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Isothermal section of the Ho–Fe–Ga ternary system at 773 K

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ABSTRACT

The isothermal section of the Ho–Fe–Ga ternary phase diagram at 773 K was constructed based on X-ray powder diffraction analysis. Fourteen binary compounds and twelve ternary compounds have been confirmed: Ho_2Fe_{17} Ho_6Fe_{23}, $HoFe_3$, $HoFe_2$, $HoGa_3$, $HoGa_2$, Ho_3Ga_5, HoGa, Ho_3Ga_2, Ho_5Ga_3, Fe_3Ga, Fe_6Ga_5, Fe_3Ga_4, $FeGa_3$, κ_1-$HoFe_{6.02-5.24}Ga_{5.98-6.76}$, κ_2-$HoFe_{4.98-4.59}Ga_{7.02-7.41}$, κ_3-$HoFe_{17-14.07}Ga_{0-2.93}$, κ_4-$HoFe_{13.39-8.45}$ $Ga_{3.61-8.55}$, κ_5-Ho_2FeGa_8, κ_6-$HoFe_{3-2.52}Ga_{0-0.48}$, κ_7-$HoFe_{2.36-1.91}Ga_{0.64-1.09}$, κ_8-Ho_2FeGa_8, κ_9-$HoFe_{2-1.46}$ $Ga_{0-0.54}$, κ_{10}-$HoFe_{1.28-1.16}Ga_{0.72-0.84}$, κ_{11}-$HoFe_{0.43-0.34}Ga_{1.57-1.66}$, and κ_{12}-$HoFe_{0.26-0.19}Ga_{1.74-1.81}$. The maximum solid solubilities of Ga in $HoFe_2$, $HoFe_3$ and Ho_2Fe_{17} were determined to be 18.1, 11.9 and 15.4 at.%, respectively. The structures of the ternary compounds were refined by Rietveld refinement method. It was shown that all the solid solutions in the ternary system are formed by random distribution of Ga and Fe on the transition metal sites.

1. Introduction

Element substitution of rare earth (R) or transition metal (T) in R–T compounds is one of the effective ways to improve the magnetic properties of materials [1]. Owing to the unique interactions of gallium with the R and T atoms in R–T alloys, the crystal structure, Curie temperature and other magnetic properties of R–T–Ga compounds depend strongly on the gallium concentration. For example, the Curie temperatures (T_c) of $R_2Fe_{17-x}Ga_x$ (R = Y, Sm Gd, Tb, Ho and Tm) varied significantly with the Ga concentration [2]. Systematic studies showed that the phase relations and structural characteristics of $R_2Fe_{17-x}Ga_x$ (R = Rare earth) compounds depend strongly on the Ga content. With increasing Ga content, a structural transformation from the hexagonal Th_2Ni_{17}-type structure to the rhombohedral Th_2Zn_{17}-type structure was observed in $R_2Fe_{17-x}Ga_x$. The Curie temperature of the compound increased firstly with the Ga concentration, reached a maximum value and then decreased. The exchange interaction in $R_2Fe_{17-x}Ga_x$ with different Ga concentration varied between Fe atoms, but almost unchanged between R atom and Fe atom [3]. In addition, the compounds $RFe_{12-x}Ga_x$ derived from the $ThMn_{12}$-type structure, such as RFe_6Ga_6, can be stabilized by the addition of Ga to the R–Fe binary systems [4].

The phase diagrams of the Ho–Co–Ga, Sm–Co–Ga, Er–Fe–Ga and Sc–Fe–Ga ternary systems show that there are rich ternary compounds with various structures in R–Co (Fe)–Ga ternary systems [5]. However, there are also some inconsistent reports on the stability of the compounds and the phase relations of the systems involving gallium. For Ho–Ga binary system, two binary compounds Ho_3Ga_2 (Gd_3Ga_2 -type) [6] and Ho_3Ga_5 (Tm_3Ga_5 -type) [7] was reported, but the Ho_3Ga_2 was not shown while the Ho_3Ga_5 was speculative drawn with dot line in the Ho–Ga phase diagram in Ref. [8]. Although the isothermal section of the Ho–Fe–Ga ternary system at 870 K has been reported by Raghavan [9], there still exists some unreasonable issues regarding the existence of the compounds and phase boundaries. For instance, it is unreasonable for the coexistence of the solid solution of $HoFe_{0.1-0.2}Ga_{2.9-2.8}$ (τ_4) and the compound $HoGa_3$ with the same cubic $AuCu_3$- type structure (S.G, *Pm*-3*m*) at the same temperature. The compounds R_4FeGa_{12} (R = Y, Er, Ho, Dy and Tb), with a cubic $U_4Fe_6Ga_7$-type structure, in some R–Fe–Ga system were reported recently [9,10], but the compound Ho_4FeGa_{12} was not shown in the isothermal section at 870 K reported by Raghavan et al. [9]. Therefore, the structure and the composition of $Ho(Fe,Ga)_3$(τ_4) warrants a further confirmation. In addition, it was reported that the structure of $R(Fe,Ga)_{12}$ (R = Gd, Tb) [11,12] compound transformed from $ThMn_{12}$-type structure (S.G. *I*4/*mmm*) to $ScFe_6Ga_6$-type structure (*Immm*) with the decrease of the gallium content at 773 K, whereas the $ScFe_6Ga_6$ type structure of $HoFe_{5.9}Ga_{6.1}$ compound was stable up to 1073 K [13]. However, the isothermal section of Ho–Fe–Ga at 870 K showed that the $HoFe_{12-x}Ga_x$ crystallized in the $ThMn_{12}$-type structure within the whole homogeneity range without any change in structure. A series of isothermal sections at 773 K of R–Fe–Ga tenary system, such as Tb–Fe–Ga [11], Nd–Fe–Ga [14] and Gd–Fe–Ga [12], have been determined by our group. In the Ho–Fe–Ga system, the compounds Ho_2FeGa_8 and Ho_4FeGa_{12} are heavy fermion materials. Constructing the isothermal section of Ho–Fe–Ga at 773 K will be helpful for exploring new ternary compounds,designing novel magnetic func-

