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The crystal structure of an Al-rich titanite from Grisons, Switzerland

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Abstract

The structure of an Al-rich titanite has been refined in several space groups to provide data on a natural titanite and to evaluate the structural effects of the coupled substitution $(Al,Fe)^{3+} + (OH,F)^{-} = Ti^{4+} + O^{2-}$. Titanite from Grisons, Switzerland, $Ca(Ti^{4+}_{0.90}Al^{3+}_{0.09}Fe^{3+}_{0.01})O_{0.98}SiO_{3.96}(OH_{0.08}F_{0.02})$, is monoclinic with $a = 7.050(3)$, $b = 8.681(4)$, and c 6.539(2)Å and $\beta = 113.90(3)°$. Anisotropic refinement in space group $A2/a$ ($R_w = 0.048$) yielded results similar to those obtained by Mongiorgi and di Sanseverino (1968) for titanite from Zillertal except that the mean Ti–O bond length is smaller due to substitution of Al for Ti in the octahedral site. The orientation of the maximum thermal vibrational displacement for most atoms subparallel to **a** reflects positional disordering due to the development of a domain texture. The details of the $P2_1/a$ refinement ($R_w = 0.065$) are comparable to those of synthetic $P2_1/a$ titanite (Speer and Gibbs, 1976). Despite extensive $Al^{3+} \rightarrow Ti^{4+}$ substitution, the alternating long and short Ti–O(1) bond lengths, (1.970 and 1.768Å, Fig. 1) which reflect the amount of displacement of the Ti atom from the geometric center of the Ti octrahedron are the same as for the synthetic $P2_1/a$ titanite at 25°C (Taylor and Brown, 1976). The extreme distortion of some of the Si and Ti polyhedra and unreasonable bond distances cast doubt on the reliability of refinement in space group $P2_1$ constrained by only 21 weak maxima of type $h0l$, h = odd. The weak maxima are the result of diffuse h-relplanes. It is possible that the h-relplanes are due either to linear positional ordering or to chemical cation ordering in the octahedral sites.

Introduction

The space group of synthetic titanite, $CaTiOSiO_4$, is $P2_1/a$ (Robbins, 1968; Speer and Gibbs, 1976), the diffraction pattern showing sharp but weak $k + l$ = odd reflections in violation of the A-centering of the previously reported space group $A2/a$ of natural titanites (Zachariasen, 1930; Mongiorgi and di Sanseverino, 1968). Refinement of the structure (Speer and Gibbs, 1976) showed that the sharp but weak $k + l$ = odd reflections are due to displacement of the Ti atoms from the geometric centers of the octahedra.

The observation of diffuse $k + l$ = odd reflections on long exposure single crystal photographs of natural titanites led Speer and Gibbs (1976) to conclude that the structure of stoichiometric synthetic titanite consists essentially of a single domain of $P2_1/a$ symmetry while that of natural titanite consists of a large and variable number of $P2_1/a$ domains related to one another by half turn parallel to **b**. This brings all atoms in two neighboring domains into coincidence except Ti which in effect is linearly disordered, resulting in the observed diffuse streaking of the $k + l$ = odd reflections. Out-of-step linear domain formation in natural titanites appears to be favored by the substitution, $(Al,Fe)^{3+} + (OH,F)^{-} = Ti^{4+} + O^{2-}$, with the $k + l$ = odd reflections becoming unobservable above ~ 20 mole percent substituents (Higgins and Ribbe, 1976). The quasi-mirror displacement of the "Ti" atoms either towards or away from the domain boundaries (Fig. 4 in Taylor and Brown, 1976) provides the necessary charge balance at the sites of R^{3+} and OH/F substitution, respectively. The present study was undertaken to determine the effects of extensive Al^{3+} for Ti^{4+} substitution on the titanite structure.

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[1] To obtain a copy of Table 1, order document AM-84-240 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, DC 20009. Please remit $5.00 in advance for microfiche.

0003–004X/84/0708–0725$02.00

Experimental

A titanite crystal (0.11 × 0.11 × 0.14 mm) of composition

$$Ca(Ti_{0.90}Al_{0.09}Fe^{3+}_{0.01})O_{0.98}SiO_{3.96}(OH_{0.08}F_{0.02})$$

from Grisons, Switzerland (VPI&SU-43; Higgins and Ribbe, 1976) was used for data collection. Grisons titanite was chosen because the substitution is primarily $Al^{3+} + OH^- \rightarrow Ti^{4+} + O^{2-}$, whereas in samples having more extensive substitution (up to 24 mole% octahedral substituents; Higgins and Ribbe, 1976), Fe^{3+} and F^- as well as Al^{3+} and OH^- are major substituents. Consistent with earlier observations (Higgins and Ribbe, 1976) only the more intense reflections compatible with $A2/a$ symmetry were observable even on long exposure (100 hours) precession and Weissenberg photographs. A 140 hour Laue photograph taken down the c-axis of the intensity crystal showed only two very weak and diffuse h-relplanes of modulated intensity. The unit cell parameters a = 7.050(3), b = 8.681(4), c = 6.539(2)Å and β = 113.90(3)° were obtained by least squares refinement of 12 high-angle reflections (2Θ > 50°) collected using a Picker 4-circle diffractometer and Mo$K\alpha$ radiation.

