

## Substitution of Ti for Si in titanite and new end-member cell dimensions for titanite

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### Abstract

Enlargement of the lattice parameters, particularly the *b*-dimension, of titanites synthesized at high temperatures ( $\geq 700^\circ\text{C}$ ) in the system  $\text{CaO-TiO}_2\text{-SiO}_2(\pm\text{H}_2\text{O})$ , can be accounted for by substitution of Ti for Si. The unit-cell dimensions of the ideal end-member,  $\text{CaTiSiO}_5$ , extrapolated from the linear relationship between tetrahedral site occupancies and unit-cell dimensions of synthetic samples are approximately;  $a = 7.054\text{\AA}$ ,  $b = 8.703\text{\AA}$ ,  $c = 6.551\text{\AA}$  and  $\beta = 113.77^\circ$ . Enlargement of the *b* dimension to  $8.724\text{\AA}$  corresponds to the presence of Ti in approximately 6% of the tetrahedral sites.

### Introduction

During an experimental investigation of compositional variations in titanite (sphene) in the system  $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2\text{-H}_2\text{O}$  (Hollabaugh, 1980) attempts were made to synthesize and characterize the ideal, end-member composition,  $\text{CaTiSiO}_5$ , for purposes of comparison with Al-bearing solid solutions. Unit-cell dimensions of titanite synthesized in the system  $\text{CaO-TiO}_2\text{-SiO}_2$  in the presence and absence of water were found to be significantly smaller than those previously reported (Robbins, 1968; Speer and Gibbs, 1976) suggesting compositional variations. A brief investigation was undertaken to determine the nature and extent of these solid solutions.

### Procedures

#### *Experimental details*

Starting materials were prepared as mechanical mixtures of high purity ( $>99.99\%$ ) oxides and synthetic minerals including  $\text{CaTiO}_3$ ,  $\text{CaSiO}_3$ ,  $\text{TiO}_2$  and  $\text{SiO}_2$  (Hollabaugh, 1980).

Conventional hydrothermal techniques including cold-seal pressure vessels and sealed gold tubes were used for hydrothermal experiments. Titanite

was synthesized at 2 kbar in two experiments which yielded crystals large enough for electron microprobe analysis: S152R,  $800^\circ\text{C}$ , 51 days duration, solid composition (mole %) 33.3 CaO, 33.3  $\text{TiO}_2$ , 33.3  $\text{SiO}_2$ ;  $\text{H}_2\text{O}$  17 wt.%; S250,  $700^\circ\text{C}$ , 38 days duration, solid composition (mole%) 31 CaO, 31  $\text{TiO}_2$ , 38  $\text{SiO}_2$ ;  $\text{H}_2\text{O}$  17 wt.% (Hollabaugh, 1980). Titanite was also synthesized from a mixture of  $\text{CaSiO}_3$  and  $\text{TiO}_2$  which was heated to a temperature over  $1400^\circ\text{C}$  at one atmosphere in a carbon crucible using an induction furnace and then allowed to air-cool. A sample of titanite synthesized at the National Bureau of Standards (Robbins, 1968) was also available for this study.

#### *Unit-cell parameters*

Unit-cell dimensions (Table 1) were determined from X-ray powder patterns, using either  $\text{CdF}_2$  (French, 1970) or rutile (Swanson and Tatge, 1973) as an internal standard (Hollabaugh, 1980). X-ray diffraction patterns were scanned at  $1/4^\circ 2\theta/\text{min}$ . using Ni-filtered  $\text{CuK}\alpha$  radiation. Two oscillations were measured and averaged for each peak. X-ray reflections were indexed with reference to the structure refinement of Speer and Gibbs (1976) and assigned unit weights. Unit-cell dimensions were

Table 1. Unit-cell dimensions of titanite

Sample	a(Å)	b(Å)	c(Å)	$\beta$ (°)	V(Å <sup>3</sup> )
S152R	7.057(1)*	8.707(3)	6.554(2)	113.80(3)	368.4(1)
S250	7.056(1)	8.707(1)	6.552(1)	113.77(2)	368.4(1)
Induction Furnace	7.058(2)	8.709(2)	6.553(1)	113.74(2)	368.7(1)
Robbins**	7.065(5)	8.723(5)	6.567(5)	113.86(3)	370.3
Robbins***	7.067(1)	8.724(2)	6.560(1)	113.80(2)	370.0(1)
Speer and Gibbs#	7.069(2)	8.722(5)	6.566(8)	113.86(2)	370.2(1)
Takenouchi##	7.066(9)	8.705(5)	6.561(9)	113.93(2)	368.9

\*Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 7.057(1) indicates an esd of 0.001.  
 \*\*Robbins (1968).  
 \*\*\*Robbins' sample; this study.  
 #Speer and Gibbs (1976).  
 ## Takenouchi (1971).

refined using the least-squares program of Appleman and Evans (1973) based on 12–15 X-ray reflections per sample.

