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New quaternary alumosilicides with $Y_3NiAl_3Ge_2$-type structures

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Eight rare-earth nickel alumosilicides $R_3NiAl_3Si_2$ (R = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) were synthesized by arc melting and their crystal structures were studied by X-ray powder diffraction. They are isotypic to $Y_3NiAl_3Ge_2$, Pearson symbol *hP*9, space group *P*-62*m*. The hexagonal structure type $Y_3NiAl_3Ge_2$ (Z = 1) is a quaternary variant of the binary type Fe_2P (Z = 3) and the ternary types β_1-K_2UF_6, Lu_3CoGa_5, $Zr_3Cu_4Si_2$, and ZrNiAl. It belongs to a family of structures with trigonal prismatic coordination of the small atoms (Ni and Ge).

Quaternary alumosilicide / X-ray powder diffraction / Crystal structure / Isotypic compounds

Introduction

Four-component systems R–T–Al–Si, where R is a rare-earth metal and T is a 3*d*-element Mn, Fe, Co or Ni, have been investigated with the purpose to establish the existence of quaternary compounds. According to Pearson's Crystal Data [1] and the Handbook of Inorganic Substances [2], eight compounds in these systems have been reported. The crystal structures of the compounds belong to four structure types, $Ce_4Fe_2(Fe_{0.03}Al_{0.97})Al_6Si_8$ (Pearson symbol *oS*42, space group *Cmmm*, isotypic compounds with Pr, Nd, and Sm) [3], $Yb_5Fe_4Al_{17}Si_6$ (*tP*32, *P*4/*mmm*) [4], $Sm_2Ni(Ni_{0.27}Si_{0.73})Al_4Si_6$ (*tP*28, *P*4/*nmm*) [5], and $TbFe_4Al_9Si_6$ (*tP*80, *P*4$_2$/*nmc*, isotypic compound with Er) [6]. The crystal structures of the eight compounds were determined by X-ray single crystal diffraction. In the structure types defined on compounds with Yb or Tb the chemical elements are arranged in an ordered manner, whereas in the structure types with Ce or Sm partial disorder is observed, in particular, there are statistic mixtures of Al and Fe, or Ni and Si, atoms, respectively.

A larger number of quaternary compounds is known in the systems R–T–Al–Ge. The crystal structures of these intermetallics belong to eleven structure types, seven of which were determined in four-component systems: $Er_5Ni_3Al_3Ge_4$ (Pearson symbol *oP*30, space group *Pmmn*) [7], $Y_3NiAl_3Ge_2$ (*hP*9, *P*-62*m*) [8], $Tb_2NiAl_4Ge_2$ (*tI*18, *I*4/*mmm*) [9], $Ce_2NiAl_{5.77}Ge_{2.64}$ (*tI*38, *I*4/*mmm*) [9], $Ce_2CoAl_7Ge_4$ (*tP*28, *P*-42$_1$*m*) [10], $SmNiAl_4Ge_2$ (*hR*24, *R*-3*m*) [11], and $Pr(Ni_{0.2}Al_{0.5}Ge_{0.3})_2$ (*oS*6, *Cmm*2) [12]. The first six types are characterized by well-defined compositions and ordered distribution of the elements in the structures, whereas the last type exhibits Ni/Al/Ge disorder. Complete rows of isotypic compounds are not observed for any of the structure types; the majority of the compounds are formed by rare-earth metals of the yttrium subgroup. The maximum number of compounds, 40, was found for the structure type $Y_3NiAl_3Ge_2$ in R–T–Al–Ge systems with R = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and T = Mn, Fe, Co, Ni [13-17].

The aim of the present work was to search for representatives of the structure type $Y_3NiAl_3Ge_2$ in R–Ni–Al–Si systems. Considering that Ge and Si are analogue with respect to their electronic and size factors, the probability of existence of isotypic compounds $R_3TAl_3Si_2$ is rather high.

