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Letter

Crystal structure and magnetic properties of $YbZn_{8.3–9.2}Ga_{2.7–1.8}$ with $BaHg_{11}$ structure type

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ABSTRACT

The ternary $YbZn_{8.3–9.2}Ga_{2.7–1.8}$ compound has been synthesized by reacting the elements at 900 °C, followed by annealing at 400 °C. The crystal structure of the compound was solved from single crystal as well as powder X-ray counter data. The above mentioned compound crystallizes in a cubic symmetry, with $BaHg_{11}$ structure type (space group $Pm\overline{3}m$, Pearson symbol $cP36$). The study of the magnetic properties of the compound reveals a diamagnetic behavior.

1. Introduction

Numerous of the rare earth and *d*-metal alloy systems are interesting both as from scientific viewpoint as from industrial applications. Some of them, with complex valuable properties (magnetic materials, superconductors, and hydrogen storage alloys, etc.), are already being used in different branches of industry. Among these compounds, special place have been occupied by cerium, europium or ytterbium intermetallics, with their unusual electronic and magnetic properties, such as heavy-fermion superconductivity, Kondo behavior, anomalous magnetism and intermediate valence.

Results on the determination of the new ternary phases and construction of the isothermal section of the phase diagrams for the Yb–Zn–In and Yb–Zn–Ga systems have been recently published [1,2]. One ternary compound, $YbZn_{1-x}In_{1+x}$ ($x = 0.3$), with UHg_2-type structure, was indentified in the Yb–Zn–In system at 400 °C. The Yb–Zn–Ga system is characterized by the existence of four ternary phases: $YbZn_xGa_{4-x}$, $0.75 \le x \le 2$ ($BaAl_4$-type), $YbZn_xGa_{4-x}$, $0.25 \le x \le 0.5$ ($CaCu_{0.15}Ga_{3.85}$-type), $Yb_3Zn_{11-x}Ga_x$, $3.5 \le x \le 4.2$ (La_3Al_{11}-type) and $YbZn_{11-x}Ga_x$, $1.8 \le x \le 2.7$ ($BaHg_{11}$-type). The partial isothermal section of the Yb–Zn–Al system at 400 °C has been presented in Ref. [3]. According to the reported data [4–8], there are seventeen intermediate ternary compounds in the Yb–Zn–Al system, namely, $YbZn_{1.46–1.67}Al_{0.54–0.33}$ ($MgZn_2$-type), $YbZn_{0.99–1.32}Al_{1.01–0.68}$ ($MgNi_2$-type), $YbZn_{2.12–2.6}Al_{0.88–0.4}$ ($CeNi_3$-type), $YbZn_{0.92–1.08}Al_{2.08–1.92}$ ($PuNi_3$-type), $Yb_3Zn_{4–6.16}Al_{7–4.84}$ (La_3Al_{11}-type), $YbZn_{1.65}Al_{2.35}$ ($BaAl_4$-type), $Yb_8Zn_{41.4–48.5}Al_{24.6–17.5}$ ($Yb_6Cu_{17}Al_{49}$-type), $Yb_2Zn_{15.61}Al_{0.71}$ (derived from U_2Zn_{17}-type), $Yb_{6.4}Zn_{46.8}Al_{3.4}$ (own type), $YbZn_{9.21}Al_{1.29}$ (derived from $SmZm_{11}$-type), $Yb_3Zn_{17.7}Al_{4.3}$ (Ce_3Zn_{22}-type) and $YbZn_{8.5}Al_{2.5}$ ($BaHg_{11}$-type).

The present work is part of the systematic investigation of such systems and shows the results on the crystal structure and magnetic properties of the ternary $YbZn_{8.3–9.2}Ga_{2.7–1.8}$ compound.

2. Experimental details

Starting materials for the $YbZn_{11-x}Ga_x$ alloys preparation were metals with nominal purities >99.95 wt.% (ytterbium ingots, zinc tear drops and gallium pieces). Each sample was synthesized by melting directly the elements inside quartz ampoules under vacuum (10^{-5} Torr). The reactions were first performed at 900 °C, the ampoules being hold at that temperature for 1 h, followed by their cooling in air and further under running water. The obtained samples resulted as soft reaction products with metallic-like lustres. They were examined by X-ray powder diffraction technique. No reaction with the quartz ampoules was observed. Finally, ingots were cut into small pieces, sealed in evacuated quartz tubes and annealed at 400 °C for 20 days inside a vertical oven. After the heat treatments, the samples were quenched, by submerging the quartz tubes in cold water, and analysed.

