Ni-Ga BINARY PHASE RELATIONS AT 700 ℃[①]

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ABSTRACT As the solid foundation of building ternary phase relations, Ni-Ga binary phase relations at 700 ℃ were experimentally determined by X-ray powder diffraction and the confusion in the previous reports was clarified. The arc-melting was adopted to prepare the samples and ensure the full mixing of starting elements. Five intermetallic compounds were obtained, i. e., $Ni_{1-x}Ga_x$, Ni_3Ga, $Ni_{13}Ga_9$, NiGa and Ni_2Ga_3, but Ni_5Ga_3, Ni_3Ga_2, Ni_3Ga_4 and $NiGa_4$ phases were not found in experiment. Their lattice parameters and the powder X-ray diffraction patterns including the *d*-value and the indices of crystallographic planes were given as a reference to determine exact ternary phase relations of Ni-Ga-Sb(As).

Key words Ni-Ga binary phase relation lattice constant intermetallic compound

1 INTRODUCTION

Efforts to design new metallization processes in the ongoing miniaturization of electronic and optoelectronic devices would benefit from an enhanced understanding of the chemistry, microstructure and morphology of metallic contacts to compound semiconductors (M/ III-V SC)[1], such as Ni/ GaAs[2-5], Ni/ GaSb[1], and so on. Previous work has demonstrated the need for phase diagrams in rationalizing the reactions of metals with III-V SC and in researching stable contacts[6]. Therefore, the knowledge of which phase is in thermodynamic equilibrium with the III-V SC is of practical importance. Unfortunately, these phase diagrams are not easily available because of the difficulty in the preparation of samples and the complication of the phase relations including the unclear solubility limits. For example, up to now, many reports about the Ni-Ga-Sb (or As) ternary phase diagram are not clear or different with each other. Even in Ni-Ga binary system, the different intermetallic phases were reported at a certain isothermal section. This is very confused and therefore needs a more exact testification. Especially, the isothermal section at 700 ℃ of Ni-Ga binary phases has not been reported.

The knowledge of the binary phase relations is a basis of the building of the ternary phase relations. It is impossible to succeed in mapping out a correct ternary phase diagram without a clear binary phase relations. Therefore, it is most important to define the binary phases that border the diagram.

This paper deals with Ni-Ga binary system in the isothermal section at 700 ℃. The arc-melting method was adopted for the preparation of the samples which is different from the method of the direct combination of the elements reported by most of authors. This ensured an enough mixing of the elements at high temperature. First, an isothermal section at 700 ℃ of the phase diagram was experimentally determined. Then, as a reference for correctly determining the ternary phases afterwards, their X-ray diffraction patterns including the *d*-value and the indices of the crystallographic planes were given.

2 EXPERIMENTAL

All alloy samples with a mass of about 1.2 g were prepared by arc-melting the appropriate

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amount of the starting elements (Ni ingots and Ga ingots) in an atmosphere of ultra-pure argon gas. The purity of Ni and Ga is higher than 99.9%. The samples were remelted several times to ensure full mixing. The massloss during the melting process was less than 2%. The obtained samples were sealed in quartz capsules that had a vacuum of 1.3 Pa, annealed at 700 ℃ for 20~30 days and then the samples were quickly quenched into water at RT. The annealing temperature was controlled within ±5 ℃.

The phase identification of the samples was carried out by X-ray powder diffraction in a M18AHF X-ray diffractometer with CuK_α radiation (50kV, 200mA). High purity Si was added to the samples as an internal standard to correct the 2θ position of the diffraction peaks.

