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REFINEMENT OF THE CRYSTAL STRUCTURE OF THE NEWLY DISCOVERED PHOSPHIDE $Ho_2Pd_4P_3$

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The new ternary phosphide $Ho_2Pd_4P_3$ was synthesized and structurally characterized by single-crystal *X*-ray diffraction. The compound crystallizes in the hexagonal space group *P*-62*m* (Pearson symbol *hP*36), adopting the $Hf_2Co_4P_3$-type structure with lattice parameters a = 13.1727(4), c = 4.0150(2) Å, and V = 603.34(5) Å³. Structural refinement converged to R_1 = 0.0157 and wR_2= 0.0351. Comparative analysis with the related ternary rare earth and transition metal phosphides revealed close structural relations between the $Hf_2Co_4P_3$ and $Ho_5Ni_{19}P_{12}$ types, differing mainly in the occupancy of the 3*f* (*x*00) Wyckoff site. The results suggest the presence of concentration polymorphism among rare-earth palladium phosphides between the boundary compositions $RE_2Pd_4P_3$ and $RE_5Pd_{19}P_{12}$.

Keywords: holmium, palladium, phosphide, X-ray single crystal diffraction, crystal structure.

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1. Introduction

There is a wide variety of three-component phosphides of rare earth metals (*RE*) and 3*d*-, 4*d*-, and 5*d*-transition metals (*T*) [1, 2]. Scientists around the world dedicated a large amount of works to studying the mentioned compounds with a metal to phosphorous ratio of 2:1 [3, 4]. The most distributed compositions of compound are $RE_2T_{12}P_7$, $RE_2T_4P_3$, RET_2P_2, *RET*P, RET_4P_{12}, RET_3P_2, RET_5P_3 and some others [1, 2]. However, the phosphides with transition metals are pretty common, compounds with palladium as a transition component are still less investigated in comparison with related systems.

The structure of $Hf_2Co_4P_3$-type [5] and its derivatives $Ho_5Ni_{19}P_{12}$ [6], $Sc_5Pd_{19}P_{12}$ [7], $Nd_5Cu_{17.8}P_{12}$ [8], and $Ce_5Cu_{19}P_{12}$ [9] are widespread in the systems *RE*–*T*–P, where *RE* – rare earth metals, *T* – transition metals. All these structures are closely related as a result of substitution of large *RE*-atoms by smaller atoms of transition metals in 3*f* Wyckoff site. Nevertheless, recently new ternary phosphides of palladium, namely $Ho_5Pd_{19}P_{12}$ [10] and $Tb_2Pd_4P_3$ [11] with the $Ho_5Ni_{19}P_{12}$ [6] and $Hf_2Co_4P_3$ [5] types of structure, respectively, have been reported. In some papers, several pairs of compounds with the composition $RE_2T_4P_3$–$RE_5T_{19}P_{12}$ have been reported [12–16]. Among mentioned systems, the series $Sc_5Co_{19}P_{12}$–$Sc_2Co_4P_3$, and $Sc_5Ni_{19}P_{12}$–$Sc_2Ni_4P_3$ [12], $Zr_5Co_{19}P_{12}$ [13]–$Zr_2Co_4P_3$ [14], $Hf_5Co_{19}P_{12}$ [12]–$Hf_2Co_4P_3$ [5], and $Gd_5Co_{19}P_{12}$ [15]–$Gd_2Co_4P_3$ [16] were published. Because of the tiny divergence between phosphides with $Ho_2Co_4P_3$ [2] and $Ho_5Ni_{19}P_{12}$ [3] structures types that have been observed within the same ternary system, the formation of the series of solid solutions was assumed by Jeitschko et al. [12].

