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Phase Relations in the Nb–Sb–Si and Nb–Sb–P Systems

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Abstract—Phase relations in the systems Nb–Sb–Si (0–70 mol % Sb) and Nb–Sb–P (0–50 mol % P) have been studied by X-ray diffraction, and the 1070-K isothermal sections of their phase diagrams have been constructed. The existence of the compound NbSbSi (PbFCl structure) has been confirmed. Both systems contain a few substitutional solid-solution series: $Nb_3(Sb,Si)$ and $Nb_3(Sb,P)$ (Cr_3Si structure, limiting compositions $Nb_3Sb_{0.55}Si_{0.45}$ and $Nb_3Sb_{0.8}P_{0.2}$), $Nb_3(Si,Sb)$ and $Nb_3(P,Sb)$ (Ti_3P structure, limiting compositions $Nb_3Si_{0.6}Sb_{0.4}$ and $Nb_3P_{0.5}Sb_{0.5}$), Nb(P,Sb) (NbAs structure, limiting composition $NbP_{0.8}Sb_{0.2}$), and $Nb(Si,Sb)_2$ ($CrSi_2$ structure, limiting composition $NbSi_{1.65}Sb_{0.35}$). Phase equilibria in related systems are analyzed.

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INTRODUCTION

The Nb–Sb–Si system is known to contain a compound of composition NbSbSi with the PbClF structure (sp. gr. *P4/nmm*, $a = 3.639$, $c = 8.179$ Å) [1]. Transition metal–antimony–phosphorus systems have been studied little, except for those containing titanium and zirconium [2]. Phase-diagram data for the Nb–Sb–P system are not available in the literature. The purpose of this work was to study the phase relations in the Nb–Sb–Si and Nb–Sb–P systems.

EXPERIMENTAL

The Nb–Sb–Si and Nb–Sb–P systems were studied using ≃1-g samples prepared from 99.7+%-pure metal and red phosphorus powders. After pressing at 4.9 MPa in a steel die, the green compacts were sintered at 1070 K for 150 h in evacuated silica ampules. Next, the samples were ground, re-pressed, and sintered in ampules at 1070 K for an additional 200 h. The sintered Nb–Sb–P samples were studied with no further processing. Most of the Nb–Sb–Si samples were arc-melted in an argon atmosphere and then annealed at 1070 K (or another temperature) for 800 h in evacuated silica tubes, followed by quenching in cold water without breaking the vacuum. In our studies, we used only those samples which differed in weight from the starting mixture by no more than 2%. The phase composition of the samples was determined by X-ray diffraction (XRD) with DRON-2.0 (FeK_α radiation) and DRON-3M (CuK_α) diffractometers (scan step $\Delta(2\theta) = 0.05°$; counting time per data point, 10–20 s). Lattice parameters were refined by least squares fitting using CSD software [3].

RESULTS AND DISCUSSION

The phase relations in the Nb–Sb–Si and Nb–Sb–P systems were studied at 1070 K in the regions 0–70 mol % Sb and 0–50 mol % P, respectively.

First, the compounds known in the constituent binary systems were shown to exist at 1070 K. The Nb–Si system is known to contain the compounds Nb_3Si (Ti_3P structure), α-Nb_5Si_3 (W_5Si_3), and $NbSi_2$ ($CrSi_2$) [2]. The compounds existing in the Nb–Sb system are Nb_3Sb (Cr_3Si), Nb_5Sb_4 (Ti_5Te_4), and $NbSb_2$ ($OsGe_2$) [2, 4]. The Sb–Si system contains no solid solutions. The eutectic is located at 99.7 mol % Sb, with a melting point of 903 K [5]. In the Nb–P system, we obtained all the phosphides, except those with a mole fraction of P above 0.50, which form at elevated pressures: Nb_3P (Ti_3P), Nb_2P (Nb_2P), Nb_7P_4 (Nb_7P_4), Nb_5P_3 (Nb_5P_3), Nb_8P_5 (Nb_8P_5), and NbP (NbAs) [2]. The crystal data for all the phases existing in the Nb–Sb–Si and Nb–Sb–P systems are summarized in Tables 1 and 2.

