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CRYSTAL STRUCTURE OF THE NEW ARSENIDE LuNiAs

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Crystal structure of the new ternary arsenide LuNiAs has been established using powder X-ray diffraction data: YbPtP type structure, space group $P\text{-}6m2$, $a = 0.40121(4)$ nm, $c = 0.37032(5)$ nm; $R_I = 0.0339$, $R_P = 0.0496$, $R_{wP} = 0.0660$. This compound is a new member of the isotypic series of the ternary arsenides with equimolar composition LnNiAs, where Ln – rare earth metal.

Key words: crystal structure, rare-earth metal, transition metal, nickel, arsenide.

Ternary systems containing rare earth metal, nickel and arsenic have not been studied widely, and the isothermal sections of the respective phase diagrams have been constructed only for several Ln–Ni–As systems, where Ln = Y, La, Ce, Sm, Ho, and Er [1–5]. Number of ternary arsenides being found in these systems varied from five compounds for the Ho–Ni–As system to seven in the case of Ce–Ni–As and Er–Ni–As ones. Existence of the series of the isotypic ternary arsenides LnNiAs, where Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm, has been reported earlier [2]. Crystal structure of the ternary phase CeNiAs was determined applying the Rietveld method using powder diffraction X-ray data, the arsenide crystallizes with the hexagonal YbPtP type structure [6] (the same atomic distribution has been established earlier for the ternary silicide LiBaSi [7]), for other isotypic compounds only lattice parameters were refined using powder diffraction data. Later the series of the LnNiAs compounds (Ln = La–Nd, Sm, Gd, Dy–Yb) [8] was found to have a closely related hexagonal structure which is very similar or identical with the structure reported for the series LnPtAs and LnNiP, where structure determination from single crystal data were carried out for YPtAs [6] and TbNiP [9], respectively. It should be noted what only powder diffraction data were used for the LnNiAs crystal structure determination, and other closely related hexagonal structures such as ScAuSi or NdPtSb cannot be ruled out [8].

For the Lu–Ni–As ternary system existence of only three ternary arsenides has been reported, namely $LuNi_4As_2$ ($ZrFe_4Si_2$-type structure) [10], $Lu_2Ni_{12}As_7$ ($Zr_2Fe_{12}P_7$-type structure) [11], and $Lu_{13}Ni_{25}As_{19}$ ($Tm_{13}Ni_{25}As_{19}$-type structure) [12]. Therefore, the main goals of our investigation were synthesis and crystal structure determination of the ternary arsenide of lutetium and nickel with equimolar composition.

Starting materials for the samples preparation were ingots of the lutetium, nickel powder, and crystalline arsenic (all with a stated purity better than 99.9 wt. %). Mixtures of rare earth chips and powders of nickel and arsenic with the stoichiometric ratio and total mass of 1 g were pressed into pellets. The pellets were placed into evacuated fused silica tube and slowly heated to 1 070 K (100 K per 24 hours), kept at this temperature over 240 h,

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and then cooled to room temperature by switching off the furnace. The sintered samples were ground, pressed again into pellets, and then arc-melted in purified argon atmosphere. Finally, the samples were annealed in evacuated fused silica tubes at 1 070 for 4 weeks, and quenched into cold water without breaking the tubes. The final mass of the annealed samples did not deviate from the initial mass of the unreacted mixtures by more than 2 %.

All samples were investigated by X-ray phase and structural analysis using DRON-3M diffractometer (Cu $K\alpha$-radiation, graphite monochromator, $\theta/2\theta$ scan mode, scanning limits $2\theta = 20–100\,°$, scanning step 0.05 degree of 2θ, time of measurement 8–10 sec in every point). For the X-ray data treatment WinCSD software was used [13]. The atomic positional and displacement parameters were refined from powder diffraction data using the full-profile Rietveld method [14].

The new ternary arsenide of lutetium and nickel with equimolar composition LuNiAs was found to be isotypic with YbPtP phosphide [6] (the same LiBaSi-type structure [7]), experimental details and refined atomic parameters for the LuNiAs crystal structure are listed in Tables 1 and 2, respectively. The reasonable values of the residual factors of the structure reliability confirmed that the compound indeed adopts the YbPtP-type structure with the fully ordered atomic distribution in the crystallographic sites $1a$, $1d$, and $1f$ of the space group P-6m2. The X-ray diffraction pattern of the LuNiAs compound is given in Fig. 1, one can observe a good correlation between experimental and calculated ones. However, structure type YPtAs in the case of LuNiAs compound is also possible, but this assumption can be confirmed only by X-ray single crystal or high precision powder diffraction data investigation.

