

The crystal structure of synthetic titanite, CaTiOSiO_4 , and the domain textures of natural titanites

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Abstract

The crystal structure of synthetic titanite ($a = 7.069(2)$, $b = 8.722(5)$, $c = 6.566(8)$, $\beta = 113.86(2)^\circ$, $P2_1/a$) has been refined by least-squares methods to an unweighted $R = 0.043$. Chains of corner-sharing TiO_6 octahedra running parallel to the a -cell edge are crosslinked by silicate tetrahedra to form a TiOSiO_4 framework that accommodates Ca in irregular 7-coordination polyhedra. Diffraction data of the type $k + l$ odd which violate the diffraction rules of the previously reported $A2/a$ space group are ascribed to an "off-centered" displacement of the titanium atom from the geometrical center of each octahedron, resulting in long (1.974 Å) and short (1.766 Å) Ti–O bonds alternating along the chains. The displacement is such that Ti is shifted in the $+a$ -direction in one-half of the chains and in the $-a$ -direction in the other half. This arrangement implies that $P2_1/a$ titanite is antiferroelectric. Long-exposure single-crystal photographs of several natural titanites show diffuse $k + l$ odd diffraction data, indicating that natural specimens may consist of domains of $P2_1/a$ titanite related by a half-turn parallel to b . The coupled substitution of Fe and Al for Ti and OH for O appears to favor domain formation.

Introduction

Titanite (CaTiOSiO_4) is a sparse yet widely distributed accessory mineral commonly found in metamorphic and igneous rocks and their associated pegmatites. It was first described by Pictet in 1787 and designated titanite (Klaproth, 1795) to conform with its chemical composition. The common wedge-shaped habit of titanite accounts for its also being called sphene, a name having originated from a Greek word meaning wedge (Haüy, 1801). Because of its extreme dispersive power, birefringence, and color, titanite has been cut into spectacular gemstones. Because they are soft and not durable, they are not in general highly prized.

The crystal structure of titanite was first investigated by Zachariasen (1930), who described it as consisting of independent silicate ions bonded together with TiO_6 octahedra to form a network with Ca tucked into 7-fold coordinated sites in the resulting cavities. In order to clarify the wide range of Si–O distances reported by Zachariasen (1.54–1.74 Å), Mongiorgi and Riva di Sanseverino (1968) undertook a reinvestigation of the structure using multiple-film Weissenberg techniques and obtained Si–O bond lengths in close agreement with those reported for

other orthosilicates. In addition, a new set of unit cell parameters was chosen and titanite's space group was transformed from $C2/c$ to $A2/a$ to conform with rules set forth by the Commission on Crystallographic Data. The axial transformation from Zachariasen's $C2/c$ cell to Mongiorgi and Riva di Sanseverino's $A2/a$ cell is (101/010/ $\bar{1}00$). The axial transformation to a right-handed coordinate system as suggested by Donnay and Ondik (1973) and the setting for the $P2_1/a$ space group used in this study is ($\bar{1}0\bar{1}$ /010/100). The axial transformation from Mongiorgi and Riva di Sanseverino's cell to that of Donnay and Ondik is ($\bar{1}00$ /010/ $00\bar{1}$).

Recently, Dr. D. A. Hewitt of this department synthesized dry several single crystals of titanite which he kindly donated for this crystallographic study. Upon examination of the single-crystal photographs, we were surprised to discover that synthetic titanite's space group symmetry is actually $P2_1/a$ instead of $A2/a$ as previously reported for natural titanite. In addition, long-exposure single-crystal photographs of several natural specimens showed diffuse reflections in violation of the diffraction rules of $A2/a$. Later we learned in a literature search that Robbins (1968) had reported the $P2_1/a$ space group symmetry for synthetic titanite. Because no report of

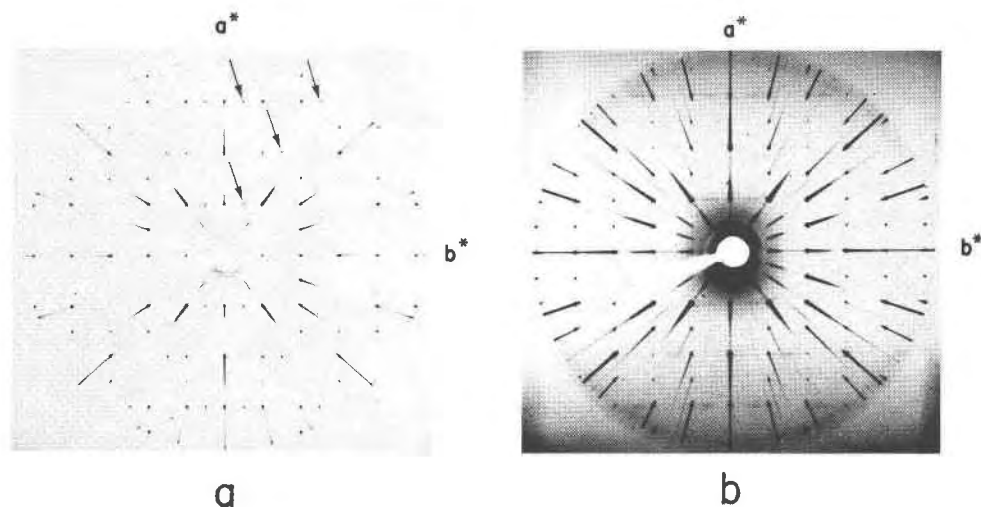


FIG. 1. Precession photographs ($hk0$ level, $\mu = 30^\circ$, $\text{MoK}\alpha$ radiation) of (a) synthetic primitive titanite and (b) natural titanite. Some reflections violating $k + l = 2n$ are shown by arrows for synthetic titanite. Precession axis is c with a^* vertical and b^* horizontal.

any further study was found, we undertook a crystal structure analysis of $P2_1/a$ titanite and a study of the diffuse reflections exhibited by certain natural specimens (Speer and Gibbs, 1974), the results of which are reported here.

