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Synthesis methods and unit-cell volume of end-member titanite ($CaTiOSiO_4$)

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ABSTRACT

Unit-cell parameters of synthetic, end-member titanite ($CaTiOSiO_4$) critically depend on the synthesis conditions, as is shown for studies reported in the literature and for new samples reported here. Our study suggests that phase-pure samples are likely to be obtained only if they are synthesized entirely below the solidus. In contrast, samples synthesized either directly from melt or by annealing of glass tend to have higher unit-cell volumes, contain Si-rich and Ca-Si–rich phase impurities, and may be nonstoichiometric. The observed variations in cell parameters among the samples strongly correlate with synthesis methods and can be explained by vacancies in the Ca or Si site or both. This result is particularly important because the thermodynamic properties currently in use for titanite are based on samples synthesized from melts of stoichiometric composition and thus are suspect even though they have been determined carefully. To establish a reference point for future studies concerned with the chemical and physical properties of this material we report our findings along with a redetermination of the unit-cell parameters [$a = 7.062(1)$, $b = 8.716(2)$, and $c = 6.559(1)$ Å; $\beta = 113.802(9)°$, $V=369.4(3)$ Å^3] from powder X-ray data of synthetic, stoichiometric titanite.

INTRODUCTION

Variations in unit-cell volume and composition of synthetic, end-member, titanite ($CaTiOSiO_4$) were first documented by Hollabaugh and Rosenberg (1983). Those authors attributed the larger unit-cell parameters and volume of some synthetic samples to the substitution of Ti^{4+} for Si^{4+} in the tetrahedral site. The mechanism was proposed mainly on the basis of microprobe analyses. In this paper we show that a stronger correlation exists between synthesis method and the observed variations in unit-cell volume.

In the course of a phase-equilibrium study involving titanite, we attempted to synthesize end-member titanite ($CaTiOSiO_4$) powder samples using oxide mixtures and stoichiometric glass. Optical examination and unit-cell refinements of these samples suggested that the choice of synthesis path affects the unit-cell volume as well as the phase purity of the sample. A literature search also revealed that synthesis of end-member titanite ($CaTiOSiO_4$) either by direct and slow crystallization from melt or by annealing glasses of the appropriate composition resulted in samples with larger volumes in comparison with samples synthesized below the solidus (Table 1; Fig. 1): In addition, the samples with the larger unit-cell parameters appear to be nonstoichiometric (e.g., Robbins 1968; Manning and Bohlen 1992) and to contain phase impurities either Ca- and Si-rich or Si-rich, or both (e.g., Tanaka et al. 1988; this study) or $CaSiO_3$ and TiO_2 (Manning and Bohlen 1992). To elucidate the origin of these differences we compared our data with previously reported electron microprobe (EMP) analyses and unit-cell refinement of single crystal and powder samples.

EXPERIMENTAL PROCEDURES

Synthesis

Detailed descriptions of the synthesis procedures for samples extracted from the literature can be found in the original papers (Table 1). The samples in this study were synthesized from glass of $CaTiOSiO_4$ composition (sample no. 93-1) and from a mechanical mixture of $CaSiO_3$ and TiO_2 (JMC 810420) (i.e., sample no. 94-2 and 96-1). The $CaSiO_3$ had been synthesized from a mechanical mixture of $CaCO_3$ (ALFA lot 050980) and SiO_2 (JM S50389B), which had been dried at 400 °C for 4 h, and at 1000 °C for 30 h, respectively, before weighing. The $CaCO_3$-SiO_2 mixture was ground in ethanol in an automatic agate mortar for 3 h. The mixture was decarbonated by gradual heating from 500 to 1000 °C over a period of 24 to 30 h and then reacted at 1100 °C. During annealing it was ground several times until optical examination and powder X-ray diffraction suggested that only wollastonite was present. The final product was stored in a desiccator. Before weighing, $CaSiO_3$ and TiO_2 were dried at 1100 °C for 5 and 30 h, respectively. The titanite glass (Table 3: sample no. glass 93) was synthesized by melting an equimolar mixture of $CaSiO_3$-TiO_2 in a platinum crucible at 1400 °C for 16 h, cooling to 1000 °C at 360 °C/min, and quenching in air. The product, an opaque white glass, was crushed and then ground in ethanol in an agate mortar for 2 h.

