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Phosphides with $Zr_2Fe_{12}P_7$-Type Structure

W. JEITSCHKO, D. J. BRAUN, R. H. ASHCRAFT,* AND R. MARCHAND†

Institut für Anorganische und Analytische Chemie, Universität Giessen, D-6300 Giessen, West Germany

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Twenty-six ternary phosphides $Ln_2T_{12}P_7$ (Ln = lanthanoid, T = Fe, Co, Ni) were prepared for the first time by reaction of the elemental components in liquid tin or by reaction of the components in evacuated silica tubes. The analysis of their powder patterns indicates their isotypism with $Zr_2Fe_{12}P_7$. Their lattice constants are reported. $Gd_2Ni_{12}As_7$ also crystallizes with that structure.

Introduction

Little is known about ternary compounds in lanthanoid-transition metal-pnicogen systems. Recently we reported on $LaFe_4P_{12}$ (*1*), $La_6Ni_6P_{17}$ (*2*), and isostructural polyphosphides, as well as ternary lanthanoid-transition metal phosphides, arsenides, and antimonides with $ThCr_2Si_2$-type structure (*3*). In the course of these studies we have occasionally observed second- or third-phase products, whose diffraction patterns we could index with hexagonal cells corresponding to $Zr_2Fe_{12}P_7$ (*4*). We have now investigated the formation of such compounds in a more systematic way.

Experimental

Samples were prepared from stoichiometric mixtures of the elemental components (stated purities greater than 99.5%) using liquid tin (>99.9%) as a reaction medium. This method was already used by Jolibois (*5*) to synthesize NiP_2 and NiP_3. Filings of the rare earth elements were prepared in a dry box under argon or petrolether. The transition metals and red P were in the form of powders. The tin contents of the mixtures varied between 75 and 80 at.%. The samples were sealed under vacuum in silica tubes and heated for 7 days at 1070°K. After cooling, the tin matrices of the samples were dissolved in moderately concentrated hydrochloric acid (~1 : 1) which did not greatly affect the ternary phosphides.

Guinier powder patterns of the products were recorded with α-quartz ($a = 4.91304$, $c = 5.40463$ Å) as standard. Cell constants were refined by computerized least-squares calculations. The standard deviations of Table I are those of the refinements and do not reflect possible homogeneity ranges. Several samples were also prepared by direct reaction of intimate mixtures of the elemental components in evacuated silica tubes. They were heated at 920°K for 12 hr, followed by 4 hr at 1250°K. After grinding and coldpressing, the samples were resealed in silica tubes and annealed at 1250°K for 15 hr. The lattice constants of the phases obtained that way were within three standard deviations of the phases obtained by the tin flux method. $Gd_2Ni_{12}P_7$ and the only arsenide we have attempted to prepare,

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* Present address: Department of Chemistry, Rice University, Houston, Texas.

† On leave of absence from Laboratoire de Chimie Minérale C, Université de Rennes, France.

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TABLE I

LATTICE DIMENSIONS OF NEW $Zr_2Fe_{12}P_7$-TYPE PHASES[a]