Experimental

The titanite crystals used in this study were synthesized from a mix having the bulk composition CaCO_3

$\text{TiO}_2 \cdot \text{SiO}_2$. The CO_2 was driven off at $\sim 1000^\circ\text{C}$ prior to melting in a platinum crucible at $\sim 1400^\circ\text{C}$ and 1 atm. The resulting material was homogenized by repeated cycles of crushing, remelting, and quenching. After the last melting, the material was crystallized at $\sim 1200^\circ\text{C}$ for several weeks and then

cooled. Figure 1a is a precession photograph exposed about c of one of the crystals selected from the crystallized mix. The more intense reflections on the film are consistent with space group $A2/a$; however, weaker ones with indices $hk0$, k odd, violate the diffraction rules for the A -centered translation group. This result taken in conjunction with data obtained from other single-crystal photographs shows the space group symmetry of synthetic titanite to be $P2_1/a$.

The cell parameters of the crystal ($0.10 \times 0.10 \times 0.12$ mm) selected for the structure analysis were obtained from a least-squares refinement of more than twenty 4θ values of hkl reflections recorded with the single-crystal diffractometer. Table 1 compares these cell parameters with those obtained by previous

TABLE 1. Crystallographic data for titanite*

	Zachariasen (1930)	Monglorgi + Riva di Sanseverino (1968) redetermined by Cerny + Riva di Sanseverino (1972)	Robbins (1968)	this study
a	7.06 Å	7.062(1) Å	7.065(5) Å	7.069(2) Å
b	8.70	8.705(1)	8.723(5)	8.722(5)
c	6.55	6.553(1)	6.567(5)	6.566(8)
β	113.95°	$113.82^\circ(1)$	$113.86^\circ(3)$	$113.86^\circ(2)$
Cell volume	370 \AA^3	$368.49(6) \text{ \AA}^3$	370.3 \AA^3	$370.22(6) \text{ \AA}^3$
Reported space group	$A2/a(C2/c)$	$A2/a$	$P2_1/a(P2_1/n)$	$P2_1/a$
Calculated density		3.53 g/cc	3.52 g/cc	3.52 g/cc
Locality	Lindvikskollen, Norway	Zillertal, Italy	synthetic	synthetic

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

workers for natural and synthetic titanite. Our values for synthetic titanite are statistically identical with those obtained by Robbins (1968). More than 1100 non-equivalent intensity data were recorded using an automated four circle X-ray goniostat, Nb-filtered Mo radiation, and a scintillation counter. The resultant data were corrected for Lorentz and polarization effects and converted to unscaled $|F_{\text{obs}}|$ values with a program written by C. T. Prewitt. Initially, no corrections were made for primary and secondary extinction. No absorption correction was made ($\mu_{\text{MoK}\alpha} = 38.8 \text{ cm}^{-1}$).

A least-squares refinement of the titanite structure in space group $P2_1/a$ was calculated using the program of Busing *et al.* (1962), form factor curves for neutral atoms taken from Doyle and Turner (1968), and 888 reflections whose intensities were more than four times the estimated standard deviations of their measurements. The positional parameters of titanite obtained by Mongiorgi and Riva di Sanseverino (1968) were used as starting values with small, random displacements (± 0.01) added to the positional parameters of those atoms no longer on special positions. As the center of symmetry chosen as their origin is not present in $P2_1/a$, a new origin was chosen at the remaining center of symmetry. Three cycles of refinement assuming isotropic temperature factors for all the atoms gave an R -value of 0.10. After conversion to anisotropic temperature factors, further least-squares calculations resulted in several temperature factor coefficients that tested non-positive definite. Because the important details of the structure are contained in the relatively weak $|F_{\text{obs}}|$, $k + l$ odd diffraction data, a refinement again assuming anisotropic temperature factors was carried out using only $|F_{\text{obs}}| < 24.5$ wherein an R -value of 0.057 was obtained. Using these results as starting parameters, a refinement using $|F_{\text{obs}}| < 46$ was calculated and resulted in an R -value of 0.043. At this point, all the data were corrected for secondary extinction effects using a program written by Dr. G. Chiari of the University of Turin, Italy, which makes use of the relation:

$$|F_{\text{calc}}| = |F_{\text{obs}}| (1 + gI_{\text{calc}}).$$

The refinement was completed using all the observational data by simultaneously varying all positional and anisotropic thermal parameters. The $|F_{\text{obs}}|$'s and the final $|F_{\text{calc}}|$'s are given in Table 2. Positional and thermal parameters (Table 3), bond distances and angles (Table 4), and thermal ellipsoid data (Table 5) were obtained from the results of the final cycle of

refinement which yielded an unweighted residual of $R = 0.042$. Unit weighting of the data was considered adequate in that it gave nearly constant values $\omega|\Delta F^2|$ for ten equal sized groups of increasing $|F_{\text{obs}}|$'s, consistent with the criteria for a good weighting scheme.

Discussion of the structure

The dominant structural units in titanite are chains of corner-sharing TiO_6 octahedra running parallel to the a cell edge. The repeat unit in the chain is defined by two tilted octahedra which share a common oxygen atom designated O_1 . While the oxygen atoms surrounding the titanium atoms form a nearly regular octahedra, the titanium atoms are displaced from the geometrical centers of the octahedra, resulting in alternating long (1.974 Å) and short (1.766 Å) $\text{Ti}-\text{O}_1$ bonds. The four remaining $\text{Ti}-\text{O}$ bond distances are longer than either of the $\text{Ti}-\text{O}_1$ bonds and range between 1.984 Å and 2.025 Å. The off-center displacement of the Ti is also reflected in the $\text{O}_1-\text{Ti}-\text{O}$ angles with the average of the four angles involving the shorter bond being wider than those involving the larger bond (Fig. 2). Two chains per unit cell are related by a center of symmetry, one chain having the octahedral titanium displaced in the $+a$ direction from the geometrical center of the octahedra and the other chain having the titanium displaced in the $-a$ direction. These chains are cross-linked by silicate tetrahedra sharing the remaining four oxygens: O_2 , O_3 , O_4 , O_5 . The silicate tetrahedra share oxygen atoms with four separate TiO_6 octahedral groups in three separate chains. The oxygen atoms O_3 and O_5 belong to the same chain while O_2 and O_4 are shared by two chains. This produces a $[\text{TiOSiO}_4]^{-2}$ framework with large cavities enclosing calcium atoms in irregular 7-coordination polyhedra. This coordination is based on a limiting $\text{Ca}-\text{O}$ bond length of 3.0 Å, which seems reasonable considering that the next closest cation, Si, is at a distance of 3.066 Å. The $\text{Si}-\text{O}$ bond length variations in the silicate ion are small ranging from 1.641 Å to 1.647 Å, despite a range of $\langle \text{O}-\text{Si}-\text{O} \rangle$ from 108.3° to 110.8° and a range of $\zeta(\text{O})$ from 1.96 to 2.24. Moreover, neither of these parameters may be used to satisfactorily rationalize the small $\text{Si}-\text{O}$ bond length variations that do occur in titanite. A stereoscopic pair of the titanite structure is shown in Figure 3.

