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Interaction between the components in Tm-Cr-Ge system at 1070 K

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The phase equilibrium diagram of the Tm–Cr–Ge ternary system was constructed at a temperature 1070 K based on the results of X-ray phase, microstructural analyzes and energy-dispersive X-ray spectroscopy in the whole concentration range. At the temperature of investigation, two new ternary compounds are realized in the system: TmCr₆Ge₆ (SmMn₆Sn₆ structure type, space group *P6/mmm*, *a*=0.51506(1), *c*=0.82645(2) nm) and Tm₄Cr₄Ge₇ (Zr₄Co₄Ge₇ structure type, space group *I4/mmm*, *a*=1.39005(9), *c*=0.54441(1) nm). Inclusion of Cr atoms in the structure of the binary germanide TmGe₂ (structure type ZrSi₂) up to 10 at. % Cr leads to the formation of a solid solution TmCr_xGe₂ (*x* = 0-0.33).

Keywords: intermetallics, ternary system, phase equilibria, crystal structure.

Received 04 April 2022; Accepted 09 October 2022.

Introduction

The study of multicomponent metallic systems is a prerequisite for finding and creating new functional materials with important properties for practical application. Experimental studies of the interaction between the components in metallic systems provide important information about the conditions of formation, temperature stability, composition and crystal structure of intermetallic phases, which serve as the basis for the search of new materials. R-M-Ge ternary systems (R – rare earth element, M – transition metal) are characterized by a significant number of ternary compounds and structure types in which they crystallize [1]. Among R-M-Ge systems ternary systems with rare earths, germanium and chromium are not studied enough, phase equilibrium diagrams are constructed only for Y, Nd, Gd and Er [2-5]. According to the literature data, R-Cr-Ge systems are characterized by a small number of compounds, among which the most studied are series of RCrGe₃, RCr₆Ge₆ and RCr_xGe₂ compounds.

The study of the physical properties of individual series of compounds of R-Cr-Ge systems, in particular RCrGe₃ (R = La-Nd, Sm) with perovskite structure, showed that these germanides are ferromagnetically

ordered with rather high Curie temperatures (from 60 to 155 K) [6]. R₁₁₇Cr₅₂Ge₁₁₂ compounds (R = Nd, Sm, Gd) with a giant unit cell (structure type Tb₁₁₇Fe₅₂Ge₁₁₂, *a*~2.9 nm) are promising thermomagnetic materials because the complexity of the crystal structure provides low thermal conductivity [3, 7]. Analysis of the literature data shows that ternary compounds RCr₆Ge₆ (R = Y, Tb–Er) are formed with rare-earth metals of the yttrium subgroup [8, 9], and belong to the HfFe₆Ge₆ (or MgFe₆Ge₆) structure type. According to the measurements of the magnetic properties the presence of magnetic ordering at low temperatures has been established for RCr₆Ge₆ germanides (R = Tb, Dy, Er) [8, 10]. It was shown that sublattices of rare earth elements and chromium are characterized by different directions of the magnetic moments of atoms.

There is no information in the literature on the study of the Tm-Cr-Ge system and ternary germanides with thulium and chromium. Taking into account the lack of results regarding the phase equilibrium diagram and the formation of ternary compounds, this paper presents experimental results of study the interaction between the components in the Tm-Cr-Ge system at 1070 K.

I. Experimental methods

To study the interaction of thulium with chromium and germanium alloys were synthesized by a direct twofold arc-melting of the constituent elements (metals were used in the form of ingots, with purity of thulium 99.9 wt.%; chromium, purity of 99.99 wt.%; and germanium, purity of 99.999 wt.%) under high purity Ti-gettered argon atmosphere on a water-cooled copper bottom. For better homogenization the samples were remelted twice. The weight loss during the preparation of the samples was less than 1 % of the total mass, which was 1 g for each sample. For heat treatment, the alloys were placed in vacuum quartz ampoules and annealed at 1070 K for 700 h, followed by quenching in cold water without breaking the ampoules. X-ray phase analysis of the samples was carried out using the powder patterns obtained at room temperature on DRON-4.0 (FeK α radiation) diffractometer. The observed diffraction intensities were compared with reference powder patterns of binary phases, known ternary germanides and pure elements (programme PowderCell [11]). To control the chemical composition of the synthesized samples, determine the exact content of components in the phases and confirm the results of X-ray phase analysis we used the method of energy-dispersive X-ray spectroscopy (EDRS) (electron microscope TESKAN VEGA 3 LMU, equipped by an X-ray analyzer with energy dispersive spectroscopy). At least five measurements were taken to obtain the average value for each phase in each sample.