3 RESULTS AND DISCUSSION

In the Ni-Ga binary phase relations at 700 ℃, as outlined in Fig. 1, fifteen samples with different nominal stoichiometric compositions (such as Ni∶Ga(mole) = 4∶1, 7∶3, 3∶2, 1∶1, 3∶7, 1∶4, 1∶9) were prepared in the arc-melting furnace and five intermetallic compounds were determined by powder X-ray diffraction, i.e., $Ni_{1-x}Ga_x$, Ni_3Ga, $Ni_{13}Ga_9$, NiGa and Ni_2Ga_3, as described below (also see Tables 1~5):

No. 1 Ni∶Ga= 4∶1 —$Ni_{1-x}Ga_x$,
No. 2 Ni∶Ga= 7∶3 —Ni_3Ga+ Ni,
No. 3 Ni∶Ga= 3∶2 —$Ni_{13}Ga_9$+ NiGa,
No. 4 Ni∶Ga= 1∶1 —NiGa+ Ni
No. 5 Ni∶Ga= 3∶7 —Ni_2Ga_3+ Ga
No. 6 Ni∶Ga= 1∶4 —Ni_2Ga_3+ Ga
No. 7 Ni∶Ga= 1∶9 —Ni_2Ga_3+ Ga

Up to now, all intermetallic phases obtained by previous investigations[8-11] in Ni-Ga binary system are Ni_3Ga, Ni_5Ga_3, Ni_3Ga_2, $Ni_{13}Ga_9$, NiGa, Ni_3Ga_4, Ni_2Ga_3, $NiGa_4$.

However, recent years, most of reports were concentrated on the isothermal section at 600 ℃[1-3, 7]. Guerin R and Guivarc'h A[2] reported that the existing Ni-Ga binary phases of the isothermal section at 600 ℃ were Ni_3Ga, Ni_3Ga_2, NiGa and Ni_2Ga_3, but afterwards, Le

Table 1 *d*-values and indices of crystallographic planes of identified phases $Ni_{1-x}Ga_x$ from sample No. 1

Nominal composition Ni∶Ga= 4∶1		Identified phases $Ni_{1-x}Ga_x$	
d/ Å	I/I_0	*H K L*	*d*/ Å
2.0599	69	1 1 1	2.0600
1.7849	100	2 0 0	1.7849
1.3540	6	-	-
1.2610	23	2 2 0	1.2610

$Ni_{1-x}Ga_x$ with space group Fm$\bar{3}$m, lattice type of cubic, cell const a= 3.5674(8) Å

Table 2 *d*-values and indices of crystallographic planes of identified phases Ni_3Ga and Ni from sample No. 2

Nominal composition Ni∶Ga= 7∶3		Identified phases			
		Ni_3Ga		Ni	
d/ Å	I/I_0	*H K L*	*d*/ Å	*H K L*	*d*/ Å
2.5276	7	1 1 0	2.5277		
2.0747	100	1 1 1	2.0747		
2.0439	23			1 1 1	2.0439
1.7987	29	2 0 0	1.7987		
1.4675	7	2 1 1	1.4676		
1.2724	32	2 2 0	1.2724		
1.2429	15			2 2 0	1.2429

Ni_3Ga with space group Pm$\bar{3}$m, lattice type of cubic, cell const a= 2.596(2) Å; and Ni with space group Fm3m, lattice type of cubic, cell const a= 3.518(5) Å

Clanche *et al*[1] reported that the intermetallic compounds were Ni_3Ga, Ni_5Ga_3, $Ni_{13}Ga_9$, NiGa and Ni_2Ga_3 in the same isothermal section. Guivarc'h A *et al*[7] also reported that the stable phases were Ni_3Ga, Ni_3Ga_2, $Ni_{13}Ga_9$, NiGa, Ni_2Ga_3 at 600 ℃ isothermal section. Zheng X Y *et al*[3] considered that the stable binary phases at 600 ℃ were Ni_3Ga, Ni_5Ga_3, $Ni_{13}Ga_9$, NiGa, Ni_2Ga_3, $NiGa_4$. However, we did not find Ni_5Ga_3, Ni_3Ga_2, Ni_3Ga_4 and $NiGa_4$ in the isothermal section at 700 ℃ in our experiments. For the phases of Ni_5Ga_3, Ni_3Ga_4 and $NiGa_4$, their existing temperature ranges[10] are < 741 ℃, < 542 ℃, < 363 ℃, respectively. So the phases of Ni_3Ga_4 and $NiGa_4$ should not appear at 700 ℃. The only exception in our exper-