Experimental

Samples of nominal composition $R_{33.3}Ni_{11.1}Al_{33.4}Si_{22.2}$ (R = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were synthesized from the elements (purity of $R \geq 99.75$, Ni $\geq$ 99.99, Al $\geq$ 99.998, Si $\geq$ 99.999 mass%) by arc melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere (using Ti as a getter). The ingots were annealed at 600°C under vacuum in quartz ampoules for 1 month and subsequently quenched in cold water. The weight loss during the preparation of the samples was less than 1 % of the total mass, which was 1 g for each alloy.

The crystal structures of the new compounds were established by X-ray powder diffraction. Data for polycrystalline samples were collected on an automatic diffractometer STOE STADI P (Cu $K\alpha_1$ radiation, $\lambda = 1.5406$ Å, in the angular range $6 \leq 2\theta \leq 110.625°$ with a step of 0.015° and scan time 250 s). The structural parameters were refined by the Rietveld method [18], using the program DBWS [19]. The structure drawings were made with the program ATOMS [20].

Results and discussion

The X-ray diffraction of the alloys annealed at 600°C showed that the samples with Y, Gd, Tb, Dy, Ho, Er, Tm, and Lu contained the compound $R_3NiAl_3Si_2$, which is new for these rare earths. The crystal structures effectively belong to the $Y_3NiAl_3Ge_2$ type. In addition to the new compounds $R_3NiAl_3Si_2$, all the samples contained a small quantity (~ 4 mass%) of a secondary phase, *R*Si with TlI-type structure (*oS*8, *Cmcm*). The sample with Yb did not contain the phase "$Yb_3NiAl_3Si_2$", but the formation of the ternary compound Yb_2AlSi_2 with Mo_2FeB_2-type structure (*tP*10, *P*4/*mbm*) was confirmed. The cell parameters refined for the *R*Si compounds (*R* = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) and Yb_2AlSi_2 are in good agreement with those reported in the literature [1]. Based on the X-ray diffraction data, the structural parameters of the compounds $R_3NiAl_3Si_2$ (*R* = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) were determined.

Details of the structural refinements, refinable atomic coordinates and displacement parameters of the eight new compounds $R_3NiAl_3Si_2$ are listed in Table 1. As expected, the cell parameters refined for the new compounds decrease with decreasing radius of the rare-earth metal [21] from Gd to Lu (Fig. 1). A comparison of the experimental and calculated diffraction diagrams for $Lu_3NiAl_3Si_2$ is shown in Fig. 2. Relevant interatomic distances for the eight new compounds are presented in Table 2.

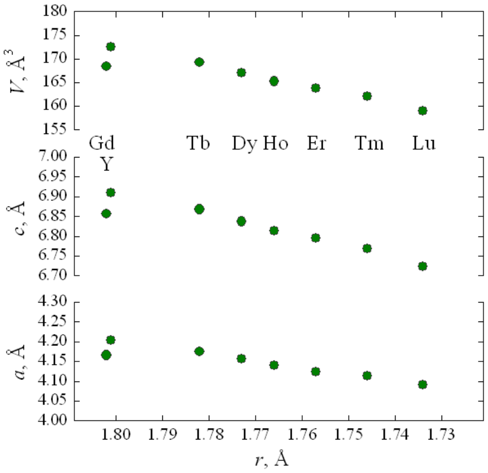

Fig. 1 Unit-cell parameters of $R_3NiAl_3Si_2$ compounds.

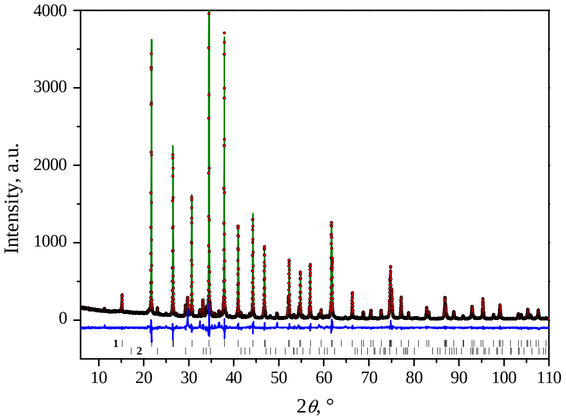

Fig. 2 Experimental, calculated and difference between experimental and calculated X-ray powder diffraction patterns (Cu $K\alpha_1$ radiation) for the sample $Lu_{33.3}Ni_{11.1}Al_{33.4}Si_{22.2}$. Vertical bars indicate the positions of the reflections of $Lu_3NiAl_3Si_2$ (1) and LuSi (2).

