Isothermal Section of the Co-Gd-Sn Ternary System Between 0 and 55 at.% Sn at 500 °C

J.L. Yan, Y. Xu, Q.X. Long, J.M. Zhu, and Y.H. Zhuang

The isothermal section of the Co-Gd-Sn system between 0 and 55 at.% Sn at 500 °C was investigated by means of powder x-ray diffraction. Five ternary phases were identified or confirmed: Gd_6Co_2Sn, $Gd_3Co_8Sn_4$, $Gd_3Co_6Sn_5$, Gd_4CoSn_8, and $Gd_3Co_4Sn_{13}$. A new ternary phase $Gd_{117}Co_{57}Sn_{112}$ with $Dy_{117}Co_{57}Sn_{112}$-type structure, space group $Fm\bar{3}m$, and lattice parameter $a = 3.0023$ (4) nm was found. The ternary rare earth compound $Gd_3Co_8Sn_4$ presents a homogeneity range of 20 to 27 at.% Sn along the 20 at.% Gd iso-concentration line. Comparison of this section with those of the Co-Gd-Sn system reported in the literature was made and the differences were discussed.

1. Introduction

Since the discovery of the giant magnetocaloric effect (MCE) in $Gd_5Si_xGe_{4-x}$ compounds in 1997,[1] a number of rare-earth-based (especially Gd-based) intermetallic compounds, such as $RECo_2$ and RE_5M_4 (where RE = a rare-earth element and M = Si, Ge, or Sn), have been widely studied for their structure and MCE properties in search of high-performance room temperature magnetic refrigerant materials.[2] Some efforts were made in the substitution of a third element M (M = Al, Si, Ga, Ge, Sn) for Co in the $RECo_2$ compound.[3,4] Our previous work showed that the solid solubility of Sn in $RECo_2$ is very limited (<2 at.% Sn).[4] In addition, the isothermal sections of the RE-Co-Sn ternary systems found in the literature for RE = Nd,[5] Gd,[6] Dy,[7] and Er[8] have shown the existence of rich ternary rare earth stannides with interesting magnetic properties.[9-11] Among these systems, the Co-Gd-Sn system has attracted much attention. Seven ternary compounds Gd_6Co_2Sn,

$GdCo_3Sn$, $Gd_4Co_3Sn_3$, $GdCoSn$, $GdCo_2Sn_2$, $GdCo_6Sn_6$, and $Gd_3Co_4Sn_{13}$ have been reported by Skorlozdra et al.[6] in the Co-Gd-Sn system, as listed in Table 1. Interestingly, four of these ternary phases have a Co:Sn ratio of 1:1. In this work, we re-investigated the partial phase equilibrium in the Co-Gd-Sn ternary system at 500 °C (up to 55 at.% Sn), with emphasis placed on the regions along the line between $Gd_4Co_3Sn_3$ and CoSn.

The phase diagrams of the binary Co-Gd,[17-19] Co-Sn,[17,20,21] and Gd-Sn[17,22,23] systems have been well assessed. Buschow[24] first reported eight compounds, namely Gd_2Co_{17}, $GdCo_5$, Gd_2Co_7, $GdCo_3$, $GdCo_2$, Gd_4Co_3, $Gd_{12}Co_7$, and Gd_3Co, in the Co-Gd binary system, later Ge et al.[25] confirmed the existence of the above compounds except for $Gd_{12}Co_7$, and mentioned that $GdCo_5$ phase decomposes into Gd_2Co_{17} and Gd_2Co_7 at 850 °C. Gd_2Co_{17} and Gd_2Co_7 are dimorphic, but their transformation temperatures are unknown. In the Co-Sn system,[21] there are three compounds at 500 °C: Co_3Sn_2, CoSn, and $CoSn_2$. Polymorphic transformation of Co_3Sn_2 occurs at about 560 °C. On the Gd-rich side (50 to 100 at.% Gd) of the assessed Gd-Sn phase diagram,[17,22,23] five compounds, namely Gd_3Sn, Gd_5Sn_3, Gd_5Sn_4, Gd_8Sn_7, and $Gd_{11}Sn_{10}$, were reported. The structures of phases Gd_3Sn and Gd_8Sn_7 are unknown. The crystal structure data for the binary phases relevant to this study are listed in Table 2.

