Preparation of Single Crystals of a New Compound, Ta_5B_6 by the Aluminium-Flux Method

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Single crystals of a new compound Ta_5B_6 was prepared by the high temperature aluminium solution method using tantalum and boron powder as starting materials in an argon atmosphere. The experimental conditions for obtained single crystals of relatively large size were established. The optimum conditions for growing Ta_5B_6 single crystals were found to include atomic ratios of starting materials B/Ta=1.2 and Al/Ta=8.38, soaking temperature 1650 °C, soaking time 5 h and a cooling rate of 25 °C h^{-1}. Single crystals of Ta_5B_6, having a grey color and metallic luster, were generally obtained in the form of an irregular or trapezoidal shape: the latter crystals were enclosed by two large {010} planes. The largest crystals prepared have maximum dimensions of about 0.12 mm×0.13 mm×0.23 mm. The crystals are orthorhombic with a space group of either *Cmm*2, *Cm*2*m*, *C*222, or *Cmmm* and the unit cell dimensions a=3.1385(10) Å, b=22.609(7) Å, c=3.2865(8) Å, and V=233.20(12) Å^3. The X-ray density is 13.808(2) g cm^{-3}. The present study of growing Ta_5B_6 crystals is the first single crystal growth study of a V_5B_6 type crystal.

The transition metal binary borides have several unique chemical and physical properties, which are of great importance in many cases from technological applications. Among their attractive properties are high melting points, chemical stability, high electrical and thermal conductivity, high hardness and high mechanical toughness.[1]

Previously, the properties of most borides have been studied on polycrystalline specimens. The need for precise data have led to an increased interest in the preparation of single crystals of these materials. Preparation of single crystals of the binary borides is fairly difficult because of their melting points and chemical stability. The simplest method of preparing single crystals of borides, in terms of growth technology at lower temperatures, is provided by the crystal growth from solution in metallic melts.[2] Several reports have been published in recent years on the growth of single crystals of binary borides from metallic solutions. For example, the preparation of pure zirconium and hafnium diborides from copper, tin and lead melts has been studied.[3] Single crystals of the incongruently melting borides Mo_2B_5 and W_2B_5 have been prepared from an aluminium solution.[4] We reported earlier the growth of single crystals of TiB_2, ZrB_2, HfB_2, VB, V_3B_4, VB_2, NbB_2, TaB, TaB_2, CrB, Cr_3B_4, Cr_2B_3, CrB_2, $W_2B_{5-x}(WB_2)$, and $Mo_2B_{5-x}(MoB_2)$ from an aluminium-flux soaked at 1300—1550 °C for 1—10 h.[5—7] From the experimental results of these reports it is apparent that a great number of transition metals react with boron in metallic melts to form borides.

In the tantalum-boron system the intermediate phases Ta_2B, Ta_3B_2, TaB, Ta_3B_4, and TaB_2 have been reported.[8,9] Recently we have prepared small crystals of TaB and TaB_2 from tantalum and boron powder as starting materials using an aluminium-flux technique.[10] Further detailed experiments on the Ta–B system have led us to obtain a new binary metal boride, Ta_5B_6 in single crystalline form. In the present paper, we report the experimental conditions for growing the new boride as well as its crystallographic data.