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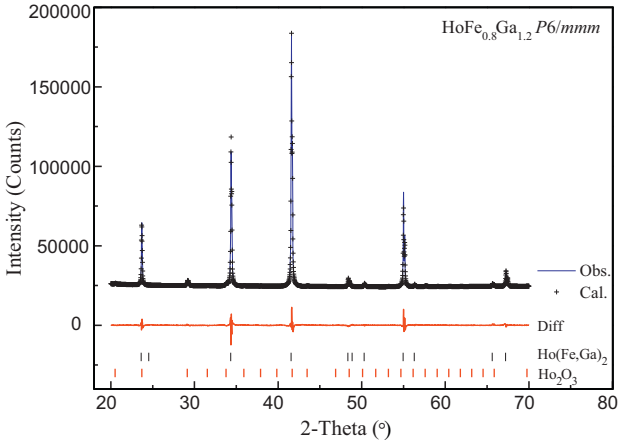

Fig. 1. XRD Rietveld refinement result of the compound $HoFe_{0.2}Ga_{1.8}$ at 773 K.

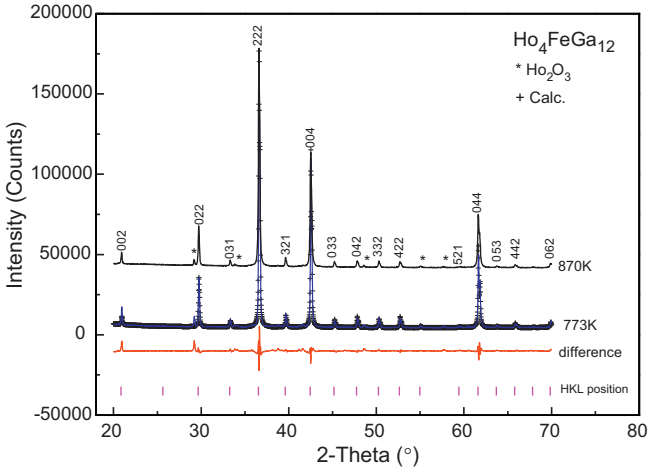

Fig. 3. XRD Rietveld refinement result of the compound Ho_4FeGa_{12}.

tional materials, and for crystal growth of the compounds, etc. It also helps to answer the questions mentioned above.

2. Experimental procedure

Polycrystalline Ho–Fe–Ga alloys were prepared by arc melting technique using a non-consumable tungsten electrode and a water-cooled copper tray in pure argon atmosphere. The holmium, iron and gallium metals with purity higher than 99.9% were used as starting materials. Titanium was used as an oxygen getter during the melting process. The alloys were re-melted at least three times to ensure complete fusion and composition homogeneity. The melted buttons were sealed in evacuated quartz tubes, in which titanium chips were placed as an oxygen getter, and then put in a resistance furnace for homogenization annealing. The homogenization annealing was performed at 1123 K for 20 days for the Fe-rich alloys with Ho less than 20 at.% and Ga less than 55 at.%, while at 873 K for 20 days for other alloys. The alloys were cooled from their homogenization temperatures to 773 K, and then kept at 773 K for 5 days followed by quenching in liquid nitrogen. About 170 samples in total were prepared in this work. X-ray powder diffraction (XRD) data were collected by a Bruker D8 Advance SS/18 kW diffractometer with CuKα radiation. JADE 5.0 and Topas 3.0 software were used for phase analysis and structure refinement.

3. Results and discussion

3.1. Phase analysis

X-ray diffraction analysis in the present study confirmed the existence of fourteen binary compounds in the Ho–Fe–Ga ternary system at 773 K, which is in good agreement with the reports on the related binary phase diagrams in Ref. [8] except for the Ho_3Ga_2 and Ho_3Ga_5 in Ho–Ga binary system. The XRD pattern of the alloy with composition of $Ho_{54}Ga_{46}$ (in at.%) consists of the patterns of Ho_3Ga_2, HoGa and a small amount of Ho_2O_3, instead of those for Ho_5Ga_3 and HoGa phases. The trace amount of Ho_2O_3 may be formed by active Ho and the trace of O_2 during heat treatment,