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Sample no. 93-1 was synthesized by annealing this glass for 48 h at 1100 °C with two cycles of grinding in between. Petrographic examination suggested that only titanite was present. However, backscattered electron imaging and energy dispersive spectrometer (EDS) analysis revealed the presence of Ca- and Si-rich, or Si-rich impurities along grain edges. In addition, synchrotron powder X-ray diffraction suggested the possible presence of at least one phase impurity: One peak at ~ 4.1 Å could not be assigned to titanite.

Sample no. 94-2 was synthesized by first reacting dry a $CaSiO_3$-TiO_2 mechanical mixture for 14 d at 1285 °C and at 1150 °C for 13 d with several cycles of 2–3 h grinding between annealing. Subsequently, 0.6 g from this white powder were loaded with 50 ml H_2O in a gold capsule and reacted at 750 °C and 2 kbar for 7 d. Neither backscattered electron imaging nor X-ray diffraction suggested the presence of impurities.

The third sample (no. 96-1) was synthesized by reacting in a platinum crucible, dry and at 1 atm, an equimolar mixture of $CaSiO_3$-TiO_2 at 1100 °C for 14 d and 1200 °C for 21 d with cycles of thorough grinding during annealing. Optical examination during EMP analysis revealed traces of $CaSiO_3$ (3–5 grains) and one grain of SiO_2 as unreacted cores in titanite grains. Careful EMP analysis of titanite grains showed them to have end-member composition.

Electron microprobe analysis

The synthetic samples were analyzed with a four-spectrometer CAMEBAX electron microprobe. Analytical conditions were an accelerating voltage of 15 kV, a beam current of 20 nA, a 1–5 μm beam, and counting times of 60 s. Titanite (C.M. Taylor Corporation) was used as standard. The ability to directly analyze O, using a multi-layered WSi crystal, was a big advantage over previous studies, which had to infer O from charge-balance considerations. The carbon-coated surface of the probe mounts and that of a brass cylinder, coated together with the samples, were checked against the surface of a brass cylinder that had been coated at the same time as the standards. The raw data were reduced with the PAP and ZAF correction routines. No differences were observed. During the analysis the standards were also analyzed to check for reproducibility. Analyses were accepted if the sums of the elements were 100 ± 2 wt%, and they are presented in Table 2.

Unit-cell refinement

The X-ray measurements were done on beamline X7a (Cox et al. 1988) at the National Synchrotron Light Source in Brookhaven National Laboratory (BNL) and on ID30 of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The data for sample no. 94-2 were collected at X7a (BNL) with a wavelength of 0.6925(2) Å selected from a channelcut Ge (111) monochromator with a linear position-sensitive detector (psd) operating in the escape mode under a krypton gas pressure of 43 psi (Smith 1991). The detector was moved in steps of 0.25° 2θ. The data were binned using the central 2° of the linear psd yielding a pattern containing 723 reflections between 5 and 50° 2θ ($\sin\theta/\lambda_{max}$ = 0.6103 Å^{-1}). The peak full-width at half-minimum (FWHM) ranged between 0.048 and 0.062° 2θ. The data for samples 93-1 and 96-1 were collected on ID30 at ESRF. A very fine fraction obtained by selecting only the particles remaining suspended after 2 min sedimentation was loaded in a hole in a steel foil 200 μm thick to form a cylindrical disk of 200 μm in height and 100 μm in diameter. This disk was then centered on an X-ray beam with 0.4350(3) Å wavelength. Data were collected for 30 min on a Fuji image plate (IP) that was subsequently read on a Molecular Dynamics Phosphor2 IP reader, and were corrected for IP-reader induced distortion (by means of a reference grid pattern exposed immediately before the experiment) as well as tilt of the IP relative to the incident beam. Intensities were then integrated along the full Debye rings to obtain a conventional intensity versus 2θ angle profile. All 2-d data analysis was done using the program fit2d (Hammersley 1995). Unit-cell refinements were done using LeBail's algorithm (LeBail 1992) as implemented on the Rietveld analysis program GSAS (Larson and Von Dreele 1994). Peak profile functions were fitted using a multiterm Simpson's rule integration (Howard 1982) of the pseudo-Voigt function described by Thompson et al. (1987) as implemented in GSAS. No zero point was refined as this was accounted for during 2-d image processing.