The description of the coordination polyhedra is given on the example of the compound $Lu_3NiAl_3Si_2$. The smaller atoms (Ni and Si) are characterized by a trigonal-prismatic environment with additional atoms above all the side faces of the prisms: for Ni – Al_6Lu_3 and for Si – Lu_6Al_3 [22]. The polyhedron of the Al site is a cuboctahedron $Lu_6Ni_2Al_2Si_2$, and that of the Lu site is a pentagonal prism with eight additional atoms, $Lu_6Ni_2Al_6Si_4$: five atoms above the side faces of the prism, two above the bases of the prism, and another Ni atom beyond one of the edges of the prism. One unit cell of the structure of $Lu_3NiAl_3Si_2$ and the coordination polyhedra of the atoms are shown in Fig. 3.

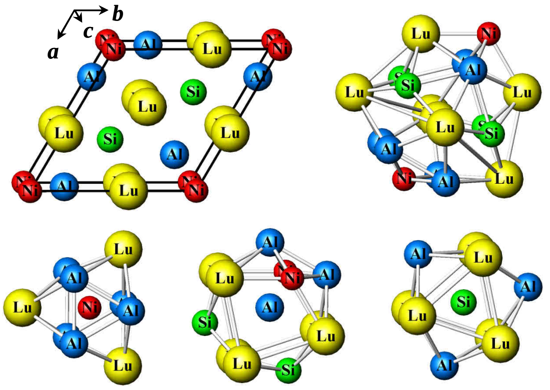

Fig. 3 Unit cell of the structure of the $Lu_3NiAl_3Si_2$ compound and coordination polyhedra of the atoms.

The hexagonal structure type $Y_3NiAl_3Ge_2$ (*Z* = 1) is the only possible quaternary substitution derivative in space group *P*-62*m* of the binary type Fe_2P (*Z* = 3) – $Fe_3PFe_3P_2$, since each chemical element occupies a distinct crystallographic position. To date the existence of four of the six

Table 1 Details of the structural refinements of the compounds $R_3NiAl_3Si_2$ (space group P-62m, R in 3f: x 0 0, Ni in 1a: 0 0 0, Al in 3g: x 0 ½, Si in 2d: ⅓ ⅔ ½, Z = 1).

