

New compound in the system Sc–Cr–B

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Abstract

The isothermal section of the phase diagram of Sc–Cr–B system at 800°C is constructed using the data of X-ray analysis. CrB₂ dissolves up to 5 mol% of ScB₂, and ScB₂ dissolves up to about 20 mol% of CrB₂. A new boride Sc₂CrB₆ was found and its crystal structure was established by single-crystal X-ray diffraction: Y₂ReB₆ type, space group *Pbam*, *Z* = 4, *a* = 8.7909(4), *b* = 11.0541(6), *c* = 3.2996(1) Å, diffractometer Kappa CCD-Nonius, MoK α , *R*_F = 0.047, *R*_w = 0.064.

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1. Introduction

The large experimental and theoretical information on the interaction between components in ternary *Ln–Me–B* systems (where *Ln* is a rare-earth (RE), and *Me* is a transition metal) is saved for the present time [1–4]. Borides and boride-based materials find practical application due to their specific physical and chemical characteristics. Sc–*Me–B* systems are of a particular interest, as scandium metal, having the electronic structure of a *d*-element, shows also properties of a RE. Nevertheless, ternary systems containing scandium, transition metal and boron are insufficiently well investigated in the whole concentration regions. Phase diagrams are only constructed for Sc–{W, Re}–B [4] and Sc–{Fe, Co, Ni}–B [2] systems. In the Sc–W–B system, a wide solid solution exists on the basis of ScB₂, reaching <30 mol% of “WB₂”; no ternary borides are found. In Sc–Re–B ScB₂ dissolves up to 20 mol% of ReB₂ and there is a ternary compound Sc₂ReB₆ with the structure of the Y₂ReB₆ type [1]. In the Sc–{Fe, Co, Ni}–B systems there are no significant solid solutions on the basis of binary phases, and one, four and five ternary borides, respectively are revealed, in particular, compounds Sc*Me*B₄ with the structure of the YCrB₄ type [1] are formed.

This work is devoted to the Sc–Cr–B system, which has not been studied systematically before. A super-

conducting compound of composition Sc_{2.15}Cr_{0.55}B_{*x*} (*x* < 0.01), which is identified as a metastable phase, stabilized by boron, with structure of Ti₂Ni type (space group *Fd3m*, *a* = 12.33 Å) is mentioned in Ref. [5].

1.1. Binary systems

According to the phase diagram the Sc–B system, ScB₂ and ScB₁₂ compounds are formed congruently [2,6,7]. Six binary borides are shown in the phase diagram of the Cr–B system: the phases CrB and CrB₂ are formed congruently, Cr₂B, Cr₅B₃, Cr₃B₄ are formed by peritectic reactions, and CrB₄ is formed by a peritectoid reaction [2,8]. The compounds Cr₂B, CrB, Cr₃B₄ and CrB₂ have insignificant homogeneity ranges. The solubility of boron in chromium at 1570°C is 0.38–0.48 at% [2]. There are data about the existing of boron-rich phases ScB₁₉ (*P*4₁2₁2 or *P*4₃2₁, *a* = 10.2915(4), *c* = 1.42463(9) Å) [9], ScB_{~28} (*R*3̄*m*, *a* = 10.966, *c* = 24.088) [10], and CrB_{~41} (*R*3̄*m*, *a* = 10.9637, *c* = 23.8477) [11], which are not reflected at the corresponding phase diagrams. Also, it is not established finally if ScB_{~28} and CrB_{~41} are individual compounds or intercalating solid solutions of the transition metals into the β -rh boron structure. ScB₁₉ have been obtained by the borothermal reduction of Sc₂O₃ by amorphous boron, and, probably, the structure is stabilized by admixtures. As soon as we did not investigate a boron-rich region we did not examine a forming the boron-rich compounds.

