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Interaction of the components in the Gd-Mn-Sn ternary system at 873 and 673 K

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The interaction of the components in the Gd-Mn-Sn ternary system was studied using the methods of X-ray and microstructure analyses, in the whole concentration range. The isothermal sections of the phase diagrams of the Gd-Mn-Sn system were constructed at 873 and 673 K. At both temperatures of investigation the Gd-Mn-Sn system is characterized by formation of two ternary compounds: $GdMn_6Sn_6$ ($MgFe_6Ge_6$ structure type, space group *P*6/*mmm*) and $Gd_4Mn_4Sn_7$ ($Zr_4Co_4Ge_7$ structure type, space group *I*4/*mmm*). The formation of the interstitial solid solution $GdMn_xSn_2$ based on $GdSn_2$ ($ZrSi_2$-type) binary compound was observed up to 10 at. % Mn at 873 K and 673 K. The existence of the substitutional solid solution based on $GdMn_2$ ($MgCu_2$-type) was observed up to 5 at.% Sn and 3 at. % Sn at 873 K and 673 K, respectively.

Keywords: inetmetallics, ternary system, phase equilibria, crystal structure, solid solution.

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Introduction

Intermetallics of rare earth metals (R) cause the special attention of the scientists as a basis for searching and creation of new perspective magnetic materials. Partially, widely studied the magnetic properties of compounds contained magnetic rare earths and magnetic *d*-elements (iron, cobalt, nickel). The basic step for searching of new materials is investigation of component interaction in metallic systems which give the possibility to determine the temperature and concentration range of existence of intermediate phases, influence of some factors on their stability, as important characteristics for next study of physical properties. During investigation of the ternary stannides with rare earths and manganese (R = Y, Pr, Nd, Sm, Gd-Lu) the existence of the ternary compounds with stoichiometry 1:6:6 was found and it was established that they crystallize with $MgFe_6Ge_6$, $HoFe_6Sn_6$, and $SmMn_6Sn_6$ structure types [1-7]. Among RMn_6Sn_6 stannides the $SmMn_6Sn_6$ compound is characterized by three structural modifications with $MgFe_6Ge_6$, YCo_6Ge_6 and $SmMn_6Sn_6$ (disordered variant of $HfFe_6Ge_6$-type) structure types depending on temperature of annealing. Magnetic property measurements of RMn_6Sn_6 compounds indicated considerable influence of manganese atoms on magnetic behavior of these compounds which order ferro- or ferrimagnetically with temperature of magnetic ordering higher that room temperature (including the compounds with nonmagnetic rare earth metals Y, Lu) [3-6, 8]. In the most R-Mn-Sn systems also the ternary compounds with $Zr_4Co_4Ge_7$ structure type were found [9]. It worth to note that except the compounds with $Zr_4Co_4Ge_7$ and $MgFe_6Ge_6$ structure types for stannides with manganese, Tm and Lu the formation of compounds with $Hf_3Cr_2Si_4$-type was found [10], and Mg_5Si_6-type is realized only for $Yb_4Mn_2Sn_5$ stannide [11].

Taking into account the low melting temperature of tin (505.05 K), the most of the studied R-M-Sn ternary systems (M – *d*-element) were investigated at 670 K [12]. The higher temperature of annealing used during investigation of some R-{Cu,Ag}-Sn and R-Ni-Sn systems indicated an influence of temperature factor on stability of ternary compounds with high Sn content [13, 15]. With the aim to study an influence of annealing temperature on interaction of the components, formation of solid solutions and stability of intermediate phases we studied the Gd-Mn-Sn system at 873 and 673 K. Experimental results of this investigation are given in the presented work.

I. Experimantal

To study the phase equilibria in the Gd-Mn-Sn system 31 ternary and 13 binary samples were prepared by arc melting of the constituent elements (content of the basic component not lower than 99.9 wt. %). The homogenizing annealing of separate particles of the synthesized alloys was performed in the evacuated up to 0.1 Pa quartz tubes for 720 hours at temperatures 873 K and 673 K with subsequently quenching in ice water. X-ray phase analysis of the samples was carried out using the powder patterns obtained on DRON-2.0 (Fe$K\alpha$ radiation) diffractometer. The observed diffraction intensities were compared with reference powder patterns of binary, known ternary phases and pure elements. The chemical and phase compositions of the obtained samples were examined by Scanning Electron Microscopy (SEM) using REMMA-102-02 scanning electron microscope. The data for the crystal structure refinements were collected at room temperature using STOE STADI P diffractometer (graphite monochromator, Cu$K_{\alpha 1}$ radiation, 20 - 100° 2θ range with scanning step 0.02°). Calculations of the crystallographic parameters and theoretical patterns were performed using the WinPLOTR [16] program packages.

