Fragments of isothermal sections of the Gd-Ge(Si)-Ga systems phase diagrams at 800^{0}C

Golovataya N.V., Markiv V.Ya., Belyavina N.M.

Taras Shevchenko University, 64/13, Volodymyrska str., 01601, Kyiv, Ukrain,

nata.hoff@mail.ru

The Gd-rich alloys of the Gd-Ge(Si)-Ga systems have been studied by the X-ray powder diffraction. The parts of the isothermal sections of these systems (800 ^{0}C, up to 33.3 at. % Gd) have been constructed. Four ternary compounds were found to exist here, namely, 1-$GdGe_{1.0-0.7}Ga_{1.0-1.3}$ (α-$ThSi_2$-type structure), 2-$Gd_{11}Ge_9Ga_1$ ($Ho_{11}Ga_{10}$), 1-$GdSi_{0.9-0.6}Ga_{1.1-1.4}$ (α-$ThSi_2$) and 2-$GdSi_{0.9-0.6}Ga_{0.1-0.4}$ (CrB). One of these compounds (2-$Gd_{11}Ge_9Ga_1$) is in fact the Ga-stabilized solid solution on the base of the high temperature $Gd_{11}Ge_{10}$ compound. Extended solid solutions on the base of the most Gd-{Si,Ge,Ga} binary compounds was shown to form in the Gd-Ge(Si)-Ga systems.

Introduction

Creation of a new gadolinium-containing functional materials is based on an experimental study of the appropriate multicomponent phase diagrams (their isothermal sections), as well as on a study of the crystal structures and physical properties of the synthesized first intermetallic compounds. Taking into account that Gd_5Ge_4 and Gd_5Si_4 compounds possess a giant *magnetocaloric* effect here we present results of determining the phase equilibria in the Gd–Ge–Ga and Gd–Si–Ga ternary systems (800^{0}C, 33.3–100 at. % Gd).

The Gd–Ge, Gd–Ga and Gd-Si basal phase diagrams have been studied well in Refs. [1-7]. These systems are characterized by existing of numerous compounds (Tab. 1). The Ge-Ga and Si-Ga systems are eutectic type [8, 9] and they do not contain intermetallics.

Experimental part

173 Gd-rich alloys (80 in the Gd-Ge-Ga system and 93 in the Gd-Si-Ga system) were prepared by the arc melting of gadolinium (99.85 wt. %), germanium (99.999%), silicium (99.99%) and gallium (99.999%) under purified argon atmosphere. The ingots were remelted several times in order to ensure perfect homogeneity. After arc melting the samples were wrapped into the molybdenum foil, sealed in the evacuated quartz tubes and annealed at 800 °C for 1400 h.

The X-ray powder diffraction data were collected with a DRON-3 automatic diffractometer (Cu$K\alpha$ radiation) [10]. The diffraction patterns were obtained in a discrete mode under the following scanning parameters: the observation range 2θ was 20–85°, the step scan was 0.05°, the counting time per step was 5 s (for phase analyses) and

Table 1.

Crystal structure data for binary system compounds.

