Chemistry of Metals and Alloys

Chem. Met. Alloys 6 (2013) 75-80
Ivan Franko National University of Lviv
www.chemetal-journal.org

The ternary system Hf–Ga–Sb at 600ºC

Iryna TOKAYCHUK[1]*, Yaroslav TOKAYCHUK[1], Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
* *Corresponding author. Tel.: +380-32-2394506; e-mail: i.tokaychuk@gmail.com*
Present address: Scientific Consulting Company "Structure-Properties", Sakharova St. 33, 79026 Lviv, Ukraine

Received May 28, 2013; accepted June 19, 2013; available on-line November 4, 2013

The isothermal section at 600ºC of the phase diagram of the ternary system Hf–Ga–Sb was constructed in the whole concentration range, using X-ray powder diffraction. Limited solid solutions based on the binary compounds HfGa (17 at.% Sb), Hf_5Ga_3 (11 at.% Sb), and Hf_5Sb_3 (3 at.% Ga) were observed. Four ternary compounds form at 600ºC: Hf_2GaSb_3 (structure type Zr_2CuSb_3, Pearson symbol *tP*6, space group *P*-4*m*2, *a* = 3.89841(8), *c* = 8.62650(19) Å), $HfGa_{0.1}Sb_{0.9}$ (FeSi, *cP*8, $P2_13$, *a* = 5.5752(3) Å), Hf_5GaSb_3 (Hf_5CuSn_3, *hP*18, $P6_3/mcm$, *a* = 8.4747(5), *c* = 5.7190(5) Å), and $Hf_5Ga_{1.84\text{-}0.72}Sb_{1.16\text{-}2.28}$ (Nb_5SiSn_2, *tI*32, *I*4/*mcm*, *a* = 10.84972(15), *c* = 5.50154(8) Å for composition $Hf_5Ga_{1.51(2)}Sb_{1.49(2)}$). The ternary phases, except $HfGa_{0.1}Sb_{0.9}$, are characterized by full or partial ordering of the Ga and Sb atoms.

Hafnium / Gallium / Antimony / X-ray powder diffraction / Phase diagram / Crystal structure / Solid solution

Introduction

The ternary systems {Ti,Zr,Hf}–Ga–Sb have not yet been systematically investigated. In the systems with Ti and Zr, the existence of Mn_5Si_3-type (Pearson symbol *hP*16, space group $P6_3/mcm$) solid solutions and of the W_5Si_3/Nb_5SiSn_2-type (Pearson symbol *tI*32, space group *I*4/*mcm*) ternary compounds Ti_5GaSb_2 and $Zr_5Ga_{0.8}Sb_{2.2}$ has been reported [1-3].

Short time ago the isothermal section at 600ºC of the phase diagram of the ternary system Hf–Ga–Sn was constructed in the whole concentration range, and the crystal structures of the ternary phases formed in it, were reported [4-6]. Solid solutions with up to 17 at.% Sn based on the binary gallides HfGa (structure type ThIn, Pearson symbol *oP*24, space group *Pbcm*) and Hf_5Ga_3 (structure type Mn_5Si_3) were observed. The structure of the limiting composition of the solid solution $HfGa_{1-x}Sn_x$ ($x \approx 0.33$) is characterized by an ordered distribution of Ga and Sn atoms, representing an own structure type, Hf_3Ga_2Sn (Pearson symbol *oP*24, space group *Pbcm*), which is the first ternary ordering derivative of the structure type ThIn. Based on the binary stannide Hf_5Sn_3 (structure type Mn_5Si_3), an interstitial solid solution containing up to 11.1 at.% Ga is formed. The structure of the limiting composition of the solid solution $Hf_5Ga_xSn_3$ ($x = 1$) is also characterized by an ordered distribution of Ga and Sn atoms, and belongs to the structure type Hf_5CuSn_3 (Pearson symbol *hP*18, space group $P6_3/mcm$), which is a ternary ordered derivative of the structure type Ti_5Ga_4 (filled up Mn_5Si_3 type). A ternary compound, $Hf_5Ga_{1.24\text{-}0.52}Sn_{1.76\text{-}2.48}$, with a homogeneity range of 9 at.% Ga (Sn), was found in the Hf–Ga–Sn system at 600ºC. Its crystal structure belongs to the structure type Nb_5SiSn_2, which is an ordered ternary variant of the W_5Si_3 type.

