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The System Yb–Co–P

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Phase equilibria in Yb–Co–P system have been investigated at 870 K by X-ray analysis. The existence of early known compounds $Yb_2Co_{12}P_7$ (structure $Zr_2Fe_{12}P_7$), $YbCo_5P_3$ (structure YCo_5P_3), $YbCo_3P_2$ (structure $HoCo_3P_2$), $Yb_6Co_{30}P_{19}$ (own structure) and $Yb_5Co_{19}P_{12}$ (structure $Sc_5Co_{19}P_{12}$) has been confirmed. Atomic coordinates in structures $Yb_2Co_{12}P_7$ (powder method $R_F = 0.049$) and $YbCo_3P_2$ (single crystal method, $R_F = 0.0393$) have been determined.

Key words: X-ray, phase diagram, ternary compound, phosphide

To present time isothermal sections of phase diagrams of {La,Gd,Tb}Co–P [1–3] systems have been given. Other RE–Co–P-type systems (RE – rare-earth metal) investigated only with the purpose to obtain compounds of known types of structure. Thus, phosphides $RE_2Co_{12}P_7$, (structure $Zr_2Fe_{12}P_7$), $RECo_5P_5$ (structure YCo_5P_3), $LaCo_5P_3$ (own structure), $RECo_3P_2$ (structure $HoCo_3P_2$), $RECo_8P_5$ (structure $LaCo_8P_5$), $RE_6Co_{30}P_{19}$ (structure $Yb_6Co_{30}P_{19}$), RECoP (structure PbFCl), RCo_2P_2 (structure $CeAl_2Ga_2$) were obtained. The subject of our work was the investigation of phase equilibria in Yb–Co–P system, possible obtaining of new ternary phosphides formed and the full determination of their structures. From the literature the existence of 5 ternary phosphides in the region of 0–0.55 molar parts of phosphorus of the Yb–Co–P system, *i.e.* $Yb_2Co_{12}P_7$ [5], $YbCo_5P_3$ [6], $Yb_5Co_{19}P_{12}$ [7], $Yb_6Co_{30}P_{19}$ [8], $YbCo_3P_2$ [9] is known. These compounds, except $YbCo_3P_2$ (obtained by arc melting), were obtained using the tin flux method. During experimental work, information about the boundary systems Yb–Co, Yb–P, Co–P [10,11] was used.

EXPERIMENTAL

Samples for investigation of phase equilibria were prepared by two main methods – the heating of previously pressed powder mixtures of pure components in sealed evacuated silica tubes at 870 K and arc melting of applicable binary cobalt and ytterbium phosphides in an atmosphere of purified argon, followed by heat treatment at 870 K not less than 600 hours. Composition of samples, synthesized for investigation of phase equilibria in the Yb–Co–P system, is shown in Fig. 1. Single crystals of ternary phosphides were obtained by arc melting. The pure components mixtures for crystals growth were preheated at 870 K for 48 hours. Heating of pure components mixtures in sealed niobium tubes in argon atmosphere was also used for crystals growth. X-ray phase analysis was made by matching the experimental powder diffraction patterns (DRON-3M, CoK$_{\alpha}$-radiation, step of 2θ-scanning 0.05° in 2θ ranges 20–90°; STOE STADI P, Huber Guinier camera, CoK$_{\alpha 1}$-radiation, Image Plate detector) with data calculated from literature by using CSD software [12].