### Chemical analysis

Synthetic titanites were analyzed by means of an electron microprobe (accelerating voltage 15 kv) using wavelength dispersive methods, mineral standards (synthetic rutile, natural garnet and albite) and Bence–Albee matrix correction procedures. The reported compositions (Table 2) are based on an average of 10–15, 10 second, point analyses.

## Discussion

### Substitutions in titanite

The unit-cell dimensions of synthetic titanites measured in this study and in studies by Takenouchi (1971), Robbins (1968), and Speer and Gibbs (1976) are given in Table 1 and compared graphical-

Table 2. Electron microprobe analyses of synthetic titanites

Sample Number	S152R	S250	Induction Furnace	Robbins	Stoichiometric
Weight Percent Oxides					
CaO	28.29	28.20	28.87	29.24	28.60
TiO <sub>2</sub>	41.74	41.36	41.49	43.78	40.75
SiO <sub>2</sub>	30.47	30.28	30.25	29.26	30.65
Total	100.50	99.84	100.61	102.28	
Atoms Per Unit Cell, Assuming 20 Anions					
Ca	3.936	3.949	4.020	4.025	4.000
Ti	4.075	4.066	4.056	4.229	4.000
Si	3.957	3.959	3.932	3.759	4.000
Total	11.968	11.974	12.008	12.013	12.000
Percent of Si Site Not Filled by Si					
	1.075	1.025	1.700	6.025	0.0

ly in Figure 1. Titanites synthesized by Robbins (1968) and Speer and Gibbs (1976) have significantly larger unit-cell dimensions than those synthesized by Takenouchi (1971) and in the present investigation. The chemical compositions of four synthetic titanites were determined by electron microprobe analysis in an attempt to identify the substitution responsible for this difference.

The titanite synthesized by Robbins (1968) has a significant excess of Ti and a comparable deficiency in Si (Table 2) which suggests substitution of Ti for Si. It also has the largest unit-cell parameters (Table 1), particularly the *b* dimension and unit-cell volume (Fig. 1), of the four samples determined in the present investigation.

Substitution of Ti for Si should expand the size of the tetrahedral site since <sup>IV</sup>Ti<sup>4+</sup> (0.42Å) is considerably larger than <sup>IV</sup>Si<sup>4+</sup> (0.26Å; Shannon, 1976). In the titanite structure isolated SiO<sub>4</sub> tetrahedra are located and act as linkages between chains of TiO<sub>6</sub> octahedra; the chains run parallel to the *a* axis. An increase in the size of the tetrahedral site enlarges the *b* and, to a smaller extent, the *c* and *a* dimensions; enlargement of *a* requires distortion of the octahedral chains.

The synthetic titanite used by Speer and Gibbs (1976) in their crystal structure determination also has a large *b* lattice parameter and a large unit-cell volume (Table 1, Fig. 1). Analysis by Higgins and Ribbe (1976) showed a slight Ca-deficiency which was attributed to the presence of small amounts of CaSiO<sub>3</sub> in the sample. It seems likely that some Ti may also substitute for Si in this titanite.

Titanites synthesized in the present investigation have smaller unit-cell dimensions, particularly *b*

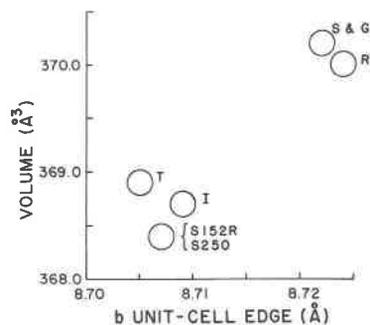


Fig. 1. Variation of unit-cell volume with *b* cell-edge of synthetic titanites. Unit-cell dimensions and their estimated standard deviations are given in Table 1. S and G, Speer and Gibbs (1976); T, Takenouchi (1971); R, Robbins sample, this study; I, induction furnace, this study; S152R and S250, this study.

parameters and unit-cell volumes (Table 1, Fig. 1) than the titanite synthesized by Robbins (1968) and their chemical compositions are also closer to that of stoichiometric titanite (Table 2). Thus, it appears that substitution of Ti for Si accounts for the larger unit-cell dimensions observed in investigations by Robbins (1968) and Speer and Gibbs (1976). The relatively small  $b$  cell dimension of Takenouchi's (1971) synthetic titanite which has been attributed to misindexing (Higgins and Ribbe, 1976) is probably due to its close approach to ideal stoichiometry.

Titanites crystallized under hydrothermal conditions (S152R and S250, Table 2) are also slightly Ca-deficient. In these samples the Ti-excess is sufficient to compensate for all of the Si-deficiency and most of the Ca-deficiency. The remaining Ca-deficiency ( $\sim 0.02$  atoms/formula unit) may be due to analytical error or to the substitution of small amounts of  $(\text{OH})^-$  for  $\text{O}^{2-}$  according to the equation,  $\text{Ca}^{2+} = 2\text{H}^+$ . In the presence of excess water, partial substitution of  $(\text{OH})^-$  for the underbonded O(1), coupled with site vacancies, is possible in titanite (Rosenberg, 1974). Vacancies in Ca-sites have little or no effect on unit-cell dimensions (Cérny and Riva di Sanseverino, 1972), whereas substitution of  $(\text{OH})^-$  for O(1) might be expected to enlarge unit-cell dimensions slightly.