Several compounds have been identified in the binary systems that delimit the ternary system Hf–Ga–Sb [7]. The phase diagrams of the systems Hf–Ga and Ga–Sb have been constructed in the whole concentration range [8]. In the system Hf–Sb the existence of five binary phases has been reported. The equiatomic hafnium antimonide, HfSb, exists in two polymorphic forms. The presumed high-temperature modification of $HfSb_2$ was later shown to be off-stoichiometric and crystallize with a new structure type [9].

In this work we present the results of an experimental investigation of the phase equilibria and crystal structures of the phases observed in the ternary system Hf–Ga–Sb at 600ºC. We have recently reported the crystal structures of the ternary phases Hf_2GaSb_3 [10] and $Hf_5Ga_{1.51}Sb_{1.49}$ [11] and preliminary results of the determination of the crystal structure of Hf_5GaSb_3 [12].

Experimental

11 two-component and 96 three-component alloys were synthesized from high-purity metals

(Hf ≥ 99.9 wt.%, Ga ≥ 99.99 wt.%, Sb ≥ 99.97 wt.%) by arc melting, using a tungsten electrode and a water-cooled copper hearth under a Ti-gettered argon atmosphere. To achieve homogeneity, the samples were melted twice. After the synthesis the alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, and annealed at 600ºC for 720 h. Finally the ampoules were quenched into cold water. The weight losses, which were controlled at all stages of the synthesis, did not exceed 1 wt.% of the total mass, which was approximately 1 g for each alloy.

Phase analysis and structure refinements were carried out using X-ray powder diffraction data collected on diffractometers DRON-2.0M (Fe *K*α-radiation, angular range $20 \le 2\theta \le 110$-120^o, step 0.05º) and STOE Stadi P (Cu $K\alpha_1$-radiation, angular range $6\text{-}10 \le 2\theta \le 110^o$, step 0.015º). The profile and structural parameters were refined by the Rietveld method, using the program package FullProf Suite [13].

Results and discussion

Binary systems

The existence of 12 binary compounds at 600ºC in the boundary systems Hf–Ga, Hf–Sb and Ga–Sb was confirmed. Crystallographic data for the binary compounds in the system Hf–Ga can be found in [4]; data for the compounds in the systems Hf–Sb and Ga–Sb, including literature data and unit-cell parameters refined in this work, are summarized in Table 1.

Isothermal section at 600ºC of the phase diagram of the system Hf–Ga–Sb

The isothermal section at 600ºC of the phase diagram of the ternary system Hf–Ga–Sb was constructed in the whole concentration range (Fig. 1). It consists of 19 single-phase, 39 two-phase and 21 three-phase fields. The ternary phase Hf_2GaSb_3 forms the highest number of equilibria (8). The binary compounds HfGa and Hf_5Ga_3 dissolve 17 and 11 at.% Sb, respectively; the compound Hf_5Sb_3 dissolves 3 at.% Ga. The other binary compounds do not dissolve noticeable amounts of the third component. Four ternary compounds were found in the system at 600ºC.

Solid solutions $HfGa_{1-0.66}Sb_{0-0.34}$ and $Hf_5Ga_{3-2.12}Sb_{0-0.88}$

The substitutional solid solution $HfGa_{1-x}Sb_x$ (x = 0-0.34, a = 9.1609(10)-9.282(2), b = 8.5097(8)-8.639(3), c = 5.6384(6)-5.6255(15) Å) was studied by X-ray powder diffraction. It was found that substitution of Sb for Ga in the binary gallide HfGa takes place up to the composition Hf_3Ga_2Sb, similarly to what was observed for the ternary system Hf–Ga–Sn [4]. The crystal structure of the limiting composition belongs to the structure type Hf_3Ga_2Sn (Pearson symbol *oP*24, space group *Pbcm*). Replacement of Ga atoms by larger Sb atoms leads to an increase of the unit-cell parameters a and b and a decrease of the parameter c.

