

The synthesis and crystal structure of CaAlFSiO₄, the Al-F analog of titanite

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ABSTRACT

Aluminum-rich titanites [Ca(Ti,Al)(O,F)SiO₄] with $X_{Al} > 0.53$ [$X_{Al} = Al/(Al+Ti)$], including the pure end-member CaAlFSiO₄, were synthesized for the first time in a high-pressure experimental study. The crystal structure of CaAlFSiO₄ was determined by Rietveld analysis of an X-ray powder diffraction pattern. CaAlFSiO₄ is monoclinic, belongs to the space group *A2/a*, and has the unit-cell dimensions $a = 6.9149(2)$ Å, $b = 8.5064(1)$ Å, $c = 6.4384(2)$ Å, and $\beta = 114.684(2)^\circ$. The unit-cell volume is less than 93% of CaTiOSiO₄, which is consistent with the natural occurrence of Al-rich titanite in high-*P* rocks. Although previous studies suggested that titanite with $X_{Al} > 0.5$ is possibly not stable, this study demonstrates that complete solid solution occurs between CaTiOSiO₄ and CaAlFSiO₄. The similarity of the crystal structures of titanite and CaAlFSiO₄ explains why in natural Al-rich titanite the end-member CaAlFSiO₄ generally dominates over the hypothetical end-member CaAlOHSiO₄, which under geological conditions is stable in a different crystal structure.

INTRODUCTION

Al-rich titanite [Ca(Ti,Al)(O,F,OH)SiO₄] has been the focus of many previous mineralogical studies (Higgins and Ribbe 1976; Smith 1981; Oberti et al. 1991) because Al is one of the most common and abundant substituents for Ti in natural titanite (Franz and Spear 1985; Sobolev and Shatsky 1990; Krogh et al. 1990; Carswell et al. 1996). Moreover, the substitution appeared to be pressure and temperature dependent and thus could be of interest for geothermobarometry (Smith 1981; Enami et al. 1993). The two coupled substitution reactions that account for the formation of Al-bearing titanite are $Ti^{4+} + O^{2-} = Al^{3+} + F^-$ and $Ti^{4+} + O^{2-} = Al^{3+} + OH^-$. Hence Al-rich titanite is made up of the three end-members CaTiOSiO₄ [titanite], CaAlFSiO₄, and CaAlOHSiO₄. Although the end-member titanite occurs in nature and its crystal structure is known (Speer and Gibbs 1976), to our knowledge CaAlFSiO₄ has never been found or synthesized before, and neither has the pure CaAlOHSiO₄ end-member been reported. The mineral vuagnatite [CaAlOHSiO₄] is chemically equivalent to the AlOH end-member of Al-rich titanite, but its crystal structure (McNear et al. 1976) is different to that of titanite and thus it does not represent the AlOH-component of titanite solid solution.

The extent of solid solution between these end-members was previously discussed. Because the maximum amount of Al-substitution ($X_{Al} \approx 0.5$) reported from natural titanite (Franz and Spear 1985) is comparable to that of the first and only high-*PT* experimental investigation of Al- and F-bearing titanite with $X_{Al} = 0.53$ (Smith 1981), previous studies (Franz and Spear 1985; Oberti et al. 1991) pointed out that the Al-content in titanite appears to be restricted to $X_{Al} < 0.5$ (note that earlier studies usually did not distinguish between the two aluminum-end-members due to lack of OH- and F-analyses). Oberti et al. (1991)

investigated several natural Al-rich titanites ($X_{Al} < 0.37$), documenting changes in the crystal structure with increasing X_{Al} . They discussed various crystal structural features that might be responsible for the apparent mixing gap at $X_{Al} > 0.5$, but clear evidence for a crystal structural constraint was still missing.

The present study extends the information on Al-rich titanite summarized by Oberti et al. (1991) by providing crystal structural data for the end-member CaAlFSiO₄. Results from high-*PT* experiments in the binary system CaTiOSiO₄-CaAlFSiO₄ are reported that show complete solid solution.

EXPERIMENTAL METHODS

Synthesis of CaAlFSiO₄

The synthesis of CaAlFSiO₄ was carried out at 35 to 38 kbar and 1100 °C using the piston cylinder apparatus at the Geology Department, Australian National University. Run times varied from 21 to 24 h (see Table 1 for individual run conditions; samples G-295, G-296, G-297). The starting material was a powder of synthetic fluorite (Specpure) and anorthite in equal molar proportions, seeded with about 10 wt% CaAlFSiO₄. CaAlFSiO₄ does not nucleate without the presence of seeds. Thus CaAlFSiO₄ seeds had to be prepared in several cycles from titanite, anorthite and fluorite. In the first cycle, a mix of fluorite and anorthite (1:1) and about 1 wt% titanite seeds was run at 35 kbar and 1100 °C for 24 h, resulting in titanite solid solution with about 99 mol% of the CaAlFSiO₄ end-member, besides smaller amounts of zoisite, fluorite, and kyanite (G-274, Table 1). This product was then used as seed material for subsequent cycles. After three cycles, titanium could no longer be detected using scanning electron microscopy, and the material was used as seeds for CaAlFSiO₄ synthesis. The anorthite of the starting mix was crystallized from glass at 1000 °C, 1 atm for 24 h with several cycles of crushing and heating. The glass was prepared by melting Al₂O₃, SiO₂, and CaCO₃ at 1600 °C and 1 atm, with subsequent quenching in water.

