The crystal structure of Ho$_4$Ni$_{11}$In$_{20}$

Yuriy Tyvanchuk$^{1,*}$, Volodymyr Svitlyk$^{2,3}$, Yaroslav Kalychak$^1$

$^1$Department of Analytical Chemistry, Ivan Franko National University of Lviv, UA-79005 Lviv, Ukraine
$^2$Department of Chemistry, McMaster University, Hamilton L8S 4M1, ON, Canada
$^3$Swiss-Norwegian Beamlines at European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France

Received 2 November 2011; Accepted 16 November 2011

Abstract: The polycrystalline Ho$_4$Ni$_{11}$In$_{20}$ was obtained by arc-melting of the elements. The subsequent high temperature procedure was used for single crystal growth. Crystal structure of the compound was investigated by X-ray single crystal method: U$_4$Ni$_{11}$Ga$_{20}$ type, C2/m, a = 22.4528(17), b = 4.2947(3), c = 16.5587(13) Å, β = 124.591(5)°, R1 = 0.0276, wR2 = 0.0493 for 1989 independent reflections with |I|>2σ(I).

The structure is composed of three-dimensional network from Ni and In atoms in which Ho atoms fill distorted pentagonal channels.

Keywords: Intermetallics • Crystal structure • X-ray diffraction

© Versita Sp. z o.o.

1. Introduction

Among rare earth - transition metal - indium systems, the Ni - based systems are the most interesting with respect to the formation of numerous intermetallic compounds and their various physical properties [1]. According to the review works [1,2] investigation of the systems run intensively but they are completed only for Ce-Ni-In [3] with construction of isothermal section of the phase diagram. At 870 K the Ho-Ni-In system was so far characterized by the HoNi$_9$In$_2$ [4], HoNi$_4$In [5], Ho$_{10}$Ni$_9$In$_{20}$ [6], HoNi$_{10.5}$In$_{16.5}$ [7,8], Ho$_{10.5}$Ni$_7$In [9], Ho$_{10}$Ni$_7$In [10], Ho$_{10}$Ni$_7$In$_{11}$ [11] and Ho$_{13.35}$Ni$_{17}$In$_{3.48}$ [12] intermetallic compounds. Recent phase analytical investigation in this system at high indium content revealed existence of a new ternary Ho$_4$Ni$_{11}$In$_{20}$ compound. Earlier, the existence of R$_{Ni}_{11}$In$_{20}$ (R=Y, Gd, Tb, Dy) [13,14] was found in this region, and the Ho$_{Ni}_{11}$In$_{20}$ compound belonging to the U$_{Ni}_{11}$Ga$_{20}$ [15] or Ho$_{Ni}_{10}$Ga$_{21}$ [16] type structure was supposed. In this work results of the single crystal studies of the Ho$_4$Ni$_{11}$In$_{20}$ compound together with crystallographic analysis are presented.

2. Experimental procedure

Sample of a total weight of 1 g was obtained by a standard melting procedure: the amounts of the elements appropriate for the nominal composition of Ho$_4$Ni$_{11}$In$_{20}$ were arc-melted under pure argon atmosphere on a water cooled copper hearth with a tungsten electrode and titanium serving as a getter. Ingots of holmium of the purity not lower than 99.85 wt.%, nickel 99.92 wt.%, and indium 99.99 wt.% were used as the starting elements. After the arc-melting procedure, Ho$_4$Ni$_{11}$In$_{20}$ sample was obtained only as a polycrystalline alloy. Special heat treatment was used for the growth of Ho$_4$Ni$_{11}$In$_{20}$ single crystals. For this, the sample was placed in a zirconia crucible and evacuated to vacuum of 10$^{-6}$ bar. The sample was heated up to 1270 K and cooled to 870 K within 1 h and kept at this temperature for 3 h. Finally, the sample was cooled to room temperature by switching off the furnace. No reaction of the sample with the crucible was detected.

X-ray powder patterns were recorded with CuKα radiation (Philips PANalytical X’Pert Pro type
The single crystals were selected by mechanical fragmentation of the alloy. Single crystal X-ray diffraction was performed on the STOE IPDS II diffractometer with the MoKα radiation in the whole reciprocal sphere at room temperature. The single crystal investigated on the diffractometer was studied by the energy dispersive analysis of X-rays (EDX) using a JEOL JSM-7000F electron microscope with internal standards.

3. Results and discussion

Analysis of symmetry and systematic extinctions in reflections based on the single crystal data of Ho$_4$Ni$_{11}$In$_{20}$ suggested monoclinic centrosymmetric cell with $C2/m$, $Cm$ and $C2$ as possible space groups. The atomic positions of Dy$_{4}$Ni$_{10.80}$In$_{20.20}$ [14] were taken as a starting model and the structure was successfully refined with anisotropic displacement parameters for all atoms with SHELXL-97 [17]. All significant details concerning the data collections and structure refinement are listed in Table 1. The final difference Fourier synthesis revealed no significant residual peaks. The atomic parameters and anisotropic displacement parameters are listed in Tables 2 and 3. Further data on the structure refinement are available: Fachinformationszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD – 423747. The interatomic distances are listed in Table 4.

Phase analysis of XRD data of polycrystalline sample showed the existence of three phases: Ho$_4$Ni$_{11}$In$_{20}$ and minor additions of Ni$_2$In$_3$ and metallic indium. The lattice parameters obtained from least-squares fits [18] of the Ho$_4$Ni$_{11}$In$_{20}$ powder data are: $a=22.459(2)$, $b=4.2947(3)$, $c=16.5587(13)$ Å, $β=124.634(5)$°. The lattice parameters determined from the powder and the single crystals analysis agree well.

The atomic content obtained from the EDX analysis of the measured single crystal is 12.76 for Ho, 30.67 for Ni, 56.57 for In (in at.%, with an overall accuracy of 2%). These values are very close to the composition obtained from the structural refinement.

The Ho$_4$Ni$_{11}$In$_{20}$ adopts the U$_4$Ni$_{11}$Ga$_{20}$ type structure which is closely related to the Ho$_4$Ni$_{10}$Ga$_{21}$ type [15]. The difference between these two types lies in the different atomic occupation of the 2(d) 0 1/2 1/2 position. In U$_4$Ni$_{11}$Ga$_{20}$ this site is occupied by the atoms of d-element, while in Ho$_4$Ni$_{10}$Ga$_{21}$ it is occupied by the atoms of p-element. For Dy$_{4}$Ni$_{10.80}$In$_{20.20}$ [14] the Ni/In mixed occupation of the 2(d) site has been observed, whereas for compounds with Y, Gd and Tb only Ni