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Dedicated to the memory of Stepan Oryshchyn

SINGLE CRYSTAL STRUCTURE STUDY OF THE NEW TERNARY PHOSPHIDE $Re_{0.44-0.51}Ni_{0.56-0.49}P$

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New ternary phosphide $Re_{0.44-0.51}Ni_{0.56-0.49}P$ has been synthesized from the pure elements and its crystal structure has been determined using X-ray single crystal data: MnP-type structure, space group *Pnma*, $a = 0.5460(2)$ nm, $b = 0.3274(4)$ nm, $c = 0.6014(3)$ nm, $R_F = 0.0370$, $R_w = 0.0381$ (for the composition $Re_{0.44}Ni_{0.56}P$); and $a = 0.5430(1)$ nm, $b = 0.3259(2)$ nm, $c = 0.5992(2)$ nm, $R_F = 0.0356$, $R_w = 0.0386$ (for the composition $Re_{0.51}Ni_{0.49}P$). Lattice parameters obtained from X-ray powder data ($a = 0.54311(5)$ nm, $b = 0.32606(3)$ nm, $c = 0.59917(6)$ nm for the sample composition $Re_{0.4}Ni_{0.6}P$) correlate well with the single crystal data.

Keywords: rhenium, nickel, phosphide, X-ray single crystal diffraction, crystal structure.

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1. Introduction

Ternary system Re-Ni-P was first studied in whole concentration region by X-ray powder diffraction, and isothermal section of the phase diagram at 700 °C was constructed [1]. Four ternary phosphides were synthesized in the system: $Re_2Ni_3P_5$, $Re_{0.6}Ni_{0.4}P$, $ReNi_2P_6$, and $ReNiP_4$. Crystal structure was determined only for the phosphide $Re_{0.6}Ni_{0.4}P$ using X-ray single crystal data with visual assessment of the intensity of the reflection, but obtained value of reliability factor was very high ($R = 0.15$) [2]. Therefore, the aim of our work was reinvestigation of the Re–Ni–P system in the region of 50 at. % of phosphorus content.

2. Experimental details

Three-component samples for investigation were prepared from powders of rhenium, nickel and red phosphorus (all with stated purity more than 99.9 wt. %), which were mixed in stoichiometric amounts and pressed into pellets. All pellets were sealed in evacuated silica ampoules, then slowly heated to 800 °C (200 degrees per day) and sintered at this temperature for 80–100 h. To reach thermodynamic equilibrium all samples were crushed, carefully mixed, again pressed into pellets, and sealed in evacuated silica ampoules, which were heat treated at 800 °C for 800–1 000 h. After heat treatment all samples were quenched in cold water without breaking the ampoules.

For the synthesis of the single crystals special heat treatment of the samples using a high frequency furnace was performed: pre-sintered samples of the definite compositions were placed into molybdenum crucibles, sealed into evacuated silica tubes, and then gradually heated to 1 250 °C during 100 h, kept at this temperature for 2 h, and slowly cooled in a furnace to room temperature. The single crystals were obtained from the crushed samples.

All samples were examined using X-ray powder diffraction: Imaging Plate Guinier Camera G670, Cu$K_{\alpha1}$ radiation, $2\theta_{max} = 100^{\circ}$. Determination of the crystal structure was performed using X-ray single crystal diffraction: diffractometers STOE IPDS I (AgK_{α} radiation) and Rigaku AFC7 (MoK_{α} radiation). For all calculations WinCSD software [3] was used.