Experimental

The synthesis of crystals was carried out in a resistance furnace equipped with a tantalum heating element. The starting materials were tantalum metal powder (particle size, −325 mesh: purity, 99.9%), crystalline boron (particle size, −115 mesh: purity, 99.5%) and aluminium metal chips (purity, 99.995%). The starting materials were placed in an alumina crucible (purity, 99.8%) and heated at a rate of 300 °C h^{-1} up to a temperature of 1650 °C in an argon atmosphere. After the specimen was kept at this temperature for 5 h and cooled to 1000 °C at a rate of 25 °C h^{-1}, it was cooled to room temperature by switching off the electric power of the furnace. After cooling, the as-grown crystals in the reaction mixtures were separated from the solidified matrix by dissolving the excess metal in 6 mol dm^{-3} hydrochloric acid for about 5 days. The experimental conditions for each run as well as the crystalline phases obtained are shown in Table 1. The crystalline phases and the unit cell dimensions were examined using a powder X-ray diffractometer (Rigaku Denki Co., Ltd., RU-200) with monochromatic Cu $K\alpha$ radiation (wavelength λ=1.541743 Å) or an XDC 1000 Guinier–Hägg foucusing X-ray powder diffraction camera with strictly monochromatic Cu $K\alpha_1$ radiation (wavelength λ=1.5405981 Å) and semiconductor grade silicon (purity, 99.9999%, a=5.431065Å) as internal calibration standard.[11] The Guinier–Hägg film was used for measuring X-ray diffraction intensities, which was performed with a Line Scanner (Model LS-18).[12] The relative amounts of the product phases can be assumed to be proportional to the relative intensities of the phases disregarding absorption and possibly preferred orientation effects.[13] The non-overlapping diffraction lines I_{221} (TaB), I_{150} (Ta_5B_6), I_{121}(Ta_3B_4), and I_{101}(TaB_2) were selected for calculation of the relative intensities. The relative intensity of a phase is defined as

Table 1. Preparation Conditions of Ta_5B_6 Crystals from Molten Aluminium Solution, Soaked at 1650 °C for 5 h

Run. No.	Composition of starting material (atomic ratio)			Phases identified			
	Ta	B	Al				
1	1	1.10	100.60	TaB,	Ta_3B_4,	Ta_5B_6	
2	1	1.15	100.60	TaB,	Ta_3B_4,	Ta_5B_6	
3	1	1.20	100.60	Ta_3B_4,	Ta_5B_6,	TaB	
4	1	1.25	100.60	Ta_3B_4,	Ta_5B_6,	TaB	
5	1	1.30	100.60	Ta_3B_4,	Ta_5B_6,	TaB,	TaB_2
6	1	1.35	100.60	Ta_3B_4,	TaB_2,	Ta_5B_6	
7	1	1.40	100.60	Ta_3B_4,	TaB_2,	Ta_5B_6	
8	1	1.20	3.35	TaB,	Ta_5B_6,	Ta_3B_4	
9	1	1.20	8.38	Ta_5B_6,	TaB,	Ta_3B_4	
10	1	1.20	16.77	Ta_5B_6,	Ta_3B_4,	TaB	
11	1	1.20	50.30	Ta_3B_4,	Ta_5B_6,	TaB	
12	1	1.20	100.60	Ta_3B_4,	Ta_5B_6,	TaB	
13	1	1.20	217.96	Ta_3B_4,	TaB,	TaB_2,	Ta_5B_6

The starting materials for Run Nos. 1 to 7 consist of 2.00 g Ta, 0.13 to 0.17 g Boron and 30.0 g Al, the starting materials for Run Nos. 8 to 13 consist of 2.00 g Ta, 0.14 g Boron and 1.0 to 65.0 g Al.

$$I_i(\text{rel.}) = I_i / \sum_{j=1}^{n} I_j$$

where i, j=TaB, Ta_5B_6, Ta_3B_4, and TaB_2.

Some crystals were examined to collect data on crystal plane orientations or other crystal data using Weissenberg, oscillation and precession cameras, and a four-circle type automatic diffractometer (Rigaku Denki Co., Ltd., AFC-6), equipped with a graphite monochrometer using Mo $K\alpha$ radiation (wavelength λ=0.710678 Å). Binocular microscope and scanning electron microscope (SEM)(JEOL, JSM-840) were used for morphological investigations. The aluminum content of the crystals was analyzed using an electron probe microanalyzer (EPMA)(JEOL, JSM-35C). The X-ray density was determined using the results of the unit cell dimension measurements and the assumption that Ta_5B_6 is iso-structural with V_5B_6.

