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## THE CRYSTAL CHEMISTRY OF TIN IN TITANITE

### INTRODUCTION

Titanite  $\text{CaTi}[\text{O}|\text{SiO}_4]$  is an orthosilicate that crystallizes in the monoclinic system ( $P2_1/a$  or  $A2/a$  space groups). The structure of titanite consists of chains of Ti-octahedra that are bonded by isolated Si-tetrahedra. The large seven-fold Ca sites and the under-bonded O1 sites are between octahedral and tetrahedral sites (Ribbe 1980). This structure enables substitutions of many elements. Titanites, especially those that form in postmagmatic stage are scavengers for trace elements, e.g. Nb, Sn, Ta, Y, U, Th and REE, which occur in concentrations too low to form their own minerals.

Tin replaces titanium in octahedral sites according to the scheme of isomorphism  $\text{Sn}^{4+} \Leftrightarrow \text{Ti}^{4+}$  (Paul *et al.* 1981).

According to the experimental data of Takenouchi (1971), titanite  $\text{CaTi}[\text{O}|\text{SiO}_4]$  and malayaite  $\text{CaSn}[\text{O}|\text{SiO}_4]$  form a complete solid solution above 650-700°C. Kunz *et al.* (1997) found that a 10 mol% substitution of Sn changes the synthetic titanite symmetry from  $P2_1/a$  to  $A2/a$ . Tin-bearing titanites are rare in nature. Ramdohr (1935) described titanite containing 10 wt% of Sn (~ 19 mol%). Recently, titanites containing 1,41 wt% of Sn (Černý *et al.* 1995) and 2,12 wt% of Sn (Janeczek 1996) have been described.

### ANALYTICAL METHODS

Microscopic observations of thick sections were performed using a Carl Zeiss ore microscope. BSE (back-scattered electron) images were obtained using an ESEM – XL 30 TMP (Philips/Fei) scanning microscope with an EDS (EDAX) detector. Electron-probe microanalyses were performed using a Cameca SX 100 in the WDS-mode.

### RESULTS

Elevated concentrations of Sn in pegmatite titanites from Michałowice (Karkonosze Massif), Żółkiewka and Zimnik (Strzegom-Sobótka Massif) were established on the basis of electron-probe microanalyses (Table 1). The presence of such concentrations of Sn was made possible by the low concentration of Ti in these systems. As noted above, titanite scavenges trace elements, among others

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tin, occurring in concentrations too low to form minerals such as, e.g., cassiterite SnO<sub>2</sub>.

Table 1. Chemical compositions of Sn-rich titanites

	ideal	Marškov Černý <i>et al.</i>	Żółkiewka Janeczek	Michałowice	Żółkiewka I	Żółkiewka II	Zimnik I	Zimnik II
CaO	28.60	26.88	27.06	23.13	25.44	24.13	25.33	26.22
Y <sub>2</sub> O <sub>3</sub>				5.09	0.02	0.00	0.00	0.00
Na <sub>2</sub> O		0.09		0.07	0.05	0.13	0.05	0.00
TiO <sub>2</sub>	40.75	18.68	25.02	29.59	25.95	19.88	23.68	23.80
Nb <sub>2</sub> O <sub>5</sub>		4.86	3.33	0.62	6.01	6.10	3.45	3.46
Ta <sub>2</sub> O <sub>5</sub>		10.76	1.44	0.66	1.18	5.59	2.58	2.21
SnO <sub>2</sub>		0.77	7.40	4.06	7.54	11.87	14.33	15.41
Al <sub>2</sub> O <sub>3</sub>		6.62	4.05	2.20	2.01	1.37	1.03	0.94
Fe <sub>2</sub> O <sub>3</sub>		0.16	*1.42	2.43	1.10	2.31	1.47	1.49
SiO <sub>2</sub>	30.65	29.21	29.48	27.95	28.74	26.88	28.03	24.62
Total	100.00	98.03	100.32	95.79	98.04	98.27	99.95	98.13
Number of ions based on 3 cations								
Ca <sup>2+</sup>	1.00	1.01	0.99	0.88	0.96	0.97	0.98	1.04
Y <sup>3+</sup>				0.10	0.00	0.00	0.00	0.00
Na <sup>+</sup>		0.01		0.00	0.00	0.01	0.00	0.00
Ti <sup>4+</sup>	1.00	0.49	0.64	0.79	0.69	0.56	0.64	0.66
Nb <sup>5+</sup>		0.08	0.05	0.01	0.10	0.10	0.06	0.06
Ta <sup>5+</sup>		0.10	0.01	0.01	0.01	0.06	0.03	0.02
Sn <sup>4+</sup>		0.01	0.10	0.06	0.11	0.18	0.21	0.23
Al <sup>3+</sup>		0.27	0.16	0.09	0.08	0.06	0.04	0.04
Fe <sup>3+</sup>		0.00	0.04	0.07	0.03	0.06	0.04	0.04
Si <sup>4+</sup>	1.00	1.02	1.00	0.99	1.02	1.00	1.01	0.91
Total	3.00	2.99	2.99	3.00	3.00	3.00	3.00	3.00

\* Total Fe as FeO.

In all cases, titanite crystallized after secondary albite and almost at the same time as (Mg-Fe)-chlorites in the final hydrothermal stage under conditions between the prehnite-pumpellyite and zeolite facies,

The 0,23 Sn a.p.f.u. (Zimnik, Strzegom-Sobótka massif) is the highest reported concentration of Sn in natural titanite. It suggests a wider possible range of miscibility than has been described in the literature to-date.

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