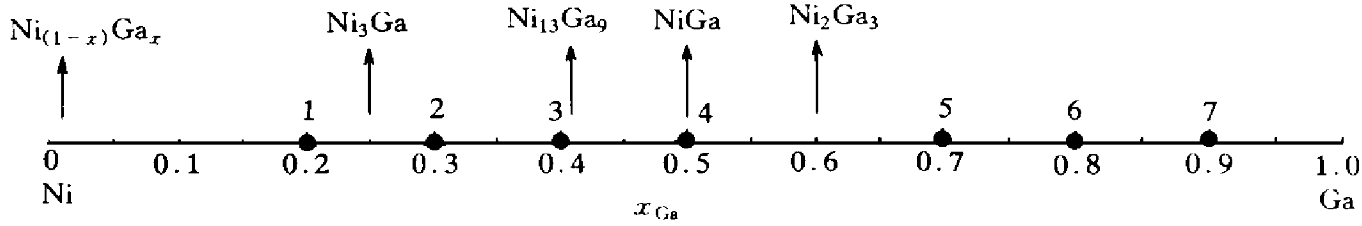

Fig. 1　Sample composition and phase relations in Ni-Ga binary system at 700 ℃

Table 3　*d*-values and indices of crystallographic planes of identified phases $Ni_{13}Ga_9$ and NiGa from sample No. 3

Nominal composition Ni∶Ga=3∶2		Identified phases				Nominal composition Ni∶Ga=3∶2		Identified phases			
		$Ni_{13}Ga_9$		NiGa				$Ni_{13}Ga_9$		NiGa	
d/Å	I/I_0	$H\ K\ L$	d/Å	$H\ K\ L$	d/Å	d/Å	I/I_0	$H\ K\ L$	d/Å	$H\ K\ L$	d/Å
5.6610	1	1 1 0	5.6536			1.4098	22	4 4 4	1.4079		
4.0296	1	2 0 2	4.0183			1.3930	1	4 2 5	1.3929		
3.6957	1	3 1 1	3.7032			1.3589	2	5 5 2	1.3589		
3.4293	1	2 2 1	3.4274			1.3310	1	8 2 6	1.3302		
3.0931	1	0 2 1	3.0906			1.3171	1	9 3 4	1.3159		
2.9936	2	$\bar{1}$ 1 1	2.9875			1.2901	1			2 1 0	1.2901
2.8877	3			1 0 0	2.8877	1.2705	1	0 6 1	1.2718		
2.8202	10	4 0 3	2.8258			1.2514	1	2 6 0	1.2513		
2.6019	4	4 2 2	2.5999			1.2431	2	5 1 6	1.2429		
2.5061	7	1 3 0	2.5026			1.2306	1	1 5 3	1.2308		
2.3007	23	6 0 3	2.3036			1.2258	1	7 5 3	1.2245		
2.2276	15	3 3 1	2.2288			1.2041	1	3 3 5	1.2036		
2.0980	1	6 0 2	2.0966			1.1944	1	4 6 1	1.1944		
2.0439	73	5 1 4	2.0418	1 1 0	2.0439	1.1808	30			2 1 1	1.1808
2.0188	100	$\bar{2}$ 1 1	2.0155			1.1666	1	2 2 5	1.1663		
1.9918	67	6 2 3	1.9895			1.1523	11	12 0 6	1.1518		
1.9749	30	0 4 0	1.9735			1.1441	1	7 1 0	1.1450		
1.8864	2	3 3 0	1.8845			1.1027	1	10 4 6	1.1022		
1.7925	1	4 2 4	1.7905			1.0907	1	$\bar{1}$ 1 4	1.0909		
1.7743	1	2 4 0	1.7741			1.0754	1	11 3 4	1.0753		
1.6676	1			1 1 1	1.6676	1.0575	4	$\bar{6}$ 2 1	1.0571		
1.5774	1	$\bar{1}$ 3 2	1.5768			1.0519	7	1 5 4	1.0521		
1.5595	1	6 2 1	1.5585			1.0219	2			2 2 0	1.0219
1.5485	2	1 5 1	1.5492			0.9953	2	5 7 4	0.9950		
1.4904	2	9 1 4	1.4922			0.9881	1	11 3 3	0.9881		
1.4789	1	3 5 1	1.4775			0.9633	1	0 2 5	0.9637	3 0 0	0.9633
1.4451	36			2 0 0	1.4451	0.9581	1	2 8 2	0.9583		
1.4243	12	8 0 2	1.4240								