Thirty-four hundred and one reflection intensities in the quadrants $\bar{h}\bar{k}l$ and $h\bar{k}l$ (2Θ = 5–90°) were collected using a 0.05% 2Θ step scan, a 2-second step count and a 20-second background count. Because of the possible presence of weak maxima in the diffuse h-relplanes, lattice extinctions were neglected during data collection. As a result weak $k + l$ = odd maxima violating A-centering and very weak $h0l$, h = odd maxima violating a-glide symmetry were subsequently observed. The $h0l$, h = odd reflections were not only weaker but significantly fewer in number (21) than the $k + l$ = odd reflections (138). Three standard reflections measured every 40 reflections showed no significant change with time. The data were corrected for Lorentz and polarization effects and absorption (μ = 39 cm^{-1}). Symmetry equivalent structure factors were averaged and those for which $F_o < 3\sigma(F_o)$ were rejected leaving 1221 structure factors for refinement. Since it was likely that the observed weak $k + l$ = odd and $h0l$, h = odd reflections were contributions from the diffuse h-relplanes of modulated intensity commonly observed in natural titanites (Speer and Gibbs, 1976), structure refinement was first undertaken in space group $A2/a$ and, then in subsequently lower symmetry space groups ($P2_1/a$ and $P2_1$) as required by the addition of these weak maxima to the data set.

Refinement was carried out using a modified version of ORFLS (Busing et al., 1962). The form factor tables corrected for anomalous dispersion (Vol. 3, International Tables for X-ray Crystallography) were constructed from the data of Doyle and Turner (1968) for neutral atoms. The observed structure factors (F_o) were weighted on the basis of $1/\sigma^2_{Fo}$, where σF_o is the standard deviation of F_o.

A2/a refinement

Refinement was initiated in space group $A2/a$ using the atom positions of Mongiorgi and di Sanseverino (1968) and omitting the 159 weak $k + l$ = odd and $h0l$, h = odd reflections. Preliminary cycles of refinement varying scale factors (one for

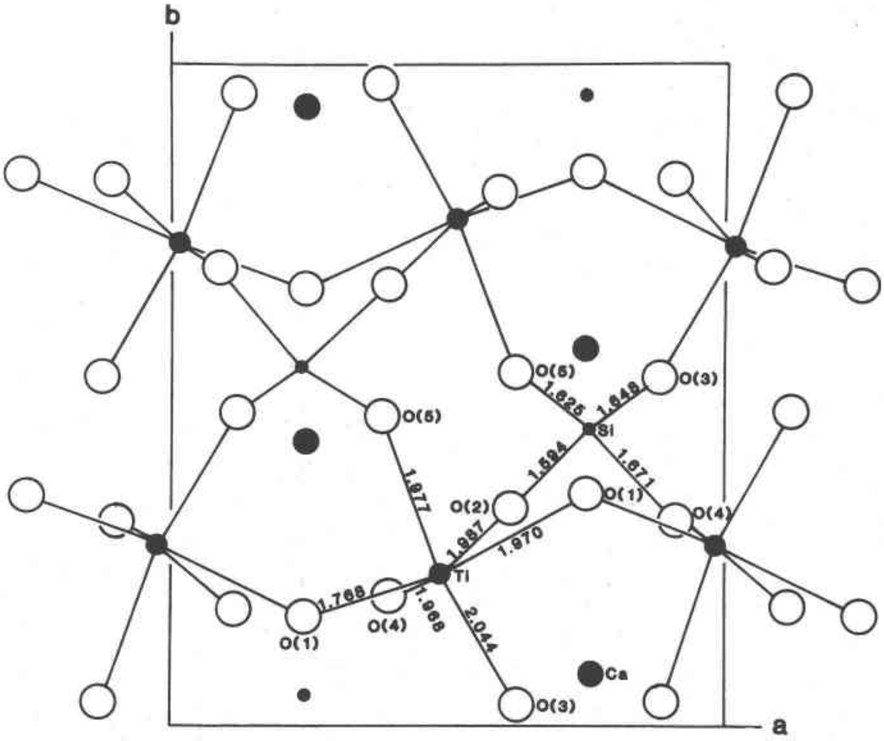

Fig. 1. The $P2_1/a$ structure of Grisons titanite projected on (001) showing the details of octahedral and tetrahedral coordination.

each of two filter thicknesses), positional parameters, and temperature factors revealed a secondary extinction problem. Twelve reflections for which $F_c - F_o$ was greater than 10% of F_o were subsequently removed from the refinement and the refinement rapidly converged to $R = 0.061$ and $R_w = 0.048$ using an anisotropic temperature factor model. The observed and calculated structure factors are given in Table 1,[1] atom positional and anisotropic thermal parameters in Table 2, magnitudes and orientations of the thermal ellipsoids in Table 3 and selected interatomic distances and angles in Table 4.