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2. Experimental

The sample buttons, each weighing 3 g, were prepared by arc melting of Gd (99.9 wt.%), Co (99.9 wt.%), and Sn (99.99 wt.%) on a water-cooled copper hearth with a nonconsumable tungsten electrode under pure argon atmosphere. Each button was turned over and re-melted three times for improved homogeneity. For most alloys, the weight losses were found to be less than 1% after melting. Subsequently, the samples were sealed in an evacuated quartz tube, annealed at elevated temperature for 30 days,

Table 1 Crystallographic data for the ternary compounds in the Co-Gd-Sn system

Phase	Space group	Structure type	Lattice parameters, nm			Ref.
			a	b	c	
Gd_6Co_2Sn	$Immm$	Ho_6Co_2Ga	0.9522	0.9502	0.9995	[6]
			0.9530(2)	1.0012(2)	0.9505(2)	This work
$GdCo_3Sn$	$P6_3/mmc$	$BaLi_4$	0.8893		0.7506	[12,13]
$Gd_3Co_8Sn_4$	$P6_3mc$	$Lu_3Co_{7.77}Sn_4$	0.8907		0.7502	[14]
			0.8910(1)		0.7511(1)	This work
$Gd_4Co_3Sn_3$	Unknown					[6]
$GdCoSn$	$Pnma$	$TiNiSi$	0.7319	0.4671	0.7464	[6]
$GdCo_2Sn_2$	Unknown					[6]
$GdCo_6Sn_6$	$P6/mmm$	YCo_6Ge_6	0.5352		0.4279	[6]
$Gd_3Co_6Sn_5$	$Immm$	La_3Al_{11}	0.4314	1.2422	0.9742	[15]
			0.4310(1)	1.2416(2)	0.9735(1)	This work
$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	$Dy_{117}Co_{57}Sn_{112}$	3.0023(4)			This work
Gd_4CoSn_8	$Cmcm$	$CeNiSi_2$	0.4449	1.657	0.4400	[16]
			0.4451(1)	1.6601(2)	0.4399(1)	This work
$Gd_3Co_4Sn_{13}$	$Pm\bar{3}n$	$Pr_3Rh_4Sn_{13}$	0.9518			[16]
			0.9498(1)			This work

Table 2 Crystallographic data for the binary compounds relevant to the studied isothermal section of the Co-Gd-Sn system[16]

Phase	Space group	Structure type	Lattice parameters, nm			β, °
			a	b	c	
Gd_2Co_{17}	$R\bar{3}m$	Th_2Zn_{17}	0.8377		1.2198	
Gd_2Co_{17}	$P6_3/mmc$	Th_2Ni_{17}	0.8378		0.8139	
$GdCo_5$	$P6/mmm$	$CaCu_5$	0.4974		0.3973	
Gd_2Co_7	$R\bar{3}m$	Er_2Co_7	0.5024		3.632	
Gd_2Co_7	$P6_3/mmc$	Ce_2Ni_7	0.5022		2.419	
$GdCo_3$	$R\bar{3}m$	$NbBe_3$	0.5026		2.4456	
$GdCo_2$	$FdR\bar{3}m$	Cu_2Mg	0.7262			
Gd_4Co_3	$P6_3/m$	Ho_4Co_3	1.159		0.4055	
$Gd_{12}Co_7$	$P2_1/c$	$Ho_{12}Co_7$	0.841	1.139	1.402	138.8
Gd_3Co	$Pnma$	Fe_3C	0.705	0.954	0.632	
$\alpha\text{-}Co_3Sn_2$	$Pnma$	Ni_3Sn_2	0.7085	0.5216	0.8194	
$CoSn$	$P6/mmm$	$CoSn$	0.5268		0.4249	
$CoSn_2$	$I4/mcm$	$CuAl_2$	0.6363		0.5456	
Gd_3Sn	Unknown					
Gd_5Sn_3	$P6_3/mcm$	Mn_5Si_3	0.9020		0.6568	
Gd_5Sn_4	$Pnma$	Sm_5Ge_4	0.8046	1.553	0.8102	
Gd_8Sn_7	Unknown					
$Gd_{11}Sn_{10}$	$I4/mmm$	$Ho_{11}Ge_{10}$	1.167		1.715	

and then cooled down slowly to 500 °C and kept for 14 days before quenching in liquid nitrogen. X-ray powder diffraction (XRD) data were collected on a Rigaku D/Max 2500 V diffractometer with Cu Kα and a graphite monochromator. The experimental XRD patterns were analyzed using JADE5 software[26] by comparing them with the powder diffraction files (PDF release2002) and the calculated ones obtained by using the PowderCell program.[27]