Nb–Sb–Si system. The Nb–Sb–Si samples prepared as described above contained no NbSbSi. In view of this, a number of samples of this composition were sintered at 770, 870, and 1070 K and then annealed at the same temperature for 600 h. The phase compositions of those samples are listed in Table 3.

It can be seen from Table 3 that, after the syntheses at 770 and 870 K, the only phase detected by XRD in the NbSbSi samples was Si; the other phases were X-ray amorphous. Only at 1070 K was the compound NbSbSi obtained, with impurities of other phases.

Since Nb_3Si in two- and three-phase Nb–Sb–Si samples had slightly increased lattice parameters and Nb_3Sb had reduced lattice parameters, we studied phase relations along the 75 mol % Nb join in order to ascertain the formation of substitutional solid solutions. From the composition dependences of lattice parameters for the

Table 1. Crystal data for phases of the Nb–Sb–Si system

Phase	Structure type	Sp. gr.	*a*, Å	*b*, Å	*c*, Å	Source
Nb	W	$Im\bar{3}m$	3.3014			[7]
			3.3161 (4)			This work
Si	C (diamond)	$Fd\bar{3}m$	5.42996			[7]
			5.4266 (8)			This work
Sb	α-As	$R\bar{3}m$	4.3084		11.247	[7]
			4.3051 (5)		11.281 (3)	This work
Nb_3Sb	Cr_3Si	$Pm\bar{3}m$	5.2643			[2]
			5.270 (2)			This work
$Nb_3Sb_{0.55}Si_{0.45}$*			5.207(2)			This work
Nb_5Sb_4	Ti_5Te_4	$I4/m$	10.314		3.5566	[2]
			10.436 (3)		3.542 (2)	This work
$NbSb_2$	$OsGe_2$	$C2/m$	10.218	3.630 (β = 120.03°)	8.315	[2]
			0.230 (2)	3.6310 (7) (β = 120.029(8)°)	8.3289 (6)	This work
Nb_3Si	Ti_3P	$P4_2/n$	10.224		5.189	[2]
			10.228 (8)		5.192 (4)	This work
$Nb_3Si_{0.6}Sb^{*}_{0.4}$			10.224 (3)		5.298 (3)	This work
Nb_5Si_3	W_5Si_3	$I4/mcm$	10.224		5.189	[2]
			10.076 (4)		5.096 (3)	This work
$\simeq Nb_5Si_{2.6}Sb^{*}_{0.4}$			10.076 (4)		5.096 (3)	This work
$NbSi_2$	$CrSi_2$	$P6_222$	4.819		6.592	[2]
			4.802 (4)		6.592 (3)	
$NbSi_{1.65}Sb^{*}_{0.35}$			4.790 (5)		6.490 (4)	This work
NbSbSi	PbFCl	$P4/nmm$	3.6388		8.179	[1]
			3.572 (2)		8.310 (4)	This work

* Limit of the solid solution.

$Nb_3(Sb,Si)$ and $Nb_3(Si,Sb)$ solid solutions (Fig. 1), we determined their limits. The lattice parameters of the limiting solid solutions are indicated in Table 1.

$NbSi_2$ dissolves up to 10 mol % Sb, as follows from the composition dependences of lattice parameters for this solid solution (Fig. 2). Its lattice parameters decrease with increasing antimony content. Similar results were obtained earlier for solid solutions between a transition metal and antimony, e.g., $Ni_{1-x}Sb_x$ and $V_{1-x}Sb_x$ [6].

The Nb_5Si_3-based solid solution (W_5Si_3 structure) extends to the composition $\simeq Nb_5Si_{2.6}Sb_{0.4}$.