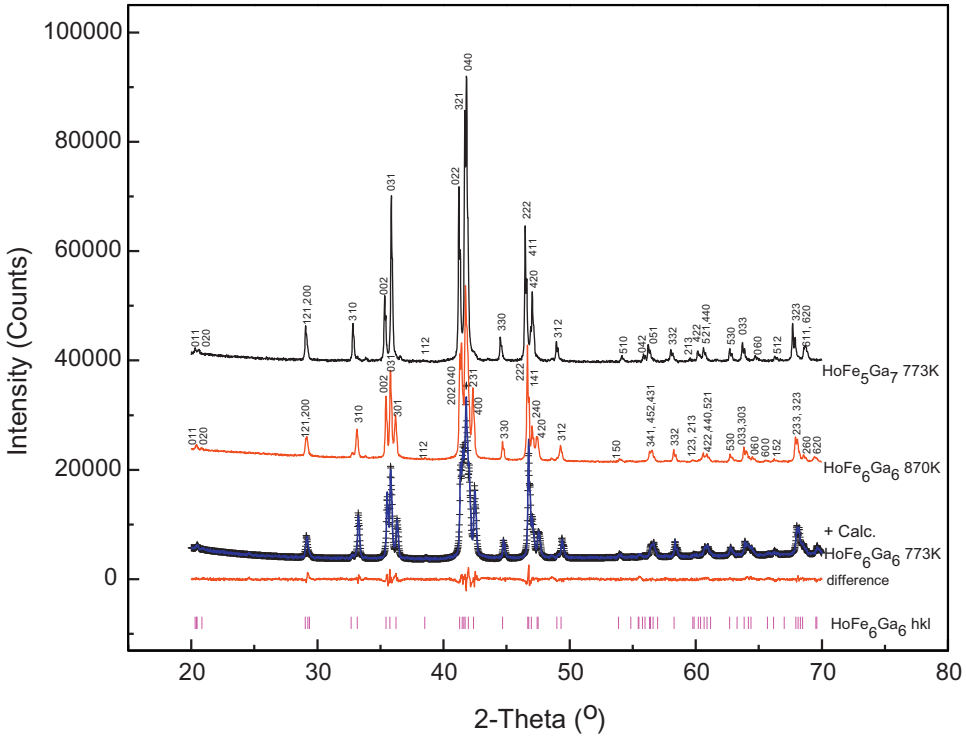

Fig. 2. XRD Rietveld refinement result of the compounds of $HoFe_{12-x}Ga_x$.

Table 1
Crystallographic data of the elements and the compounds in the Ho–Fe–Ga ternary system at 773 K.

Phase	Ga (at.%)	Space group	Structure type	Lattice parameters (nm)			Reference
				a	*b*	*c*	
Ho		$P6_3/mmc$	Mg	0.3609		0.5697	[9]
α-Fe		$Im\bar{3}m$	W	0.2932			[9]
Ga		*Cmca*	Ga	0.4520	0.7660	0.4526	[9]
$HoFe_2$		$Fd\bar{3}m$	$MgCu_2$	0.73			[9]
Ho_6Fe_{23}		$Fm\bar{3}m$	Th_6Mn_{23}	1.2032			[9]
Ho_5Ga_3		*P4/nnc*	Si_3Ba_5	0.7586		1.4001	[9]
Ho_3Ga_2		*I4/mcm*	Gd_3Ga_2	1.1489		1.470	[9]
				1.150(2)		1.4766(3)	This work
HoGa		*Cmcm*	CrB	0.433	1.09	0.409	[9]
Ho_3Ga_5		*pnma*	Tm_3Ga_5	1.1347	0.9630	0.6046	[9]
				1.1370(6)	0.96093(6)	0.60517(4)	This work
$HoGa_2$		*P6/mmm*	AlB_2	0.4281		0.4042	[9]
$HoGa_3$		$Pm\bar{3}m$	$AuCu_3$	0.4235			[9]
Fe_3Ga		$Pm\bar{3}m$	$AuCu_3$	0.3679			[9]
Fe_6Ga_5		*C2/m*	Fe_6Ge_5	1.0058	0.7946	0.7747	[9]
				$\beta = 109.33^\circ$			
Fe_3Ga_4		*C2/m*	Fe_3Ga_4	1.0091	0.7666	0.7866	[9]
				$\beta = 106.67^\circ$			
$FeGa_3$		$P4_2/mnm$	$FeGa_3$	0.6263		0.6556	[9]
κ_1-$HoFe_{6.02-5.24}Ga_{5.98-6.76}$	46.0-52.0	*Immm*	$ScFe_6Ga_6$	0.5060	0.8521	0.8644	[9]
				0.5049–0.5076	0.8541–0.8577	0.8624–0.8658	This work
κ_2-$HoFe_{4.98-4.59}Ga_{7.02-7.41}$	54.0-57.0	*I4/mmm*	$ThMn_{12}$	0.8570		0.5053	[5]
				0.8643–0.8667		0.5087–0.5091	This work
κ_3-$Ho_2Fe_{17-14.07}Ga_{0-2.93}$	0–15.4	$P6_3/mmc$	Th_2Ni_{17}	0.8458–0.8547		0.8285–0.8348	This work
κ_4-$Ho_2Fe_{13.39-8.45}Ga_{3.61-8.55}$	19.5–45.0	$R\bar{3}m$	Th_2Zn_{17}	0.8787		1.2604	[16]
				0.8555–0.8781		1.2538–1.2607	This work
κ_5-Ho_2FeGa_8		*P4/mmm*	Ho_2CoGa_8	0.4226		1.1088	[9]
				0.4230		1.1085	This work
κ_6-$HoFe_{3-2.52}Ga_{0-0.48}$	0–11.9	$R\bar{3}m$	$NbBe_3$	0.5110–0.5146		2.453–2.468	This work
κ_7-$HoFe_{2.36-1.91}Ga_{0.64-1.09}$	16.0–27.3	$P6_3/mmc$	$CeNi_3$	0.5154–0.5195		1.6679–1.6532	This work
κ_8-Ho_4FeGa_{12}	70.5–72.5	$Im\bar{3}m$	$U_4Fe_6Ga_7$	0.8510–0.8518			This work
κ_9-$HoFe_{2-1.46}Ga_{0-0.54}$	0–18.1	$Fd\bar{3}m$	$MgCu_2$	0.7317–0.7411			This work
κ_{10}-$HoFe_{1.28-1.16}Ga_{0.72-0.84}$	24.0–28.0	$P6_3/mmc$	$MgZn_2$	0.5297–0.5274		0.8628–0.8640	This work
κ_{11}-$HoFe_{0.43-0.34}Ga_{1.57-1.66}$	52.5–55.5	*Imma*	$CeCu_2$	0.4356–0.4354	0.7045–07024	0.7602–0.7611	This work
κ_{12}-$HoFe_{0.26-0.19}Ga_{1.74-1.81}$	58.0–60.5	*P6/mmm*	AlB_2	0.4344–0.4356		0.3626–0.3593	This work

leading to small deviation of the composition of the sample from the nominal one, which has very limited effect on the analysis of the phases and phase relationship in the Ho–Fe–Ga ternary system. Therefore, the compound Ho_3Ga_2 should be a stable one under our experimental conditions. In the same way, the alloy $Ho_{42}Ga_{58}$ is found to be composed of HoGa, Ho_3Ga_5 and Ho_2O_3 phases. Thus, the existence of Ho_3Ga_5 compounds is confirmed. The existence of Ho_3Ga_2 and Ho_3Ga_5 was also confirmed at 870 K [9]. The Rietveld refinement results of the XRD patterns of the two alloys mentioned above are included as supplementary information.