3. Results and Discussion

Eight compounds in the Co-Gd binary system were confirmed to exist. Gd_2Co_{17} and Gd_2Co_7 were found to crystallize at 500 °C with the Th_2Zn_{17} and Er_2Co_7 structure types, respectively. Evidence for the existence of $Gd_{12}Co_7$ was given by the ternary alloy samples in the three-phase

region of Gd_6Co_2Sn, $Gd_{12}Co_7$, and Gd_3Co. $GdCo_5$ was found to be a metastable phase at 500 °C; its eutectoid decomposition to Gd_2Co_{17} and Gd_2Co_7 is incomplete. This was also the case in our previous studies of the Gd-Dy-Co[28] and Gd-Tb-Co[29] ternary systems. The $GdCo_5$ metastable phase is thus not presented in this isothermal section.

In the composition range of our investigation (up to 55 at.% Sn), the existence of the binary phases Co_3Sn_2 and CoSn in the Co-Sn system as well as Gd_5Sn_3, Gd_5Sn_4, and $Gd_{11}Sn_{10}$ in the Gd-Sn system were confirmed. No Gd_3Sn phase was observed. In the XRD pattern of an alloy with Gd_3Sn nominal composition, only of two phases, Gd and Gd_5Sn_3 were evident. In the Gd-Sn system, Gd_5Sn_3 is a stable phase while the binary alloy samples containing 40 to 55 at.% Sn were rapidly pulverized in air. The Gd_5Sn_4 and $Gd_{11}Sn_{10}$ phases could only be identified by comparing XRD patterns of some binary and ternary alloys in the region close to their stoichiometric composition with their theoretical powder patterns. The existence of Gd_8Sn_7 remains unknown because of its unknown structure and the difficulty of obtaining a sound XRD pattern due to the high chemical reactivity of the relevant alloys. This pulverization phenomenon for binary alloys containing more than 40 at.% Sn is commonly found in the rare earth-Sn systems, as mentioned in the studies of phase equilibria in the Nd-Co-Sn system,[5] Pr-Fe-Sn system,[30] Gd-Fe-Sn system,[31] and Dy-Ag-Sn system,[32] etc.

It is suggested that these samples are subjected to rapid hydrolysis and oxidization in atmospheric conditions.

Phase relations in the ternary system Co-Gd-Sn at 497 °C (0 to 55 at.% Sn) and at 397 °C (>55 at.% Sn) were previously investigated by Skorlozdra et al.[6] They reported the existence of seven ternary compounds and gave the structures of Gd_6Co_2Sn, GdCoSn, and $GdCo_6Sn_6$. Our literature study showed that in addition to the above seven compounds, three ternary stannides $Gd_3Co_8Sn_4$,[14] $Gd_3Co_6Sn_5$,[15] and Gd_4CoSn_8[16] have also been reported. Their theoretical diffraction intensities were calculated in this study for phase identification.

By extensive x-ray analysis of 120 alloys, the partial isothermal section of the ternary Co-Gd-Sn system at 500 °C was determined, as shown in Fig. 1. (The alloys prepared and their XRD analysis results are indicated in Fig. 1 with symbols.) The results of phase identification and the lattice parameters of each phase from XRD measurements are listed in Table 3 for selected alloys. The existence of compounds Gd_6Co_2Sn, $Gd_3Co_8Sn_4$, $Gd_3Co_6Sn_5$, Gd_4CoSn_8, and $Gd_3Co_4Sn_{13}$ were confirmed and one new compound $Gd_{117}Co_{57}Sn_{112}$ was found. The lattice parameters determined in this work for all these six ternary compounds are also listed in Table 1.