Calculations and indexing of powder diffraction patterns were performed using the WinCSD software package [12] (determination of the unit cell parameters). For the crystal structure refinements the diffraction data were collected at room temperature using STOE STADI P diffractometer (graphite monochromator, Cu K α_1 radiation). The coordinates of atoms, occupancy of the crystallographic sites, and isotropic displacement parameters were refined with the FullProf Suite software package [13].

II. Experimental results

Information on the phase diagrams of Tm-Cr, Tm-Ge and Cr-Ge binary systems which delimit the Tm-Cr-Ge system was used from handbooks [14, 15]. The phase diagram of the Tm-Cr system belongs to the monotectic type, binary compounds are absent in the system. In the Cr-Ge system, five binary compounds are formed by peritectic transformations: Cr₃Ge (Cr₃Si-type), Cr₅Ge₃ (W₅Si₃-type for high-temperature modification), Cr₁₁Ge₈ (Cr₁₁Ge₈-type), CrGe (FeSi-type), and Cr₁₁Ge₁₉ (Mn₁₁Si₁₉-type). Cr₃Ge compound is characterised by homogeneity region. For Cr₅Ge₃ germanide polymorphic transformation is observed at a temperature of 1275 K. There is no information in the literature about the crystal structure of low-temperature modification of Cr₅Ge₃ binary. In our study, the compound with Cr₅Ge₃ stoichiometry was not identified at the temperature of investigation. X-ray phase analysis of the sample with corresponding composition showed two binary compounds Cr₃Ge and Cr₁₁Ge₈ in equilibrium.

According to reported phase diagram [14] in the Tm-Ge system at 1070 K binary compounds Tm₅Ge₃ (Mn₅Si₃-type), Tm₅Ge₄ (Sm₅Ge₄-type), Tm₁₁Ge₁₀ (Ho₁₁Ge₁₀-type), TmGe (TiJ-type), Tm₃Ge₄ (Er₃Ge₄-type), Tm₂Ge₃ (Tm₂Ge₃-type), TmGe_{1.9} (TmGe_{1.9}-type), and TmGe₂ (ZrSi₂-type) exist. Information about the compound TmCr₃ (DyGe₃-type), which is obtained at high temperature and pressure, and germanide Tm₂Ge₅ (Er₂Gr₅-type), synthesized by induction melting was reported in [16, 17]. Under used in our work conditions the compound TmGe_{1.9} was not identified, the Tm₃Ge₄ compound belongs to the Gd₃Ge₄ structure type [18]. Crystallographic characteristics of the binary compounds which are realised at the temperature of our study in the Tm-Ge and Cr-Ge systems are listed in Table 1.

The phase equilibrium diagram of the Tm-Cr-Ge system is constructed at 1070 K based on the X-ray phase, microstructural analyses and energy-dispersive X-ray spectroscopy of the prepared samples (Fig. 1). Phase compositions of the selected alloys of the Tm-Cr-Ge system are given in Table 2.

Table 1

Crystallographic characteristics of the binary compounds of Tm-Ge and Cr-Ge systems.

