Contribution to the investigation of the ternary Lu–Cu–Sn system

L. ROMAKA[1]*, V.V. ROMAKA[1], V. DAVYDOV[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
  Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
* *Corresponding author. E-mail: romakal@franko.lviv.ua*

A detailed study of the Lu-Cu-Sn ternary system was performed in the composition range Cu–LuCu$_5$–LuCuSn–Sn at 670 K. The crystal structure of two previously unknown stannides formed in this region was determined using X-ray powder diffraction. The Lu$_{1.8}$Cu$_{9.2}$Sn$_{2.8}$ compound crystallizes in the Dy$_{1.9}$Cu$_{9.2}$Sn$_{2.8}$ structure type (space group $P6_3/mmc$), whereas the Lu$_3$Cu$_4$Sn$_4$ stannide belongs to the Tm$_3$Cu$_4$Sn$_4$ structure type (space group $C2/m$). The formation of a substitutional solid solution LuCu$_{5-x}$Sn$_x$ up to 15 at.% Sn was observed.

Stannides / Phase diagrams / Crystal structure / X-ray powder diffraction

Introduction

A previous study of the phase equilibria in the Lu-Cu-Sn ternary system at 670 K allowed us to find three ternary compounds, as reported in [1,2]. The crystal structure was determined for LuCuSn, at first based on a CaIn$_2$-type structure (space group (SG) $P6_3/mmc$) with a mixture (0.5Cu + 0.5Sn) in the 4(f) position [3]. A more detailed study performed in [4], using X-ray powder and single crystal diffraction and Mössbauer spectroscopy, led to the LiGaGe structure type (SG $P6_3mc$, an ordered non-centrosymmetric variant of the CaIn$_2$ type with full occupancy of all atomic positions) for the LuCuSn compound. The crystal structure of the two other compounds, found at the compositions Lu$_{15}$Cu$_{65}$Sn$_{20}$ and Lu$_{28}$Cu$_{36}$Sn$_{36}$ was not determined.

With regard to the work in progress on the R–Cu–Sn ternary systems formed by the rare earths, in this paper we report the data obtained during a partial revision of the Lu-Cu-Sn system and the crystal structure determination of two new intermetallics, Lu$_{1.8}$Cu$_{9.2}$Sn$_{2.8}$ and Lu$_3$Cu$_4$Sn$_4$.

Experimental

The samples were prepared by arc melting the constituent elements (Lu, Tm purity 99.9 wt. %, Cu 99.99 wt. %, and Sn 99.999 wt. %) under a purified, Ti-gettered, argon atmosphere with a non-consumable tungsten electrode and a water-cooled copper hearth. The overall weight losses were generally less than 1 wt. %. The alloys were annealed at 670 K in evacuated quartz tubes for 720 hours, and subsequently quenched in ice water. Independently, part of the samples with compositions Lu$_{15}$Cu$_{65}$Sn$_{20}$, Lu$_{28}$Cu$_{36}$Sn$_{36}$, and Tm$_{28}$Cu$_{36}$Sn$_{36}$ was annealed at 770 K (720 hours) to check the temperature range of existence of the formed compounds.

X-ray phase analysis of the samples was carried out using the powder patterns obtained on DRON-2.0m (Fe K_α radiation) and Philips PW1720 (Cu K_α radiation) powder diffractometers. The observed diffraction intensities were compared with reference powder patterns of known binary and ternary phases. For the crystal structure refinements the powder patterns obtained on Bruker D8 (graphite monochromator, Cu $K_{\alpha1}$ radiation, 20–100° 2θ range with scanning step 0.02° and 20 s exposure time), and HZG 4A automatic diffractometers (CuK_α radiation, 15–150° 2θ range with scanning step 0.05° and 20 s exposure time) were used. The calculations of the crystal structure parameters were accomplished using the CSD [5] and WinPLOTR [6] program packages.

