PHYSICS AND CHEMISTRY OF SOLID STATE
V. 23, No. 4 (2022) pp. 633-639
Section: Chemistry

DOI: 10.15330/pcss.23.4.633-639

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 23, № 4 (2022) С. 633-639
Хімічні науки

UDC: 546.882

ISSN 1729-4428

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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: $TmCr_6Ge_6$ ($SmMn_6Sn_6$ structure type, space group *P*6/*mmm*, *a*=0.51506(1), *c*=0.82645(2) nm) and $Tm_4Cr_4Ge_7$ ($Zr_4Co_4Ge_7$ structure type, space group *I*4/*mmm*, *a*=1.39005(9), *c*=0.54441(1) nm). Inclusion of Cr atoms in the structure of the binary germanide $TmGe_2$ (structure type $ZrSi_2$) up to 10 at. % Cr leads to the formation of a solid solution $TmCr_xGe_2$ (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 $RCrGe_3$, RCr_6Ge_6 and RCr_xGe_2 compounds.

The study of the physical properties of individual series of compounds of R-Cr-Ge systems, in particular $RCrGe_3$ (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]. $R_{117}Cr_{52}Ge_{112}$ compounds (R = Nd, Sm, Gd) with a giant unit cell (structure type $Tb_{117}Fe_{52}Ge_{112}$, *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 RCr_6Ge_6 (R = Y, Tb−Er) are formed with rare-earth metals of the yttrium subgroup [8, 9], and belong to the $HfFe_6Ge_6$ (or $MgFe_6Ge_6$) structure type. According to the measurements of the magnetic properties the presence of magnetic ordering at low temperatures has been established for RCr_6Ge_6 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 re-melted 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 (Fe$K\alpha$ 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 $K\alpha_1$ 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: Cr_3Ge (Cr_3Si-type), Cr_5Ge_3 (W_5Si_3-type for hight-temperature modification), $Cr_{11}Ge_8$ ($Cr_{11}Ge_8$-type), CrGe (FeSi-type), and $Cr_{11}Ge_{19}$ ($Mn_{11}Si_{19}$-type). Cr_3Ge compound is characterised by homogeneity region. For Cr_5Ge_3 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 Cr_5Ge_3 binary. In our study, the compound with Cr_5Ge_3 stoichiometry was not identified at the temperature of investigation. X-ray phase analysis of the sample with corresponding composition showed two binary compounds Cr_3Ge and $Cr_{11}Ge_8$ in equilibrium.

According to reported phase diagram [14] in the Tm-Ge system at 1070 K binary compounds Tm_5Ge_3 (Mn_5Si_3-type), Tm_5Ge_4 (Sm_5Ge_4-type), $Tm_{11}Ge_{10}$ ($Ho_{11}Ge_{10}$-type), TmGe (TlJ- type), Tm_3Ge_4 (Er_3Ge_4-type), Tm_2Ge_3 (Tm_2Ge_3-type), $TmGe_{1.9}$ ($TmGe_{1.9}$-type), and $TmGe_2$ ($ZrSi_2$- type) exist. Information about the compound $TmCr_3$ ($DyGe_3$-type), which is obtained at high temperature and pressure, and germanide Tm_2Ge_5 (Er_2Gr_5-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 Tm_3Ge_4 compound belongs to the Gd_3Ge_4 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.
			a	*b*	*c*	
$TmGe_2$	*Cmcm*	$ZrSi_2$	0.4004(2)	1.5708(6)	0.3907(1)	This work
Tm_2Ge_3	*C*12/*c*1	Tm_2Ge_3	0.90577	0.66386 β=115.678	0.77596	[19]
Tm_3Ge_4	*Cmcm*	Gd_3Ge_4	0.3987(3)	1.0495(5)	1.4069(5)	This work
TmGe	*Cmcm*	TlJ	0.4189(3)	1.0492(6)	0.3875(5)	This work
$Tm_{11}Ge_{10}$	*I*4/*mmm*	Ho11Ge10	1.0554(5)		1.5899(6)	This work
Tm_5Ge_4	*Pnma*	Sm_5Ge_4	0.7293(3)	1.4417(6)	0.7198(5)	This work
Tm_5Ge_3	*P*6$_3$/*mcm*	Mn_5Si_3	0.8337(3)		0.6231(3)	This work
Cr_3Ge	*Pm*-3*n*	Cr_3Si	0.4624(1)			This work
$Cr_{11}Ge_8$	*Pnma*	$Cr_{11}Ge_8$	1.3171	0.4939	1.5775	[20]
CrGe	*P*2$_1$3	FeSi	0.47971(3)			This work
$Cr_{11}Ge_{19}$	*P*-4*n*2	$Mn_{11}Si_{19}$	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.

