Journal of Solid State Chemistry 184 (2011) 1715–1718

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

$SmZn_{11}$-type derivative compound in the Yb–Zn–Al system: Crystal structure and magnetic properties

O. Stelmakhovych [a,b], B. Stelmakhovych [a], K. Uhlířová [b], S. Mašková [b], L. Havela [b,*], Ya. Kalychak [a]

[a] Department of Analytical Chemistry, Ivan Franko National University of Lviv, Kyryla & Mefodija Str. 6, 79005 Lviv, Ukraine
[b] Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague 2, Czech Republic

ARTICLE INFO

Article history:
Received 26 February 2011
Received in revised form
6 May 2011
Accepted 8 May 2011
Available online 17 May 2011

Keywords:
Intermetallics
Crystal growth
Crystal structure
Magnetization
Differential thermal analysis
Chemical analysis

ABSTRACT

Crystal structure and magnetic properties are reported for $Yb_{3.50}Zn_{32.1}Al_{1.4}$ prepared in single-crystalline form. It adopts the $SmZn_{11}$-type of structure (SG $P6/mmm$) with lattice parameters $a=0.90458(1)$, $c=0.88547(1)$ nm. The phase composition was analyzed by XRD, chemical and electron microprobe analysis. The ytterbium atoms in this compound are in the non-magnetic $4f^{14}$ state.

1. Introduction

Crystal structures of newly discovered intermetallic compounds in the very rich Yb–Zn–Al system have been recently investigated extensively. The data on structures of several intermetallics were reported, namely: $Yb_{25.39}Zn_{138.2}Al_{7.7}$ (YCd_6-type of structure, SG Im-3) [1], $Yb_{3.36}Zn_{30.94}Al_{4.34}$ ($SmZn_{11}$-type of structure, SG $P6/mmm$) [2], $Yb_{6.4}Zn_{46.8}Al_{3.4}$ ($Yb_{6.4}Zn_{46.8}Al_{3.4}$-type of structure, SG $P6/mmm$) [2], $Yb_{12.4}Zn_{96.8}Al_{4.4}$ (U_2Zn_{17}-type of structure, SG $P6_3/mmc$) [2], $Yb_3Zn_{17.7}Al_{4.3}$ (Ce_3Zn_{22}-type of structure, SG $I4_1/amd$) [2], $Yb_3Zn_{6.16\text{-}4}Al_{4.84\text{-}7}$ (La_3Al_{11}-type of structure, SG $Immm$) [3], and $Yb_8Zn_{48.5\text{-}41.4}Al_{17.5\text{-}24.6}$ ($Yb_8Cu_{17}Al_{49}$-type of structure, SG $I4/mmm$) [3], $YbZn_{0.996}Al_{1.004}$ ($MgNi_2$-type of structure, SG $P6_3/mmc$) [4], $YbZn_{0.88}Al_{1.12}$ ($MgCu_2$-Fd-3m) [4], $YbZn_{2.50}Al_{0.50}$ ($CeNi_3$-type of structure, SG $P6_3/mmc$) [4], $YbZn_{1.92}Al_{1.08}$ ($PuNi_3$- or $NbBe_3$-type of structure, R-3m) [4]. We continued mapping the Yb–Zn–Al ternary phase diagram, which still indicated existence of previously unknown compounds $YbZn_{8.5}Al_{2.5}$ ($BaHg_{11}$-type of structure, SG Pm-3m) [5], $Yb_4Zn_{20.3}Al_{12.7}$ ($Yb_8Cu_{17}Al_{49}$-type of structure, SG $I4/mmm$) [6] and $YbZn_{1.65}Al_{2.35}$ ($BaAl_4$-type of structure, SG $I4/mmm$) [7].

Magnetic properties of the compounds in the Yb–Zn–Al system are practically unknown. The first results for the compound $Yb_{25.39}Zn_{138.2}Al_{7.7}$ (YCd_6-type of structure) were reported by Fornasini et al. [1]. Magnetization, electrical resistivity and specific heat measurements revealed that ytterbium atoms in this compound are in the non-magnetic $4f^{14}$ state.