Phase	Temperature (^{0}C) and mode of formation	Structure type	Lattice constants, nm			Ref.
			a	*b*	*c*	
		Gd-Ge system				
Gd_5Ge_3	1790, *L* [1)]	Mn_5Si_3	0.858	-	0.645	[1]
Gd_5Ge_4	1690, *P*	Sm_5Ge_4	0.769	1.475	0.776	[1]
$Gd_{11}Ge_{10}$	-	$Ho_{11}Ge_{10}$	1.093	-	1.667	[3]
GdGe	1570, *P*	CrB	0.433	1.079	0.398	[1]
γ-Gd_2Ge_3	1415, *P*	-	-	-	-	[1]
β-Gd_2Ge_3	1210-1070, *S*	-	-	-	-	[1]
α-Gd_2Ge_3	833, *S*	AlB_2	0.3973	-	0.4179	[1]
β-Gd_3Ge_5	808, *Pd*	α-$GdSi_2$	0.4130	0.4096	1.376	[4]
α-Gd_3Ge_5	<600, *S*	α-$ThSi_2$	0.412	-	1.372	[1]
$GdGe_2$	-	RGe_2	0.8047	0.8270	1.498	[5]
$GdGe_{2.57}$	890-850, *P*	$YGe_{3.5}$	2.093	0.410	0.394	[1]
		Gd-Si system				
Gd_5Si_3	1748, *P*	Mn_5Si_3	0.8503	-	0.6401	[6]
Gd_5Si_4	1774, *P*	Sm_5Ge_4	0.7500	1.4730	0.7749	[6]
GdSi	1835, *L*	FeB	0.7980	0.3854	0.5749	[6]
β-$GdSi_{1.5}$	1625, *P*	-	-	-	-	[6]
α-$GdSi_{1.5}$	700, *S*	AlB_2	0.6869	-	0.4173	[6]
β-$GdSi_{2-x\ x=0.28-0.11}$	1590, *P*	α-$ThSi_2$	0.4100	-	1.361	[6]
α-$GdSi_{2-x\ x=0.28-0.11}$	425-700, *S*	α-$GdSi_2$	0.4067-0.40808	0.39966-0.40041	1.3482-1.3442	[6]
		Gd-Ga system				
Gd_5Ga_3	1090, *P*	Cr_5B_3	0.7726	-	1.4170	[7]
Gd_3Ga_2	1110, *P*	Gd_3Ga_2	1.1666	-	1.5061	[7]
GdGa	1195, *P*	CrB	0.4337	1.0977	0.4104	[7]
$GdGa_2$	1400, *L*	AlB_2	0.4224-0.4270	-	0.4140-0.4210	[7]
$GdGa_6$	405, *P*	$PuGa_6$	0.5946	-	0.7601	[7]

[1)] Phases are formed from liquid (*L)*, as a result of peritectic reaction (*P),* formation in solid state (*S).*

the observation range 2θ was 20–125°, the step scan was 0.02°, the counting time per step was 8 s (for crystal structure investigation). The peak positions and integral intensities of the observed reflections were determined using the full profile analysis. After removal of the Cu$K\alpha_2$ components the diffraction profiles were fitted by the Lorentz function. The peak positions and integral intensities have been calculated with accuracy no less than ±(0.001–0.005)° and ±(5–10)%, respectively.

In order to determine the phase compositions and to refine the lattice constants of the identified phases we used the original software program packages with special banks for the X-ray diffraction data and for the crystal structures of intermetallic and inorganic compounds [10]. The tests of the trial structure models and the structural parameter refinements (including texture [11]) were carried out using original software [10], too.

Results and discussion

As a result of the X-ray phase analysis four ternary intermetallic compounds were found to exist in the alloys annealed at 800°C of the Gd-Ge-Ga and Gd-Si-Ga systems. Two of them (1-$GdGe_{1.0-0.7}Ga_{1.0-1.3}$ and 1-$GdSi_{0.9-0.6}Ga_{1.1-1.4}$) contained 33.3 at. % Gd. Both these compounds have extended homogeneity ranges: from 34 to 43 at. % Ga for 1-$GdGe_{1.0-0.7}Ga_{1.0-1.3}$ and from 37 to 47 at. % Ga for 1-$GdSi_{0.9-0.6}Ga_{1.1-1.4}$. The 2-$Gd_{11}Ge_9Ga_1$ compound had a very narrow homogeneity range and contained 52.4 at. % Gd. The 2-$GdSi_{0.9-0.5}Ga_{0.1-0.5}$ compound was found to contain 50 at. % Gd and extend from 3 to 25 at. % Ga.

The diffraction patterns of the 1-$GdSi_{0.88}Ga_{1.12}$ and 1-$GdGe_{0.71}Ga_{1.29}$ compounds are similar each other. Considering that crystal structure of the 1-$GdGe_{0.71}Ga_{1.29}$ phase was shown to belong to the α-$ThSi_2$-type structure (a=0.4154 nm, c=1.4440 nm) [12], the diffraction pattern of the 1-$GdSi_{0.88}Ga_{1.12}$ compound has been also indexed well by the tetragonal unit cell (a=0.41269(4) nm, c=1.4295(1) nm). Taking into account both obtained values of the lattice constants and peculiar arrangement of the diffraction peaks, α-$ThSi_2$-type structure has been selected as a trial model for the 1-$GdSi_{0.88}Ga_{1.12}$ phase. The crystal structure refinement in this model has led to a good agreement of the observed and calculated intensities at the X-ray pattern. The final results for the crystal structure of the 1-$GdSi_{0.88}Ga_{1.12}$ compound are: space group $I4_1/amd$, 4 Gd in 4(a) 0 3/4 1/8; (3.52Si+4.48Ga) in 8(e) 0 3/4 z with z=0.5433(4). The reliability factor R_I=0.07 for 75 independent reflections.