Table 3. Magnitudes and orientations of principal axis of the thermal ellipsoids for Grisons titanite, space group *A2/a*

Atom	Axis r_i	rms amplitude, Å	Angle (°) with respect to: +a	+b	+c
Ca	1	0.063(2)*	90	0	90
	2	0.071(2)	100(1)	90	146(1)
	3	0.170(2)	10(1)	90	124(1)
Ti	1	0.061(2)	91(5)	83(13)	24(1)
	2	0.067(2)	71(1)	160(6)	91(13)
	3	0.142(2)	19(1)	71(1)	114(1)
Si	1	0.051(4)	90	0	90
	2	0.065(3)	100(62)	90	146(62)
	3	0.067(5)	10(62)	90	124(62)
O(1)	1	0.066(1)	1(9)	90	115(9)
	2	0.072(6)	90	180	90
	3	0.104(5)	89(9)	90	25(9)
O(2)	1	0.056(5)	68(4)	112(6)	51(6)
	2	0.083(5)	73(8)	145(8)	125(7)
	3	0.107(5)	28(6)	64(8)	122(6)
O(3)	1	0.071(4)	93(44)	50(34)	132(55)
	2	0.075(7)	137(15)	61(40)	44(56)
	3	0.090(4)	48(13)	54(9)	82(13)

*Estimated standard deviations in parentheses refer to the last decimal place.

P2₁/a refinement

Prior to structure refinement in space group $P2_1/a$, 138 weak and diffuse $k + l$ = odd reflections were added to the data set. Because of the linear disordering produced by the domain texture, these "reflections" are only maxima in reciprocal lattice planes of modulated intensity (Speer and Gibbs, 1976) and, therefore, represent only a limited amount of data. This is in sharp contrast to the $k + l$ = odd data used in the refinement of the $P2_1/a$ structure of synthetic titanite where in the absence of a domain texture the reflections are discrete intensity maxima.

The starting positional parameters were those of synthetic $P2_1/a$ titanite (Speer and Gibbs, 1976). The coordinate and isotropic temperature factor refinement rapidly converged to $R = 0.085$ and $R_w = 0.065$. Despite application of a secondary extinction correction and constraining of the cations and O(1) to movement in only the x direction (Taylor and Brown, 1976) several oxygen atoms still had negative anisotropic temperature factors. This is probably due in large part to the use of limited modulated relplane intensity data for this lower symmetry model. The observed and calculated structure factors are given in Table 1, the atom positional and thermal parameters in Table 5 and selected interatomic distances and angles in Table 6.

P2₁ refinement

The absence of *a*-glide symmetry (evinced by the presence of weak $h0l$, h = odd reflections) left two possible space groups, centrosymmetric space group $P2_1/m$ and acentric space group $P2_1$. Since the atom positions are not compatible with mirror symmetry, additional refinement was carried out in space group $P2_1$. Initial coordinates and temperature factors were taken from the final cycle of refinement in $P2_1/a$, with the addition of 1/4 to each x coordinate being needed to bring atom positions into coincidence between the two space groups. Furthermore, the loss of *a*-glide symmetry required the addition of a second identical atom for each entered in the $P2_1/a$ refinement.

The refinement converged to $R = 0.077$ and $R_w = 0.060$ with non-positive isotropic temperature factors for Si(1) and O(3a). The residual (~0.33) for the 21 weak $h0l$, h = odd reflections was comparable to that for all reflections of similar intensity. Of the atom pairs in the $P2_1$ structure, Si(1)–Si(2) and O(3a)–O(3b) are two of the most crystallographically equivalent (Table 7). Their correspondingly high positional parameter correlations (correlation coefficients for xyz of atom pair Si(1)–Si(2) are 0.37, 0.50 and 0.92; respectively) and inclusion of weak relplane data are more than likely responsible for the non-positive temperature factors. Atom coordinates and isotropic temperature factors are given in Table 7. Selected interatomic distances and angles are listed in Table 8. Table 1 contains the observed and calculated structure factors.

Structural configurations and discussion

A2/a structure

The structure of natural titanite from Zillertal (Tyrol) was first accurately determined by Mongiorgi and di

Table 2. Atom positional and anisotropic thermal parameters for Grisons titanite, space group *A2/a*

Atom	x	y	z	B***	β_{11}**	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	1/4	0.1672(1)	0	0.67(3)	1026(22)	103(6)	318(17)	0	-71(15)	0
Ti	1/2	0	1/2	0.61(2)	760(15)	160(6)	204(11)	151(9)	63(10)	-8(8)
Si	3/4	0.1831(1)	0	0.35(4)	210(20)	68(10)	231(23)	0	84(18)	0
O(1)	3/4	0.0714(3)	1/2	0.50(10)	262(46)	137(21)	592(56)	0	230(42)	0
O(2)	0.9098(3)	0.0664(2)	0.1855(3)	0.40(7)	358(32)	189(15)	242(34)	83(19)	1(30)	30(19)
O(3)	0.3818(3)	0.2107(2)	0.3974(3)	0.37(7)	340(32)	164(15)	320(34)	46(20)	154(27)	36(19)

*Estimated standard deviations given in parentheses refer to the last decimal place.
** $\beta_{ij} \times 10^{-5}$
***Isotropic temperature factors are from last cycle before changing to anisotropic temperature factors.