	a (Å)	c (Å)	V (Å^3)	c/a
$Pr_2Fe_{12}P_7$	9.2039(9)	3.6878(4)	270.55	0.4007
$Nd_2Fe_{12}P_7$	9.1856(7)	3.6769(3)	268.68	0.4003
$Sm_2Fe_{12}P_7$	9.1558(8)	3.6653(3)	266.09	0.4003
$Gd_2Fe_{12}P_7$	9.1448(4)	3.6528(2)	264.55	0.3994
$Tb_2Fe_{12}P_7$	9.1333(11)	3.6460(5)	263.39	0.3992
$Dy_2Fe_{12}P_7$	9.1148(9)	3.6363(4)	261.63	0.3989
$Ho_2Fe_{12}P_7$	9.1053(6)	3.6340(3)	260.92	0.3991
$Er_2Fe_{12}P_7$	9.0978(4)	3.6274(2)	260.01	0.3987
$Tm_2Fe_{12}P_7$	9.0898(4)	3.6191(2)	258.96	0.3981
$Yb_2Fe_{12}P_7$	9.0914(10)	3.6154(4)	258.79	0.3977
$Lu_2Fe_{12}P_7$	9.0688(9)	3.6180(4)	257.69	0.3990
$Ce_2Co_{12}P_7$	9.0776(9)	3.6553(4)	260.85	0.4027
$Pr_2Co_{12}P_7$	9.1300(9)	3.6606(4)	264.25	0.4009
$Nd_2Co_{12}P_7$	9.1065(9)	3.6499(5)	262.13	0.4008
$Sm_2Co_{12}P_7$	9.0853(7)	3.6330(3)	259.71	0.3998
$Eu_2Co_{12}P_7$	9.0753(6)	3.6284(3)	258.80	0.3998
$Gd_2Co_{12}P_7$	9.0669(6)	3.6230(3)	257.93	0.3996
$Tb_2Co_{12}P_7$	9.0557(8)	3.6094(4)	256.34	0.3986
$Dy_2Co_{12}P_7$	9.0465(9)	3.6016(4)	255.27	0.3981
$Ho_2Co_{12}P_7$	9.0383(7)	3.5956(3)	254.38	0.3978
$Er_2Co_{12}P_7$	9.0252(6)	3.5913(3)	253.34	0.3979
$Tm_2Co_{12}P_7$	9.0215(7)	3.5867(3)	252.80	0.3976
$Yb_2Co_{12}P_7$	9.0206(8)	3.5788(3)	252.20	0.3967
$Lu_2Co_{12}P_7$	9.0001(10)	3.5722(4)	250.59	0.3969
$Gd_2Ni_{12}P_7$	9.085(3)	3.702(1)	264.6	0.4075
$Yb_2Ni_{12}P_7$	9.045(2)	3.649(1)	258.6	0.4034
$Gd_2Ni_{12}As_7$	9.367(1)	3.8328(8)	291.2	0.4092

[a] Standard deviations in the least significant digits are given in parentheses.

$Gd_2Ni_{12}As_7$, were obtained by direct reaction of the elemental components. We have previously unsuccessfully attempted to synthesize arsenides in these ternary systems by the tin flux method (*3*).

Results and Discussion

The powder patterns of the new compounds are similar to that of $Zr_2Fe_{12}P_7$ and were indexed with analogous hexagonal cells (Table I). Calculated powder patterns assuming positional parameters as determined for $Zr_2Fe_{12}P_7$ (*4*) were in good agreement with the observed patterns. As an example, the evaluation of the pattern of $Er_2Fe_{12}P_7$ is shown in Table II.

So far the $Zr_2Fe_{12}P_7$-type structure was reported only for the prototype (*4*), although similar cell dimensions were also observed for $Mg_{2.5}Ni_{11.5}P_7$ (*7*). The present investigation shows that this structure is very common for the rare earth-transition metal phosphides. In the iron- and cobalt-containing combinations, which we have investigated with all lanthanoids (except Pm), we have obtained this structure for most compositions (Table I). In the few samples where we used Ni as the transition metal component, we have also found phases with this structure, and the successful preparation of $Gd_2Ni_{12}As_7$ shows that corresponding arsenides can also be synthesized.