II. Results and discussion

For construction of the phase diagrams of Gd-Mn-Sn ternary system at 873 K and 673 K we prepared and analyzed 31 ternary and 13 binary alloys. After annealing all synthesized samples were examined by X-ray phase and microstructure analyses. The isothermal sections of the Gd-Mn-Sn system at 873 K and 673 K are presented in Figs. 1, 2, respectively. In the Mn-Sn and Gd-Mn binary systems the presence of the all binary compounds corresponding to the reference data [17-20] was confirmed at both temperature of investigation. At 873 K only two compounds – Mn_3Sn, Mn_2Sn, were formed in Mn-Sn system that corresponds to the reported phase diagram according to which $MnSn_2$ binary exists up to ~820 K. According to EDX data the homogeneity range of Mn_2Sn compound is limited by $Mn_{67.81}Sn_{32.11}$ and $Mn_{63.87}Sn_{36.73}$ compositions. $GdMn_2$ binary at stoichiometric composition crystallizes in $MgCu_2$ structure type. To check the formation of $GdMn_2$ binary with $MgZn_2$-type [21] in course of our investigation two alloys with $Gd_{37}Mn_{63}$ and $Gd_{40}Mn_{60}$ compositions were prepared and annealed at 673 and 873 K. Performed phase analysis of the $Gd_{37}Mn_{63}$ and $Gd_{40}Mn_{60}$ samples indicated the presence of the main cubic phase $GdMn_2$ with $MgCu_2$-type and Gd. In the Gd-Sn binary system at both temperatures of annealing the existence of binaries Gd_5Sn_3 (Mn_5Si_3-type), Gd_5Sn_4 (Sm_5Ge_4-type), $Gd_{11}Sn_{10}$ ($Ho_{11}Ge_{10}$-type), $GdSn_2$ ($ZrSi_2$-type), Gd_3Sn_7 (Gd_3Sn_7-type) and $GdSn_3$ was confirmed. $GdSn_3$ binary is characterized by polymorphic transformation at ~ 665 K, thus at 873 K belongs to Cu_3Au structure type [19], and at 673 K is characterized by orthorhombic structure of $GdSn_{2.75}$-type [20].

A formation of interstitial solid solutions based on the RSn_2 (R- rare earths of Yttrium group) series of binary compounds with $ZrSi_2$ structure was studied and reported in Ref. [22]. During investigation of Gd-Mn-Sn system the existence of interstitial solid solution $GdMn_xSn_2$ based on the $GdSn_2$ binary ($ZrSi_2$-type) was observed. The solubility of Mn atoms was found to be up to 10 at. % ($GdMn_{0.33}Sn_2$) at both temperatures 873 K and 673 K. The lattice parameters change from a = 0.4431(2), b = 1.6408(8), c = 0.4325(4) nm (for

