Incorporation of rare earth elements in titanite: Stabilization of the *A2/a* dimorph by creation of antiphase boundaries

John M. Hughes,[1] Erich S. Bloodaxe,[1] John M. Hanchar,[2]* and Eugene E. Foord[3]

[1]Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.
[2]Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180–3590, U.S.A.
[3]U.S. Geological Survey, P.O. Box 25046, MS 905, Denver Federal Center, Denver, Colorado 80225, U.S.A.

Abstract

The atomic arrangement of a natural rare-earth-rich titanite and two synthetic rare-earth-doped titanites have been refined in space group *A2/a*, and the atomic arrangement of an undoped *P2₁/a* synthetic titanite was also refined for comparison.

Previous work has shown that titanite possesses a domain structure, with domains formed of like-displaced Ti atoms in the [100] octahedral chains. *P2₁/a* titanite results when the crystal is formed of a single domain, but as Ti-reversal sites occur in the octahedral chain the apparent *A2/a* structure results from the average of antiphase domains. Antiphase boundaries occur at O1, which is alternately overbonded or underbonded at the boundaries, depending on the displacement of the neighboring Ti atoms. Type 2 antiphase boundaries exist where two Ti atoms are displaced away from the intervening O1 atom and are energetically unfavorable because of underbonding of that O1 atom. However, substitution of a trivalent rare earth element in the adjacent Ca^{2+} site relieves that underbonding, favoring the creation of type 2 antiphase boundaries and stabilization of the *A2/a* dimorph. The results of high-precision crystal structure analyses demonstrate that rare earth substituents for Ca stabilize the *A2/a* dimorph at lower substitution levels than required for octahedral substitutions.

Introduction and previous work

Titanite, $CaTiSiO_5$, is a common accessory mineral in igneous and metamorphic rocks, and it plays a major role in the rare earth element (REE) distribution in rocks that contain the phase. Of particular interest in titanite is the accommodation of REE and the concomitant charge-balancing substitution for the $Ca^{2+} \leftrightarrow REE^{3+}$ exchange.

Natural *P2₁/a* and *A2/a* titanites have been reported, and many authors have addressed the paradox. Speer and Gibbs (1976) described the structure of titanite on the basis of domains of Ti-octahedral chains with like-displaced (along [100]) Ti atoms and conjectured on the relationship between domain volume and temperature and composition. They noted that the *A2/a* dimorph of titanite is stable at temperatures above ~220 °C in synthetic titanites and that sufficient substitutions for Ti in the octahedral chains allow Ti reversal sites and decrease the volume of domains such that the apparent structure is *A2/a* at lower temperatures.

Taylor and Brown (1976) examined the phase transition in synthetic titanites as a function of temperature and elucidated structural changes that occur with that variable. More recently, Zhang et al. (1995) have elucidated the spectroscopic and thermochemical properties of the $CaTiSiO_5$ dimorphs, and Van Heurck et al. (1991) provided electron diffraction and electron microscopic images of the phase and evaluated the nature of the antiphase boundaries at conditions near the transition temperature. Ghose et al. (1991) undertook a detailed high-temperature X-ray diffraction study of the phase transition and presciently noted that "vacancies and defects pinning the domain boundaries may drastically alter the transition behavior and affect the domain mobility," an observation germane to the present study.

Substitution of REE elements in titanite is of interest beyond the mere elucidation of the polyhedral response to substitution of the larger REE element for Ca. Because the antiphase boundaries in titanite create underbonding or overbonding at the bridging oxygen (O1) in the octahedral chain, antiphase boundaries are energetically unfavorable in unsubstituted titanite. However, as REE^{3+} substitute for Ca^{2+}, the increased bonding to O1 may make type 2 antiphase domain boundaries favorable, as the increased bonding from the REE can relieve the underbonding of O1.