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Table 1
Crystal characteristics of the binary compounds in Sc–B and Cr–B systems [1]

Boride	Space group	Structure type	Lattice parameters (Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
Cr ₂ B	<i>Fddd</i>	Mg ₂ Cu	14.837	7.338	4.255
Cr ₅ B ₃	<i>I4/mcm</i>	Cr ₅ B ₃	5.472		10.098
CrB	<i>Cmcm</i>	CrB	2.969	7.858	2.932
Cr ₃ B ₄	<i>Immm</i>	Ta ₃ B ₄	2.984	13.02	2.953
CrB ₂	<i>P6/mmm</i>	AlB ₂	2.969		3.066
CrB ₄	<i>Immm</i>	CrB ₄	4.7441	5.4773	2.8659
ScB ₂	<i>P6/mmm</i>	AlB ₂	3.146		3.517
ScB ₁₂	<i>Fm$\bar{3}m$</i>	UB ₁₂	7.402		

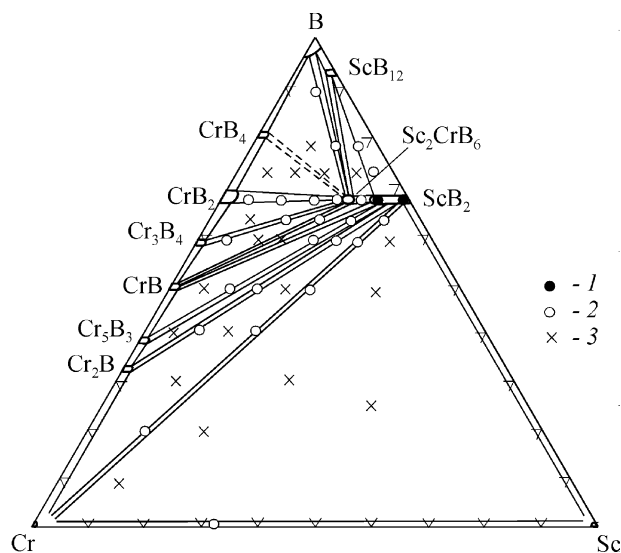


Fig. 1. Isothermal section of the phase diagram of the Sc–Cr–B system at 800°C: 1—one-phase samples, 2—two-phase samples, 3—three-phase samples.

The phase diagram of Sc–Cr system is of eutectic type with the limited solubility of the components; no binary compounds are found [12]. The solubility of Cr in α -Sc at 990°C is 0.4 at%, in β -Sc at 1090°C it is near 2 at%; solubility of Sc in Cr is smaller than 0.1 at% [13].

During the present investigation we have confirmed the existence of all binary compounds, which are presented in Table 1 and in Fig. 1, the only exception is CrB₄, which is formed in solid state. We did not investigate the boron-rich and scandium-rich regions of the system.

2. Experimental

2.1. Synthesis

For preparing samples we used powders of boron (with a purity of 99.4%), chromium (99.98%) and Sc ingots (99.93%). The chromium and boron powders

were first mixed together and then pressed into pellets. These were melted together with Sc pieces in an arc furnace using a non-consumable tungsten electrode in a Ti-gettered argon atmosphere. The total mass of each sample was about 2 g. In order to ensure homogeneity, the samples were turned over and remelted several times. All prepared samples were heat treated at 800°C in evacuated silica tubes for not less than 1000 h to reach equilibrium. Finally samples were quenched in cold water. The samples prepared were partially pulverized and analyzed using powder and single crystal X-ray analyses.

2.2. X-ray analysis

Phase compositions of samples (as-cast and/or annealed) were determined using powder diffractometers DRON-3M (CuK α , step-by-step mode of registration of reflections θ – 2θ by scanning, $2\theta = 20$ – 130° , $\Delta 2\theta = 0,05^\circ$, time of an exposition in each point 20 s), and CPS 120 INEL equipped with a position-sensitive detector covering 120° in 2θ (CuK α_1 , elemental silicon was taken to determine a cubic spline calibration function to describe the 2θ vs. channel number function). Lattice parameters were refined by a least-squares method using the CSD package [14].

Crystal structure determination of a new boride Sc₂CrB₆ was carried out on single-crystal using reflection intensities collected on an automated diffractometer Kappa Nonius with a CCD detector. Refinement of the atomic parameters was performed using the CSD package [14].

3. Results and discussion

3.1. Phase equilibria

We investigated 45 ternary samples in the Sc–Cr–B system. Mutual solubility of isotypic borides CrB₂ and ScB₂ (AlB₂ structure type) is observed: CrB₂ dissolves up to 5 mol% of ScB₂; its lattice parameters in a two-phase sample (CrB₂ + Sc₂CrB₆) are $a = 2.9802(7)$, $c = 3.113(1)$ Å slightly higher than the lattice parameters of CrB₂ (Table 1). ScB₂ dissolves about 20 mol% of CrB₂, therefore the ScB₂ lattice parameters decrease down to $a = 3.1205(6)$, $c = 3.461(3)$ Å in a sample, which contained both phases ScB₂ and Sc₂CrB₆. Thus the solid solution on the basis of ScB₂ diboride with the greater metal atomic size ($r_{Cr} = 1.29$ Å, $r_{Sc} = 1.606$ Å [16]) is larger. Other binary borides practically do not dissolve the third component.