Results and Discussion

Conditions of Synthesis for Ta_5B_6 Crystals. The synthesis was performed under constant conditions of heating rate 300 °C h^{-1}, soaking temperature 1650 °C, soaking time 5 h, cooling rate 25 °C h^{-1} and an atomic ratio Al/Ta =100.60. The atomic ratio B/Ta in the starting material was varied from 1.10 to 1.40 (Run No. 1 to 7). The amount of tantalum in the starting material was fixed at 2 g throughout all the experiments. The crystalline phases obtained were identified by X-ray powder diffraction. The results are listed in Table 1, and typical X-ray diffraction patterns are shown in Fig. 1. As seen from Table 1 and Fig. 1, four kinds of tantalum borides, i.e., TaB, the new phase Ta_5B_6, Ta_3B_4, and TaB_2 were formed, while crystals of Ta_2B, Ta_3B_2, AlB_2,[14] α-AlB_{12},[15,16] β-AlB_{12},[14] γ-AlB_{12},[17] and $Ta_5Al_3B_x$[18] were not detected by powder X-ray diffraction. The variation of the atomic ratio of the starting materials gave different product phases. With increased boron concentration, more boron-rich phases are formed. The desired Ta_5B_6 crystals were invariably obtained as a phase mixture for all atomic ratios B/Ta in the starting material (Run No. 1 to 7). However, the relative X-ray intensity of formed Ta_5B_6 became remarkably large for B/Ta=1.20 to B/Ta=1.30. From Table 1 (Run No. 1 to 7), it is evident that the most favorable atomic ratio B/Ta for obtaining Ta_5B_6 crystals is 1.20.

The influence of the amount of molten aluminium used in the crystal growth of Ta_5B_6 was studied under constant conditions of soaking temperature 1650 °C, soaking time 5 h and already established atomic ratio of the starting materials B/Ta=1.20. The results of the powder X-ray analysis of the product specimens are presented in Table 1 (Run No. 8 to 13) and Fig. 2. In all experiments on influence of the amount of aluminium solution, Ta_5B_6 crystals were obtained as a phase mixture together with crystals of TaB and Ta_3B_4 or TaB_2 for Al/Ta=3.35 to 217.96. When starting materials with the atomic ratio of Al/Ta=8.38 were used, the Ta_5B_6 phase shows the strongest relative X-ray intensity. However, from starting materials containing a very small amount of aluminium (Al/Ta=3.35)(Run No. 8) and from those containing larger amount of aluminium (Al/Ta>16.77) (Run No. 10 to 13), only small amounts of Ta_5B_6 crystals were obtained.

It is clear from the above results that for all B/Ta and Al/Ta atomic ratios of the starting materials, Ta_5B_6 crystals were obtained as a phase mixture together with crystals of TaB and Ta_3B_4 or TaB_2. The relative X-ray intensity of formed Ta_5B_6 became remarkably large for soaking temperature 1650 °C, soaking time 5 h, and the atomic ratios of the starting materials: B/Ta=1.2 and Al/Ta=8.38.

Ta_5B_6 crystals were deposited in substantial quantities on the wall and bottom of the alumina crucible.