Although no hydrogen was present in the synthetic titanite, Isetti and Penco (1968) and Beran (1970) have shown for natural OH-bearing titanites that the

hydrogen-oxygen bond direction lies in the (010) plane nearly normal to *a* and parallel to the principal optical vibration axis *X*. Being aware of the fact that $\zeta(O_1) = 1.62$, Zachariasen (1930) and Sahama (1946)

have proposed replacement of O_1 by OH, Cl, or F to satisfy its valency. Hence hydrogen when present is probably associated with O_1 and lies in the (010) plane with the O_1 -H vector nearly normal to *a*.

TABLE 2. Observed and calculated structure factors for titanite

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}					
0	0	0	1.4970	0.2234	-1	5	0	0.4900	1.1842	-1	3	1	0.3550	1.3347	-1	2	0	5.9990	5.5638	-2	0	0	7.2200	6.9934	-1	8	2	18.4466	18.7778
1	0	0	1.4970	0.2234	1	5	0	0.4900	1.1842	1	3	1	0.3550	1.3347	1	2	0	5.9990	5.5638	2	0	0	7.2200	6.9934	1	8	2	18.4466	18.7778
2	0	0	1.4970	0.2234	2	0	1	0.4900	1.1842	2	0	1	0.4900	1.1842	2	0	1	0.4900	1.1842	3	0	1	0.4900	1.1842	2	0	1	0.4900	1.1842
3	0	0	1.4970	0.2234	3	0	0	0.4900	1.1842	3	0	0	0.4900	1.1842	3	0	0	0.4900	1.1842	4	0	0	0.4900	1.1842	3	0	0	0.4900	1.1842
4	0	0	1.4970	0.2234	4	0	0	0.4900	1.1842	4	0	0	0.4900	1.1842	4	0	0	0.4900	1.1842	5	0	0	0.4900	1.1842	4	0	0	0.4900	1.1842
5	0	0	1.4970	0.2234	5	0	0	0.4900	1.1842	5	0	0	0.4900	1.1842	5	0	0	0.4900	1.1842	6	0	0	0.4900	1.1842	5	0	0	0.4900	1.1842
6	0	0	1.4970	0.2234	6	0	0	0.4900	1.1842	6	0	0	0.4900	1.1842	6	0	0	0.4900	1.1842	7	0	0	0.4900	1.1842	6	0	0	0.4900	1.1842
7	0	0	1.4970	0.2234	7	0	0	0.4900	1.1842	7	0	0	0.4900	1.1842	7	0	0	0.4900	1.1842	8	0	0	0.4900	1.1842	7	0	0	0.4900	1.1842
8	0	0	1.4970	0.2234	8	0	0	0.4900	1.1842	8	0	0	0.4900	1.1842	8	0	0	0.4900	1.1842	9	0	0	0.4900	1.1842	8	0	0	0.4900	1.1842
9	0	0	1.4970	0.2234	9	0	0	0.4900	1.1842	9	0	0	0.4900	1.1842	9	0	0	0.4900	1.1842	10	0	0	0.4900	1.1842	9	0	0	0.4900	1.1842
10	0	0	1.4970	0.2234	10	0	0	0.4900	1.1842	10	0	0	0.4900	1.1842	10	0	0	0.4900	1.1842	11	0	0	0.4900	1.1842	10	0	0	0.4900	1.1842
11	0	0	1.4970	0.2234	11	0	0	0.4900	1.1842	11	0	0	0.4900	1.1842	11	0	0	0.4900	1.1842	12	0	0	0.4900	1.1842	11	0	0	0.4900	1.1842
12	0	0	1.4970	0.2234	12	0	0	0.4900	1.1842	12	0	0	0.4900	1.1842	12	0	0	0.4900	1.1842	13	0	0	0.4900	1.1842	12	0	0	0.4900	1.1842
13	0	0	1.4970	0.2234	13	0	0	0.4900	1.1842	13	0	0	0.4900	1.1842	13	0	0	0.4900	1.1842	14	0	0	0.4900	1.1842	13	0	0	0.4900	1.1842
14	0	0	1.4970	0.2234	14	0	0	0.4900	1.1842	14	0	0	0.4900	1.1842	14	0	0	0.4900	1.1842	15	0	0	0.4900	1.1842	14	0	0	0.4900	1.1842
15	0	0	1.4970	0.2234	15	0	0	0.4900	1.1842	15	0	0	0.4900	1.1842	15	0	0	0.4900	1.1842	16	0	0	0.4900	1.1842	15	0	0	0.4900	1.1842
16	0	0	1.4970	0.2234	16	0	0	0.4900	1.1842	16	0	0	0.4900	1.1842	16	0	0	0.4900	1.1842	17	0	0	0.4900	1.1842	16	0	0	0.4900	1.1842
17	0	0	1.4970	0.2234	17	0	0	0.4900	1.1842	17	0	0	0.4900	1.1842	17	0	0	0.4900	1.1842	18	0	0	0.4900	1.1842	17	0	0	0.4900	1.1842
18	0	0	1.4970	0.2234	18	0	0	0.4900	1.1842	18	0	0	0.4900	1.1842	18	0	0	0.4900	1.1842	19	0	0	0.4900	1.1842	18	0	0	0.4900	1.1842
19	0	0	1.4970	0.2234	19	0	0	0.4900	1.1842	19	0	0	0.4900	1.1842	19	0	0	0.4900	1.1842	20	0	0	0.4900	1.1842	19	0	0	0.4900	1.1842
20	0	0	1.4970	0.2234	20	0	0	0.4900	1.1842	20	0	0	0.4900	1.1842	20	0	0	0.4900	1.1842	21	0	0	0.4900	1.1842	20	0	0	0.4900	1.1842