Compound	Space group	Structure type	Lattice parameters, nm			Ref.
			<i>a</i>	<i>b</i>	<i>c</i>	
TmGe ₂	<i>Cmcm</i>	ZrSi ₂	0.4004(2)	1.5708(6)	0.3907(1)	This work
Tm ₂ Ge ₃	<i>C12/c1</i>	Tm ₂ Ge ₃	0.90577	0.66386 $\beta=115.678$	0.77596	[19]
Tm ₃ Ge ₄	<i>Cmcm</i>	Gd ₃ Ge ₄	0.3987(3)	1.0495(5)	1.4069(5)	This work
TmGe	<i>Cmcm</i>	TiJ	0.4189(3)	1.0492(6)	0.3875(5)	This work
Tm ₁₁ Ge ₁₀	<i>I4/mmm</i>	Ho ₁₁ Ge ₁₀	1.0554(5)		1.5899(6)	This work
Tm ₅ Ge ₄	<i>Pnma</i>	Sm ₅ Ge ₄	0.7293(3)	1.4417(6)	0.7198(5)	This work
Tm ₅ Ge ₃	<i>P6₃/mcm</i>	Mn ₅ Si ₃	0.8337(3)		0.6231(3)	This work
Cr ₃ Ge	<i>Pm-3n</i>	Cr ₃ Si	0.4624(1)			This work
Cr ₁₁ Ge ₈	<i>Pnma</i>	Cr ₁₁ Ge ₈	1.3171	0.4939	1.5775	[20]
CrGe	<i>P2₁3</i>	FeSi	0.47971(3)			This work
Cr ₁₁ Ge ₁₉	<i>P-4n2</i>	Mn ₁₁ Si ₁₉	0.5790		5.1870	[21]

Microstructural and X-ray spectral analyzes were used to confirm the chemical and phase composition of the samples. Microphotographs of some alloys are presented in Fig. 2.

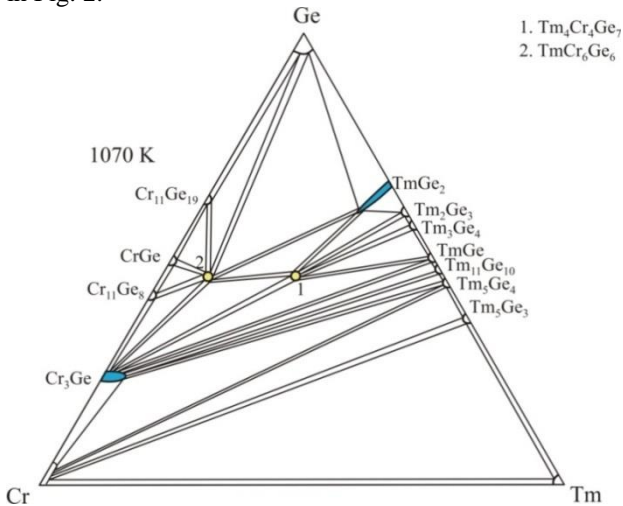


Fig. 1. Isothermal section of the Tm–Cr–Ge system at 1070 K.

According to the results of X-ray phase and EPM analyzes at a temperature of 1070 K in the Tm–Cr–Ge system the formation of two new ternary germanides TmCr_6Ge_6 and $\text{Tm}_4\text{Cr}_4\text{Ge}_7$ was established. Crystallographic characteristics of the ternary compounds are given in Table 3.

Analysis of the diffraction pattern of the $\text{Tm}_8\text{Cr}_{46}\text{Ge}_{46}$ sample showed the formation of the TmCr_6Ge_6 compound, which is isostructural to the previously studied germanides RCr_6Ge_6 ($R=Y, \text{Gd-Er}$) [8, 9]. The performed calculation of the crystal structure of the TmCr_6Ge_6 compound indicated that it belongs to the SmMn_6Sn_6 structure type (space group $P6/mmm$), which is a disordered variant of the HfFe_6Ge_6 structure type [22]. Atomic coordinates, isotropic displacement parameters of the atoms are gathered in Table 4. In the model of the SmMn_6Sn_6 structure type for the TmCr_6Ge_6 structure, as well as for the studied by neutronography TbCr_6Ge_6 [10], the partial distribution of Tm atoms and Ge1 atoms in two crystallographic positions is observed:

$\text{Tm}1(1a, 0, 0, 0)/\text{Tm}1(1b, 0, 0, 1/2)$;

$\text{Ge}1(2e, 0, 0, 0.3474(4))/\text{Ge}1(2e, 0, 0, 0.1386(2))$. The

Table 2

Phase composition and EPMA data for individual samples of the Tm–Cr–Ge system.