3. Results and discussion

According to the results of the phase analysis of the synthesized samples the existence of the earlier known binary phosphide Re_3P_4 (space group $C2/m$, Cr_3S_4-type structure, $a = 1.2173$ nm, $b = 0.30149$ nm, $c = 0.6039$ nm, $\beta = 114.05^{\circ}$ [4, 5]), as well as a new ternary phase with the refined composition $Re_{0.44–0.51}Ni_{0.56–0.49}P$ was revealed. However, any reflections inherent to the earlier reported ternary phase $Re_{0.6}Ni_{0.4}P$ (space group $Imm2$, $a = 0.6068(4)$ nm, $b = 0.31914(2)$ nm, $c = 0.5568(4)$ nm [2]) were not observed in the powder patterns of the samples being synthesized. This new ternary phosphide $Re_{0.44–0.51}Ni_{0.56–0.49}P$ has the close to $Re_{0.6}Ni_{0.4}P$ composition, but entirely different crystal structure. This ternary phosphide was found to be in equilibrium with the binary phosphide Re_3P_4.

For the crystal structure determination of the new ternary phosphide two single crystals were found in the samples of the starting compositions $Re_{20}Ni_{30}P_{50}$ and $Re_{25}Ni_{25}P_{50}$. Crystal data, experimental details and results of the crystal structure refinement are summarized in Table 1. Previous single crystal investigation revealed the orthorhombic symmetry (Laue class mmm) for both crystals with the lattice parameters given in Table 1. Crystal structure of the phosphide $Re_{0.44–0.51}Ni_{0.56–0.49}P$ was solved using direct methods in a space group $Pnma$ with the help of the program complex WinCSD [3].

Atomic positional and displacement parameters in anisotropic approximation are given in Tables 2 and 3. Crystal structure of the new phosphide $Re_{0.44–0.51}Ni_{0.56–0.49}P$ belongs to the MnP-type structure with statistical distribution of the rhenium and nickel atoms in one crystallographic position 4*c*, whereas the second position 4*c* is fully occupied by phosphorus atoms. Since the atoms of rhenium and nickel are characterized by relatively close values of atomic radii ($r_{Re} = 0.1371$ nm, $r_{Ni} = 0.1246$ nm [6]) it can cause the formation of a small homogeneity range for the compound (~3.5 at. %).

Another confirmation of the existence of such homogeneity range is the observed change in the lattice parameters of the phase $Re_{0.44-0.51}Ni_{0.56-0.49}P$ in the samples with different ratios of Re and Ni for the stable content of phosphorus (50 at. % of P), according to the X-ray diffraction analysis.

Interatomic distances in the structure of $Re_{0.44–0.51}Ni_{0.56–0.49}P$ (Table 4) are in good correlation with the respective sum of the atomic radii of the pure components.

Projection of the $Re_{0.44–0.51}Ni_{0.56–0.49}P$ structure on *xz*-plane and coordination polyhedra of the atoms are shown in Fig. 1. The crystal structure of the phosphide $Re_{0.44–0.51}Ni_{0.56–0.49}P$ belongs to the binary type MnP, which is deformed derivative of the NiAs-type [7, 8]. As a result of the cell deformation the hexagonal symmetry of the structure (NiAs-type, space group $P6_3/mmc$) changes to orthorhombic symmetry (MnP-type, space group $Pnma$).

Table 1

Crystal data and structure refinement details for $Re_{0.44}Ni_{0.56}P$ and $Re_{0.51}Ni_{0.49}P$