The diffraction patterns of the ternary 2-$GdSi_{0.9-0.5}Ga_{0.1-0.5}$ and binary GdGa (Tab. 1) compounds are mutually similar. Proceeding from this fact, CrB-type structure has been suggested for the 2-$GdSi_{0.8}Ga_{0.2}$ phase. So, the pattern of this compound has been indexed well by orthorhombic cell with a=0.4313(1) nm, b=1.0679(4) nm, c=0.3883(1) nm as well as their crystal structure has been successfully refined in a frame of the CrB-type model.

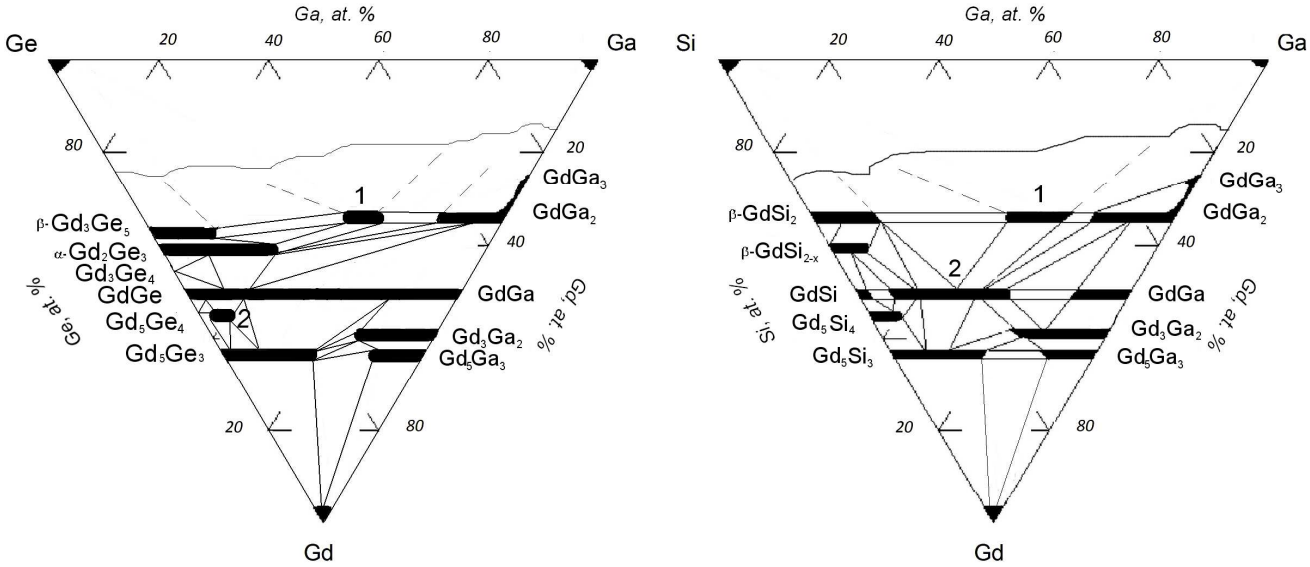
The final results for the 2-$GdSi_{0.8}Ga_{0.2}$ compound are: space group $Cmcm$, 4 Gd in 4(c) 0 y 1/4 with y=0.1388(8); (3.2 Si+0.8 Ga) in 4(c) 0 y 1/4 with y=0.436(2). The reliability factor for 44 independent reflections is equal to 0.045. It should be noted that although the GdGa and 2-$GdSi_{0.9-0.5}Ga_{0.1-0.5}$ compounds was found to be

isostructural the two-phase region has been fixed between them.

The crystal structure of the 2-$Gd_{11}Ge_9Ga_1$ phase belongs to the $Ho_{11}Ge_{10}$-type structure. This phase in fact is a Ga-stabilized solid solution on the base of the high-temperature $Gd_{11}Ge_{10}$ binary compound (Tab. 1).