In this study a variety of REE-bearing titanites, both natural and synthetic, have been submitted to crystal structure analysis to allow examination of the structural response to substitutions of the rare earth elements and the effect of concomitant altervalent substitutions for Ti

TABLE 1. Crystal data and results of refinement for $A2/a$ and $P2_1/a$ titanites

	Natural	La-Al	Dy-Al	$P2_1/a$
$a(\text{Å})$	7.0425(16)	7.0348(12)	7.0280(17)	7.057(1)
$b(\text{Å})$	8.7155(16)	8.7119(17)	8.7025(20)	8.710(2)
$c(\text{Å})$	6.5376(11)	6.5498(8)	6.5434(15)	6.555(1)
$\beta(°)$	113.629(15)	113.712(12)	113.6813(18)	113.84(2)
$V(\text{Å}^3)$	367.6(2)	367.5(2)	366.5(2)	368.5(2)
Scan type	θ-2θ	θ-2θ	θ-2θ	θ-2θ
Scan time (s)	$\leq$50	$\leq$60	$\leq$90	$\leq$90
θ limits (°)	0–30	0–30	0–30	0–30
Data collected	2250	2256	2253	4260
	$\pm h, +k, \pm l$	$\pm h, +k, \pm l$	$\pm h, +k, \pm l$	$\pm h, \pm k, \pm l$
R_{merge}	0.015	0.008	0.020	0.020
No. of observations (3σ)	378	460	299	572
No. of variable parameters	42	43	43	74
R	0.019	0.017	0.019	0.031
R_w	0.020	0.033	0.020	0.047
Goodness-of-Fit	0.973	0.997	1.003	1.023
Difference peaks (e/Å^3)				
(+)	0.29	0.29	0.31	0.77
(−)	0.44	0.42	0.32	0.85

that affect antiphase boundaries in the domain structure in titanite. The results suggest that REE substituents have a large effect on the $A2/a \leftrightarrow P2_1/a$ phase transition, an effect that has not been previously elucidated.

EXPERIMENTAL METHODS

Three crystals of REE-bearing titanite were obtained. The natural crystal was described by Foord et al. (1993), who reported the formula as: $(Ca_{0.86}REE_{0.12}Na_{0.01})_{0.99}$ $(Ti_{0.63}Fe^{3+}_{0.20}Al_{0.07}Mg_{0.04}Mn^{3+}_{0.03}Nb_{0.02}Sn_{0.01})_{1.00}(Si_{0.99}$ $Al_{0.01})_{1.00}$ $O_4(O_{0.78}F_{0.22})$. In addition to this natural crystal, two synthetic crystals were prepared that were doped with REE substituents, with the charge-balancing reaction of REE + Al $\leftrightarrow$ Ca + Ti. The pure $CaTiSiO_5$ phase was also synthesized to be used for structure comparisons of the dimorphs. Crystals of composition $(Ca_{0.95}La_{0.05})$ $(Ti_{0.95}Al_{0.05})SiO_5$, $(Ca_{0.95}Dy_{0.05})(Ti_{0.95}Al_{0.05})SiO_5$, and Ca-$TiSiO_5$ were synthesized using a modification of the method discussed in Speer and Gibbs (1976). SiO_2, TiO_2, Al_2O_3, $CaCO_3$, and REE_2O_3 starting materials were mixed in a clean glass bottle with a screw cap rotating at a slow speed in a lathe chuck for at least 15 min. The CO_2 was driven off at 700–950 °C in a Deltech $MoSi_2$ vertical-tube furnace prior to melting at 1400 °C in a 25 ml platinum crucible with a tightly fitting Pt lid. The temperature of the furnace and the location of the hot spot within the furnace were determined using a Pt-$Pt_{90}Rh_{10}$ (type S) thermocouple; temperature uncertainties were typically ± 2 °C. The material was homogenized through four cycles of melting, quenching, and crushing. After the final melting the furnace was cooled to 1200 °C and the titanite was allowed to crystallize for two to three weeks depending on the batch that was synthesized. The furnace was then slowly cooled to 600 °C over the course of 12 h. Finally, the furnace was cooled to room temperature and the titanite crystals were removed.

X-ray intensity data for the four phases were collected on an Enraf-Nonius CAD4 diffractometer utilizing graphite-monochromated Mo$K\alpha$ radiation. Unit-cell parameters

were refined (no symmetry constraints) using diffraction angles from 25 automatically centered reflections. Crystal data are given in Table 1, which records details of data collection and structure refinement.

The SDP package of computer programs (Frenz 1985) was used throughout the solution and refinement. Intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. Absorption effects were corrected using 360° ψ-scan data. Symmetry-equivalent reflections were averaged, and neutral-atom scattering factors with terms for anomalous dispersion were used throughout the structure calculations. Reflections were weighted proportionally to $1/\sigma^2$ and only reflections with $I > 3\sigma_I$ were used in the refinement.