Table 4. Selected interatomic distance (Å) and angles (°) for Grisons titanite, space group *A2/a*

Atoms	Distance	Atoms	Distance	Angle at metal atom
SiO_4 tetrahedron				
Si-O(2)^2 2x	1.631(2)	O(2)-O(2)^2	2.556(4)	103.2(1)
-O(3)^{5,7} 2x	1.634(2)	O(2)-O(3)^5 2x	2.713(3)	112.4(1)
		O(2)-O(3)^7 2x	2.652(3)	108.6(1)
		O(3)^5-O(3)^7	2.697(5)	111.3(2)
mean =	1.633		2.664	109.4
TiO_6 octahedron				
Ti-O(1)^1 2x	1.868(1)	O(1)-O(2)^2 O(1)^1-O(2)^3	2.716(3)	89.85(9)
-O(2)^{2,3} 2x	1.976(2)			
-O(3)^1 2x	2.009(2)			
mean	= 1.951	O(1)-O(2)^3 O(1)^1-O(2)^2	2.723(3)	90.15(9)
mean Ti-O(1)	= 1.868	O(1)-O(3) O(1)^1-O(3)^1	2.691(3)	87.80(10)
mean Ti-O(x)	= 1.993	O(1)-O(3)^1 O(1)^1-O(3)	2.796(3)	92.20(10)
		O(2)^2-O(3) O(2)^3-O(3)^1	2.814(3)	89.83(8)
		O(2)^3-O(3) O(2)^2-O(3)^1	2.823(3)	90.17(8)
		mean =	2.761	90.00
CaO_7 polyhedron				
Ca-O(1)^5	2.269(3)	O(1)^5-O(3)^2 2x	3.039(3)	80.98(5)
-O(2)^{1,3} 2x	2.397(2)	-O(3)^{5,7} 2x	2.691(3)	66.20(4)
-O(3)^2 2x	2.409(2)	O(2)^1-O(2)^3	2.556(4)	64.44(9)
-O(3)^{5,7} 2x	2.627(2)	O(2)^{1,3}-O(3)^2 2x	2.823(3)	71.94(7)
		-O(3)^{5,7} 2x	3.554(3)	89.94(7)
		O(3)^2-O(3)^{5,7} 2x	3.092(5)	75.63(10)
		-O(3)^{5,7} 2x	3.774(3)	96.99(9)
mean =	2.448		3.116	79.06

1 = -x,-y,-z; 2 = 1/2-x,y,-z; 3 = 1/2+x,-y,z; 4 = x,1/2+y,1/2+z; 5 = -x,1/2-y,1/2-z; 6 = 1/2-x,1/2+y,1/2-z; 7 = 1/2+x,1/2-y,1/2+z transformations relating coordinates to those of Table 2 .

*Estimated standard deviations given in parentheses refer to the last decimal place.

Table 5. Atom positional and isotropic thermal parameters for Grisons titanite, space group *P*2$_1$/*a*

Atom	x	y	z	B
Ca	0.2327(3)	0.9172(1)	0.7545(3)	0.44(1)
Ti	0.5149(2)	0.7541(2)	0.2493(3)	0.32(1)
Si	0.7562(7)	0.9327(1)	0.7570(7)	0.24(2)
O(1)	0.7465(14)	0.8213(4)	0.2362(10)	0.38(4)
O(2)	0.9209(11)	0.8231(8)	0.9376(13)	0.58(7)
O(3)	0.3837(14)	0.9652(10)	0.1421(14)	0.52(8)
O(4)	0.9010(10)	0.3109(7)	0.4345(11)	0.22(5)
O(5)	0.3798(14)	0.4562(10)	0.6523(14)	0.35(8)

*Estimated standard deviations given in parentheses refer to the last decimal place.

Sanseverino (1968). The results of our anisotropic refinement of Grisons titanite in space group *A2/a*, although more precise, are only slightly different from those reported by Mongiorgi and di Sanseverino (1968) (obtained using a multiple film technique) and probably reflect the compositional differences between the two titanites. While the mean Si–O bond lengths are the same for both structures, the Si tetrahedron is considerably more regular in the Grisons titanite with the Si–O(2) and Si–O(3) bonds being the same within the error of measurement. Both the mean Ca–O and mean Ti–O distances are 0.01Å smaller in the Grisons titanite. In the case of the Ti polyhedron this is probably the result of greater Al^{3+} for Ti^{4+} substitution in the octrahedral site. Since the Grisons titanite contains a stoichiometric amount of Ca, the larger size of this site in the Zillertal titanite may reflect minor RE element substitution.

Both the Ca and Ti atoms have large root mean square amplitudes (r_3, Table 3) nearly parallel to the **a**-axis due to the positional disordering of these cations attendant to the formation of out-of-step linear domains (Speer and Gibbs, 1976; Higgins and Ribbe, 1976).

*P*2$_1$/*a* structure

The steric details of the Grisons titanite structure at this intermediate stage of refinement are more similar to those

Table 6. Selected interatomic distances (Å) and angles (°) for Grisons titanite, space group *P*2$_1$/*a*

