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Structure of Pentanickel Titanium Diboron Oxide, $Ni_5TiB_2O_{10}$

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Abstract. $M_r = 523\cdot0$, orthorhombic, *Pbam*, $a = 12\cdot221\,(2)$, $b = 9\cdot199\,(2)$, $c = 2\cdot996\,(1)$, $V = 336\cdot8$ Å^3, $Z = 2$, $D_x = 5\cdot16$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 14\cdot97$ mm^{-1}, $F(000) = 504$, $T = 293$ K, R is 0·021 for 1042 reflections. The titanium atom partially occupies the smallest of four octahedral sites. (Ni,Ti) octahedra share edges and corners to form a 3D framework in which B occupies triangular interstices. The oxygen atoms are in approximate cubic closest packing as in the NiO structure.

Introduction. In a study of the NiO–TiO_2 system, Shimura & Kawamura (1976) described a new orthorhombic phase with composition Ni_5TiO_7 prepared by the Na_2O–B_2O_3 flux method. A chemical analysis of this phase by Armbruster (1981) indicated the presence of boron, which was not detected by the above authors. The correct chemical formula is $Ni_5TiB_2O_{10}$, which gives better agreement with the observed density of 5·14 Mg m^{-3} (Shimura & Kawamura, 1976). A structural analysis of this compound was undertaken to provide more information on the stereochemistry of Ni–Ti oxides and to complement our previous work in the NiO–TiO_2 system (Armbruster & Lager, 1981; Lager, Armbruster, Ross, Rotella & Jorgensen, 1981).

Experimental. Crystal prismatic in shape, 100 × 46 × 46 μm; grown from oxide mixture and Na_2O–B_2O_3 flux during cooling from 1573 K; intensity data (ω-scan technique; $\sin\theta/\lambda \leq 0\cdot905$ Å^{-1}; $0 \leq h \leq 22$, $0 \leq k \leq 16$, $0 \leq l \leq 5$) collected with Nonius CAD-4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation) in bisecting mode; unit-cell parameters from least-squares refinement of 20 automatically centered reflections ($10 \leq \theta \leq 20°$); 1190 unique reflections measured; 1042 with $I > 3\sigma(I)$ used in subsequent calculations; three standard reflections monitored every 100 reflections showed no significant variation (± 1%); Lp correction, empirical absorption correction, using ψ scans with 5 reflections, transmission factors ranged from 0·86 to 1·0; structure solution by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); space group *Pbam* chosen after refinements did not converge in *Pba*2; initially all metal atoms considered to be Ni; Ti atom assigned to octahedral site with anomalously large isotropic B (see *Discussion*); scale, primary and secondary extinction parameters, positional parameters, anisotropic temperature factor coefficients varied in the final cycle of refinement; function minimized $\sum w(F_o - F_c)^2$; $w = \sigma^2(F_o)$; $R = 0\cdot021$, $wR = 0\cdot039$,

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$S = 3{\cdot}17$, max. $\Delta/\sigma = 0{\cdot}10$; refined extinction parameters [Becker & Coppens (1974, 1975) formalism] for Lorentzian domain distribution: $r = 2{\cdot}4\ (3) \times 10^4$, $g = 0{\cdot}45\ (3) \times 10^4$ (domain size: $2{\cdot}4 \times 10^{-4}$ cm, mosaic spread 7·2″); anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); all calculations performed on IBM 3330 computer at the University of Bern with the program *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). Final difference Fourier maps indicate max. and min. peaks of 1·2 and $-1{\cdot}0$ e Å^{-3}.

Discussion. Atomic parameters and metal–oxygen distances are listed in Tables 1* and 2, respectively. The polyhedral drawing in Fig. 1 (*STRUPLO'*82; Fischer, 1983) illustrates the characteristic feature of the structure: zigzag chains of edge-sharing (Ni,Ti) octahedra parallel to **b** (Fig. 2). Adjacent chains are linked by corners and edges to form a three-dimensional framework in which the boron atoms occupy the triangular interstices between chains. Oxygen atoms in each chain are arranged in approximate cubic closest packing as in NiO. The titanium atom probably occupies the smallest of the four octahedral sites [Ni/Ti]. Addition of Ti to this site in the early stages of refinement reduced the isotropic temperature factor from 0·8 to 0·4 Å^2 (a value in better agreement with *B*'s for the three Ni sites) and decreased the *R* value from 0·052 to 0·036. The assignment of Ti to this position was also confirmed by a site occupancy factor refinement of Ti with the constraint Ti = 1—Ni yielding 0·51 (1) Ti. Site occupancy refinements on all other Ni positions show that Ni(1), Ni(2) and Ni(3) do not contain significant Ti concentrations. Mean Ni—O distances are similar to those reported for Ni—Ti spinels (2·07 Å), NiO (2·08 Å) and $NiTiO_3$ (2·08 Å) (Armbruster & Lager, 1981; Lager *et al.*, 1981; Shirane, Pickert & Ishikawa, 1959).