Correct assignment of space group (i.e., $P2_1/a$ vs. $A2/a$) was critical in the refinement but in retrospect was not difficult. Long-exposure (8 h) b-axis precession photographs were taken of the synthetic La-Al phase using Polaroid film; no reflections that violated the A centering were noted, even among the $40l$ reflections, the reflections that are among the strongest violations of the centering in $P2_1/a$ titanite. Upon refinement of the superior diffractometer data, it was found for all crystals that the refinement succeeded only in one space group ($A2/a$ for REE-bearing natural and synthetic titanite, and $P2_1/a$ for the undoped synthetic phase). During attempts to refine in the incorrect space group, either the refinement would not converge or large numbers of atoms would refine with nonpositive-definite thermal ellipsoids, indicative of incorrect assignment of space group. Convergence in the correct space group was rapid and routine.

As noted in many previous refinements of the titanite atomic arrangement, the thermal vibration of the Ca site is markedly anisotropic, with the value of β_{11} markedly greater than the other principal axes of the thermal vibration ellipsoid. This observation was manifested in all the present structures, most noticeably in the natural phase, where β_{11} was deemed unusually high (0.0160 Å^2), and thus a model of split sites was attempted. Although the

TABLE 2. Positional parameters and equivalent isotropic displacement factors for A2/a titanites

	x	y	z	B(Å²)
		Ti		
Natural	½	0	½	0.75(1)
La-Al	½	0	½	0.693(8)
Dy-Al	½	0	½	0.64(1)
		Ca		
Natural	¼	0.16684(7)	0	1.54(1)
La-Al	¼	0.16873(6)	0	1.058(8)
Dy-Al	¼	0.16923(9)	0	1.01(2)
		Si		
Natural	¾	0.1828(1)	0	0.67(2)
La-Al	¾	0.18265(7)	0	0.417(9)
Dy-Al	¾	0.1825(1)	0	0.58(2)
		O1		
Natural	¾	0.0744(3)	½	0.88(4)
La-Al	¾	0.0696(2)	½	0.69(3)
Dy-Al	¾	0.0707(4)	½	0.91(6)
		O2		
Natural	0.9127(2)	0.0667(2)	0.1834(3)	1.10(3)
La-Al	0.9115(2)	0.0662(1)	0.1853(2)	0.77(2)
Dy-Al	0.9112(3)	0.0663(2)	0.1851(3)	0.86(4)
		O3		
Natural	0.3798(3)	0.2105(2)	0.3949(2)	1.03(3)
La-Al	0.3826(2)	0.2108(1)	0.3970(2)	0.68(3)
Dy-Al	0.3819(3)	0.2105(2)	0.3968(3)	0.79(4)

Note: Anisotropically refined atoms are given in the form of their isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*\beta_{(1,1)} + b^2*\beta_{(2,2)} + c^2*\beta_{(3,3)} + ab(\cos \gamma)*\beta_{(1,2)} + ac(\cos \beta)*\beta_{(1,3)} + bc(\cos \alpha)*\beta_{(2,3)}]$.

single Ca site is reported here, that site can be successfully refined as two half-occupied sites at $(¼ \pm x', \sim0.17, 0)$, where $x' \cong 0.018$. However, despite the fact that somewhat more realistic β_{11} values resulted, there was no significant decrease in the final R value; thus the single Ca site model is reported.

Occupancy of the Ca site was measured by one of two methods. For the natural phase, electron occupancy of the Ca site was released and refined to 1.186(1) Ca atoms/site. For the synthetic phases nominally with $Ca_{0.95}REE_{0.05}$ and $Ti_{0.95}Al_{0.05}$ at the Ca and Ti sites, respectively, refinement was undertaken by refining the value of x in (Ca_xREE_{1-x}) and (Ti_xAl_{1-x}) for the Ca and Ti sites, respectively, using appropriate scattering factors. For La-Al–substituted titanite, site occupancies for the Ca and Ti sites, respectively, refined to $Ca_{0.96}La_{0.04}$ and $Ti_{0.91}Al_{0.09}$. For Dy-Al titanite the site occupancies refined to $Ca_{0.97}Dy_{0.03}$ and $Ti_{0.85}Al_{0.15}$.