Atoms	Distance	Atoms	Distance	Angle at metal atom
SiO_4 tetrahedron				
Si-O(2)	1.594(7)*	O(2) -O(3)^1	2.712(10)	113.5(5)
-O(3)^1	1.648(9)	-O(4)^2	2.570(10)	103.8(4)
-O(4)^2	1.671(9)	-O(5)^3	2.607(12)	108.2(5)
-O(5)^3	1.625(12)	O(3)^1-O(4)^2	2.694(12)	108.5(5)
		-O(5)^3	2.700(14)	111.2(4)
mean =	1.635	O(4)^2-O(5)^3	2.724(13)	111.5(5)
TiO_6 octahedron				
Ti-O(1)	1.768(10)	O(1) -O(1)^3	3.735(14)	175.1(3)
-O(1)^3	1.970(10)	-O(2)^3	2.648(9)	89.5(3)
-O(2)^3	1.987(8)	-O(3)	2.685(13)	89.2(4)
-O(3)	2.044(9)	-O(4)^2	2.747(14)	94.5(4)
-O(4)^2	1.968(9)	-O(5)^1	2.766(11)	95.1(3)
-O(5)^1	1.977(9)	O(1)^3-O(2)^3	2.696(14)	85.9(3)
		-O(3)	2.824(11)	89.4(3)
mean	= 1.952	-O(4)^2	2.790(10)	90.2(4)
		-O(5)^1	2.700(13)	86.3(3)
mean Ti-O(1)	= 1.869	O(2)^3-O(3)	2.899(12)	92.0(3)
		-O(4)^2	3.950(12)	174.3(4)
mean Ti-O(x)	= 1.994	-O(5)^1	2.728(11)	87.0(3)
		O(3) -O(4)^2	2.890(12)	92.1(4)
		-O(5)^1	4.019(12)	175.6(4)
		O(4)^2-O(5)^1	2.756(13)	88.6(4)
CaO_7 polyhedron				
Ca-O(1)^1	2.275(4)	O(1)^1-O(2)^3	4.536(8)	143.5(2)
-O(2)^3	2.501(7)	-O(3)	2.925(10)	78.4(3)
-O(3)	2.354(9)	-O(3)^1	2.684(11)	64.5(3)
-O(3)^1	2.707(7)	-O(4)^1	4.448(7)	150.8(2)
-O(4)^1	2.322(6)	-O(5)^3	2.699(13)	67.8(3)
-O(5)^2	2.472(9)	-O(5)^2	3.154(10)	83.2(3)
-O(5)^3	2.549(10)	O(2)^3-O(3)	2.899(12)	73.3(3)
		-O(3)^1	3.521(10)	85.0(2)
mean =	2.454	-O(4)^1	2.570(8)	64.3(2)
		-O(5)^3	4.734(11)	139.2(3)
		-O(5)^2	4.315(11)	120.4(3)
		O(3) -O(3)^1	4.328(11)	67.6(2)
		-O(4)^1	4.225(10)	129.3(3)
		-O(5)^3	3.756(11)	100.0(3)
		-O(5)^2	4.756(12)	160.4(3)
		O(3)^1-O(4)^1	4.506(8)	127.1(2)
		-O(5)^3	4.807(12)	124.9(1)
		-O(5)^2	3.709(9)	94.0(3)
		O(4)^1-O(5)^3	3.592(12)	94.9(3)
		-O(5)^2	2.756(11)	70.1(3)
		O(5)^2-O(5)^3	3.187(16)	78.8(3)

1 = -x,-y,-z,; 2 = 1/2-x,1/2+y,-z; 3 = 1/2+x,1/2-y,z

*Estimated standard deviations given in parentheses refer to the last decimal place.

reported for synthetic $P2_1/a$ titanite without a domain texture (Speer and Gibbs, 1976; Taylor and Brown, 1976) than they are to the $A2/a$ structure. The most notable difference is the marked increase in distortion of the Si and Ti coordination polyhedra as compared to those in the $A2/a$ structure (Table 9). This involves bond length distortion in the Si polyhedron and bond length and bond angle distortion in the Ti polyhedron. The mean value of the pseudo-*A*-centering related bond lengths (i.e., mean Si–O(2,4) in space group $P2_1/a$ are identical (within the error of measurement) to the corresponding bond lengths in the $A2/a$ structure. This increase in distortion is attributed to the Ca, Si, Ti and O(1) going from special positions in the $A2/a$ structure to general positions in the $P2_1/a$ structure.

As first noted by Taylor and Brown (1976) and confirmed in this study, bond angle variance parameters (Robinson et al., 1971) are not by themselves an adequate measure of polyhedral distortion in the titanite structure.

Table 7. Atom positional and isotropic thermal parameters for Grisons titanite, space group $P2_1$

Atom	x	y	z	B
Ca(1)	0.5001(4)	0.9179(2)	0.7498(5)	0.55(3)
Ca(2)	0.0253(4)	0.0835(2)	0.2442(5)	0.48(4)
Ti(1)	0.7662(6)	0.7559(5)	0.2486(6)	0.42(4)
Ti(2)	0.7356(6)	0.2491(6)	0.7506(6)	0.35(4)
Si(1)	0.9971(19)	0.9305(7)	0.7583(17)	0.75(6)
Si(2)	0.4912(9)	0.0653(6)	0.2462(13)	-0.01(4)
O(1a)	0.9889(23)	0.8162(11)	0.2459(39)	0.40(10)
O(1b)	0.5011(26)	0.1736(11)	0.7686(18)	0.31(11)
O(2a)	0.1671(31)	0.8214(21)	0.9456(29)	0.93(20)
O(2b)	0.3261(20)	0.1799(15)	0.0682(21)	0.18(10)
O(3a)	0.6327(20)	0.9608(15)	0.1389(19)	-0.06(10)
O(3b)	0.8748(31)	0.0421(27)	0.8595(36)	1.13(26)
O(4a)	0.1547(24)	0.3046(12)	0.4304(24)	0.36(11)
O(4b)	0.3534(17)	0.6808(15)	0.5626(21)	0.14(11)
O(5a)	0.6278(32)	0.4544(23)	0.6533(34)	0.93(22)
O(5b)	0.8612(19)	0.5339(14)	0.3432(22)	0.16(11)

*Estimated standard deviations given in parentheses refer to the last decimal place.