Our results were used to identify phase equilibria in the region 0–70 mol % Sb and to construct the 1070-K isothermal section of the Nb–Sb–Si phase diagram (Fig. 3).

Nb–Sb–P system. Phase relations in the Nb–Sb–P system were studied in the region 0–50 mol % P at 1070 K, using samples prepared by double sintering.

The 75 mol % Nb join contains terminal substitutional solid solutions. The composition dependences of their lattice parameters (Fig. 4) demonstrate that the extent of the Nb_3P-based solid solution exceeds that of the Nb_3Sb-based solid solution.

The Sb solubility in NbP reaches 10 mol % (Fig. 5). The other binary compounds dissolve insignificant amounts of the third component. The lattice parameters of the phases existing in the Nb–Sb–P system are listed in Table 2.

The 1070-K phase equilibria in the composition region studied are illustrated in Fig. 6.

The Nb–Sb–Si and Nb–Sb–P systems differ somewhat in phase relations. The Nb–Sb–Si system contains the ternary compound NbSbSi (PbFCl structure), whereas in the Nb–Sb–P system no compounds were identified. The likely reason for this is that antimony and silicon differ in properties more significantly than antimony and phosphorus. At the same time, both systems contain Nb_3E-based (E = *p*-element) solid solutions with *p*-element substitutions. In the case of Sb and Si substitutions, the solubility is slightly higher in comparison with Sb and P, because Sb and Si differ less in atomic radius and electronegativity ($r_{Sb} = 0.141$ nm,

Table 2. Crystal data for phases of the Nb–Sb–P system

Phase	Structure type	Sp. gr.	*a*, Å	*b*, Å	*c*, Å	Source
Nb_3S	Cr_3Si	$Pm\bar{3}m$	5.2643			[2]
			5.270(2)			This work
$Nb_3Sb_{0.8}P_{0.2}$*			5.205(5)			This work
Nb_5Sb_4	Ti_5Te_4	$I4/m$	10.314		3.5566	[2]
			10.436(3)		3.542(2)	This work
$NbSb_2$	$OsGe_2$	$C2/m$	10.218	3.630	8.315	[2]
				(β = 120.03°)		
			10.231(1)	3.631(1)	8.329(4)	[2]
				(β =120.03(2)°)		
Nb_3P	Ti_3P	$P4_2/n$	10.128		5.089	[2]
			10.125(8)		5.094(6)	This work
$Nb_3P_{0.5}Sb_{0.5}$*			10.137(5)		5.126(5)	This work
Nb_2P	Nb_2P	*Pmma*	18.079	3.425	13.858	[2]
			18.07(1)	3.419(2)	13.896(8)	This work
Nb_7P_4	Nb_7P_4	$C2/m$	14.9503	3.4398	13.8478	[2]
				(β = 104.74°)		
			14.917(5)	3.431(4)	13.838(6)	This work
				(β = 104.54(9)°)		
Nb_5P_3	Nb_5P_3	*Pnma*	25.384	3.433	11.483	[2]
			25.441(1)	3.440(4)	11.469(9)	[2]
Nb_8P_5	Nb_8P_5	*Pbam*	26.1998	9.4652	3.4641	[2]
			26.087(9)	9.425(3)	3.424(2)	[2]
NbP	NbAs	$I4_1md$	3.3324		11.3705	[2]
			3.338(1)		11.3728(6)	This work
$NbP_{0.8}Sb_{0.2}$*			3.342(1)		11.391(6)	This work

* Limit of the solid solution.

