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Phase Equilibria in Y–Ag–P and Nd–Ag–P Systems

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Phase equilibria were established in the Y–Ag–P and Nd–Ag–P ternary systems up to 80 at.% of P at 400°C. The isothermal sections have been built basing on X-ray phase analysis.

Key words: phase diagram, ternary system, phosphides

Phase diagrams of the Y–Ag [1], Nd–Ag [2,3], Ag–P [4], Nd–P [5] boundary binary systems are presented in [6]. There is no phase diagram available for Y–P. Three compounds, YP, Y_2P and YP_2, exist in this system. Their crystal structures were not reported. Crystallographic data of the initial components and binary phases of the Y–Ag–P and Nd–Ag–P ternary systems are listed in Table 1. Phase equilibria in the Y–Ag–P and Nd–Ag–P ternary systems have not been studied yet. Among Ln–Ag–P related ternary systems, where Ln = rare-earth elements, only the Ce–Ag–P system has been studied [24]. The existence of the phosphide with the approximate composition $CeAgP_2$ (*I*4/*mmm* space group, $a = 0.4002(1)$ nm, $c = 2.042(2)$ nm) at 800°C and its decomposition at 400°C has been reported [24]. The $LnAg_xP_y$ ternary compounds (*Cmmm* space group, $CeCu_{1,12}P_{1,97}$ structure type), where Ln = La, Ce, Pr are known, but their lattice parameters were not reported [25]. Therefore, the Y–Ag–P and Nd–Ag–P ternary systems become the subjects of our investigation to construct isothermal sections of these systems at 400°C and to obtain ternary compounds and to determine their crystal structures. The reaction temperature 400°C for these systems is chosen, because the AgP_2 and Ag_3P_{11} compounds exist up to 400°C [4].

Table 1. Crystallographic data for the boundary phases in the Y–Ag–P and Nd–Ag–P systems.

Phase	Pearson symbol	Space group	Prototype	Lattice parameter, nm			β,°	Ref.
				a	*b*	*c*		
β-Y	*cF*4	*Fm*3*m*	Cu	0.583	–	–	–	7
α-Y	*hP*2	$P6_3/mmc$	Mg	0.3663	–	0.5814	–	8
Nd	*hP*2	$P6_3/mmc$	La	0.3659	–	1.1799	–	9
Ag	*cF*4	*Fm*3*m*	Cu	0.4086	–	–	–	10
AgP_2	*mP*12	$P2_1/c$	CuP_2	0.62167	0.50587	0.7806	113.48	11
Ag_3P_{11}	*mC*28	*Cm*	Ag_3P_{11}	1.2999	0.7555	0.6612	118.84	12
$Y_{14}Ag_{51}$*	*hP*68	*P*6/*m*	$Gd_{14}Ag_{51}$	1.2637	–	0.9300	–	13
YAg_2	*tI*6	*I*4/*mmm*	$MoSi_2$	0.3691	–	0.9241	–	14
YAg	*cP*2	*Pm*3*m*	CsCl	0.3619	–	–	–	15
$Nd_{14}Ag_{51}$*	*hP*68	*P*6/*m*	$Gd_{14}Ag_{51}$	1.2726	–	0.9389	–	16

Table 1 (continuation)

$NdAg_2$	*ol*12	*Imma*	KHg_2	0.4772	0.7027	0.8153	–	17
NdAg	*cP*2	*Pm*3*m*	CsCl	0.3716	–	–	–	18
YP	*cF*8	*Fm*3*m*	NaCl	0.5652	–	–	–	19
NdP	*cF*8	*Fm*3*m*	NaCl	0.5838	–	–	–	20
NdP_2	*mP*12	$P2_1/c$	$NdAs_2$	0.40018	0.65385	1.0098	105.72	21,22
NdP_5	*mP*12	$P2_1/m$	NdP_5	0.4938	0.9551	0.5444	103.27	23

*At 21.5 at.% of rare-earth elements.