$Ni_{13}Ga_9$ with space group C2/m, latice type of monoclinic and cell consts a = 13.822 Å, b = 7.894 Å, c = 8.478 Å, β = 35.88°; and NiGa with space group Fm3m, lattice type of cubic, cell const a = 2.8898(7) Å

iments was Ni_5Ga_3, which should occur but was not observed in our experiments in spite of many verification tests have been carried out, so the temperature range for the occurrence of Ni_5Ga_3 stable phase needs to be determined through further experiments. Our experimental results were nearly similar to that of the report of Guivarc' h A *et al*[7], except for the Ni_3Ga_2 phase which should not appear according to its existing temperature range (790 ℃< t < 947 ℃)[10]. The Ni_3Ga_2 phase crystallized in the B8$_{1.5}$ structure between 790 ℃ and 947 ℃[12], below this temperature it undergoes a transition from a hexagonal γ-Ni_3Ga_2 to a monoclinic phase $Ni_{13}Ga_9$ at 790 ℃ ±30 ℃, which may be regarded as a distorted superlattice structure and whose vacancies and nickle atoms became ordered[13]. This is consistent with our results that $Ni_{13}Ga_9$ monoclinic phase, not hexagonal Ni_3Ga_2, occurs at 700 ℃ (see Fig. 2 and Table 3).

As we know, the pure Ni belongs to cubic lattice with the lattice constant a= 3.518 Å, but a little amount of Ga can be dissolved into the lattice of Ni and forms $Ni_{1-x}Ga_x$, the lattice constant a increases from 3.518 Å to 3.567 Å without change of the lattice type. In fact, there exist different solubility limits in Ni (Ga), Ni_3Ga, NiGa, Ni_2Ga_3 and so on [2, 3], so the lattice parameters would change within certain soluble ranges. The X-ray diffraction pattern of Ni_3Ga is similar to that of Ni, but the weak diffraction line (110), (211) and the larger lattice constant a= 3.596 Å indicate the Ni_3Ga phase (see Fig. 3 and Table 2). NiGa compound is a stable phase and is easily formed with a cubic lattice (see Table 4). Two phases of Ni_2Ga_3 and Ga coexist in the samples of No. 5~ 7. The lattice type of Ga was reported to belong to orthorhombic structure with the lattice parameters a= 4.524 Å, b= 4.523 Å and c= 7.661 Å in Pearson' s Handbook of Crystallographic Data for Intermetallic Phases (1991), but we only obtained a tetragonal structure with the lattice parameters a= 4.523 (3) Å, c= 7.666 (3) Å.

Table 4 *d*-values and indices of crystallographic planes of identified phases NiGa and Ni from sample No. 4

Nominal composition Ni∶ Ga= 1∶ 1		Identified phases NiGa		Ni	
d/ Å	I/I_0	HKL	d/ Å	HKL	d/ Å
2.0365	100	1 1 0	2.0365	1 1 1	2.0365
1.6681	2	1 1 1	1.6681		
1.4448	1	2 0 0	1.4448		
1.4395	1				
1.2944	1	2 1 0	1.2944		
1.2429	3			2 2 0	1.1429

GaNi with space group Pm$\bar{3}$m, lattice type of cubic, cell const a= 2.891(2) Å; and Ni with space group Fm3m, lattice type of cubic, cell const a= 3.517(2) Å

Overall, the existing stable phases at 700 ℃ should be Ni_3Ga, $Ni_{13}Ga_9$, NiGa and Ni_2Ga_3.