Skorlozdra et al.[6] reported that the $GdCo_3Sn$ compound has a small homogeneity range of 20 to 25 at.% Sn. We prepared six alloy samples along the iso-concentration line of 20 at.% Gd with the concentration of Sn varying from
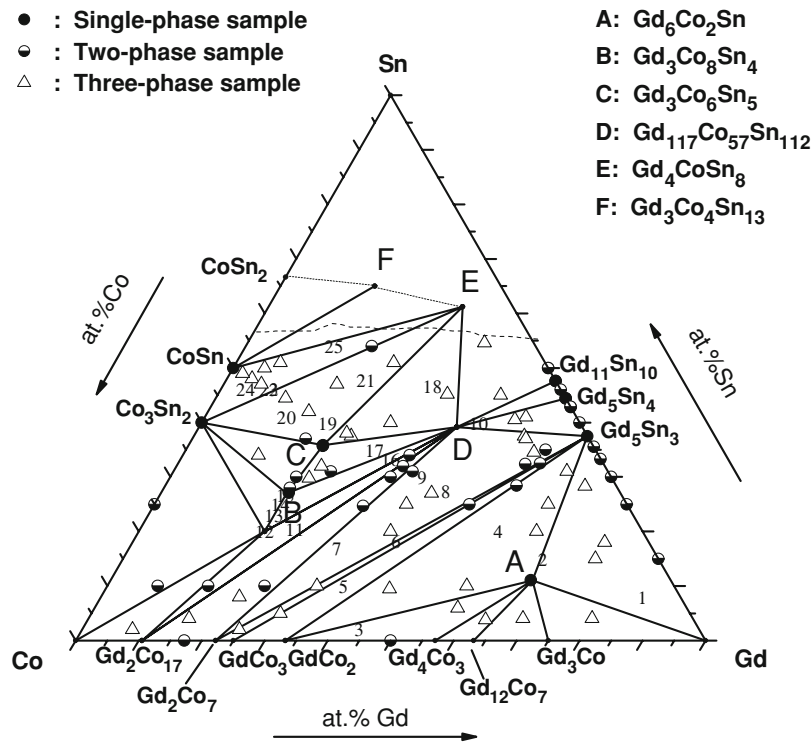

Fig. 1 Partial isothermal section of the Co-Gd-Sn ternary system at 500 °C (0 to 55 at.% Sn). The alloys prepared and their XRD analysis results are shown with symbols. Results of phase identification and lattice parameters from XRD analysis are reported in Table 3 for the numbered alloy samples

Table 3 Quantitative analysis for selected alloys in the Co-Gd-Sn system at 500 °C

No.	Alloy composition, at.%			Phases	Space group	Lattice parameters, nm		
	Gd	Sn	Co			a	b	c
1	86	8	6	Gd_6Co_2Sn	$Immm$	0.9519(3)	0.9997(1)	0.9492(2)
				Gd_5Sn_3	$P6_3/mcm$	0.9002(2)		0.6554(2)
				Gd	$P6_3/mmc$	0.3638(5)		0.5784(3)
2	67	15	18	Gd_6Co_2Sn	$Immm$	0.9530(2)	1.0012(2)	0.9505(2)
				Gd_5Sn_3	$P6_3/mcm$	0.9027(3)		0.6573(1)
3	44	2	54	$GdCo_2$	$Fd\bar{3}m$	0.7263(1)		
				Gd_6Co_2Sn	$Immm$	0.9517(6)	0.9984(2)	0.9502(2)
				Gd_4Co_3	$P6_3/m$	1.1586(5)		0.4060(2)
4	57	20	23	Gd_5Sn_3	$P6_3/mcm$	0.9023(3)		0.6575(2)
				Gd_6Co_2Sn	$Immm$	0.9512(3)	1.0004(3)	0.9532(2)
				$GdCo_2$	$Fd\bar{3}m$	0.7276(2)		
5	38	10	53	Gd_5Sn_3	$P6_3/mcm$	0.9024(2)		0.6577(3)
				$GdCo_2$	$Fd\bar{3}m$	0.7276(2)		
				$GdCo_3$	$R\bar{3}m$	0.5053(3)		2.459(1)
6	42	18	40	Gd_5Sn_3	$P6_3/mcm$	0.8973(3)		0.6529(2)
				Gd_2Co_7	$R\bar{3}m$	0.5018(3)		3.624(1)
				$GdCo_3$	$R\bar{3}m$	0.5023(4)		2.442(2)
7	33	17	50	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0019(6)		
				Gd_5Sn_3	$P6_3/mcm$	0.8993(7)		0.6543(4)
				Gd_2Co_7	$R\bar{3}m$	0.5034(3)		3.631(2)
8	45	28	28	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0051(5)		
				Gd_5Sn_3	$P6_3/mcm$	0.8988(2)		0.6558(2)
				Gd_2Co_7	$R\bar{3}m$	0.5024(3)		3.628(2)
9(a)	40	30	30	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0085(2)		
				Gd_5Sn_3 (trace)	$P6_3/mcm$			
				Gd_2Co_7 (trace)	$R\bar{3}m$			
10	44	40	16	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0023(4)		
11	25	20	55	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0112(4)		
				Gd_2Co_{17}	$R\bar{3}m$	0.8397(3)		1.2225(4)
				$Gd_3Co_8Sn_4$ (trace)				
12	20	20	60	$Gd_3Co_8Sn_4$	$P6_3mc$	0.8903(3)		0.7415(3)
				Gd_2Co_{17} (trace)				
13(a)	20	23	57	$Gd_3Co_8Sn_4$	$P6_3mc$	0.8906(2)		0.7477(2)
14	20	25	55	$Gd_3Co_8Sn_4$	$P6_3mc$	0.8891(2)		0.7474(2)
15	20	27	53	$Gd_3Co_8Sn_4$	$P6_3mc$	0.8910(1)		0.7511(1)
16(a)	33	33	33	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0092(2)		
				$Gd_3Co_8Sn_4$	$P6_3mc$	0.8914(4)		0.7490(4)
17	30	35	35	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0142(2)		
				$Gd_3Co_8Sn_4$	$P6_3mc$	0.8942(4)		0.7468(5)
				$Gd_3Co_6Sn_5$	$Immm$	0.4319(2)	1.2448(4)	0.9757(4)
18	33	47	20	$Gd_{117}Co_{57}Sn_{112}$	$Fm\bar{3}m$	3.0191(1)		
				Gd_4CoSn_8	$Cmcm$	0.445(5)	1.6604(1)	0.440(6)
				$Gd_3Co_6Sn_5$	$Immm$	0.4319(2)	1.2449(5)	0.9749(6)
19(a)	20	40	40	$Gd_3Co_6Sn_5$	$Immm$	0.4310(1)	1.2416(2)	0.9735(1)
				Gd_4CoSn_8	$Cmcm$	0.4444(3)	1.6591(8)	0.4396(2)
				Co_3Sn_2	$Pnma$	0.7072(3)	0.5202(2)	0.8188(2)
20	13	41	46	$Gd_3Co_6Sn_5$	$Immm$	0.4311(1)	1.2424(3)	0.9752(3)
				Gd_4CoSn_8	$Cmcm$	0.4448(2)	1.6583(6)	0.4403(1)
				Co_3Sn_2	$Pnma$	0.7094(1)	0.52170(8)	0.8206(2)
21	22	48	30	$Gd_3Co_6Sn_5$	$Immm$	0.4311(1)	1.2418(2)	0.9742(2)
				Gd_4CoSn_8	$Cmcm$	0.4446(1)	1.6570(4)	0.4395(1)
				Co_3Sn_2 (trace)	$Pnma$			