Compound		$Y_3NiAl_3Si_2$	$Gd_3NiAl_3Si_2$	$Tb_3NiAl_3Si_2$	$Dy_3NiAl_3Si_2$	$Ho_3NiAl_3Si_2$	$Er_3NiAl_3Si_2$	$Tm_3NiAl_3Si_2$	$Lu_3NiAl_3Si_2$
Cell parameters, Å:	a	6.85746(9)	6.90979(8)	6.86802(8)	6.83711(9)	6.81341(9)	6.79541(8)	6.76825(9)	6.72303(7)
	c	4.16590(6)	4.20368(5)	4.17427(6)	4.15675(5)	4.13947(6)	4.12357(5)	4.11438(6)	4.09142(5)
Cell volume V, Å^3		169.65(1)	173.81(1)	170.51(1)	168.27(1)	166.41(1)	164.90(1)	163.22(1)	160.15(1)
Density D_X, g cm^{-3}		4.529	6.378	6.552	6.745	6.893	6.995	7.150	7.475
FWHM parameters:	U	0.047(2)	0.083(3)	0.062(5)	0.051(4)	0.038(3)	0.048(2)	0.048(1)	0.031(2)
	V	-0.021(2)	-0.039(4)	-0.027(4)	-0.042(3)	-0.011(2)	-0.035(2)	-0.005(2)	-0.001(2)
	W	0.0098(6)	0.0127(5)	0.0139(7)	0.0164(6)	0.0085(7)	0.0116(5)	0.0104(2)	0.0098(4)
Mixing parameter η		0.479(7)	0.581(6)	0.671(6)	0.648(7)	0.826(6)	0.703(6)	0.582(4)	0.611(6)
Asymmetry parameter C_M		-0.057(8)	-0.044(7)	-0.037(8)	-0.081(7)	-0.083(8)	-0.064(8)	-0.077(5)	-0.095(5)
Texture parameter G, direction [001]		0.907(2)	0.935(2)	0.915(2)	0.899(1)	0.919(3)	0.943(2)	0.912(1)	0.904(1)
Atomic coordinates:	$x(R)$	0.5919(2)	0.5951(2)	0.5932(2)	0.5924(2)	0.5945(2)	0.5937(2)	0.5906(1)	0.5904(1)
	x(Al)	0.2337(7)	0.2298(11)	0.2320(13)	0.2348(12)	0.2399(13)	0.2367(11)	0.2359(9)	0.2351(10)
Isotropic displacement parameters, Å^2:	$B_{iso}(R)$	1.22(2)	0.75(7)	0.91(5)	0.99(6)	0.88(2)	0.87(6)	0.85(4)	0.92(2)
	B_{iso}(Ni)	1.16(11)	0.86(13)	0.83(11)	1.03(12)	0.97(9)	0.99(14)	0.92(10)	0.95(12)
	B_{iso}(Al)	1.41(13)	0.90(14)	1.12(11)	1.14(11)	1.09(11)	1.38(15)	1.23(13)	1.06(14)
	B_{iso}(Si)	1.05(18)	0.77(19)	0.72(15)	1.01(14)	0.97(12)	0.94(12)	0.90(13)	0.86(17)
Reliability factors:	R_B	0.0509	0.0626	0.0517	0.0521	0.0603	0.0536	0.0497	0.0486
	R_p	0.0257	0.0321	0.0218	0.0192	0.0255	0.0218	0.0247	0.0187
	R_{wp}	0.0387	0.0414	0.0307	0.0258	0.0313	0.0285	0.0309	0.0344

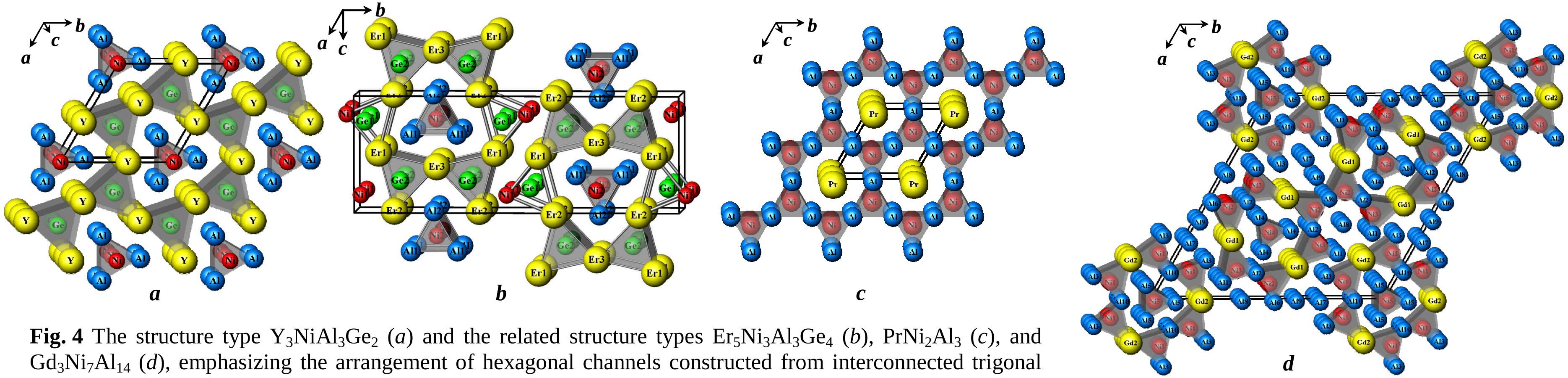

Fig. 4 The structure type $Y_3NiAl_3Ge_2$ (*a*) and the related structure types $Er_5Ni_3Al_3Ge_4$ (*b*), $PrNi_2Al_3$ (*c*), and $Gd_3Ni_7Al_{14}$ (*d*), emphasizing the arrangement of hexagonal channels constructed from interconnected trigonal prisms and centered by isolated columns of trigonal prisms or isolated atoms.