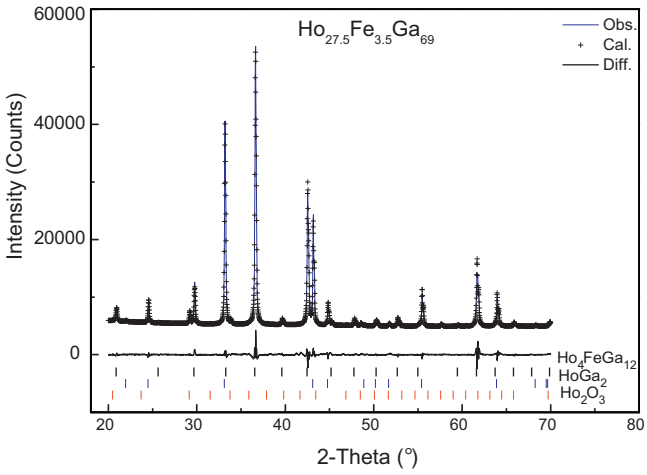

Fig. 4. XRD Rietveld refinement result of the alloy $Ho_{27.5}Fe_{3.5}Ga_{69}$ at 870 K.

Twelve ternary compounds or solid solutions are identified in the Ho–Fe–Ga ternary system at 773 K: κ_1-$HoFe_{6.02-5.24}Ga_{5.98-6.76}$, κ_2-$HoFe_{4.98-4.59}Ga_{7.02-7.41}$, κ_3-$HoFe_{17-14.07}Ga_{0-2.93}$, κ_4-$HoFe_{13.39-8.45}$ $Ga_{3.61-8.55}$, κ_5-Ho_2FeGa_8, κ_6-$HoFe_{3-2.52}Ga_{0-0.48}$, κ_7-$HoFe_{2.36-1.91}Ga_{0.64-1.09}$, κ_8-Ho_4FeGa_{12}, κ_9-$HoFe_{2-1.46}$ $Ga_{0-0.54}$, κ_{10}-$HoFe_{1.28-1.16}Ga_{0.72-0.84}$, κ_{11}-$HoFe_{0.43-0.34}Ga_{1.57-1.66}$ and κ_{12}-$HoFe_{0.26-0.19}Ga_{1.74-1.81}$. The crystal structural types, composition ranges, and lattice parameters of the compounds and solid solution are listed in Table 1. The structural parameters of ternary compounds, except for the well known solid solutions $Ho_2Fe_{17-x}Ga_x$ (κ_3), $HoFe_{3-x}Ga_x$ (κ_6) and $HoFe_{2-x}Ga_x$ (κ_9), derived from Rietveld refinements are listed in Table 2. The ternary compound $HoFe_{0.26-0.19}Ga_{1.74-1.81}$($\kappa_{12}$) was also reported to be stable at 870 K [9] but its structure type was not given. The results of Rietveld refinement (Fig. 1) indicate that κ_{12} has an AlB_2-type structure with space group *P6/mmm*, the same as $HoGa_2$. It is interesting to note that solubility of iron in $HoGa_2$ is negligibly small, whereas the homogeneity range is about 6.2–8.7 at.% Fe in κ_{12}, but they have same hexagonal AlB_2-type structure. The lattice of κ_{12} expands in *a* and *b* directions and shrinks in *c* direction comparing to that of $HoGa_2$ to ensure structural stability. The *a*/*c* ratio of κ_{12} and $HoGa_2$ is about 1.20, and 1.06, respectively. In comparison to the isothermal section at 870 K [9], some salient difference is observed in the isothermal section at 773 K. The solid solution phase $HoFe_{12-x}Ga_x$ at 773 K crystallizes in the $ScFe_6Ga_6$-type structure (*Immm*) for $x = 5.98–6.76$ and in the $ThMn_{12}$-type structure (S.G. *I4*/*mmm*) for $x = 7.02–7.41$ (Fig. 2), while it crystallized in the $ThMn_{12}$-type structure in the whole homogeneity range ($x = 5.9–6.9$) at 870 K [9]. Our experimental results also reveal that the structure of $Ho(Fe,Ga)_{12}$ transformed from $ThMn_{12}$-type

Table 2
Refined cell and atomic parameters for nine ternary compounds.