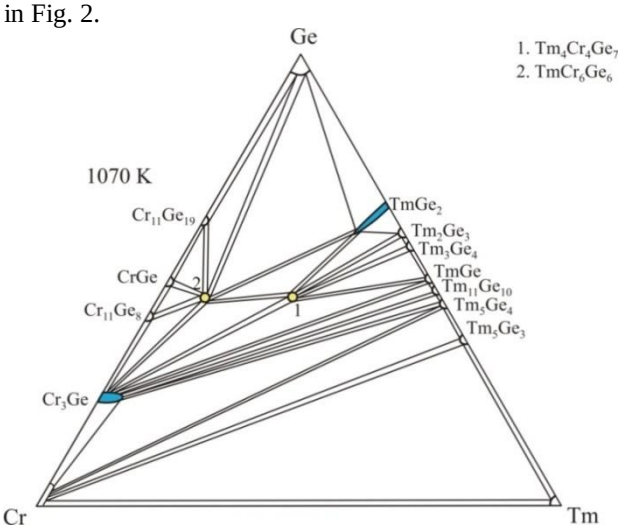


Fig. 1. Isothermal section of the Tm–Cr–Ge system at 1070 K.

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 $Tm_4Cr_4Ge_7$ was established. Crystallographic characteristics of the ternary compounds are given in Table 3.

