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Crystal Structure of Ordered Calzirtite $Ca_2Zr_5Ti_2O_{16}$

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Abstract – The crystal structure of calzirtite $Ca_2Zr_5Ti_2O_{16}$ from the Kusa titanium–magnetite deposit at the South Ural massif has been studied ($a = 15.189$, $c = 10.111$ Å, sp. gr. $I4_1/acd$, $Z = 8$, Enraf–Nonius diffractometer, 772 reflections with $|F| > 3\sigma(F)$, MoK_α-radiation, $R_{hkl} = 0.0356$). The splitting of the Zr position with the cubic coordination observed earlier is confirmed. A distinctive feature of the specimen studied in comparison with the specimens investigated earlier is the ordered distribution of cations over the positions of an octahedron, a seven-vertex polyhedron, and cubes of two types.

The model of the structure of the mineral calzirtite was first suggested by Pyatenko and Pudovkina in 1961 [1] as a fluorite-type structure with a thrice enlarged *a* and doubly enlarged *c* parameters. The structure was suggested as being built by Ti-octahedra, seven-vertex Zr polyhedra, and two types of cubes filled with Ca and Zr plus Ca, respectively. Later on, a more detailed study was performed on a synthesized powder specimen (the synthesis temperature 1200°C) with the use of 112 reflections ($R = 0.031$) [2]. This study indicated somewhat different cation distribution over the structure positions: an octahedron was occupied by a Ti atom with a small addition of Zr, and one of the cubes [the *M*(1) position] was occupied by Zr (85%) plus Ti (15%). In fact, this position is split into two positions spaced by 0.51 Å filled with equal probabilities. The structural study of a single crystal of the mineral from ultrabasic alkali rocks from the Jacupiranza deposit in Brazil [3] confirmed the splitting of the *M*(1) position, which, in this case, could be associated with the high crystallization temperature of the magmatic rocks (~800°C). Nevertheless, it is believed [3] that the position in an octahedron is occupied by Ti together with Nb and Fe atoms that participate in the isomorphous substitution of Ti, whereas the *M*(1) cube is filled with Zr atoms alone.

The object of the present study was a calzirtite specimen from the rodingite mineral association of the Zelenets mine of the South Ural massif's Kusa titanium–magnetite deposit. The main accompanying minerals in the specimen are clinochlore, hydrotalcite, manasseite, perovskite, magnesioferrite, etc. Calzirtite forms small colorless inclusions in finely grained perovskite and clinochlore aggregates. The powder X-ray diffraction patterns (obtained on a DRON-3.5 diffractometer, CoK_α-radiation) was close to the reference pattern of calzirtite, but had several weak superstructural reflections. The chemical microprobe analysis (CAMEBAX) of the specimens performed by I.M. Kulikova (from the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of the Russian Academy of Sciences) showed the presence of (in wt %): ZrO_2, 67.55; CaO, 12.51; TiO_2, 18.01; HfO_2, 1.59; ThO_2, 0.01; V_2O_3, 0.01; FeO, 0.09; MgO, 0.03; MnO, 0.03; SrO, 0.59; Ce_2O_3, 0.03; Yb_2O_3, 0.01; and K_2O, 0.01; which leads to the formula $(Ca_{1.97}Sr_{0.05}Fe_{0.01}Mg_{0.01})_{\Sigma 2.04} \cdot (Zr_{4.84}Hf_{0.07})_{\Sigma 4.91}Ti_{2.05}O_{16}$ characterized by the absence of any noticeable amounts of isomorphous impurities that can be written in an idealized form as $Ca_2Zr_5Ti_2O_{16}$.

The parameters of the tetragonal unit cell were determined and refined by 22 reflections on a CAD-4F Enraf-Nonius automatic diffractometer (MoK_α radiation, graphite monochromator) to yield: $a = 15.189(2)$, $c = 10.111(2)$ Å, $V = 2332.7$ Å^3, $Z = 8$, $\rho_{calc} = 5.06$ g/cm^3. The space group was determined from the extinctions as $I4_1/acd$. The experimental set of diffraction reflections obtained within the half-sphere of the reciprocal space ($\sin\theta/\lambda < 0.7$ Å^{-1}) on a $0.4 \times 0.3 \times 0.35$ mm large crystal on the same diffractometer had 5796 reflections with $I > 2\sigma(I)$. Upon averaging over the symmetrically equivalent reflections ($R_{av} = 0.046$) the set had 772 reflections with $|F| > 3\sigma(F)$. All the calculations were performed by the AREN system of programs [4].