Phase	Atom	Site	*x*	*y*	*z*	Occ
κ_1-$HoFe_6Ga_6$ S.G. *Immm*, $ScFe_6Ga_6$-type, *a* = 5.0590(5) Å, *b* = 8.5218(8) Å, *b* = 8.6749(5) Å, R_{exp} = 0.9%, R_{wp} = 1.81%, R_B = 0.278%	Ho	2a	0	0	0	1
	Ga1	4e	0.3354(7)	0	0	1
	Fe1	4f	0.2591(9)	1/2	0	1
	Ga2	4g	0	0.3425(8)	0	1
	Ga3	4h	0	0.8111(8)	1/2	1
	Fe3	8k	1/4	1/4	1/4	1
κ_2-$HoFe_{4.84}Ga_{7.16}$ S.G. *I4/mmm*, $ThMn_{12}$-type, *a* = 8.6436(4) Å, *c* = 5.0879(3) Å, R_{exp} = 5.34%, R_{wp} = 13.75%, R_B = 3.66%	Ho	2a	0	0	0	1
	$Fe_{0.78}Ga_{0.32}$	8f	1/4	1/4	1/4	1
	$Fe_{0.15}Ga_{0.85}$	8i	0.6607(4)	0	0	1
	$Fe_{0.38}Ga_{0.62}$	8j	0.2856(4)	1/2	0	1
κ_4-$Ho_2Fe_9Ga_8$ S.G.$R\bar{3}m$, Th_2Zn_{17}-type, *a* = 8.7555(2) Å, *c* = 12.5597(3) Å, R_{exp} = 0.97%, R_{wp} = 2.08%, R_B = 0.35%	Ho	6c	0	0	0.3498(5)	1
	Fe	6c	0	0	0.1154 (1)	1
	Fe	9d	1/2	0	1/2	1
	$Fe_{0.15}Ga_{0.85}$	18h	0.3139(9)	0	0	1
	$Fe_{0.85}Ga_{0.15}$	18f	0.5	0.5	0.1571(7)	1
κ_5-Ho_2FeGa_8 S.G. *P4/mmm*, Ho_2CoGa_8-type, *a* = 4.230(1) Å, *c* = 10.085(2) Å, R_{exp} = 1.16%, R_{wp} = 3.58%, R_B = 2.32%	Fe	1a	0	0	0	1
	Ga1	2e	0	1/2	1/2	1
	Ho	2g	0	0	0.3104(4)	1
	Ga2	2h	1/2	1/2	0.2925(7)	1
	Ga3	4i	0	1/2	0.1138(3)	1
κ_7-$HoFe_{2.08}Ga_{0.92}$ S.G. $P6_3/mmc$, $CeNi_3$-type, *a* = 5.1799(1) Å, *c* = 16.6376(5) Å, R_{exp} = 0.96%, R_{wp} = 2.20%, R_B = 0.44%	Ho	2c	1/3	2/3	1/4	1
	Ho	4f	1/3	2/3	0.0375(3)	1
	Fe	2a	0	0	0	1
	$Fe_{0.48}Ga_{0.52}$	2b	0	0	1/4	1
	$Fe_{0.62}Ga_{0.38}$	2d	1/3	2/3	3/4	1
	$Fe_{0.69}Ga_{0.31}$	12k	0.826(1)	0.652(2)	0.1277(4)	1
κ_8-Ho_4FeGa_{12} S.G.$Im\bar{3}m$, $U_4Fe_6Ga_7$-type, *a* = 8.5112(3) Å, R_{exp} = 1.22%, R_{wp} = 5.74%, R_B = 1.21%	Ho	8c	1/4	1/4	1/4	1
	Fe	2a	0	0	0	1
	Ga	12d	1/4	0	1/2	1
	Ga	12e	0.2799(6)	0	0	1
κ_{10}-$HoFe_{1.26}Ga_{0.74}$ S.G. $P6_3/mmc$, $MgZn_2$-type, *a* = 5.2742(2) Å, *c* = 8.6284(3) Å, R_{exp} = 1.0%, R_{wp} = 3.8%, R_B = 1.77%	Ho	4f	1/3	2/3	0.0555(3)	1
	$Fe_{0.63}Ga_{0.37}$	2a	0	0	0	1
	$Fe_{0.63}Ga_{0.37}$	6h	0.829(5)	0.656(1)	1/4	1
κ_{11}-$HoFe_{0.38}Ga_{1.62}$, S.G. *Imma*, $CeCu_2$-type, *a* = 4.3549(1) Å, *b* = 7.0447(2) Å, *c* = 7.6062(2) Å, R_{exp} = 1.2%, R_{wp} = 6.12%, R_B = 4.22%	Ho	4e	0	1/4	0.5308(3)	1
	$Fe_{0.19}Ga_{0.81}$	8h	0	0.0393(5)	0.1680(5)	1
κ_{12}-$HoFe_{0.2}Ga_{1.8}$ S.G. *P6/mmm*, AlB_2-type, *a* = 4.34325(8) Å, *c* = 3.62566(9) Å, R_{exp} = 1.29%, R_{wp} = 6.34%, R_B = 1.81%	Ho	1a	0	0	0	1
	$Fe_{0.1}Ga_{0.9}$	2d	1/3	2/3	1/2	1

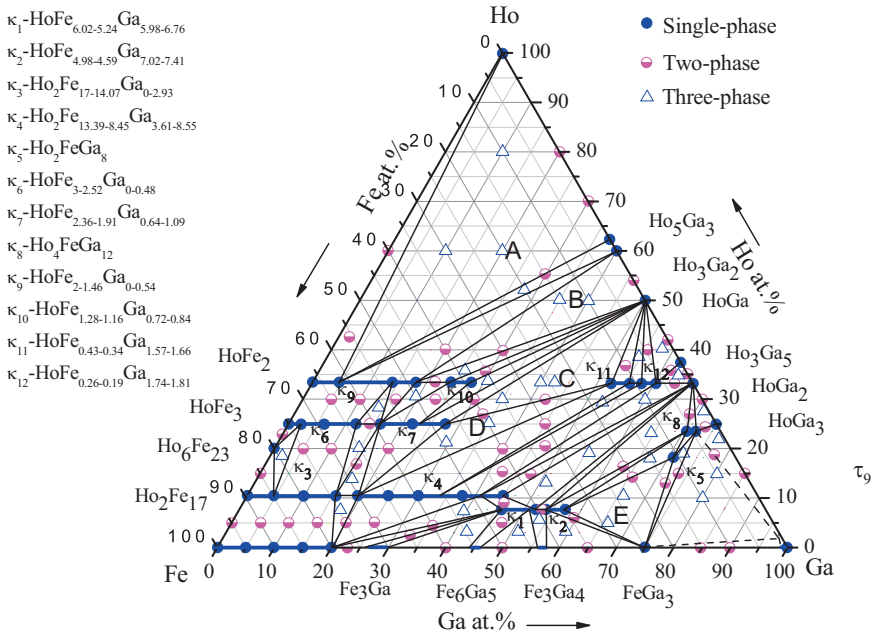

Fig. 5. The isothermal section of the Ho–Fe–Ga ternary system at 773 K.