The polycrystalline samples were studied by X-ray powder diffraction method. A PANalytical X'Pert Pro diffractometer (Cu Kα-radiation) was used for this purpose. The scans were taken in the $\theta/2\theta$ mode with the following parameters: 2θ region, 15–120°; step scan, 0.03°; counting time per step, 20 s. The theoretical powder patterns were calculated with the help of the PowderCell program [9]. The lattice parameters were obtained by least-squares fitting using the Latcon program [10]. The FullProf [11] program was used for Rietveld refinements. Pseudo–Voigt profile shape function was used. The background was refined with a polynomial function.

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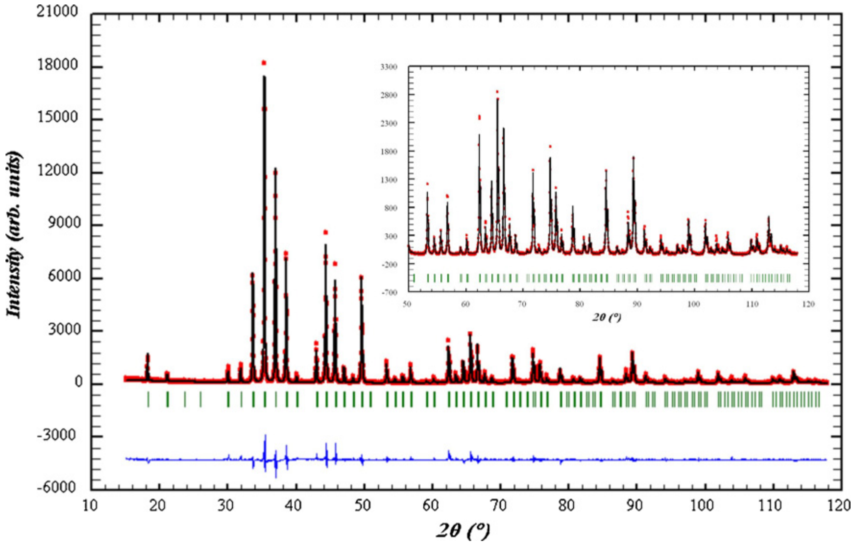

Fig. 1. Rietveld refinement of the sample $Yb_{8.3}Zn_{75.5}Ga_{16.2}$ (red circles – experimental, black line – theoretical and blue line – difference data, green bars – Bragg positions). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1
Parameters for data collection and structural refinement of $YbZn_{11-x}Ga_x$ compound.

Chemical formula	$YbZn_9Ga_2$	$YbZn_{8.6}Ga_{2.4}$
Structure type	$BaHg_{11}$	$BaHg_{11}$
Space group, *Z*	$Pm\bar{3}m$ (No. 221), 3	$Pm\bar{3}m$ (No. 221), 3
Pearson symbol	*cP*36	*cP*36
Cell parameters		
a	8.41640(8)Å	8.42850(7)Å^3
V	596.183(9)Å	598.757(9)Å^3
Diffractometer	PANalytical X'Pert Pro	PANalytical X'Pert Pro
Radiation	Cu Kα-radiation	Cu Kα-radiation
Data range and counting step (deg 2θ)	15–120, 0.03	15–120, 0.03
Counting time (s)	20	20
Number of reflection	117	123
Number of refined parameter	21	21
Rietveld reliability factors (%)		
R_p, R_{wp}	8.34, 10.6	9.67, 12.3
R_{Bragg}, R_F	5.19, 3.60	6.34, 4.23
χ^2	3.73	5.65

Table 2
Atomic coordinates and thermal parameters for $YbZn_9Ga_2$ compound.

Atom	Site	*x*	*y*	*z*	B_{iso} (Å^2)
Yb	3*c*	0	1/2	1/2	0.56(3)
M1	1*a*	0	0	0	1.06(12)
M2	8*g*	0.34172(16)	0.34172(16)	0.34172(16)	1.22(5)
M3	12*i*	0	0.23145(16)	0.23145(16)	0.98(4)
M4	12*j*	1/2	0.15356(13)	0.15356(13)	0.42(4)

M = 0.82Zn + 0.18 Ga.

Table 3
Atomic coordinates and thermal parameters for $YbZn_{8.6}Ga_{2.4}$ compound.