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The research in similar vein was conducted for *RE*–*T*–P systems based on Cu, Co [17], Ru and Ir [18]. Furthermore, the existence of homologous compounds not only with rare earth and transition metals such as La, Ce, Sc, Zr, and Hf but with alkaline earth elements (e. g. Ca, Sr) have been reported [19, 20]. Accordingly, to reported results of investigations we can assume that phosphides of this series are quite flexible in order to the valence electron concentration. However, phosphides with the same composition $Th_5Fe_{19}P_{12}$ [21] and $Yb_5Ni_{19}P_{12}$ [22] differ from typical representatives derived from $Ho_2Co_4P_3$ structure by their lattice and connectivity pattern. Summarizing the reported data, we can assume the existence of similar structural relationships in Ho–Pd–P system, which require further scientific attention.

The aim of this work is to synthesize the new phosphide $Ho_2Pd_4P_3$, study its crystal structure and atomic arrangement, and discuss the similarities between $Ho_2Pd_4P_3$ and $Ho_5Pd_{19}P_{12}$ structures.

2. Experimental

The direct solid-state synthesis method was employed for the preparation of the samples in the present study. To obtain the single crystals of the new ternary phosphide $Ho_2Pd_4P_3$, a mixture of the starting elements – fillings of holmium, and powders of palladium and red phosphorus (all of stated purity better than 99.99 wt. %, Alfa Aesar, Johnson Matthey Company) – was prepared in a stoichiometric ratio of Ho:Pd:P = 26:41:33. The thoroughly mixed powders were pressed into a pellet under a pressure of 5 MPa, with total mass of sample approximately 0.8 g.

The pressed pellet was then sealed in evacuated silica tube (filled with high-purity argon at 0.4 bar) using alumina crucible as container. The sealed sample was gradually heated to 1000 °C for 72 hours, followed by sintering for five days and subsequent slow cooling to room temperature. After cooling, the resulting sample was mechanically crushed, and single crystals of the phosphide $Ho_2Pd_4P_3$ were manually extracted.

Single-crystal X-ray diffraction (XRD) data were collected at room temperature using a Rigaku AFC7 diffractometer equipped with a Saturn 724+ CCD detector and employing Mo Kα radiation (λ = 0.71073 Å). The intensity data were processed, and all crystal structure determination and refinement calculations were performed using the SIR-92 [23] and SHELXL [24] software packages.

3. Results and discussion

The analysis of the Laue symmetry 6/*mmm*, together with the absence of any systematic extinction conditions and the refined hexagonal unit cell parameters listed in Table 1, indicates that the newly synthesized ternary phosphide of holmium and palladium crystallizes in the hexagonal space group *P*-62*m*. Examination of the intensity distribution and systematic arrangement of reflections in the *X*-ray single-crystal diffraction patterns confirmed that the overall diffraction symmetry and intensity statistics are consistent with those expected for compounds adopting the $Hf_2Co_4P_3$-type structure. Consequently, this structure type was selected as the initial model for the refinement of the crystal structure of new phosphide resulting in its refined composition $Ho_2Pd_4P_3$.

Table 1

Crystal data and structure refinement details for the compound $Ho_2Pd_4P_3$

Refined composition	$Ho_2Pd_4P_3$
Space group	*P*-62*m*
Formula units per cell, *Z*	4
Lattice parameters: *a*, Å	13.1727(4)
c, Å	4.0150(2)
Cell volume, *V*, Å^3	603.34(5)
F(000), *e*	1452
Calculated density, g cm^{-3}	9.340
Absorption coefficient, mm^{-1}	38.234
Diffractometer	Rigaku
Radiation/wavelength λ, Å	MoK_α/0.71073
Mode of refinement	*F*(*hkl*)
Number of atoms/sites in cell	36/10
θ range for data collection º	3.093−32.474
N(*hkl*) measured	4667
Independent reflections/parameters	839 / 45
Reflections with $I > 2\sigma(I)$	831
h(min), *k*(min), *l*(min)	−19, −8, −5
h(max), *k*(max), *l*(max)	11, 19, 5
Goodness-of-fit on F^2	1.054
Final *R* values R_1/wR_2 [$I > 2\sigma(I)$]	0.0153/0.0346
Final *R* values R_1/wR_2	0.0157/0.0351
Largest diff. peak/hole (e-nm$^{-3}\cdot 10^3$)	1.314/−1.268

The $Hf_2Co_4P_3$ structure type [5] is characterized by three distinct crystallographic positions for the rare-earth (or large size) atoms, four sites for the transition-metal atoms, and three for phosphorus atoms. Structural refinement of $Ho_2Pd_4P_3$, based on a fully ordered atomic distribution, converged smoothly to low residuals listed in Table 1, indicating an excellent fit between the observed and calculated structure factors.