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TABLE 1. Experimental details

Expt. no.	T (°)	P (kbar)	t* (h)	Mix†	Run result	X _{Al} -range in Tnt	Comments
G-312	1100	15	22	1:9	Tnt	0.01-0.24	Tnt zoned, X _{Al} from core to rim
G-183	1100	30	21	1:1	Tnt	0.43-0.56	
G-184	1000	30	30	1:1	Tnt	0.44-0.50	
G-185	1200	30	22	1:1	Tnt	0.39-0.50	
G-186	1300	30	22	1:1	Tnt Melt	0.25-0.67	Tnt zoned, X _{Al} from core to rim
G-187	1100	25	36	1:1	Tnt	0.46-0.47	
G-194	1100	25	25	2:1	Tnt	0.50-0.69	
G-313	1100	25	23	3:1	Tnt Zoi Fluo	0.05-0.88	Tnt zoned, X _{Al} from core to rim
G-198	1100	10	23	10:1	Tnt An Fluo Sill	0.34-0.36	
G-199	1100	25	26	10:1	Tnt Zoi Fluo Ky	0.85	
G-200	1100	25	21	20:1	Tnt Zoi Fluo Ky	0.87-0.90	
G-201	1100	25	20	99:1	Tnt Zoi Fluo Ky	0.90-0.95	
G-203	1100	25	80	99:1	Tnt Zoi Fluo Ky	0.85-0.90	
G-264	1100	22	21	99:1	Tnt Zoi Fluo Ky	0.87-0.96	
G-265	1100	15	23	99:1	Tnt An Fluo	0.54-0.57	
G-266	1100	35	20	99:1	Tnt Zoi Fluo Ky	0.97-1.00	
G-268	1050	35	47	99:1	Tnt Zoi Fluo Ky	0.95-1.00	
G-274	1100	35	16	99:1	Tnt Zoi Fluo Ky	0.97-1.00	
G-275	1100	35	22	99:1	Tnt Zoi Fluo Ky	0.96-0.99	starting material was G-274
G-276	1100	35	24	999:1	Tnt Zoi Fluo Ky	0.98-0.99	seed material was G-275
G-278	1100	35	21	1:0	Tnt Zoi Fluo Ky	0.98-1.00	seed material was G-276
G-280	1100	35	23	1:0	Tnt Zoi Fluo Ky	0.99-1.00	seed material was G-278
G-282	1100	35	39	1:0	Tnt Zoi Fluo Ky	0.98-1.00	seed material was G-280
G-295	1100	35	24	1:0	Tnt Zoi Fluo Ky	1.00	seed material was G-280
G-296	1100	38	21	1:0	Tnt Zoi Fluo Ky	1.00	seed material was G-280
G-297	1100	35	23	1:0	Tnt Zoi Fluo Ky	1.00	seed material was G-278 and G-280

Notes: Tnt = titanite; An = anorthite; Zoi = F-rich zoisite; Fluo = fluorite; Sill = sillimanite; Ky = kyanite.

* Run Duration.

† Ratio of CaAlFSiO₄ to CaTiOSiO₄.

For each CaAlFSiO₄ synthesis run about 140 mg of mix was filled in 3 mm diameter silver-palladium capsules (Ag₇₅Pd₂₅), which were then dried at 110 °C for 1 h before welding shut. The pressure medium enclosing the capsule was boron-nitride and a surrounding salt-sleeve with zero friction correction. The pressure readings during the experiments are precise within 1%. The temperature was monitored by a Pt-Pt₉₀Rh₁₀ thermocouple and was regulated automatically by a EUROTHERM controller. The accuracy of the temperature measurements was ±5 °C. The grain size of all run products was <10 μm.

Synthesis of titanite solid solution Ca(Ti,Al)(O,F)SiO₄

Titanite solid solution over a range of compositions was synthesized under various pressures and temperatures (Table 1) from two different starting mixes: Anorthite + fluorite (molar proportion 1:1) and grossular + quartz + kyanite + fluorite (molar proportion 1:1:2:3), both mixed with various amounts of titanite. The preparation of anorthite is described above. Synthetic fluorite (Specpure), SiO₂ (Aerosil, Degussa), natural kyanite (Northern Territory, Australia, Fe₂O₃ < 0.4 wt%) and synthetic grossular and titanite were used. Grossular was made from glass at 1200 °C, 25 kbar for 26 h using the piston cylinder apparatus. Titanite was crystallized from glass at 1100 °C, 1 atm for four weeks with several cycles of heating and crushing. Both the grossular and titanite glass were prepared from the oxides and CaCO₃ at 1450 °C and 1 atm, and quenched in water.

Silver-palladium capsules (Ag₇₅Pd₂₅) of 2 mm diameter were filled with about 10 mg mix and dried at 110 °C before welding shut. Salt or salt and pyrex-sleeves were used as outer pressure media. The grain size of all run products was <10 μm.

SEM

Quantitative analyses were obtained with a JEOL JSM-6400 scanning electron microscope, Link ISIS EDS, at 15 kV and 1 nA, at the Electron Microscopy Unit, Australian National University. Analyses were calculated using ZAF-correction. Analyzed elements were silicon, titanium, aluminum, calcium, fluorine, and oxygen.