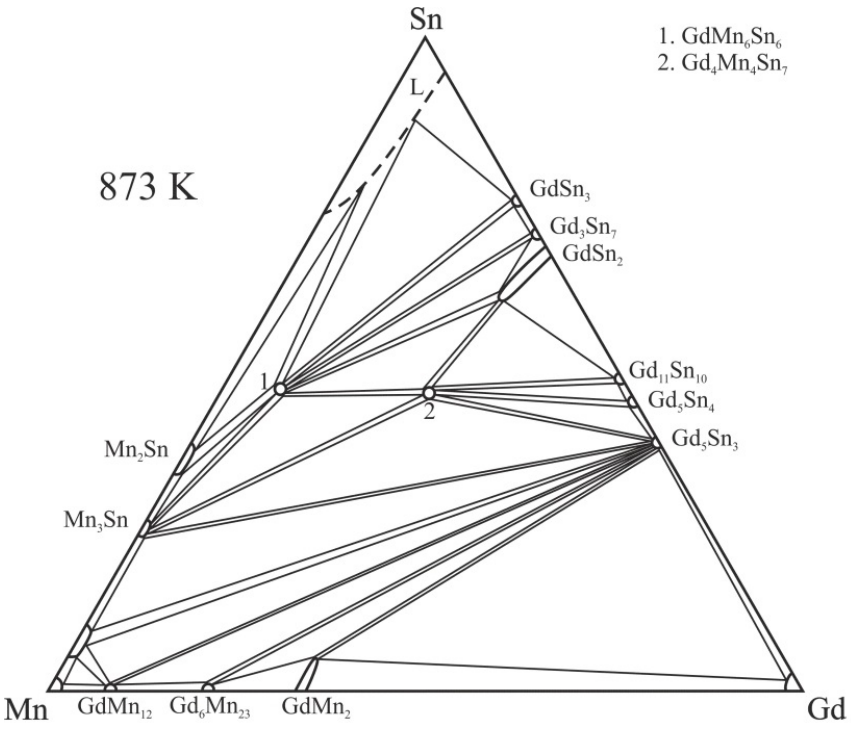


Fig. 1. Isothermal section of Gd-Mn-Sn system at 873 K.

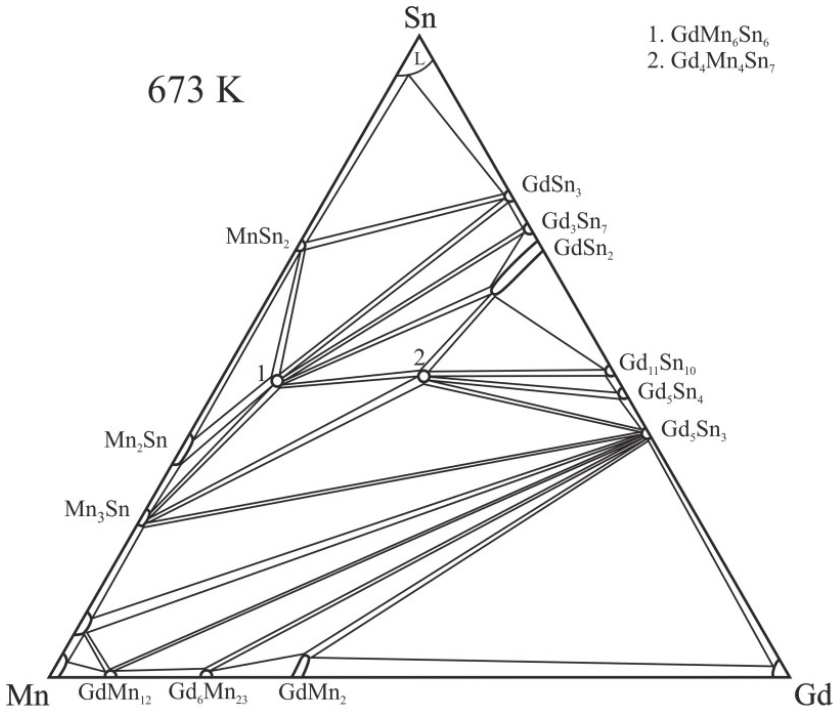
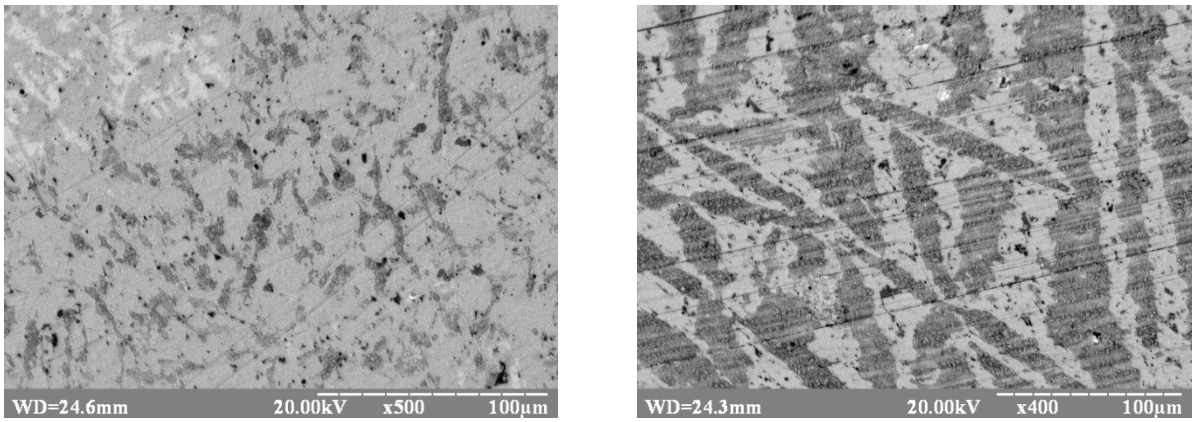


Fig. 2. Isothermal section of Gd-Mn-Sn system at 673 K.