Results and discussion

In the present work a detailed investigation of the Lu–Cu–Sn ternary system was performed in the composition range Cu–LuCu$_5$–LuCuSn–Sn at 670 K. Data concerning the phase diagrams and crystallographic characteristics of the binary phases of the Cu–Sn and Lu–Cu systems as assessed by Massalski [7] and Villars and Calvert [8], were used

Table 1 Atomic coordinates and isotropic displacement parameters for $Lu_{1.8}Cu_{9.2}Sn_{2.8}$ (SG $P6_3/mmc$).

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \cdot 10^2$ (nm^2)
Lu1	2*a*	0	0	0	1.22(2)
Lu2[a]	2*d*	1/3	2/3	3/4	1.59(2)
Cu1	12*k*	0.1630(2)	0.3260(2)	0.14207(3)	0.06(2)
Cu2	4*f*	1/3	2/3	0.04197(7)	2.09(4)
Cu3	2*b*	0	0	1/4	2.06(5)
Sn1	4*f*	1/3	2/3	0.58428(3)	0.97(2)
(Sn,Cu)[a]	2*c*	1/3	2/3	1/4	1.59(2)

[a] occupation of Lu2 – 0.80(1); (Sn,Cu) – 0.83Sn + 0.17Cu

for our investigation. Previous investigations of the Cu-rich corner of the *R*-Cu-Sn ternary systems where *R* = Y, La–Yb showed the formation of ternary phases at the composition $R_{15}Cu_{70}Sn_{15}$, crystallizing with CeCu$_6$-type structure [9,10]. Thus, it was decided to perform a detailed study of this range also in the Lu–Cu–Sn system to check for the possible existence of an analogous compound with Lu. The phase analysis of the powder pattern of the corresponding ingots showed the formation of a substitutional solid solution $LuCu_{5-x}Sn_x$ up to about 15 at.% Sn (including the composition $Lu_{15}Cu_{70}Sn_{15}$) based on the LuCu$_5$ binary (*ST* AuBe$_5$) (Fig. 1). At a higher Sn content a new
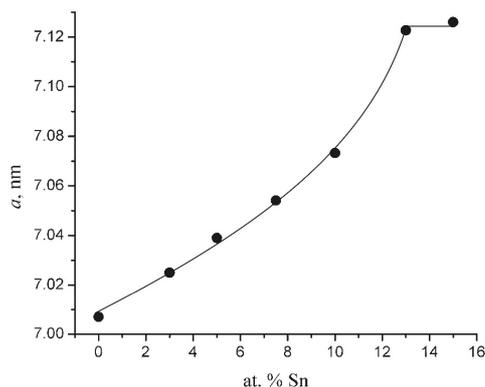

Fig. 1 The variation of the cell parameter *a vs.* composition for the $LuCu_{5-x}Sn_x$ solid solution.

ternary compound with composition $Lu_{15}Cu_{65}Sn_{20}$ was found. The powder pattern of the $Lu_{15}Cu_{65}Sn_{20}$ alloy was successfully indexed on the basis of a hexagonal lattice with cell parameters $a = 0.501254(7)$, $c = 2.04491(4)$ nm. The crystal structure appeared to be very similar to $Nd_7Cu_{35}Sn_{11}$ [11] and $Ho_{7.3}Cu_{37}Sn_{11}$ [12], both related to the CeNi$_5$Sn structure. A detailed crystal structure investigation performed on the $Lu_{15}Cu_{65}Sn_{20}$ sample showed that this structure belongs to the $Dy_{1.9}Cu_{9.2}Sn_{2.8}$ structure type (space group $P6_3/mmc$) [13], which is a partly disordered substitution variant of the CeNi$_5$Sn structure. The final atomic parameters, refined to $R_p = 0.113$, $R_{wp} = 0.154$, $R_{Bragg} = 0.056$, are listed in Table 1. The observed, calculated, and difference X-ray patterns for the $Lu_{1.8}Cu_{9.2}Sn_{2.8}$ compound are presented in Fig. 2. The series of isotypic $R_{1.9}Cu_{9.2}Sn_{2.8}$ compounds, where *R* is Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Yb,