TEM

Diffraction patterns of CaAlF SiO₄ were investigated at 300 kV using a Philips EM 430T at the Research School of Earth Sciences, Australian National University. The camera constant was calibrated against thallium chloride, the uncertainty of the measurements is 1%. The sample (G-297) was finely ground, dispersed on a carbon-coated copper grid, and mounted on a tilt-rotate holder.

XRD

Powder-diffraction data were collected at room temperature with a Siemens D501 diffractometer at the Geology Department, Australian National University. The diffractometer was equipped with a curved graphite monochromator, a scintillation detector, and CuKα radiation was used. The diffraction data were recorded in four passes over a range of 10 to 100°2θ, using a step width of 0.02° at a scan speed of 0.5° per minute.

IR

Infra-red spectra were recorded using a Bruker IFS 28 FT-IR spectrometer and microscope. Single grains of sample material were investigated individually. KBr pellets were not used.

Raman

The LaserRaman spectra were recorded on a Dilor SuperLabram spectrometer equipped with a holographic notch filter, 600 and 1800 g/mm gratings, and a liquid N₂ cooled, 2000 × 450 pixel CCD detector. The sample was illuminated with 514.5 nm laser excitation from a Spectra Physics model 2017 argon ion laser, using 5 mW power at the samples, and a single second accumulation. A 100× microscope objective was used to focus the laser beam and collect the scattered light. The focused laser spot on the samples was approximately 1 mm in diameter. Wavenumbers are accurate to * 1 cm⁻¹ as determined by plasma and neon emission lines.

Structure refinement

Rietveld refinement using up to 50 parameters was performed on sample G-297 (Table 1) with the computer program RIETAN-94 (Izumi 1993), which uses the pseudo-Voigt function as profile-shape function, and the *International Tables for Crystallography* (Wilson et al. 1992) as the database. All four phases present in the sample (85 wt% CaAlFSiO₄, 10 wt% zoisite, 2 wt% fluorite, and 3 wt% kyanite) were accounted for in the refinement. Refined non-atomic parameters included scale factors (4), specimen-displacement (1), background (8), profile-shape parameters (12), preferred orientation (3), and unit-cell parameters (7). Neutral atom scattering factors were chosen for all atoms. The unit-cell parameters of kyanite and fluorite were fixed.

RESULTS

Titanite solid solution

The results of 19 experiments synthesizing titanite solid solution over a range of compositions span the entire spectrum of possible Ti-Al exchange including the end-members titanite and CaAlFSiO₄ (Fig. 1; Table 1). This is the first time that titanite is reported with X_{Al} >> 0.53. Moreover, complete solid solution between CaTiOSiO₄ and CaAlFSiO₄ is observed, showing that there is no crystal structural constraint in the titanite structure that precludes the occupation of the octahedral sites with more than 50% Al.

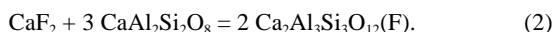
CaAlFSiO₄ synthesis

The results of three experiments carried out under comparable run conditions (G-295 to G-297, Table 1) are identical. They consist of a mixture of CaAlFSiO₄ (>70 wt%), F-rich zoisite (<20 wt%), fluorite (<10 wt%), and traces of kyanite.

The formation of CaAlFSiO₄ and F-rich zoisite in the experiments from fluorite and anorthite can be described by the reactions



and



The composition of the synthetic CaAlFSiO₄ is close to ideal with a deviation of less than 0.05 apfu of all analyses from the end-member composition. The average chemical formula from 26 SEM analyses of CaAlFSiO₄ calculated on the basis of three cations is Ca_{1.012}Al_{0.991}F_{0.991}Si_{0.997}O_{3.998}.

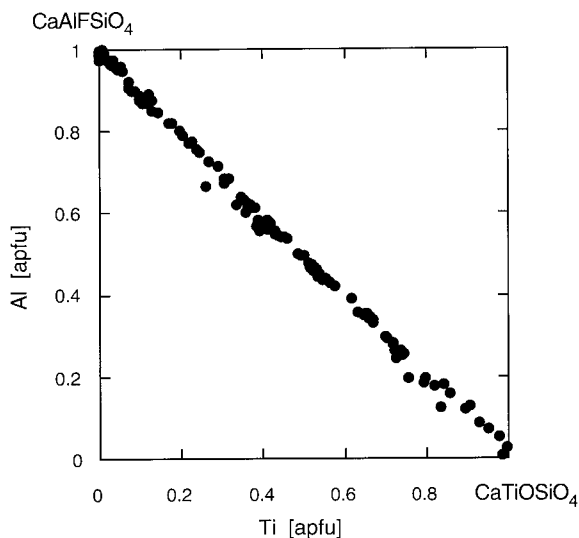


FIGURE 1. Al vs. Ti atoms per formula unit in synthetic binary titanite solid solution Ca(Ti,Al)(O,F)SiO₄ from various experiments carried out under a range of pressures and temperatures (see Table 1).