DISCUSSION

Inspection of unit-cell volumes of our samples and those from the literature (Table 1) as a function of synthesis method suggests that the samples can be divided into two groups. The first group consists of crystals synthesized either by slow crystallization of stoichiometric melts (i.e., Robbins 1968; Brower and Robbins 1969; Tanaka et al. 1988) or by subsolidus recrystallization of glasses with $CaTiOSiO_4$ composition (Speer and Gibbs 1976; Taylor and Brown 1976; Ghose et al. 1991; This study: sample no. 93-1). These synthetic titanite samples on average have large unit cells regardless of whether single crystals or powders were used in the cell refinement. The second group consists of synthetic titanite samples that were synthesized entirely below the solidus and tend to have smaller unit cells (i.e., Takenuchi 1971; Hollabaugh and Rosenberg 1983: S152R and S250; This study: samples 94-2 and 96-1). Some ambiguity exists regarding the synthesis conditions of one of the Hollabaugh and Rosenberg (1983) titanites (Table 1: 8c; Fig. 1: open square). Although this titanite was synthesized at a nominal temperature (1400 ± 50 °C) higher than the melting point (1382 ± 5 °C), no glass was detected optically (Rosenberg, written communication). Thus, it may be assigned to the second group of synthetic titanite.

To test whether the observed differences might be an artifact of the different experimental procedures for unit-cell determination, we determined the unit-cell parameters of two of our samples (93-1 vs. 96-1) using exactly the same experimental procedure as well as identical data-processing and refinement procedures. The two samples show a significant difference in cell volume. We

TABLE 1. Unit-cell parameters of synthetic titanite ($CaTiOSiO_4$) samples

Unit-cell para-meters	Melt/glass-derived samples*							
	Single-crystal X-ray diffraction					Powder X-ray diffraction		
	(1)‡	(2)‡	(3a)	(3b)	(3c)	(4)	(5)	(6)
a (Å)	6.567(5)	6.57(1)	7.069(2)	7.068(3)	7.0722(5)	7.081(4)	7.065(3)	7.0673(2)
b (Å)	8.723(5)	8.72(1)	8.722(5)	8.714(3)	8.7302(7)	8.736(3)	8.719(4)	8.7201(2)
c (Å)	7.454(5)	7.45(1)	6.566(8)	6.562(2)	6.5672(5)	6.569(3)	6.562(3)	6.5649(2)
β (°)	119.52(3)	119.50	113.86(2)	113.82(2)	113.84(2)	113.89(4)	113.84(4)	113.835(2)
V (Å³)	370.3 ± 0.5	370.26 ± 0.65	370.22(6)	369.7 ± 0.5	370.875 ± 0.055	371.54 ± 1.01	369.7(5)	370.07(2)

Notes: Numbers in parentheses are the reported deviations by the authors, or standard error for Taylor and Brown 1976. If uncertainties for the volume were not reported then they were estimated (i.e., ±) using the equation $\delta y = [\Sigma((\partial y/\partial x_i)\cdot\delta x_i)^2]^{1/2}$. (1) = Robbins 1968; (2) = Brower and Robbins 1969; (3) = sample synthesized by D. Hewitt at VPI subsequently studied by (a) Speer and Gibbs 1976, (b) Taylor and Brown 1976, and (c) Ghose et al. 1991; (4) = Tanaka et al. 1988; (5) = Manning and Bohlen 1992; (6) = this study 93-1; (7) = Takenuchi 1971; (8) = Hollabaugh and Rosenberg 1983, (a) S152R, (b) S250, (c) Induction furnace; (9) this study, (a) 96-1 and (b) 94-2.