	Single crystal 1	**Single crystal 2**
Starting sample composition	$Re_{0.20}Ni_{0.30}P_{0.50}$	$Re_{0.25}Ni_{0.25}P_{0.50}$
Refined composition	$Re_{0.44}Ni_{0.56}P$	$Re_{0.51}Ni_{0.49}P$
Calculated density, g/cm^3	9.00(2)	9.66(1)
Structure type, space group	MnP, *Pnma*	
Formula units, Z	4	
Lattice paramerers, nm: a	0.5460(2)	0.5430(1)
b	0.3274(4)	0.3259(2)
c	0.6014(3)	0.5992(2)
V, nm^3	0.1075(2)	0.1060(1)
Diffractometer	STOE IPDS I	Rigaku AFC7
Radiation and wavelength, nm	Ag $K\alpha$, 0.056087	Mo $K\alpha$, 0.071069
Absorption coefficient, cm^{-1}	335.44	708.41
$2\theta_{max}$; $(\sin\theta/\lambda)_{max}$	47.65; 0.720	68.15; 0.788
Reflections measured	684	782
Range h, k, l	$-7 \le h \le 7$	$-8 \le h \le 8$
	$-4 \le k \le 4$	$-5 \le k \le 5$
	$-8 \le l \le 8$	$-9 \le l \le 9$
Mode of refinement	$F(hkl)$	
Number of atoms in cell	8.0	
Number of free parameters	14	
Reflections with $F(hkl) > 4\sigma F(hkl)$	342	272
Extinction	0.001(1) (Sheldrick-1)	0.074(8) (Sheldrick-2)
Weighing scheme	$1/[\sigma F^2+0.0012F_o^2]$	$1/\ln(F_o^4)$
Goodness-of-fit on F^2	1.060	1.030
Final R-values: R_F, R_w	0.0370, 0.0381	0.0356, 0.0386
Largest diff. peak and hole (e Å^{-3})	1.08/–0.90	2.15/–1.40

Table 2

Atomic positional and equivalent displacement parameters in the structures of $Re_{0.44}Ni_{0.56}P$ and $Re_{0.51}Ni_{0.49}P$

Atom	Site	x/a	y/b	z/c	$^*B_{eq}\times10^2$, nm^2
Single crystal 1 – $Re_{0.44}Ni_{0.56}P$					
M (0.44(1) Re + + 0.56(1) Ni)	4c	0.9964(4)	1/4	0.3008(2)	0.72(2)
P	4c	0.3046(12)	1/4	0.4262(8)	0.95(10)
Single crystal 2 – $Re_{0.51}Ni_{0.49}P$					
M (0.51(1) Re + + 0.49(1) Ni)	4c	0.9961(1)	1/4	0.3010(1)	0.98(2)
P	4c	0.3034(5)	1/4	0.4252(5)	0.82(5)

$^*B_{eq} = 1/3[B_{11}\, a^{*2}\, a^2 + ...\, 2B_{23}\, b^*\, c^*\, b\, c \cos\alpha]$.

Table 3

Anisotropic displacement parameters ($B^{*}\times10^{2}$, nm^{2}) of atoms in the structures of $Re_{0.44}Ni_{0.56}P$ and $Re_{0.51}Ni_{0.49}P$

Atom	B_{11}	B_{22}	B_{33}	B_{13}
Single crystal 1 – $Re_{0.44}Ni_{0.56}P$				
M	0.65(4)	1.13(4)	0.44(4)	–0.05(4)
P	1.4(2)	0.57(14)	0.86(13)	–0.1(2)
Single crystal 2 – $Re_{0.51}Ni_{0.49}P$				
M	0.68(3)	1.68(4)	0.58(3)	0.05(1)
P	0.96(9)	0.72(9)	0.79(9)	0.09(7)

* $B_{12} = B_{23} = 0$.

Table 4

Interatomic distances (δ) and coordination numbers (CN) of atoms in the structures of $Re_{0.44}Ni_{0.56}P$ and $Re_{0.51}Ni_{0.49}P$

Atom	δ, nm **$Re_{0.44}Ni_{0.56}P$**	δ, nm **$Re_{0.51}Ni_{0.49}P$**	CN
M – P	0.2340(3)	0.2351(6)	10
– 2P	0.2383(2)	0.2393(4)	
– 2P	0.2420(2)	0.2439(5)	
– P	0.2483(3)	0.2484(5)	
– 2*M*	0.2783(1)	0.2797(3)	
– 2*M*	0.2888(1)	0.2902(1)	
P – *M*	0.2340(3)	0.2351(6)	6
– 2*M*	0.2383(2)	0.2393(4)	
– 2*M*	0.2420(2)	0.2439(5)	
– *M*	0.2483(3)	0.2484(5)	