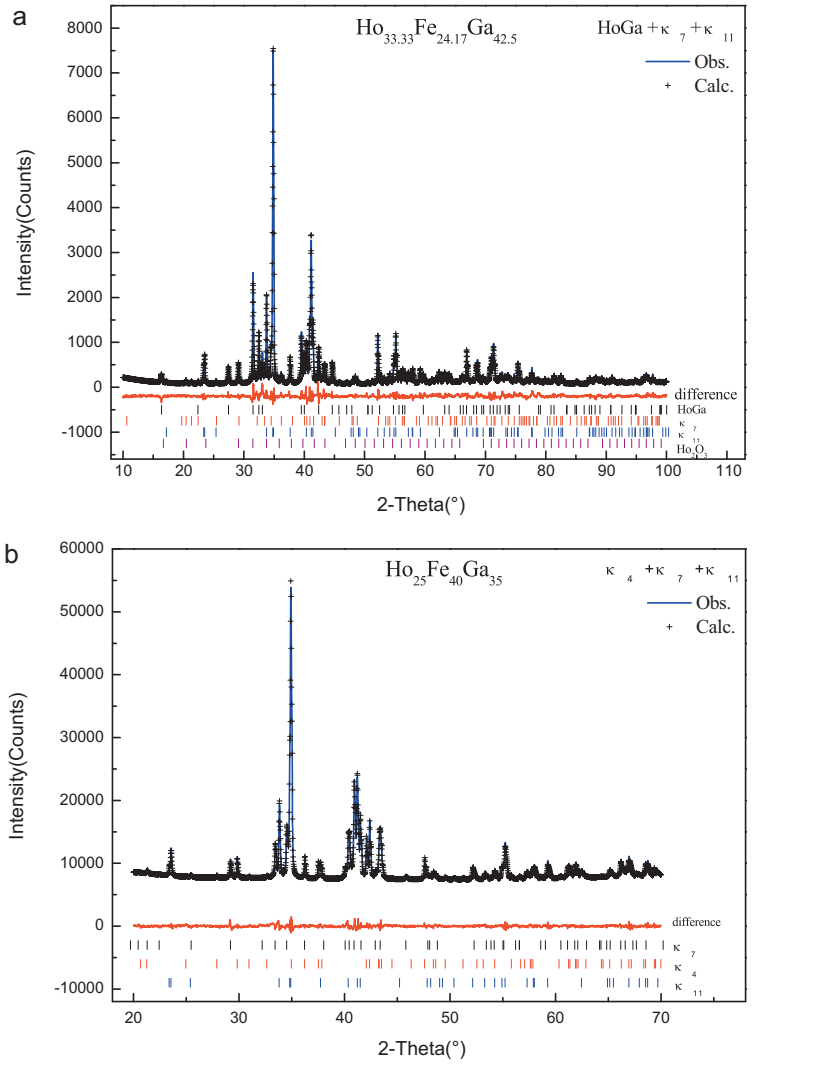

Fig. 6. XRD Rietveld refinement result of the Ho–Fe–Ga alloy. (a): $Ho_{33.33}Fe_{24.17}Ga_{42.5}$ (labeled with C in Fig. 5); (b): $Ho_{25}Fe_{40}Ga_{35}$ (labeled with D in Fig. 5).