We expected the mineral under study to be isostructural to calzirtite from Brazil [3], therefore we performed the refinement by using the initial coordinates from [3], but with the use of the the atomic-scattering curves (*f*-curves) for Zr and Ti in the cationic *M*-positions and with the Zr(1) atom being placed into the center of inversion. The least-squares procedure in the isotropic approximation decreased the *R*-factor from 0.31 down to 0.23, whereas the thermal parameter for Zr(1) with the cubic coordination was twice as high as that for Zr(2) in the seven-vertex polyhedron. The displacement of Zr(1) from the center of inversion to the general position with the occupancy 0.5 provided the structure

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Table 1. Positional and thermal parameter

Atom	x/a	y/b	z/c	B_{eq}, Å^2
Zr(1)	0.5134(1)	0.2366(1)	0.8750(1)	1.50(3)
Zr(2)	0.8383(1)	0.2321(1)	0.3604(1)	1.02(2)
Ti	0.3320(1)	0.0820(1)	0.3750(1)	0.55(3)
Ca	0.6678(1)	0.0822(1)	0.3750(1)	0.64(3)
O(1)	0.2435(2)	0.1719(2)	0.7054(3)	0.75(6)
O(2)	0.0654(2)	0.1707(2)	−0.0059(3)	0.77(6)
O(3)	0.6141(2)	0.1667(2)	0.0014(3)	0.96(6)
O(4)	0.2502(1)	0.0373(3)	0.4999(1)	0.78(8)
O(5)	0.2498(1)	0.1806(3)	0	0.70(8)

Table 2. Interatomic distances (Å)

Ti-octahedron		Zr-cube	
Ti–O(4)	1.897(1) × 2	Zr(1)–O(2)	2.046(3) × 2
O(1)	1.959(3) × 2	O(2)	2.087(3) × 2
O(3)	1.989(3) × 2	O(3)	2.258(3) × 2
	⟨1.948⟩		⟨2.130⟩
		Zr(1)	0.575(1)
Zr-seven-vertex polyhedron		**Ca-cube**	
Zr(2)–O(2)	2.068(3)	Ca–O(5)	2.319(3) × 2
O(5)	2.101(1)	O(2)	2.444(3) × 2
O(1)	2.154(3)	O(4)	2.539(3) × 2
O(3)	2.182(3)	O(1)	2.571(3) × 2
O(1)	2.199(3)		⟨2.491⟩
O(2)	2.199(3)		
O(3)	2.199(3)		
	⟨2.157⟩		

refinement to R_{hkl} = 0.11 and with allowance for absorption (μ = 64.7 cm^{-1}) by the DIFABS program [5] to R = 0.054, with the thermal parameter of the Zr(1) atom being normalized. The refinement in the anisotropic approximation with allowance for extinction yielded R_{hkl} = 0.0356.

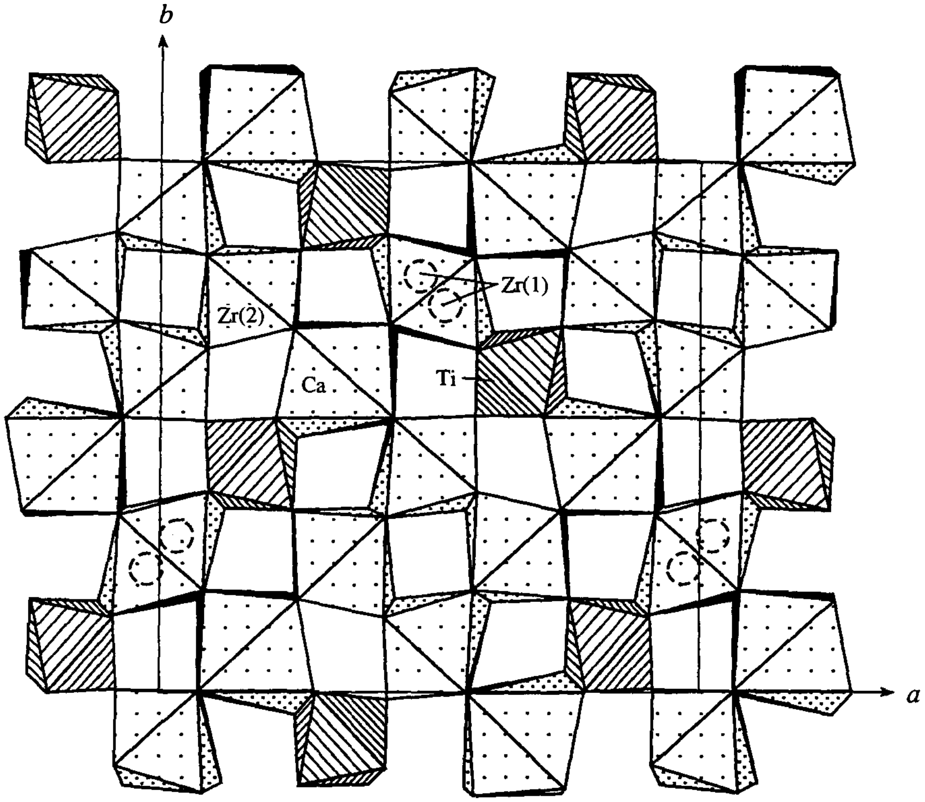
The final atomic coordinates are listed in Table 1, and the corresponding interatomic distances are given in Table 2.