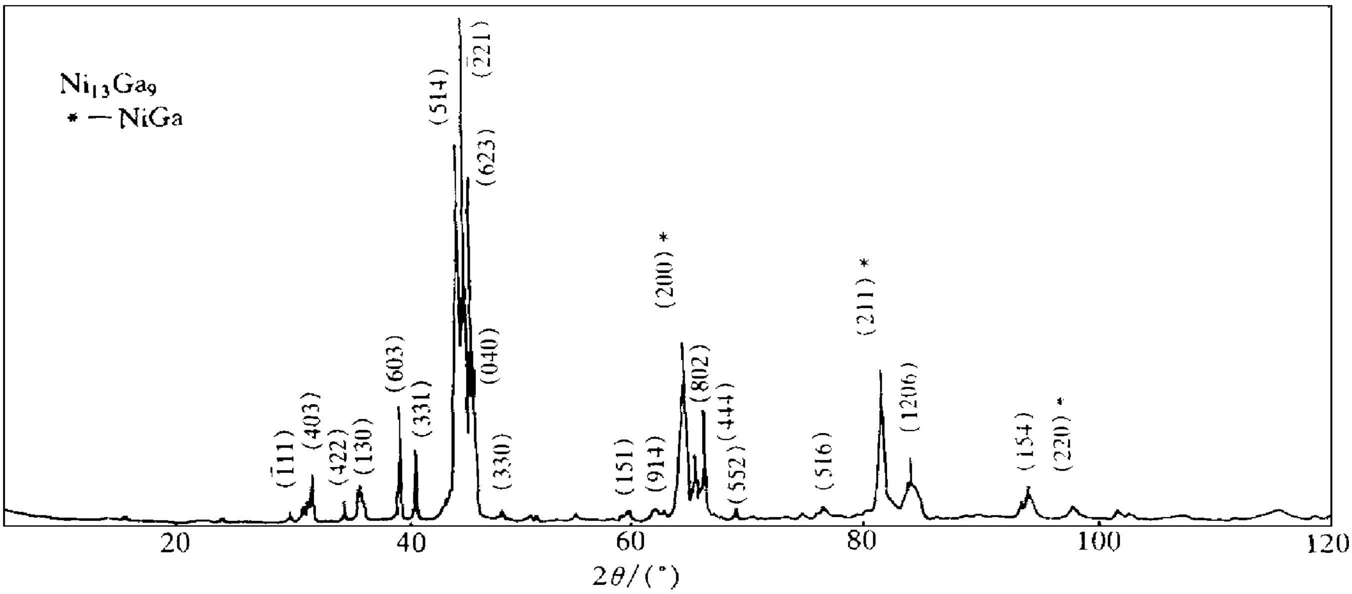

Fig. 2 X-ray diffraction pattern for two phases of $Ni_{13}Ga_9$ and NiGa from sample No. 3

The confusion in Ni-Ga binary phase relations at 600~ 700 ℃ was clarified in our experiments. Their crystal structures were analyzed and as a representative, the X-ray diffraction patterns of the samples (No. 2, No. 3, No. 4, No. 6) were given (see Fig. 2– 4). The lattice parameters and the indices of crystallographic phanes were determined so as to investigate further their ternary phase relations with Sb (or As).

4 CONCLUSIONS

Ni-Ga binary phase relations at 700 ℃ were experimentally determined by X-ray powder diffraction. The arc-melting method was adopted for the preparation of the samples. Five inter-

