.182(3)	
	O5	2.183(3)	
Mean		2.142	

	O1 - M2 -	O1^1	88.4(2)
		O3	98.4(1)
		O3^1	88.4(1)
		O4	94.6(1)
	O1 - M2 -	O3	88.4(1)
		O3^1	98.4(1)
		O4^1	94.6(1)
	O3 - M2 -	O4	93.1(1)
		O4^1	79.7(1)
	O3 - M2 -	O4	79.7(1)
		O4^1	93.1(1)
	O4 - M2 -	O4^1	82.6(2)
	M2-M2^1		3.524(1)
M2^1-M4	M4^1-M2		3.809(1)
M2-M4	M2^1-M4^1		3.863(1)
	M4^1-M4^1		3.867(1)
	O1-O4, O1-O4^1		2.848(4)
	O4-O3, O4^1-O3^1		2.860(4)
	O1-O3, O1-O3^1		2.908(4)
	O4-O3^1, O4^1-O3		2.982(4)
	O4-O2, O4^1-O2		3.088(4)
	O3-O2, O3^1-O2		3.084(4)

the error contribution to $|F_o|$ from counting statistics alone) is 0.025. Transmission factors for F_o calculated by the analytical method of De Meulenaer and Tompa (1965), varied from 0.790 to 0.822.

Computer programs for data reduction and structure solution are part of the ANUCRYS package implemented on the UNIVAC 1100/42 ANU by Drs. P. O. Whimp and D. Taylor.

STRUCTURE SOLUTION AND REFINEMENT

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography,* volume 4 (1974) and were corrected for both real and imaginary anomalous components. The refinement was carried out using the full-matrix least-squares program SFLS (Prewitt, 1966), which minimizes the function $\Sigma\, w(|F_o| - k|F_c|)^2$, where k is an overall scale factor and w is the weight of an observation taken as unity in the initial stages and later as $w(hkl) = 1/\sigma_2^2$ where $\sigma_2 = \{\sigma_1^2 + 0.25[0.03(F_o)]^2\}^{1/2}$.

Refinement using the coordinates and site occupancies of Pyatenko and Pudovkina (1961) was unsuccessful. A second refinement using only the cation positions and occupancies converged to an R index of 0.25. A three-dimensional difference Fourier map showed that the O2

Table 2. Atomic coordinates and thermal parameters for Jacupiranga calzirtite

ATOM	SITE	OCCUPANCY	X	Y	Z	Beq. (Å^2)
M(1)	16(f)	0.5 Zr	0.01264(4)	0.01264(4)	1/4	0.93
M(2)	16(f)	0.75Ti+0.1Fe+0.15Nb	0.16809(4)	0.16809(4)	1/4	0.50
M(3)	16(f)	1.0 Ca	0.33281(5)	0.33281(5)	1/4	0.56
M(4)	32(g)	1.0 Zr	0.16152(2)	0.01780(2)	0.48578(4)	0.37
O(1)	16(e)	1.0 Oxy	1/4	0.2130(3)	1/8	0.87
O(2)	16(e)	1.0 Oxy	1/4	0.4303(3)	1/8	0.56
O(3)	32(g)	1.0 Oxy	0.2433(2)	0.0776(2)	0.3309(3)	0.93
O(4)	32(g)	1.0 Oxy	0.1135(2)	0.0827(2)	0.1236(3)	0.95
O(5)	32(g)	1.0 Oxy	0.0655(2)	0.0795(2)	0.6193(3)	0.84

ATOM	U11*	U22	U33	U12	U13	U23
M(1)	0.0140(11)	0.0140(11)	0.0073(6)	-0.0064(12)	0.0011(10)	-0.0011(10)
M(2)	0.0065(5)	0.0065(5)	0.0060(4)	0.0001(6)	-0.0006(5)	0.0006(5)
M(3)	0.0069(6)	0.0069(6)	0.0074(6)	0.0001(8)	-0.0007(7)	0.0007(7)
M(4)	0.0047(12)	0.0041(2)	0.0051(2)	0.0002(5)	0.0010(4)	-0.0001(2)
O(1)	0.008(5)	0.014(2)	0.011(3)	0	0	-0.003(3)
O(2)	0.008(4)	0.008(2)	0.006(2)	0	0	-0.000(2)
O(3)	0.017(10)	0.009(2)	0.010(2)	-0.006(4)	0.001(3)	-0.000(2)
O(4)	0.014(10)	0.011(2)	0.011(2)	-0.002(5)	-0.000(4)	0.000(2)
O(5)	0.017(10)	0.008(2)	0.007(2)	-0.002(4)	-0.001(3)	-0.000(2)

$$*\exp[-2\pi^2(U_{11}h^2\underline{a}^{*2}+U_{22}k^2\underline{b}^{*2}+U_{33}l^2\underline{c}^{*2}+2U_{12}hk\underline{a}^*\underline{b}^*+2U_{13}hl\underline{a}^*c^*+2U_{33}kl\underline{b}^*c^*)]$$