21	0	0	1.4970	0.2234	21	0	0	0.4900	1.1842	21	0	0	0.4900	1.1842	21	0	0	0.4900	1.1842	22	0	0	0.4900	1.1842	21	0	0	0.4900	1.1842
22	0	0	1.4970	0.2234	22	0	0	0.4900	1.1842	22	0	0	0.4900	1.1842	22	0	0	0.4900	1.1842	23	0	0	0.4900	1.1842	22	0	0	0.4900	1.1842
23	0	0	1.4970	0.2234	23	0	0	0.4900	1.1842	23	0	0	0.4900	1.1842	23	0	0	0.4900	1.1842	24	0	0	0.4900	1.1842	23	0	0	0.4900	1.1842
24	0	0	1.4970	0.2234	24	0	0	0.4900	1.1842	24	0	0	0.4900	1.1842	24	0	0	0.4900	1.1842	25	0	0	0.4900	1.1842	24	0	0	0.4900	1.1842
25	0	0	1.4970	0.2234	25	0	0	0.4900	1.1842	25	0	0	0.4900	1.1842	25	0	0	0.4900	1.1842	26	0	0	0.4900	1.1842	25	0	0	0.4900	1.1842
26	0	0	1.4970	0.2234	26	0	0	0.4900	1.1842	26	0	0	0.4900	1.1842	26	0	0	0.4900	1.1842	27	0	0	0.4900	1.1842	26	0	0	0.4900	1.1842
27	0	0	1.4970	0.2234	27	0	0	0.4900	1.1842	27	0	0	0.4900	1.1842	27	0	0	0.4900	1.1842	28	0	0	0.4900	1.1842	27	0	0	0.4900	1.1842
28	0	0	1.4970	0.2234	28	0	0	0.4900	1.1842	28	0	0	0.4900	1.1842	28	0	0	0.4900	1.1842	29	0	0	0.4900	1.1842	28	0	0	0.4900	1.1842
29	0	0	1.4970	0.2234	29	0	0	0.4900	1.1842	29	0	0	0.4900	1.1842	29	0	0	0.4900	1.1842	30	0	0	0.4900	1.1842	29	0	0	0.4900	1.1842
30	0	0	1.4970	0.2234	30	0	0	0.4900	1.1842	30	0	0	0.4900	1.1842	30	0	0	0.4900	1.1842	31	0	0	0.4900	1.1842	30	0	0	0.4900	1.1842
31	0	0	1.4970	0.2234	31	0	0	0.4900	1.1842	31	0	0	0.4900	1.1842	31	0	0	0.4900	1.1842	32	0	0	0.4900	1.1842	31	0	0	0.4900	1.1842
32	0	0	1.4970	0.2234	32	0	0	0.4900	1.1842	32	0	0	0.4900	1.1842	32	0	0	0.4900	1.1842	33	0	0	0.4900	1.1842	32	0	0	0.4900	1.1842
33	0	0	1.4970	0.2234	33	0	0	0.4900	1.1842	33	0	0	0.4900	1.1842	33	0	0	0.4900	1.1842	34	0	0	0.4900	1.1842	33	0	0	0.4900	1.1842
34	0	0	1.4970	0.2234	34	0	0	0.4900	1.1842	34	0	0	0.4900	1.1842	34	0	0	0.4900	1.1842	35	0	0	0.4900	1.1842	34	0	0	0.4900	1.1842
35	0	0	1.4970	0.2234	35	0	0	0.4900	1.1842	35	0	0	0.4900	1.1842	35	0	0	0.4900	1.1842	36	0	0	0.4900	1.1842	35	0	0	0.4900	1.1842
36	0	0	1.4970	0.2234	36	0	0	0.4900	1.1842	36	0	0	0.4900	1.1842	36	0	0	0.4900	1.1842	37	0	0	0.4900	1.1842	36	0	0	0.4900	1.1842
37	0	0	1.4970	0.2234	37	0	0	0.4900	1.1842	37	0	0	0.4900	1.1842	37	0	0	0.4900	1.1842	38	0	0	0.4900	1.1842	37	0	0	0.4900	1.1842
38	0	0	1.4970	0.2234	38	0	0	0.4900	1.1842	38	0	0	0.4900	1.1842	38	0	0	0.4900	1.1842	39	0	0	0.4900	1.1842	38	0	0	0.4900	1.1842
39	0	0	1.4970	0.2234	39	0	0	0.4900	1.1842	39	0	0	0.4900	1.1842	39	0	0	0.4900	1.1842	40	0	0	0.4900	1.1842	39	0	0	0.4900	1.1842
40	0	0	1.4970	0.2234	40	0	0	0.4900	1.1842	40	0	0	0.4900	1.1842	40	0	0	0.4900	1.1842	41	0	0	0.4900	1.1842	40	0	0	0.4900	1.1842
41	0	0	1.4970	0.2234	41	0	0	0.4900	1.1842	41	0	0	0.4900	1.1842	41	0	0	0.4900	1.1842	42	0	0	0.4900	1.1842	41	0	0	0.4900	1.1842
42	0	0	1.4970	0.2234	42	0	0	0.4900	1.1842	42	0	0	0.4900	1.1842	42	0	0	0.4900	1.1842	43	0	0	0.4900	1.1842	42	0	0	0.4900	1.1842
43	0	0	1.4970	0.2234	43	0	0	0.4900	1.1842	43	0	0	0.4900	1.1842	43	0	0	0.4900	1.1842	44	0	0	0.4900	1.1842	43	0	0	0.4900	1.1842
44	0	0	1.4970	0.2234	44	0	0	0.4900	1.1842	44	0	0	0.4900	1.1842	44	0	0	0.4900	1.1842	45	0	0	0.4900	1.1842	44	0	0	0.4900	1.1842
45	0	0	1.4970	0.2234	45	0	0	0.4900	1.1842	45	0	0	0.4900	1.1842	45	0	0	0.4900	1.1842	46	0	0	0.4900	1.1842	45	0	0	0.4900	1.1842
46	0	0	1.4970	0.2234	46	0	0	0.4900	1.1842	46	0	0	0.4900	1.1842	46	0	0	0.4900	1.1842	47	0</								