Refined atomic coordinates and anisotropic displacement parameters for the $Ho_2Pd_4P_3$ structure are listed in Tables 2 and 3.

Table 2

Coordinates of atoms and their equivalent displacement parameters for $Ho_2Pd_4P_3$

Atom	Wyckoff site	Atomic coordinates			U_{eq}, Å^2
		x	*y*	*z*	
Ho1	3*g*	0.81321(5)	0	½	0.00791(14)
Ho2	3*f*	0.44258(5)	0	0	0.00865(14)
Ho3	2*c*	⅓	⅔	0	0.00921(16)
Pd1	6*k*	0.35914(8)	0.48855(5)	½	0.01019(2)
Pd2	6*j*	0.18567(8)	0.37622(7)	0	0.00864(14)
Pd3	3*g*	0.26947(8)	0	½	0.0101(16)
Pd4	1*a*	0	0	0	0.0054(3)
P1	6*k*	0.1713(2)	0.48074(2)	½	0.0068(5)
P2	3*f*	0.17377(2)	0	0	0.0071(7)
P3	3*f*	0.65073(2)	0	0	0.0081(7)

Table 3

Anisotropic displacement parameters (U [a]) of atoms for $Ho_2Pd_4P_3$

Atom	U_{11}, Å^2	U_{22}, Å^2	U_{33}, Å^2	U_{12}, Å^2
Ho1	0.0079(3)	0.0079(3)	0.0080(3)	0.00393(14)
Ho2	0.0090(2)	0.0090(2)	0.0081(3)	0.0046(2)
Ho3	0.0091(2)	0.0091(2)	0.0095(3)	0.00454(11)
Pd1	0.0116(3)	0.0125(4)	0.0097(3)	0.0084(3)
Pd2	0.0081(3)	0.0081(3)	0.0078(3)	0.0026(3)
Pd3	0.0137(5)	0.0102(3)	0.0075(5)	0.0068(3)
Pd4	0.0050(4)	0.0050(4)	0.0061(7)	0.0025(2)
P1	0.0062(11)	0.0074(12)	0.0065(11)	0.0031(9)
P2	0.0083(12)	0.0090(15)	0.0043(15)	0.0045(8)
P3	0.0090(17)	0.0070(11)	0.0088(15)	0.0045(8)

[a] $U_{13} = U_{23} = 0$.

The interatomic distances (Table 4) and anisotropic displacement parameters (Table 3) obtained for all atoms are in good agreement with the expected values for compounds adopting this structure type. Together with the fairly low *R*-values and the insignificant residual electron density, this confirms the accuracy of the model and the absence of significant atomic disorder.

Furthermore, the observed Ho–Pd, Ho–P, and Pd–P bond lengths correspond well to the sums of the metallic radii of holmium and palladium, and the covalent radius of the phosphorus atoms: *r*(Ho) = 1.743 Å, *r*(Pd) = 1.376 Å, *r*(P) = 1.10 Å [25], supporting the established atomic arrangement. The shortest distances were observed for the next bonds: δ(Ho2–Pd2) = 2.9806 Å, δ(Ho2–P3) = 2.742 Å, δ(Ho1–P2) = 2.934 Å, δ(Pd2–P3) = 2.3529 Å, and δ(Pd3–P2) = 2.2894 Å. However, the observed reduction of interatomic distances in almost all cases does not exceed 5% of the corresponding sums of the atomic radii, which is typical for intermetallics. Only in the case of the Pd3–P2 bond the reduction in distance about 7.5 % was observed, which may indicate a slight covalent interaction.