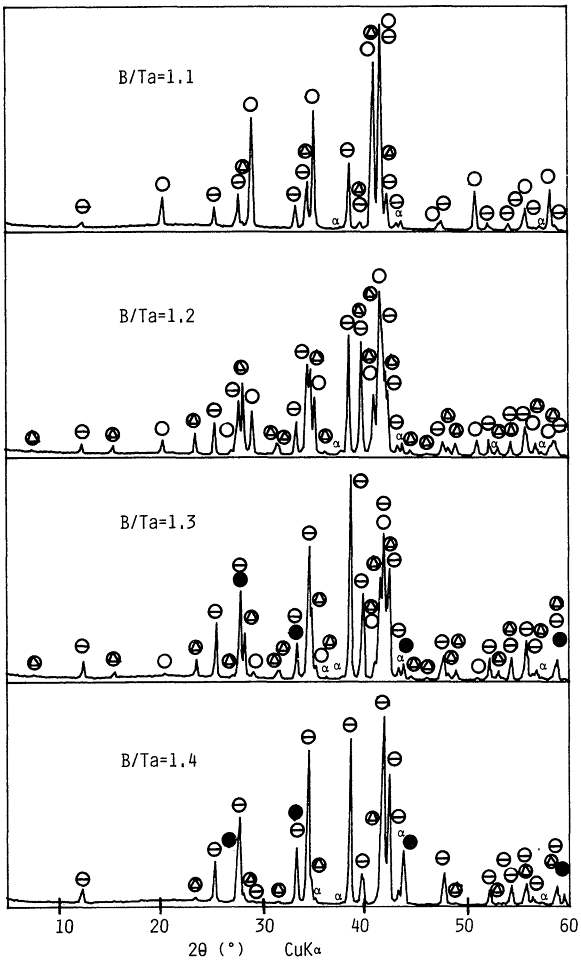

Fig. 1. Powder X-ray patterns (diffractometer data, Cu $K\alpha$ radiation) of the products obtained from several starting materials with various compositions. The atomic ratio Al/Ta of the starting materials is fixed at 100.60. The starting materials are heated at 1650 °C for 5 h. (◎) Ta_5B_6, (○) TaB, (⊖) Ta_3B_4, (●) TaB_2, (α) α-Al_2O_3.

This was because the crystals sank in the aluminum solution due to the difference in density between Ta_5B_6 (d_{calc}=13.808 g cm^{-3}) and aluminum (d^{20}= 2.6989 g cm^{-3}).[19] A SEM photograph of the Ta_5B_6 crystals obtained is shown in Fig. 3. The shape of the Ta_5B_6 crystals was mostly irregular, though there were trapezoidally shaped crystals, enclosed by two large {010} planes. Ta_5B_6 crystals had a grey color and metallic luster. The largest crystals prepared had maximum dimensions of about 0.12 mm×0.13 mm× 0.23 mm. Although the Ta_5B_6 crystals were not analysed chemically, the electron microprobe analysis showed that the aluminium concentration in the crystals is generally below the detection limit (<0.05% Al). Occasionally, however, higher values were registered. They were shown to originate in small closed pores containing aluminium or in minute fragments of Al_2O_3 (from the crucible) adhering to the crystal surface. Accordingly, the solid solubility of aluminium in Ta_5B_6 could be negligible. In addition to aluminium, only traces of iron and silicon were detected, which suggests that the crystals were very pure. The EPMA technique was also used to measure the distribution of tantalum and boron on the surface of the crystals obtained by varying the atomic ratio of the starting materials (B/Ta, Al/Ta), soaking temperature, and soaking time. From these examinations it can be concluded that the distribution of Ta and B in the crystal surface is homogeneous.

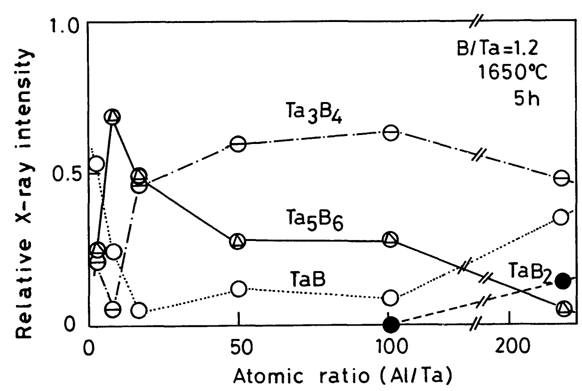

Fig. 2. Relative X-ray intensity of each phase in the products obtained from several starting materials with various aluminium contents. The atomic ratio B/Ta is fixed at 1.2. The starting materials are heated at 1650 °C for 5 h.