* Sample was synthesized either by slow crystallization of $CaTiOSiO_4$ melts or by subsolidus recrystallization of $CaTiOSiO_4$ glasses.

† Sample was synthesized either in air or hydrothermally.

‡ Refined in space group $P2_1/n$ whereas the rest of the samples were refined in space group $P2_1/a$.

§ Method of synthesis is unclear.

therefore conclude that their difference is real and must be a result of the synthesis path. Because the differences are found for several studies, we suspect a crystal-chemical cause. The disparity between samples 94-2 and 96-1 most likely reflects the actual differences in X-ray data collection strategies (i.e., different stations with different detectors, wavelength, and sample mounts) and not the effect of OH^- substitution.

The values for unit-cell axes of end-member ($CaTiOSiO_4$) titanite predicted by Higgins and Ribbe (1976) compare better with the samples synthesized at subsolidus conditions than with the melt or glass derived ones. Therefore we suspect that the titanite derived from melt or glass may deviate from stoichiometry. To explain the inferred relationship among synthesis method, crystal chemistry, and unit-cell volume, we need to consider the possible substitution mechanisms, which can only involve the elements of the formula unit (Ca, Ti, Si, and O, plus vacancies), in the synthetic samples considered here. From a crystal-chemical viewpoint there are two simple mechanisms that could lead to an isostructural increase of the cell volume at constant temperature: (1) substitution of some atoms, most likely cations, by an ion that is larger than the regular cation, and (2) vacancies within the lattice. Isochemical valence change must also be taken into consideration, especially for the Ti site where Ti^{3+} could substitute for Ti^{4+}, with a corresponding charge-balancing anionic substitution or vacancy.

The presence of Ti^{3+} on the octahedral site could explain an increase in the *a* axis and thus also in cell volume, because in the titanite structure the Ti octahedra are arranged in corner-linked chains parallel to *a* (e.g., Speer and Gibbs 1976). However, such a mechanism is rather unlikely because it implies a reducing environment during synthesis, and most syntheses have been performed in air. This is also in agreement with spectroscopic studies (Waychunas 1987) that found no compelling evidence for tetrahedral Ti in a series of silicates including titanite, despite sometimes strong Si deficiencies and negative Si-Ti correlation. It may apply though to one of the two titanite crystals of Tanaka et al. (1988), which was originally melt-grown in an N_2 atmosphere and subsequently annealed at 1300 °C for 24 h in air. There is a small possibility that grains in this powder may contain Ti^{3+}. However, we dismiss Ti^{3+} as the main cause for the unit-cell variation because such a mechanism is sample specific and cannot explain the variations observed in all samples.

The inference of tetrahedral Ti^{4+} (Hollabaugh and Rosenberg, 1983) is not supported by direct evidence. According to them, Ti^{4+} substitution for Si^{4+} in the tetrahedral site should correlate with an increase in unit-cell volume and the length of the *b* axis. However, if the data of Robbins (1968) for $CaTiGeO_5$ are taken into account, then substitution of a cation larger than Si^{4+} in the tetrahedral site may lead to an increase in all axes with the following sequence in relative increase: $b > c > a$. We do not observe a prominent correlation of volume with the length of the *b* axis. The change in cell volume correlates strongly with all three cell axes (Table 3), with only a slightly higher correlation for the *b* axis. Nonetheless, the maximum relative change is about the same for the *a* and *b* axes (3.5%), which is slightly higher than that of the *c* axis (2.5%). Therefore, this finding suggests that the expansion is mainly isotropic and it is not in accordance with a model of cell expansion driven by Ti^{4+} on the tetrahedral site. A linear regression fit of the unit-cell axes vs. unit-cell volume data may appear to favor this model because the observed regression R^2 statistics are 0.89, 0.94, and 0.88 for the *a, b,* and *c* axis, respectively. However, this observation only indicates how well the linear model (i.e., $y = ax + b$) accounts for the variability of the observations.