Analysis of the diffraction pattern of the $Tm_8Cr_{46}Ge_{46}$ sample showed the formation of the $TmCr_6Ge_6$ compound, which is isostructural to the previously studied germanides RCr_6Ge_6 (R=Y, 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 *P*6/*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:
Tm1(1*a*, 0, 0, 0)/Tm11(1*b*, 0, 0, 1/2);
Ge1(2*e*, 0, 0, 0.3474(4))/Ge11(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. %		
			a	*b*	*c*	Tm	Cr	Ge
$Tm_{55}Cr_{15}Ge_{30}$	Tm_5Ge_3	Mn_5Si_3	0.8332(3)		0.6232(3)	62.88	1.16	35.96
$Tm_{53.02}Cr_{15.14}Ge_{31.84}$	(Cr)	W	0.2892(3)				100.0	
$Tm_5Cr_{70}Ge_{25}$	Cr_3Ge	Cr_3Si	0.4632(3)					
	$Tm_{11}Ge_{10}$	$Ho_{11}Ge_{10}$	1.0556(5)		1.5922(4)			
$Tm_{45}Cr_{25}Ge_{30}$	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	
$Tm_{10}Cr_{55}Ge_{35}$	$TmCr_6Ge_6$	$SmMn_6Sn_6$	0.5150(3)		0.8263(4)	7.21	46.45	46.34
$Tm_{11.12}Cr_{54.36}Ge_{34.52}$	Cr_3Ge	Cr_3Si	0.4628(2)			2.74	72.65	24.61
	$Tm_4Cr_4Ge_7$	$Zr_4Co_4Ge_7$	1.3900(5)		0.5444(4)	25.67	26.84	47.49
$Tm_{40}Cr_{20}Ge_{40}$	$Tm_{11}Ge_{10}$	$Ho_{11}Ge_{10}$	1.0554(5)		1.5899(6)	51.72	1.09	47.19
$Tm_{40.49}Cr_{18.95}Ge_{40.56}$	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
$Tm_{15}Cr_{45}Ge_{40}$	Cr_3Ge	Cr_3Si	0.4628(3)			1.87	73.76	24.37
$Tm_{12.91}Cr_{45.60}Ge_{41.49}$	$TmCr_6Ge_6$	$SmMn_6Sn_6$	0.5151(2)		0.8264(3)	7.48	47.26	45.26
	$Tm_4Cr_4Ge_7$	$Zr_4Co_4Ge_7$	1.3901(4)		0.5445(3)	25.53	26.97	47.50
$Tm_5Cr_{50}Ge_{45}$	$TmCr_6Ge_6$	$SmMn_6Sn_6$	0.5150(3)		0.8264(3)	7.62	46.54	45.84
$Tm_{4.93}Cr_{49.60}Ge_{45.47}$	CrGe	FeSi	0.4794(3)				48.93	51.07
	$Cr_{11}Ge_8$	$Cr_{11}Ge_8$	Not determined				56.89	43.11
$Tm_{45}Cr_{10}Ge_{45}$	$Tm_{11}Ge_{10}$	$Ho_{11}Ge_{10}$	1.0555(5)		1.5903(6)		51.72	48.28
$Tm_{44.60}Cr_{10.91}Ge_{44.49}$	TmGe	TlJ	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
$Tm_{25}Cr_{25}Ge_{50}$	$TmCr_{1-x}Ge_2$	$CeNiSi_2$	0.4094(7)	1.5600(7)	0.3982(5)	31.90	9.09	59.01
$Tm_{25.13}Cr_{25.61}Ge_{49.26}$	$TmCr_6Ge_6$	$SmMn_6Sn_6$	0.5150(2)		0.8265(2)	7.82	47.57	44.61
	$Tm_4Cr_4Ge_7$	$Zr_4Co_4Ge_7$	1.3899(4)		0.5444(4)	26.34	27.03	46.63
$Tm_{40}Cr_{10}Ge_{50}$	Tm_3Ge_4	Gd_3Ge_4	0.3979(4)	1.0492(6)	1.4054(6)	43.59		56.41
$Tm_{39.81}Cr_{11.04}Ge_{49.15}$	TmGe	TlJ	0.4189(3)	1.0492(6)	0.3875(5)	49.33		50.67
	$Tm_4Cr_4Ge_7$	$Zr_4Co_4Ge_7$	1.3900(5)		0.5444(5)	26.90	26.27	46.83
$Tm_{20}Cr_{25}Ge_{55}$	$TmCr_6Ge_6$	$SmMn_6Sn_6$	0.5150(2)		0.8265(2)	7.95	44.84	47.21
$Tm_{18.87}Cr_{24.04}Ge_{57.09}$	$TmCr_{1-x}Ge_2$	$CeNiSi_2$	0.4093(1)	1.5598(2)	0.3984(1)	29.63	10.51	59.86
	(Ge)	(C)	0.5649(4)					100.00
$Tm_{20}Cr_{20}Ge_{60}$	$TmCr_6Ge_6$	$SmMn_6Sn_6$	0.5151(3)		0.8265(4)	7.53	45.36	47.11
$Tm_{18.92}Cr_{21.03}Ge_{60.05}$	$TmCr_{1-x}Ge_2$	$CeNiSi_2$	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		
				a	*b*	*c*
1	$Tm_4Cr_4Ge_7$	$Zr_4Co_4Ge_7$	*I4/mmm*	1.39005(9)	–	0.54441(1)
2	$TmCr_6Ge_6$	$SmMn_6Sn_6$	*P6/mmm*	0.51506(1)	–	0.82645(2)