Table 3. Phase composition of NbSbSi-containing samples prepared by sintering at different temperatures

Annealing temperature, K	Sample composition	Phase composition	*a*, Å	*c*, Å
770	NbSbSi	Si	5.433(1)	
870	NbSbSi	Si	5.440(2)	
1070	NbSbSi	NbSbSi	3.572(2)	8.310(4)
		$NbSi_2$ (tr)	4.802(1)	6.577(2)
		Si (tr)	5.4360(7)	
	$Nb_{40}Sb_{25}Si_{35}$	NbSbSi	3.576(3)	8.313(7)
		$Nb_5Si_3(W_5Si_3)$	9.939(3)	5.146(4)
		$NbSi_2$	4.799(2)	6.573(2)

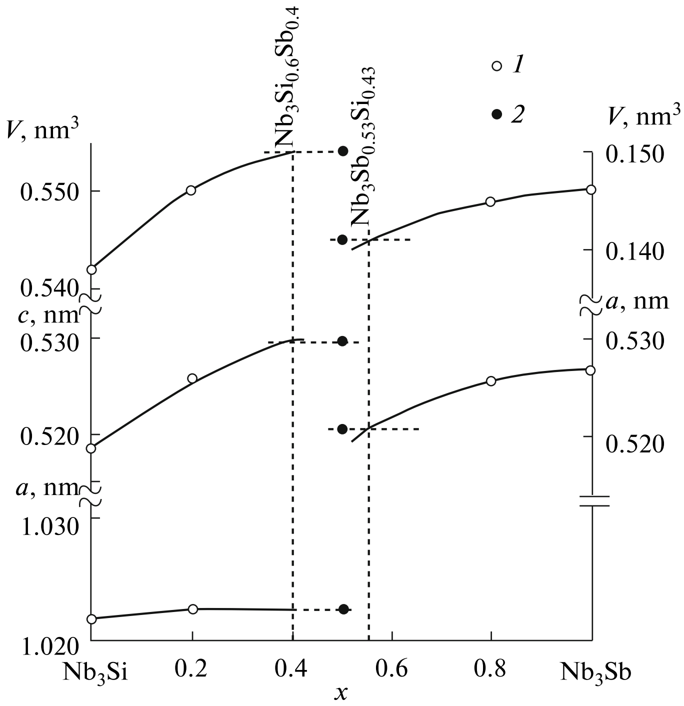

Fig. 1. Composition dependences of lattice parameters for the $Nb_3Si_{1-x}Sb_x$ and $Nb_3Sb_{1-x}Si_x$ substitutional solid solutions: (*1*) single- and (*2*) two-phase samples.

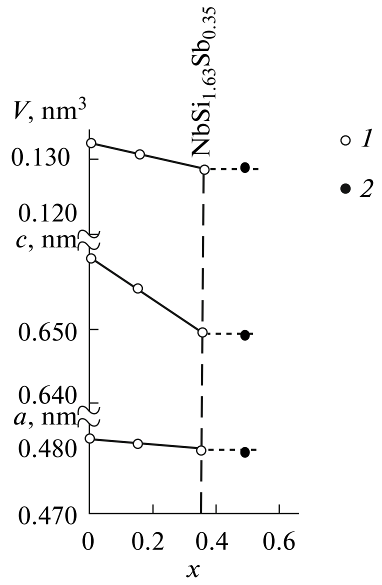

Fig. 2. Composition dependences of lattice parameters for the $NbSi_{2-x}Sb_x$ substitutional solid solution: (*1*) single- and (*2*) two-phase samples.