The solid solution $Hf_5Ga_{3-x}Sb_x$ (x = 0-0.88, a = 7.9601(10)-8.0986(8), c = 5.6779(8)-5.6436(5) Å) was also studied by X-ray powder diffraction. Substitution of Sb atoms for Ga atoms in the hexagonal Mn_5Si_3-type structure produces an increase of the parameter a and the unit-cell volume, to a decrease of the parameter c (Fig. 2).

Ternary compounds

The structure of the ternary compound **Hf_2GaSb_3** was determined by X-ray powder diffraction [10]. It crystallizes with the structure type Zr_2CuSb_3, which represents a ternary ordered derivative of the UAs_2 type (Pearson symbol *tP*6, space group *P*-4*m*2, a = 3.89841(8), c = 8.62650(19) Å).

Table 1 Crystallographic data for the binary compounds of the systems Hf–Sb and Ga–Sb.

Compound	Structure type	Pearson symbol	Space group	Unit-cell parameters, Å			Reference
				a	*b*	*c*	
Hf_3Sb	Ni_3P	*tI*32	*I*-4	11.1899	–	5.6364	[14]
				11.1723(11)	–	5.6255(6)	this work
Hf_5Sb_3	Y_5Bi_3	*oP*32	*Pnma*	7.4075	8.718	1.0736	[15]
				7.3865(9)	8.6843(10)	10.7192(12)	this work
rt-HfSb	ZrSb	*oS*24	*Cmcm*	3.779	10.338	13.842	[16]
				3.7738(9)	10.334(3)	13.893(4)	this work
ht-HfSb	FeSi	*cP*8	$P2_13$	5.59	–	–	[17]
rt-$HfSb_2$	$TiAs_2$	*oP*24	*Pnnm*	14.96	9.86	3.85	[18]
				14.9629(2)	9.8503(12)	3.8403(4)	this work
‘ht-$HfSb_2$‘	UAs_2	*tP*6	*P*4/*nmm*	3.92	–	8.68	[17]
Hf_5Sb_9	Hf_5Sb_9	*tP*28	*P*4/*n*	8.7483	–	8.6646	[9]
GaSb	ZnS	*cF*8	*F*-43*m*	6.0963	–	–	[19]
				6.0935(4)	–	–	this work