Tables 2 and 3 contain positional parameters and equivalent isotropic displacement parameters for $A2/a$ and $P2_1/a$ titanite, respectively, and Tables 4[1] and 5[1] contain anisotropic thermal parameters for the two phases. Table 6 contains selected bond lengths for the structures,

TABLE 3. Positional parameters and equivalent isotropic displacement factors for synthetic $P2_1/a$ titanite

	x	y	z	B(Å²)
Ti	0.50877(7)	0.7521(2)	0.2496(1)	0.54(1)
Ca	0.2444(1)	0.91827(8)	0.7503(2)	0.97(1)
Si	0.7503(1)	0.93281(9)	0.7504(2)	0.21(2)
O1	0.7489(3)	0.8207(3)	0.2484(5)	0.55(4)
O2	0.9110(3)	0.8170(4)	0.9360(4)	0.51(5)
O3	0.3828(3)	0.9601(4)	0.1462(5)	0.49(5)
O4	0.9110(4)	0.3157(4)	0.4354(4)	0.57(5)
O5	0.3818(3)	0.4612(4)	0.6481(4)	0.53(5)

Note: Anisotropically refined atoms are given in the form of their isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*\beta_{(1,1)} + b^2*\beta_{(2,2)} + c^2*\beta_{(3,3)} + ab(\cos \gamma)*\beta_{(1,2)} + ac(\cos \beta)*\beta_{(1,3)} + bc(\cos \alpha)*\beta_{(2,3)}]$.

and Table 7[1] lists observed and calculated structure factors from the refinements.

DISCUSSION OF STRUCTURES

Speer and Gibbs (1976) described the dominant structural unit of titanite as kinked [100] chains of corner-sharing TiO_6 octahedra; adjacent octahedra in the chains are linked by sharing O1 atoms (Fig. 1).

Natural $P2_1/a$ and $A2/a$ titanites have been reported, and numerous authors have addressed the paradox. Speer and Gibbs (1976) noted that although in the primitive dimorph the Ti-coordinating O atoms form a regular octahedron, the Ti atoms are displaced from the geometric center of the octahedra, a displacement that results in alternating long and short Ti-O1 bonds along the chain (Table 6). Taylor and Brown (1976) showed that synthetic titanite crystallizes in the primitive space group and noted that reflections that violate A-centering are weak but sharp. Upon heating, however, the reflections become diffuse to the point where they disappear at ~220 °C and the A-centered dimorph is stable. Taylor and Brown attributed the phase change to shifts in Ti atom position, wherein the Ti atoms gradually shift toward the octahedron center with increasing temperature until they are centered within the octahedron at ~220 °C.

The apparent $A2/a$ structure of titanite results from the domain texture of the phase. Speer and Gibbs (1976) sug-

TABLE 6. Selected bond lengths (Å) in titanite samples

|	Natural	La-Al	Dy-Al		$P2_1/a$
Ca-O1	2.255(3)	2.279(2)	2.263(3)	Ca-O1	2.274(3)
Ca-O2	2.407(2)	2.418(1)	2.419(2)	Ca-O2	2.430(3)
Ca-O2'	2.407(2)	2.418(1)	2.419(2)	Ca-O4	2.399(3)
Ca-O3	2.399(2)	2.4112(9)	2.408(2)	Ca-O3	2.403(3)
Ca-O3''	2.399(2)	2.4112(9)	2.411(2)	Ca-O5	2.424(3)
Ca-O3'''	2.641(2)	2.615(1)	2.615(2)	Ca-O3'	2.657(3)
Ca-O3''''	2.641(2)	2.615(1)	2.615(2)	Ca-O5'	2.591(3)
Mean	2.450(6)	2.452(3)	2.450(6)		2.454(8)
Ti-O1	1.8765(9)	1.8604(5)	1.862(1)	Ti-O1	1.799(3)
Ti-O1'	1.8765(9)	1.8604(5)	1.862(1)	Ti-O1'	1.938(3)
Ti-O2	1.995(2)	1.984(1)	1.984(2)	Ti-O2	1.979(3)
Ti-O2'	1.995(2)	1.984(1)	1.984(2)	Ti-O4	1.987(3)
Ti-O3	2.022(2)	2.015(1)	2.013(2)	Ti-O3	2.011(3)
Ti-O3'	2.022(2)	2.015(1)	2.013(2)	Ti-O5	2.020(3)
Mean	1.965(4)	1.953(2)	1.953(4)		1.956(7)
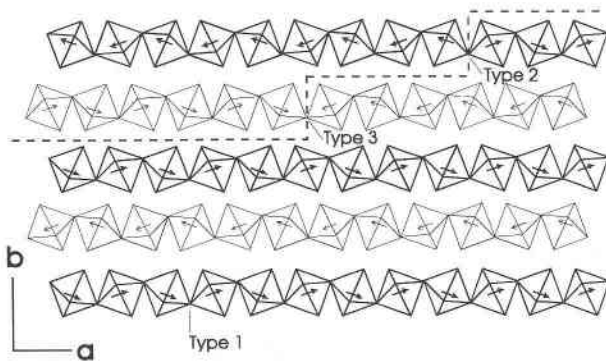
FIGURE 1. The [100] octahedral chains in titanite; octahedra are linked by corner sharing of O1 atoms. Arrows depict direction of Ti movement from octahedron center. Antiphase boundaries are depicted by dashed line, and bold and light octahedra are above and below plane of page, respectively. Type 1, 2, and 3 O1 atoms are shown. Modified slightly from Taylor and Brown (1976).