The existence of a new ternary boride Sc₂CrB₆ is revealed and data on its crystal structure determination are listed below. Its refined lattice parameters have the following values: in equilibrium with CrB₂ $a = 8.723(3)$,

$b = 10.991(4)$, $c = 3.282(1)$ Å, and in equilibrium with ScB_2 $a = 8.7909(4)$, $b = 11.054(6)$, $c = 3.2996(1)$ Å. From the given data it is evident that the Sc_2CrB_6 boride is characterized by a small homogeneity range; its limits need further refinement.

In the investigated samples we did not observe a metastable $\text{Sc}_{2.15}\text{Cr}_{0.55}\text{B}_x$ ($x < 0.01$) compound with the structure of Ti_2Ni type [5]. Isothermal section of the phase diagram of the Sc–Cr–B system at 800°C , constructed on the basis of the X-ray phase analysis, is given in Fig. 1.

3.2. Crystal structure

The single crystal of the new ternary compound in the form of a long prism with the dimensions $0.05 \times 0.05 \times 0.277$ mm was extracted from a two-phase alloy of $\text{Sc}_5\text{Cr}_{35}\text{B}_{60}$ composition, that also contained CrB_2 . The crystal structure was studied using the intensity data collected on the automated diffractometer Kappa Nonius-CCD (Table 2). It is established, that the compound crystallizes with an orthorhombic symmetry;

Table 2
Crystal data and structure refinement for Sc_2CrB_6 boride

Space group	<i>Pbam</i> (No. 55)
Unit cell dimensions, Å	$a = 8.7909(4)$ $b = 11.0541(6)$ $c = 3.2996(1)$
<i>Z</i>	4
Cell volume, Å ³	320.64(4)
Calculated density, g/cm ³	4.2831(6)
Number of atoms in cell	36.0
Number of atom sites	9
Number of free parameters	56
Diffractometer	Kappa CCD-Nonius
Radiation and wavelength	MoK α , 0.71073
Mode of refinement	$F(hkl)$
Restrictions	$ F_{hkl} > 4.00\sigma(F)$
θ range and maximum $\sin \theta/\lambda$	2.91° – 37.04° ; 0.846
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 14$, $-3 \leq l \leq 5$
Reflections collected	2562
Reflections used ($F > 4\sigma(F)$)	1003 ($R_\sigma = 0.0376$)
Extinction formalism	Sheldrick-1 0.001343
Largest diff. peak and hole, e/Å ³	2.26; -1.35
Weighing scheme	Varying
Goodness-of-fit on F	1.200
Scale factor	0.820(1)
Final R indices ($(F > 4\sigma(F))$)	$R_F = 0.047$; $R_w = 0.064$
$R_\sigma = \sum \sigma F_o^2 / \sum F_o^2$	
$R_F = \sum F_o - F_c / \sum F_o$	
$R_w = 1 / \sum F_c^2 + 0.004 F_o^2$	
$\text{GoF} = (\sum w(F_o^2 - F_c^2)^2 / (n-p))^{1/2}$ with $w = 1 / (\sigma^2(F_o^2) + (a \times P)^2 + b \times P)$, n is the number of observed reflections, p is the number of parameters refined.	

Note: $T = 20(2)^\circ\text{C}$, graphite monochromator, the refinement method was full-matrix least-squares on F .

Table 3
Atomic and equivalent isotropic parameters (B_{eq}) for Sc_2CrB_6 (space group *Pbam*)

Atom	Position	x	y	z	B_{eq} (Å ²) ^a
Sc1	4 <i>g</i>	0.82230(8)	0.08623(6)	0	0.56(1)
Sc2	4 <i>g</i>	0.44456(8)	0.12870(6)	0	0.35(1)
Cr1	4 <i>g</i>	0.14313(7)	0.18254(6)	0	0.51(1)
B1	4 <i>h</i>	0.0541(5)	0.0651(4)	1/2	0.64(7)
B2	4 <i>h</i>	0.2555(5)	0.0800(4)	1/2	0.55(6)
B3	4 <i>h</i>	0.2973(5)	0.2378(4)	1/2	0.59(7)
B4	4 <i>h</i>	0.1295(5)	0.3197(4)	1/2	0.64(7)
B5	4 <i>h</i>	0.4805(5)	0.2875(4)	1/2	0.59(7)
B6	4 <i>h</i>	0.0973(5)	0.4737(4)	1/2	0.68(7)