The formation of zoisite under anhydrous conditions was unexpected, because to the authors knowledge the existence of F-rich zoisite has never been reported in the literature before. The average structural formula for zoisite synthesized in this study is Ca_{2.06}Al_{2.94}Si_{3.00}O_{12.48}F_{0.43}. It was calculated from 17 SEM analyses on the basis of 8 cations. The surplus of O²⁻ and deficiency of F⁻ compared to the ideal formula as used in reaction 2, together with a charge unbalance of -0.46 for this chemical formula, suggests the presence of about 0.46 apfu H⁺ in the form of OH⁻. This changes the above formula to Ca_{2.06}Al_{2.94}Si_{3.00}O_{12.02}F_{0.43}(OH)_{0.46}. The presence of structurally bound OH in zoisite in sample G-297 was confirmed with IR and Raman spectroscopy. Water contamination of the supposedly dry experiments is possible. Even though the starting mix was dried inside the open capsules at 110 °C before welding, water contamination cannot be excluded entirely during the subsequent welding process that involves cooling of the capsule using water-soaked sleeves. Note that for 140 mg sample it requires only 0.00014 g of water contamination to account for 10% of the product to be the above zoisite composition. The formation of F-rich zoisite (reaction 2) instead of CaAlFSiO₄ (reaction 1) accounts for the presence of “left-over” fluorite in the run product. The presence of kyanite in the reaction products indicates slight deviation of the starting mix from ideal composition.

It is most likely that F-rich zoisite and fluorite in these experiments are metastable, and only persist because of nucleation problems of CaAlFSiO₄ or incomplete reaction due to slow diffusion rates. A high activation energy for nucleation is suggested by the fact that mixes without seeds react to form F-rich zoisite and fluorite, whereas seeded mixes react to form up to 100% CaAlFSiO₄. Incomplete reaction is indicated by the textures of the reaction products. Fluorite and F-rich zoisite are typically preserved as isolated grains surrounded by CaAlFSiO₄.

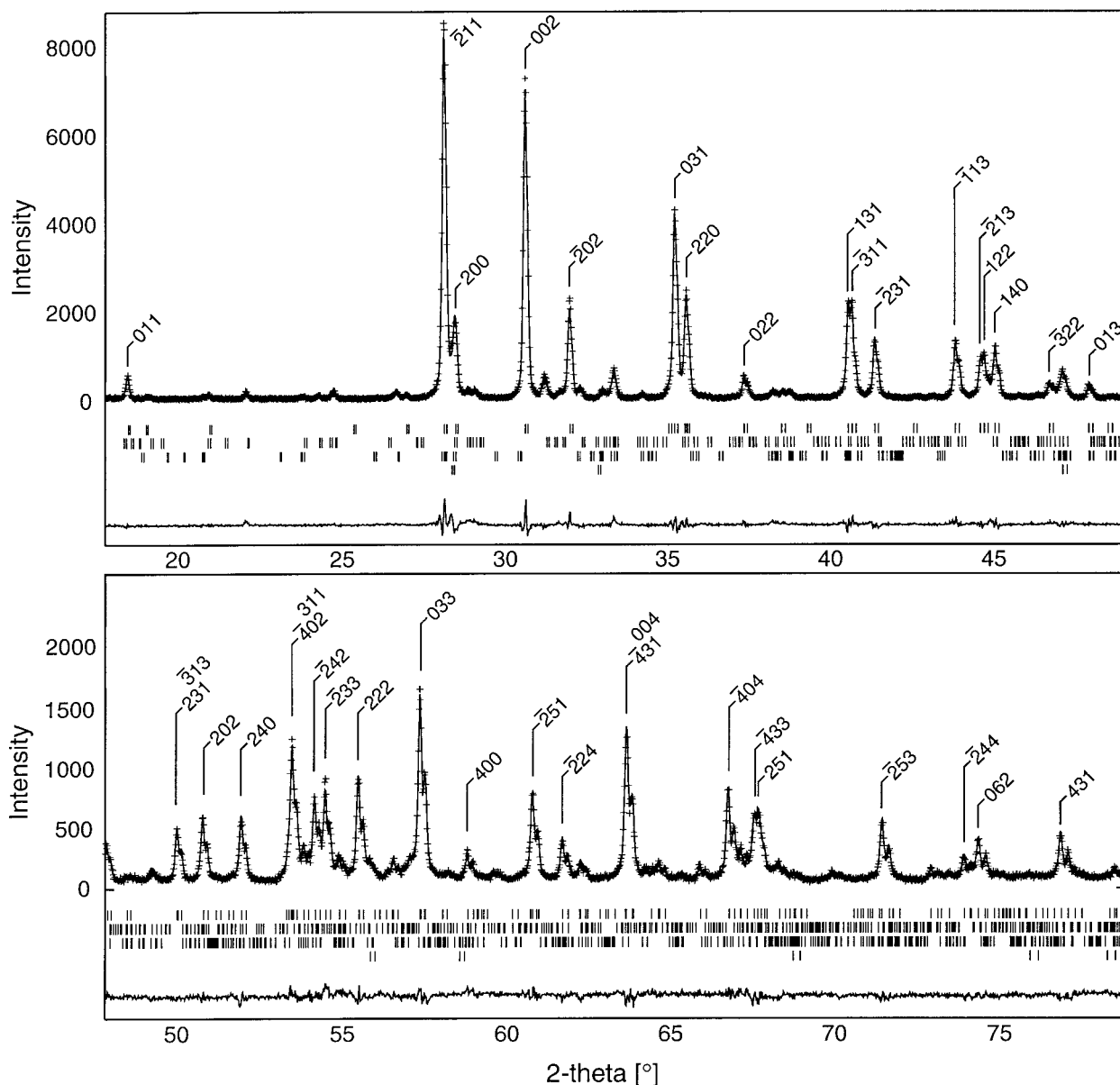


FIGURE 2. X-ray powder diffraction pattern and Rietveld refinement result of CaAlFSiO₄ with traces of zoisite, kyanite, and fluorite (sample G-297). Crosses represent the raw diffraction data, the upper solid curve is the calculated trace, and the lower solid curve shows the difference between the two. Positions of all *hkl* reflections are indicated by vertical bars (four rows from top to bottom: CaAlFSiO₄, Zoisite, Kyanite, Fluorite), major reflections of CaAlFSiO₄ are indexed. Note the difference in scale between the two parts of the figure.

