REFINEMENT OF THE CRYSTAL STRUCTURE OF THE ARSENIDE HfNiAs

Makara I. A., Zhak O. V.
Ivan Franko National University of Lviv, Analytical Chemistry Department
igor1994makara@gmail.com

Existence of the ternary arsenide of hafnium and nickel HfNiAs has been reported earlier by [1]. The crystal structure of the isotypic ternary arsenide with cobalt HfCoAs was determined by the same authors using single crystal X-ray data. Both compounds crystallize with orthorhombic Co_2Si type structure (space group *Pnma*). However for the compound HfNiAs only the lattice parameters were refined from powder diffraction data: a = 0.6421(2), b = 0.3760(2), c = 0.7331(3) nm [1]. The goals of our investigation were synthesis and crystal structure determination of the ternary arsenide of hafnium and nickel with equiatomic composition.

Samples for investigation were prepared using arc-melting procedure of the preliminary sintered pellets obtained from the stoichiometric mixtures of starting materials: powders of hafnium and nickel, and crystalline arsenic (all with a stated purity better than 99.9 wt. %). The samples were heat treated in evacuated fused-silica tubes at 1 070 K during 1 month and quenched in cold water without breaking the tubes. Samples were investigated by X-ray powder diffraction method (diffractometer DRON-3M, Cu $K\alpha$-radiation). For the X-ray data treatment and refinement of the atomic coordinates and displacement parameters CSD software was used [2]. The atomic parameters were refined using the full-profile Rietveld method.

The ternary arsenide HfNiAs was found to crystallize with the orthorhombic crystal structure of the TiNiSi type structure (space group *Pnma*), refined lattice parameters are a = 0.64000(6), b = 0.38050(2), c = 0.73378(5) nm, cell volume V = 0.17869(5) nm^3, number of formula units Z = 4, final R-values are R_I = 0.0428, R_P = 0.0413, R_{wP} = 0.0554. The coordinates and displacement parameters of atoms in the HfNiAs crystal structure are listed in Table.

Table. Atomic parameters in the HfNiAs crystal structure

Atoms	Site	*x/a*	*y/b*	*z/c*	$B_{izo,}$ nm^2 10^2
Hf	4*c*	0.0273(5)	1/4	0.6875(4)	0.82(8)
Ni	4*c*	0.1433(11)	1/4	0.0688(9)	0.9(2)
As	4*c*	0.2685(13)	1/4	0.3844(12)	1.2(2)

The TiNiSi structure is an ordered ternary superstructure of the Co_2Si binary type, where all sorts of the atoms are regularly occupy the crystallographic sites. Arsenic atoms in the structure of HfNiAs are centered the trigonal prisms formed by the metal atoms only, whereas coordination polyhedra of the nickel atoms are the orthorhombic prisms formed by the all atom types. Coordination polyhedra of the largest hafnium atoms are the distorted pentagonal prisms also formed by the all atom types.

[1] Kleinke H., Franzen H. F. Crystal Structures, Bonding and Electronic Structures of MM'As, a Series of New Ternary Arsenides (M= Zr, Hf; M'= Fe, Co, Ni) // Z. Anorg. Allg. Chem. – 1998. – Vol. 624. – P. 51–56.
[2] Akselrud L., Grin Yu. WinCSD: Software Package for Crystallographic Calculations (Version 4) // J. Appl. Crystallogr. – 2014. – Vol. 47. – P. 803–805.