Nominal composition/EPMA data, at. %	Phase	Structure type	Lattice parameters, nm			EPMA data, at. %		
			<i>a</i>	<i>b</i>	<i>c</i>	Tm	Cr	Ge
$\text{Tm}_{55}\text{Cr}_{15}\text{Ge}_{30}$ $\text{Tm}_{53.02}\text{Cr}_{15.14}\text{Ge}_{31.84}$	Tm_5Ge_3	Mn_5Si_3	0.8332(3)		0.6232(3)	62.88	1.16	35.96
	(Cr)	W	0.2892(3)				100.0	
$\text{Tm}_5\text{Cr}_{70}\text{Ge}_{25}$	Cr_3Ge	Cr_3Si	0.4632(3)					
	$\text{Tm}_{11}\text{Ge}_{10}$	$\text{Ho}_{11}\text{Ge}_{10}$	1.0556(5)		1.5922(4)			
$\text{Tm}_{45}\text{Cr}_{25}\text{Ge}_{30}$	Tm_5Ge_3	Mn_5Si_3	0.8330(4)		0.6234(4)	62.77		37.23
	Tm_5Ge_4	Sm_5Ge_4	0.7293(3)	1.4417(6)	0.7198(5)	56.14		43.86
	(Cr)	W	0.2888(3)				100.0	
$\text{Tm}_{10}\text{Cr}_{55}\text{Ge}_{35}$ $\text{Tm}_{11.12}\text{Cr}_{54.36}\text{Ge}_{34.52}$	TmCr_6Ge_6	SmMn_6Sn_6	0.5150(3)		0.8263(4)	7.21	46.45	46.34
	Cr_3Ge	Cr_3Si	0.4628(2)			2.74	72.65	24.61
	$\text{Tm}_4\text{Cr}_4\text{Ge}_7$	$\text{Zr}_4\text{Co}_4\text{Ge}_7$	1.3900(5)		0.5444(4)	25.67	26.84	47.49
$\text{Tm}_{40}\text{Cr}_{20}\text{Ge}_{40}$ $\text{Tm}_{40.49}\text{Cr}_{18.95}\text{Ge}_{40.56}$	$\text{Tm}_{11}\text{Ge}_{10}$	$\text{Ho}_{11}\text{Ge}_{10}$	1.0554(5)		1.5899(6)	51.72	1.09	47.19
	Tm_5Ge_4	Sm_5Ge_4	0.7489(5)	1.444(7)	0.7541(5)	55.66		44.34
	Cr_3Ge	Cr_3Si	0.4632(3)			3.95	71.60	24.45
$\text{Tm}_{15}\text{Cr}_{45}\text{Ge}_{40}$ $\text{Tm}_{12.91}\text{Cr}_{45.60}\text{Ge}_{41.49}$	Cr_3Ge	Cr_3Si	0.4628(3)			1.87	73.76	24.37
	TmCr_6Ge_6	SmMn_6Sn_6	0.5151(2)		0.8264(3)	7.48	47.26	45.26
	$\text{Tm}_4\text{Cr}_4\text{Ge}_7$	$\text{Zr}_4\text{Co}_4\text{Ge}_7$	1.3901(4)		0.5445(3)	25.53	26.97	47.50
$\text{Tm}_5\text{Cr}_{50}\text{Ge}_{45}$ $\text{Tm}_{4.93}\text{Cr}_{49.60}\text{Ge}_{45.47}$	TmCr_6Ge_6	SmMn_6Sn_6	0.5150(3)		0.8264(3)	7.62	46.54	45.84