Determination of the crystal structure

The X-ray powder-diffraction pattern of CaAlFSiO₄ (Fig. 2) is comparable to that of titanite (space group $P2_1/a$) and Al-rich titanite (space group $A2/a$; Higgins and Ribbe 1976). The space group $A2/a$ was confirmed for CaAlFSiO₄ by the absence of $k + l = 2n + 1$ reflections from the diffraction pattern of zone [102] (Fig. 3) (Higgins and Ribbe 1976; Speer and Gibbs 1976). The starting coordinates for the refinement process were those of a titanite with $X_{Al} = 0.09$ in space group $A2/a$ (Hollabaugh and Foit 1984). For the CaAlFSiO₄ refinement the octahedral site was fully occupied with Al, and the O1-site with F. Occupancies

of all sites were fixed at 1.0 assuming ideal composition. The refinement result is shown in Figure 2, with $R_{wp} = 9.99$, $R_c = 6.62$, $S = 1.51$, and $R_B = 3.42$, as defined in Young (1993). The unit-cell dimensions of CaAlFSiO₄, atom coordinates, bond-lengths and bond-angles and other structural information are summarized in Tables 2 to 4.

DESCRIPTION AND DISCUSSION OF THE CRYSTAL STRUCTURE

CaAlFSiO₄ is isostructural with titanite as determined by Speer and Gibbs (1976). The CaAlFSiO₄ structure (Fig. 4) is

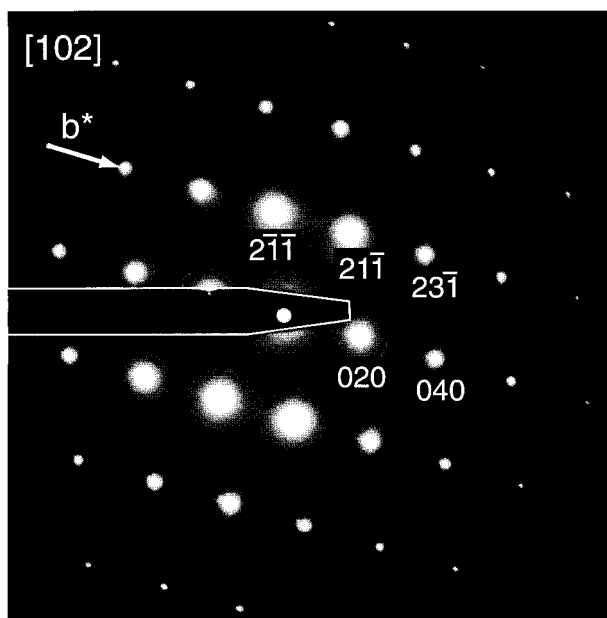


FIGURE 3. Electron diffraction pattern of CaAlFSiO₄ viewed along [102], showing the absence of $k + l = 2n + l$ reflections belonging to space group $P2_1/a$.

TABLE 2. The crystal structures of synthetic CaAlFSiO₄ and titanite*

	CaAlFSiO ₄	CaTiOSiO ₄ *
space group	$A2/a$	$P2_1/a$
unique axis	$b\uparrow$	b
unit cell content	$Z = 4$	$Z = 4$
molar weight (g/mol)	178.14	196.02
D (g/cm ³)	3.439	3.517
Unit cell dimensions		
a (Å)	6.9149(2)	7.0697(3)
b (Å)	8.5064(1)	8.7223(4)
c (Å)	6.4384(2)	6.5654(4)
β (°)	114.684(2)	113.853(4)
V (Å ³)	344.11(2)	370.27(3)
Octahedron		
mean oct-O bond (Å)	1.870	1.959
mean O-O bond (Å)	2.644	2.768
V (Å ³)	8.699	9.971
quadratic elongation	1.0013	1.0058
angle variance	2.773	—
oct-O1-oct angle (°)	141.5	141.8†
Tetrahedron		
mean Si-O bond (Å)	1.628	1.647
mean O-O bond (Å)	2.658	2.688
V (Å ³)	2.198	2.282
quadratic elongation	1.0053	1.0033
angle variance	17.077	12.566
Ca ^{IV} -site		
mean Ca-O bond	2.403	2.457

Notes: Sites occupied by fluorine or oxygen are represented by "O," the octahedral cation by "oct." Bond lengths, angles, polyhedral volumes, quadratic elongation and angle variance were calculated with the program VOLCAL (Hazen and Finger 1982). Errors of unit cell parameters of CaAlFSiO₄ as given by the program RIETAN (Izumi 1993).

* Refined by Kek et al. 1997.

† Non-standard setting was chosen for comparison with titanite.

‡ Speer and Gibbs (1976).