TABLE 8. Bond valence sums (in valence units) for O1 atoms at antiphase boundaries in $P2_1/a$ titanites with nearest-neighbor Ca and REE atoms

	Type 1	Type 2	Type 3
Ca	2.10	1.77	2.43
REE	2.41	2.08	2.74

Note: Constants from Brown (1981); Pr constants were used to represent average REE atom. Favored O1 environment is type 1 for Ca and type 2 for REE.

gested that in $P2_1/a$ titanite all Ti atoms in a given octahedral chain are like-displaced, i.e., they are all displaced in the same direction away from the octahedron center along the entire chain; thus primitive titanite is essentially a single domain. As impurities increase, however, "mistakes" occur in the structure that create domains of like-displaced Ti atoms and anti-phase boundaries between regions of opposite-displaced Ti atoms (Fig. 1). At each anti-phase boundary, which occurs at an O1 atom, Ti-reversal sites occur such that the two Ti atoms adjacent to an O1 atom in the chain are both displaced away from the O1 or toward the O1 atom. As noted by Taylor and Brown (1976), this yields three types of O1 atoms in the octahedral chains of titanite (Fig. 1): (1) the normal O atom (their "type 1") with one Ti displaced toward and the other away from O1 (bond valence sum on this O1 = 2.10 v.u., Table 8); (2) an O1 at a domain boundary where both Ti atoms are displaced away from O1 ("type 2"; O1 valence sum = 1.77 v.u.); and (3) an O1 at a domain boundary where both Ti atoms are displaced toward the O1 site ("type 3"; O1 valence sum = 2.43 v.u.). They suggested that titanite "will react in such a way as to minimize the number of type 2 and type 3 O1 sites leading to domain boundaries;" such O1 atoms are either significantly underbonded (type 2) or overbonded (type 3). However, although in unsubstituted titanite the existence of type 2 and type 3 O1 atoms is energetically unfavorable, in titanites with a REE substituent for Ca, type 2 O1 atoms may be favored as a method of balancing the increased charge of the trivalent substituent.

The volume of individual domains in titanite can be reduced by incorporating substituents for Ti in the octahedral site, substituents that can act as Ti-reversal sites in the octahedral chains and thus terminate a domain in [100]. Higgins and Ribbe (1976) demonstrated that as the mol percent of the Ti substituents increased, the $h0l$ reflections that violate the A centering become more diffuse

(i.e., domain volume decreases and number of domains increases) to the point at approximately 20 mol% [6](Fe,Al), at which the diffuse reflections disappear completely, yielding an average $A2/a$ structure.

Substitutions of REE, although unstudied, can also effect octahedral substitutions by coupling REE^{3+} + $(Fe,Al)^{3+}$ ↔ Ca^{2+} + Ti^{4+}, as the charge-balancing substituent for Ti will also favor Ti-reversal sites in the octahedral chain. The substitution of REE elements, however, is of interest beyond providing concomitant Ti-reversal sites in the octahedral chain in the titanite atomic arrangement. The altervalent substitution in which REE^{3+} elements substitute in the Ca site has a unique affect on O1, the nearest ligand to the Ca site occupant.

Type 2 O1 atoms exist at antiphase boundaries at which both neighboring (along [100]) Ti atoms are displaced away from the intervening O1, leaving the O1 atom underbonded by 0.23 v.u. The O1 atom bonds to the two Ti atoms and the Ca atom and provides the shortest bond to Ca. As noted above, type 2 O1 atoms are energetically unfavorable in unsubstituted titanite because that O1 is underbonded; however, substitution of a trivalent REE for Ca^{2+} relieves that underbonding.