was investigated earlier by our research team [13], and it was shown that this structure consists of fragments of $R_{0.9}Cu_{4.2}Sn_{0.8}$ and a hypothetical structure of composition "RCu_5Sn_2". A crystal chemical analysis showed that the interatomic distances between the rare-earth atom in the position 2*d* and the Sn/Cu atoms in the position 2*c* are shorter (0.291–0.311 nm) than the sum of the corresponding atomic radii, which could be explained by partial occupation of the site 2*d*. Some difference in the occupation of the 2*d* site by rare earth elements was observed for $R_{1.9}Cu_{9.2}Sn_{2.8}$ compounds. Additional investigation of alloys with 1–3 at.% deviations of each component from the stoichiometry did not show any significant homogeneity range.

Another series of $R_3Cu_4Sn_4$ stannides (*R* = Y, Ce, Nd, Gd-Tm) was found earlier at 770 K and the crystal structure was studied [11,14-16]. These compounds crystallize with Gd$_3$Cu$_4$Ge$_4$-type structure (SG *Immm*). From single crystal data it was established [16] that the Tm$_3$Cu$_4$Sn$_4$ compound also has a monoclinic modification (SG *C2/m*), derived by deformation from the orthorhombic Gd$_3$Cu$_4$Ge$_4$ structure. The phase analysis performed on powder pattern samples near the composition $Lu_{28}Cu_{36}Sn_{36}$ showed that these phases appeared to be very similar to the