In Fig. 1 the cell volumes of the iron- and

TABLE II

GUINIER POWDER PATTERN OF $Er_2Fe_{12}P_7$[a]

h k l	d_c	d_o	I_c	I_o
1 0 0	7.8789	7.9110	4	vvw
1 1 0	4.5489	4.5490	4	vw
2 0 0	3.9395	—	2	—
0 0 1	3.6273	—	<1	—
1 0 1	3.2949	3.2967	10	w
2 1 0 1 2 0	2.9780	2.9789	3 6	w
1 1 1	2.8361	2.8342	2	vvw
2 0 1	2.6684	2.6693	7	w
3 0 0	2.6263	2.6270	11	w
2 1 1 1 2 1	2.3017	2.3005	31 100	vvs
2 2 0	2.2745	2.2750	13	w
1 3 0 3 1 0	2.1852	2.1852	5 6	w
3 0 1	2.1273	2.1252	10	w
4 0 0	1.9697	1.9693	12	w
2 2 1	1.9270	1.9274	3	vvw
1 3 1 3 1 1	1.8718	1.8718	10 7	m
0 0 2	1.8137	1.8133	27	s
2 3 0 3 2 0	1.8076	1.8072	5 1	vw
1 0 2	1.7674	—	<1	—
4 0 1	1.7310	—	1	—
4 1 0 1 4 0	1.7193	1.7193	28 2	s
1 1 2	1.6847	—	1	—
2 0 2	1.6475	—	1	—
3 2 1 2 3 1	1.6178	1.6186	4 13	m
5 0 0	1.5758	—	1	—
1 4 1 4 1 1	1.5536	—	1 <1	—
2 1 2 1 2 2	1.5490	1.5497	1 3	vw
3 3 0	1.5163	1.5166	5	vw
3 0 2	1.4924	1.4926	6	vw
2 4 0 4 2 0	1.4890	—	<1 <1	—
5 0 1	1.4453	1.4451	8	vw
2 2 2	1.4180	1.4179	9	vw
5 1 0 1 5 0	1.4151	—	<1 2	—
3 3 1	1.3990	—	<1	—
1 3 2 3 1 2	1.3956	1.3954	3 5	vw

[a] The calculated pattern was generated by a computer program (*6*) assuming positional parameters as found for $Zr_2Fe_{12}P_7$ (*4*)

cobalt-containing compounds are shown together with the volumes of the rare earth monophosphides (*8*). For comparison, only half of the volumes of the *Ln*P (NaCl-type) compounds are plotted. Thus all volumes correspond to two *Ln* atoms. The volume decrease with increasing weight of the *Ln* component is due to the well-known lanthanoid contraction. It can, however, be seen that the slope is steeper for the *Ln*P compounds, than for the $Ln_2T_{12}P_7$ compounds. This is probably due to the stiffness of the $T_{12}P_7$ "framework" which prevents the *Ln* component from showing its optimal partial volume.

We were not successful in preparing the $La_2T_{12}P_7$ (T = Fe, Co) compounds. Apparently La is too big to be accommodated in the $Fe_{12}P_7$ and $Co_{12}P_7$ partial structures under our experimental conditions. Under these conditions we also did not obtain a $Zr_2Fe_{12}P_7$-type phase in the system Eu–Fe–P. The products contained $EuFe_2P_2$ (*3*) and Fe_2P (*9*) as major components.

In the series $Gd_2T_{12}P_7$ and $Yb_2T_{12}P_7$, where T = Fe, Co, Ni, the Co compounds have the smallest average atomic volume, even though the atomic volume of elemental Ni is lower than that of elemental Co. This behavior is also observed for many silicides and germanides (*10*) including $ThCr_2Si_2$-type silicides and germanides, although not for $ThCr_2Si_2$-type phosphides and arsenides (*3*), where the Ni compounds have the smallest volume. In oxides, the relative sizes of Fe, Co, and Ni depend on their oxidation states, coordination number *CN*, and their being in high or low spin states: For T^{2+} ions with $CN = 4$, Ni^{2+} is the smallest; for low spin T^{2+} ions, Fe^{2+} is the smallest; and for low spin T^{3+} ions and $CN = 6$, Co^{3+} is the ion with the smallest effective ionic radius (*11*).

