Journal of Alloys and Compounds 671 (2016) 114–121

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Crystal structure and low-temperature properties of a novel cerium stannide Ce_3RuSn_6

V. Gribanova [a], D. Gnida [b], E.V. Murashova [a], A.V. Gribanov [a, *], D. Kaczorowski [b]

[a] Department of Chemistry, Moscow State University, GSP-1, Moscow 119991, Russia
[b] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form
5 February 2016
Accepted 8 February 2016
Available online 9 February 2016

Keywords:
Intermetallics
Crystal structure
Electrical transport
Magnetoresistance
Magnetic measurements

ABSTRACT

A novel ternary compound Ce_3RuSn_6 was synthesized as a single phase polycrystalline alloy. Its crystal structure was solved by direct methods and refined from the single crystal X-ray diffraction data down to R1 = 0.038 for 1021 independent reflections with $I > 2\sigma(I)$ and 36 variable parameters. The compound crystallizes with an orthorhombic unit cell of the Yb_3CoSn_6 type (space group *Cmcm*, lattice parameters: $a = 4.6744$ (4), $b = 16.8542$ (15), $c = 13.3227$ (12) Å), in which Ce atoms occupy two independent crystallographic sites. Physical behavior in Ce_3RuSn_6 was studied by means of magnetic susceptibility, electrical resistivity and heat capacity measurements, performed down to 0.4 K in magnetic fields up to 9 T. The compound exhibits ferromagnetic ordering below $T_C = 3$ K. Its thermodynamic and electrical transport properties in the paramagnetic and ordered states are strongly influenced by Kondo effect with the characteristic temperature very close to T_C.

1. Introduction

Ce-based intermetallics exhibit very rich spectrum of anomalous properties (valence instability, Kondo lattice behavior, heavy fermions, unconventional superconductivity, quantum criticality, non-Fermi liquid features), which are governed by strong electronic correlations resulting from the hybridization between 4*f*-electronic orbitals of rare earth atoms and conducting band [1]. Among these phases, several ternary compounds with noble metals and *p*-elements have been comprehensively studied due to their unique behaviors. In the system Ce–Ru–Sn, five ternaries have been reported to date: heavy fermion systems $CeRuSn_3$ [2–4] and $Ce_3Ru_4Sn_{13}$ [5,6], Kondo insulator $CeRu_4Sn_6$ [6–10], valence fluctuator CeRuSn [11–14], and putative ferrimagnet $Ce_{13}Ru_2Sn_5$ [15].

In this paper, we report for the first time on the formation of a novel ternary compound from the Ce–Ru–Sn system, namely Ce_3RuSn_6, describe its crystal structure and its low-temperature physical properties.

2. Experimental details

2.1. Synthesis

Polycrystalline sample of Ce_3RuSn_6 was synthesized by arc-melting the constituents (purity: cerium 99.85 mass %, ruthenium 99.99 mass %, tin 99.99 mass %) taken in the molar ratio 3:1:6. The melting procedure was performed on a copper hearth under purified argon atmosphere using zirconium as a getter. To promote homogeneity, the melting was repeated several times with the button turned over between each melting. The total weight loss after melting was less than 0.2 mass %. No further heat treatment was applied.

2.2. Sample characterization

The prepared material was examined by energy-dispersive X-ray (EDX) spectroscopy on a Carl Zeiss LEO EVO 50XVP scanning electron microscope (SEM). The accuracy in determining the chemical composition was 0.8 at.%.

Differential thermal analysis (DTA) was performed in the temperature interval from 298 K to 1723 K (heating/cooling rate 20 K/min, sample mass 6.2 mg) using a Netzsch STA449 F1 apparatus equipped with a Platinum RT analyzer.

* Corresponding author.
E-mail address: avgri@mail.ru (A.V. Gribanov).

http://dx.doi.org/10.1016/j.jallcom.2016.02.074
0925-8388/

2.3. X-ray single crystal diffraction

For structural analysis, a suitable small single crystal was selected from the surface of the prepared sample. X-ray diffraction (XRD) experiment was carried out on a Bruker APEX-II diffractometer equipped with a CCD area detector employing monochromated MoK_α radiation (λ = 0.71073 Å) at 296 (2) K. The obtained XRD intensities were collected and derived using the program Bruker SAINT [16]. Absorption correction was performed with the program SADABS [17]. The crystal structure was solved by direct methods and refined with the SHELXS-97 and SHELXL-97 programs [18]. Atomic parameters were standardized using the program STRUCTURE TIDY [19].

2.4. X-ray powder diffraction analysis

Powder XRD data were collected at 296 (2) K employing a STOE STADI P transmission X-ray diffractometer, equipped with a linear position-sensitive detector (monochromated Cu$K\alpha_1$ radiation with λ = 1.54056 Å; $5^\circ \leq 2\theta \leq 90^\circ$, step scan 0.01°, counting time 10 s/point). The lattice parameters were calculated with the STOE WinXpow program package [20]. Quantitative Rietveld refinement of the powder XRD pattern was performed with the FULLPROF program [21,22], employing internal tables for X-ray atomic form factors. As a starting model for the structure refinement, the atomic order obtained from the single crystal XRD experiment was taken. Structure and polyhedra were visualized using the program DIAMOND [23].