$$^a B_{\text{eq}} = 1/3(B11a^2a^2 + \dots 2B23b^*c^*bc \cos \alpha).$$

Table 4
Anisotropic parameters (B , Å²) for Sc_2CrB_6 ^{a,b}

Atom	$B11$	$B22$	$B33$	$B12$
Sc1	0.57(2)	0.52(2)	0.57(2)	0.03(2)
Sc2	0.34(2)	0.34(2)	0.37(2)	-0.02(1)
Cr1	0.52(2)	0.50(2)	0.50(2)	-0.03(1)
B1	0.57(12)	0.66(12)	0.68(13)	-0.07(10)
B2	0.65(11)	0.49(11)	0.51(11)	0.06(9)
B3	0.71(12)	0.49(11)	0.59(12)	-0.03(9)
B4	0.72(12)	0.55(11)	0.63(13)	0.04(10)
B5	0.56(12)	0.56(11)	0.63(12)	0.03(9)
B6	0.75(12)	0.48(11)	0.80(13)	0.03(9)

$$^a T = \exp(-1/4(B11a^2h^2 + \dots 2B23b^*c^*kl)).$$

$$^b B13 = B23 = 0.$$

unit cell parameters, refined by a least-squares method are as follows: $a = 8.7909(4)$, $b = 11.0541(6)$, $c = 3.2996(1)$ Å; possible space groups are: *Pbam* and *Pba2*. Using the obtained data we suppose that the crystal structure of the compound belongs to the Y_2ReB_6 type (*Pbam* space group) [1]. This was confirmed by the structure investigation. The atomic parameters in the structure were defined by direct methods using the program SIR-97 [15]. Refinement of a model in space group *Pbam* was carried out using CSD software [14]. Crystal data of the structure are listed in Table 2. As a result of structure determination, the Sc_2CrB_6 formula of the new compound is confirmed, as well as its isotypism with the Y_2ReB_6 structure type ($Z = 4$, $\rho_{\text{calc}} = 4.2831(6)$ g/cm³). The final coordinates and equivalent thermal atomic parameters of Sc_2CrB_6 are given in Table 3; the anisotropic thermal factors are listed in Table 4.

The interatomic distances (δ) in the structure of Sc_2CrB_6 boride are given in Table 5. They are close to the sum of atomic radii of the components [16]. Shortening is observed only between atoms Sc2–Sc2 ($\delta = 3.007(1)$ Å; $2r_{\text{Sc}} = 3.212$ Å), Sc2–Cr ($\delta = 2.716(1)$, $2.721(1)$ Å; $r_{\text{Sc}} + r_{\text{Cr}} = 2.896$ Å) and Sc2–B4 ($\delta = 2.386$ Å; $r_{\text{Sc}} + r_{\text{B}} = 2.486$ Å). Obviously,