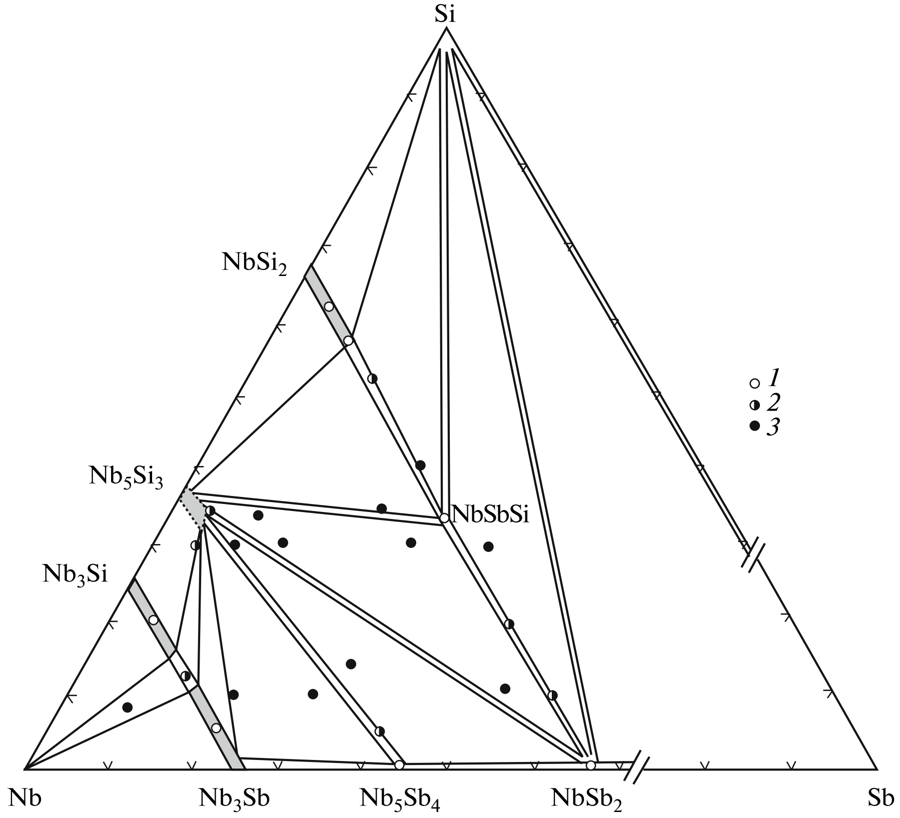

Fig. 3. Phase equilibrium diagram of the Nb–Sb–Si system at 1070 K: (*1*) single-, (*2*) two-, and (*3*) three-phase samples.

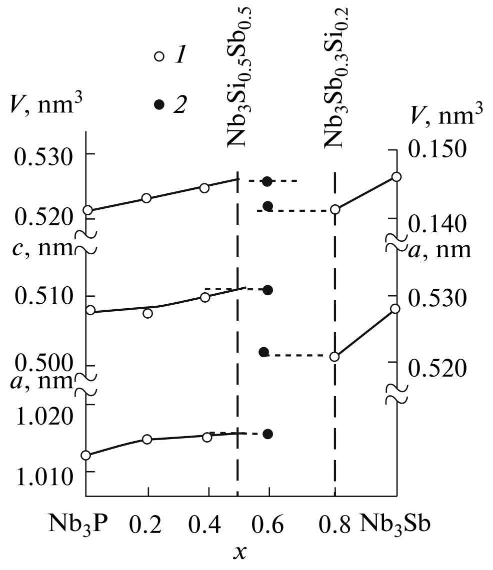

Fig. 4. Composition dependences of lattice parameters for the $Nb_3P_{1-x}Sb_x$ and $Nb_3Sb_{1-x}P_x$ substitutional solid solutions: (*1*) single- and (*2*) two-phase samples.

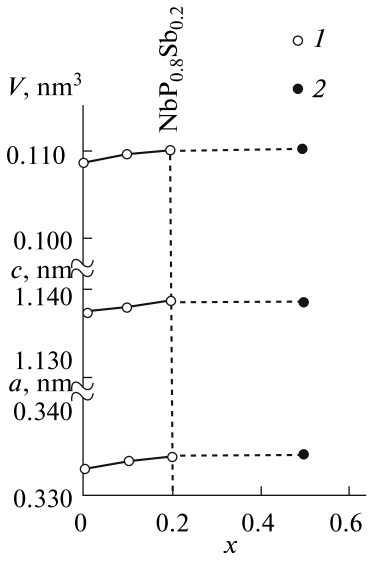

Fig. 5. Composition dependences of lattice parameters for the $NbP_{1-x}Sb_x$ substitutional solid solution: (*1*) single- and (*2*) two-phase samples.