	CrGe	FeSi	0.4794(3)				48.93	51.07
	$\text{Cr}_{11}\text{Ge}_8$	$\text{Cr}_{11}\text{Ge}_8$	Not determined				56.89	43.11
$\text{Tm}_{45}\text{Cr}_{10}\text{Ge}_{45}$ $\text{Tm}_{44.60}\text{Cr}_{10.91}\text{Ge}_{44.49}$	$\text{Tm}_{11}\text{Ge}_{10}$	$\text{Ho}_{11}\text{Ge}_{10}$	1.0555(5)		1.5903(6)		51.72	48.28
	TmGe	TIJ	0.4191(3)	1.0491(6)	0.3874(4)	48.69		51.31
	Cr_3Ge	Cr_3Si	0.4630(4)			1.97	73.40	24.63
$\text{Tm}_{25}\text{Cr}_{25}\text{Ge}_{50}$ $\text{Tm}_{25.13}\text{Cr}_{25.61}\text{Ge}_{49.26}$	$\text{TmCr}_{1-x}\text{Ge}_2$	CeNiSi_2	0.4094(7)	1.5600(7)	0.3982(5)	31.90	9.09	59.01
	TmCr_6Ge_6	SmMn_6Sn_6	0.5150(2)		0.8265(2)	7.82	47.57	44.61
	$\text{Tm}_4\text{Cr}_4\text{Ge}_7$	$\text{Zr}_4\text{Co}_4\text{Ge}_7$	1.3899(4)		0.5444(4)	26.34	27.03	46.63
$\text{Tm}_{40}\text{Cr}_{10}\text{Ge}_{50}$ $\text{Tm}_{39.81}\text{Cr}_{11.04}\text{Ge}_{49.15}$	Tm_3Ge_4	Gd_3Ge_4	0.3979(4)	1.0492(6)	1.4054(6)	43.59		56.41
	TmGe	TIJ	0.4189(3)	1.0492(6)	0.3875(5)	49.33		50.67
	$\text{Tm}_4\text{Cr}_4\text{Ge}_7$	$\text{Zr}_4\text{Co}_4\text{Ge}_7$	1.3900(5)		0.5444(5)	26.90	26.27	46.83
$\text{Tm}_{20}\text{Cr}_{25}\text{Ge}_{55}$ $\text{Tm}_{18.87}\text{Cr}_{24.04}\text{Ge}_{57.09}$	TmCr_6Ge_6	SmMn_6Sn_6	0.5150(2)		0.8265(2)	7.95	44.84	47.21
	$\text{TmCr}_{1-x}\text{Ge}_2$	CeNiSi_2	0.4093(1)	1.5598(2)	0.3984(1)	29.63	10.51	59.86
	(Ge)	(C)	0.5649(4)					100.0 0
$\text{Tm}_{20}\text{Cr}_{20}\text{Ge}_{60}$ $\text{Tm}_{18.92}\text{Cr}_{21.03}\text{Ge}_{60.05}$	TmCr_6Ge_6	SmMn_6Sn_6	0.5151(3)		0.8265(4)	7.53	45.36	47.11
	$\text{TmCr}_{1-x}\text{Ge}_2$	CeNiSi_2	0.4091(6)	1.5600(6)	0.3983(5)	30.27	10.57	59.16
	(Ge)	(C)	0.5647(3)					100.0