Atom	Site	*x*	*y*	*z*	B_{iso} (Å^2)
Yb	3*c*	0	1/2	1/2	0.84(3)
M1	1*a*	0	0	0	0.41(12)
M2	8*g*	0.34147(17)	0.34147(17)	0.34147(17)	1.20(6)
M3	12*i*	0	0.22985(17)	0.22985(17)	1.14(5)
M4	12*j*	1/2	0.15242(15)	0.15242(15)	0.46(4)

M = 0.78Zn + 0.22 Ga.

Table 4
Crystal data and structure refinement for $YbZn_{8.6}Ga_{2.4}$.

Empirical formula	$YbZn_{8.6}Ga_{2.4}$
Rel. mass	2702.17
Crystal system	Cubic
Space group, Z	$Pm\bar{3}m$ (No. 221), 3
Pearson symbol	*cP*36
Cell parameters	
a	8.4151(16) Å
V	595.9(2) Å^3
Formula units per cell	3
Calculated density	7.546 g/cm^3
Crystal shape and color	Block, silvery
Diffractometer	Enraf–Nonius Mach III
Wavelength	Mo K_α (λ = 0.71073 Å)
Monochromator	Graphite
Temperature	293(2) K
Absorption coefficient	44.982 mm^{-1}
F(0 0 0)	1207
θ Range for data collection	2.42–29.86°
Scan type	ω–2θ
Range in *h k l*	±11, ±11, ±11
Total no. reflections	6430
Independent reflection	219
Reflections with $I > 2\sigma(I)$	197
R_{eq}, R_σ	0.1939, 0.0509
Structure refinement	SHELXL-97 (Sheldrick-1997)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	214/0/16
Goodness-of-fit on *F*	0.856
Final *R* indices[a]	$R1 = 0.0283$, $wR2 = 0.0712$
R indices (all data)	$R1 = 0.0317$, $wR2 = 0.0744$
Weighting scheme[b]	$a = 0.0750$, $b = 0$
Extinction coefficient	0.0094(10)
Largest diff. peak/hole	3.558/−1.738e/Å^3

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR2 = \{\sum w[(F_o{}^2 - F_c{}^2)^2]/\sum w[(F_o{}^2)^2]\}^{½}$.

[b] $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, in which $P = (F_o{}^2 + 2F_c{}^2)/3]$.

Table 5
Atom coordinates and isotropic displacement parameters for $YbZn_{8.6}Ga_{2.4}$.

Atom	Site	*x*	*y*	*z*	U_{eq} (Å^2)
Yb	3*c*	0	½	½	0.0072(3)
M1	1*a*	0	0	0	0.0076(7)
M2	8*g*	0.34126(13)	0.34126(13)	0.34126(13)	0.0167(4)
M3	12*i*	0	0.23184(10)	0.23184(10)	0.0103(3)
M4	12*j*	½	0.15401(9)	0.15401(9)	0.0071(3)

M = 0.78Zn + 0.22 Ga.

Table 6
Anisotropic displacement parameters for $YbZn_{8.6}Ga_{2.4}$.

Atom	U11	U22	U33	U23	U13	U12
Yb	0.0106(4)	0.0055(3)	0.0055(3)	0	0	0
M1	0.0076(7)	0.0076(7)	0.0076(7)	0	0	0
M2	0.0167(4)	0.0167(4)	0.0167(4)	0.0070(4)	0.0070(4)	0.0070(4)
M3	0.0116(6)	0.0097(4)	0.0097(4)	0.0000(4)	0	0
M4	0.0077(5)	0.0068(4)	0.0068(4)	0.0011(4)	0	0

High quality crystals in the form of blocks were selected from the crushed samples obtained by slowly cooling from the ~950 °C to room temperature within 10 h. Single crystal intensity data were collected at room temperature using a four-circle Enraf–Nonius Mach III diffractometer with graphite monochromatized Mo Kα-radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. Empirical absorption corrections were applied on the basis of Ψ-scan data. Crystal structure was successfully refined using Shelxl-97 [12] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. Starting atom parameters were taken from the fitting of X-ray powder diffraction data.

Magnetic measurements were done on the annealed polycrystalline sample using a multicharacterization system MAGLAB 2000 (Oxford Instruments), in the temperature range 1.7–300 K and under applied magnetic fields up 5 T. Corrections taking into account the diamagnetic signal of the sample holder were done.