Table 1

Crystallographic characteristics of the ternary compounds in Gd-Mn-Sn system

Compound	Structure type	Space group	Lattice parameters, nm		
			a	*b*	*c*
$GdMn_6Sn_6$	$MgFe_6Ge_6$	*P*6/*mmm*	0.55304(9)	–	0.9014(2)
$Gd_4Mn_4Sn_7$	$Zr_4Co_4Ge_7$	*I*4/*mmm*	1.5246(8)	–	0.5892(5)

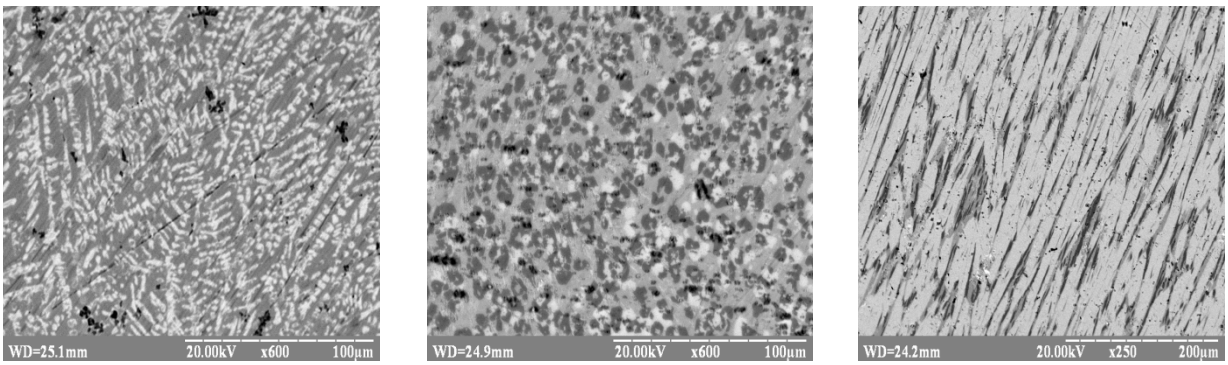


а б

Fig. 3. Electron micrographs and phase compositions of the alloys at 873 K: *a)* $Gd_{28}Mn_{26}Sn_{46}$ (light phase – $GdMn_xSn_2$, grey phase – $Gd_4Mn_4Sn_7$, dark phase – $GdMn_6Sn_6$), *b)* $Gd_{29}Mn_{19}Sn_{52}$ (light phase – $GdMn_xSn_2$ ($Gd_{30.45}Mn_{9.40}Sn_{60.15}$), grey phase – $Gd_4Mn_4Sn_7$).

$GdSn_2$ compound) to a = 0.4446(7), b = 1.6461(8), c = 0.4368(5) nm (for $Gd_{30}Mn_{10}Sn_{60}$ sample). Limited composition of the solid solution was confirmed by results of EDX analysis ($Gd_{30.45}Mn_{9.40}Sn_{60.15}$, Fig. 3,b). Phase analysis of samples in the ternary part of Gd-Mn-Sn system close to the Gd-Mn binary system indicated the formation of the substitutional solid solution based on $GdMn_2$ binary compound ($MgCu_2$ structure type) up to 3 at. % Sn at 673 K and up to 5 at. % Sn at 873 K (a = 0.77515(6) – 0.77638(7) nm). Significant solubility of the third component in other binary compounds of Mn-Sn, Gd-Mn i Gd-Sn system was not observed under used conditions.