TABLE 3. Fractional atomic coordinates, isotropic thermal parameters (Å²) and bond-valence sums (BVS) of synthetic CaAlFSiO₄

Site	Atom	x	y	z	B_{iso}	BVS*
Ca	Ca	1/4	0.1637(2)	0	1.50(7)	2.20
Al	Al	1/2	0	1/2	1.75(7)	3.03
Si	Si	3/4	0.1860(4)	0	1.21(8)	3.97
O1	F	3/4	0.0709(5)	1/2	1.15(12)	1.25
O2	O	0.9031(5)	0.0667(4)	0.1904(5)	0.80(11)	1.98
O3	O	0.3887(6)	0.2011(4)	0.4031(6)	0.79(10)	1.99

Note: Errors as given by the program RIETAN (Izumi 1993), see discussion in text.

* Calculated with the program EUTAX (Bresle and O'Keeffe 1991).

TABLE 4. Selected bond lengths and angles of synthetic CaAlFSiO₄

Octahedron	Bond lengths (Å)	Angles on Al (°)	Tetrahedron or Ca ^{IV} -site	Bond lengths (Å)	Angles on Si (°)
Al-O1 ×2	1.831		Si-O2 ×2	1.603	
Al-O2 ×2	1.905		Si-O3 ×2	1.653	
Al-O3 ×2	1.873		O2-O2'	2.482	101.4
O1-O2 ×2	2.619	89.0	O2'-O3 ×2	2.706	112.4
O1-O2' ×2	2.665	91.0	O2-O3' ×2	2.680	110.8
O1-O3 ×2	2.560	87.5	O3-O3'	2.691	109.0
O1-O3' ×2	2.677	92.5			
O2-O3 ×2	2.662	89.6	Ca-O1	2.258*	
O2-O3' ×2	2.681	90.4	Ca-O2 ×2	2.319*	
			Ca-O3 ×2	2.383*	
			Ca-O3' ×2	2.579*	

* These four entries pertain to the Ca^{IV}-site.

composed of kinked chains parallel to [100] of corner-sharing AlF₂O₄ octahedra, which are interlinked by isolated SiO₄ tetrahedra in a way such that each tetrahedron shares two corners with neighboring octahedra of one chain and the other two corners with octahedra of two different chains. This AlFSiO₄-network contains large sevenfold-coordinated sites that accommodate Ca.

The bridging atom occupying site O1 in the octahedral chain is F. This position for F in titanite solid solution was proposed by Higgins and Ribbe (1976) on the basis of bond-strength calculations. In the CaAlFSiO₄, refinement F was placed exclusively on this bridging site, which is justified given the overbonded character of this position in the CaAlFSiO₄ structure (Table 3). The bond valence sums for most other sites are close to ideal values, which supports our structural model. The Ca-site is slightly overbonded mainly due to shortening of the Ca-O2 bond (Table 4) by about 0.1 Å compared to those in titanite (Table 11 in Kek et al. 1997).

Thermal parameters

The large absolute values of all thermal parameters (Table 3) are unrealistic. For comparison, isotropic atomic displacement parameters determined with single-crystal X-ray diffractometry for an Al-rich titanite $X_{Al} = 0.36$ by Oberti et al. (1991, sample HEL697) are 1.15 (Ca), 1.00 (oct), 0.41 (Si), 0.66 (O1), 0.66 (O2), and 0.59 (O3). Note that the errors obtained from the Rietveld refinement (Table 3) are probably underestimated, which is a problem previously recognized by, for example, Sakata and Cooper (1979) and Scott (1983). Because temperature factors correlate strongly with other 2θ -dependent refinable parameters, they can act as a sink for sys-

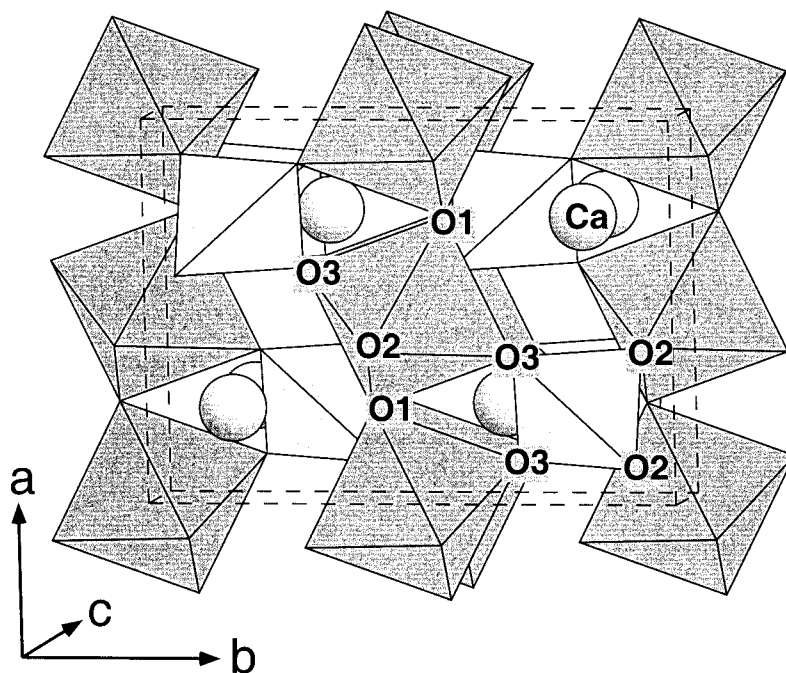


FIGURE 4. Crystal structure of CaAlFSiO₄ (ATOMS, Dowty 1993). Stippled lines represent the unit-cell boundaries.

tematic errors in the modeling of the profile. In this case the definition of the background at high angle was difficult due to strong peak overlap (Fig. 2). If the background was chosen too high, the large thermal parameters could represent the compensation for this mismatch.