Gd$_3$Cu$_4$Ge$_4$ type, but the structure refinements using this starting model were not satisfactory. Thus, for further crystal structure calculations the starting model of the monoclinic Tm$_3$Cu$_4$Sn$_4$ structure was chosen. The reflections in the powder pattern of the $Lu_3Cu_4Sn_4$ phase were well indexed in space group *C2/m* with the parameters $a = 1.58842(4)$, $b = 0.43644(1)$, $c = 0.68851(2)$ nm, $\beta = 114.538(2)°$. The final atomic parameters, refined to $R_p = 0.024$, $R_{wp} = 0.032$, $R_{Bragg} = 0.097$, are listed in Table 2. The observed, calculated, and difference X-ray patterns for the $Lu_3Cu_4Sn_4$ compound are shown in Fig. 3, and a model of the crystal structure is presented in Fig. 4. Further investigations showed that the same compound was observed also after annealing at 770 and 870 K. During this work it was decided to perform detailed crystal structure calculations also for the Tm$_3$Cu$_4$Sn$_4$ compound annealed at 670 K. The results of the structure refinements confirmed the Gd$_3$Cu$_4$Ge$_4$ type structure $(a = 0.45957(3)$, $b = 0.70193(4)$, $c = 1.50963(9)$ nm). Refined atomic
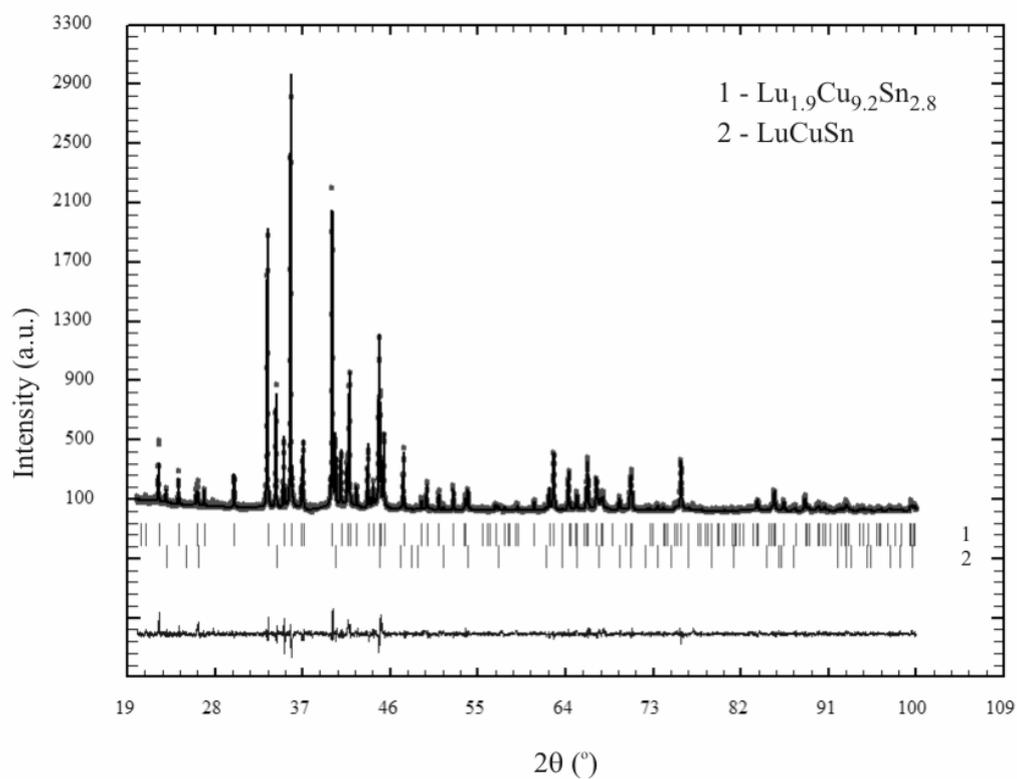
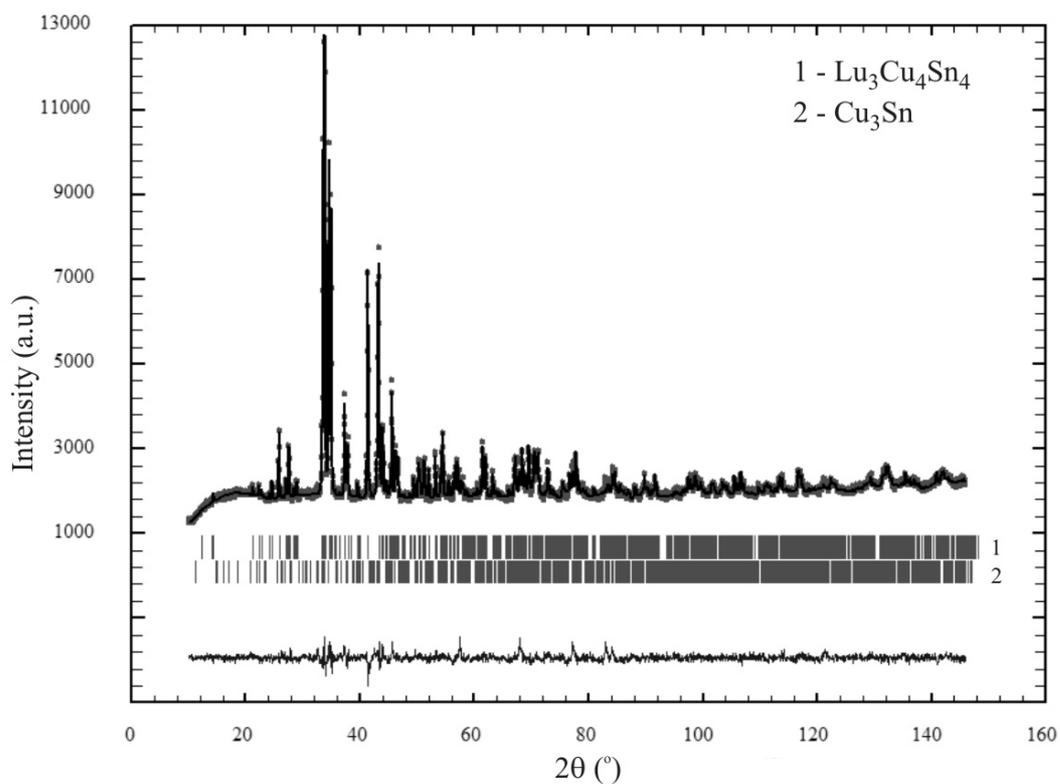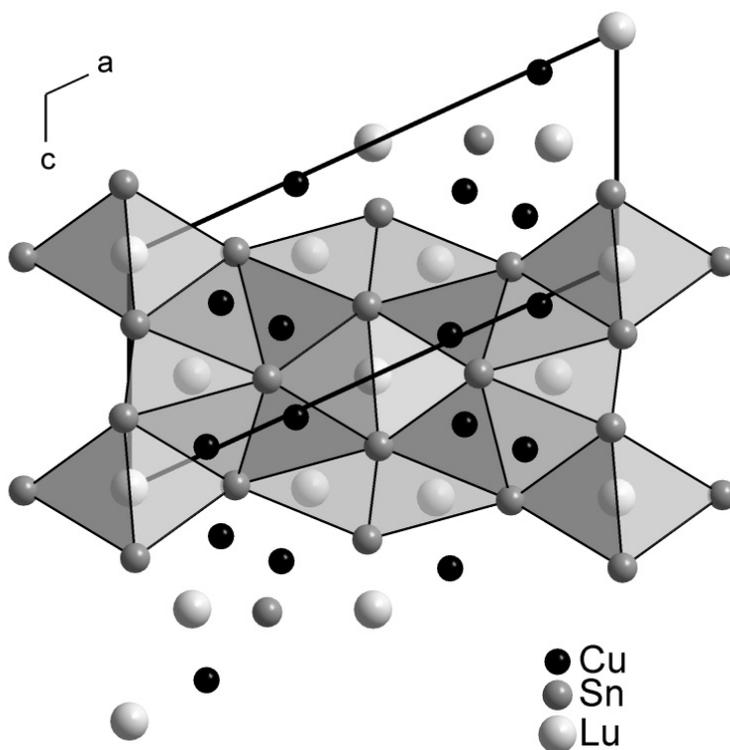**Fig. 2** The observed, calculated, and difference X-ray patterns for the $Lu_{15}Cu_{65}Sn_{20}$ alloy.