Bond sums for the three types of O1 environments illustrated in Figure 1 are listed in Table 8. As shown there, in an unsubstituted titanite type 1 O1 atoms are favored, and, as noted previously, type 2 and 3 antiphase boundaries are energetically unfavorable. Thus, at low temperatures, the $P2_1/a$ dimorph is favored and domain volume is large. With the substitution of REE, however, it can be suggested that a type 2 antiphase boundary must be created to relieve the underbonding on O1; the normally unfavorable type 2 O1 atom becomes a stabilizing nearest neighbor of the REE substituent (Table 8). Thus, REE substituents stabilize the type 2 O1 antiphase boundary and perform "double duty" in producing antiphase boundaries by making type 2 O1 atoms energetically favorable and by providing a coupled (Fe,Al) ↔ Ti substituent reversal site [as noted by Taylor and Brown (1976) the octahedral substituent need not be spatially coupled with charges at the O1 site]. Thus, REE substituents greatly favor the $A2/a$ dimorph. As noted by Higgins and Ribbe (1976), the $A2/a$ dimorph is stabilized at 20 mol% substitution in the Ti site of the octahedral chains. In the synthetic samples analyzed herein, that dimorph was stabilized at 5% Al substitution in the Ti sites, but with each REE substituent also creating an antiphase

boundary. Thus trivalent REE substituents are apparently more effective in stabilizing the $A2/a$ dimorph than octahedral substituents.

In a manner similar to the stabilizing influence of trivalent REE substituents on type 2 antiphase boundaries, monovalent substituents such as Na may reduce the overbonding at type 3 antiphase boundaries by an amount sufficient to make those antiphase boundaries energetically favorable. Calculation of bond valence sums on a type 3 O1 atom assuming a substituent Na atom in the Ca site yields 2.17 v.u., in contrast to 2.43 v.u. for a Ca atom in the site. Thus Na, which is known to substitute in titanite in minor amounts, may stabilize type 3 antiphase boundaries. We are attempting to synthesize a titanite with minor substitutions ($\leq 1\%$) of Na + REE $\leftrightarrow$ 2Ca to determine if the $A2/a$ dimorph can be stabilized by creation of type 2 and type 3 antiphase boundaries, with no substitutions for Ti in the octahedral chains.

ACKNOWLEDGMENTS

REFERENCES CITED

Brown, I.D. (1981) The bond-valence method: An empirical approach to chemical structure and bonding. In M. O'Keeffe and A. Navrotsky, Eds., Structure and bonding in crystals, volume 2, p. 1–30. Academic, New York.

Foord, E.E., Hlava, P.F., Erd, R.C., and Lichte, F.E. (1993) Rhyolite-hosted REE-Fe-Nb-bearing titanite from Willow Spring Draw, Sierra County, New Mexico, U.S.A. Abstracts, Rare Earth Minerals: Chemistry, Origin, and Ore Deposits Conference, p. 39–41. Mineralogical Society of Great Britain and Ireland, London.

Frenz, B.A. (1985) Enraf-Nonius Structure Determination Package. In SDP Users Guide, Version 4. Enraf-Nonius, Delft, The Netherlands.

Ghose, S., Ito, Y., and Hatch, D.M. (1991) Paraelectric-antiferroelectric phase transition in titanite, $CaTiSiO_5$. I. A high temperature X-ray diffraction study of the order parameter and transition mechanism. Physics and Chemistry of Minerals, 17, 591–603.

Higgins, J.B. and Ribbe, P.H. (1976) The crystal chemistry and space groups of natural and synthetic titanites. American Mineralogist, 61, 878–888.

Speer, J.A. and Gibbs, G.V. (1976) The crystal structure of synthetic titanite, $CaTiOSiO_4$, and the domain textures of natural titanites. American Mineralogist, 61, 238–247.

Taylor, M. and Brown, G.E. (1976) High-temperature structural study of the $P2_1/a \leftrightarrow A2/a$ phase transition in synthetic titanite, $CaTiSiO_5$. American Mineralogist, 61, 435–447.

Van Heurck, C., Van Tendeloo, G., Ghose, S., and Amelinckx, S. (1991) Paraelectric-antiferroelectric phase transition in titanite, $CaTiSiO_5$. II. Electron diffraction and electron microscope studies of the transition dynamics. Physics and Chemistry of Minerals, 17, 604–610.

Zhang, M., Salje, E.K.H., Bismayer, U., Unruh, H.-G., Wruck, B., and Schmidt, C. (1995) Phase transition(s) in titanite $CaTiSiO_5$: An Infrared spectroscopic, dielectric response and heat capacity study. Physics and Chemistry of Minerals, 22, 41–49.