2.5. Physical properties measurements

Magnetic measurements were performed in the temperature range 1.72–400 K and in external fields up to 5 T using a Quantum Design SQUID magnetometer. The electrical resistivity was measured over the temperature interval 0.4–300 K and in magnetic fields up to 9 T employing a Quantum Design PPMS platform and standard ac four-probe technique. Heat capacity measurement was carried out in the temperature range 0.4–7 K by relaxation method using the same Quantum Design PPMS platform.

3. Results and discussion

3.1. Crystal structure

In the SEM study, the prepared Ce_3RuSn_6 alloy showed a microstructure with regions of slightly different darkness (Fig. 1a),

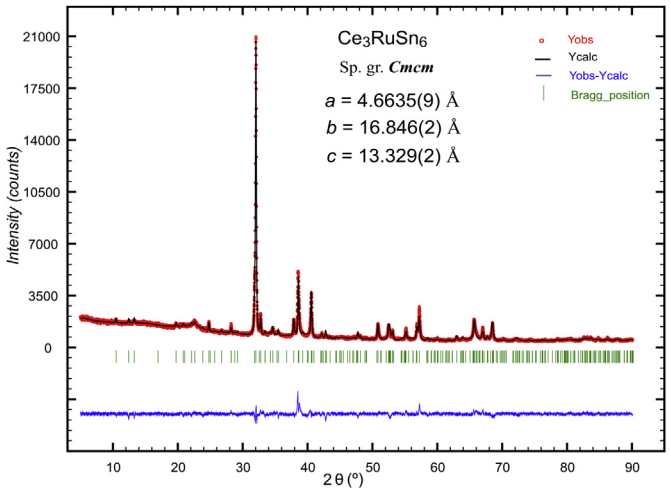

Fig. 2. Experimental (circles) and Rietveld refined (solid line) powder X-ray diffraction patterns of Ce_3RuSn_6. The curve in the bottom is a difference between the measured and calculated data. The ticks mark positions of the Bragg peaks.

however the EDX analysis revealed the same composition at all the points examined. This finding implies that the entire sample was homogeneous, and thus the dissimilar regions should be attributed to crystallites with different crystallographic orientation. The quantitative EDX measurements over the surface areas marked in Fig. 1b, resulted in the composition $Ce_{30.4}Ru_{10.4}Sn_{59.2}$ (at.%), which is very close to the ideal one. The melting temperature of 1524.15 (50) K was determined from the DTA measurement, without any thermal effects below this value.

The structural study showed Ce_3RuSn_6 to crystallize in the orthorhombic structure of the Y_3CoSn_6-type (space group *Cmcm*) [24] with the lattice parameters: a = 4.6744 (4), b = 16.8542 (15), c = 13.3227 (12) Å. The structure refinement based on the single crystal XRD data was performed down to R1 = 0.038 for 1021 independent reflections with $I > 2\sigma(I)$ (36 refined parameters). The powder XRD data confirmed this result (see Fig. 2). Details on the performed X-ray diffraction experiments and the structure refinements are gathered in Table 1. The refined atomic coordinates and the equivalent atomic displacement parameters are given in Table 2, while the anisotropic atomic displacement parameters are listed in Table 3. As can be inferred from the latter table, the anisotropic displacement ellipsoids of all the atoms have a nearly spherical form, and their overall sizes are reasonable. The main

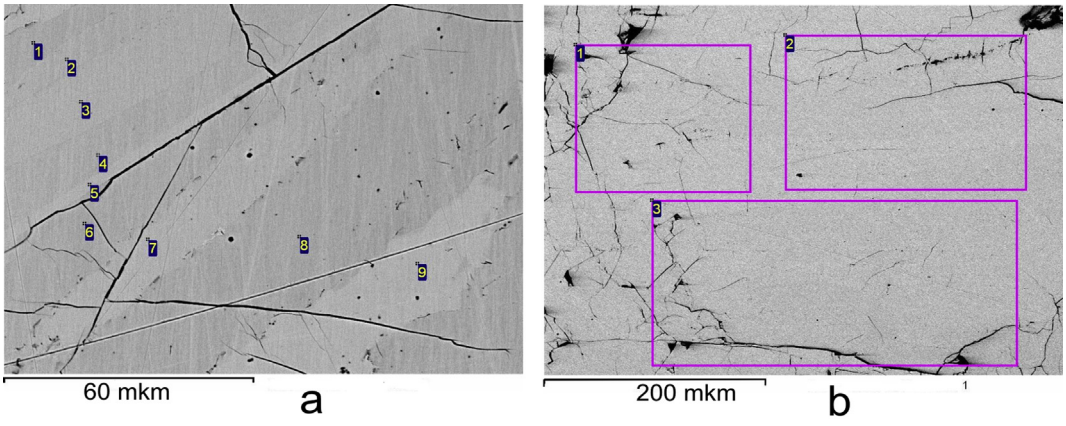

Fig. 1. Microstructure of the $Ce_{30}Ru_{10}Sn_{60}$ (at.%) alloy obtained with scanning electron microscope. Marked are (a) the measured points and (b) the measured surface areas.