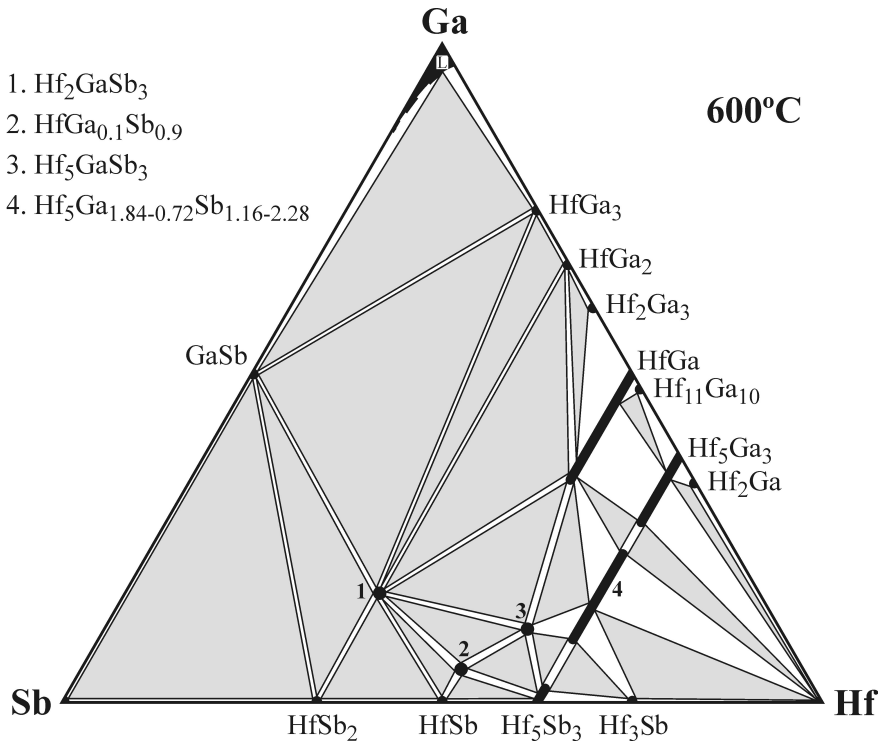

Fig. 1 Isothermal section of the phase diagram of the system Hf–Ga–Sb at 600ºC.

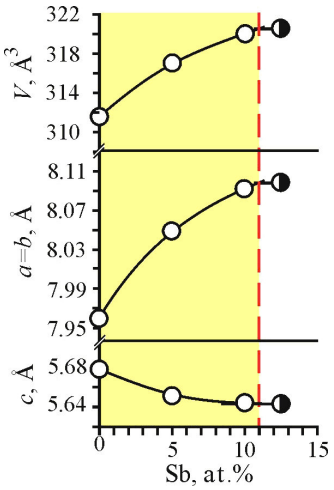

Fig. 2 Unit-cell parameters as a function of the Sb content in the solid solution $Hf_5Ga_{3-x}Sb_x$ (x = 0-0.88).

The crystal structure of the ternary compound **$HfGa_{0.1}Sb_{0.9}$** was studied on X-ray powder diffraction data (diffractometer DRON-2.0M). It crystallizes with the structure type FeSi (Pearson symbol *cP*8, space group $P2_13$, a = 5.5752(3) Å) and is probably part of the solid solution of the high-temperature modification of binary compound HfSb, stabilized by Ga at 600°C. The unit-cell parameters of the ternary phase are smaller than those reported for the corresponding binary compound [17], thereby confirming partial substitution of Ga atoms for Sb atoms. Experimental details and crystallographic data for $HfGa_{0.1}Sb_{0.9}$ are listed in Table 2, atomic coordinates and isotropic displacement parameters in Table 3, and interatomic distances and coordination numbers in Table 4. The atoms of the *p*-block elements occupy one of the two atom sites, forming a statistical mixture M = 0.10(3)Ga + 0.90(3)Sb. The content of the unit cell and the coordination polyhedra of the two sites in the structure of $HfGa_{0.1}Sb_{0.9}$ are shown in Fig. 3. Both sites have similar coordination polyhedra, namely trigonal prisms with one additional atom: $\underline{Hf}M_7$ and $\underline{M}Hf_7$.

The structure of the ternary compound **Hf_5GaSb_3** was determined from X-ray powder diffraction data collected on a diffractometer STOE Stadi P. It crystallizes with the structure type Hf_5CuSn_3 (Pearson symbol *hP*18, space group $P6_3/mcm$, a = 8.4747(5), c = 5.7190(5) Å). As stated above, this type represents a ternary ordered variant of the Ti_5Ga_4 structure type, which is a filled derivative of the Mn_5Si_3-type structure. In contrast to the ternary system Hf–Ga–Sn, where a continuous solid solution $Hf_5Ga_xSn_3$ (x = 0-1) was observed [4], the structure type Hf_5CuSn_3 is here adopted by a distinct ternary compound, Hf_5GaSb_3, whereas the structure of binary Hf_5Sb_3 belongs to a different structure type. Experimental details and crystallographic data for Hf_5GaSb_3 are listed in Table 2, atomic coordinates and isotropic displacement parameters in Table 5, interatomic distances and coordination numbers in Table 6. Fig. 4 shows the content of the unit cell and the coordination polyhedra of the crystallographically independent atoms in the structure of Hf_5GaSb_3.