Table 8. Selected interatomic distances (Å) and angles (°) for Grisons titanite, space group $P2_1$

Atoms	Distance	Atoms	Distance	Angle at metal atom
SiO_4 tetrahedra				
Si(1)-O(2a)	1.63(2)*	O(2a)-O(3b)	2.70(3)	113(1)
-O(3b)	1.61(3)	-O(4a)	2.59(2)	103(1)
-O(4a)	1.67(1)	-O(5b)	2.59(2)	104(1)
-O(5b)	1.67(2)	O(3b)-O(4a)	2.75(4)	114(1)
		-O(5b)	2.69(3)	110(1)
mean = 1.64		O(4a)-O(5b)	2.76(2)	112(1)
Si(2)-O(2b)	1.61(1)	O(2b)-O(3a)	2.77(2)	114(1)
-O(3a)	1.70(2)	-O(4b)	2.55(2)	104(1)
-O(4b)	1.63(1)	-O(5a)	2.60(2)	109(1)
-O(5a)	1.58(3)	O(3a)-O(4b)	2.70(2)	109(1)
		-O(5a)	2.69(3)	110(1)
mean = 1.63		O(4b)-O(5a)	2.65(2)	111(1)
TiO_6 octahedra				
Ti(1)-O(1a)	1.66(2)	O(1a)-O(1b)	3.63(3)	175(1)
-O(1b)	1.98(2)	-O(2b)	2.62(2)	90(1)
-O(2b)	2.01(1)	-O(3a)	2.64(2)	91(1)
-O(3a)	2.00(1)	-O(4a)	2.69(3)	95(1)
-O(4a)	1.99(2)	-O(5b)	2.77(2)	96(1)
-O(5b)	2.05(1)	O(1b)-O(2a)	2.71(2)	85(1)
		-O(3a)	2.82(2)	90(1)
mean = 1.95		-O(4a)	2.79(2)	89(1)
		-O(5b)	2.65(2)	82(1)
		O(2b)-O(3a)	2.86(2)	91(1)
		-O(4a)	3.99(2)	173(1)
		-O(5b)	2.78(2)	86(1)
		O(3a)-O(4a)	2.93(2)	94(1)
		-O(5b)	4.05(2)	172(1)
		O(4a)-O(5b)	2.80(2)	88(1)
Ti(2)-O(1a)	2.02(2)	O(1a)-O(1b)	3.84(3)	174(1)
-O(1b)	1.83(2)	-O(2a)	2.73(4)	88(1)
-O(2a)	1.92(2)	-O(3b)	2.76(3)	86(1)
-O(3b)	2.03(2)	-O(4b)	2.82(2)	90(1)
-O(4b)	1.97(1)	-O(5a)	2.78(3)	89(1)
-O(5a)	1.94(2)	O(1b)-O(2a)	2.66(2)	90(1)
		-O(3b)	2.70(3)	89(1)
mean = 1.95		-O(4b)	2.75(2)	92(1)
		-O(5a)	2.80(2)	96(1)
		O(2a)-O(3b)	2.81(3)	90(1)
		-O(4b)	3.89(2)	177(1)
		-O(5a)	2.69(2)	88(1)
		O(3b)-O(4b)	2.84(2)	90(1)
		-O(5a)	3.97(3)	175(1)
		O(4b)-O(5a)	2.79(2)	91(1)