The P atoms in the $Zr_2Fe_{12}P_7$ structure are all isolated from each other and thus no P–P bonds exist. Because P is the most electronegative component in the $Ln_2T_{12}P_7$ compounds, its 3*s* and 3*p* states will be filled and P

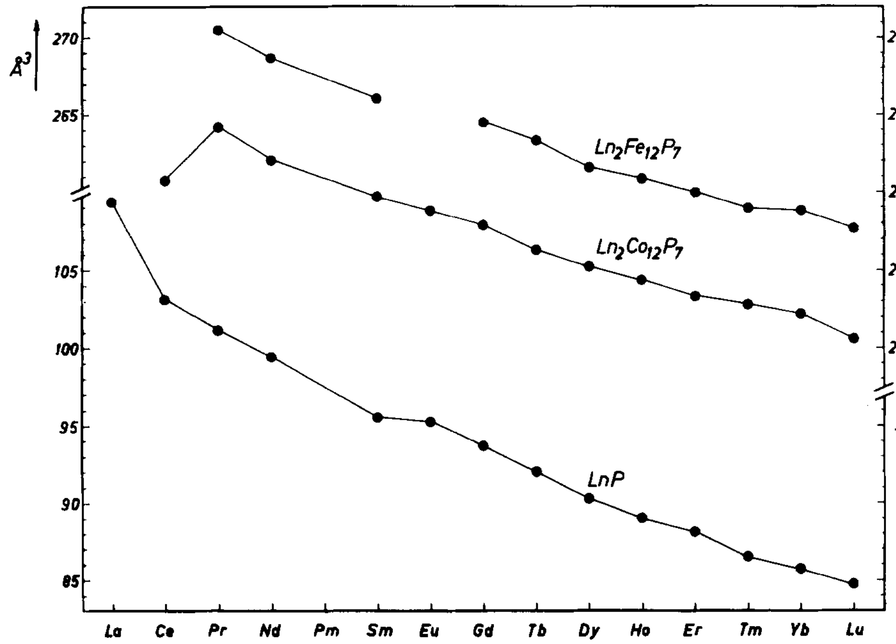

FIG. 1. Cell volumes of $Zr_2Fe_{12}P_7$-type compounds as compared to the volumes of *Ln*P compounds with NaCl-type structure. For the *Ln*P compounds only one-half of the volume of the *F*-centered cell is plotted. Thus all plotted volumes contain two lanthanoid atoms.

obtains a formal oxidation number of −3. The volume plot indicates Ce in $Ce_2Co_{12}P_7$ to be tetravalent, while the other lanthanoids are trivalent in their respective $Ln_2T_{12}P_7$ compounds. In the extreme ionic formulation (where shared bonding electrons are counted as to belong to the more electronegative partner) formulas $Ce_2^{4+}Co_{12}^{1.08+}P_7^{3-}$ and $Ln_2^{3+}T_{12}^{1.25+}P_7^{3-}$ are obtained. Many short Fe–Fe distances in $Zr_2Fe_{12}P_7$ indicate substantial Fe–Fe bonding.

The $Zr_2Fe_{12}P_7$-type structure belongs to a family of structures which all have a metal-to-metalloid ratio of 2:1. Usually the metal atoms are of two kinds with different size and coordination. They form trigonal prisms which contain the metalloid atoms. The coordination of the metalloid atoms thus consists of nine metals: six at the corners of the trigonal prism and three outside the rectangular faces of the prism. The five structure types of this family differ in the way that these prisms are linked to one another (*12*, *13*). The most simple types are the hexagonal, ordered Fe_2P, e.g., NbMnSi (*14*), and the orthorhombic TiNiSi (*15*) structure types. They were found for many ternary borides (*16*), silicides, and germanides (*17*), as well as phosphides (*18*) and arsenides (*19–21*). So far only silicides are known to crystallize with the more complicated UNi_5Si_3-type structure (*13*) and to our knowledge, the $Hf_2Co_4P_3$-type stucture (*12*) has not been found yet for any other composition.

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