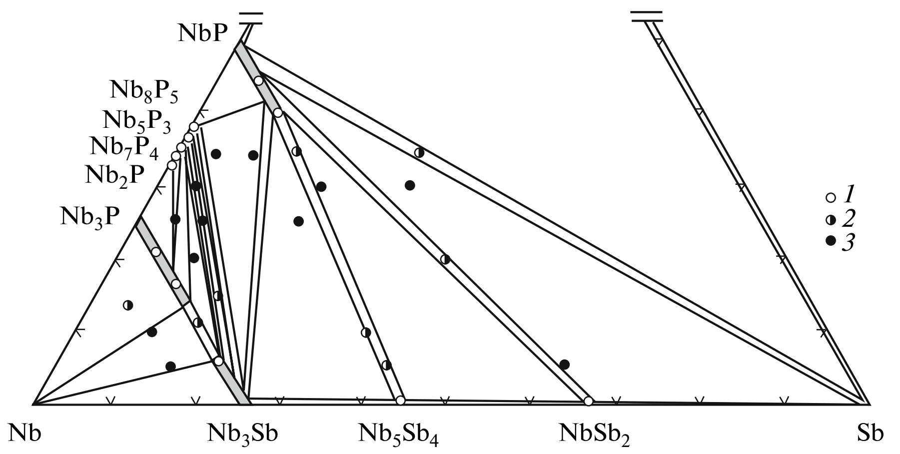

Fig. 6. Phase equilibrium diagram of the Nb–Sb–P system at 1070 K in the region 0–50 mol % P: (*1*) single-, (*2*) two-, and (*3*) three-phase samples.

$r_{Si} = 0.117$ nm, $r_P = 0.110$ nm, $\chi_{Sb} = 2.04$, $\chi_{Si} = 1.9$, $\chi_P = 2.1$ [7, 8]).

The Nb–Sb–Si system is similar in phase relations to other M–Sb–Si systems, in particular to the Zr–Sb–Si system, which contains two compounds, Zr_5SiSb_3 (Ti_5Ga_4) and $ZrSi_{0.7}Sb_{1.3}$ (PbFCl) [1, 2, 9], and to the V–Sb–Si system [2, 10], in which P substitutes for Si in most of the binary compounds to form substitutional solid solutions.

The phase relations in the Nb–Sb–P system are simpler in comparison with the systems Ti–Sb–P and, especially, Zr–Sb–P, which contain the ternary compounds Ti_2SbP, Zr_2SbP, Hf_2SbP (Cr_2AlC or Ti_2SC (ordered TiAs type) structure) [2, 11], and Zr_5Sb_3P (Ti_5Ge_4). The Nb–Sb–P system contains no compound with the Nb_2SbP stoichiometry, in contrast to the titanium, zirconium, and hafnium systems, probably because the binary phosphides TiP, ZrP, and HfP have a hexagonal TiAs-type structure, whereas NbP has a tetragonal NbAs-type structure. The formation of two compounds in the zirconium system is associated with the larger atomic radius and lower electronegativity of zirconium in comparison with the other transition metals ($r_{Zr} = 0.1602$ nm, $r_{Nb} =$

0.1468 nm, $\chi_{Zr} = 1.4$, $\chi_{Nb} = 1.6$ [7, 8]). Thus, the phase relations in the M–Sb–P systems are considerably influenced by the nature of the transition metal M.

The phase relations in the Nb–Sb–P and Nb–Sb–Si systems differ markedly from those in the Nb–Si–P system [12, 13], which contains the ternary compound Nb_5Si_3P (Mn_5Si_3-related structure), with no analogue in the Nb–Si–Sb system, even though antimony and phosphorus belong to the same periodic group.