Thus, in accordance with data [2, 3], Zr(1) statistically occupies two positions at a close distance from the center of inversion (0.28 Å) (see the figure). As shows the local valence balance performed by the Brown method [6], the nearest environment of the Zr(1) atom can be considered either as a trigonal prism with the distances to the O atoms ranging within 2.05 - 2.26 Å or as a cube with two additional anions at a distance of 2.75 Å. The second version is characterized by a slightly worsened local balance at the O(3) anion (the corresponding value in Table 3 is given in brackets), but shows better valence balance at the cation (3.8 instead of 3.6). The splitting of the M(1) position observed first on powder patterns and confirmed by the studies on single crystals is interpreted in [2, 3] as a tendency towards attaining a valence balance. At the same time, a more probable reason of the splitting seems to be different dimensions of a large polyhedron (a cube) and a Zr atom. This discrepancy is even more pronounced for the Ti atom, and thus makes its entering into a cube together with Zr (as was indicated in [2]) to be even less probable. Large dimensions of a Zr-polyhedron M(1) seem to determine a somewhat overestimated B_{eq} value, which leads to to an assumption on partial substitution of Zr atoms by Ti.

Table 3. Local valence balance at anions (according to Brown)

Atom	Zr(1)	Zr(2)	Ti	Ca	V_i	$\|\Delta\| i$
O(1)		0.54 + 0.48	0.68	0.20	1.90	0.10
O(2)	0.69	0.68 + 0.48		0.28	2.13	0.13
O(3)	0.41	0.50 + 0.48	0.62		2.01	0.01
	(+0.11)				(2.12)	(0.12)
O(4)			0.80 × 2	0.21 × 2	2.02	0.02
O(5)		0.63 × 2		0.39 × 2	2.04	0.04
Σ					10.10	0.30
					(10.21)	(0.41)

Note: D = 3(4)%, $|\Delta|_{max}$ = 6.5%.



A fragment of the calzirtite structure projected onto the (001) plane; Ti octahedra are hatched, the dot lines indicate seven-vertex polyhedra and cubes, the circles denote the split Zr positions.

Of all the polyhedra in the calzirtite structure, the titanium octahedron seems to be the most regular one. The "cubes" occupied by Zr plus Ca atoms are strongly distorted and are, in fact, slightly twisted tetragonal prisms. The Ti-octahedron is connected to Zr(2) seven-vertex polyhedra by its apical vertices and to the Ca and Zr(1) prisms by the edges; the seven-vertex polyhedra and prisms share edges. Thus, all the polyhedra participate in the formation of a dense mixed framework.

The distinctive feature of the structure is complete ordering of the cation positions (Table 4). The disorder indicated in the earlier studies seems to be associated with the conditions of the structure formation at elevated temperature and more complicated chemical composition of the specimens used.

Table 4. Chemical composition and mean distances (Å) in cation polyhedra of the calzirtite structures

Polyhedron; ⟨*M*–O⟩	[1]	[2]	[3]	Present study
M(1)	Ca	$Zr_{0.86}Ti_{0.14}$	Zr	Zr
M(2)	Zr	Zr	Zr	Zr
M(3)	Ti	$Ti_{0.95}Zr_{0.07}$	$Ti_{1.5}Nb_{0.29}Fe_{0.18}$	Ti
M(4)	$Ca_{0.41}Zr_{0.59}$	Ca	Ca	Ca
⟨*M*(1)–O⟩		2.26	2.265	2.284
⟨*M*(2)–O⟩		2.16	2.142	2.157
⟨*M*(3)–O⟩		1.95	1.943	1.948
⟨*M*(4)–O⟩		2.47	2.452	2.468

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