Characterization of the Single Crystals. The Ta_5B_6 crystals obtained were examined in Weissenberg and precession cameras. A crystal of the size, 0.08 mm× 0.09 mm×0.13 mm, was selected for single-crystal X-ray diffraction analysis. An oscillation photograph taken with the c axis as rotation axis displayed mirror symmetry perpendicular to the rotation axis. The Weissenberg (zero and first layer) and oscillation photographs showed that the symmetry is orthorhombic. The approximate cell dimensions were found to be a=3.17 Å, b=22.65 Å, and c=3.29 A. The observed systematic extinctions were:

$$hkl: h+k=2n$$

$$hk0: h+k=2n$$

$$h00: h=2n$$

$$0k0: k=2n$$

The presented extinction conditions and the symmetry observed lead to the possible space groups $Cmm2$, $Cm2m$, $C222$, and $Cmmm$.[20] A precession photograph of the a*-b* plane was taken using Cu K radiation and μ=25° (Fig. 4). The photograph shows that the crystal has no satellites or intergrown phases. The basic crystal data are collected in Table 2. The unit cell dimensions presented in the Table were obtained from Guinier–Hägg X-ray powder diffrac-

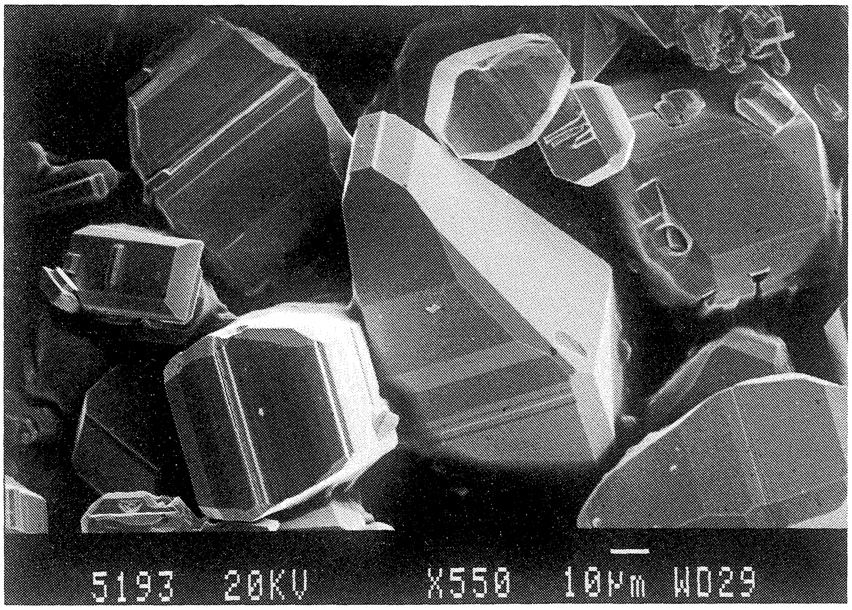

Fig. 3. Scanning electron microphotograph of Ta_5B_6 single crystals.

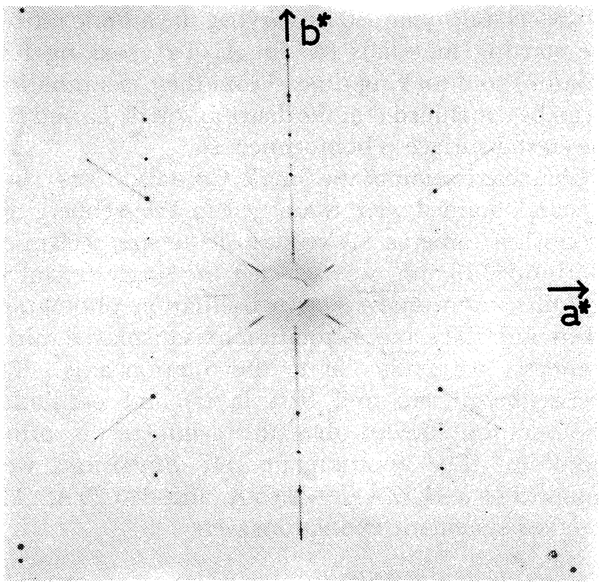

Fig. 4. A precession photograph of a Ta_5B_6 single crystal. c axis, zero-level, $\mu=25°$; Cu K, Ni filter.