The available EMP analyses of melt and glass-derived titanites that also have on average large unit cells are quite variable. For example, Tanaka et al. (1988) report ideal stoichiometry for their sample. In contrast, Manning and Bohlen (1992) and Hollabaugh and Rosenberg (1983) report 5 and ~6 mol% excess Ti^{4+}, respectively. However, the data of Hollabaugh and Rosenberg (1983) that

Table 1.—*Extended*

Unit-cell parameters	Subsolidus-derived samples†					
	Powder X-ray diffraction					
	(7)	(8a)	(8b)	(8c)§	(9a)	(9b)
a (Å)	7.066(9)	7.057(1)	7.056(1)	7.058(2)	7.0629(1)	7.0611(1)
b (Å)	8.705(5)	8.707(3)	8.707(1)	8.709(2)	8.7173(2)	8.7138(1)
c (Å)	6.561(9)	6.554(1)	6.553(1)	6.553(1)	6.5601(1)	6.5586(1)
β (°)	113.93(2)	113.80(2)	113.77(2)	113.74(2)	113.796(1)	113.809(1)
V (Å^3)	368.9 ± 0.59	368.4(1)	368.4(1)	368.7(2)	369.57(1)	369.20(1)

refers to the titanite crystal synthesized by Robbins (1968) may be problematic as the reported sum of the oxides is slightly greater than 102 wt%. Finally, Higgins and Ribbe (1976) report a 3% Ca deficiency for the sample used by Speer and Gibbs (1976), Taylor and Brown (1976), and Ghose et al. (1991).

Our EMP analyses for the synthetic titanites of this study (Table 3) indicate that (1) Ca, Ti, and O wt% in all samples compare very well within error with each other and most importantly with ideal titanite stoichiometry, (2) Ti wt% in all samples is slightly higher than the ideal, and finally (3) the Si content of samples 94-2 and 96-1 compares well with ideal titanite, whereas sample 93-1 appears to be Si deficient. From the analyses we also observe that Ti^{4+} is negatively correlated to both Si^{4+} and O^{2-}. Apparent excess Ti^{4+} can compensate for apparent Si^{4+} and O^{2-} deficiencies when atomic fractions are calculated assuming eight ions. Although we could accept the possibility of Ti^{4+} substituting for Si^{4+}, the possibility of a cation substituting for an anion is not reasonable. Therefore, we conclude that the apparent excess titanium is probably an artifact caused by grain overlap, fluorescence, and the difference in the beam-sample interaction volume between heavy and light elements. The above suggests, although it cannot conclusively prove, that Si deficiency is a real possibility for sample no. 93-1. Moreover, Si deficiency is compatible with the presence of the observed Si-rich, or Ca- and Si-rich impurities in this titanite. For all these reasons we do not believe that tetrahedral Ti^{4+} is the dominant cause of the high volumes of glass and melt-derived titanites.