EXPERIMENTAL

To investigate the Y–Ag–P and Nd–Ag–P ternary systems, we prepared samples by two different methods, depending on the phosphorus content. For sample preparation, a powder of red phosphorus (99.9 wt.%), the fillings of yttrium and neodymium (99.9 wt.%) and a powder of silver (99.98 wt.%) were used. Samples were prepared from freshly ground powder of P, which was mixed with Y and Nd fillings and Ag powder and then pressed into pellets at 7.9 MPa, using a 6 to 8 mm steel die without a lubricant. Samples with 0–33 at.% of P were then arc melted in argon atmosphere. All prepared alloys were heat-treated at either 400°C for 1000 hours in evacuated quartz tube, followed by quenching in cold water. Each sample with 33–80 at.% P content was sealed in an evacuated quartz ampoule and slowly heated (100 K/day) to 400°C. After an annealing time of 250 hours the samples were quenched by removing them from the furnace. Then, the samples were ground, pressed and heated in an evacuated silica tube at 400°C during 1000 hours and quenched in cold water. The total mass of each sample was about 1 g.

For single crystal growth of the ternary compounds the chemical transport reaction *via* a gas phase was used. Initial pure components in stoichiometric ratios or powdered previously annealed samples were placed into an evacuated quartz tube together with a small amount of iodine tincture. The total masses of the ternary samples and of the iodine tincture were about 1 and 0.15 g, respectively. The reaction took place during 250 h at two-zone heating with the temperature of the 'hot' and the 'cold' end of the ampoule at 800 and 600°C, respectively.

Phase analysis was carried out by using X-ray powder films, obtained in RKD-57.3 chambers (Cr K radiation) and diffractograms (diffractometer DRON-3M, CuK_α radiation, 2ϑ–$2\vartheta_{max}$ = 20–100°, $\Delta 2\vartheta$ = 0.05°). Precise lattice parameters and standard deviations were obtained by least square refinement using CSD software [26].

RESULTS AND DISCUSSION

The isothermal section of Y–Ag–P system has been constructed using the results of X-ray powder phase analysis of samples annealed at 400°C (Fig. 1). The compositions of the samples are shown in Fig. 1. The yttrium monophosphide YP in the Y–Ag–P system exists in equilibrium with the initial components and binary compounds. Results of crystallographic phase analysis on a series of representative ternary samples are listed in Table 2. Practically no variation of the lattice dimensions exists among the initial components and binary compounds and their corresponding data in ternary samples, which suggests the absence of mutual solid solubilities among Y, Ag, and the binary compounds of side binary systems. We have not studied the homogeneity range of the $Y_{14}Ag_{51}$, because of existence of the detailed data about it in [13]. Therefore, according to these data, the homogeneity range of the $Y_{14}Ag_{51}$ is presented from 21.5 up to 25.5 at. % Y in Fig. 1.