This study was completed while GAL was a visiting fellow of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung at the Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Switzerland.

Table 1. *Fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j .$$

The site occupation of Ni/Ti is 0·50 Ni + 0·50 Ti.

	x	y	z	U_{eq}
Ni(1)	0·0	0·0	0·50	0·0056
Ni(2)	0·28270 (3)	0·50067 (4)	0·0	0·0040
Ni(3)	0·50	0·0	0·0	0·0043
Ni/Ti	0·11412 (3)	0·26068 (4)	0·50	0·0040
B	0·1401 (2)	0·7268 (4)	0·50	0·0045
O(1)	0·9242 (2)	0·8820 (2)	0·0	0·0071
O(2)	0·7380 (2)	0·8477 (2)	0·50	0·0053
O(3)	0·1444 (2)	0·3911 (3)	0·0	0·0080
O(4)	0·1409 (2)	0·8762 (2)	0·50	0·0053
O(5)	0·4580 (2)	0·1503 (2)	0·50	0·0055

Table 2. *Metal and boron–oxygen distances* (Å) *with e.s.d.'s in parentheses*

Bond multiplicity is given in square brackets.

[4] Ni(1)–O(1)	2·068 (1)	[2] Ni/Ti–O(1)	2·046 (1)
[2] Ni(1)–O(4)	2·065 (2)	[1] Ni/Ti–O(2)	2·064 (2)
Mean	2·067	[2] Ni/Ti–O(3)	1·955 (2)
		[1] Ni/Ti–O(5)	2·076 (2)
[1] Ni(2)–O(1)	2·039 (2)	Mean	2·024
[2] Ni(2)–O(2)	2·118 (1)		
[1] Ni(2)–O(3)	1·968 (2)	[1] B–O(2)	1·379 (3)
[2] Ni(2)–O(4)	2·104 (1)	[1] B–O(4)	1·375 (5)
Mean	2·075	[1] B–O(5)	1·390 (3)
		Mean	1·381
[2] Ni(3)–O(3)	2·029 (2)		
[4] Ni(3)–O(5)	2·102 (1)		
Mean	2·078		

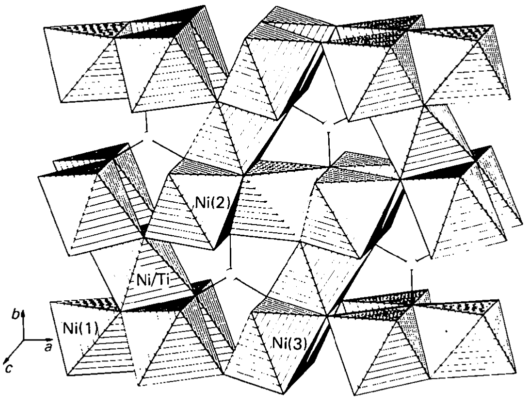

Fig. 1. Drawing of the unit cell of $Ni_5TiB_2O_{10}$ illustrating the zigzag chains of (Ni,Ti) octahedra and the triangular coordination of B (depicted as circles).

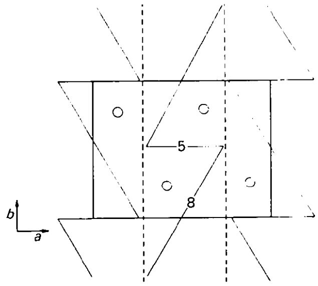

Fig. 2. Schematic drawing of the structure parallel to (001) illustrating the relationship between octahedral chains. The numbers 8 and 5 refer to the number of octahedra comprising each segment of the chain. The *b* glide is indicated by dashed lines. The circles represent B atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42331 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of 24 New Polytypes of Tin Disulphide*