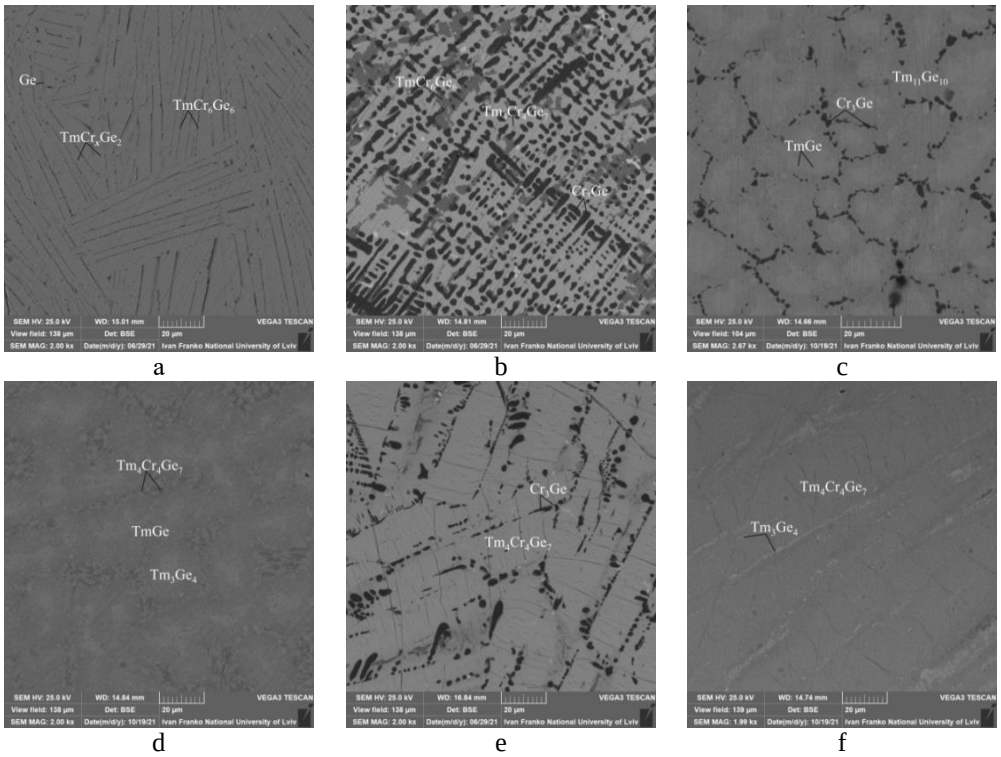


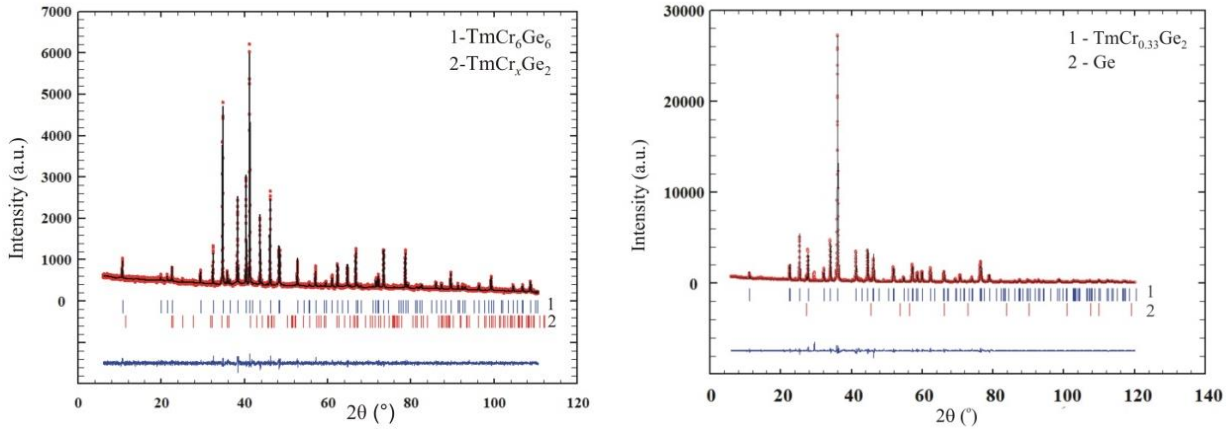
Fig. 2. Electron microphotographs of the Tm–Cr–Ge alloys:$Tm_{20}Cr_{25}Ge_{55}$ (a), $Tm_{10}Cr_{55}Ge_{35}$ (b), $Tm_{45}Cr_{10}Ge_{45}$ (c), $Tm_{40}Cr_{10}Ge_{50}$ (d), $Tm_{20}Cr_{40}Ge_{40}$ (e), $Tm_{37}Cr_{10}Ge_{53}$ (f).