Although the absolute values of thermal parameters might be erroneous, their relative values are significant. Whereas the relative magnitudes of the thermal parameters of Ca, O2, and O3 in CaAlFSiO₄ are comparable to titanite, those of Al, Si, and O1 seem too high. The high thermal parameter observed for the O1-site could be partly explained if the assumption of full occupancy by F was wrong, and trace amounts of F (<0.05 apfu) are replaced by OH in the sample. Trace amounts of structurally bound OH in one phase other than zoisite were detected with IR spectroscopy in the bulk sample (single grains of CaAlFSiO₄ large enough to be analyzed individually could not be separated). Disorder of F and O, which could also account for high thermal parameters, is unlikely given the already large bond valence sum for the O1-site (Table 3). High thermal parameters for Al and Si could be caused by some disordering in the octahedral and tetrahedral sites, resulting in local distortion of the crystal lattice. Diffuse scattering in the electron diffraction patterns which could indicate such disorder, however, could not be observed. A single-crystal diffraction study is necessary to obtain more reliable information about the thermal motion of the atoms and possible chemical and displacive disorder in the structure of CaAlFSiO₄.

Polyhedral distortion

Whereas the AlF₂O₄ octahedron in CaAlFSiO₄ is quite regular, the SiO₄ tetrahedron is very distorted. It has one very short

edge (O2-O2 = 2.482 Å), two short and two long Si-O bonds (Si-O2 = 1.603 Å, Si-O3 = 1.653 Å), a small O2-Si-O2 angle (101.4°), and large angle variance and quadratic elongation values (Hazen and Finger 1982) (Table 2). This is surprising, because SiO₄ tetrahedra generally behave as rigid units that hardly deviate from ideal bond lengths and angles, whereas octahedra deform more easily. Although a short O2-O2 edge and a small O2-Si-O2 angle of the tetrahedron is typical for most minerals in the titanite structure, uneven Si-O bonds as described above are unusual for this group.

To double-check the coordinates of our structure model, the refinement was repeated with hard constraints on the Si-O (1.624 Å) and O-O bond lengths (2.652 Å) of the tetrahedron. When the constraints were softened at the end of the refinement process, all atoms moved back to the positions forming the distorted tetrahedron. Because the overall fit (R_{wp}) improved by several percent after releasing the constraints, the distortion of the tetrahedron in CaAlFSiO₄ at room pressure and temperature seems to be real. Bond valence sums calculated for the same structure, but with Si located at the equidistant point of the tetrahedron, are 2.13 (Ca), 3.94 (Si), 1.88 (O2), and 2.05 (O3), (those of the Al- and O1-site remain unchanged, Table 2). This shows that off-centering of Si improves the bond-valence sums of all tetrahedral atoms, but slightly worsens that of Ca.

Hammonds et al. (1998) suggest that due to the absence of rigid-unit modes from the titanite structure, formation of solid solutions in this structure requires distortion of the polyhedra to accommodate cations of different size. This is consistent with the distortion of the tetrahedron in CaAlFSiO₄ but does not explain why in this case only the tetrahedra appear to take up the strain.

Comparison with titanite structure

The crystallographic data of titanite and CaAlFSiO₄ are compared in Table 2. Due to the smaller ionic radii of Al and F compared to Ti and O, all unit-cell dimensions of CaAlFSiO₄ are shorter, and its unit-cell volume is at least 7% smaller than that of titanite. This is consistent with the occurrence of natural Al-rich titanite in high-*P* and/or low-*T* rocks. The crystal lattice of CaAlFSiO₄ is more compact especially along the octahedral chain, resulting in smaller octahedral and Ca-sites, whereas the tetrahedral volume is comparable to that of titanite. Even though the major difference between the two end-members lies in the octahedral chains, their kinking angle (oct-O1-oct, Table 2) is almost identical. Changes in the crystal structure of titanite with increasing Al-content ($0.00 < X_{Al} < 0.37$) were investigated by Oberti et al. (1991). Extrapolation of their crystal structure data to $X_{Al} = 1.0$, especially the trends in site-volumes and the stable kinking-angle, are in general agreement with this study. The slight underestimate of the decrease in unit cell and polyhedral volume with X_{Al} by Oberti et al. (1991) compared to this study is either due to the fact that the crystals analyzed by them contained other substituents like Fe³⁺, which dilate the structure, or to non-linear changes in crystal structure dimensions between the two end-members. The polyhedral geometry they reported is comparable to that found in CaAlFSiO₄ in that the tetrahedra are more distorted with larger quadratic elongation and angle variance values compared to the octahedra. The Si-O distances determined for Al-rich titanite by Oberti et al. (1991), however, only vary over a narrow range (1.633 to 1.640 Å) unlike those in CaAlFSiO₄. This does not necessarily mean that the distortion of the Si-O bonds is restricted to $X_{Al} > 0.37$ also in the pure binary system CaTiOSiO₄-CaAlFSiO₄. It has to be considered that the tetrahedral geometry in the natural crystals examined by Oberti et al. (1991) might be influenced by the presence of hydrogen bonds.