According to phase and microstructure analyses in the Gd-Mn-Sn system at both temperatures 873 K and 673 K the presence of two ternary compounds $GdMn_6Sn_6$ and $Gd_4Mn_4Sn_7$ was confirmed. Both $GdMn_6Sn_6$ and $Gd_4Mn_4Sn_7$ stannides are characterized by narrow



a **b** **c**

Fig. 4. Electron micrographs and phase compositions of the alloys at 673 K: *a)* $Gd_{42}Mn_{46}Sn_{12}$ (light phase – Gd_5Sn_3, grey phase – $GdMn_{2-x}Sn_x$ (up to 3 at. % Sn)), *b)* $Gd_{10}Mn_{52}Sn_{38}$ (light phase – $Gd_4Mn_4Sn_7$, grey phase – $GdMn_6Sn_6$, dark phase –Mn_3Sn), *c)* $Gd_{19}Mn_{39}Sn_{42}$ (light phase – $Gd_4Mn_4Sn_7$, grey phase – $GdMn_6Sn_6$, dark phase – Mn_3Sn).

Table 2

Atomic coordinates and isotropic displacement parameters for $GdMn_6Sn_6$ compound

Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	$B_{iso.}\cdot 10^2$ (nm^2)
Gd	1*a*	0	0	0	1.55(1)
Mn	6*i*	1/2	0	0.2481(5)	0.34(10)
Sn1	2*e*	0	0	0.3370(4)	0.78(8)
Sn2	2*c*	1/3	2/3	0	0.40(9)
Sn3	2*d*	1/3	2/3	1/2	0.40(10)

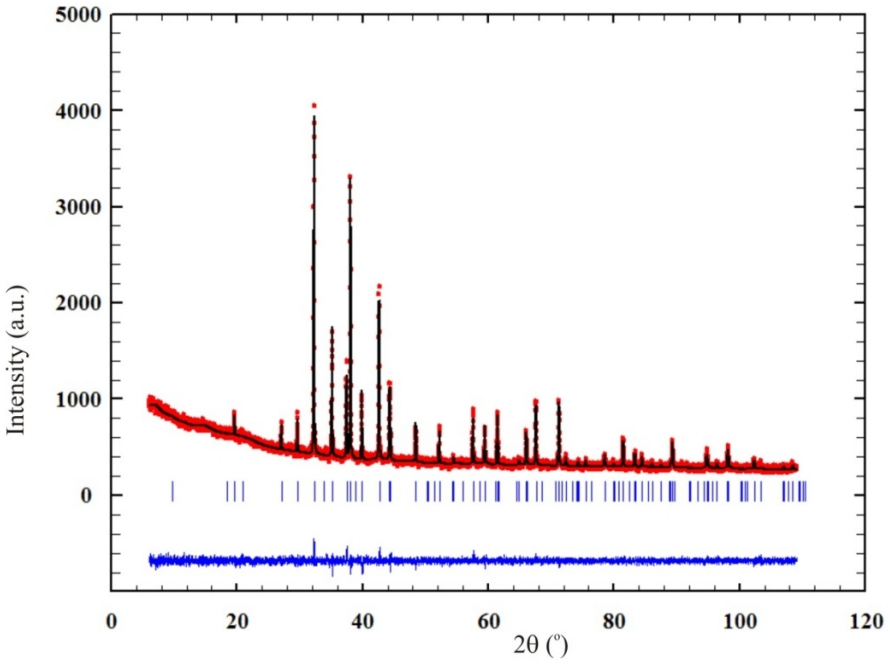


Fig. 5. The observed, calculated and difference X-ray patterns of $GdMn_6Sn_6$ compound.

homogeneity ranges at investigated temperatures. Crystallographic characteristics of ternary compounds are given in Table 1. The SEM pictures and phase compositions of some alloys are shown in Figs. 3, 4.

The existence of the $GdMn_6Sn_6$ compound with $MgFe_6Ge_6$ structure type and its lattice parameters were reported earlier [23]. During present work, the crystal structure of this stannide was refined by X-ray powder diffraction method. Performed structure refinement confirmed that $GdMn_6Sn_6$ belongs to $MgFe_6Ge_6$ structure type (space group *P6/mmm*, a = 0.55369(2) nm, c = 0.90270(4) nm, R_p = 0.0378, R_{wp} = 0.0484, R_{Brag} = 0.0455). Refined atomic parameters are listed in Table 2. The observed, calculated and difference X-ray patterns of the $GdMn_6Sn_6$ compound are shown in Fig. 5.