Table 2. Crystal Data of Ta_5B_6 Single Crystal

Formula unit	Ta_5B_6
Crystal system	Orthorhombic
a/Å	3.1385(10)
b/Å	22.609(7)
c/Å	3.2865(8)
V/Å^3	233.20(12)
Space group	$Cmm2$ or $Cm2m$ or $C222$ or $Cmmm$
$d_{\text{X-ray}}$/g cm^{-3}	13.808(2)
Z	2

tion films.21)

The cell dimensions presented are in good agreement with those obtained by using a four-circle single crystal diffractometer. Guinier–Hägg X-ray diffraction intensities for Ta_5B_6 are presented in Table 3 together with observed and calculated interplanar spacings (d_{obs} and d_{calc}, respectively). The diffraction data for Ta_5B_6 are very similar to those reported for V_5B_6 (Space group $Ammm$, $a=3.058$ Å, $b=21.25$ Å, $c=2.974$ Å.22) A complete structure determination and refinement of Ta_5B_6 has been carried out and was reported at the 32nd IUPAC Congress.23) It showed that Ta_5B_6 is iso-structural with V_5B_6 as anticipated. A complete description of the structure refinement will be published shortly.24) The present study of the new compound, Ta_5B_6 is the first crystal growth study of a material crystallizing in the V_5B_6-type structure.

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References

1) B. Aronsson, T. Lundström, and S. Rundqvist, "Borides, Silicides and Phosphides," Methuen, London (1965).

2) T. Lundström, *J. Less-Common Metals*, **100**, 215 (1984).

3) R. Keiffer and G. Jangg, *Powder Metall. Int.*, **5**, 25 (1973).

4) V. N. Gurin, M. M. Korsukova, S. P. Nikanorov, I. A. Smirnov, N. N. Stepanov, and S. G. Shul'man, *J. Less-Common Metals*, **47**, 265 (1976).

5) I. Higashi, Y. Takahashi, and T. Atoda, *J. Crys. Growth*, **33**, 207 (1976).

Table 3. Powder X-Ray Diffraction Data of Ta$_5$B$_6$

h	k	l	d_{calc}	d_{obs}	I/I_1
0	2	0	11.305	11.301	4.0
0	4	0	5.652	5.655	10.3
0	6	0	3.768	3.771	16.9
0	0	1	3.287	3.288	7.0
0	2	1	3.156	3.158	57.7
1	1	0	3.109	3.111	1.3
1	3	0	2.897	2.899	2.9
0	4	1	2.841	2.842	20.2
0	8	0	2.826	2.826	5.5
1	5	0	2.578	2.579	79.3
0	6	1	2.477	2.477	6.7
0	10	0	2.261	2.261	64.4
1	1	1	2.258	—	—
1	7	0	2.251	2.252	6.7
1	3	1	2.173	2.173	100.0
0	8	1	2.143	2.143	81.2
1	5	1	2.029	2.030	11.9
1	9	0	1.961	1.961	6.9
0	12	0	1.884	1.884	6.4
0	10	1	1.863	—	—
1	7	1	1.857	1.857	26.1
1	11	0	1.720	1.720	25.6
1	9	1	1.684	1.684	12.3
0	0	2	1.643	1.643	49.3
0	12	1	1.635	1.638	4.9
0	2	2	1.626	1.626	1.5
0	14	0	1.615	1.615	4.1
0	4	2	1.578	1.577	17.1
2	0	0	1.569	1.567	5.4
2	2	0	1.554	1.554	1.4
1	11	1	1.522	1.522	5.1
1	13	0			
2	4	0	1.512	1.512	3.2
0	6	2	1.506	1.506	6.8
1	1	2	1.453	1.451	4.9
0	14	1	1.449	1.446	7.5
2	6	0			
1	3	2	1.429	—	—
0	8	2	1.421	1.421	3.0
2	0	1	1.416	1.416	5.3
0	16	0	1.413	1.413	13.0
2	2	1	1.405	1.405	35.7
1	5	2	1.386	1.386	71.3
1	13	1	1.381	1.381	85.0
2	4	1	1.373	1.374	12.2
2	8	0			
1	15	0	1.359	1.359	24.1
0	10	2	1.328	1.329	46.5
1	7	2			
2	6	1	1.326	—	—
0	16	1	1.298	1.299	1.7
2	10	0	1.289	1.289	29.8
2	8	1	1.266	1.266	55.3
1	9	2	1.260	1.261	8.8
0	18	0	1.256	1.256	1.6
1	15	1			
0	12	2	1.238	1.239	8.0
1	17	0	1.225	1.225	8.1
2	12	0	1.206	1.207	17.7
2	10	1	1.200	—	—
1	11	2	1.188	1.188	29.0
0	18	1	1.173	1.173	55.8
0	14	2	1.152	1.152	4.9
1	17	1	1.148	—	—
2	0	2	1.135	1.135	50.6
2	12	1	1.132	1.133	4.8
0	20	0	1.130	1.130	7.1
2	2	2			
2	14	0	1.125	1.125	4.0
1	13	2	1.116	1.116	9.0
2	4	2	1.113	1.113	2.9
1	19	0			