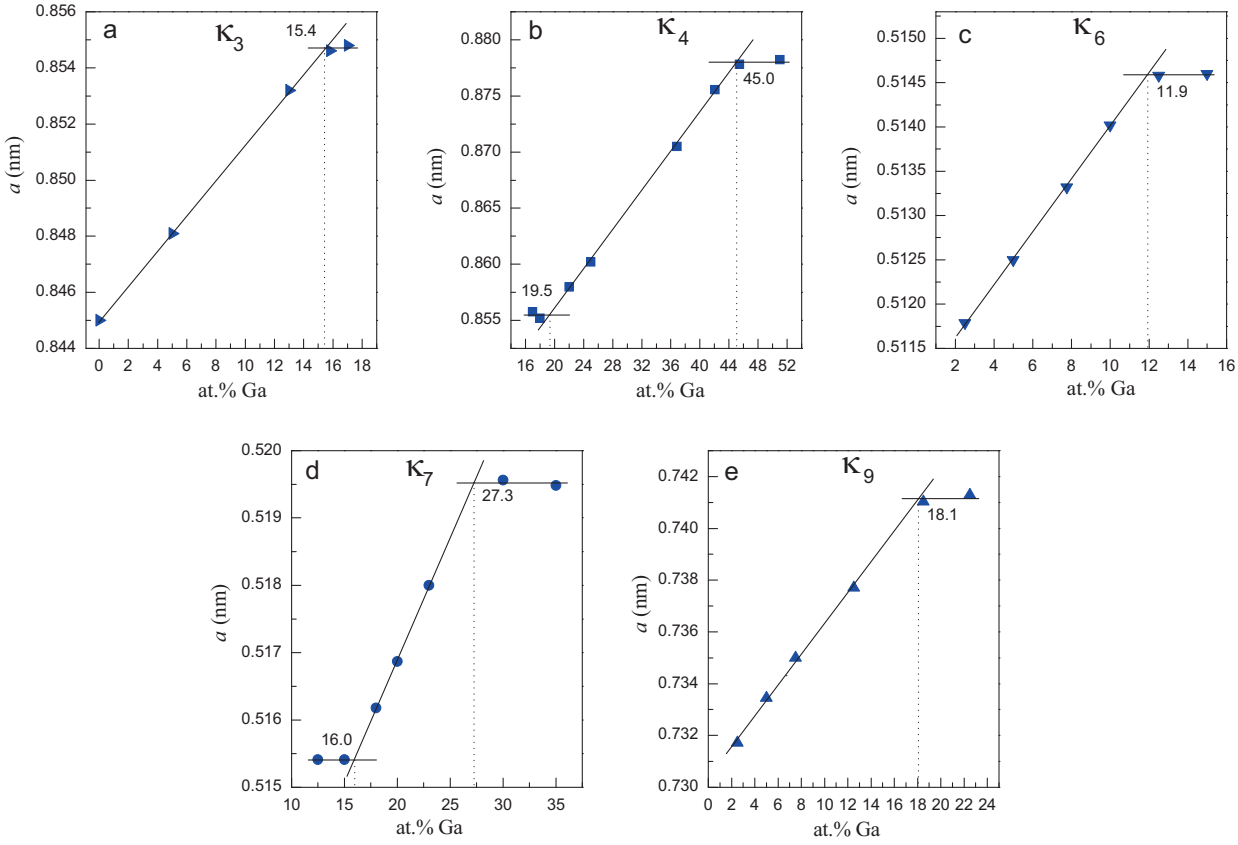

Fig. 7. Variation of the lattice parameter a with Ga content for determination of the solid solubility of Ga in the ternary solid solutions (a: κ_3; b: κ_4; c: κ_6; d: κ_7; e: κ_9).

structure (S.G. *I*4/*mmm*) to $ScFe_6Ga_6$-type structure (*Immm*) with the decrease of the gallium content at 870K. The compound Ho_4FeGa_{12} was identified at 773 K (Fig. 3), which crystallized in an cubic $U_4Fe_6Ga_7$-type structure (S.G. *Im*-3*m*) with the lattice parameter almost double that of Ho(Fe,Ga)$_3$ (τ_4) reported at 870 K. The composition of Ho_4FeGa_{12} is very close to that of Ho(Fe,Ga)$_3$ (τ_4). The XRD pattern of the Ho_4FeGa_{12} alloy, which was annealed at 870 K and then quenched in liquid nitrogen, manifested that it still holds the $U_4Fe_6Ga_7$-type structure even at 870 K (Fig. 3). The Rietveld refinement result of the XRD pattern of the alloy $Ho_{27.5}$ $Fe_{3.5}Ga_{70.8}$, which is located in the $HoGa_2$ + Ho(Fe,Ga)$_3$ (τ_4) two-phase region in the section at 870 K, also showed that the alloy consisted of Ho_4FeGa_{12} and $HoGa_2$ with a small amount of Ho_2O_3 impurity at 870 K (Fig. 4). The so-called Ho(Fe,Ga)$_3$ (τ_4) phase was not observed at both 773 K or 870 K in present work. Unlike $HoGa_2$ and Ho(Fe,Ga)$_2$(τ_6) mentioned above, the existence of Ho(Fe,Ga)$_3$ (τ_4) is questionable, because the iron has no obvious solubility in $HoGa_3$ and it cannot re-dissolve in $HoGa_3$ with a larger solubility by adjusting the lattice parameter ratio of *a*/*c* in cubic system with the same $AuCu_3$- type structure. Thus, the so-called Ho(Fe,Ga)$_3$ (τ_4) should not exist but be replaced by Ho_4FeGa_{12} at 870 K.

3.2. Isothermal section at 773 K

By comparing and analyzing the XRD patterns of the samples and identifying the phases in each sample, we have constructed the isothermal section of the Ho–Fe–Ga ternary system at 773 K as shown in Fig. 5. It is composed of 26 single-phase regions, 58 two-phase regions and 33 three-phase regions. The X-ray diffraction patterns for some representative alloys located in some three-phase regions are shown in Fig. 6 and as supplementary materials. The alloy $Ho_{60}Fe_{20}Ga_{20}$ (label with A in Fig. 5) was located in the $HoFe_2$ + Ho_5Ga_3 + Ho three-phase region; the alloy $Ho_{50}Fe_{10}Ga_{40}$ (label with B in Fig. 5) was located in the Ho_3Ga_2 + HoGa + $HoFe_2$ three-phase region; the alloys $Ho_{33.33}Fe_{24.17}Ga_{42.5}$ (label with C in Fig. 5) was located in the HoGa + κ_7 + κ_{11} three-phase region (Fig. 6a); the alloys $Ho_{25}Fe_{40}Ga_{35}$ (label with D in Fig. 5) was located in the κ_4 + κ_7 + κ_{11} three-phase region (Fig. 6b); the alloy $Ho_5Fe_{29}Ga_{66}$ (label with E in Fig. 5) was located in the κ_2 + κ_5 + $FeGa_3$ three-phase region, respectively.

The homogeneity ranges of the single-phase regions were determined by phase-extinction method (extrapolating *I*–*x* curve to *I* = 0) or lattice parameter method (kinks on the composition dependence of lattice parameters). The variation of the lattice parameters of κ_3, κ_4, κ_6, κ_7 and κ_9 with Ga content are shown in Fig. 7(a)–(e), which show that the homogeneity ranges at 773 K are from19.5 to 45.0 at.% Ga for κ_4, and from 16.0 to 27.3 at.% Ga for κ_7, respectively, while the maximum solid solubilities of Ga in κ_3, κ_6 and κ_9 at 773 K are determined to be 15.4, 11.9, and 18.1 at.% Ga, respectively. Similarly, the homogeneity ranges are from 46 to 52 at.% Ga for κ_1, 54 to 57 at.% Ga for κ_2, 70.5 to 72.5 at.% Ga for κ_8, 24.0 to 28.0 at.% Ga for κ_{10}, 52.5 to 55.5 at.% Ga for κ_{11}, and 58.0 to 60.5 at.% Ga for κ_{12}, respectively (Table 1). For the Fe–Ga binary system, the homogeneity ranges of the solid solutions are 0–20.0 at.% Ga for α-Fe, 27.0–30.0 at.% Ga for Fe_3Ga,44.5–46.0 at.% Ga for Fe_6Ga_5, 56.5–58.0 at.% Ga for Fe_3Ga_4, respectively, according to the binary Fe–Ga phase diagram [15].