Table 3   Continued

No.	Alloy composition, at.%			Phases	Space group	Lattice parameters, nm		
	Gd	Sn	Co			a	b	c
22	8	46	46	Gd_4CoSn_8	*Cmcm*	0.4451(1)	1.6625(4)	0.4407(1)
				Co_3Sn_2	*Pnma*	0.7102(2)	0.5215(2)	0.8196(2)
				$Gd_3Co_6Sn_5$	*Immm*	0.4322(2)	1.2450(4)	0.9769(3)
23	8	46	46	Gd_4CoSn_8	*Cmcm*	0.4451(1)	1.6601(2)	0.4399(1)
				Co_3Sn_2	*Pnma*	0.7098(1)	0.5219(1)	0.8208(1)
				CoSn (trace)				
24	4	46	50	Co_3Sn_2	*Pnma*	0.7074(3)	0.5211(2)	0.8198(4)
				CoSn	*P6/mmm*	0.5318(2)		0.4281(2)
				Gd_4CoSn_8	*Cmcm*	0.4450(2)	1.6592(9)	0.4397(2)
25	14	54	32	Gd_4CoSn_8	*Cmcm*	0.4440(4)	1.653(1)	0.4389(3)
				$Gd_3Co_4Sn_{13}$	$Pm\bar{3}n$	0.9498(1)		
				CoSn	*P6/mmm*	0.5347(5)		0.4294(6)

(a) Two alloy samples had been prepared at this composition. Results listed in this table had been confirmed by repetitive experiments

20 to 30 at.%. Analysis of the diffraction patterns of these alloys indicated the existence of a phase with a homogeneity range of 20 to 27 at.% Sn. Our results indicated that this phase is better described by the $Gd_3Co_8Sn_4$ structure rather than the $GdCo_3Sn$ structure.