#### Unit-cell dimensions of ideal titanite

At present, the unit-cell dimensions of end-member titanite,  $\text{CaTiSiO}_5$ , are not well-known. Ideal compositions, natural or synthetic, are not available for study but the unit-cell parameters of the end-member can be estimated by indirect methods.

Si-deficiency in synthetic titanites appears to be entirely accounted for by substitution of Ti for Si. Assuming that a linear relationship exists between Si-deficiency (mole%; Table 2) and unit-cell parameters (Table 1) an extrapolation to ideal titanite composition (Si-deficiency = 0) can be carried out (Fig. 2). This estimate yields the unit-cell parameters:  $a = 7.054\text{\AA}$ ;  $b = 8.703\text{\AA}$ ;  $c = 6.551\text{\AA}$  and  $\beta = 113.77^\circ$ . Considering the estimated standard deviations of the refined unit-cell dimensions (Table 1) and the limited data available, the last decimal place is only an approximation.

Higgins and Ribbe (1976) showed that a linear relationship exists between the effective octahedral cation radius and the unit-cell parameters of natural titanites, assuming that variations in unit-cell dimensions are due to substitution of Al and Fe for Ti and that natural titanites contain stoichiometric Si.

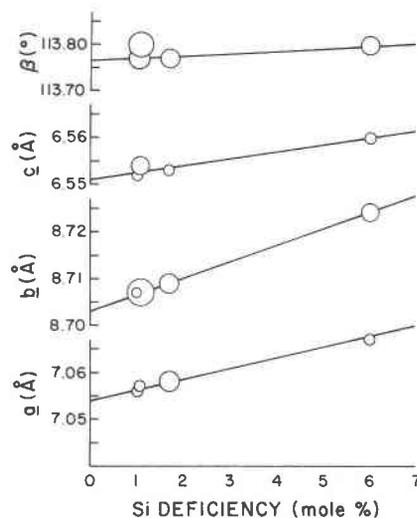


Fig. 2. Variation of  $a$ ,  $b$ ,  $c$  and  $\beta$  lattice parameters with Si-deficiency. Size of symbols approximates estimated standard deviation of lattice parameters. Correlation coefficients of regression lines:  $a$ ,  $r > 0.99$ ;  $b$ ,  $r > 0.99$ ;  $c$ ,  $r = 0.97$ ;  $\beta$ ,  $r = 0.43$ .

Unit-cell dimensions of the ideal end-member estimated from this study are:  $a = 7.060\text{\AA}$ ;  $b = 8.710\text{\AA}$  and  $c = 6.556\text{\AA}$ . These values are intermediate between the unit-cell dimensions estimated for end-member titanite in the present investigation and those obtained for the titanites of Robbins and of Speer and Gibbs (Table 1), although the  $b$  dimensions is closer to the value obtained in the present study.

A slight Si-deficiency is often observed in natural titanite (Deer *et al.*, 1962). This suggests that the assumption of Si stoichiometry by Higgins and Ribbe (1976) may not be fully justified and, therefore, that the effective tetrahedral cation radius may play a role in determining unit-cell dimensions. Since the extent of tetrahedral substitution is small, its effect on unit-cell dimensions will be slight. However, the linear relationship between effective octahedral cation radius and lattice parameters (Higgins and Ribbe, 1976) may be slightly displaced due to tetrahedral substitution. If a slight enlargement of unit-cell dimensions does occur in natural titanite due to Si-deficiency, it is probably caused by substitution of Al or  $\text{Fe}^{3+}$  both of which enter tetrahedral sites more easily than does Ti (Hartman, 1969).

#### Conclusions

Substitution of Ti for Si occurs in titanites synthesized at high temperatures in the system  $\text{CaO-TiO}_2\text{-SiO}_2$  resulting in enlargement of lattice pa-

rameters, particularly the  $b$  dimension. The lattice parameters of ideal, end-member titanite,  $\text{CaTiSiO}_5$ , obtained by extrapolating linear relationships between tetrahedral site occupancies and unit-cell dimensions are approximately:  $a = 7.054\text{\AA}$ ;  $b = 8.703\text{\AA}$ ;  $c = 6.551\text{\AA}$  and  $\beta = 113.77^\circ$ . Enlargement of the  $b$  dimension to  $8.724\text{\AA}$  corresponds to the presence of Ti in approximately 6% of the tetrahedral sites. Si-deficiencies compensated by substitutions of Al or  $\text{Fe}^{3+}$  in tetrahedral sites may be responsible for a slight enlargement in the unit-cell dimensions of natural titanites.

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