Table 3

Crystallographic characteristics of the ternary compounds in the Tm–Cr–Ge system.						
N	Compound	Structure type	Space group	Lattice parameters, nm		
				<i>a</i>	<i>b</i>	<i>c</i>
1	Tm ₄ Cr ₄ Ge ₇	Zr ₄ Co ₄ Ge ₇	<i>I4/mmm</i>	1.39005(9)	–	0.54441(1)
2	TmCr ₆ Ge ₆	SmMn ₆ Sn ₆	<i>P6/mmm</i>	0.51506(1)	–	0.82645(2)

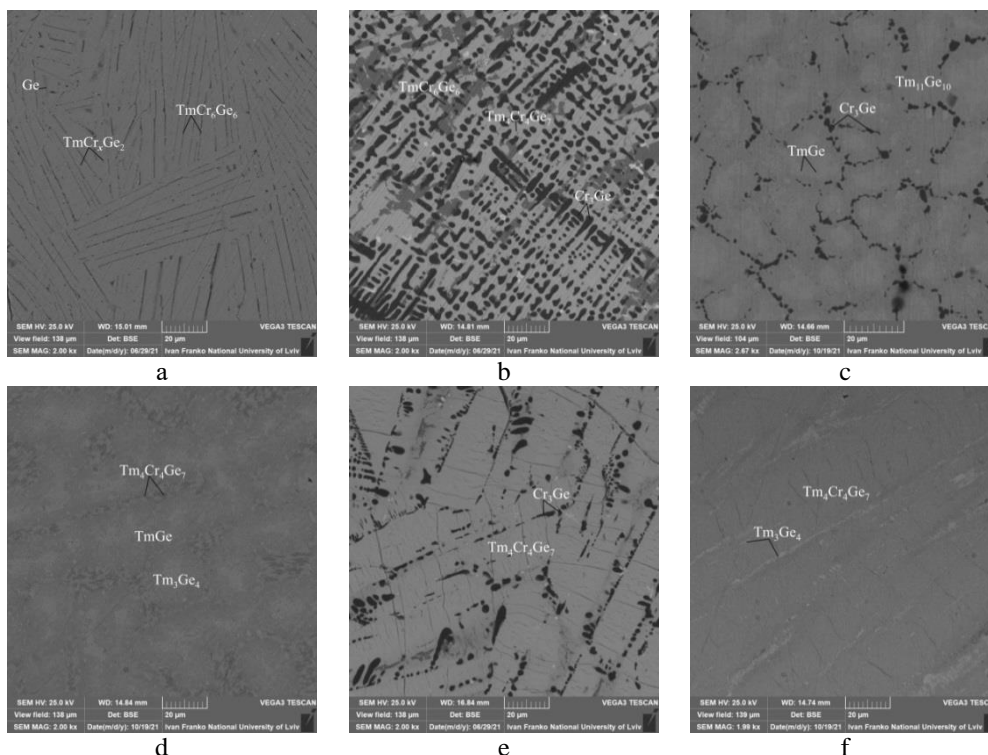


Fig. 2. Electron microphotographs of the Tm–Cr–Ge alloys: Tm₂₀Cr₂₅Ge₅₅ (a), Tm₁₀Cr₅₅Ge₃₅ (b), Tm₄₅Cr₁₀Ge₄₅ (c), Tm₄₀Cr₁₀Ge₅₀ (d), Tm₂₀Cr₄₀Ge₄₀ (e), Tm₃₇Cr₁₀Ge₅₃ (f).

experimental, calculated and difference X-ray diffraction patterns for Tm₈Cr₄₆Ge₄₆ sample are shown in Fig. 3, a.

During the study of the system at 1070 K, the formation of a new ternary compound with the composition ~Tm₂₇Cr₂₇Ge₄₆ was established. According to EPMA data composition of the compound is Tm_{26.45}Cr_{27.22}Ge_{46.33}. Analysis of the diffraction pattern of the sample Tm₂₇Cr₂₇Ge₄₆ and the calculated lattice periods (*a* = 1.39005 (9), *c* = 0.54441 (1) nm) indicated that the compound belongs to the Zr₄Co₄Ge₇ structure type (space group *I4/mmm*). Sample Tm₁₀Cr₅₅Ge₃₅ contains TmCr₆Ge₆, Tm₄Cr₄Ge₇ compounds and Cr₃Ge binary in equilibrium (Fig. 2b).

According to the literature data [23] formation of the ternary germanides RCr_xGe₂ with CeNiSi₂ structure type was found for rare earth elements where R = Sm, Gd–Er. In the case of the Tm–Cr–Ge system, the binary germanide TmGe₂ crystallizes in the ZrSi₂-type and, in the ternary part inclusion of Cr atoms results in formation of the TmCr_xGe₂ solid solution up to Cr content ~10 at. %. Solubility limit of Cr in the TmCr₂ binary was determined by change of the lattice parameters (*a* = 0.4004 (2) - 0.4095 (7) nm, *b* = 1.5708 (6) - 1.5601 (1) nm,

c = 0.3907 (1) - 0.3983 (5) nm) and electron probe microanalysis (Tm_{29.96}Cr_{10.19}Ge_{59.85}). An increase of the unit cell volume with increasing of Cr content confirms the formation of an inclusion-type solid solution (from *V* = 0.2457 nm³ for TmGe₂ to *V* = 0.2544 nm³ for the sample Tm₃₀Cr₁₀Ge₆₀). Structure calculations of the sample Tm₃₀Cr₁₀Ge₆₀ (Fig. 3, b) showed that the inclusion of Cr atoms in the tetragonal-prismatic voids of the structure (crystallographic position 4*c* 0 *y* 1/4) of the binary germanide TmGe₂ with ZrSi₂-type corresponds to the CeNiSi₂ structure type (space group *Cmcm*, Tm 4*c*, *y* = 0.3948(5); Cr 4*c*, *y* = 0.1683(1); Ge1 4*c*, *y* = 0.0467(1); Ge2 4*c*, *y* = 0.7598(7)). Tm₂₀Cr₂₅Ge₅₅ sample contains main phase TmCr_xGe₂ in equilibrium with TmCr₆Ge₆ compound and Ge (Fig. 2a).