Table 2 Interatomic distances (δ) in the eight new compounds $R_3NiAl_3Si_2$.

Atoms		δ, Å							
		Y	Gd	Tb	Dy	Ho	Er	Tm	Lu
R	-1 Ni	2.7985(7)	2.7978(7)	2.7939(6)	2.7868(8)	2.7628(6)	2.7610(7)	2.7709(7)	2.7538(7)
	-4 Si	2.9419(7)	2.9713(3)	2.9490(3)	2.9350(3)	2.9269(3)	2.9162(3)	2.9027(1)	2.8846(1)
	-2 Al	3.2022(3)	3.2131(5)	3.2014(6)	3.1921(6)	3.1738(7)	3.1655(5)	3.1615(5)	3.1454(5)
	-4 Al	3.2206(4)	3.2847(6)	3.2419(8)	3.2090(6)	3.1814(6)	3.1837(5)	3.1678(3)	3.1486(4)
	-4 *R*	3.5983(4)	3.6375(4)	3.6085(4)	3.5894(4)	3.5846(4)	3.5722(4)	3.5469(2)	3.5225(2)
Ni	-6 Al	2.6281(2)	2.6342(2)	2.6258(3)	2.6262(3)	2.6373(5)	2.6150(2)	2.6041(2)	2.5852(2)
	-3 *R*	2.7985(7)	2.7978(7)	2.7939(6)	2.7868(8)	2.7628(6)	2.7610(7)	2.7709(7)	2.7538(7)
Al	-2 Ni	2.6281(2)	2.6342(2)	2.6258(3)	2.6262(3)	2.6373(5)	2.6150(2)	2.6041(2)	2.5852(2)
	-2 Si	2.6932(3)	2.7321(5)	2.7053(6)	2.6801(5)	2.6474(6)	2.6554(5)	2.6481(4)	2.6343(5)
	-2 Al	2.7758(6)	2.7503(9)	2.7598(9)	2.7806(8)	2.8311(9)	2.7860(9)	2.7654(7)	2.7381(8)
	-2 *R*	3.2022(3)	3.2131(5)	3.2014(6)	3.1921(6)	3.1738(7)	3.1655(5)	3.1615(5)	3.1454(5)
	-4 *R*	3.2206(4)	3.2847(6)	3.2419(8)	3.2090(6)	3.1814(6)	3.1837(5)	3.1678(3)	3.1486(4)
Si	-3 Al	2.6932(3)	2.7321(5)	2.7053(6)	2.6801(5)	2.6474(6)	2.6554(5)	2.6481(4)	2.6343(5)
	-6 *R*	2.9419(7)	2.9713(3)	2.9490(3)	2.9350(3)	2.9269(3)	2.9162(3)	2.9027(1)	2.8846(1)

possible ternary derivatives of the Fe_2P type is known: β_1-K_2UF_6, Lu_3CoGa_5, $Zr_3Cu_4Si_2$ (all $Z = 1$) and ZrNiAl ($Z = 3$) [23].

The structure of the $Y_3NiAl_3Ge_2$ type can be considered as an arrangement of trigonal prisms of composition Y_6 centered by Ge atoms. The prisms form infinite columns (common bases) running along the crystallographic direction **c**, and in the **ab** plane each prism is connected to two other prisms *via* common edges. As a result, hexagonal channels are formed, in which isolated columns of trigonal prisms of composition Al_6, centered by Ni atoms, are located. Similar structure fragments, hexagonal channels, are also present in related aluminide structures: the quaternary type $Er_5Ni_3Al_3Ge_4$ (*hP*9, *P*-62*m*) [7] and the ternary types $PrNi_2Al_3$ (*hP*6, *P*/6*mmm*) [24] and $Gd_3Ni_7Al_{14}$ (*hP*72, *P*-62*m*) [25] (Fig. 4).

Conclusions

The quaternary compounds $R_3NiAl_3Si_2$ (*R* = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) adopt the structure type $Y_3NiAl_3Ge_2$, which belongs to a family of structures with trigonal prismatic coordination of the small atoms (Ni and Ge). The Ni- and Ge-centered trigonal prisms form infinite columns *via* common triangular faces. The columns of Ge-centered prisms (Y_6) share prism edges and form a 3D framework with six-membered rings in the (001) plane, whereas the columns of Ni-centered prisms (Al_6) are isolated and located in the channels of the framework.