TABLE 3. Positional and thermal atomic parameters for titanite ($\beta_{ij} \times 10^{-5}$)*

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B**	B _{eq} ***
Ca	.2424(2)	.9184(1)	.7512(2)	1039(26)	129(11)	294(25)	24(13)	-50(21)	11(14)	.52(3)	1.00
Ti	.5134(1)	.7542(1)	.2495(1)	348(16)	117(9)	179(20)	11(10)	64(14)	10(11)	.01(3)	0.44
Si	.7486(2)	.9330(1)	.7490(2)	224(25)	67(13)	105(29)	-1(16)	47(22)	1(17)	-.07(4)	0.27
O(1)	.7499(6)	.8202(4)	.2502(7)	413(69)	191(38)	686(91)	38(45)	346(67)	46(54)	.35(10)	0.77
O(2)	.9108(6)	.8162(4)	.9347(6)	565(78)	222(40)	271(100)	25(45)	18(73)	7(50)	.17(10)	0.75
O(3)	.3827(5)	.9608(4)	.1459(6)	443(73)	276(42)	279(99)	42(45)	107(70)	47(51)	.27(10)	0.71
O(4)	.9122(6)	.3165(4)	.4368(6)	572(77)	224(40)	195(97)	55(45)	57(72)	39(49)	.13(10)	0.71
O(5)	.3813(5)	.4601(4)	.6468(6)	391(71)	172(38)	323(98)	58(43)	78(68)	66(49)	.15(10)	0.60

* Estimated standard deviations are in parentheses and refer to the last decimal place(s).

** Isotropic temperature factors from last cycle of refinement before changing to anisotropic temperature factors.

*** Equivalent isotropic temperature factors calculated using the expression of Hamilton (1959).

The off-center displacement of Ti in an octahedron is characteristic of oxygen-octahedral ferroelectrics. The antiparallel displacements of the titanium atoms in adjacent chains in titanite would compensate the electric moments produced by the ionic displacements, resulting in a net zero electric polarization for the unit cell. This state for a dielectric crystal is called antiferroelectric.

The domain texture of titanite

The lattice upon which the titanite structure is built is nearly *A*-face centered. The crystal structure refinement shows that only the small, off-center displacement of the titanium atoms significantly violates the *A*-face centering. This phenomenon is also revealed in the diffraction pattern of titanite by the behavior of the types of reflections: $k + l$ odd and $k + l$ even. Diffraction data of the type $k + l$ odd which violate the *A*-centered lattice symmetry are relatively weak as compared with $k + l$ even reflections (Fig. 1a). In long-exposure single-crystal photographs of the natural titanites, these $k + l = \text{odd}$ reflections are diffuse (Fig. 1b). The cause of the diffuse nature of these reflections may be discovered by carefully examining their shape and intensity distribution.

Long-exposure Laue and precession photographs, taken with filtered Mo radiation, show that the diffuse scattering is localized on reciprocal lattice planes (relplanes) with modulated intensities (Fig. 4). These two-dimensional relplanes have extensions entirely in the (100). According to Wooster (1962) and Comès *et al.* (1970) this is indicative of a one-dimensional lattice disorder parallel to the [100]. Furthermore, the varying intensity within the diffuse relplanes has

been shown by Guinier (1963) and Vainshtein (1966) to be a result of a one-dimensional lattice wherein the vectors forming the repeat not only vary about some average length but also in direction to some small degree.

While these constraints could be met by a number of atoms, the structure refinement clearly shows that the difference between an *A*-centered structural refinement of a natural titanite (Mongiorgi and Riva di Sanseverino, 1968) and a primitive structure refinement is the position of the titanium atoms. We suggest that natural titanites consist of numerous domains of $P2_1/a$ titanite related by a half-turn parallel to *b*. This would bring all atoms into coincidence except the titanium atoms because of their off-centering. This non-coincidence of the titanium atoms would yield the necessary linear disorder required by the space-averaging effect of the scattered X-rays. The addition of a half-turn to the $P2_1/a$ space group would give the apparent $A2/a$ space group of natural titanites.

Long-exposure Laue photographs (168 hrs) of the synthetic titanite show very weak relplanes, indicating the presence of domains although the crystal is essentially a single domain. The existence of these domains in the synthetic titanite may be related to the largest axes of the thermal ellipsoids of Ti, Ca, Si, O(2), O(3), O(4), and O(5), all being nearly parallel to *a* (Table 5).

The coupled substitution of Fe and Al for Ti and OH, Cl, and F for O₁ appears to favor domain formation in natural titanites, (*i.e.*, (Fe,Al) + (OH,Cl,F) \rightleftharpoons Ti + O₁). Synthetic titanite (Robbins, 1968; this study) is essentially a single domain resulting in a space group of $P2_1/a$, whereas all natural titanites

examined as a part of this study and by Higgins (1975) possess diffuse $k + l$ odd reflections. It is thought that if a titanium atom is off-centered in the octahedra, all other titanium atoms in the octahedral chain are off-centered in the same direction through polarization of the common corner oxygen atoms. As