Table 2 Experimental details and crystallographic data for the ternary phases $HfGa_{0.10(3)}Sb_{0.90(3)}$ and Hf_5GaSb_3.

Compound		$HfGa_{0.10(3)}Sb_{0.90(3)}$	Hf_5GaSb_3
Formula weight M_r		295.037	1327.423
Structure type		FeSi	Hf_5CuSn_3
Pearson symbol		*cP*8	*hP*18
Space group		$P2_13$	$P6_3/mcm$
Unit-cell parameters:	*a*, Å	5.5752(3)	8.4747(5)
	c, Å	–	5.7190(5)
Unit-cell volume *V*, Å^3		173.29(2)	355.71(4)
Formula units per cell *Z*		4	2
Density D_X, g cm^{-3}		11.313	12.398
Preferred orientation: value / [direction]		–	0.925(3) / [001]
Scan mode		$\theta/2\theta$	$\theta/2\theta$
Range 2θ, º		29-115	6-110
Step size, º		0.05	0.015
Scan time per step, s		3	380
Profile parameters	*U*	0.058(8)	0.043(4)
	V	-0.041(8)	-0.011(3)
	W	0.072(9)	0.0359(6)
Shape parameter		0.67(2)	0.393(5)
Asymmetry parameters		0.09(2), 0.05(7)	–
Number of refined parameters		13	17
Reliability factors:	R_B	0.0583	0.0676
	R_F	0.0423	0.0534
	R_p	0.0543	0.0784
	R_{wp}	0.0690	0.0915
	χ^2	3.5	2.3

Table 3 Atomic coordinates and isotropic displacement parameters for $HfGa_{0.1}Sb_{0.9}$.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Hf	4*a*	0.3911(18)	0.3911(18)	0.3911(18)	0.48(2)
M [a]	4*a*	0.0856(18)	0.0856(18)	0.0856(18)	0.95(3)

[a] *M* = 0.10(3)Ga + 0.90(3)Sb

Table 4 Interatomic distances and coordination numbers in the structure of $HfGa_{0.1}Sb_{0.9}$.

Atoms		*d*, Å	Coordination number
Hf	– 3 *M* [a]	2.873(14)	7
	– 1 *M* [a]	2.950(14)	
	– 2 *M* [a]	3.115(14)	
M [a]	– 3 Hf	2.873(14)	7
	– 1 Hf	2.950(14)	
	– 3 Hf	3.115(14)	

[a] *M* = 0.10(3)Ga + 0.90(3)Sb

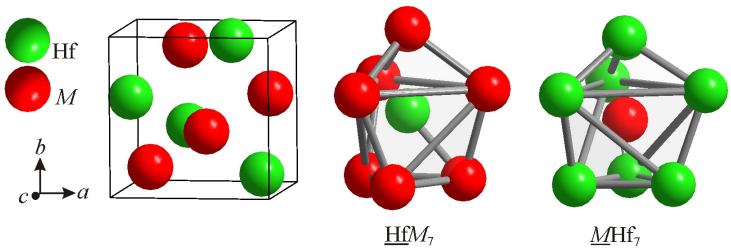

Fig. 3 Unit-cell content and coordination polyhedra of the two sites in the structure of $HfGa_{0.1}Sb_{0.9}$.

Table 5 Atomic coordinates and isotropic displacement parameters for Hf_5GaSb_3.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Hf1	6*g*	0.2694(4)	0	¼	0.85(5)
Hf2	4*d*	⅓	⅔	0	0.51(7)
Ga	2*b*	0	0	0	0.91(4)
Sb	6*g*	0.6143(6)	0	¼	0.55(8)

Table 6 Interatomic distances and coordination numbers in the structure of Hf_5GaSb_3.