In addition to the difference mention above between the isothermal sections reported for *T* = 870 K [9] and we determined at 773 K, the tie-line between Ho(Fe,Ga)$_2$(τ_8) (S.G. $P6_3/mmc$) and Ho(Fe,Ga)$_2$ (τ_7) (S.G. *Imma*) reported at 870 K [9] does not exist at 773 K. Instead, the two three-phase regions: HoGa + τ_7 + τ_8, τ_7 + τ_8 + Ho(Fe,Ga)$_3$ (τ_5), and a two-phase region of τ_7 + τ_5 at 870 K changed to two three-phase region of HoGa + κ_7 + κ_{11}, HoGa + κ_7 + κ_{10}, and a two-phase region of HoGa + κ_{10} at 773K.

4. Conclusion

The isothermal section of the Ho–Fe–Ga ternary system was constructed at 773 K. It consists of 26 single-phase regions, 58 two-phase regions and 33 three-phase regions. There are fourteen binary compounds and twelve ternary compounds at 773 K. The structures of the ternary compounds were refined by Rietveld refinement technique. A new compound, Ho_4FeGa_{12} is identified and stable up to 870 K. The solid solubilities of all the ternary solid solution phases were determined based upon XRD phase analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.10.072.

References

[1] N. Tang, J.L. Wang, Y.H. Gao, W.Z. Li, Fuming Yang, F.R. de Boer, Magnetic properties of $R_2(Fe_{1-x}Ga_x)_{17}$ compounds with R = Y, Sm, Dy, Ho, J. Magn. Magn. Mater. 140–144 (1995) 979–980.
[2] F. Maruyama, Exchange interaction in $R_2Fe_{17-x}Ga_x$ (R = Y, Sm, Gd, Tb, Ho and Tm) compounds, J. Solid State Chem. 178 (2005) 3020–3026.
[3] M. Venkatesan, K.V.S. Rama Rao, U.V. Varadaraju, Structural, magnetic and exchange interaction studies on $R_2Fe_{17-x}Ga_x$ (R = Tm, Er and Sm) compounds, Physica B 291 (2000) 159–172.
[4] F. Weitzer, K. Hiebl, P. Rogl, Y.N. Grin, Magnetism and crystal chemistry in $REFe_{12-x}Ga_x$ (RE = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and (Zr, Pr)$(Fe_{1-x}Co_x)_{12-y}Ga_y$, J. Appl. Phys. 68 (1990) 3512–3517.
[5] P. Villars, A. Prince, H. Okamoto, Handbook of Ternary Alloy Phase Diagrams, Materials Park, OH: ASM Int., 1995.
[6] V.Ja. Markiv, T.I. Zhunkovskaja, N.N. Beljavina, Ternary phase diagram of the system Y–Sc–Ga and the crystal stucture of RE_2Ga_3 (RE = Sc Y, Tb, Dy, Ho, Er, Tm, Yb, Lu), Dopovidi Akademii Nauk Ukrains'koi RSR, Seriya A: Fizico-Matematichni Ta Tekhnichni Nauki 83 (3) (1981) 85–87.
[7] S.P. Yatsenko, R.E. Hladyschewsky, O.M. Sitschewitsch, V.K. Belsky, A.A. Semyannikov, Ju.N. Hryn, Ya.P. Yarmolyuk, Kristallstruktur von Ho_3Ga_2 and isotypen verbindungen, J. Less-Comm. Metal. 115 (1) (1986) 17–22.
[8] T.B. Massalski, H. Okamoto, Binary Alloy Phase Diagram, Materials Park, OH: ASM Int., 1990.
[9] V. Raghavan, Fe–Ga–Ho (iron–gallium–holmium), J. Phase Equilib. 22 (2) (2001) 143–144.
[10] B.L. Drake, F. Grandjean, M.J. Kangas, E.K. Okudzeto, A.B. Karki, M.T. Sougrati, D.P. Young, G.J. Long, J.Y. Chan, Crystal growth, transport, and the structural and magnetic properties of Ln_4FeGa_{12} with Ln = Y, Tb, Dy, Ho, and Er, Inorg. Chem. 49 (2010) 445–456.
[11] J.Q. Li, M. Ouyang, D.C. Liu, F.S. Liu, W.Q. Ao, The isothermal section of the Tb–Fe–Ga ternary system at 773 K, Intermetallics 17 (2009) 733–737.
[12] D.C. Liu, J.Q. Li, M. Ouyang, F.S. Liu, W.Q. Ao, The phase relations in the Gd–Fe–Ga ternary system at 500 °C, J. Alloy Compd. 479 (2009) 134–139.
[13] F. Weitzer, K. Hiebl, P. Rogl, N. Yu Grin, Magnetism and crystal chemistry in $REFe_{12-x}Ga_x$ (RE = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and MM = mischmetal) and (Zr,Pr) $(Fe_{1-x}Co_x)_{12-y}Ga_y$, J. Appl. Phys. 68 (7) (1990) 3512–3517.
[14] J.Q. Li, W.H. Zhang, Y.J. Yu, F.S. Liu, W.Q. Ao, J.L. Yan, The isothermal section of the Nb–Fe–Ga ternary system at 773 K, J. Alloy Compd. 487 (2009) 116–120.
[15] H. Okamoto, Fe–Ga (Iron–Gallium), J. Phase Equilb. Diff. 25 (2004) 100.
[16] P. Villars, Pearson's Handbook of Crystallographic Data, Materials Park, OH: ASM Int., 1997, pp. P1715–P1716.