Comparing the investigated in our work Gd-Mn-Sn

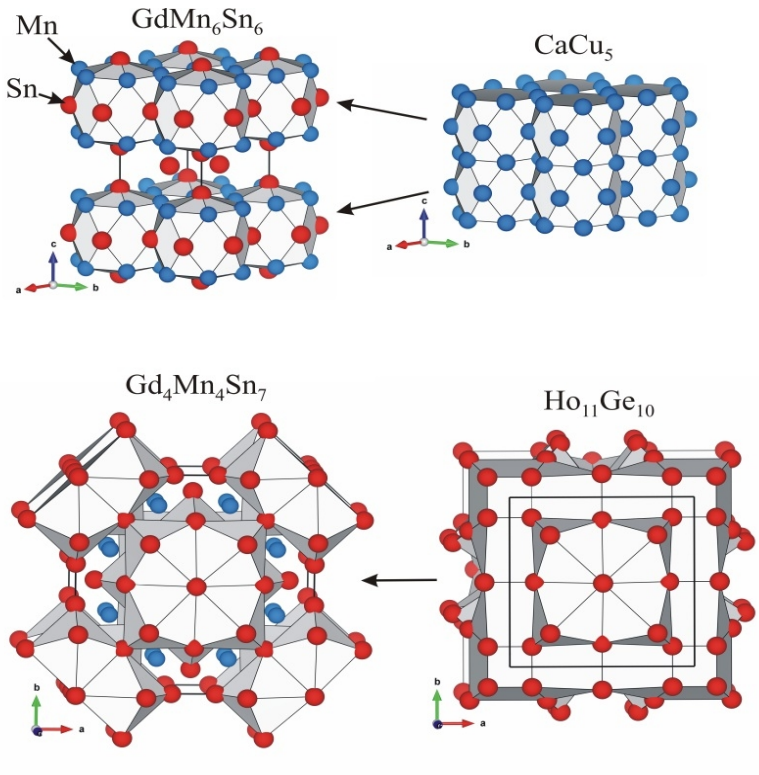


Fig. 6. Stacking of polyhydra in the structures $GdMn_6Sn_6$ and $CaCu_5$ (top), $Gd_4Mn_4Sn_7$ and $Ho_{11}Ge_{10}$ (bottom).

system with studied earlier {Y, Ce, Dy}-Mn-Sn and known in the literature ternary compounds [12] we may note that the R–Mn–Sn ternary systems contain a relatively small number of ternary phases. Series of stannides with $CeNiSi_2$ and $Gd_3Cu_4Ge_4$ structure types are formed only in the systems with rare earths of Cerium group. R-Mn-Sn systems here R is a rare earth element of Yttrium group are characterized by formation of the ternary compounds with $Zr_4Co_4Ge_7$-type and $MgFe_6Ge_6$ structure types, which are realized in studied Gd-Mn-Sn system.

The structural analysis of ternary compounds formed in the Gd-Mn-Sn system with regard on the coordination polyhydra for smallest and bigger atoms showed that they are related to corresponding structures of the binary compounds (Fig. 6). The structure of $Gd_4Mn_4Sn_7$ is a derivative from the $Ho_{11}Ge_{10}$ structure type in which crystallizes $Gd_{11}Sn_{10}$ binary compound. Main structural fragment is octahedron with additional atoms formed by Sn atoms around Gd atoms. Structure of $GdMn_6Sn_6$ compound is derivative from the structure of $GdMn_{12}$ binary [24] which contains fragments of hexagonal $CaCu_5$-type. Main structural fragment is hexagonal prism with six additional atoms formed by Sn atoms around Gd atoms and its deformed derivatives.

Conclusions

Performed in our work investigation of component interaction in the Gd-Mn-Sn system at 673 and 873 K indicated the stability of $GdMn_6Sn_6$ and $Gd_4Mn_4Sn_7$ formed ternary compounds at both temperature of investigation. An influence of the temperature of annealing takes place in character of the phase equilibria in the part of Gd-Mn-Sn system closed to Mn-Sn binary system, above 50 at. % Sn. It is caused by increasing of the liquidus range with increasing of temperature up to 873 K and subsequently absence of $MnSn_2$ binary. Increasing of annealing temperature from 673 to 873 K results in increasing of solubility of Sn in the $GdMn_2$ binary (from 3 to 5 at. %).

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[1]. B. Malaman, G. Venturini, B. Roques, Mater. Res. Bull. 23, 1629 (1988).
[2]. R.V. Skolozdra, in: K.A. Gschneidner, Jr. and L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 24, 1997, p. 399.
[3]. F. Weitzer, A. Leithe Jasper, K. Hiebl, P. Rogl, J. Appl. Phys. 73, 8447 (1993).
[4]. B. Malaman, G. Venturini, B. Chafik El Idrissi, E. Ressouche, J. Alloys Compd. 252, 41 (1997).
[5]. B. Chafik El Idrissi, G. Venturini, B. Malaman, D. Fruchart, J. Less-Common Met. 175, 143 (1991).
[6]. T. Mazet, R. Welter, B. Malaman, J. Magn. Magn. Mater. 204, 11 (1999).