Table 1

Experimental details and crystallographic data for the LuNiAs compound

Structure type	YbPtP (LiBaSi)
Space group, number of the formula units	P -6m2, Z = 1
Lattice parameters, nm: a	0.40121(4)
c	0.37032(5)
Unit cell volume, V, nm^3	0.05162(2)
Density calculated, g/cm^3	9.926(3)
Absorption coefficient, cm^{-1}	1148.29
Diffractometer	DRON-3M
Radiation and wavelength	Cu$K\alpha$, λ = 0.154185 nm
Mode of refinement	Full profile Rietveld method
Number of atoms in cell	3
Number of reflections / parameters for refinement	19 / 4
$2\theta_{max}$ and $(\sin\theta/\lambda)_{max}$	100.00 0.497
Final R-values	R_I = 0.0339, R_P = 0.0496, R_{wP} = 0.0660

It must be noted that the investigated sample contained a small amount of additional phase LuNi$_4$As$_2$ (ZrFe$_4$Si$_2$-type structure; space group $P4_2/mnm$; refined lattice parameters a = 0.7170(1) nm, c = 0.3747(1) nm are in the good agreement with literature data [10]), which is obviously in equilibrium with the investigated LuNiAs compound.

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Table 2

Atomic positional and isotropic displacement parameters for LuNiAs

Atoms	Wyckoff site	x/a	y/b	z/c	$B_{iso} \times 10^2$, nm^2
Lu	1a	0	0	0	0.65(6)
Ni	1d	1/3	2/3	1/2	1.4(2)
As	1f	2/3	1/3	1/2	1.1(2)

Interatomic distances in the structure of the LuNiAs compound are nearly the same as the respective sums of the atomic radii of the components: $r_{Lu} = 0.1718$ nm, $r_{Ni} = 0.1246$ nm, $r_{As} = 0.121$ nm [15]. The shortest distances are observed between atoms of nickel and arsenic (see Table 3). A distance reducing being observed in this case is less then 6 % of the respective sum of the atomic radii values. This fact confirms the predominant contribution of the metallic type bonding in the structure of the new compound.
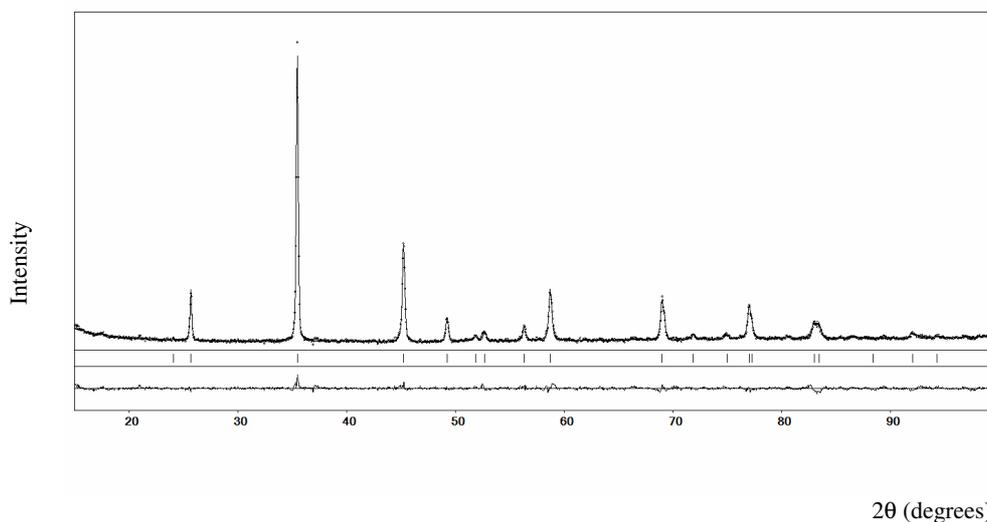
Fig. 1. Observed (points), calculated (solid line) and difference X-ray diffraction patterns of the LuNiAs compound (Cu$K\alpha$ radiation)

Table 3

Interatomic distances (δ) and coordination numbers (CN) of atoms in the LuNiAs structure

Atoms	δ, nm	CN
Lu – 6Ni	0.29655(2)	20
– 6As	0.29655(2)	
– 2Lu	0.37033(5)	
– 6Lu	0.40121(3)	
Ni –3As	0.23164(2)	9
– 6Lu	0.29655(2)	
As – 3Ni	0.23164(2)	9
– 6Lu	0.29655(2)	

The projection of LuNiAs structure on the *XY*-plane and the coordination polyhedra (CP) of atoms are shown in Fig. 2. Coordination polyhedra are similar to corresponding CP of atoms in the YbPtP structure and typical for the most of the ternary compounds in the *RE*-Ni-{P, As} systems [16]. The coordination number (CN) of lutetium atom is rather large, and coordination sphere is formed by all three types of atoms. The Lu atom has 20 neighbours, the polyhedron [Lu(Lu$_8$Ni$_6$As$_6$)] can be described as the hexagonal prism formed by Ni and As atoms with lateral sides and bases capped by additional atoms of Lu. CNs of nickel and arsenic atoms are smaller, and their polyhedra are the trigonal prisms formed by the six Lu atoms in both cases with the three additional atoms of As (for Ni atoms) and Ni (for As atoms), respectively. It should be mentioned that trigonal prismatic coordination is the most common for the phosphorus and arsenic atoms in the crystal structures of the ternary compounds with rare earth and 3*d*-transition metals, especially Fe, Co and Ni [16].
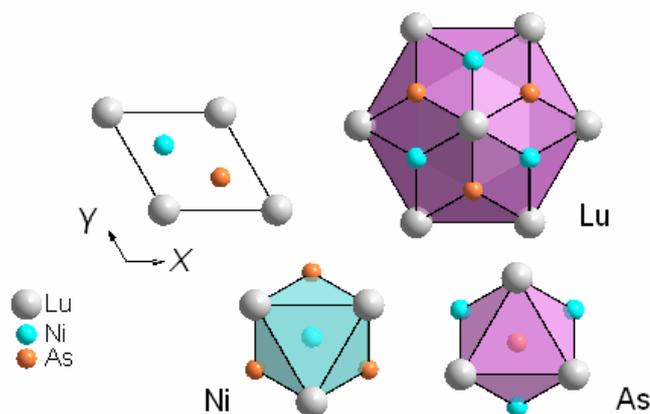
Fig. 2. Projection of the LuNiAs structure onto the *XY*-plane and CP of the individual atoms