3. Results and discussion

The as-prepared as well as annealed at 400 °C the $YbZn_{11-x}Ga_x$ samples were first studied by means of X-ray powder diffraction data. XRD of the single phases was well indexed by a cubic unit cell ($a \sim 8.42$ Å). Lattice parameters, characteristic intensity of the peaks and composition AB_{11} indicated on the $BaHg_{11}$ structure type (space group $Pm\bar{3}m$) for the above mentioned compound. Crystal structure refinement for the $Yb_{8.3}Zn_{75.5}Ga_{16.2}$ alloy using Rietveld method confirmed this prediction (Fig. 1). Homogeneity range of this compound at 400 °C covers the composition from $YbZn_{9.2}Ga_{1.8}$ to $YbZn_{8.3}Ga_{2.7}$. Lattice parameters increase (from $a = 8.4131(1)$ Å, $V = 595.47(1)$ Å^3 for $x = 1.8$ to $a = 8.4360(1)$ Å, $V = 600.35(1)$ Å^3 for $x = 2.7$, respectively) due to the increasing of the gallium content in $YbZn_{11-x}Ga_x$. Table 1 shows parameters for data collection and structural refinements of $YbZn_9Ga_2$ and $YbZn_{8.6}Ga_{2.4}$ phases. Atomic coordinates and thermal parameters for above sites phases are presented in Tables 2 and 3, respectively.

Single crystal X-ray diffraction studies have also been performed for this compound. Details of the data collection and structure refinements of a crystal extracted from the alloy with $Yb_{8.3}Zn_{71.7}Ga_{20}$ (=$YbZn_{8.6}Ga_{2.4}$) nominal composition are presented in Table 4. Final atom coordinates and displacement parameters are given in Tables 5 and 6.

Fig. 2 shows the atom coordinations and the interatomic distances in the structure of $YbZn_{8.6}Ga_{2.4}$. Coordination polyhedra for the Yb atoms are 20-vertex polyhedral [$YbM2_8M3_4M4_8$] (coordination number 20). The M1 atoms are located in a cuboactahedra [$M1M3_{12}$] (CN 12). The nearest neighbors of the M2 atoms form distorted icosahedra [$M2Yb_3M2_3M3_3M4_3$] (CN 12). For the M3 and M4 atoms the coordination polyhedra are 12- and 10-vertex polyhedra [$M3YbM1M2_2M3_4M4_4$] (CN 12) and [$M4Yb_2M2_2M3_4M4_2$] (CN 10), respectively. The values of the interatomic distances are in good agreement with the sums of the atomic radii of the respective components ($r_{Yb} = 1.93$ Å, $r_{Zn} = 1.39$ Å, $r_{Ga} = 1.39$ Å) [13]. The shortest Yb–M bonds occurring in the structure of this compound range from 3.187 to 3.191 Å. The shortest M–M distances, which are less than the sum of r_{Zn} (or r_{Ga}), range from 2.592 to 2.759 Å.

The temperature and magnetic field dependence of the magnetization are shown in Figs. 3 and 4, respectively. The data show that this compound is diamagnetic for temperatures higher than 100 K. Below that temperature there is no sign of magnetic ordering down to 2 K. Such results, as expected, point to a nonmagnetic divalent state of ytterbium in $YbZn_9Ga_2$, which is typical for numerous ytterbium-based compounds. Among some Yb–Zn–X sytem