Coordination polyhedra of the phosphorus atoms in the $Re_{0.44–0.51}Ni_{0.56–0.49}P$ structure are deformed trigonal prisms formed by the metal atoms, and coordination number of P-atom is 6. Larger atoms of the statistical mixture of Re and Ni (called *M*) are in the centers of the deformed octahedrons formed by P atoms with four additional *M* atoms, due to what coordination number of *M*-atom is equal 10 (see Fig. 1). In accordance with P.I. Kripiakevych [7] this structure belongs to the class 11.II – structures with both trigonal-prismatic and octahedral coordination of smaller atom.

In the $Re_{0.44–0.51}Ni_{0.56–0.49}P$ structure (MnP-type) empty trigonal prisms formed by the atoms of metals alternates with the trigonal prisms centered by the phosphorus atoms in a similar mode as in the NiAs-type structure. The filled prisms are connected with each other by the edges, resulting in their lateral faces forming corrugated planes (Fig. 2).

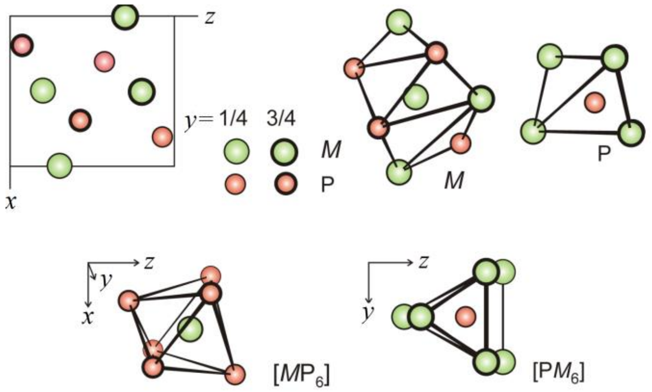

Fig. 1. Projection of the $Re_{0.44-0.51}Ni_{0.56-0.49}P$ structure on *xz*-plane, coordination polyhedra of the atoms, deformed octahedrons [*M*P_6] and trigonal prisms [PM_6]

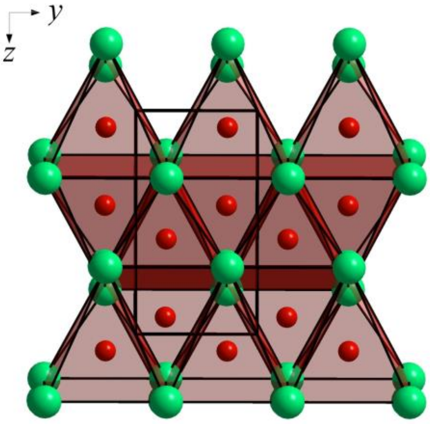

Fig. 2. Combination of the trigonal prisms [PM_6] in the $Re_{0.44-0.51}Ni_{0.56-0.49}P$ structure

Empty prisms are superimposed on the bases of the filled ones and for the form are their mirror images. The relative position of the filled prisms is similar to the combination of trigonal prisms in the structure of the Mn_5Si_3-type, in which the prism strips form hexagonal rings. On the other hand, in the structure of $Re_{0.44–0.51}Ni_{0.56–0.49}P$ (MnP-type) atoms of the metal (*M*) form zigzag-like chains parallel to the *z*-axis, and the atoms of phosphorus form zigzag-shaped chains along the *x*-axis [8].

4. Conclusions

Crystal structure of the new ternary phosphide $Re_{0.44–0.51}Ni_{0.56–0.49}P$ was determined using X-ray single crystal data: space group *Pnma*, MnP-type structure, *a* = 0.5460(2)–0.5430(1) nm, *b* = 0.3274(4)–0.3259(2) nm, *c* = 0.6014(3)–0.5992(2) nm. The small homogeneity range (~3.5 at. %) caused by the statistical distribution of the rhenium and nickel atoms in the crystallographic position 4*c*.