TABLE 4. Interatomic distances (Å) and angles (°) in titanite*

Atoms	Distance	Atoms	Distance	Angle at metal atom
Si-0(2)	1.646(4)	0(2)-0(3)	2.735(6)	112.3(2)
-0(3)	1.647(4)	-0(4)	2.581(5)	103.5(2)
-0(4)	1.641(4)	-0(5)	2.666(6)	108.1(2)
-0(5)	<u>1.646(4)</u>	0(3)-0(4)	2.672(6)	108.7(2)
		-0(5)	2.719(6)	111.3(2)
		0(4)-0(5)	2.736(5)	<u>112.7(2)</u>
mean	1.645			mean 109.4
Ti-0(1)	1.766(4)	0(1)-0(1)	3.739(9)	179.7(5)
-0(1)	1.974(6)	-0(2)	2.727(6)	92.9(2)
-0(2)	1.984(5)	-0(3)	2.697(6)	90.8(2)
-0(3)	1.991(5)	-0(4)	2.728(6)	93.2(2)
-0(4)	2.014(4)	-0(5)	2.793(5)	94.6(2)
-0(5)	<u>2.025(4)</u>	0(1)-0(2)	2.737(8)	87.3(2)
mean	1.959	-0(3)	2.807(6)	89.5(2)
mean		-0(4)	2.716(5)	86.7(2)
Ti-0(1)	1.870	-0(5)	2.703(6)	85.1(2)
mean Ti-0(x),		0(2)-0(3)	2.833(5)	90.0(2)
x ≠ 1	2.003	-0(4)	3.969(7)	173.9(2)
		-0(5)	2.832(6)	89.7(2)
		0(3)-0(4)	2.825(6)	89.9(2)
		-0(5)	4.034(5)	174.5(2)
		0(4)-0(5)	2.831(5)	89.8(2)
Ca-0(1)	2.281(4)	0(1)-0(2)	4.512(5)	146.8(2)
-0(2)	2.428(4)	-0(3)	3.052(6)	81.4(2)
-0(3)	2.399(5)	-0(3)	2.697(6)	65.4(1)
-0(3)	2.672(5)	-0(4)	4.519(5)	148.5(2)
-0(4)	2.414(4)	-0(5)	3.059(6)	81.1(1)
-0(5)	2.425(5)	-0(5)	2.704(6)	67.1(1)
-0(5)	<u>2.587(5)</u>	0(2)-0(3)	2.833(6)	71.8(1)
mean	2.458	-0(3)	3.555(5)	88.2(1)
		-0(4)	2.581(5)	64.4(1)
		-0(5)	4.274(6)	123.5(1)
		-0(5)	4.637(6)	135.2(1)
		0(3)-0(3)	3.075(8)	74.4(1)
		-0(4)	4.288(6)	125.9(1)
		-0(5)	4.766(8)	162.3(1)
		-0(5)	3.792(7)	98.9(1)
		0(3)-0(4)	4.637(6)	131.4(1)
		-0(5)	3.787(7)	95.8(1)
		-0(5)	4.815(8)	132.6(1)
		0(4)-0(5)	2.831(5)	71.6(1)
		-0(5)	3.570(5)	91.0(1)
		0(5)-0(5)	3.104(8)	76.5(1)
		Ti-0(1)-Ti		141.8(2)
		Si-0(2)-Ti		144.3(2)
		Si-0(3)-Ti		128.4(2)
		Si-0(4)-Ti		139.0(2)
		Si-0(5)-Ti		125.3(2)

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

TABLE 5. Magnitude and orientation of the principal axes of the thermal ellipsoids for titanite*

Atom, axis	rms displacement (Å)	Angle (°) with respect to:		
		+a	+b	+c
Ca, r ₁	0.067(4)	83(2)	130(26)	50(19)
r ₂	0.073(3)	86(3)	40(25)	56(19)
r ₃	0.170(2)	171(1)	91(1)	58(1)
Ti, r ₁	0.057(3)	91(3)	79(12)	152(6)
r ₂	0.067(3)	94(5)	12(11)	78(11)
r ₃	0.091(2)	176(5)	94(5)	65(3)
Si, r ₁	0.044(6)	87(7)	89(39)	159(8)
r ₂	0.051(5)	89(10)	1(36)	89(37)
r ₃	0.072(4)	177(8)	89(10)	68(7)
0(1), r ₁	0.076(10)	162(27)	77(50)	54(21)
r ₂	0.084(9)	81(49)	18(37)	108(33)
r ₃	0.116(7)	106(9)	102(13)	138(10)
0(2), r ₁	0.068(13)	100(7)	85(20)	146(8)
r ₂	0.092(8)	95(11)	7(15)	83(17)
r ₃	0.124(7)	169(8)	96(11)	56(7)
0(3), r ₁	0.069(13)	91(13)	78(13)	152(14)
r ₂	0.098(8)	32(43)	121(42)	117(15)
r ₃	0.107(8)	122(43)	146(40)	86(23)
0(4), r ₁	0.058(15)	93(7)	78(14)	150(10)
r ₂	0.093(8)	102(13)	17(14)	74(14)
r ₃	0.119(7)	167(12)	102(13)	66(7)
0(5), r ₁	0.064(12)	76(12)	128(18)	55(17)
r ₂	0.090(9)	96(37)	42(22)	50(28)
r ₃	0.099(8)	164(18)	104(30)	60(29)

* Estimated standard deviations are given in parentheses and refer to the last decimal place(s).

Fe and Al substitute for Ti with a coupled OH, F, or Cl for O₁ substitution, the electronic configuration changes, and this trend need not follow. The Ti atoms may be off-centered in either direction along *a* on either side of the non-titanium-containing octahedra.

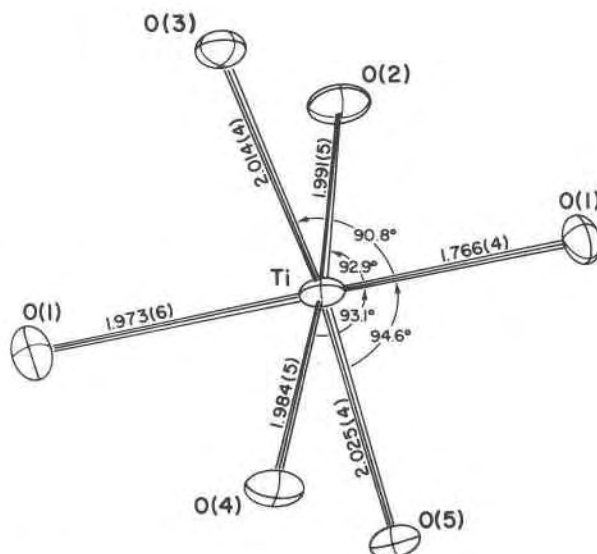


FIG. 2. The titanium octahedra in synthetic $P2_1/a$ titanite.

