

## IRON IN TITANITE: A MÖSSBAUER-SPECTROSCOPY STUDY

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### ABSTRACT

Natural and synthetic samples of titanite have been investigated using  $^{57}\text{Fe}$  Mössbauer spectroscopy. Both ferrous and ferric iron are found in the natural samples. Ferric iron, octahedrally co-ordinated, occurs in two different environments, caused by domain formation in the octahedral chains. Domain boundaries that cross-cut the octahedral chains prevent the  $P2_1/a \rightleftharpoons A2/a$  change in symmetry observed for pure  $\text{CaTiSiO}_5$  at elevated temperatures.

**Keywords:** titanite, Mössbauer spectroscopy, synthesis, X-ray data, domain boundaries.

### SOMMAIRE

On a étudié des échantillons naturels et synthétiques de titanite par spectroscopie Mössbauer du  $^{57}\text{Fe}$ . La titanite naturelle contient à la fois  $\text{Fe}^{2+}$  et  $\text{Fe}^{3+}$ . Le fer ferrique, à coordinance octaédrique, se trouve dans deux environnements différents liés à la formation de domaines dans les chaînes d'octaédres. Les parois des domaines qui recourent ces chaînes entravent la transition en symétrie de  $P2_1/a$  à  $A2/a$ , qui caractérise le  $\text{CaTiSiO}_5$  pur à température élevée.

(Traduit par la Rédaction)

**Mots-clés:** titanite, spectroscopie Mössbauer, synthèse, diffractogramme X, parois des domaines.

### INTRODUCTION

Titanite  $\text{CaTiSiO}_5$  can form under a wide range of physical conditions and is often found as an accessory mineral in both igneous and metamorphic rocks. Its crystal structure consists of infinite parallel chains of  $\text{TiO}_6$  octahedra connected by isolated  $\text{SiO}_4$  tetrahedra (Zachariasen 1930, Mongiorgi & Riva De Sanseverino 1968). The large interstitial positions, considered to be seven co-ordinated and irregular, are occupied mainly by Ca ions. The octahedra are arranged in a zig-zag line parallel to the  $X$  axis and are connected by the  $\text{O}_1$  in a corner-sharing pattern. In the  $\text{TiO}_6$  octahedra (almost regular), the Ti atoms are displaced along the  $X$  direction ( $+X$  or  $-X$ ), giving alternating short and long  $\text{Ti}-\text{O}_1$  distances. The remaining four bonds in the Ti-octahedra are longer than either of the  $\text{Ti}-\text{O}_1$  bonds. Each  $\text{SiO}_4$  tetrahedron is linked to four different octahedra. Although the Si-O bonds within the tetrahedra are similar, the angles are different, resulting

in a distorted co-ordination polyhedron (Speer & Gibbs 1976). Chemical substitution in titanite is regulated by the criterion of ionic size (Sahama 1946, Zabavnikova 1957). Thus large ions such as Na, rare-earth elements, Mn, Sr and Ba substitute for Ca in the large seven co-ordinated site, whereas Al, Fe, Mg, Nb and Ta substitute for Ti in the smaller octahedral sites. Aluminum and ferric iron are the most important ions substituting in natural titanite; they are considered to occur through the reaction  $(\text{Al,Fe})^{3+} + (\text{F,OH})^- = \text{Ti}^{4+} + \text{O}^{2-}$ . In natural samples, little or no substitution occurs in the Si position (Higgins & Ribbe 1976), although according to Hollabaugh & Rosenberg (1983), small amounts of Al and  $\text{Fe}^{3+}$  can proxy for Si. Muir *et al.* (1984) have shown the presence of tetrahedral ferric iron in synthetic titanite.