Fig. 3 The observed, calculated, and difference X-ray patterns for the $Lu_{28}Cu_{36}Sn_{36}$ alloy.

Table 2 Atomic coordinates and isotropic displacement parameters for $Lu_3Cu_4Sn_4$ (SG $C2/m$).

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \cdot 10^2$ (nm^2)
Lu1	2a	0	0	0	0.34(3)
Lu2	4i	0.1288(1)	0	0.6426(3)	0.55(2)
Cu1	4i	0.3122(4)	0	0.6139(8)	1.01(5)
Cu2	4i	0.3408(3)	0	0.0234(8)	1.17(6)
Sn1	4i	0.2175(2)	0	0.1975(4)	1.06(3)
Sn2	4i	0.5114(2)	0	0.3103(4)	0.48(2)

Table 3 Atomic coordinates and isotropic displacement parameters for $Tm_3Cu_4Sn_4$ (SG *Immm*).

Atom	Wyckoff position	x/a	y/b	z/c	$B_{iso} \cdot 10^2$ (nm^2)
Tm1	2a	0	0	0	1.77(8)
Tm2	4j	1/2	0	0.3648(4)	1.41(12)
Cu	8l	0	0.3094(13)	0.3268(6)	0.59(12)
Sn1	4i	0	0	0.2170(4)	0.98(8)
Sn2	4h	0	0.1978(9)	1/2	0.19(8)

Fig. 4 A model of the crystal structure of the $Lu_3Cu_4Sn_4$ compound (SG $C2/m$).