The partial isothermal sections (800^0C) of the Gd-Ge(Si)-Ga systems constructed on the basis of the obtained results are shown at Fig. 1.

Formation of the extended solid solutions on the base of the Gd-{Si,Ge,Ga} binary systems was shown to be a distinctive feature of the studied ternary systems. These solid solutions are placed along the isoline corresponding to the gadolinium content in the binary compounds and possess the extending homogeneity regions. A continuous solid solution forms between the isostructural GdGa and GdGe compounds in the Gd-Ge-Ga system. It was found that solubility of gallium (at. %) in the β-Gd_3Ge_5, α-Gd_2Ge_3, Gd_5Ge_3, α-$GdSi_{1.5}$ and α-$GdSi_{2-x}$ compounds was 20, 27, 10, 5 and 15, respectively. Gd_5Ga_3, Gd_3Ga_2 and $GdGa_2$ dissolve 7, 12.5 and 13 at. % Ge (Gd-Ge-Ga system) or 12, 16 and 19 at. % Si (Gd-Si-Ga system). The GdGa compound dissolves 15 at. % Si.



a) b)

Fig. 1. Partial isothermal sections of the phase diagrams of Gd-Ge-Ga (a) and Gd-Si-Ga (b) systems at 800^0C.

Conclusions

The performed study of the alloys annealed at 800°C of the Gd-Ge(Si)-Ga systems reveal the existence of four ternary compounds, namely, 1-$GdGe_{1.0-0.7}Ga_{1.0-1.3}$ (α-$ThSi_2$-type structure), 2-$Gd_{11}Ge_9Ga_1$ ($Ho_{11}Ga_{10}$), 1-$GdSi_{0.9-0.6}Ga_{1.1-1.4}$ (α-$ThSi_2$) and 2-$GdSi_{0.9-0.6}Ga_{0.1-0.4}$ (CrB). Three of these compounds possess the extending homogeneity regions. Most of the binary compounds of the Gd-{Ge,Si,Ga} basal systems dissolve the third component (Ga, Si or Ge) and form extended solid solutions.

As a result the partial isothermal sections (800°C) of the Gd–Ge(Si)–Ga systems including mentioned above ternary compounds and solid solutions have been constructed. It can be seen that studied systems are similar each other on the compositions and crystal structures of the compounds and solid solutions. Moreover, they are also similar to the RE-Ge(Si)–Ga systems studied by authors [13].

References

[1] V.N. Eremenko, B.G. Batalin, Yu.I. Buyanov, I.M.Obushenko, *Poroshk. Metall*. **1980**, 2, 40-45, in Russian.

[2] A.B. Gokhale, G.J. Abbaschian, *Bull. Alloy Phase Diagr.* **1989**, 10(2), 147-152.

[3] A.G. Tharp, G.S. Smith, Q. Johnson *Acta Crystall.* **1966,** 20(4), 583-585.

[4] E.I. Gladyshevsky, V.V. Burnashova *Izv. AN USSR. Neorg. Mat*. **1965,** 1(1), 1508-1512, in Russian.

[5] K. Sekizawa *J. Phys. Soc. Jpn*. **1966**, 21(6), 1137-1142.

[6] H. Okamoto *J .of Phase Eq. and Diff*. **2009**, 30(2), 213-214.

[7] A. Palenzona, S. Cirafici *Bull. Alloy Phase Diagr.* **1990**, 11(1), 57-72.

[8] R. W. Olesinski, N. Kanani, G. J. Abbaschian *Bull. Alloy Phase Diagr*. **1985**, 6(4), 362-364.

[9] R. W. Olesinski, G. J. Abbaschian *Bull. Alloy Phase Diagr* **1985**, 6(3), 258-262.

[10] V. Markiv, N. Belyavina, in: *Proceedings of the Second International Scientific Conference of Engineering and Functional Materials*, EFM997, Lviv, 14–16 October, **1997**, 260.

[11] V.K. Pecharsky, L.G. Akselrud, *Krystallografiya* **1987**, 32, 874, in Russian.

[12] G. Venturini, A. Verniere *J. All. and Comp.* **2000**, 305, 7-13.

[13] Ya.O. Tokaychuk *Thesis for a degree of Candidate of Sciences in Chem., 02.00.01- Inorg.Chem., Ivan Franko National University of Lviv*, **2004**.