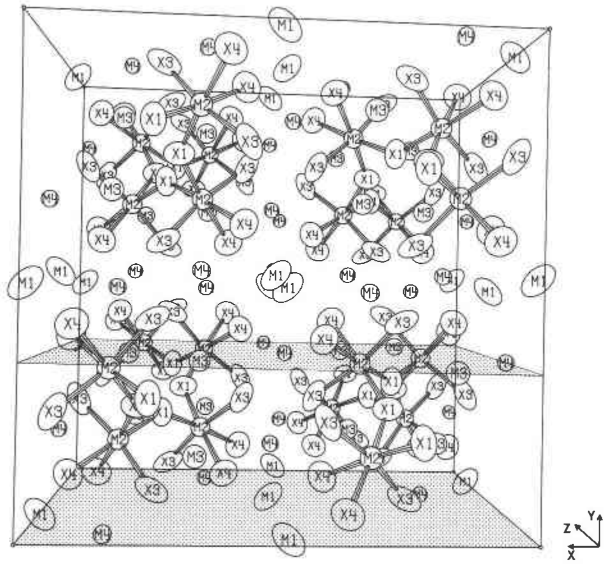

Fig. 1. ORTEP II (Johnson, 1976) drawing of calzirtite showing all metal atoms in the unit cell. The octahedral coordination spheres are also illustrated. Two planes are shaded at $y = 0$ and $y = \frac{1}{3}$. M1 = Zr; M2 = Ti, Fe, Nb; M3 = Ca; M4 = Zr; X1–X5 = oxygen.

oxygen was incorrectly placed by Pyatenko and Pudovkina (1961), the site occupancies were not correct, and there was positional disorder at the M1 site. Adjustment of site-occupancies, splitting of the M1 site and refinement of all variables resulted in an R index of 0.049 for an isotropic thermal model.

Conversion to anisotropic temperature factors reduced the R and R_w indices to 0.040 and 0.049 respectively. A correction for secondary extinction (Zachariasen, 1963) was also included and refined to a final value of 4.6(2) × 10^{-4}. An analysis of $w(|F_o| - |F_c|)$ vs. F_o and $\sin\theta/\lambda$ showed no systematic trends, indicating an adequate weighting scheme. The standard deviation of an observation of unit weight was 1.76.

A difference Fourier map calculated at this stage showed the largest residual peak to be 2 e Å^{-3} at (0.03, 0.03, 0.25). Final atomic parameters are presented in Table 2. Bond lengths and angles are given in Table 3, and structure factors are listed in Table 4.[2]

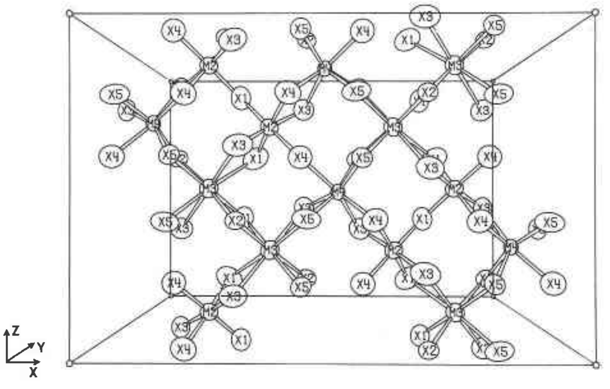

Fig. 2. Diagram of the plane of metal atoms shaded in Fig. 1 at $y = \frac{1}{3}$. The completed coordination spheres of the cations have been included.

