Crystal growth of CsCl-type Yb$_{0.24}$Sn$_{0.76}$Ru

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ABSTRACT

The Yb–Ru–Sn ternary system was investigated and a new material, Yb$_{0.24}$Sn$_{0.76}$Ru, with a simple cubic crystal structure, was discovered. Yb$_{0.24}$Sn$_{0.76}$Ru has a smaller lattice parameter $a = 3.217(4)$ Å, than its isostructural YbRu analogue ($a = 3.360$ Å). Both X-ray diffraction and electron microscopy techniques were used to refine the crystal structure of Yb$_{0.24}$Sn$_{0.76}$Ru. It was found that a new compound forms in the CsCl structure, with Ru on the 1a site and a (Yb, Sn) mixture on site 1b. The XRD Rietveld analysis provides the occupation of Yb equal to 0.24, in agreement with the single crystal nano-electron diffraction refinement, which gives the occupation 0.21.

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1. Introduction

Employing molten fluxes as solvents allows for the discovery of new, often very complex, intermetallic materials. The molten metal-flux technique has been used for crystal growth for more than a century [1]. The main advantages of this technique are the lower temperature and increased diffusion rate in comparison to other commonly used methods. Without doubt, this growth method is an important tool in solid state chemistry, especially when utilized as a way of discovering new materials. This method is also a first choice for exploration of systems containing highly volatile elements such as Mg, Yb or Sb, where synthesis by arc-melting or radio-frequency heating of pure elements is problematic or simply impossible.

The molten metal-flux is a relatively easy technique, but severely limited. Two of the limitations seem to be the most critical: (1) the flux used should form no high temperature stable binary compounds with any of the reacting components; (2) the separation of the crystals from the flux should be possible. The commonly used methods of separation are the centrifugation technique and/or the chemical etching of the post-growth product. Although Sn metal is routinely used as a flux medium for the growth of single crystals of intermetallics, pnictides and oxypnictides, Pb metal has an important advantage compared to Sn. It can be very easily, and in a clean way, be dissolved using a mixture of acetic acid and H$_2$O$_2$.

Here we present the crystal growth details of a new (Yb$_{0.24}$Sn$_{0.76}$)Ru compound, obtained from a high temperature solution with Pb as a flux medium. We focus on the crystal structure refinement by means of X-ray diffraction and electron microscopy analysis.

2. Experimental details

Regularly shaped cube-like single crystals of (Yb$_{0.24}$Sn$_{0.76}$)Ru were grown from high temperature solution. The starting high purity (99.9% Ru, 99.99% Sn, 99.999% Pb and 99.9% Yb) metals in the ratio of Yb:Ru:Sn:Pb = 1.1:2:1:1.5 were placed in an alumina crucible and sealed under vacuum in a quartz tube. A different Yb concentration was also employed as discussed later. The tube was heated to 1150 °C and kept at that temperature for 6 h, then cooled at the rate of 5 °C/h to 650 °C, at which temperature the excess Pb was spun off with the aid of a centrifuge. This process removes almost all the Pb flux, however, an additional etching treatment, in the 1:1 mixture of H$_2$O$_2$ and acetic acid, is required to remove traces of Pb remaining on the crystals’ faces. Traces of remnant Pb were detected by magnetic susceptibility (MPMS-SQUID) and electrical resistivity measurements, which

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clearly show a partial superconducting transition close to 7 K when some Pb remains on the crystals.

Selected crystals were ground and characterized by powder X-ray diffraction, performed on a Scintag XDS 2000 diffractometer with CuKα radiation (λ=0.15460 nm). Data were collected in the 2θ range of 10–115° with a step size of 0.02°. Rietveld refinement of the structure was achieved using TOPAS software. Electron microscopy analysis was performed with a Philips CM200 with a field emission gun, operated at 200 kV. Electron diffraction was recorded on image plates with spot sizes less than 10 nm. Exposure times ranged from 1 to 3 s (condenser aperture 10 μm) for the diffraction patterns used for structure refinement and 15–30 s (condenser aperture 70 μm) for the convergent beam electron diffraction (CBED) pattern. The least squares refinement package MSLS [2] was employed to analyze the single crystal nano-electron diffraction data. This software, explicitly taking dynamical electron diffraction into account, has been proven to determine crystal structure with the same accuracy as single-crystal X-ray diffraction.