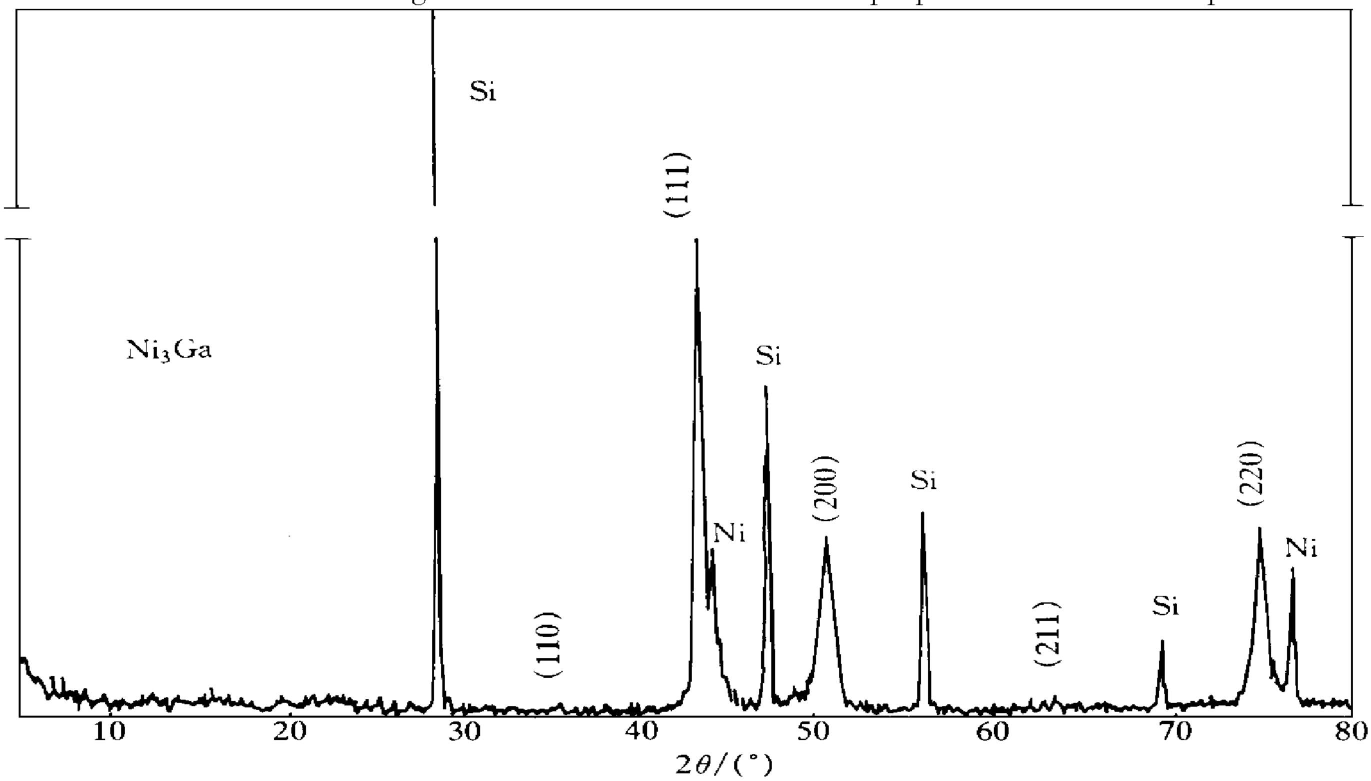

Fig. 3 X-ray diffraction pattern for two phases of Ni_3Ga and Ni from sample No. 2