References

[1] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2018/19.

[2] P. Villars, K. Cenzual, R. Gladyshevskii (Eds.), *Handbook of Inorganic Substances 2017*, De Gruyter, Berlin, Germany, 2017, 1955 p.

[3] B. Sieve, S. Sportouch, X.Z. Chen, J.A. Cowen, P.W. Brazis, C.R. Kannewurf, V. Papaefthymiou, M.G. Kanatzidis, *Chem. Mater.* 13 (2001) 273-283.

[4] X. Ma, J.B. Whalen, H.B. Cao, S.E. Latturner, *Chem. Mater.* 25 (2013) 3363-3372.

[5] X.Z. Chen, S. Sportouch, B. Sieve, P.W. Brazis, C.R. Kannewurf, J.A. Cowen, R. Patschke, M.G. Kanatzidis, *Chem. Mater.* 10 (1998) 3202-3211.

[6] B. Sieve, D.L. Gray, R.W. Henning, A.J. Schultz, M.G. Kanatzidis, *Chem. Mater.* 20 (2008) 6107-6115.

[7] P. Demchenko, J. Konczyk, G. Demchenko, R. Gladyshevskii, V. Pavlyuk, *Acta Crystallogr. C* 62 (2006) i29-i31.

[8] J.T. Zhao, E. Parthé, *Acta Crystallogr. C* 46 (1990) 2273-2276.

[9] B. Sieve, P.N. Trikalitis, M.G Kanatzidis, *Z. Anorg. Allg. Chem.* 628 (2002) 1568-1574.

[10] N.J. Ghimire, L. Civale, J.D. Thompson, F. Ronning, E.D. Bauer, S.K. Cary, S. Eley, N.A. Wakeham, P.F.S. Rosa, T. Albrecht Schmitt, Y. Lee, M. Janoschek, C.M. Brown, *Phys. Rev. B* 93 (2016) 205141.

[11] B. Sieve, X. Chen, J.A. Cowen, P. Larson, S.D. Mahanti, M.G. Kanatzidis, *Chem. Mater.* 11 (1999) 2451-2455.

[12] N. Muts, L. Akselrud, R. Gladyshevskii, *Coll. Abstr. IX Int. Conf. Crystal Chem. Intermet. Compd.*, Lviv, 2005, p. 151.

[13] N. Semuso, Yu. Lutsyshyn, S. Pukas, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 55 (2014) 135-141.

[14] N. Semuso, S. Pukas, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 59 (2018) 90-97.

[15] N. Semuso, Yu. Lutsyshyn, S. Pukas, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 57 (2016) 89-96.

[16] N. Semuso, S. Pukas, Ya. Tokaychuk, R. Gladyshevskii, *Solid State Phenom.* 289 (2019) 21-27.

[17] W. He, W. Zeng, G. Lin, *J. Alloys Compd.* 627 (2015) 307-312.

[18] R.A. Young (Ed.), *The Rietveld Method*, Oxford University Press, Oxford, United Kingdom, 1995, 298 p.

[19] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, *J. Appl. Crystallogr.* 28 (1995) 366-367.

[20] E. Dowty, *ATOMS. A Computer Program for Displaying Atomic Structures*, Kingsport, TN, USA, 1999.

[21] E. Teatum, K. Gschneidner, J. Waber, *Report No. LA-2345*, US Department of Commerce, Washington, D.C., USA, 1960.

[22] P.I. Kripyakevich, *Structure Types of Intermetallic Compounds*, Nauka, Moscow, 1977, 288 p. (in Russian).

[23] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *TYPIX. Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*, Springer-Verlag, Berlin, Germany, 1993/1994, Vols. 1-4, 1596 p.

[24] R.M. Rykhal, O.S. Zarechnyuk, Yu.I. Kuten, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* 8 (1978) 1136-1138.

[25] S. Pukas, R. Gladyshevskii, *Acta Crystallogr. C* 71 (2015) 996-1000.