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Abstract. The structures of 24 new polytypes of SnS_2 obtained from a vapour phase are presented: $8H_1$: $(f2f1)_2/(211)_2$ (*t*–*o*–*f*/Zhdanov notations); $10H_2$: $f2of1f2f1/2(11)_2211$; $12H_1$: $tf5tf1of1/22122111$; $12H_2$: $f2(o)_2f1f2f1/2(11)_3211$; $14H_2$: $f2(o)_2f1f2of1/2(11)_32(11)_2$; $22H_1$: $(f5f1f1)_3(t)_2/22(2121)_3$; $24H_1$: $f5f1f1f2f2f1f1f5f1f1(t)_2/2221212111212121$; $40H_2$: $(f5f1f1)_6(t)_2/22(2121)_6$; $42H_1$: $(f1f5f1)_6(o)_3/(2121)_6(11)_3$; $44H_1$: $(f1f5f1)_3o(f1f5f1)_2(o)_2f1f5f1o/(2121)_311(2121)_2(11)_2212111$; $24R_2$: $f2f2f1f1/211121$; $30R_2$: $f5f1f1(t)_2/222121$; $36R_1$: $f1f5f1(o)_3/2121(11)_3$; $42R_2$: $f5f1f1f2f2f1f1/2121211121$; $48R_2$: $(f5f1f1)_2(t)_2/22(2121)_2$; $54R_1$: $f1f5f1of1f5f1(o)_2/2121112121(11)_2$; $72R_1$: $f5f1f1f2f2f1of1(f2f1)_2/212121112111211211$; $84R_2$: $(f1f5f1)_2(f1f5f1o)_2/(2121)_2(212111)_2$; $96R_1$: $(f1f5f1)_3(o)_2f1f5f1(o)_2/(2121)_3(11)_22121(11)_2$; $96R_2$: $(f1f5f1)_3of1f5f1(o)_3/(2121)_3112121(11)_3$; $114R_1$: $(f1f5f1o)_4f1f5f1/(212111)_42121$; $132R_2$: $(f1f5f1o)_3(o)_4f1f5f1(o)_3/(212111)_3(11)_42121(11)_3$; $138R_1$: $(f5f1f1)_7(t)_2/22(2121)_7$; $144R_1$: $(f1f5f1o)_2(f1f5f1)_2of1f5f1(o)_6/(212111)_2(2121)_2112121(11)_6$.

Experimental. Crystals of SnS_2 were grown from vapour phase by the method of chemical transport. Starting materials were SnS_2 and SnI_4 powders, temperature of crystallization was in the range 670–1170 K (Pałosz, Pałosz & Gierlotka, 1984). Crystals – platelets from 1 × 1 × 0·01 to 10 × 20 × 0·1 mm – examined by X-rays in cylindrical camera with 43 mm radius and 0·7 mm collimator. Oscillation method with a^* axis as rotation axis and with angle between incident beam (Co *K* radiation) and *c* axis varying between 15 and 30°. The method used here for the determination of the structures of 24 new polytypes of SnS_2 is similar to that described previously and used for CdI_2 and SnS_2 polytypes (Pałosz, 1982; Pałosz, Pałosz & Gierlotka, 1985). This method is based on the comparison of the experimental and theoretical intensity diagrams prepared for $10.l$ and $1\bar{1}.l$ reflexions where $1{\cdot}5 \le l/N \le 2{\cdot}5$ and N is the number of S layers in a polytype cell. In the analysis of the theoretical models of the polytype cells formulae found for structural series were used (Pałosz, 1982; Pałosz *et al.*, 1985). For each polytype under investigation calculations of reflexion intensities were performed for a certain number of theoretical models: for a few models for simple polytypes (*e.g.* $8H$, $10H$, $22H$, $30R$) and up to about 20 models for complicated polytypes (*e.g.* $24H_1$, $44H_1$, $132R_2$, $144R_1$). The diagrams presented in Figs. 1–24 compare the measured values of reflexion intensities with those calculated for models corresponding to the identified polytypes of SnS_2.† The temperatures of growth of these polytypes are given in Table 1, where the polytype

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* *Editorial note:* The Zhdanov notation used in this and the two following papers is a simplified version of the recommendations approved by the International Union of Crystallography *Ad-Hoc* Committee on the Nomenclature of Disordered, Modulated and Polytype Structures [Guinier, Bokij, Boll-Dornberger, Cowley, Ďurovič, Jagodzinski, Krishna, de Wolff, Zvyagin, Cox, Goodman, Hahn, Kuchitsu & Abrahams (1984). *Acta Cryst.* A**40**, 399–404].

† Figs. 1–24 and tables listing calculated and observed intensities for SnS_2 polytypes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42251 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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