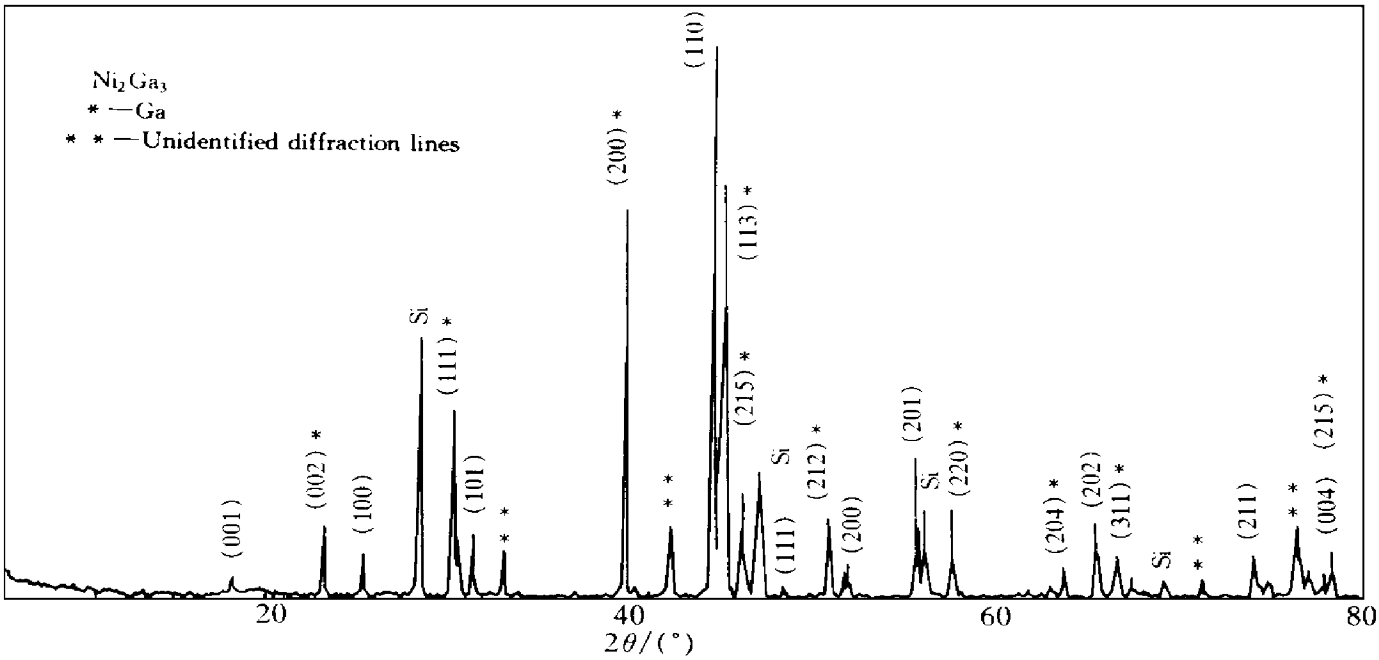

Fig. 4 X-ray diffraction pattern for two phases of Ni_2Ga_3 and Ga from sample No. 7

Table 5 *d*-values and indices of crystallographic planes of identified phases Ni_2Ga_3 and Ga from sample No. 6

Nominal composition Ni∶Ga= 1∶4		Identified phases				Nominal composition Ni∶Ga= 1∶4		Identified phases			
		Ni_2Ga_3		Ga				Ni_2Ga_3		Ga	
d/Å	I/I_0	*H K L*	*d*/Å	*H K L*	*d*/Å	*d*/Å	I/I_0	*H K L*	*d*/Å	*H K L*	*d*/Å
4.9023	3	0 0 1	4.9023			1.9547	59			2 1 1	1.9548
3.8388	6			0 0 2	3.8389	1.7859	6			2 0 2	1.7859
3.5197	6	1 0 0	3.5198			1.7642	4	2 0 0	1.7642	1 0 4	1.7642
2.9558	31			1 1 1	2.9558	1.6522	21	2 0 1	1.6522		
2.9262	24			1 0 2	2.9262	1.6002	3			2 2 0	1.6002
2.8520	18	1 0 1	2.8520	2 0 4	1.4634	1.4633	5				
2.7123	19					1.4264	28	2 0 2	1.4264		
2.2598	14			2 0 0	2.2598	1.4048	10			3 1 1	1.4048
2.1265	35					1.3252	5	2 1 0	1.3253		
2.0410	11					1.2782	2	2 1 1	1.2782	0 0 6	1.2782
2.0236	100	1 1 0	2.0236			1.2689	10				
2.0032	58	1 0 2	2.0033			1.2426	8				
1.9939	55			1 1 3	1.9940	1.2211	4	0 0 4	1.2211	2 1 5	1.2211

Ni_2Ga_3 with space group $P\bar{3}m1$, lattice type of hexagonal, cell consts $a = 4.054(4)$ Å, $c = 4.885(5)$ Å; and Ga with space group Abma, lattice type of tetragonal, cell consts $a = 4.523(3)$ Å, $c = 7.666(3)$ Å

metallic compounds, $Ni_{1-x}Ga_x$, Ni_3Ga, $Ni_{13}Ga_9$, NiGa and Ni_2Ga_3 were obtained, but Ni_5Ga_3, Ni_3Ga_4 and $NiGa_4$ were not found, which were different from previous reports. The confusion in Ni-Ga binary phase relations at 600 ~ 700 ℃ was clarified in our experiments. Their lattice parameters, the X-ray diffraction patterns including the *d*-value and the indices of crystallographic planes were given.

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