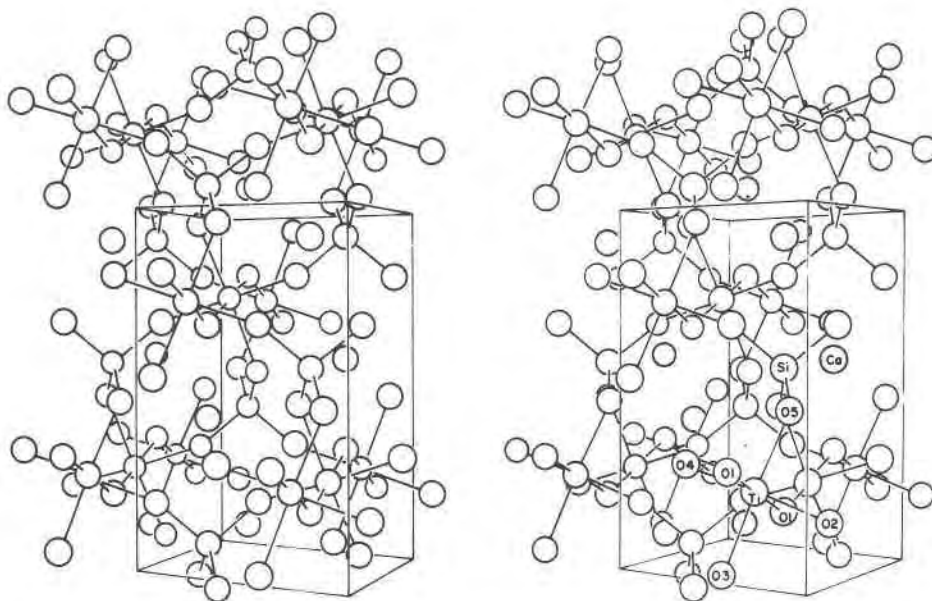


FIG. 3. Stereoscopic pair of the crystal structure of $P2_1/a$ titanite. b is vertical and a is directed away from the viewer, parallel to the octahedral chain.

Increased chemical substitution in titanite would gradually increase the number of antiferroelectric domains, and the space group would gradually appear to change from $P2_1/a$ to $A2/a$.

Relation of titanite to other compounds

A framework of corner-sharing octahedral chains cross-linked by tetrahedra has been shown by various

authors (Kokkoros, 1938; Baur, 1959; Mayer and Völlenklee, 1972) to be a basic feature of a number of compounds. Table 6 is an expanded list and includes some interesting synthetic analogs of titanite. Mayer and Völlenklee (1972) believe that structures of this type are derivatives of the structure of $\text{GeOH}[\text{PO}_4]$, which contains chains of corner-sharing $\text{GeO}_5(\text{OH})$ octahedra cross-linked by phosphate tetrahedral oxyanions. The phosphate ion shares its oxygen atoms with four separate $\text{GeO}_5(\text{OH})$ groups in three separate chains, and the large cavities formed by this framework are unoccupied. Depending on the formal charges of the octahedral and tetrahedral cations of the derivative structures, these cavities may be either vacant or occupied. Closely related to these compounds are a group of tetragonal compounds, many being polymorphs of the previous compounds. Here the octahedral chains with their cross linking tetrahedra are rotated and straightened so that the chains parallel a four-fold symmetry axis. In addition, the tetrahedra cross link four separate octahedral chains. The cavities formed by this framework may be either vacant (*i.e.* αVOSO_4) or occupied (*i.e.* $\text{Na}_2\text{TiOSiO}_4$). Mongiorgi and Riva di Sanseverino (1968) extend this notion a step further and consider a comparison between titanite and narsarsukite. In narsarsukite, the TiO_6 octahedral chains are cross linked by Si_4O_{10} groups rather than by SiO_4 tetrahedra, and sodium occupies the irregular 7-coordinate cavities.

The only naturally occurring silicate isostructural

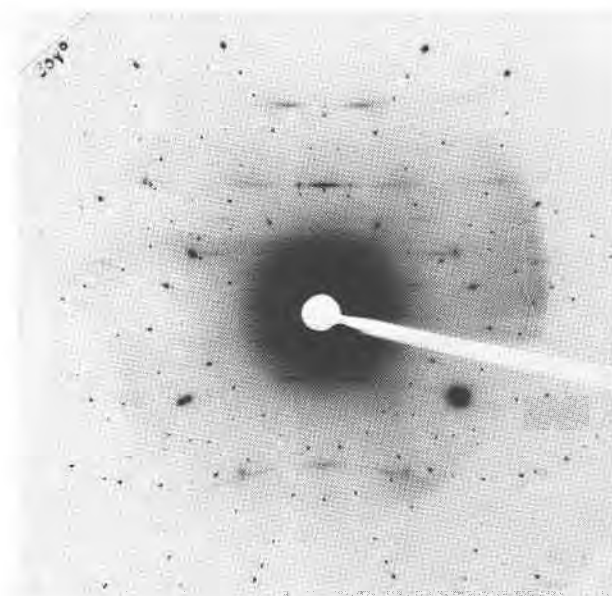


FIG. 4. Laue photograph (Mo radiation) of a natural titanite. c parallels the X-ray beam, and the symmetry plane is vertical.