experimental, calculated and difference X-ray diffraction patterns for $Tm_8Cr_{46}Ge_{46}$ 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 ~$Tm_{27}Cr_{27}Ge_{46}$ 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 $Tm_{27}Cr_{27}Ge_{46}$ and the calculated lattice periods (a =1.39005 (9), c = 0.54441 (1) nm) indicated that the compound belongs to the $Zr_4Co_4Ge_7$ structure type (space group *I4/mmm*). Sample $Tm_{10}Cr_{55}Ge_{35}$ contains $TmCr_6Ge_6$, $Tm_4Cr_4Ge_7$ compounds and Cr_3Ge binary in equilibrium (Fig. 2b).

According to the literature data [23] formation of the ternary germanides RCr_xGe_2 with $CeNiSi_2$ 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 $TmGe_2$ crystallizes in the $ZrSi_2$-type and, in the ternary part inclusion of Cr atoms results in formation of the $TmCr_xGe_2$ solid solution up to Cr content ~10 at. %. Solubility limit of Cr in the $TmCr_2$ 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 nm^3 for $TmGe_2$ to V = 0.2544 nm^3 for the sample $Tm_{30}Cr_{10}Ge_{60}$). Structure calculations of the sample $Tm_{30}Cr_{10}Ge_{60}$ (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 $TmGe_2$ with $ZrSi_2$-type corresponds to the $CeNiSi_2$ 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)). $Tm_{20}Cr_{25}Ge_{55}$ sample contains main phase $TmCr_xGe_2$ in equilibrium with $TmCr_6Ge_6$ 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 Cr_3Ge (Cr_3Si 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 Cr_3Ge, a = 0.4632(2) nm for sample $Tm_4Cr_{71}Ge_{25}$. 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



a b

Fig. 3. The experimental (circles), calculated (line) and difference (bottom) X-ray diffraction patterns for $Tm_8Cr_{46}Ge_{46}$ sample (a) and for $Tm_{30}Cr_{10}Ge_{60}$ 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*	$B_{iso.}\cdot 10^2$ (nm^2)	*G*
Tm1	1*a*	0	0	0	0.92(1)	0.929(4)
Tm11	1*b*	0	0	1/2	0.92(1)	0.053(3)
Cr	6*i*	1/2	0	0.2506(2)	0.74(5)	1
Ge1	2*e*	0	0	0.3474(4)	0.58(6)	1.894(6)
Ge11	2*e*	0	0	0.1386(2)	0.58(6)	0.071(4)
Ge2	2*c*	1/3	2/3	1/2	0.86(5)	1
Ge3	2*d*	1/3	2/3	0	0.52(7)	1