The combination of crystallographic evidence, bond length analysis, and refinement parameters unambiguously confirms that $Ho_2Pd_4P_3$ is a new member of the $Hf_2Co_4P_3$ structural family within the $RE_2T_4P_3$ compounds.

Recently, we reported the crystal structure determination of isotypic phosphide $Tb_2Pd_4P_3$ with the same $Hf_2Co_4P_3$ type structure, and the unit cell projection and coordination polyhedra of atoms were in detail described in Ref. [11]. The same atomic arrangement is observed for new phosphide $Ho_2Pd_4P_3$ including trigonal prismatic coordination for all phosphorus atoms as mostly typical for the ternary rare earth and transition metal phosphides [2].

The peculiarities of crystal structures of $Hf_2Co_4P_3$ and $Ho_5Ni_{19}P_{12}$ types as well as some related ones, are discussed in detail in our earlier works [10, 11]. Therefore, the crystal structure of the new ternary phosphide $Ho_2Pd_4P_3$ (Z = 4) is closely related to that of the previously reported compound $Ho_5Pd_{19}P_{12}$ ($Ho_5Ni_{19}P_{12}$-type structure, Z = 1) [10]. The main difference between these two structures is the occupancy of the 3*f* (*x*00) crystallographic site. In the $Ho_5Pd_{19}P_{12}$ structure, this position is populated by Pd atoms. In contrast, in the $Ho_2Pd_4P_3$ structure (with a unit-cell composition of $Ho_8Pd_{16}P_{12}$), the same site is fully occupied by Ho atoms.

The crystal structures of the $Ho_2Pd_4P_3$ and $Ho_5Pd_{19}P_{12}$ discussed here belong to a family of two-layered structures characterized by a metal-to-metalloid ratio of 2:1. Their crystal structures are built from trigonal prisms from metal atoms centered by phosphorus, that form network with well-defined layers mutually shifted by 1/2 along the *c*-axis, which are stacked and interconnected through rare-earth metal atoms in case of $Hf_2Co_4P_3$ structure, while in the $Ho_5Ni_{19}P_{12}$ structure part of building units are connected through the atoms of transition element.

Consequently, the overall structural framework is preserved, differences in composition arise from the substitution of rare-earth atoms by transition metal at the 3*f* Wyckoff site, which leads to variations in the connectivity and relative arrangement of the polyhedral building units. These substitutions modify the local coordination environments without disrupting the characteristic two-layered structure. In particular, in these structures we can identify distinct units such as $RE_6T_{19}P_6$, $RE_8T_6P_3$, and $RE_2T_{12}P_3$, which are linked in different ways to generate distinct structure types. The connectivity and stacking patterns of these polyhedra are slightly different, resulting in various rare-earth and

transition-metal contents, while the basic framework remains the same. Characteristic arrangements feature highlight small structural rearrangements that accommodate compositional changes between related compounds, and specific *T*–*X* bonds illustrate these rearrangements. These structural relationships are clearly illustrated by the comparison of $Hf_2Co_4P_3$ and $Ho_5Ni_{19}P_{12}$ types, as shown in Fig. 1.