The substitution of Al and  $\text{Fe}^{3+}$  for Ti favors domain formation in the octahedral chains, resulting from a break in the regular displacement of the octahedral cation, giving rise to a  $A2/a$  symmetry

TABLE 1. COMPOSITION AND CELL PARAMETERS

	61	Åre	Syn550	Syn700
$\text{SiO}_2$	29.12	30.14		
$\text{Al}_2\text{O}_3$	2.38	2.66		
$\text{TiO}_2$	34.04	35.92		
$\text{Fe}_2\text{O}_3$	2.42	1.65		
MnO	0.55	0.22		
CaO	26.04	27.77		
Number of cation on basis of 5 atoms of oxygen				
Si	1.00	1.00	0.986	0.979
$\text{Fe}^{3+}$			0.014	0.021
Ti	0.884	0.896	0.945	0.952
Al	0.095	0.103		
$\text{Fe}^{3+}$	0.056	0.031	0.086	0.084
$\text{Fe}^{2+}$	0.005	0.007		
Ca	0.963	0.986	0.969	0.964
Mn	0.016	0.006		
Cell dimensions				
a Å	7.058(2)	7.044(3)	7.061(5)	7.074(5)
b Å	8.714(3)	8.711(3)	8.709(6)	8.702(4)
c Å	6.558(3)	6.511(3)	6.545(8)	6.558(5)
$\beta^\circ$	113.87(7)	113.76(6)	113.79(8)	113.84(6)
$V \text{ \AA}^3$	368.8	365.6	368.2	369.3

Natural samples: 61: Leacher See, sandstone- and magnetite-bearing volcanic rocks, Elfel, West Germany. Åre: Åreskutan, metasedimentary rock, Swedish Caledonides.

in the average structure (Speer & Gibbs 1976). Pure synthetic  $\text{CaTiSiO}_5$  belongs to space group  $P2_1/a$  (Robbins 1968); this gives way at around  $220^\circ\text{C}$  to  $A2/a$  owing to the movement of the Ti ion to the centre of the octahedron (Taylor & Brown 1976).

Early investigators of the Mössbauer spectra of iron-bearing titanite (Muir *et al.* 1984) could not fully explain the observed absorptions. The present study gives further experimental data on natural and synthetic samples, leading to an improved interpretation of the Mössbauer spectra.

### EXPERIMENTAL

Two samples of natural titanite from the Mineralogical Museum, University of Uppsala, used in this study, were characterized by X-ray-diffraction and electron-microprobe analyses (Table 1). Synthetic

$T^\circ\text{C}$	$\text{Fe}^{3+}$ (tet)				$\text{Fe}^{3+}$ (oct <sub>I</sub> )				$\text{Fe}^{3+}$ (oct <sub>II</sub> )				$\text{Fe}^{2+}$ (oct)			
	IS	Q	$\Gamma$	Int	IS	Q	$\Gamma$	Int	IS	Q	$\Gamma$	Int	IS	Q	$\Gamma$	Int
61	.25				.30	1.49	.59	.52	.57	.79	.56	.36	1.02	2.44	.41	.11
Äre	.25				.34	1.54	.92	.56	.58	.74	.48	.25	1.03	2.34	.44	.17
700	.20	1.30	.56	.14	.34	.82	.44	.55	.52	.73	.35	.31				
550	.25	.21	1.25	.57	.14	.35	.96	.40	.55	.48	.81	.42	.31			
100	.14	1.25	.57	.14	.29	.89	.40	.55	.46	.82	.42	.31				
205	.09	1.30	.57	.14	.21	.87	.40	.55	.37	.81	.42	.31				
247	.05	1.27	.57	.14	.18	.87	.40	.55	.33	.78	.42	.31				
254	.05	1.37	.57	.14	.18	.86	.40	.55	.35	.81	.42	.31				
298	.08	1.38	.57	.14	.13	.85	.40	.55	.30	.76	.42	.31				
348	.07	1.31	.57	.14	.10	.85	.40	.55	.28	.80	.42	.31				

Isomer shift (IS), Quadrupole splitting (Q) and line width ( $\Gamma$ ) in mm/s  $\pm$  0.01 mm/s. Intensity in %  $\pm$  5%.