study. According to X-ray phase analysis, ternary alloys in the Tm-Tm_5Ge_3-Cr region of the Tm-Cr-Ge system contain a binary compound Tm_5Ge_3, 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 isotypic 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 $R_{117}Cr_{52}Ge_{112}$ compounds ($Tb_{117}Fe_{52}Ge_{112}$ structure type) with a giant unit cell (*a*~2.9 nm) was established. According to the results of the currently studied R–Cr–Ge systems, the formation of a new compound $Tm_4Cr_4Ge_7$ 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 $RCr_{1-x}Ge_2$ 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 $Tm_4Cr_4Ge_7$ 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 $TmCr_{0.33}Ge_2$ 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;
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[1] P. S. Salamakha, Crystal structures and crystal chemistry of ternary rare-earth germanides, in: K.A. Gschneidner, Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare-Earths, 27, North-Holland, Amsterdam, 1999, pp. 225–338.
[2] M. Konyk, L. Romaka, L. Orovčik, V.V. Romaka, Yu. Stadnyk, Y-Cr-Ge ternary system at 1070 K, Visnyk Lviv. univ. Ser. Chem. 60(1), 38 (2019); https://doi.org/10.30970/vch.6001.038.
[3] P.S. Salamakha, Y.M. Prots, The neodymium-(vanadium, chromium, manganese)-germanium systems, J. Alloys Compd. 215, 51 (1994); https://doi.org/10.1016/0925-8388(94)90817-6.
[4] M. Konyk, L. Romaka, Yu. Stadnyk, V.V. Romaka, Isothermal section of the Gd-Cr-Ge system at 1070 K, XVIII scient. Conf. "Lviv chemical reading-2021", Lviv, 31 may-2 julay, 2021. H9 (2021).
[5] M. Konyk, L. Romaka, V.V. Romaka, Yu. Stadnyk, P. Demchenko, A. Horyn, Isothermal section at 8000C of the phase diagram of the Er-Cr-Ge ternary system, Coll. Abs. XIV Int. Conf. Cryst. Chem. Interm. Compd. September 22-26, 2019. Lviv, Ukraine, 61 (2019).
[6] H. Bie, O.Ya. Zelinska, A.V. Tkachuk, A. Mar, Structure and physical properties of rare-earth chromium germanides $RECrGe_3$ (RE=La-Na, Sm), Chem. Mater. 19, 4613 (2007); https://doi.org/10.1021/cm071276+.
[7] A.V. Morozkin, Y.D. Seropegin, V.K. Portnov, I.A. Sviridov, A.V. Leonov, New ternary compounds $R_{117}Fe_{52}Ge_{112}$ (R=Gd, Dy, Ho, Er, Tm) and $Sm_{117}Cr_{52}Ge_{112}$ of the $Tb_{117}Fe_{52}Ge_{112}$-type structure, Mater. Res. Bull. 33, 903 (1998); https://doi.org/10.1016/S0025-5408(98)00051-8.
[8] J.H.V.J. Brabers, K.H.J. Buschow, F.R. de Boer, Magnetic properties of RCr_6Ge_6 compounds, J. Alloys Compd. 77, 205 (1994); https://doi.org/10.1016/0925-8388(94)90769-2.
[9] P. Schobinger-Papamantelljsa, J. Rodriguez-Carvajalb, K.H.J. Buschow, Ferrimagnetism and disorder in the RCr_6Ge_6 compounds (R=Dy, Ho, Er, Y): a neutron study, J. Alloys Compd. 92, 256 (1997); https://doi.org/10.1016/S0925-8388(96)03109-X.
[10] P. Schobinger-Papamantellos, J. Rodriguez-Carvajal, K.H.J. Buschow, Atomic disorder and canted ferrimagnetism in the $TbCr_6Ge_6$ compound. A neutron study, J. Alloys Compd. 67, 255 (1997); https://doi.org/10.1016/S0925-8388(96)02872-1.
[11] W. Kraus, G. Nolze, POWDER CELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns, J. Appl. Crystallogr. 29, 301 (1996); https://doi.org/10.1107/S0021889895014920.