coordinates and isotropic displacement parameters are presented in Table 3 ($R_p = 0.023$, $R_{wp} = 0.029$, $R_{Bragg} = 0.055$), the observed, calculated, and difference X-ray patterns are shown in Fig. 5. The crystal structure of $Tm_3Cu_4Sn_4$ ($Gd_3Cu_4Ge_4$ type structure) is presented in Fig. 6. Detailed analyses of the interatomic distances in $Lu_3Cu_4Sn_4$ and $Tm_3Cu_4Sn_4$ did not show significant deviations from the sum of the corresponding atomic radii, except for

the shorter Sn2-Sn2 distances (0.283(2) and 0.278(1) nm for the Tm and Lu compound, respectively), which indicate covalent bonding between the atoms. As noted above, the monoclinic modification of $Tm_3Cu_4Sn_4$ was established from a single crystal study, while the orthorhombic $Gd_3Cu_4Ge_4$-type structure appeared in a $Tm_{28}Cu_{36}Sn_{36}$ alloy annealed at 670 K (or 770 K), which could be explained by the existence of two modifications of the

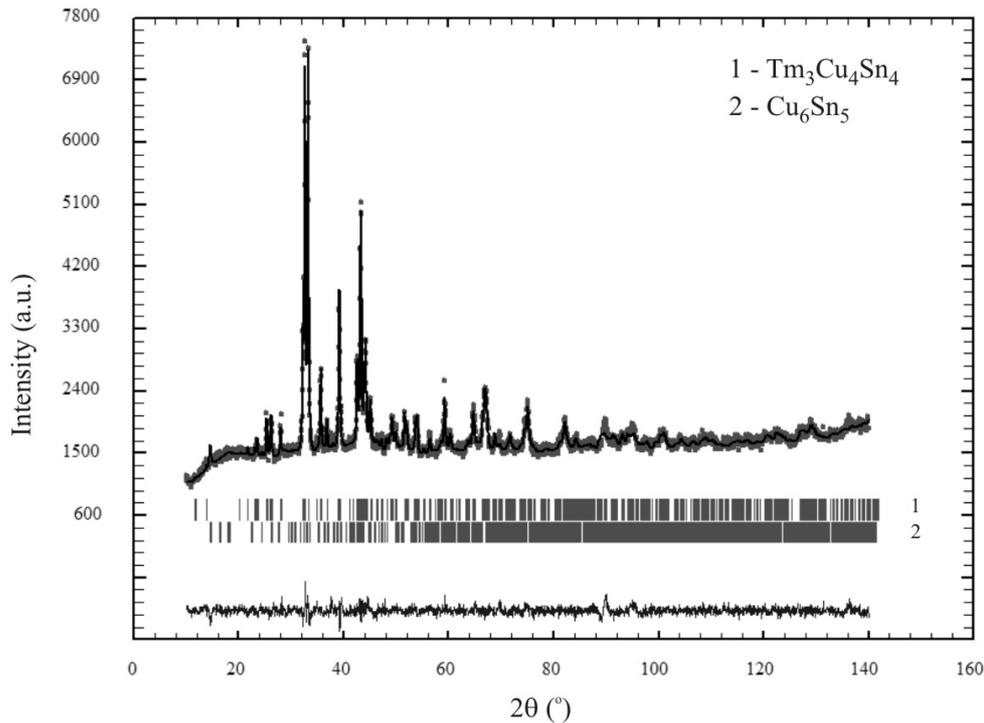**Fig. 5** The observed, calculated, and difference X-ray patterns for the $Tm_{28}Cu_{36}Sn_{36}$ alloy.

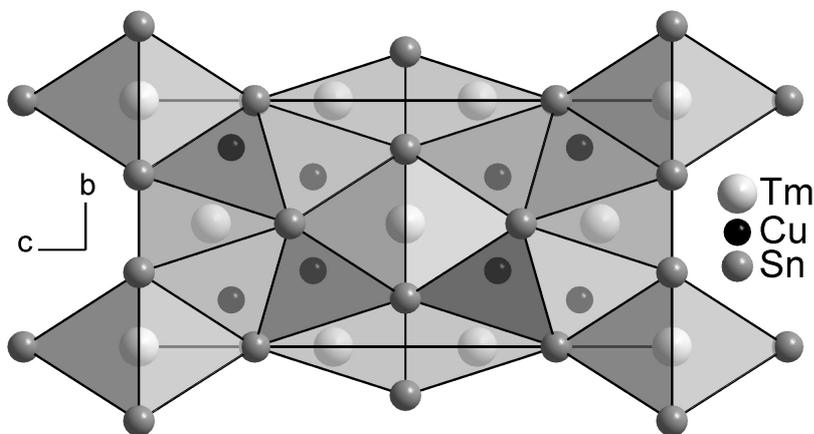**Fig. 6** A model of the crystal structure of the $Tm_3Cu_4Sn_4$ compound (SG *Immm*).