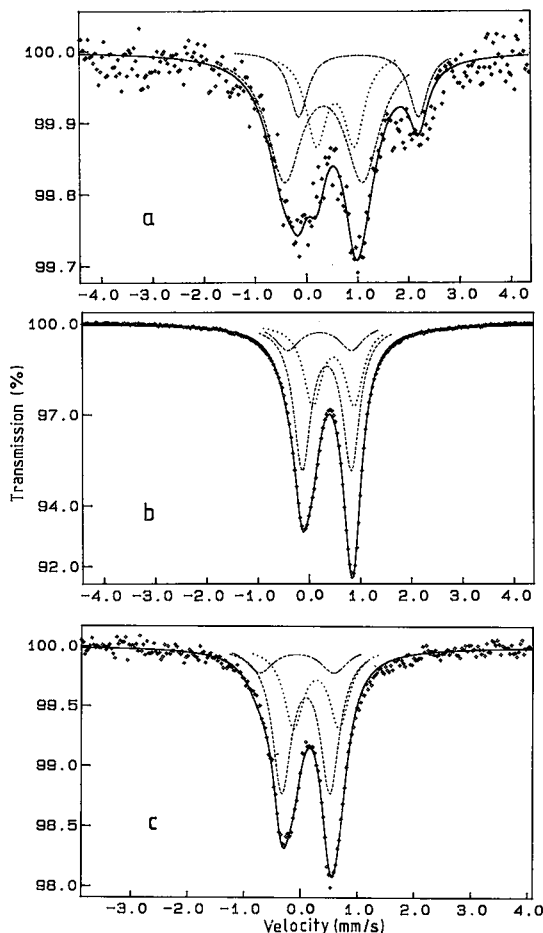


FIG. 1. Mössbauer spectra of (a) natural titanite from Åre at room temperature, (b) Syn550 at room temperature, and (c) Syn550 at  $348^\circ\text{C}$ .

titanite doped with 0.8 at. % Fe as  $^{57}\text{Fe}$  was prepared using conventional hydrothermal techniques. Conditions for the experiments were  $550$  (Syn550) and  $700^\circ\text{C}$  (Syn700) and 1 kbar pressure. To keep the oxygen fugacity high during the synthesis,  $\text{PtO}_2$  was added to the charge.

Unit-cell parameters were obtained from X-ray powder patterns using a cell-refinement program (CELNE); at least 14 reflections were used in the final refinement (Table 1). The Mössbauer spectra were obtained at room temperature as well as at elevated temperatures (for Syn550) using a furnace described by Annersten *et al.* (1982). Conventional transmission geometry was used, and calibration of the spectrometer velocity was made from natural iron foil using  $^{57}\text{Co}$  in Rh as a source. Computer-fitted spectra are shown in Figure 1, and the Mössbauer parameters are given in Table 2.

### RESULTS

Assignments of the computer-fitted absorption doublets are made from the isomer-shift values obtained (*cf.* Table 2). In the synthetic samples, prepared at a high fugacity of oxygen, only ferric iron is observed. The pattern with the smallest isomer-shift in the spectra is typical of ferric iron in tetrahedral co-ordination. The two larger isomer-shifts are assigned to ferric iron in the octahedral Ti-position. The isomer-shift values of  $0.48$ – $0.52$  mm/s were not obtained for one absorption pattern were not observed by Muir *et al.* (1984). An acceptable Lorentzian fit, however, was not obtained by the fitting of only one doublet. The incorporation of a second octahedral ferric iron improved the fit, with  $\chi^2$  dropping from  $4.8$  to  $0.8$ /datapoint.

The large isomer-shift indicates an atom of ferric iron having a smaller density of electrons, *i.e.*, situated in a larger co-ordination polyhedron. In titanite the Ca position would be a possible site. However, ferric iron substituting for Ca in such a large seven-co-ordinated polyhedron is not known in silicates (*cf.* ferric iron in plagioclase: Hofmeister & Rossman 1984).

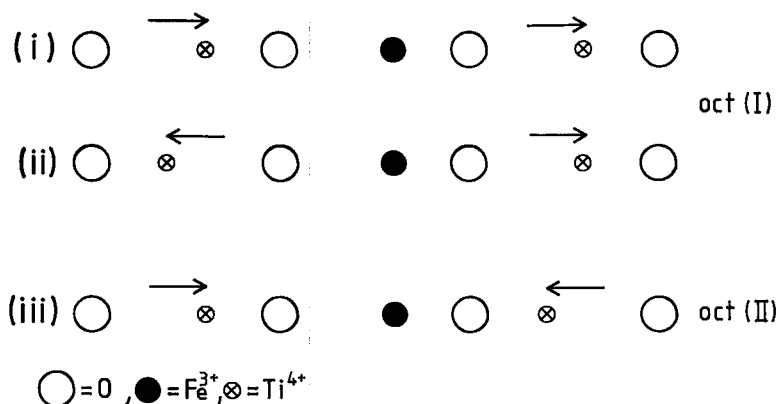


FIG. 2. Schematic view of the three possible  $P2_1/a$  geometries at the domain border below the transition temperature.