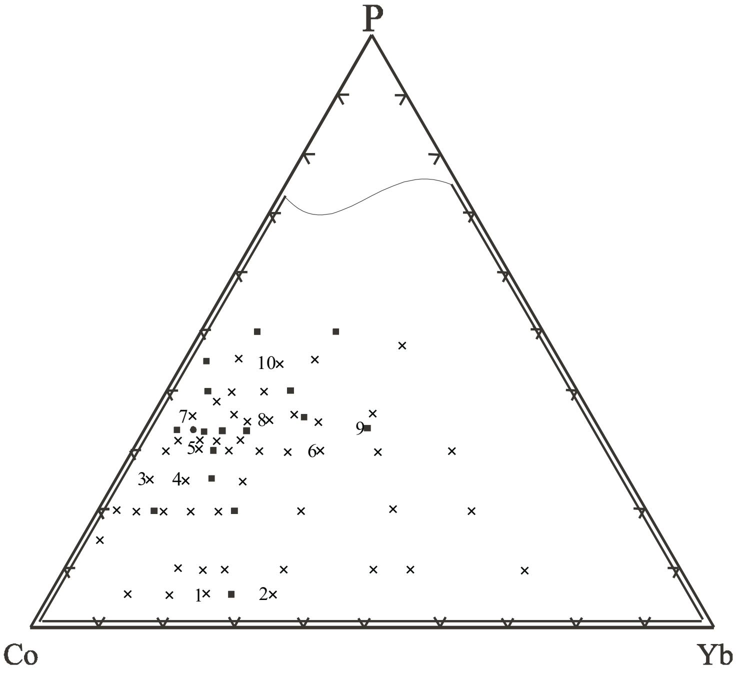

Figure 1. Phase composition of investigated samples in Yb–Co–P system (● – single phase sample, ■ – double phase sample, × – three phase sample).

RESULTS AND DISCUSSION

On the basis of phase analysis of prepared samples, the isothermal section of the Yb–Co–P phase diagram at 870 K in the range of 0–0.50 molar parts of phosphorus has been built (Fig. 2). We confirm the existence of all previously known compounds (Table 1) in the Yb–Co–P system. Phase composition of several samples is shown in Table 2. As it is seen from the cell parameters of phases from the system, they are not too different in various samples, which demonstrates the absence of homogeneity ranges of ternary compounds and solid solutions on the base of α-Co and binaries.

Table 1. Crystallographic data of compounds in Yb–Co–P system.

№	Compound	Space group	Structure	Lattice parameters, Å			Ref.
				a	*b*	c	
1	$Yb_2Co_{12}P_7$	$P\overline{6}$	$Zr_2Fe_{12}P_7$	9.020(2) 9.02654(7)	–	3.5793(6) 3.58185(4)	[5] *
2	$YbCo_5P_3$	*Pnma*	YCo_5P_3	11.756(3) 11.7726(2)	3.632(1) 3.63266(8)	10.274(4) 10.2787(2)	[6] *
3	$Yb_5Co_{19}P_{12}$	$P\overline{6}2m$	$Sc_5Co_{19}P_{12}$	12.002 12.011(2)	–	3.646 3.649(1)	[7] *
4	$YbCo_3P_2$	*Pmmn*	$HoCo_3P_2$	10.634 10.6344(2)	3.764 3.7712(1)	12.349 12.3501(3)	[8] *
5	$Yb_6Co_{30}P_{19}$	$P\overline{6}$	$Yb_6Co_{30}P_{19}$	14.703 14.734(2)	–	3.574(3) 3.583(1)	[9] *

* – Experimental values from the present work.

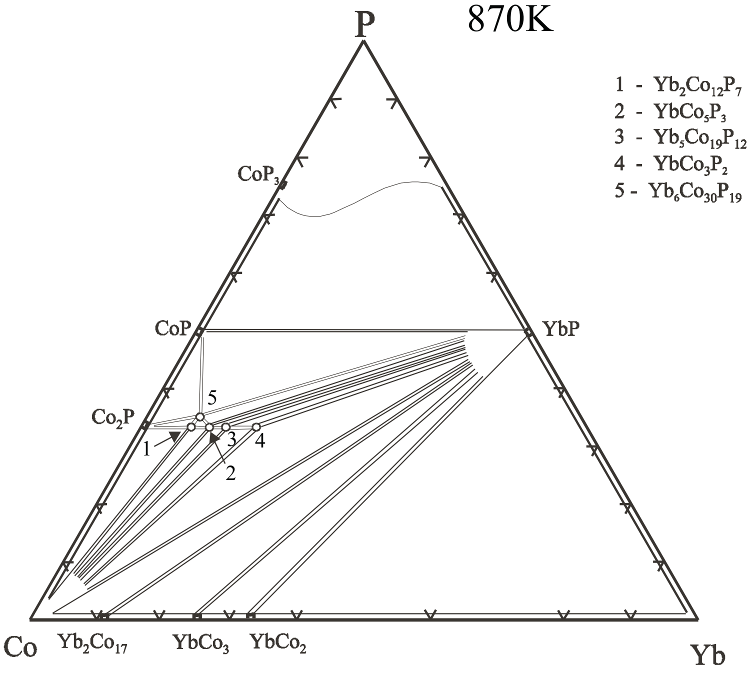

Figure 2. Isothermal section of phase diagram of the Yb–Co–P system at 870 K.

Table 2. Phase composition of selected samples from Yb–Co–P system.