CONCLUSIONS

Phase relations in the Nb–Sb–Si system were studied at 1070 K in the composition region 0–70 mol % Sb, and the existence of the NbSbSi compound (PbFCl structure) was confirmed. The system contains the following substitutional solid solutions: $Nb_3(Sb,Si)$ (Cr_3Si structure, limiting composition $Nb_3Sb_{0.55}Si_{0.45}$), $Nb_3(Si,Sb)$ (Ti_3P, $Nb_3Si_{0.6}Sb_{0.4}$), and $Nb(Si,Sb)_2$ ($CrSi_2$, $NbSi_{1.65}Sb_{0.35}$).

Phase relations in the Nb–Sb–P system were studied at 1070 K in the composition region 0–50 mol % Sb. The following substitutional solid solutions were identified: $Nb_3(Sb,P)$ (Cr_3Si structure, limiting composition $Nb_3Sb_{0.8}P_{0.2}$), $Nb_3(P,Sb)$ (Ti_3P, $Nb_3P_{0.5}Sb_{0.5}$), and Nb(P,Sb) (NbAs, $NbP_{0.8}Sb_{0.2}$).

REFERENCES

1. Johnson, V. and Jeitschko, W., PbFCl-Type Pnictides of Niobium with Silicon or Germanium, *J. Solid State Chem.*, 1973, vol. 6, pp. 306–309.
2. Villars, P., *Pearson's Handbook Desk Edition: Crystallographic Data for Intermetallic Phases*, Metals Park: American Society for Metals, 1997.
3. Aksel'rud, L.G., Grin, Yu.N., Pecharsky, V.K., and Zavalij, P.Yu., CSD 97—Universal Program Package for Single Crystal and Powder Data Treatment, Version no. 7, 1997.
4. Lomnytska, Ya.F. and Kuz'ma, Yu.B., The Nb–Sb System, *J. Alloys Compd.*, 2006, vol. 413, pp. 114–117.
5. Okamoto, H., *Desk Handbook: Phase Diagrams for Binary Alloys*, Metals Park: American Society for Metals, 2000.
6. Lomnytska, Ya.F. and Pavliv, O.P., Phase Equilibria in the V–Ni–Sb System, *Neorg. Mater.*, 2007, vol. 43, no. 6, pp. 692–697 [*Inorg. Mater.* (Engl. Transl.), vol. 43, no. 6, pp. 608–613].
7. Emsley, J., *Die Elemente*, Berlin: Walter de Gruyter, 1994.
8. *Holleman–Wiberg Lehrbuch der anorganischen Chemie*, Berlin: Walter de Gruyter, 1995, pp. 1837–1840.
9. Garcia, E. and Corbett, J.D., Chemistry in the Polar Intermetallic Host Zr_5Sb_3. Fifteen Interstitial Compounds, *Inorg. Chem.*, 1990, vol. 29, pp. 3274–3282.
10. Lomnytska, Ya.F., 1070-K Section of the V–Si–Sb Phase Diagram, *Poroshk. Metall.* (Kiev), 2007, vol. 46, nos. 9–10, pp. 60–65.
11. Boller, H., Gemischte Pnictide mit geordnetem TiP-Type (Ti_2SC-Typ), *Monatsh. Chem.*, 1973, vol. 104, pp. 166–171.
12. Lomnytska, Ya.F. and Koval', L.V., Phase Relations in the Nb–Si–P and Ta–Si–P Systems, *Zh. Neorg. Khim.*, 1996, vol. 41, no. 11, pp. 1923–1927.
13. Lomnytska, Ya.F., Oryshchyn, S.V., Kuz'ma, Yu.B., and Guerin, R., Crystal Structure of $Nb_5Si_{3-x}P_{0.5+x}$ (x = 0–0.5), *Neorg. Mater.*, 2005, vol. 41, no. 10, pp. 1212–1217 [*Inorg. Mater.* (Engl. Transl.), vol. 41, no. 10, pp. 1067–1072].