Speer & Gibbs (1976) proposed a domain structure for titanite containing impurities such as aluminum and ferric iron. Thus three different types of iron-oxygen octahedron can be considered, taking the nearest neighbors into consideration (*cf.* Fig. 2): (i) one Ti displaced toward and the other away from the impurity, *i.e.*, the domain boundary parallel to the  $X$  axis, (ii) both Ti atoms displaced away from the impurity, and (iii) both Ti atoms displaced toward the impurity. In the last two cases the domain boundary would cut across the chain of octahedra (Taylor & Brown 1976).

The polarization power of the iron on the  $\text{O}_1$  bridging ion will be larger in (i) and (ii), resulting in a higher density of electrons around the iron nucleus and a relatively small isomer-shift;  $\text{Fe}^{3+}$  is in oct(I). In (iii), where the polarization of ferric iron is reduced owing to the short distance to the neighboring small  $\text{Ti}^{4+}$  ion, the isomer shift is larger and assigned to  $\text{Fe}^{3+}$  in oct(II).

In the natural sample, a doublet with a large isomer-shift is due to ferrous iron in the octahedral position. Furthermore, two ferric iron doublets can be assigned to the octahedral sites. Line widths are, however, quite large, suggesting a partly metamict state (*i.e.*, high content of  $\text{H}_2\text{O}$  or  $\text{F}^-$ , not determined; *cf.* Muir *et al.* 1984). This conclusion is supported by the low analytical totals obtained from the microprobe analysis (*cf.* Table 1).

The computer-fitted quadrupole splitting for the oct(I) pattern is larger than that observed in the synthetic samples. Quadrupole splittings are sensitive to changes in gradient in the electrical field and thus sensitive to changes in the chemical composition. Notable here is the presence of Al in the natural samples.

The high-temperature measurements on the titanite synthesized at  $550^\circ\text{C}$  show a decrease of the

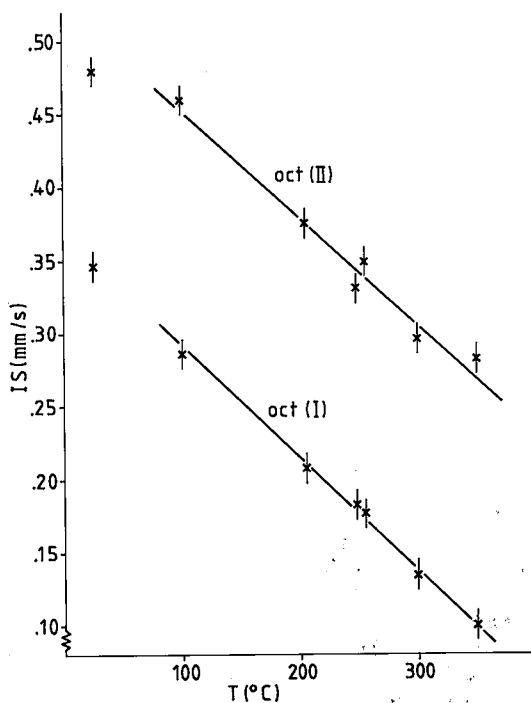


FIG. 3. Decrease of the isomer shift of octahedrally coordinated ferric iron with increasing temperature. Lines are least-squares fits of the data points (see text).

isomer shift with increasing temperature (Fig. 3). The decrease in isomer shift with temperature can be ascribed mainly to the second-order Doppler shift (SOD). Using the high-temperature approximation, the accepted value is approximately  $7.3 \times 10^{-4} \text{ mm s}^{-1}$