№ of sample of Fig. 1	Sample composition			Phase composition, cell parameters, Å		
	Yb	Co	P	I	II	III
1	25	70	5	Yb_2Co_{17} a = 8.308(2) c = 8.098(2)	$YbCo_3$ a = 7.452(1) c = 20.490(9)	YbP a = 5.5542(3)
2	32	63	5	$YbCo_3$ a = 7.455(3) c = 20.487(9)	$YbCo_2$ a = 7.2261(4)	YbP a = 5.5538(6)
3	5	70	25	Co_2P a = 5.6310(2) b = 5.5261(3) c = 6.6012(3)	α-Co a = 3.5326(9)	$Yb_2Co_{12}P_7$ a = 9.0266(2) c = 3.5811(2)
4	12	63	25	$YbCo_3P_2$ a = 10.6348(5) b = 3.7714(1) c = 12.3511(8)	$Yb_5Co_{19}P_{12}$ a = 12.0124(3) c = 3.6324(2)	α-Co a = 3.534(2)
5	10	60	30	$Yb_2Co_{12}P_7$ a = 9.0269(4) c = 3.5811(2)	$YbCo_5P_3$ a = 11.722(2) b = 3.6321(4) c = 10.278(4)	α-Co a = 0.5338(9)
6	30	40	30	$YbCo_3P_2$ a = 10.6351(8) b = 3.7713(1) c = 12.350(1)	YbP a = 5.5491(6)	α-Co a = 3.533(8)
7	8	57	35	Co_2P a = 5.6341(9) b = 5.5228(8) c = 6.608(1)	$Yb_2Co_{12}P_7$ a = 9.0271(3) c = 3.5819(1)	$Yb_6Co_{30}P_{19}$ a = 14.734(4) c = 3.583(1)

Table 2 (continuation)

8	18	47	35	$YbCo_3P_2$ a = 10.6348(9) b = 3.7722(4) c = 12.350(1)	YbP a = 5.5516(8)	$Yb_5Co_{19}P_{12}$ a = 12.0112(6) c = 3.6512(2)
9	33	33	34	YbP a = 5.5541(6)	α-Co a = 3.5368(8)	
10	20	35	45	YbP a = 5.5492(4)	CoP a = 5.0771(6) b = 3.2818(1) c = 5.5873(9)	$Yb_6Co_{30}P_{19}$ a = 14.739(6) c = 3.5826(8)

Crystal structure of $Yb_2Co_{12}P_7$ has been investigated using the X-ray powder method. Experimental conditions, atomic coordinates and atomic displacement parameters are shown in Tables 3 and 4.

Table 3. Conditions of $Yb_2Co_{12}P_7$ structure refinement.

Space group	$P\overline{6}$
a (Å)	9.02654(7)
c (Å)	3.58185(4)
Cell volume (Å^3)	252.744(7)
Number of atoms in cell	21.0
Calculated density (g/cm^3)	8.3435(2)
Absorption coefficient (1/cm)	970.88
Radiation and wavelength	X-ray 1.79020
Diffractometer	STOE STADI P
Mode of refinement	Full profile
Number of atom sites	9
Number of free parameters	24
Two-theta and $\sin(\theta/\lambda)_{max}$	99.01 0.425
R_F, R_P	0.0482 0.1176
Texture axis and parameter	[1 1 0], 1.08(2)

Table 4. Results of $Yb_2Co_{12}P_7$ structure refinement.

Atom	Position	x	y	z	Biso, Å^2
Yb1	*1(c)*	1/3	2/3	0	0.52(6)
Yb2	*1(f)*	2/3	1/3	1/2	0.51(5)
Co1	*3(j)*	0.4268(9)	0.0610(9)	0	0.78(8)
Co2	*3(j)*	0.1547(5)	0.2714(3)	0	0.79(6)
Co3	*3(k)*	0.3935(5)	0.4428(9)	1/2	0.83(7)
Co4	*3(k)*	0.2320(3)	0.0963(5)	1/2	0.83(7)
P1	*3(j)*	0.4150(14)	0.2997(12)	0	1.0(2)
P2	*3(k)*	0.1103(13)	0.4057(13)	1/2	0.9(2)
P3	*1(a)*	0	0	0	0.99(12)

Structure of $YbCo_3P_2$ phosphide was determined using the X-ray single crystal method. Experimental conditions, atomic coordinates and anisotropic parameters are reported in Tables 5–7, respectively. Partially occupied Co2 position is also confirmed by phase equilibria in the related region of phase diagram. It is not possible to occupy this position by phosphorus atoms. Values of atomic displacement parameters in $YbCo_3P_2$ structure could be caused by a stronger bonding of cobalt and phosphorus atoms in this structure. Results of the investigation show similarity of Yb–Co–P system with other RE–{Fe,Co}–P systems, both in the compound structures and in phase equilibria. RE–Ni–P systems are characterized by formation of many ternary compounds, which shows an increasing chemical activity of transition metals in the order of Fe–Co–Ni.