Atoms		*d*, Å	Coordination number
Hf1	– 2 Ga	2.694(3)	11
	– 2 Sb	2.9042(14)	
	– 1 Sb	2.923(6)	
	– 2 Sb	3.025(2)	
	– 4 Hf2	3.4422(11)	
Hf2	– 2 Hf2	2.8595(3)	14
	– 6 Sb	2.995(3)	
	– 6 Hf1	3.4422(11)	
Sb	– 2 Hf1	2.904(4)	13
	– 1 Hf1	2.923(6)	
	– 4 Hf2	2.995(3)	
	– 2 Hf1	3.025(2)	
	– 2 Sb	3.454(4)	
	– 2 Ga	3.568(2)	
Ga	– 6 Hf1	2.694(3)	14
	– 2 Ga	2.8595(3)	
	– 6 Sb	3.568(2)	

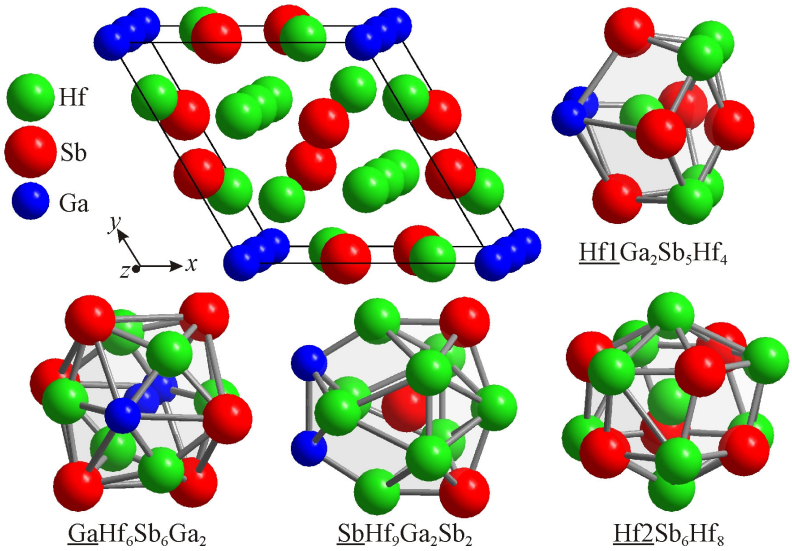

Fig. 4 Unit-cell content and coordination polyhedra of the atoms in the structure of Hf_5GaSb_3.

The ternary compound **$Hf_5Ga_{1.84-0.72}Sb_{1.16-2.28}$** crystallizes with the structure type Nb_5SiSn_2, which represents a ternary ordered derivative of the W_5Si_3 type (Pearson symbol *tI*32, space group *I*4/*mcm*, a = 10.84972(15), c = 5.50154(8) Å for composition $Hf_5Ga_{1.51(2)}Sb_{1.49(2)}$). The structure contains mixtures of Ga and Sb atoms in both available atom sites. However, a tendency towards ordering of the *p*-block elements is observed: Wyckoff position 8*h* is preferentially occupied by Sb atoms and Wyckoff position 4*a* by Ga atoms [11]. The ternary phase has a homogeneity range of 10 at.% Ga/Sb; the unit-cell parameters increase linearly (a = 10.8146-10.8921, c = 5.4895-5.5214 Å) with increasing Sb content (Fig. 5).

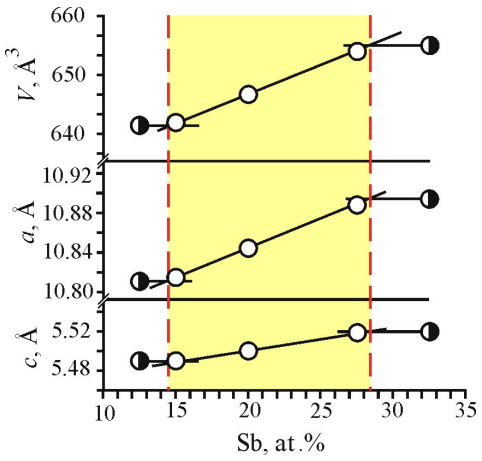

Fig. 5 Unit-cell parameters as a function of the Sb content within the homogeneity range of the ternary compound $Hf_5Ga_{1.84-0.72}Sb_{1.16-2.28}$.