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Присвячується пам'яті Степана Орищина

МОНОКРИСТАЛЬНЕ ДОСЛІДЖЕННЯ СТРУКТУРИ НОВОГО ТЕРНАРНОГО ФОСФІДУ $Re_{0,44-0,51}Ni_{0,56-0,49}P$

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Для потрійної системи Re–Ni–P раніше побудовано ізотермічний переріз діаграми стану за температури 700 °C та виявлено існування чотирьох тернарних фосфідів $Re_2Ni_3P_5$, $Re_{0,6}Ni_{0,4}P$, $ReNi_2P_6$ і $ReNiP_4$, однак лише для фосфіду $Re_{0,6}Ni_{0,4}P$ вивчено кристалічну структуру фотографічним методом монокристала з візуальною оцінкою інтенсивностей відбить за марками почорніння, причому отримано досить високе значення R-фактора (15 %). Структура решти фосфідів сьогодні невідома. Тому нашою метою було дослідження зразків системи Re–Ni–P за вмісту фосфору 50 ат. %.

Зразки для дослідження синтезували спіканням шихти з порошків чистих компонентів (усі не менше 99,9 мас. % основного компонента) за температури 800 °C протягом 80–100 год з подальшим гомогенізувальним відпалюванням за цієї ж температури тривалістю 800–1 000 год. Для синтезу монокристалів попередньо спечені зразки запаювали у молібденові тиглі, поміщали у високочастотну піч, у якій повільно нагрівали до 1 250 °C і витримували 2 год, після чого повільно охолоджували зразки з пічкою до кімнатної температури. Монокристали вилучено з розбитих зразків. Фазовий склад зразків визначено за даними порошкової дифракції (Imaging Plate Guinier Camera G670, $CuK_{\alpha 1}$ проміння), масиви інтенсивностей відбить для вивчення кристалічної структури сполук отримано на монокристальних дифрактометрах STOE IPDS (AgK_{α} проміння) та Rigaku AFC7 (MoK_{α} проміння). Усі обчислення виконано за допомогою комплексу програм WinCSD.

Кристалічна структура нового фосфіду $Re_{0,44–0,51}Ni_{0,56–0,49}P$ належить до бінарного типу MnP (просторова група *Pnma*) зі статистичним заповненням однієї позиції 4*c* атомами металів, результатом чого є незначна (~3,5 ат. %) область гомогенності цієї фази. Параметри комірки за даними методу монокристала дорівнюють $a = 0,5460(2)$, $b = 0,3274(4)$, $c = 0,6014(3)$ нм, фактори розбіжності уточнення структури $R_F = 0,0370$, $R_w = 0,0381$ (для складу $Re_{0,44}Ni_{0,56}P$) та $a = 0,5430(1)$, $b = 0,3259(2)$, $c = 0,5992(2)$ нм, $R_F = 0,0356$, $R_w = 0,0386$ (для складу $Re_{0,51}Ni_{0,41}P$). Уточнені методом полікристала величини параметрів елементарної комірки ($a = 0,54311(5)$ нм, $b = 0,32606(3)$ нм, $c = 0,59917(6)$ нм) для зразка вихідного складу $Re_{0,4}Ni_{0,6}P$ близькі до монокристальних даних. Міжатомні віддалі у структурі фосфіду $Re_{0,44–0,51}Ni_{0,56–0,49}P$ добре узгоджуються з сумами відповідних атомних радіусів компонентів.

Тернарний фосфід $Re_{0,44–0,51}Ni_{0,56–0,49}P$ перебуває в рівновазі з бінарним фосфідом ренію Re_3P_4. Існування сполуки $Re_{0,6}Ni_{0,4}P$ за умов виконаного дослідження не підтверджено.

Ключові слова: реній, нікель, фосфід, рентгенівська дифракція на монокристалах, кристалічна структура.

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