Table 5
Interatomic distances (δ) for Sc_2CrB_6 boride

Atoms	δ (Å)	Atoms	δ (Å)
Sc1–2 B3	2.560(3)	B1–B1	1.724(6)
Sc1–2 B2	2.563(3)	B1–B5	1.753(6)
Sc1–2 B5	2.570(3)	B1–B2	1.778(6)
Sc1–2 B4	2.584(3)	B1–2 Cr	2.241(3)
Sc1–2 B1	2.588(3)	B1–2 Sc1	2.588(3)
Sc1–2 B1	2.632(3)	B1–2 Sc1	2.632(3)
Sc1–2 B6	2.660(4)		
Sc1–Cr	2.986(1)	B2–B6	1.748(6)
Sc1–Cr	3.002(1)	B2–B1	1.778(6)
Sc1–Cr	3.015(1)	B2–B3	1.782(6)
Sc1–2 Sc1	3.2996(1)	B2–2 Cr	2.232(3)
Sc1–Sc2	3.330(1)	B2–2 Sc2	2.403(3)
Sc1–Sc2	3.339(1)	B2–2 Sc1	2.563(3)
Sc1–Sc2	3.354(1)		
Sc1–Sc1	3.660(1)	B3–B5	1.702(6)
		B3–B4	1.731(6)
Sc2–2 B4	2.386(3)	B3–B2	1.782(6)
Sc2–2 B2	2.403(3)	B3–2 Cr	2.221(3)
Sc2–2 B6	2.406(3)	B3–2 Sc2	2.419(3)
Sc2–2 B6	2.409(3)	B3–2 Sc1	2.560(3)
Sc2–2 B3	2.419(3)		
Sc2–2 B5	2.430(3)	B4–B6	1.726(6)
Sc2–Cr	2.716(1)	B4–B3	1.731(6)
Sc2–Cr	2.721(1)	B4–B5	1.767(6)
Sc2–Sc2	3.007(1)	B4–2 Cr	2.244(3)
Sc2–2 Sc2	3.2996(1)	B4–2 Sc2	2.386(3)
Sc2–Sc1	3.330(1)	B4–2 Sc1	2.584(3)
Sc2–Sc1	3.339(1)		
Sc2–Sc1	3.354(1)	B5–B3	1.702(6)
		B5–B1	1.753(6)
Cr–2B5	2.208(3)	B5–B4	1.767(6)
Cr–2B3	2.221(3)	B5–2Cr	2.208(3)
Cr–2B2	2.232(3)	B5–2Sc2	2.430(3)
Cr–2B1	2.241(3)	B5–2Sc1	2.570(3)
Cr–Sc2	2.716(1)		
Cr–Sc2	2.721(1)	B6–B4	1.726(6)
Cr–Sc1	2.986(1)	B6–B2	1.748(6)
Cr–Sc1	3.002(1)	B6–B6	1.806(6)
Cr–Sc1	3.015(1)	B6–2Sc2	2.406(3)
		B6–2Sc2	2.409(3)
		B6–2Sc1	2.660(4)

this is connected with the special (intermediate between L_n and Me) status of the L_n2 atom in the Y_2ReB_6 structure that is characterized by a smaller coordination number (CN=20) in comparison with the L_n1 atom (CN = 23).

3.3. Discussion

The character of the interaction between components in the Sc–Cr–B system in the range up to 66.7 at% of boron is similar to that in the Sc–W–B system investigated earlier [4], containing transition metal (W) of the same group as Cr. A solubility of the third component in the scandium diboride is observed in both systems, as well as the equilibria between this solid solution and transition metal or binary borides.

Formation of the ternary Sc_2CrB_6 boride and an absence of an isotypic compound in Sc–W–B reveal the differences in phase equilibria of those systems at higher boron contents.

The existence of borides with Y_2ReB_6 structure in Sc–Cr–B and Sc–Re–B systems [4], as well as YCrB_4 type in Sc–{Fe, Co, Ni}–B systems [2] that are characteristic for ternary $L_n\text{–}Me\text{–}B$ systems, are evidence of the tendency of Sc to behave like a lanthanoid metal. However, an important factor, which influences the formation of these structures, is the ratio of the sizes of L_n and Me atoms. The structure type YCrB_4 [1] is formed with metals, which considerably differ in their sizes ($r_{L_n}/r_{Me} > \sim 1.30$) and, accordingly, L_n atoms have CN=23, and CN of Me -atoms is 15. The structure of Y_2ReB_6 type [1] is related to YCrB_4 type, but it contains two sites for L_n atoms with CNs 23 and 20; the later CN=20 is observed in the AlB_2 structure, being characteristic for most transition metal borides. The presence of a position for L_n atom with a smaller coordination supposes also a smaller distinction of the L_n and Me atomic sizes. Indeed, in the series of $L_n\text{–}Cr\text{–}B$ (where L_n is Y, Ce–Sm, Gd–Lu) systems, in which the ratio r_{L_n}/r_{Cr} is within limits 1.411–1.33, there are borides with YCrB_4 type [2,4,17,18]. The decrease of the difference of the sizes of metal atoms in Sc–Cr–B system down to $r_{Sc}/r_{Cr} = 1.245$, results in the formation of the Y_2ReB_6 structure. For the same reason we suppose formation of isotypic ternary borides in other, yet not investigated Sc– $Me\text{–}B$ systems, where Me is V, Mn, Mo ($r_{L_n}/r_{Me} = 1.190\text{–}1.147$).

Borides with the structure of Y_2ReB_6 are also known in the systems $L_n\text{–}Al\text{–}B$, namely, Sc_2AlB_6 [19], Yb_2AlB_6 [20], Lu_2AlB_6 [21]. The Sc_2AlB_6 structure is characterized by the partially occupation of the Al position (90%). One of the reasons of that may be a decreasing of the ratio $r_{Sc}/r_{Al} = 1.147$ in comparison with other borides $L_n2\text{AlB}_6$. For the Sc_2CrB_6 the ratio r_{Sc}/r_{Cr} increases (1.245), and the corresponding position is fully occupied.