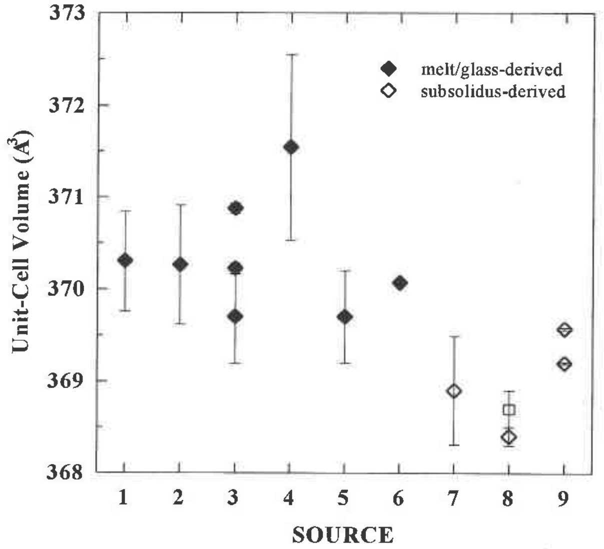

Figure 1. Plot of unit-cell volume vs. synthesis method. Numbers refer to the source of the samples and are the same as in Table 1. "Melt/glass-derived" denotes samples that were synthesized either by slow crystallization of $CaTiOSiO_4$ melts or subsolidus annealing of $CaTiOSiO_4$ glasses, whereas "subsolidus-derived" denotes titanites synthesized entirely at subsolidus conditions. Sample represented by the open square is the Induction Furnace titanite of Hollabaugh and Rosenberg (1983). This sample may belong to the subsolidus-derived titanites.

The effect of vacancies on the unit-cell volume is not straightforward (Shannon 1976). There are two possibilities: a cation that is overbonded (i.e., a bond-valence sum greater than its atomic valence) is subject to a compressional stress in its structural site (Brown 1992). It therefore exerts an expansional force on its immediate surroundings. A vacancy on this site would induce a collapsing relaxation of its surroundings, leading to a decrease in the volume. If on the other hand a given cation is underbonded (i.e., a bond-valence sum less than its atomic valence) it is in tensional stress. A vacancy on such a site would relax the coordinating O atoms by moving them away from the cation-site, resulting in an expansion of the unit cell. Of course such a crude model is applicable only if the density of the vacancies is not too high. Also extended vacancy clusters could lead to partial collapse of the structure and not only would that decrease the cell volume but also may cause more profound structural changes. However, it is observed that in wüstite ($Fe_{1-x}O$) relatively large vacancy clusters still induce an expansion of the lattice (Radler et al. 1990). Looking at the structural data for titanite, we find that in all the available studies Ti tends to be overbonded (average bond valence sum = 4.17 v.u.) whereas Ca and Si are underbonded (average bond-valence sum is 1.98 and 3.80 v.u., respectively). From a crystal chemical point of view, vacancies in the Ti site would induce a volume decrease, whereas vacancies on the Si- or Ca-site or both would result in cell expansion. We suggest that vacancies in the Si-site or Ca-site or both are the main cause of the higher volumes of melt or glass-derived titanite.

Why should titanite synthesized from melt or glass be nonstoichiometric? One possibility is that titanite melts

TABLE 2. Electron microprobe analyses of synthetic titanites from this study

Sample No. of analyses	Ideal titanite	Glass 93 17	93-1 61	94-2 28	96-1 34
Element wt%					
Ca	20.44	20.02(0.21)	20.13(0.32)	20.36(0.28)	20.47(0.48)
Ti	24.43	23.93(0.50)	24.95(0.63)	25.06(0.68)	24.83(0.61)
Si	14.32	14.31(0.46)	13.69(0.51)	14.30(0.41)	14.19(0.22)
O	40.81	40.36(0.57)	40.38(0.92)	41.20(0.58)	40.86(0.43)
Total	100.00	98.62	99.15	100.92	100.35
Formula					
Ca	1.00	0.99(0.01)	1.00(0.02)	0.99(0.02)	1.00(0.02)
Ti	1.00	0.99(0.02)	1.03(0.03)	1.02(0.03)	1.01(0.02)
Si	1.00	1.01(0.03)	0.97(0.03)	0.99(0.03)	0.99(0.02)
O	5.00	5.01(0.03)	5.00(0.05)	5.00(0.03)	5.00(0.03)

Note: Numbers in parentheses represent one standard deviation.