A comparison of our work on the Co-Gd-Sn system (Fig. 1) with those given by Skorlozdra et al.[6] (figure not shown) shows that in the composition range of Gd-Gd_2Co_7-Gd_5Sn_3, our results were in good agreement with theirs. Significant differences were found in the phase regions along the line between the reported compounds $Gd_4Co_3Sn_3$ and CoSn. In our investigation of the Co-Gd-Sn system, alloys were prepared densely around this line. Although isostructural compounds of the RECoSn with a TiNiSi type structure (space group *Pnma*) and of the $RECo_6Sn_6$ with a YCo_6Ge_6-type structure (space group *P6/mmm*) have been reported for heavy rare earths RE = Tb, Dy, Ho, Er, and Y[16] and for RE = Gd systems in Ref 6 and 33, no such phases corresponding to the structures of GdCoSn and $GdCo_6Sn_6$ were observed under our experimental conditions. Instead, analyses of the XRD patterns of alloys around the composition points of the reported GdCoSn and $Gd_4Co_3Sn_3$ compounds revealed the existence of a new phase with an approximate atomic ratio close to 2:1:2. The diffraction pattern of the new phase exhibited characteristic profile similar to the XRD pattern of compound $Dy_{117}Co_{57}Sn_{112}$ which was found during our investigation of the Dy-Co-Sn system.[7] Based on the refinement of single crystal x-ray diffraction data, $Dy_{117}Co_{57}Sn_{112}$ was reported to crystallize in a large fcc cell (space group $Fm\bar{3}m$, a = 2.9831(4) nm) with a structure type similar to the $Tb_{117}Fe_{52}Ge_{112}$ type.[34] In this work, the stoichiometry of $Gd_{117}Co_{57}Sn_{112}$ was assumed for this new phase in analogy with $Dy_{117}Co_{57}Sn_{112}$. Our preliminary structure study of this new phase $Gd_{117}Co_{57}Sn_{112}$ from powder XRD data yielded the lattice parameter a = 3.0023(4) nm, as given in Table 1. Theoretical diffraction intensities of $Gd_{117}Co_{57}Sn_{112}$ phase were then calculated to compare with the experimental ones and a

good agreement was found. Figure 2 presents the XRD pattern of alloy Gd33Co50Sn17 (alloy #7), indicating that this alloy consists of three phases: $Gd_{117}Co_{57}Sn_{112}$, Gd_2Co_7, and Gd_5Sn_3. The XRD pattern of alloy with $Gd_4Co_3Sn_3$ nominal composition is similar to that of alloy #7 and is in no way a single-phase pattern. Figure 3 shows the XRD pattern of the GdCoSn stoichiometric alloy (alloy #16). It is clearly seen that this alloy consists of the $Gd_{117}Co_{57}Sn_{112}$ and $Gd_3Co_8Sn_4$ phases.