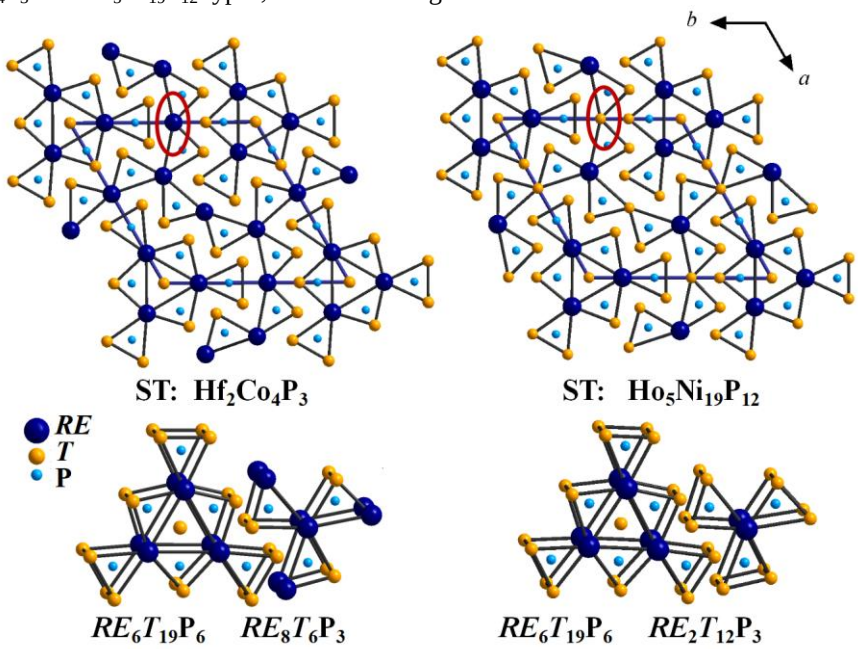


Fig. 1. Crystal structures and building motifs of $Hf_2Co_4P_3$ and $Ho_5Ni_{19}P_{12}$ types. Top: polyhedral representations of the structures with highlighted characteristic connections (red ellipses). Bottom: schematic depiction of the related structural building blocks $RE_6T_{19}P_6$, $RE_8T_6P_3$, and $RE_2T_{12}P_3$

Thus, the results we obtained reveal concentration polymorphism as described in Ref [9], namely the formation in the Ho–Pd–P system of two phosphides with close compositions $Ho_2Pd_4P_3$ and $Ho_5Pd_{19}P_{12}$ which belong to related structure types $Hf_2Co_4P_3$ and $Ho_5Ni_{19}P_{12}$, respectively. The Ho–Pd–P system is the first one among the related *RE*–Pd–P systems where the formation of two phosphides with limiting compositions $RE_2Pd_4P_3$ and $RE_5Pd_{19}P_{12}$ was detected. Meanwhile, the existence of continuous solid solution between these boundary compositions is possible, which may be caused by the mutual substitution of *RE* and palladium atoms in the 3*f* crystallographic site.

Table 4

Interatomic distances (δ, Å) and coordination numbers of atoms (CN) in the structure of $Ho_2Pd_4P_3$

Atoms		δ, Å	CN
Ho1	– 2P2	2.934(3)	18
	– 4P2	3.113(1)	
	– 2Pd4	3.1496(9)	
	– 2Pd2	3.1756(5)	
	– 4Pd3	3.2083(7)	
	–2Ho1	4.0150(3)	
Ho2	– 1P3	2.742(4)	18
	– 4P2	2.8707(1)	
	– 4Pd2	2.981(1)	
	– 2Pd4	3.038(1)	
	– 2Pd1	3.0505(8)	
	– 3Pd3	3.3135(7)	
	– 1P2	3.540(6)	
	– 2Ho3	3.877(1)	
	– 2Pd1	3.2083(7)	
	– 6P2	3.060(2)	
Ho3	– 6Pd1	3.060(2)	15
	– 2Pd1	3.2083(7)	
	– 6P2	3.2324(7)	
Pd1	– 2P1	2.424(3)	
	– 2P3	2.6784(15)	
	– 2Pd2	2.8390(8)	
	– 1Pd1	2.953(2)	
	– 2Ho2	3.055(3)	
	– 2Ho3	3.2324(3)	
	– 2Ho2	4.150(1)	