Atoms	Distance	Atoms	Distance	Angle at metal atom
CaO_7 polyhedra				
Ca(1)-O(1b)	2.22(1)	O(1b)-O(2b)	4.46(2)	146(1)
-O(2b)	2.45(1)	-O(3a)	2.88(2)	78(1)
-O(3a)	2.36(1)	-O(3b)	2.71(3)	67(1)
-O(3b)	2.66(2)	-O(4b)	4.48(2)	151(1)
-O(4b)	2.40(1)	-O(5a)	3.17(2)	86(1)
-O(5a)	2.44(2)	-O(5b)	2.65(2)	66(1)
-O(5b)	2.58(1)	O(2b)-O(3a)	2.86(2)	73(1)
		-O(3b)	3.56(3)	88(1)
mean = 2.44		-O(4b)	2.55(2)	63(1)
		-O(5a)	4.27(2)	122(1)
		-O(5b)	4.63(2)	134(1)
		O(3a)-O(3b)	3.05(3)	74(1)
		-O(4b)	4.24(2)	126(1)
		-O(5a)	4.74(2)	163(1)
		-O(5b)	3.68(2)	96(1)
		O(3b)-O(4b)	4.62(2)	131(1)
		-O(5a)	3.84(3)	98(1)
		-O(5b)	4.81(3)	133(1)
		O(4b)-O(5a)	2.79(2)	79(1)
		-O(5b)	3.58(2)	92(1)
		O(5a)-O(5b)	3.16(3)	78(1)
Ca(2)-O(1a)	2.34(1)	O(1a)-O(2a)	4.57(2)	142(1)
-O(2a)	2.51(2)	-O(3a)	2.64(2)	61(1)
-O(3a)	2.78(1)	-O(3b)	3.04(3)	81(1)
-O(3b)	2.33(2)	-O(4a)	4.43(1)	150(1)
-O(4a)	2.26(1)	-O(5a)	2.78(3)	70(1)
-O(5a)	2.52(2)	-O(5b)	3.10(2)	79(1)
-O(5b)	2.52(1)	O(2a)-O(3a)	3.57(2)	85(1)
		-O(3b)	2.81(3)	71(1)
mean = 2.47		-O(4a)	2.59(2)	66(1)
		-O(5a)	4.73(3)	140(1)
		-O(5b)	4.42(2)	123(1)
		O(3a)-O(3b)	3.05(3)	73(1)
		-O(4a)	4.52(2)	127(1)
		-O(5a)	4.82(3)	131(1)
		-O(5b)	3.85(2)	93(1)
		O(3b)-O(4a)	4.13(2)	128(1)
		-O(5a)	3.74(2)	101(1)
		-O(5b)	4.77(3)	160(1)
		O(4a)-O(5a)	3.55(3)	96(1)
		-O(5b)	2.80(2)	72(1)
		O(5a)-O(5b)	3.16(3)	78(1)

*Estimated standard deviations given in parentheses refer to the last decimal place.

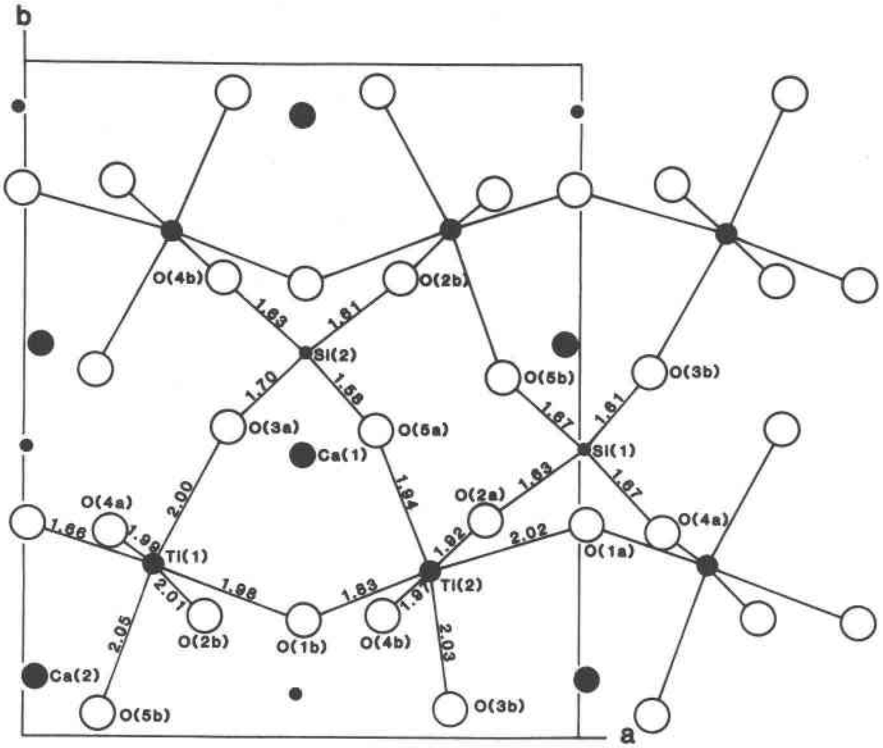

Fig. 2. The $P2_1$ structure of Grisons titanite projected on (001) showing the details of octahedral and tetrahedral coordination.

While the bond angle variances for the Si and Ti polyhedra are nearly the same for the synthetic and Grisons $P2_1/a$ structures (Table 9), bond length variances are significantly larger for the Ti octahedron in Grisons titanite. The Si–O bond length variance in Grisons titanite is greater than that observed for synthetic titanite at 25°C (Table 9) but comparable to that observed at 165°C (Taylor and Brown, 1976).

The alternating long and short Ti–O(1) bond lengths, 1.970 and 1.768Å (Fig. 1), which reflect the amount of displacement of the Ti atom from the geometric center of the Ti octahedron are the same as those reported by Taylor and Brown (1976) for synthetic $P2_1/a$ titanite at 25°C. This is somewhat surprising since the mean Ti–O distance in Grisons titanite (1.952Å) is smaller than that observed for synthetic titanite (1.956Å, Taylor and Brown, 1976; 1.958Å, Speer and Gibbs, 1976) by an amount very close to that predicted for 9% Al for Ti substitution.

The atom configuration in the synthetic titanite unit cell (Speer and Gibbs, 1976) is highly pseudo-symmetric with the Ti and Ca atoms showing the greatest deviation from true *A*-centered symmetry. The same general pattern is observed in the $P2_1/a$ structure of Grisons titanite except that while the deviation from *A*-centering for the Ti atoms is about the same, the deviations for the other atoms are significantly greater than in synthetic titanite and may reflect increased cation and OH^- substitution.