Table 5. Condition of $YbCo_3P_2$ structure determination.

Space group	*Pmmn*
a (Å)	10.6344(2)
b (Å)	3.7712(1)
c (Å)	12.3501(3)
Cell volume (Å^3)	466.099
Number of atoms in cell	36.0
Calculated density (g/cm^3)	8.7965
Absorption coefficient (1/cm)	483.37
Radiation and wavelength	Mo 0.71073
Diffractometer	Rigaku AFC7, CCD
Mode of refinement	F(hkl)^2
Restrictions	F(hkl)>4.00sig(F)
Extinction formalism	Sheldrick-2 0.000050
Number of atom sites	12
Number of free parameters	64
Two-theta and sin(θ/λ)$_{max}$	64.02 0.746
Number of measured reflections	3961
R_F, R_w	0.0393 0.0591

Table 6. Atomic coordinates and displacement parameters in $YbCo_3P_2$ structure.

Atom	Position	x	y	z	B*(eq), Å^2
Yb1	*2(b)*	1/4	1/4	0.47556(8)	0.54(2)
Yb2	*4(f)*	0.56913(5)	1/4	0.79443(5)	0.43(1)
Co1	*2(a)*	1/4	1/4	0.8395(2)	0.50(6)
Co2**	*4(e)*	1/4	0.211(13)	0.2971(3)	0.7(5)
Co3	*2(b)*	1/4	1/4	0.0115(2)	0.39(6)
Co4	*4(f)*	0.0831(2)	1/4	0.0052(2)	0.47(4)
Co5	*4(f)*	0.0476(2)	1/4	0.5685(2)	0.42(4)
Co6	*4(f)*	0.6277(2)	1/4	0.2922(2)	0.50(4)
P1	*2(a)*	1/4	1/4	0.1190(4)	0.41(10)
P2	*2(a)*	1/4	1/4	0.6514(5)	0.50(11)
P3	*4(f)*	0.0651(3)	1/4	0.3828(3)	0.39(7)
P4	*4(f)*	0.5959(3)	1/4	0.1091(3)	0.41(8)

B(eq) = 1/3[B11 a2 a2+...2B23 b c* b c cosα].

** Occupation of Co2 0.49(1) Co.

Table 7. Anisotropic displacement parameters (Å^2) in $YbCo_3P_2$ structure*.

Atom	B11	B22	B33	B13
Yb1	0.48(3)	0.48(4)	0.65(4)	0
Yb2	0.48(2)	0.40(3)	0.43(2)	–0.04(2)
Co1	0.49(8)	0.61(11)	0.39(10)	0
Co2	0.37(8)	1.3(14)	0.42(11)	0
Co3	0.14(7)	0.33(11)	0.70(11)	0
Co4	0.44(5)	0.46(8)	0.52(7)	–0.15(5)
Co5	0.36(5)	0.51(8)	0.41(7)	0.02(5)
Co6	0.80(6)	0.49(8)	0.23(7)	–0.07(5)
P1	0.35(14)	0.4(2)	0.5(2)	0
P2	0.37(15)	0.5(2)	0.7(2)	0
P3	0.30(10)	0.55(15)	0.31(13)	–0.06(9)
P4	0.30(10)	0.53(15)	0.41(14)	0.21(9)

*T = exp[–1/4(B11a*2 h2+... 2B23 b* c* k l)], B12 = B23 = 0.

The shortest interatomic distances in $Yb_2Co_{12}P_7$ and $YbCo_3P_2$ (Table 8) are close to the sum of atomic radii in pure components: metallic cobalt, ytterbium and red phosphorus. No contacts between phosphorus atoms have been observed in these compounds.

Table 8. The shortest interatomic distances in $Yb_2Co_{12}P_7$ and $YbCo_3P_2$ structures.

Atom	δ, Å	
	$Yb_2Co_{12}P_7$	$YbCo_3P_2$
Yb–Yb	3.58	3.66
Yb–Co	2.93	2.74
Yb–P	2.79	2.78
Co–Co	2.49	2.53
Co–P	2.15	2.17

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