incongruently, although this is not observed in any of the studies dealing with melting of titanite (e.g., Crowe et al. 1986). Careful new studies on titanite melting might be in order. However, even if stoichiometric titanite does melt congruently, melting of equimolar oxide mixtures might produce nonstoichiometric liquids along with small amounts of residual oxides. Using data from Robie et al. (1978), we calculate that between 1200 and 1500 °C the Gibbs Free Energy of solid or liquid titanite is higher than or close to the Gibbs Free Energy values of mechanical mixtures of $(1 + x)CaSiO_3 + (1 - x)TiO_2$, and $(1 + x)CaTiO_3 + (1 - x) SiO_2$, for $0.01 \leq x \leq 0.03$. Furthermore, the data of De Vries et al. (1955) suggest that $CaTiOSiO_4$ melts may rapidly crystallize during cooling. This suggests that there might be local minima in free energy and upon slow crystallization such melts might yield nonstoichiometric titanite with vacancies. The impurity phases could be expected to persist during prolonged annealing above 1100 °C. (Note that the thermodynamic data might also suggest a similar difficulty in subsolidus synthesis of stoichiometric titanite from oxide mixtures. The ease with which titanite can be synthesized in the subsolidus indicates that the thermodynamic data for solid titanite are in error, an issue that is discussed later in this paper.)

The presence of defects in melt- and glass-derived titanite crystals is strongly supported by the Ti, Si, and Ca X-ray maps of Tanaka et al. (1988), and indirectly, but not proved, by the scanning electron microscopy (SEM) observations of Crowe et al. (1983). Crowe et al. reported the presence of small Si-rich spheres ≤ 2 μm in apparent diameter, and Ca- or Si-rich areas (their Figures 1a and 1b) predominately within the melt-grown titanite crystals. Unfortunately they did not report the unit-cell parameters of these titanite samples.

TABLE 3. Correlation coefficient matrix of the unit-cell parameters and volumes in Table 1

	a	*b*	*c*	β	*V*
a	1.00				
b	0.87	1.00			
c	0.94	0.86	1.00		
β	0.70	0.36	0.71	1.00	
V	0.95	0.97	0.94	0.51	1.00

Crystallization from a melt or glass apparently increases the probability of obtaining titanite samples with defects, and titanite thus synthesized tends to have anomalously large volumes. Properties other than volume could also be affected. The differing conclusions in the studies of Ghose et al. (1991), Bismayer et al. (1992) and Zhang et al. (1995) regarding the behavior of titanite near its transition ($P2_1/a \leftrightharpoons A2/a$) may reflect real differences between the samples used. Ghose at al. (1991) used a crystal that came from the same synthesis batch as the samples of Speer and Gibbs (1976) and Taylor and Brown (1976), whereas Bismayer et al. (1992) and Zhang et al. (1995) used a chip from the Tanaka et al. (1988) synthesis experiment. Both crystals appear to be distinctly different. The first one (Ghose et al. 1991; Speer and Gibbs 1976; Taylor and Brown 1976) was synthesized by recrystallizing a glass of titanite composition whereas the second (Zang et al. 1995; Bismayer et al. 1991) was synthesized by slow crystallization of a stoichiometric melt.

Zhang et al. (1995) report a possible second high temperature (≥ 850 K) phase transition in this titanite sample based on their heat capacity measurements. However, if SiO_2 phase impurities are present in their sample then their observations in this temperature range may be affected by the presence of a SiO_2 phase. Furthermore, the currently available thermochemical data for titanite (Robie et al. 1978; Robie and Hemingway 1995) are based on two studies (King et al 1954; Todd and Kelley 1956) that used a synthetic titanite directly crystallized from a melt. Thus it is likely that the sample consisted of nonstoichiometric titanite plus Si- or Ca-, Si-rich phase impurities. Note that the purity of this titanite sample was estimated to be 99 mol% (King et al. 1954). We suggest that those data be used with caution, as they may not apply to stoichiometric titanite.

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