Our recent investigations on $YbZn_{8.5}Al_{2.5}$ with the $BaHg_{11}$-type of structure [5] revealed mixed valence state of the Yb atoms. Here we report on the structure and magnetic properties of single-crystalline $Yb_{3.50}Zn_{32.1}Al_{1.4}$, which adopts the $SmZn_{11}$-type of structure.

2. Experimental

2.1. Synthesis

Single crystals of the compound $Yb_{3.50}Zn_{32.1}Al_{1.4}$ were synthesized from a ternary Zn-rich flux. Appropriate amounts of the pure components were placed into alumina crucibles with quartz-wool stoppers and enclosed in sealed evacuated silica ampoules. The samples were heated up to 1030 K at a rate of 3 K/min, held for 1 h, and cooled down to 770 K at a rate of 0.05 K/min. Then the tube was removed fast from the furnace and the excess Zn was centrifuged through the quartz-wool stopper from the crystals.

2.2. Electron microprobe analysis

Microprobe analysis was carried out using a Tescan Mira I LMH microscope, with Bruker AXS and X flash detectors, and ESPRIT 18 software.

* Corresponding author. Fax: +420 22191351.
E-mail address: havela@mag.mff.cuni.cz (L. Havela).

0022-4596/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2011.05.013

2.3. Chemical analysis

The single-crystal sample was dissolved in a 10% aqueous solution of hydrochloric acid. After evaporation of the solution, the residue was dissolved in distilled water and ammonia solution was added. The ytterbium and aluminum hydroxides were precipitated and Zn^{2+} ions remained in solution as $[Zn(NH_3)_4]^{2+}$. The residue was separated by filtration. The amount of Zn in the solution was determined by complexometric titration with EDTA as a chelating agent and eriochrome black as indicator. The hydroxides residue was washed with 3% ammonia solution. Aluminum hydroxide was solved on the filter by treatment with a hot alkali solution. The amount of aluminum was estimated by complexometric back titration using standard zinc solution. The filter with the ytterbium hydroxide residue was washed until neutral reaction and dried in the desiccators. Then it was ashed in a porcelain crucible and calcined at 920 K until the mass was stable. The amount of the ytterbium was determined by gravimetric analysis in the form of Yb_2O_3.

2.4. Differential thermal analysis

DTA analysis was carried out on STA 409C NETZSCH apparatus (SiC-furnace, Pt10%Rh−Pt thermocouple) in alumina crucible under dynamic argon atmosphere in the temperature range 303–1030 K. The heating and cooling rates were 10 K/min.

2.5. Crystal structure determination

Single crystal intensities for the crystal structure determination were collected on a CAD-4 single crystal diffractometer with Ag$K\alpha$-radiation ($\lambda=0.056087$ nm) and a CCD detector in $\theta-2\theta$ mode. All calculations were performed using CSD software [8].

2.6. Magnetization measurements

Magnetization measurements were performed on single crystal sample in the temperature range 1.8–300 K and magnetic fields up to 9 T, applied along the *c*-axis and perpendicular to *c*, by means of Quantum Design PPMS equipment.

3. Results and discussion

3.1. Synthesis

The sample with the starting composition $Yb_5Zn_{81}Al_{14}$ was heated to 1030 K in a Zn flux and then cooled to 770 K. After separation of the Zn matrix and cooling to the room temperature, the single crystals in the form of hexagonal prisms up to 3 mm in length were found in the crucible. The composition of the sample from microprobe analysis is $Yb_9Zn_{85}Al_6$ (in at%). The chemical analysis of the crystals gave the composition $Yb_{9.4}Zn_{87.8}Al_{2.8}$ ($\omega_{Yb}=22.0(3)$%, $\omega_{Zn}=77.0(2)$%, $\omega_{Al}=1.0(4)$%).

3.2. Crystal structure determination

Preliminary single crystal investigations and the refinement of the lattice parameters in the hexagonal unit cell gave us a hint that this compound belongs to the $SmZn_{11}$-type of structure. This suggestion was confirmed by the refinement of atomic parameters. Basic crystallographic data and conditions of the investigation are shown in Table 1.