Analysis of the solubility of the third component in the binary compounds of the Tm–Ge and Cr–Ge systems showed that the binary germanide Cr₃Ge (Cr₃Si structure type) dissolves up to ~4 at. % Tm, which is confirmed by the results of EPM analysis and changes of the lattice parameter: *a* = 0.4624(1) nm for Cr₃Ge, *a* = 0.4632(2) nm for sample Tm₄Cr₇₁Ge₂₅. The solubility of the third component in other binary compounds of the Cr–Ge system and in most binary compounds of the Tm–Ge system is less than 2 at. % under the conditions of our

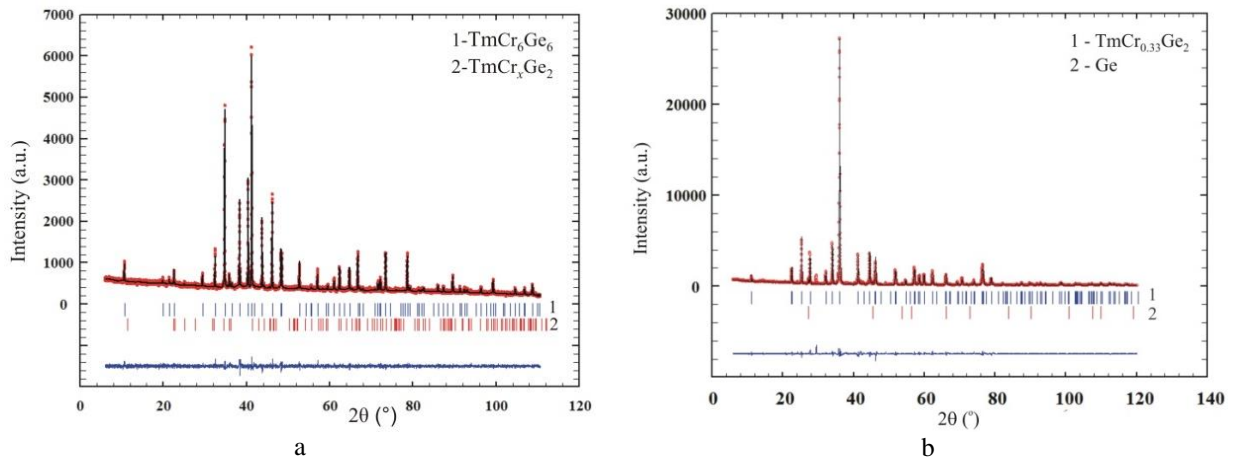


Fig. 3. The experimental (circles), calculated (line) and difference (bottom) X-ray diffraction patterns for $\text{Tm}_8\text{Cr}_{46}\text{Ge}_{46}$ sample (a) and for $\text{Tm}_{30}\text{Cr}_{10}\text{Ge}_{60}$ sample (b)

Table 4

Atomic coordinates, isotropic displacement parameters B_{iso} (nm^2) and site occupancies G in TmCr_6Ge_6 structure.

Atom	Wyckoff position	x/a	y/b	z/c	$B_{\text{iso}} \cdot 10^2$ (nm^2)	G
Tm1	1a	0	0	0	0.92(1)	0.929(4)
Tm11	1b	0	0	1/2	0.92(1)	0.053(3)
Cr	6i	1/2	0	0.2506(2)	0.74(5)	1
Ge1	2e	0	0	0.3474(4)	0.58(6)	1.894(6)
Ge11	2e	0	0	0.1386(2)	0.58(6)	0.071(4)
Ge2	2c	1/3	2/3	1/2	0.86(5)	1
Ge3	2d	1/3	2/3	0	0.52(7)	1

study. According to X-ray phase analysis, ternary alloys in the Tm-Tm₅Ge₃-Cr region of the Tm-Cr-Ge system contain a binary compound Tm₅Ge₃, Tm and Cr, which is consistent with the state diagram of the Tm-Cr system [15].