One of the major differences between CaAlFSiO₄ and titanite is in the geometry of the octahedron, which influences the space group. In CaAlFSiO₄, as in malayaite [CaSnOSiO₄] (Higgins and Ribbe 1977; Groat et al. 1996), the octahedral cation is located in the center of the octahedron, resulting in three different bonds from the central cation to the coordinating anions. In contrast to this, Ti in titanite is slightly off-set from the octahedron center, resulting in six different oct-O bonds and five different oxygen sites (Speer and Gibbs 1976). In pure titanite all Ti atoms of one octahedral chain are off-set in the same direction, and in opposite direction in the neighboring chains. The off-centering of Ti reduces the symmetry of titanite to space group $P2_1/a$.

If titanite contains small amounts of substituents such as Al and F or OH, the continuous chains of TiO₆ octahedra are interrupted, allowing the formation of antiphase domains with an apparent space group $A2/a$ (Speer and Gibbs 1976; Higgins and Ribbe 1976). The most Al-rich titanites ($0.25 \leq X_{Al} \leq 0.37$) which were characterized crystallographically (Oberti et al. 1991) belong to space group $A2/a$, but no evidence for domains was found. The space group of these high-Al titanites is consistent with that of the end-member CaAlFSiO₄.

The hypothetical end-member CaAlOHSiO₄ in the titanite structure has never been reported. Under geological conditions

CaAlOHSiO₄ is stable in a different crystal structure and occurs as the mineral vuagnatite (McNear 1976). Note that although vuagnatite cannot represent the end-member of titanite solid solution its unit-cell volume (342.5 Å³) and density (3.42 g/cm³) are comparable to those of CaAlFSiO₄ (Table 2).

Natural occurrence of Al-rich titanite

The crystal structures of CaAlFSiO₄, titanite, and vuagnatite are the key to understanding their natural occurrence and composition. Both CaAlFSiO₄ and vuagnatite have a significantly smaller unit cell volume than titanite, and thus they should be stable at higher pressures and/or lower temperatures. This is in agreement with the natural occurrence of vuagnatite in prehnite-pumpellyite facies assemblages (Sarp et al. 1976; Pabst 1977), as well as with the high Al-content of titanites predominantly reported from eclogite facies rocks (Smith 1980; Franz and Spear 1985; Krogh et al. 1990; Carswell et al. 1996).

Because vuagnatite has a different crystal structure to titanite and CaAlFSiO₄ its composition seems to be restricted to pure CaAlOHSiO₄ (Oberti et al. 1991). In contrast to this CaTiOSiO₄, CaAlFSiO₄ and the hypothetical end-member CaAlOHSiO₄ can form solid solution to various degrees in the titanite structure. Whereas natural Al-rich titanite is reported to contain up to about 53 mol% CaAlFSiO₄, this experimental study has shown that even complete solid solution is possible under appropriate *PT*-conditions (Fig. 1). However, the solubility of the CaAlOHSiO₄ component in the titanite structure seems to be restricted to values less than about 30 mol% in nature as well as in the experiment (e.g., Enami et al. 1993; Franz and Spear 1985; Hellman and Green 1979). The general dominance of F over OH in very Al-rich titanite ($X_{Al} > 0.4$) from high-pressure rocks (Sobolev and Shatsky 1990; Carswell et al. 1996) and low-temperature rocks (Enami et al. 1993) is therefore due to the fact that only a few percent of Al coupled to OH seem to be able to enter the titanite structure, whereas the amount of Al coupled to F is not restricted by the crystal lattice. However, it is possible that OH dominates F in titanite with lower Al-content ($X_{Al} < 0.4$) as observed by Enami et al. (1993). The present study agrees with Enami et al. (1993) and Carswell et al. (1996) that the two Al-end-members in Al-bearing titanite have to be treated as individual phases with different mixing properties and *PT*-dependencies.

Previous studies (e.g., Smith 1981) pointed out that the different structures of vuagnatite and titanite might be the reason for natural high-Al titanite to be restricted to $X_{Al} < 0.50$. Oberti et al. (1991) discussed several possibilities of a crystal structural limit for Al-rich titanite and "provisionally attributed [the structural limit] either to difficulties in matching the different parts of the structure or to difficulties in local charge balance at O1 at higher Al contents." Although the present study confirms that there is indeed a local charge balance problem at the O1-site in CaAlFSiO₄ as indicated by overbonded F (Table 3), it does not appear to be significant enough to destabilize the structure of CaAlFSiO₄.

The only natural titanite with an Al-content exceeding $X_{Al} = 0.5$ significantly ($X_{Al} \approx 0.65$) was reported by Franz (1987). One possible reason for the rarity of natural titanites with $X_{Al} \gg 0.50$ and absence in nature of the end-member CaAlFSiO₄ is that the equilib-

rium *PTX*-conditions are not expected in nature. Even though the synthesis conditions for CaAlFSiO₄ in this study (35 kbar and 1100 °C) can be reached in the mantle, the complete absence of titanium from a real rock may never be realized. The stability of CaAlFSiO₄ in Ti-bearing systems, like natural rocks, might be restricted to significantly higher pressures and lower temperatures not found in nature. Alternatively, titanite with $X_{Al} > 0.50$ might form in the lower crust or upper mantle, but decomposes during uplift, due to drop in pressure or change in *F* fugacity. In this case one would expect to find retrograde phases like anorthite, which was reported by Carswell et al. (1996) to have partly replaced titanite with $X_{Al} < 0.48$.

It could be speculated that the high degree of distortion of the tetrahedra in CaAlFSiO₄ has a negative effect on its stability over geological time, because small changes in pressure, temperature, or composition will shift it into stability fields of much less distorted, and thus more stable phases like for example zoisite, grossular, or kyanite.

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