Compound $GdCo_2Sn_2$ has been reported by Skorlozdra et al.[6] However, in the RE-Co-Sn systems for RE = Nd,[5] Dy,[7] and Er,[8] no such compound with a stoichiometry of 1:2:2 was observed, instead compounds with a stoichiometry of 3:6:5 were reported. Extensive studies have indicated that in the RET_2X_2 series (1:2:2), compounds RET_2X_2 with T = Fe, Co, Ni, Cu and X = Si, Ge belong to the body-centered tetragonal $ThCr_2Si_2$-type structure (space group $I4/mmm$), whereas compounds RET_2X_2 with T = Ni, Cu and X = Sn, Sb crystallize in the primitive tetragonal $CaBe_2Ge_2$-type structure (space group $P4/nmm$).[16] Compounds $RE_3Co_6Sn_5$ crystallize with a ternary ordered derivative of the orthorhombic La_3Al_{11}-type structure (space group *Immm*).[15,35] Theoretical diffraction intensities for tentative $GdCo_2Sn_2$ or $Gd_3Co_6Sn_5$ were calculated based on the above-mentioned three types of structure, and were compared with the observed diffraction patterns of relevant alloys. It has been found that no 1:2:2 compound with either the $ThCr_2Si_2$-type structure or the $CaBe_2Ge_2$-type structure exists in the Co-Gd-Sn system. The calculated diffraction intensities based on the structure of $Gd_3Co_6Sn_5$ from Ref 15 matched well with the observed diffraction patterns. Therefore, the existence of a compound with a stoichiometry of 3:6:5 is confirmed. Figure 4 shows the XRD pattern of the $GdCo_2Sn_2$ stoichiometric alloy (alloy #19). Three phases $Gd_3Co_6Sn_5$, Gd_4CoSn_8, and Co_3Sn_2 were identified. Analysis of XRD patterns of alloys #20-23 (see Table 3) can further clarify the nonexistence of the $GdCo_6Sn_6$ and $GdCo_2Sn_2$ compounds in the Co-Gd-Sn system. Three
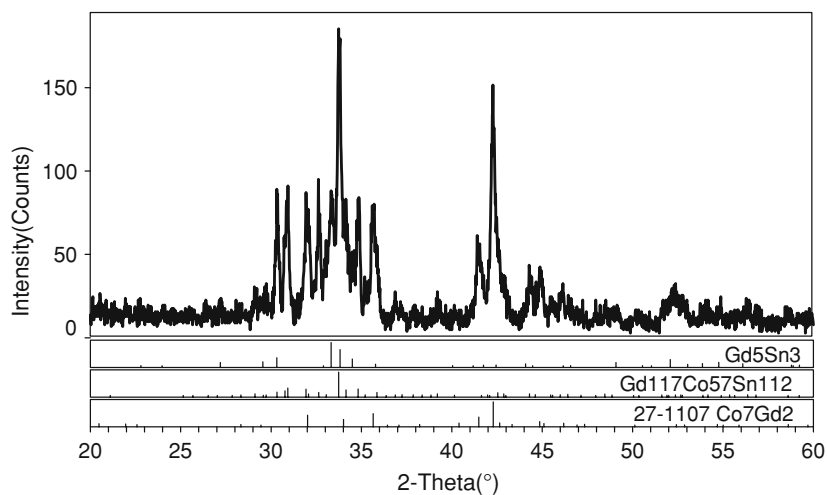
Fig. 2 XRD pattern of alloy Gd33Co50Sn17 (alloy #7): $Gd_{117}Co_{57}Sn_{112}$ + Gd_2Co_7 + Gd_5Sn_3
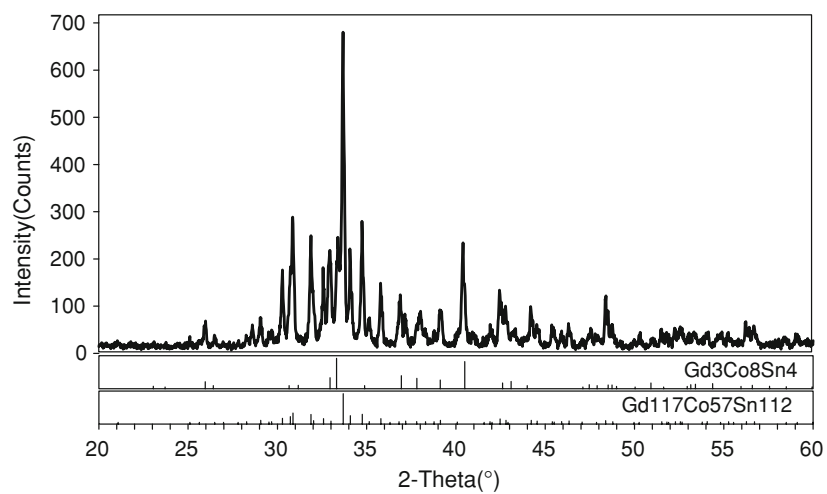
Fig. 3 XRD pattern of the alloy with GdCoSn nominal composition (alloy #16): $Gd_{117}Co_{57}Sn_{112}$ + $Gd_3Co_8Sn_4$
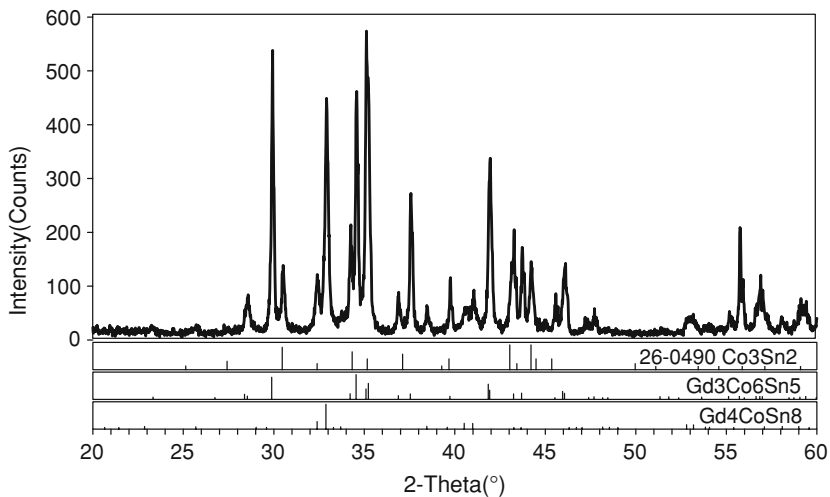
Fig. 4 XRD pattern of the alloy with $GdCo_2Sn_2$ nominal composition (alloy #19): $Gd_3Co_6Sn_5$ + Gd_4CoSn_8 + Co_3Sn_2
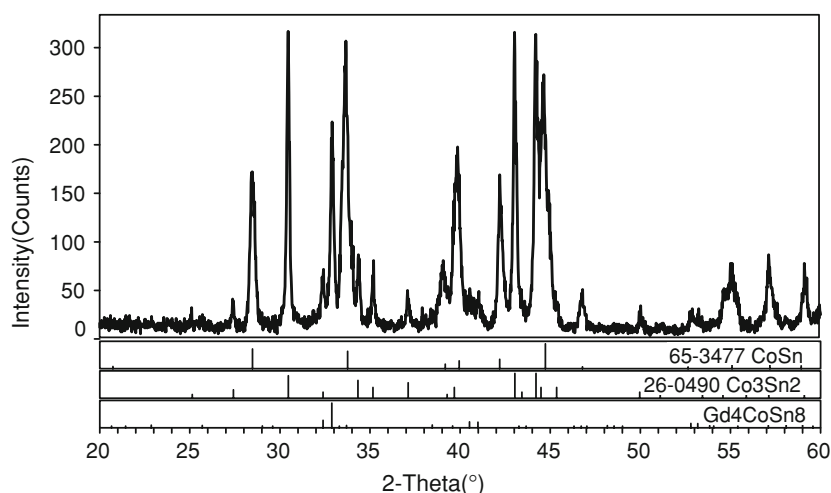
Fig. 5 XRD pattern of alloy Gd4Co50Sn46 (alloy #24): CoSn + Co_3Sn_2 + Gd_4CoSn_8