Analysis of the studied R-Cr-Ge systems (R = Nd, Y, Gd, Er, Tm) and literature data on individual ternary germanides of rare earths with chromium shows the influence of rare earth metal on the number of the formed ternary compounds and the type of their crystal structure. For rare earth metals of the yttrium subgroup the formation of the ternary germanides with stoichiometry RCr_6Ge_6 , which crystallize in the HfFe_6Ge_6 and SmMn_6Sn_6 structure types was observed. The isotopic compound TmCr_6Ge_6 was also found in the studied Tm-Cr-Ge system. RCrGe_3 germanides with BaNiO_3 -type perovskite structure are realized only with rare earth metals of the cerium subgroup. For R = Nd, Sm, Gd, the existence of the $\text{R}_{117}\text{Cr}_{52}\text{Ge}_{112}$ compounds ($\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ structure type) with a giant unit cell ($a \sim 2.9$ nm) was established. According to the results of the currently studied R-Cr-Ge systems, the formation of a new compound $\text{Tm}_4\text{Cr}_4\text{Ge}_7$ is observed only in the investigated Tm-Cr-Ge system.

In contrast to the R-Cr-Ge systems (R = Y, Gd, Er), which are characterized by the formation of ternary phases $\text{RCr}_{1-x}\text{Ge}_2$ crystallized in the CeNiSi_2 -type with defects in

position of the transition metal, in the studied Tm-Cr-Ge system a solid solution of insertion-type TmCr_xGe_2 based on the binary germanide TmGe_2 with ZrSi_2 structure type is formed.

Conclusions

Phase equilibrium diagram of the Tm-Cr-Ge ternary system is constructed at 1070 K. Based on the results of an experimental study of the interaction between the components in the Tm-Cr-Ge system at 1070 K, the formation of two new ternary germanides TmCr_6Ge_6 and $\text{Tm}_4\text{Cr}_4\text{Ge}_7$ was established. Studies of the crystal structure of the TmCr_6Ge_6 compound have indicated that it belongs to the SmMn_6Sn_6 structure type, which is a partially disordered variant of the HfFe_6Ge_6 -type. On the basis of the binary germanide TmGe_2 (ZrSi_2 -type) the formation of an insertion-type solid solution TmCr_xGe_2 up to the limit composition $\text{TmCr}_{0.33}\text{Ge}_2$ was established.

Acknowledgements

We would like to acknowledge financial support of the Ministry of Education and Science of Ukraine under Grant No. 0121U109766.

Romaka Lyubov – Ph.D., Senior Scientist of Ivan Franko National University of Lviv;
Stadnyk Yuriy – Ph.D., Senior Scientist of Ivan Franko National University of Lviv;

Romaka Vitaliy – D.Sc., doctor of material science, Institute for Solid State Research, Dresden, Germany;
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Взаємодія компонентів у системі Tm-Cr-Ge при 1070 К

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Діаграму фазових рівноваг потрійної системи Tm-Cr-Ge побудовано при температурі 1070 К за результатами рентгенофазового, мікроструктурного аналізів та енергодисперсійної рентгенівської спектроскопії в повному концентраційному інтервалі. За температури дослідження в системі утворюються дві нові тернарні сполуки TmCr₆Ge₆ (структурний тип SmMn₆Sn₆, просторова група *P6/mmm*, $a=0.51506(1)$, $c=0.82645(2)$ нм) і Tm₄Cr₄Ge₇ (структурний тип Zr₄Co₄Ge₇, просторова група *I4/mmm*, $a=1.39005(9)$, $c=0.54441(1)$ нм). Включення атомів Cr в структуру бінарного германіду TmGe₂ (структурний тип ZrSi₂) до вмісту 10 ат. % Cr приводить до утворення твердого розчину TmCr_xGe₂ ($x=0-0.33$).

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