6) S. Okada, T. Atoda, I. Higashi, and Y. Takahashi, *J. Mater. Science,* **22**, 2993 (1987).

7) S. Okada, T. Atoda, and I. Higashi, *J. Solid State Chem.,* **68**, 61 (1987).

8) J. M. Leitnaker, M. G. Bowman, and P. W. Gilles, *J. Electrochem. Soc.,* **108**, 568 (1961).

9) G. V. Samsonov and I. M. Vinitskii, "Handbook of Refractory Compounds," IFI/Plenum, New York (1980), p. 5.

10) S. Okada, T. Atoda, and Y. Takahashi, *Nippon Kagaku Kaishi,* **1985**, 1535.

11) R. D. Deslattes and A. Henins, *Phys. Rev. Lett.,* **31**, 972 (1973).

12) K. E. Johanson, T. Palm, and P.-E. Werner, *J. Phys. E.,* **13**, 1289 (1980).

13) S. Okada, T. Atoda, I. Higashi, and Y. Takahashi, *J. Less-Common Metals,* **113**, 331 (1985).

14) J. A. Kohn and D. W. Eckart, *Anal. Chem.,* **32**, 296 (1960).

15) T. Ito, I. Higashi, and T. Sakurai, *J. Solid State Chem.,* **28**, 171 (1979).

16) I. Higashi, T. Sakurai, and T. Atoda, *J. Solid State Chem.,* **20**, 67 (1977).

17) I. Higashi, *J. Solid State Chem.,* **47**, 333 (1983).

18) H. Holleck, *Monatsh. Chem.,* **95**, 552 (1964).

19) Iwanami Shoten, "Rikagaku Jiten," 3rd ed., (1976), p. 55.

20) International Tables for Crystallography. Vol. A. ed by T. Halm and D. Reidel, Dordrecht, Holland (1983).

21) S. Andersson and B. Callmer, *J. Solid State Chem.,* **10**, 219 (1974).

22) K. E. Spear and P. W. Gilles, *High Temp. Sci.,* **1**, 86 (1969).

23) H. Bolmgren, T. Lundström, S. Okada, L.-E. Tergenius, and I. Higashi, Contribution to the 32nd IUPAC Congress, Augast 2—7, Stockholm, 1989.

24) H. Bolmgren, T. Lundström, S. Okada, L.-E. Tergenius, and I. Higashi, *J. Less-Common Metals,* in press.