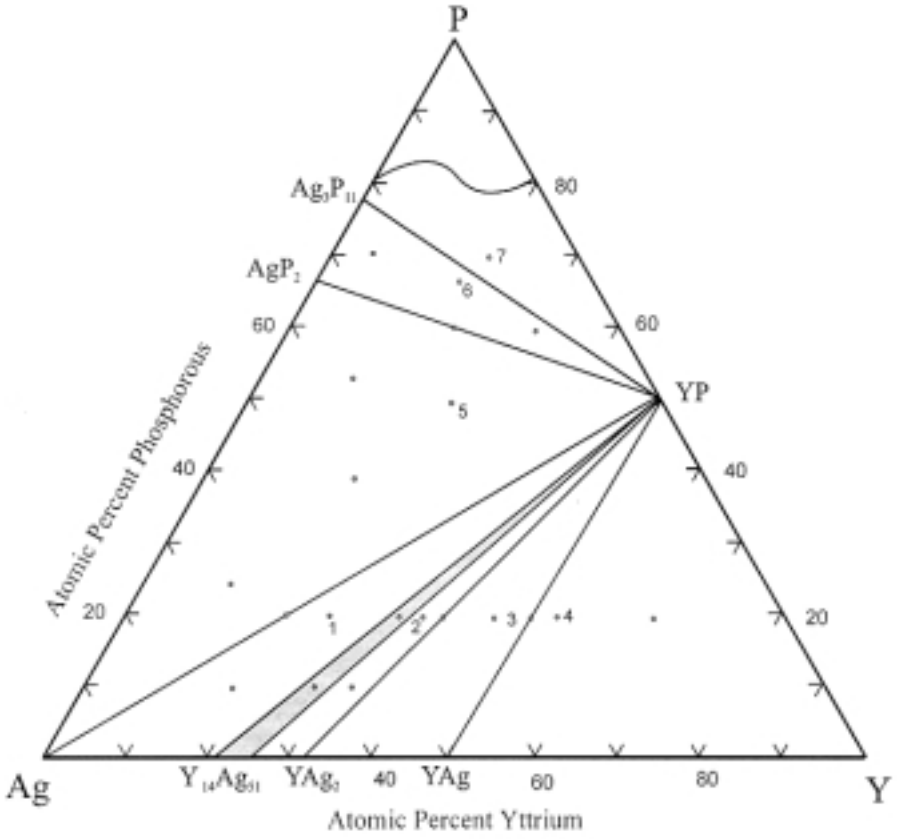

Figure 1. Isothermal section of phase equilibria diagram of the Y–Ag–P system at 400°C.

Phase relations in the Nd–Ag–P system at 400°C are shown in Fig. 2. Similar to the Y–Ag–P system, the neodymium monophosphide NdP in the Nd–Ag–P system exists in equilibrium with the initial components (Ag, Nd) and binary compounds. Also there are no mutual solid solubilities among components and the binary compounds in this system. The homogeneity range of the $Nd_{14}Ag_{51}$ compound is shown from 21.5 up to 25.5 at. % Nd in Fig. 2, corresponding to [16]. Crystallographic data of Nd–Ag–P ternary alloys annealed at 400°C are listed in Table 2.

No ternary compounds exist in the investigated Y–Ag–P and Nd–Ag–P ternary systems at 400°C. Checking a suggestion that ternary compounds could be formed at higher temperatures, we synthesized the $YAgP_2$ and $NdAgP_2$ samples by heat treatment at 600, 800 and 1000°C. But no ternary compounds have been obtained in these samples. Single crystals of YP, NdP, NdP_5 have been obtained using the chemical transport reaction via a gas phase for the samples with the same and others compositions. But, we have not obtained single crystals of ternary compounds by this method, too.

Table 2. Crystallographic data of some Y–Ag–P and Nd–Ag–P ternary alloys annealed at 400°C.

№	Composition, at.%.			Phase analysis	Lattice parameters, nm			
	Y or Nd	Ag	P		*a*	*b*	*c*	β, °
1	25	55	20	Ag	0.4088(3)	…	…	…
				YP	0.56531(2)	…	…	…
				$Y_{14}Ag_{51}$	1.2641(6)	…	0.9310(4)	…
2	37	43	20	YP	0.56507(3)	…	…	…
				$Y_{14}Ag_{51}$	1.2630(6)	…	0.9307(3)	…
				YAg_2	0.36882(4)	…	0.92436(8)	…
3	45	35	20	YP	0.56525(3)	…	…	…
				YAg_2	0.36901(5)	…	0.92410(7)	…
				YAg	0.36174(8)	…	…	…
4	57	23	20	α-Y	0.3664(2)	…	0.5821(3)	…
				YP	0.56540(4)	…	…	…
				YAg	0.36185(6)	…	…	…
5	25	25	50	Ag	0.40071(3)	…	…	…
				YP	0.56511(2)	…	…	…
				AgP_2	0.6217(2)	0.5057(2)	0.7810(3)	113.49(4)
6	18	15	67	YP	0.56509(3)	…	…	
				AgP_2	0.6218(2)	0.5060(2)	0.7807(2)	113.48(4)
				Ag_3P_{11}	1.297(2)	0.7559(1)	0.6613(1)	118.82(4)
7	20	11	69	YP	0.56514(3)	…	…	…
				Ag_3P_{11}	1.299(1)	0.7555(3)	0.6609(1)	118.84(5)
1	25	55	20	Ag	0.4083(5)	…	…	…
				NdP	0.58359(5)	…	…	…
				$Nd_{14}Ag_{51}$	1.2741(7)	…	0.93921(5)	…
2	37	43	20	NdP	0.58363(4)	…	…	…
				$Nd_{14}Ag_{51}$	1.27231(8)	…	0.93852(6)	…
				$NdAg_2$	0.4773(1)	0.7026(1)	0.8154(1)	…
3	45	35	20	NdP	0.58370(5)	…	…	…
				$NdAg_2$	0.47719(6)	0.7026(1)	0.8153(1)	…
				NdAg	0.3723(1)	…	…	…
4	57	23	20	Nd	0.3664(2)	…	0.5821(3)	…
				NdP	0.58391(5)	…	…	…
				NdAg	0.37114(7)	…	…	…
5	25	25	50	Ag	0.4075(3)	…	…	…
				NdP	0.58374(6)	…	…	…
				AgP_2	0.6217(3)	0.5059(2)	0.7809(3)	113.49(4)
6	24	15	61	NdP	0.58390(4)	…	…	
				AgP_2	0.6215(2)	0.5063(2)	0.7804(3)	113.48(4)
				Ag_3P_{11}	1.297(1)	0.7557(1)	0.6611(1)	118.82(4)
7	25	10	65	NdP	0.58384(5)	…	…	…
				NdP_2	0.40031(3)	0.65374(3)	1.0090(9)	105.8(1)
				Ag_3P_{11}	1.298(1)	0.7558(3)	0.6606(1)	118.83(5)