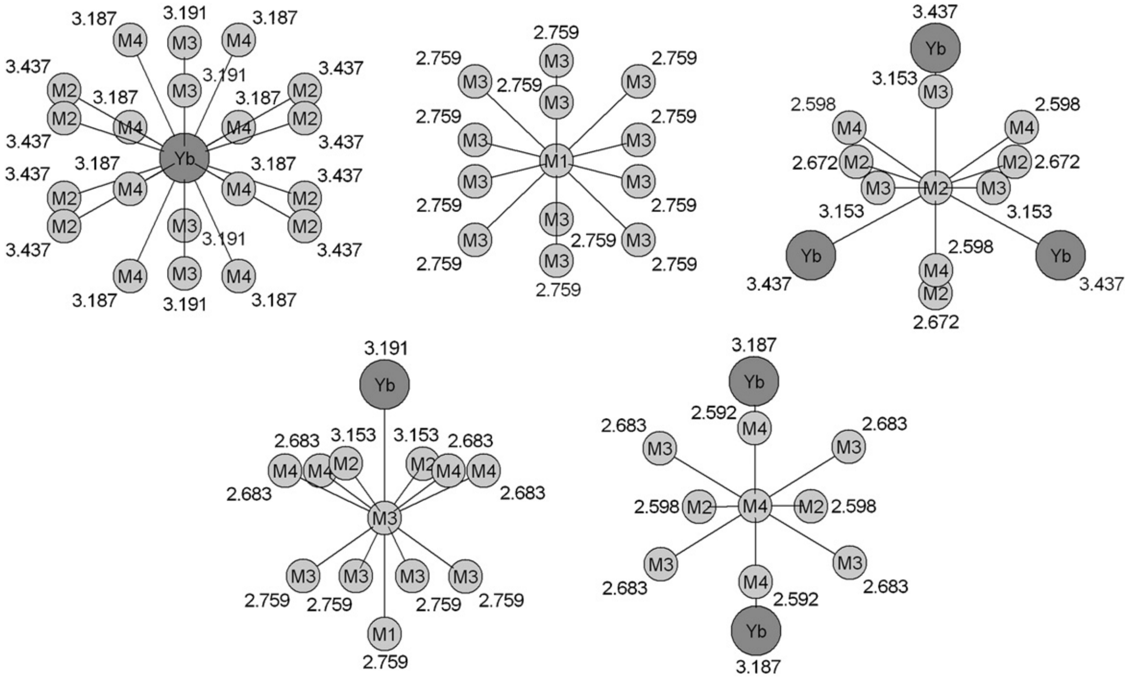

Fig. 2. Nearest-neighbor environments in the structure of $YbZn_{8.6}Ga_{2.4}$. Coordination polyhedra of the central atoms are indicated. The interatomic distances are shown in Å.

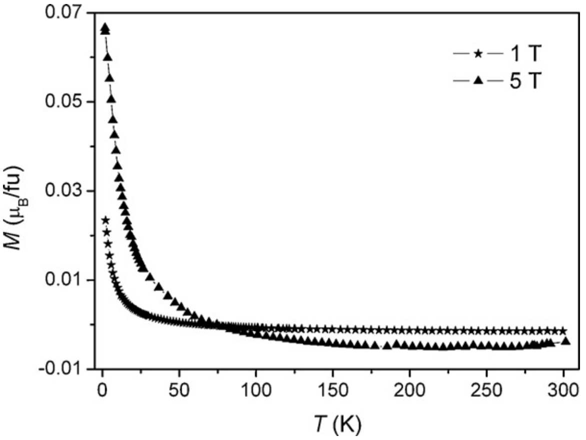

Fig. 3. Temperature dependence of the magnetization of $YbZn_9Ga_2$ taken at 1 and 5 T.

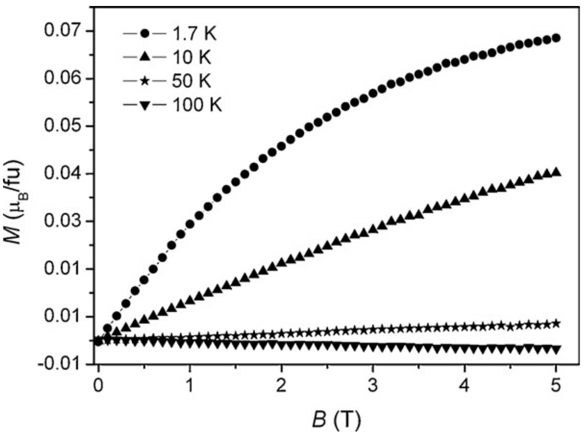

Fig. 4. Magnetic field dependence of the magnetization of $YbZn_9Ga_2$ at different temperatures.

($X = p$-metal), diamagnetic behavior was also observed for following compounds: $Yb_{3.51}Zn_{32.18}Al_{1.26}$ [3], $YbZn_{8.5}Al_{2.5}$ [8], $YbZnGa_3$ [14], YbZnIn [15], $YbZn_{0.5}Si_{1.5}$, $YbZn_2Si_2$, $YbZn_2Ge_2$ [16], YbZnSn [17], $Yb_9Zn_{4.5}Sb_9$ [18], $Yb_9Zn_4Bi_9$ [19]. Intermediate valence of ytterbium in the $Yb_4Zn_{20.3}Al_{12.7}$, $Yb_2Zn_3Ge_3$, $Yb_{14}ZnSb_{11}$ and $YbZn_2Sb_2$ compounds was suggested by the authors [3,20–22].

4. Conclusion

The new ternary $YbZn_{8.3–9.2}Ga_{2.7–1.8}$ compound was synthesized by melting the elements inside an evacuated quartz ampoule at 900 °C, followed by annealing at 400 °C. It crystallizes in the $BaHg_{11}$ structure type (space group $Pm\bar{3}m$, Pearson symbol *cP*36) with cubic lattice parameter ($a \sim 8.42$ Å). Titled compound exhibits diamagnetic behavior and does not undergo any magnetic ordering.

Acknowledgments

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