$Tm_3Cu_4Sn_4$ compound. Similar results were obtained for RNi_2Sn_2 (R = La–Sm) isotypic compounds [2], which are characterized by two polymorphic modifications, the second one formed by deformation of the tetragonal $CaBe_2Ge_2$ structure to a monoclinic one, depending on the annealing temperature.

According to the results obtained in this work for the composition range Cu–LuCu$_5$–LuCuSn–Sn of the Lu–Cu–Sn system at 670 K and 770 K the existence of two ternary $Lu_{1.8}Cu_{9.2}Sn_{2.8}$ and $Lu_3Cu_4Sn_4$ compounds was confirmed, and the formation of a $LuCu_{5-x}Sn_x$ substitutional solid solution was established.

References

[1] L.P. Komarovskaya, L.A. Mychajliv, R.V. Skolozdra, *Izv. Akad. Nauk SSSR, Met.* (4) (1989) 209.

[2] R.V. Skolozdra, in: K.A. Gschneidner, Jr., L. Eyring (Eds.), *Handbook on the Physics and*

Chemistry of Rare-Earths, Vol. 24, North-Holland, Amsterdam, 1997, Chapt. 164.

[3] L.P. Komarovskaya, R.V. Skolozdra, I.V. Filatova, *Dokl. Akad. Nauk Ukr. SSR, Ser. A* (1) (1983) 82.

[4] C.P. Sebastian, C. Fehse, H. Eckert, R.-D. Hoffmann, R. Pöttgen, *Solid State Sci.* 8 (2006) 1386.

[5] L.G. Akselrud, Yu.N. Grin, P.Yu. Zavalii, V.K. Pecharsky, V.S. Fundamenskii, CSD - universal program package for single crystal or powder structure data treatment, *Coll. Abs. 12th Eur. Crystallogr. Meet., Moscow*, Vol. 3, Nauka, Moscow, 1989, p. 155.

[6] T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows tool for powder diffraction patterns analysis, Proc. Eur. Powder Diffraction Conference (EPDIC7), *Mater. Sci. Forum* 378-381 (2001) 118.

[7] T.B. Massalski, *Binary Alloy Phase Diagrams*, ASM, Metals Park, OH, 1990.

[8] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM, Metals Park, OH, 1991.

[9] R.V. Skolozdra, L.P. Romaka, L.G. Akselrud, J. Pierre, *J. Alloys Compd.* 262-263 (1997) 346.

[10] Ya. Mudryk, O. Isnard, L. Romaka, D. Fruchart, *Solid State Commun.* 119 (2001) 423.

[11] P. Riani, M.L. Fornasini, R. Marazza, D. Mazzone, G. Zanicchi, R. Ferro, *Intermetallics* 7 (1999) 835.

[12] V. Romaka, Ya. Mudryk, L. Romaka, N. Koblyuk, *Coll. Abst. IX Inter. Conf. Cryst. Chem. Intermet. Compd.,* Lviv, Ukraine, 2005, P43.

[13] V.V. Romaka, D. Fruchart, R. Gladyshevskii, P. Rogl, N. Koblyuk, *J. Alloys Compd.*, in press.

[14] M.L. Fornasini, R. Marazza, D. Mazzone, P. Riani, G.G. Zanicchi, *Z. Kristallogr.* 213 (1998) 108.

[15] R.V. Skolozdra, L.P. Komarovskaja, L.G. Akselrud, *Ukr. Fiz. Zh.* 29 (1984) 1395.

[16] F. Thirion, J. Steinmetz, B. Malaman, *Mater. Res. Bull.* 18 (1983) 1537.