Conclusions

At 600ºC the ternary system Hf–Ga–Sb is characterized by the existence of limited solid solutions based on the binary compounds HfGa (17 at.% Sb), Hf_5Ga_3 (11 at.% Sb) and Hf_5Sb_3 (3 at.% Ga), and four ternary compounds: Hf_2GaSb_3 (structure type Zr_2CuSb_3), $HfGa_{0.1}Sb_{0.9}$ (FeSi), Hf_5GaSb_3 (Hf_5CuSn_3), and $Hf_5Ga_{1.84-0.72}Sb_{1.16-2.28}$ (Nb_5SiSn_2). Substitution of Sb atoms for Ga atoms within the homogeneity ranges of $HfGa_{1-x}Sb_x$ (x = 0-0.34), $Hf_5Ga_{3-x}Sb_x$ (x = 0-0.88) and $Hf_5Ga_{3-x}Sb_x$ (x = 1.16-2.28) leads to an increase of the unit-cell volume. The ternary phases, with the exception of $HfGa_{0.1}Sb_{0.9}$, which probably belongs to the solid solution of ht-HfGa, show a fully or partly ordered arrangement of Ga and Sb atoms.

Acknowledgements

This work was supported by the Ministry of Education and Science of Ukraine under the grants No. 0112U001279 and No. 0112U001280.

References

[1] H. Boller, E. Parthé, *Acta Crystallogr.* 16 (1963) 830-833.
[2] A.Yu. Kozlov, V.V. Pavlyuk, *Intermetallics* 11 (2003) 237-239.
[3] A.Yu. Kozlov, *PhD Thesis*, Ivan Franko National University of Lviv, 2004.
[4] I. Voznyak, Ya. Tokaychuk, R. Gladyshevskii, *Chem. Met. Alloys* 4 (2011) 175-187.
[5] I. Voznyak, Ya. Tokaychuk, V. Hlukhyy, T.F. Fässler, R. Gladyshevskii, *Chem. Met. Alloys*. 4 (2011) 166-174.
[6] I. Voznyak, Ya. Tokaychuk, V. Hlukhyy, T.F. Fässler, R. Gladyshevskii, *J. Alloys Compd.* 512 (2012) 246-251.
[7] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data. Crystal Structure Database for Inorganic Compounds*, Release 2012/13, ASM International, Materials Park (OH).
[8] P. Villars, K. Cenzual, J.L.C. Daams, F. Hulliger, T.B. Massalski, H. Okamoto, K. Osaki, A. Prince (Eds.), *Pauling File Binaries Edition*, ASM International, Materials Park (OH), 2002.
[9] A. Assoud, K.M. Kleinke, N. Soheilnia, H. Kleinke, *Angew. Chem., Int. Ed.* 43 (2004) 5260-5262.
[10] I. Tokaychuk, Ya. Tokaychuk, R. Gladyshevskii, *Diffus. Defect Data, Pt. B* 194 (2013) 1-4.
[11] I. Voznyak, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 53 (2012) 109-114.
[12] I. Tokaychuk, Ya. Tokaychuk, R. Gladyshevskii, *Coll. Abstr. 18 Int. Conf. Solid Compd. Trans. Elements*, Lisbon, Portugal, 2012, p. 101.
[13] J. Rodriguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.
[14] J.O. Willerström, S. Rundqvist, *J. Solid State Chem.* 39 (1981) 128-132.
[15] H. Kleinke, C. Felser, *J. Alloys Compd.* 291 (1999) 73-79.
[16] M.G. Haase, H. Block, W. Jeitschko, *Z. Anorg. Allg. Chem.* 627 (2001) 1941-1948.
[17] W. Rossteutscher, K. Schubert, *Z. Metallkd.* 56 (1965) 813-822.
[18] D. Eberle, K. Schubert, *Z. Metallkd.* 59 (1968) 306-308.
[19] J.F. Miller, H.L. Goering, R.C. Himes, *J. Electrochem. Soc.* 107 (1960) 527-533.