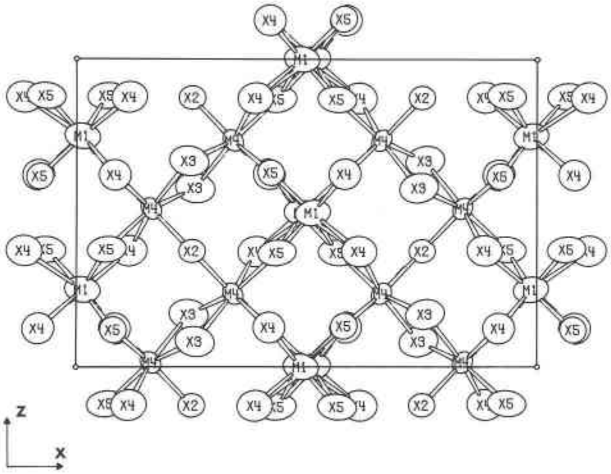

Fig. 3. Drawing of the plane of metal atoms at $y = 0$ in Fig. 1. The coordination spheres of the cations are also shown.

Description of the structure

This structure is a tetragonal distortion of the fluorite-type structure (Fig. 1). The cations are ordered into planes parallel to (010) and form two layers (at $y = \frac{1}{6}$ and $\frac{1}{3}$) containing M2, M3, and M4 cations sandwiched between layers of M1 + M4 cations (at $y = 0$ and $\frac{1}{2}$). Figure 2 shows the coordination scheme of the shaded layer at $y = \frac{1}{3}$ (Fig. 1). The plane consists of empty and filled M4(Zr) polyhedra in seven-fold coordination with oxygen, alternating with two rows of M2 octahedra and M3 cubes parallel to (001). The interstices in the M2 and M3 rows are also vacant sevenfold polyhedra. Two layers of M2,

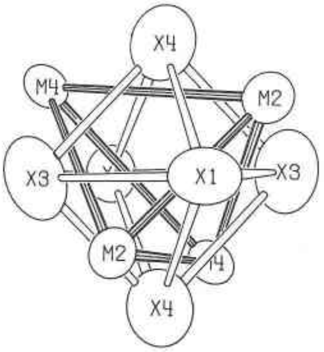

Fig. 4. Illustration of the cation tetrahedron (M2, M4) and anion octahedron (X1, X2, X3, X4) surrounding the vacant anion site at ($\frac{1}{4}$,0.5833,$\frac{1}{8}$).

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[2] To obtain a copy of Table 4 order Document AM-86-304 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit $5.00 in advance for the microfiche.

M3, and M4 cations combine to form zig-zag strings of M2 octahedra along *z* (Fig. 1). In the unit cell, 16 Ti(Nb,Fe) atoms occupy the octahedral M2 sites, 16 Ca atoms occupy the cubic M3 sites, and the seven-cornered diminished cubes (M4) contain 32 Zr atoms. A second type of layer at $y = 0$ consists of empty and full (M1) cubes containing Zr atoms and vacant and full (M4) sevenfold polyhedra in rows parallel to (001) (Fig. 3).

An unusual feature of calzirtite is the splitting of the M1(Zr) site within a distorted cube of oxygen atoms. Bond-strength calculations by Rossell (1982) showed Zr in triangular prismatic coordination to be significantly underbonded, the two more distant anions of the cube being required to satisfy the bond-strength requirements on Zr. However, the cause of the cation displacement remained unresolved. Using the more precise data of this study, bond-strength sums around Zr show that this cation is underbonded (3.80 valence units) in triangular prismatic (sixfold) coordination and fully bonded in eightfold coordination (4 valence units using the bond-strength parameters of Brown and Wu, 1976).

The metal atoms surrounding the anion vacancy at (¼,0.5833,⅛) in calzirtite form a tetrahedron and the oxygen anions form an octahedron (Fig. 4). In the ideal fluorite arrangement for calzirtite, metal-metal and oxygen-oxygen distances would be approximately 3.55 Å. The cation-cation distances of calzirtite (Table 3) are larger by 0.3 Å and the oxygen-oxygen lengths are smaller by 0.5 Å. This type of relaxation is also found in zirconolite (Rossell, 1980) and in many other anion-deficient fluorite-related superstructures (Thornber et al., 1968, $Zr_5Sc_2O_{13}$, $Zr_3Sc_4O_{12}$; Thornber and Bevan, 1970, $Zr_3Yb_4O_{12}$; Allpress et al., 1975, $CaHf_4O_9$; Rossell and Scott, 1975, $CaHf_7O_{16}$; Rossell, 1976; Rossell, 1979, Ln_3MO_7 where Ln = REE, Y, or Sc and M = Nb, Sb, or Ta).

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