[12] L. Akselrud, Yu. Grin. WinCSD: software package for crystallographic calculations (Version 4). J. Appl. Crystallogr. 47, 803 (2014); https://doi.org/10.1107/S1600576714001058.
[13] T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows tool for powder diffraction patterns analysis, Mater. Sci. Forum, 378–381, 118 (2001); https://doi.org/10.4028/www.scientific.net/MSF.378-381.118.
[14] T.B. Massalski, Binary Alloy Phase Diagrams, ASM, Metals Park, Ohio (1990).
[15] H Okamoto. Desk Handbook: Phase Diagrams for Binary Alloys, Materials Park (OH): ASM (2000).
[16] H. Fukuoka, M. Yoshikawa, K. Baba, S. Yamanaka, Preparation and structures of lanthanoid germanides, $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$ with double square Ge mesh structures, Bull. Chem. Soc. Jpn., 83, 323 (2010); https://doi.org/10.1246/bcsj.20090310.
[17] G. Venturini, Orthorhombic $TmGe_{\approx 1.9}$, with a $ZrSi_2$-$ErGe_{1.83}$ intergrowth structure, J. Alloys Compd., 308, 200 (2000); doi.org/10.1016/S0925-8388(00)00895-1.
[18] P.H. Tobash, G. DiFilippo, S. Bobev, N. Hur, J.D. Thompson, J.L. Sarrao, Structure and properties of Gd_3Ge_4. The orthorhombic RE_3Ge_4 structures revisited (RE=Y, Tb-Tm), Inorg. Chem., 46, 8690 (2007); https://doi.org/10.1021/ic7009034.
[19] G. Venturini, I. Ijjaali, B. Malaman, Vacancy ordering in AlB_2-type RGe_{2-x} compounds (R=Y, Nd, Sm, Gd-Lu), J. Alloys Compd., 284, 262 (1999); https://doi.org/10.1016/S0925-8388(98)00958-X.
[20] P. Israiloff, H. Vollenkle, A. Wittmann, The crystal structure of the compounds $V_{11}Ge_8$, $Cr_{11}Ge_8$, and $Mn_{11}Ge_8$, Monatsh. Chem., 105, 1387 (1974); https://doi.org/10.1007/BF00909876.
[21] M. Kolenda, J. Stoch, A. Szytula, Esca and magnetic studies of the Cr-Ge system, J. Magn. Magn. Mater., 20, 99 (1980); https://doi.org/10.1016/0304-8853(80)90532-6.
[22] B. Malaman, G. Venturini, B. Chafik El Idrissi, E. Ressouche, Magnetic properties of $NdMn_6Sn_6$ and $SmMn_6Sn_6$ compounds from susceptibility mesurements and neutron diffraction study, J. Alloys Compd., 252, 41 (1997); https://doi.org/10.1016/S0925-8388(96)02717-X.
[23] H. Bie, A.V. Tkachuk, A. Mar, Structure and magnetic properties of rare-earth chromium germanides $RECr_xGe_2$ (RE=Sm, Gd-Er), J. Solid State Chem. 182, 122 (2009); https://doi.org/10.1016/j.jssc.2008.10.013.

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Взаємодія компонентів у системі Tm-Cr-Ge при 1070 K

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Діаграму фазових рівноваг потрійної системи Tm–Cr–Ge побудовано при температурі 1070 K за результатами рентгенофазового, мікроструктурного аналізів та енергодисперсійної рентгенівської спектроскопії в повному концентраційному інтервалі. За температури дослідження в системі утворюються дві нові тернарні сполуки $TmCr_6Ge_6$ (структурний тип $SmMn_6Sn_6$, просторова група *P*6/*mmm*, *a*=0.51506(1), *c*=0.82645(2) нм) і $Tm_4Cr_4Ge_7$ (структурний тип $Zr_4Co_4Ge_7$, просторова група *I*4/*mmm*, *a*=1.39005(9), *c*=0.54441(1) нм). Включення атомів Cr в структуру бінарного германіду $TmGe_2$ (структурний тип $ZrSi_2$) до вмісту 10 ат. % Cr приводить до утворення твердого розчину $TmCr_xGe_2$ (*x*=0-0.33).

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