The YbPtP (or LiBaSi) structure is a first order superstructure of the binary AlB$_2$-type: ordered distribution of the atoms of the transition metal (*M*) and *p*-element (*X*) in the position 2*d* (1/3 2/3 1/2) leads to its splitting to the two positions 1*d* та 1*f*, and results the decreasing symmetry with a transition from space group *P*6/*mmm* (AlB$_2$-type) to space group *P*-6*m*2 (YbPtP-type) (see Fig. 3).

In this structure atoms of the transition metal (Pt, Ni ect.) and *p*-element (P or As) alternately centered the trigonal prisms formed by the rare-earth atoms (*R*). Such trigonal prism build layers in the structure while *M* and *X* atoms form the same net as in the structure of graphite. Layers of the rare-earth atoms (A) alternating with layers of atoms *M* and *X* (H) in order ...AHAH... [17]. Structure types ZrBeSi, EuGe$_2$ and CaIn$_2$ are also can be derived from AlB$_2$-type as shown in Fig. 3. The crystal chemical relationships between a number of AlB$_2$-related intermetallic compounds are discussed on the basis of a group-subgroup scheme in the concise and compact *B□rnighausen* formalism with respect to the aristotype AlB$_2$ in [18].

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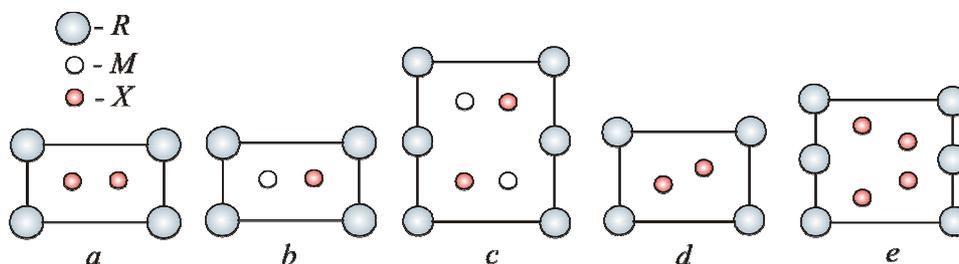
Fig. 3. Relationships between the structure types AlB_2 (*a*), YbPtP (LiBaSi) (*b*), ZrBeSi (*c*), $EuGe_2$ (*d*), and $CaIn_2$ (*e*). *R*, *M*, *X* – atoms of rare-earth, transition metal and *p*-element, respectively

On the other hand, YbPtP structure can be considered as the last member ($n = \infty$) of the homologous series of the flat hexagonal two-net structures with a metal/non-metal ratio equal or close to 2 and the general chemical formula $R_{n(n-1)}M_{(n+1)(n+2)}X_{n(n+1)+1}$, where *R, M, X* – atoms of the largest, middle and smallest size, respectively [16]. In the ternary *Ln*-Ni-{P, As} systems many compounds were found with the *Ln* content equal to 33.3 at. % and crystal structures belong to the structure types Fe_2P ($n = 1$), $Zr_2Fe_{12}P_7$ ($n = 2$), $Zr_6Ni_{20}P_{13}$ ($n = 3$) etc. Among the known Lu-Ni-As ternary compounds the arsenide $Lu_2Ni_{12}As_7$ with the $Zr_2Fe_{12}P_7$-type structure is the second member of this homologous series. So, we can predict the possible existence of new ternary Lu-Ni-As compounds with other structures of the described family.

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КРИСТАЛІЧНА СТРУКТУРА НОВОГО АРСЕНІДУ LuNiAs

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Кристалічну структуру нового тернарного арсеніду LuNiAs вивчено рентгеноструктурним методом порошку: структурний тип YbPtP, просторова група *P-6m*2, a = 0,40121(4) нм, c = 0,37032(5) nm; R_I = 0,0339, R_P = 0,0496, R_{wP} = 0.0660. Цей арсенід є новим членом ізоструктурного ряду сполук еквімолярного складу LnNiAs, де Ln – рідкісноземельний метал.

Ключові слова: кристалічна структура, рідкісноземельний метал, перехідний метал, нікель, арсенід.