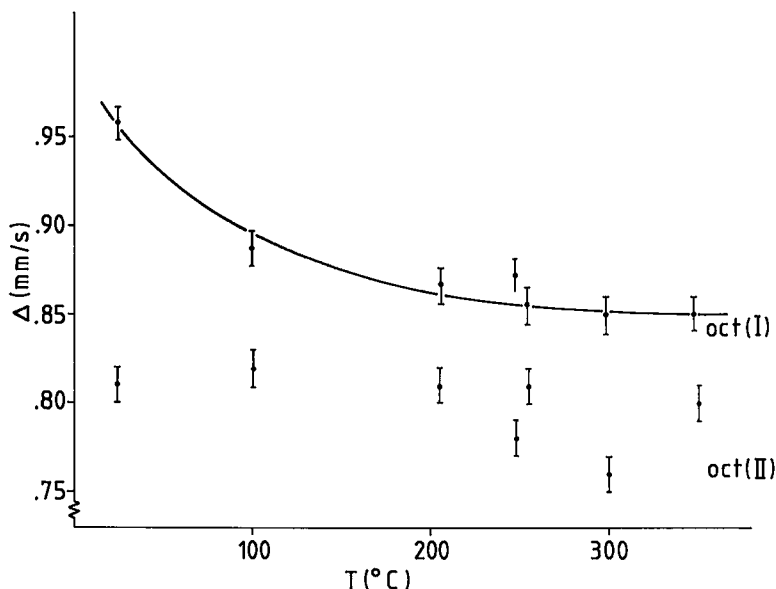


FIG. 4. Variation in quadrupole splitting of octahedrally co-ordinated ferric iron with increasing temperature. The curve drawn indicates the regular trend of the quadrupole splitting of oct(I) with increasing temperature.

deg<sup>-1</sup> (Cohen 1976). The calculated slopes for octahedral iron (Fig. 3) are  $7.8 \times 10^{-4}$  ( $R^2$  0.994) and  $7.4 \times 10^{-4}$  mm s<sup>-1</sup> deg<sup>-1</sup> ( $R^2$  0.973) for oct(I) and oct(II), respectively, in agreement with the findings of Cohen (1976).

The variation in quadrupole splitting with increasing temperature (Fig. 4) shows a smooth decrease for the oct(I) pattern up to approximately 200°C, where the curve flattens.

#### DISCUSSION AND CONCLUSIONS

In earlier Mössbauer studies on titanite, Muir *et al.* (1984) encountered difficulties in obtaining good computer-fits of the spectra. We have shown that the incorporation of an additional absorption-doublet results in improved fits; this doublet is assigned to ferric iron in a second octahedral position.

The existence of these two patterns above the transition temperature indicates the presence of two types of nonequivalent octahedrally co-ordinated iron positions in titanite with  $P2_1/a$  symmetry. Therefore, the soft-mode transition, at least for iron, will end with the maintenance of a disordered structure above the transition temperature, probably close to the domain boundary. DTA measurements on titanite (Vance & Metson 1985) support a second-order phase transition at elevated temperatures, in agreement with Taylor & Brown (1976). Our Mössbauer data support this conclusion.

Further support for their conclusions on the high-temperature behavior of titanite is furnished by the decreasing values of quadrupole splitting with increasing temperature observed for ferric iron in oct(I). Ferric iron, with its  $d^5$  configuration, has a temperature-independent quadrupole splitting. The observed decrease therefore may be explained by the displacement of the ferric iron to a more symmetrical position with increasing temperature. The data (Fig. 4) also show a gradual change, comparable to the change in intensity of the 401 reflection with increasing temperature (Taylor & Brown 1976).

The quadrupole splittings of Fe<sup>3+</sup> (oct II) have a less regular trend, indicating a small change in symmetry for this type of co-ordination polyhedron. The adjustment of the off-centre cation to a more symmetrically co-ordinated one at this type of domain boundary will involve an antiparallel movement along the  $X$  axis direction. Our data indicate that such a displacement does not occur in titanite at elevated temperatures. Thus the observed decrease in quadrupole splitting for Fe<sup>3+</sup> oct(I) will only arise from octahedral chains of type (i) (Fig. 2). In conclusion, our results indicate that the presence of domain walls that cross-cut the octahedral chains will prevent the  $P2_1/a \rightleftharpoons A2/a$  transition in titanite at elevated temperatures.

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