$P2_1$ *structure*

The most obvious feature of the $P2_1$ structure is the extreme bond length distortion of one member of each of the pseudo *a*-glide symmetry related coordination polyhedra. The distortion is unusually great in the Si(2) tetrahedron and Ti(1) octahedron where the bond lengths range from 1.58–1.70Å and 1.66–2.05Å, respectively.

In the $P2_1$ structure the zig-zag octahedral chains are no longer related by a center of symmetry and, therefore, within a given chain adjacent octahedra are no longer symmetry equivalent (Fig. 2) and two types of O(1) sites, O(1a) and O(1b), situated at mean distances of 1.84Å (2.02 + 1.66Å)/2 and 1.91Å (1.98 + 1.83Å)/2, result. Despite this the structure still retains the "off-centered" displacement of the Ti atoms resulting in the alternating long-short Ti–O(1) bonds characteristic of the $P2_1/a$ structure. Within a chain the geometries of adjacent octahedra are quite different with Ti(1) octahedron being considerably more distorted and the Ti(2) octahedron less distorted than the Ti octahedron in the $P2_1/a$ structure (Table 9). As in the $P2_1/a$ structure, the Ti(1)–O(1a) and Ti(1)–O(1b) are the shortest bond lengths in the Ti(1) octahedron, whereas, in the less distorted Ti(2) octahedron the long Ti(2)–O(1a) and short Ti(2)–O(1b) bond lengths represent the extremes (Figs. 1 and 2). Because of the appreciable distortion of the Ti(1) octahedron the difference in length between the Ti(1)–O(1) bonds (0.32Å) is appreciably greater than that between the Ti(2)–O(1) bonds (0.19Å).

Two atom pairs (Ca(1)–Ca(2) and O(1a)–O(1b) show the greatest deviation from *a*-glide symmetry in the $P2_1$ structure. However, it is difficult to attribute this to any substitutional relationship because while OH^- is thought to substitute for O(1) (Speer and Gibbs, 1976), Ca is present in stoichiometric proportions. In addition, the Ti sites, which in Grisons titanite are 10% substituted by Al^{3+} and Fe^{3+}, show the least deviation from *A*-centering. It is of interest to note that in the structure of both synthetic stoichiometric titanite, space group $P2_1/a$ (Speer and Gibbs, 1976) and Grisons titanite ($P2_1/a$ refinement), Ca like Ti shows a relatively large deviation from A-centering.

Summary and conclusions

Substitution of Al^{3+} and OH^- for Ti^{4+} and O^{2-} appears to have had very little effect on the titanite structure beyond the production of a domain texture. Comparison of the *A2/a* refinements of the "averaged" structure (i.e., without consideration of $k + l$ odd modulated maxima) of Grisons titanite (this study) to Zillertal titanite (Mongiorgi and de Sanseverino, 1968) and the $P2_1/a$ refinements of Grisons to stoichiometric synthetic titanite (Speer and Gibbs, 1976) reveal the expected reduction in the size of the Ti octahedron with increasing Al substitution.

Table 9. Bond angle and bond length variances in synthetic and natural titanites

	Structure	Grisons titanite	Synthetic titanite*	
			S&G (1976)	T&B (1976)
Si(angle)	A2/a	12.27		
Si(length)	"	0.000003		
Ti(angle)	"	1.96		
Ti(length)	"	0.0036		
Ca(length	"	0.0187		
Si(angle)	P2$_1$/a	11.61	11.98	12.20
Si(length)	"	0.00092	0.00001	0.00020
Ti(angle)	"	8.86	7.55	8.73
Ti(length)	"	0.0075	0.0078	0.0078
Ca(length)	"	0.0193	0.0145	0.0155
Si(1)(angle)	P2$_1$	22.		
Si(1)(length)	"	0.0007		
Si(2)(angle)	"	11.		
Si(2)(length)	"	0.0020		
Ti(1)(angle)	"	17.		
Ti(1)(length)	"	0.0171		
Ti(2)(angle)	"	6.		
Ti(2)(length)	"	0.0045		
Ca(1)(length)	"	0.0178		
Ca(2)(length)	"	0.0262		

*S&G (1976) = Speer and Gibbs (1976), T&B (1976) = Taylor and Brown (1976)

While the degree of distortion of the coordination polyhedra in the $P2_1/a$ model of Grisons titanite is probably "real" since it is comparable to that observed for the structure of $P2_1/a$ stoichiometric synthetic titanite, the extreme distortion of the polyhedra in the Grisons $P2_1$ refinement and the negative isotropic temperature factors may reflect the use of too limited data ($h0l$, h = odd) and the results, therefore, must be interpreted with caution.

The $h0l$, h = odd reflections measured during data collection are the result of very weak and diffuse *h*-relplanes. The h = odd reflections may be interpreted as either due to chemical cation ordering or to linear positional ordering. Most titanites form in geologic environments which are characterized by prolonged high temperatures and slow cooling rates, conditions generally conducive to ordering of substituents. It is possible that the Ti, Al and Fe atoms in Grisons titanite have adopted at least a partially ordered configuration in response to these conditions. Cation ordering in the octahedral sites would result in a loss of centrosymmetry, reduction of the space group to $P2_1$ and the appearance of ordering reflections of the type $h0l$, h = odd.

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