TABLE 6. Structural derivatives of titanite

Compound	Name	Space group	Number of octahedral chains joined per tetrahedra	Reference
$^{\circ}\text{GeOHPO}_4$		$C2/c$	3	Mayer and Völlenkle, 1972
$^{\circ}\text{FeOHSO}_4$		$Prma$ or $Pn2_1a$	3	Johansson, 1962
$^{\circ}\text{InOHSO}_4$		$Prma$ or $Pn2_1a$	3	"
$^{\circ}\text{MgH}_2\text{OSO}_4$	kieserite	$C2/c$	3	Leonhardt and Weiss, 1957
$^{\circ}\text{FeH}_2\text{OSO}_4$	szomolnokite	$C2/c$	3	Oswald, 1965
$^{\circ}\text{MnH}_2\text{OSO}_4$	szmikite	$C2/c$	3	"
$^{\circ}\text{CuH}_2\text{OSO}_4$	poitevinite	$P1$ or $P\bar{1}$	3	"
$^{\circ}\text{ZnH}_2\text{OSO}_4$	gunningite	$C2/c$	3	"
$^{\circ}\text{CoH}_2\text{OSO}_4$		$C2/c$	3	"
$^{\circ}\text{NiH}_2\text{OSO}_4$		$C2/c$	3	"
$^{\circ}\text{NiH}_2\text{OSeO}_4$		$C2/c$	3	"
$^{\circ}\text{CoH}_2\text{OSeO}_4$		$C2/c$	3	"
$^{\circ}\text{ZnH}_2\text{OSeO}_4$		$C2/c$	3	"
$^{\circ}\text{MnH}_2\text{OSeO}_4$		$C2/c$	3	"
$^{\circ}\text{VOSO}_4$	βVOSO_4	$Prma$ or $Pn2_1a$	3	Kierkegaard and Longo, 1965
$^{\circ}\text{VOPO}_4$	βVOPO_4	$Prma$ or $Pn2_1a$	3	Gopal and Calvo, 1972
$^{\circ}\text{TaOPO}_4$			3	Levin and Roth, 1970
$^{\circ}\text{NbOPO}_4$			3	"
$^{\circ}\text{VOSO}_4$	αVOSO_4	$P4/n$	4	Longo and Arnott, 1970
$^{\circ}\text{VOPO}_4$	αVOPO_4	$P4/n$	4	"
$^{\circ}\text{TaOPO}_4$		$P4/n$	4	Longo, Pierce, and Kafalas, 1971
$^{\circ}\text{NbOPO}_4$		$P4/n$	4	Longo and Kierkegaard, 1966
$^{\circ}\text{MoOPO}_4$		$P4/n$	4	Kierkegaard and Longo, 1970
$^{\circ}\text{VOMoO}_4$		$P4/n$	4	Eick and Kihlberg, 1966
$^{\circ}\text{CuClB(OH)}_4$	bandykite	$P4/n$	4	Collin, 1951
LiAlOHPO_4	amblygonite	$P\bar{1}$	3	Baur, 1959
LiAlFPO_4	montebraisite	$P\bar{1}$	3	"
NaAlFPO_4	natromontebraisite	$P\bar{1}$	3	Povarennykh, 1972
LiFeFPO_4	tavorite	$P\bar{1}$	3	Lindberg and Pecora, 1955
NaAlFAsO_4	durangite	$C2/c$	3	Kokkoros, 1938
CaTiOSiO_4	titanite	$P2_1/a$	3	this study, Robbins, 1968
CaTiOGeO_4		$P2_1/a$	3	Robbins, 1968
CaSnOSiO_4	malayaite	$A2/a$	3	Ramdohr and Strunz, 1967
$\text{Li}_2\text{TiOSiO}_4$		$P4/ramm$ (?)	4	Kim and Hummel, 1959
$\text{Na}_2\text{TiOSiO}_4$		$P4/ramm$	4	Nikitin <i>et al.</i> , 1964
$(\text{Na}, \text{Ca})(\text{Ti}, \text{Nb})\text{OSiO}_4$	fersmanite	$C2/c$		Povarennykh, 1972
CaMgFAsO_4	tilasite	$C2/c$	3	Strunz, 1937; Bladh <i>et al.</i> , 1972
CaMgFPO_4	isokite	$C2/c$	3	Povarennykh, 1972

with titanite is malayaite. Takenouchi (1971) has studied the subsolidus relations of the $\text{CaTi}[\text{SiO}_5]\text{-CaSn}[\text{SiO}_5]$ join and found complete solid solution at 700°C and 1 kb. Below $615 \pm 15^\circ\text{C}$ at 1 kb, an immiscible region exists between the two end members with the peak of the solvus at titanite₇₅ malayaite₂₅. Because of the immiscible region in the titanite-malayaite series, Takenouchi argues that tin-rich titanite and titanium-rich malayaite will rarely

occur in nature because the formation temperatures of tin ore deposits are probably lower than 500°C. Other tin-rich parageneses seem unlikely. The larger size of the tin atom in octahedral coordination is reflected in the larger cell parameters of synthetic malayaite ($a = 7.173(9) \text{ \AA}$, $b = 8.876(5) \text{ \AA}$, $c = 6.888(8) \text{ \AA}$, $\beta = 113.71^\circ$) and the $A2/a$ space group.

Of the other known cations that substitute for Ti in titanite, no end-member compositions have yet to our

knowledge been reported. These include Y and Ce, Al, Fe³⁺, Nb, Ta, and Cr. It is possible that these solid solutions are limited because either a solvus relation exists as in the case of the titanite-malayaite join or the coupled substitution needed to maintain charge balance does not occur. Other cations may be readily substituted for Ca, *i.e.* the Li and Na analogs of titanite. However, substitution of these elements results in tetragonal symmetry. The Ba analog reported by Rase and Roy (1955) has been shown to be synthetic fresnoite by Robbins (1969). Complex, coupled substitutions to maintain charge balance: Ti \rightleftharpoons Al, Fe³⁺, Nb⁵⁺, Ta⁵⁺; O₁ \rightleftharpoons Cl, F, OH; Ca \rightleftharpoons Na, Li, K, Mg, Sr appear to proceed to only a limited extent in most natural titanites. Fersmanite appears to fulfill this role for Ti \rightleftharpoons Nb; Ca \rightleftharpoons Na, but little is known about its crystal chemistry and structure.

Acknowledgments

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