phases were identified in alloys #20-22 as $Gd_3Co_6Sn_5$, Gd_4CoSn_8, and Co_3Sn_2. No diffraction peaks for the $GdCo_6Sn_6$ and $GdCo_2Sn_2$ structures were found. Evidence can also be found in Fig. 5 which presents the XRD pattern of alloy Gd4Co50Sn46 (alloy #24). The peaks corresponding to the Gd_4CoSn_8 phase are clearly seen, and thus this alloy can not be in the (CoSn + Co_3Sn_2 + $GdCo_6Sn_6$) three-phase field as shown in Ref 6. Actually, alloy #24 consists of three phases of CoSn, Co_3Sn_2, and Gd_4CoSn_8.

4. Conclusions

(1) Partial isothermal section between 0 and 55 at.% Sn of the Co-Gd-Sn ternary system at 500 °C has been determined by means of X-ray powder diffraction. This section shows some differences compared with those reported by Skorlozdra et al.[6]

(2) In the studied composition range, the existence of 12 binary compounds Gd_5Sn_3, Gd_5Sn_4, $Gd_{11}Sn_{10}$, Co_3Sn_2, CoSn, Gd_2Co_{17}, Gd_2Co_7, $GdCo_3$, $GdCo_2$, Gd_4Co_3, $Gd_{12}Co_7$, and Gd_3Co were confirmed. Gd_3Sn phase was not observed. The binary Gd-Sn alloys containing 40 to 55 at.% Sn and their adjacent ternary alloys were difficult to obtain due to their pulverization in air.

(3) Six ternary phases were found to exist at 500 °C: Gd_6Co_2Sn, $Gd_3Co_8Sn_4$, $Gd_3Co_6Sn_5$, $Gd_{117}Co_{57}Sn_{112}$, Gd_4CoSn_8, and $Gd_3Co_4Sn_{13}$. Ternary phase $Gd_{117}Co_{57}Sn_{112}$ was first reported in this work with $Dy_{117}Co_{57}Sn_{112}$-type structure, space group $Fm\bar{3}m$ and lattice parameter $a = 3.0023(4)$ nm. Ternary phases of the $Gd_4Co_3Sn_3$, GdCoSn, $GdCo_2Sn_2$, and $GdCo_6Sn_6$ compositions, which were reported by Skorlozdra et al.,[6] were not observed in this study.

(4) Our results indicated that the $GdCo_3Sn$ compound belongs to the $RE_3Co_8Sn_4$ structure. $Gd_3Co_8Sn_4$ phase shows a homogeneity range of 20 to 27 at.% Sn along the 20 at.% Gd iso-concentration line.

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