Atoms		δ, Å	CN
Pd2	–1P3	2.3529	12
	–2P1	2.4941	
	–1P2	2.5632	
	–2Pd1	2.8390	
	–2Pd3	2.9240	
	–1Ho2	2.9806	
	–2Ho1	3.2084	
	–1Ho3	3.3135	
Pd3	–3P2	2.2894	9
	–6Ho1	3.1756	
Pd4	–2P2	2.3703	12
	–2P1	2.5603	
	–4Pd2	2.9240	
	–2Ho2	3.0381	
	–2Ho1	3.1496	
P1	–2Pd1	2.4243	9
	–2Pd2	2.4941	
	–1Pd4	2.5603	
	–2Ho2	2.8707	
	–2Ho3	3.0591	
P2	–1Pd4	2.2894	9
	–2Pd3	2.3703	
	–2Pd2	2.5632	
	–4Ho1	3.1133	
P3	–2Pd2	2.3529	9
	–4Pd1	2.6784	
	–1Ho2	2.7415	
	–2Ho1	2.9347	

4. Conclusions

Single crystals of the new ternary phosphide $Ho_2Pd_4P_3$ were synthesized by direct solid-state reaction and structurally characterized by *X*-ray diffraction. The refinement converged to low residuals, confirming a fully ordered atomic arrangement of the $Hf_2Co_4P_3$ type structure: space group *P*-62*m*, lattice parameters a = 13.1727(4), c = 4.0150(2) Å. The

crystal structure of $Ho_2Pd_4P_3$ belongs to series of two layered compounds with metal-to-metalloid ratio of 2:1, where layers are mutually shifted by 1/2 along the *c*-axis. The Ho–Pd–P system demonstrates concentration polymorphism with the formation of two structurally related phosphides, $Ho_2Pd_4P_3$ and $Ho_5Pd_{19}P_{12}$. It is the first *RE*–Pd–P system where both limiting compositions have been identified, and their structural relationship suggests a possible continuous solid solution due to *RE*/Pd substitution at the 3*f* site.

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УТОЧНЕННЯ КРИСТАЛІЧНОЇ СТРУКТУРИ НОВОГО ТЕРНАРНОГО ФОСФІДУ $Ho_2Pd_4P_3$

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Кристалічну структуру нового тернарного фосфіду гольмію та паладію $Ho_2Pd_4P_3$ вивчено Х-променевим методом монокристала: просторова група *P*-62*m*, символ Пірсона *hP*36, структурний тип $Hf_2Co_4P_3$, параметри елементарної комірки a = 13,1727(4) Å, c = 4,0150(2) Å, V = 603,34(5) Å^3, R_1 = 0,0157; wR_2 = 0,0351.

Монокристали нового фосфіду для дослідження структури відібрали із розбитого зразка вихідного складу $Ho_{26}Pd_{41}P_{33}$, який синтезували спіканням спресованої шихти з вихідних компонентів високої чистоти (гольмій, паладій та червоний фосфор), повільно нагріваючи до 1 000 °C упродовж 72 год та витримуючи за цієї температури протягом п’яти діб, після чого ампулу повільно охолоджували до кімнатної температури.

Кристалічна структура нового фосфіду $Ho_2Pd_4P_3$ належить до серії двошарових сполук із співвідношенням метал–металоїд 2:1, де шари тригональних призм з атомів металів довкола атомів фосфору взаємно зміщені на 1/2 уздовж осі *c*. Беручи до уваги раніше синтезовану нами сполуку зі структурою типу $Ho_5Ni_{19}P_{12}$, можна стверджувати, що у системі Ho–Pd–P виявлено концентраційний поліморфізм, який є у співіснуванні двох структурно споріднених фосфідів $Ho_2Pd_4P_3$ і $Ho_5Pd_{19}P_{12}$. Різниця між структурами цих фосфідів полягає у різному заселенні кристалографічної позиції 3*f* (*x*00) атомами гольмію або паладію, відповідно, що й спричиняє зміну складу сполуки. Це перша серед систем *RE*–Pd–P, де було ідентифіковано представників обох граничних складів, а їхня структурна спорідненість дає змогу припустити можливість утворення між цими складами ряду неперервних твердих розчинів унаслідок заміщення *RE*/Pd у позиції 3*f*.

Ключові слова: гольмій, паладій, фосфід, Х-променева дифракція, кристалічна структура.

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