4. Conclusions

The investigation of the isothermal section at 800°C of Sc–Cr–B system shows the tendency of Sc to behave like a heavy lanthanoid metal in ternary $L_n\text{–}Me\text{–}B$ systems. Therefore, the formation of ternary compounds ScMeB_4 with the YCrB_4 structure type or Sc_2MeB_6 with the Y_2ReB_6 type are supposed in the other systems Sc– $Me\text{–}B$ where Me is transition metals of V–VII groups.

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References

- [1] Yu.B. Kuz'ma, *Crystal Chemistry of Borides*, Vyscha Shkola, Lvov, 1983 (in Russian).
- [2] Yu.B. Kuz'ma, N.F. Chaban, *Binary and Ternary Systems, Containing Boron*, Metallurgiya, Moscow, 1990 (in Russian).
- [3] S.I. Mykhalenko, N.F. Chaban, Yu.B. Kuz'ma, *Poroshk. Metall.* 1/2 (1998) 116–125 (in Russian).
- [4] S.I. Mykhalenko, L.V. Zavalij, Yu.B. Kuz'ma, L.I. Bojko, *Poroshk. Metall.* 8 (1991) 67–70 (in Russian).
- [5] P. Rogl, in: K.A. Gscheidner, L.R. Eyring (Eds.), *Handbook on the Physics and Chemistry of the Rare Earths*, Vol. 6, North-Holland, Amsterdam, 1984, p. 335.
- [6] T.B. Massalsky, *Binary Alloy Phase Diagrams*, Vol. 1, 2nd Edition, Materials Information Society, Metals Park, OH, 1990.
- [7] K.E. Spear, P.K. Liao, *Bull. Alloy Phase Diagram* 11 (1990) 321–324.
- [8] P.K. Liao, K.E. Spear, *Bull. Alloy Phase Diagram* 7 (1986) 232–237.
- [9] T. Tanaka, S. Okada, V.N. Gurin, *J. Alloys Compd.* 267 (1998) 211–214.
- [10] B. Callmer, *J. Solid State Chem.* 23 (1978) 378–391.
- [11] S. Andersson, T. Lundström, *J. Solid State Chem.* 2 (1970) 603–611.
- [12] E.I. Gladyshevsky, O.I. Bodak, *Crystal Chemistry of Rare Earth Intermetallides*, Vyscha Shkola, Lvov, 1982 (in Russian).
- [13] N.P. Lyakishev (Ed.), *Phase Diagrams of Binary Metal Systems*, Mashinostroenie, Moscow, 1997 (in Russian).
- [14] L.G. Akselrud, Yu.N. Gryn, P.Yu. Zavalij, V.K. Pecharsky, V.S. Fundamensky, in: *Proceedings of the 12th European Crystallographic Meeting*, Moscow, August 20–28, 1989, *Kristallograph.* 2 (Suppl.) (1989) 155.
- [15] G. Cascorano, A. Altomare, C. Giacobozzo, A. Guagliardi, A.G.C. Moliterni, D. Siliqi, M. Burla, G. Polidori, M. Camalli, *Acta Cryst. A* 52 (1996) 79.
- [16] N. Wiberg, in: A.F. Holleman, E. Wiberg (Eds.), *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin, New York, 1995.
- [17] N.F. Chaban, N.P. Kurylo, Yu.B. Kuz'ma, *Poroshk. Metall.* 9/10 (1997) 49–51 (in Russian).
- [18] N.F. Chaban, Yu.B. Kuz'ma, *Poroshk. Metall.* 9/10 (1999) 37–41 (in Russian).
- [19] S. Okada, T. Tanaka, A. Leithe-Jasper, Yu. Michiue, V.N. Gurin, *J. Solid State Chem.* 154 (2000) 49–53.
- [20] S.I. Mikhalenko, Yu.B. Kuz'ma, M.M. Korsukova, V.N. Gurin, *Izv. Akad. Nauk SSSR Neorg. Mater.* 16 (1980) 1941–1944.
- [21] S. Okada, Y. Yu, T. Lundstroem, K. Kudou, T. Tanaka, *Jpn. J. Appl. Phys.* 35 (1996) 4718–4722.