Thus, we can conclude that the Y–Ag–P and Nd–Ag–P ternary systems are similar to each other and to the earlier studied Ce–Ag–P system [25]. In all these systems monophosphide of rare-earth metals LnP exists in equilibrium with the components and binary compounds at 400°C. But contrary to the Ce–Ag–P system, no ternary compounds have been obtained in the investigated ternary systems at higher temperatures.

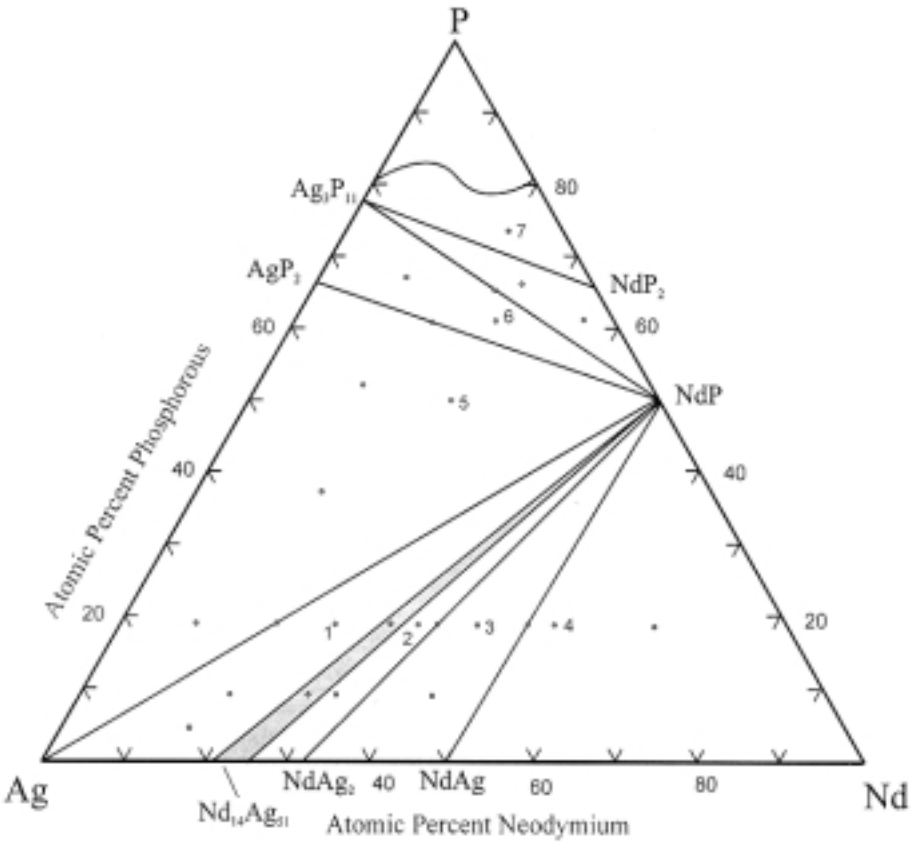

Figure 2. Isothermal section of phase equilibria diagram of the Nd–Ag–P system at 400°C.

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