[7]. V.V. Romaka, N.O. Melnychenko, Yu.K. Gorelenko, L.P. Romaka, Xth International Conference on Crystal Chemistry of Intermetallic Compounds (Lviv, 2007), p. 35.
[8]. B. Malaman, G. Venturini, R. Welter, J.P. Sanchez, P. Vulliet, E. Ressouche, J. Magn. Magn. Mater. 202, 519 (1999).
[9]. V. Romaka, L. Romaka, V. Tkachuk, Visnuk Lviv univ., Ser. chem. 52, 48 (2011).
[10]. X.-W. Lei, C.-L. Hu, J.-G. Mao, J. Solid State Chem. 183, 2031 (2010).
[11]. X.-W. Lei, G.-H. Zhong, M.-J. Li, J.-G. Mao, J. Solid State Chem. 181, 2448 (2008).
[12]. V.V. Romaka, L.P. Romaka, V.Ya. Krayovskiy, Yu.V. Stadnyk, Stannides of rare earths and transition metals (Lviv polytechnic university, Львів, 2015).
[13] V. Romaka, Yu. Gorelenko, L. Romaka, Visnyk Lviv univ. Ser. chem.. 49, 3 (2009).
[14]. L. Romaka, V.V. Romaka, E.K. Hlil, D. Fruchart, Chem. Met. Alloys 2, 68 (2009).
[15]. L. Romaka, I. Romaniv, V.V. Romaka, A. Horyn, Yu. Stadnyk, Chem.Met.Alloys 9, 135 (2016).
[16]. T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows tool for powder diffraction patterns analysis, Mater. Sci. Forum, 378–381,118 (2001).
[17]. T.B. Massalski, Binary Alloys Phase Diagrams (ASM International, Metals Park, Ohio, 1990).
[18]. U.P. Singh, A.K. Pal, L. Chandrasekaran, K.P. Gupta, Transactions of the Metallurgical Society of AIME, 242, 1661 (1968).
[19]. A. Palenzona, P. Manfrinetti, J. Alloys Compd. 201, 43 (1993).
[20]. R.V. Skolozdra, LG. Akselrud, V.K. Pecharskii, O.E. Koretskaya, Dopov.Akad. Nauk Ukr. RSR, Ser. B, 12, 51 (1986).
[21]. K. Ichinose, J. Phys. Soc. Jpn. 56, 2908 (1987).
[22]. M. Francois, G. Venturini, B. Malaman, B. Roques, J. less-Common Met. 160, 197 (1990).
[23]. B. Malaman, G. Venturini, B. Roques, Mater. Res. Bull. 23, 1629 (1988).
[24]. F.E. Wang, J.V. Gilfrich, Acta Crystallogr. 21, 476 (1966).

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Взаємодія компонентів у потрійній системі Gd-Mn-Sn при 873 і 673 K

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Методами рентгенофазового і мікроструктурного аналізів досліджено взаємодію компонентів у потрійній системі Gd-Mn-Sn у повному концентраційному інтервалі та побудовані діаграми фазових рівноваг за температур 873 K і 673 K. За обох температур дослідження в системі утворюються дві тернарні сполуки $GdMn_6Sn_6$ (структурний тип $MgFe_6Ge_6$, просторова група *P*6/*mmm*) і $Gd_4Mn_4Sn_7$ (структурний тип $Zr_4Co_4Ge_7$, просторова група I4/*mmm*). На основі бінарного станіду $GdSn_2$ зі структурою типу $ZrSi_2$ встановлено існування твердого розчину включення $GdMn_xSn_2$ до вмісту 10 ат. % Mn за температур 873 K і 673 K. На основі бінарної сполуки $GdMn_2$ (структурний тип $MgCu_2$) утворюється твердий розчин заміщення до вмісту 5 ат. % Sn при 873 K і до вмісту 3 ат. % Sn при 673 K.

Ключові слова: інтерметаліди, потрійна система, фазові рівноваги, кристалічна структура, тверді розчини.