The structure of a new compound with the $SmZn_{11}$-type of structure was reported recently by Fornasini et al. [2]. These data were used as a starting model in our refinement. The discrepancy between the composition of the obtained crystals ($Yb_{3.50(1)}Zn_{32.08(20)}Al_{1.36(16)}$) and data given in Ref. [2] ($Yb_{3.36}Zn_{30.94}Al_{4.34}$) can indicate the existence of a homogeneity range for this compound. Atomic coordinates and equivalent displacement parameters are given in Table 2. Besides the Yb positions 1(*a*) and 2(*d*) there are two positions, 2(*c*) and 4(*h*), with partial occupancy by ytterbium and zinc atoms, respectively. The smaller atoms of Zn and Al are statistically distributed in the remaining crystallographic positions. The composition of the sample obtained from X-ray analysis ($Yb_{9.47}Zn_{86.90}Al_{3.63}$, in at%) is in good agreement with the composition from the chemical analysis.

Table 1
Crystallographic data for the $Yb_{3.50}Zn_{32.1}Al_{1.4}$.

Composition	$Yb_{3.50}Zn_{32.1}Al_{1.4}$
Space group	*P*6/*mmm* (N 191)
Lattice parameters (nm)	$a=0.90458(1)$, $c=0.88547(1)$
Cell volume (nm^3); *Z*	0.62748(2); 1
Number of atomic sites	9
Number of free parameters	32
Density (calc.) (g/cm^3)	7.3167
Absorption coefficient (cm^{-1})	234.5
Mode of refinement	$F(h\,k\,l)$
Radiation (nm)	Ag$K\alpha$, 0.0560871
$2\theta_{max}$ and $\sin\theta_{max}/\lambda$	56.30 0.841
Range in *h k l*	0–17, 0–17, 0–34
Number of measured reflections	1859
Numbers of unique reflections	599
Restrictions	$F(h\,k\,l)>4\sigma(F)$
Goodness of fit	1.020
Scale factor	0.317(3)
R_{sig}, R_{eq}, R_F, R_W	0.050, 0.0430, 0.0467, 0.0507

Table 2
Atomic coordinates and thermal displacement parameters (B_{eq}) in the $Yb_{3.50}Zn_{32.1}Al_{1.4}$ structure.

Atoms	WP	Coordinates			B_{eq}(10^{-2} nm^2)
		x	*y*	*z*	
Yb1	1*a*	0	0	0	0.54(3)
Yb2	2*d*	2/3	1/3	1/2	0.56(2)
Yb3[a]	2*c*	2/3	1/3	0	0.85(8)
X1[a]	2*e*	0	0	0.3526(5)	0.68(7)
X2[a]	4*h*	2/3	1/3	0.1460(8)	0.84(11)
X3[a]	6*i*	1/2	0	0.2740(3)	1.00(5)
X4[a]	6*k*	0.2985(3)	0	1/2	0.81(4)
X5[a]	6*j*	0.3525(3)	0	0	2.33(11)
X6[a]	12*o*	0.1678(1)	2*x*	0.2411(2)	0.84(3)

[a] Yb3=0.498(10)Yb; X1=1.24(4)Zn+0.76(4)Al; X2=1.44(4)Zn; X3=6Zn; X4=6Zn; X5=5.40(12)Zn+0.60(12)Al; X6=12Zn.

Interatomic distances are in good agreement with the sum of the atomic radii of the elements (Table 3). The distances between alternative Yb3 and X2 atoms (0.1294(7) nm) in crystallographic positions 2(*c*) (1/3 2/3 1/2) and 4(*h*) (1/3 2/3 *z*, $z=0.1460(8)$) are not realized in the structure of $Yb_{3.50(1)}Zn_{32.08(20)}Al_{1.36(16)}$, as general occupancy of these sites Yb3 (24.8(5)%) and X2 (36.6(9)%) is less then 100%. Slight shortening of the distances (9.5%) between Yb3 and X5 atoms in the defective positions is observed. That can indicate the appearance of a partially covalent interaction between these atoms. The high value of displacement parameter B_{22} for the X5 atoms also points to this fact. The anisotropic displacement parameters are listed in Table 4.

3.3. Differential thermal analysis

We investigated splices of the $Yb_{3.50}Zn_{32.1}Al_{1.4}$ single crystals also using differential thermal analysis. The DTA pattern of the sample is shown in Fig. 1. One can observe significantly reproducible thermal