3. Results and discussion

Fig. 1 shows typical crystals obtained in our experiment. The relatively small size of the crystals (0.3 x 0.3 x 0.3 mm³) is a characteristic for the Heusler system, e.g. MPd₂Pb (M=Sc, Y, Gd, Tb, Dy, Ho, Er, Tm and Lu). Crystals grown in Pb flux reach the maximum size of 1 mm on side [3]. Pulverized crystals of (Yb₀.₂₄Sn₀.₇₆)Ru were studied by X-ray powder diffraction and the results, together with the Rietveld analysis, are presented in Fig. 2. The new compound was found to have the CsCl structure, space group Pm-3m, with Ru on 1a site, 0 0 0, and a (Yb, Sn) mixture on site 1b, ½ ½ ½. The calculated lattice parameter of (Yb₀.₂₄Sn₀.₇₆)Ru, a = 3.217(4) Å, is about 5% smaller than that reported for isostructural YbRu, a = 3.360 Å [4], which reflects the fact that the Yb covalent radius is larger than the Sn covalent radius. Small amount of unreacted Ru metal (4%) was also detected.

Nano-electron diffraction patterns of (Yb₀.₂₄Sn₀.₇₆)Ru show no super-reflections (see Fig. 3). These experimental results clearly show that there are no super-reflections induced by the possible Yb or Sn ordering. If the ordering of Yb/Sn exists, the symmetry of the parent CsCl structure might be broken. This possibility has been checked by the CBED pattern. As shown in Fig. 4, the CBED patterns of (Yb₀.₂₄Sn₀.₇₆)Ru along [1 0 0] and [1 1 0] show the 4mm and 2mm symmetries of the parent material, which provide supplementary evidence for no ordering of Yb and Sn. Since nano-electron diffraction and CBED are both taken from a sample area less than 10 nm, the absence of no super-reflections and no break of symmetry suggests that Yb/Sn is disordered on a single site in both long and short ranges.

The occupancy of Yb was obtained from single crystal nano-electron diffraction refinement. Eight electron diffraction datasets of (Yb₀.₂₄Sn₀.₇₆)Ru from different thickness and two main zones were refined simultaneously using the MSLS software [2]. The lowest overall R-value of 2.8% was achieved for occupancies 0.21 and 0.79 for Yb and Sn, respectively (Table 1). This result is very close to what was obtained from the Rietveld analysis of XRD pattern.

In Yb-based compounds, an important question is the Yb valence. Here, the Yb³⁺ spectral weight is strong and located around 6 eV below the Fermi level, and the bulk divalent Yb signal is absent [5]. We find that the Yb valence of 3 and f hole occupation close to 1 can be derived for (Yb₀.₂₄Sn₀.₇₆)Ru. In spectroscopy, the part missing here is usually related to as a “Kondo peak”, and the Kondo physics in other Yb compounds like YbCu₂Si², YbAl₃ or YbInCu₄ is driven by the interplay between the divalent and trivalent components [6], with Yb valence usually found between 2.6 and 2.9. It is worth noting that recently the first superconductor in an ytterbium-based heavy-fermion system was discovered [7].

![Fig. 1. SEM microscope image of typical (Yb₀.₂₆Sn₀.₇₄)Ru crystal.](image-url)
Knowing the exact concentration of Yb in (Yb\textsubscript{0.24}Sn\textsubscript{0.76})Ru, we were able to estimate the effective magnetic moment of Yb as 4.4, which is very close to the expected value of the free trivalent Yb\textsuperscript{3+} ion (4.54\mu_B). In addition, the presence of Yb\textsuperscript{3+} was independently proved by XPS and XANES experiments [5].

In the new compound, (Yb\textsubscript{0.24}Sn\textsubscript{0.76})Ru, more than 75% of 1b site is occupied by Sn, which is interesting taking into account the fact that an equivalent SnRu binary compound does not exist. Our initial goal was to synthesize YbRu\textsubscript{2}Sn with the cubic, L\textsubscript{21} Heusler structure. However the crystal growth conditions (slow cooling rate) favor the so-called B\textsubscript{2}-type disorder, which is a well-known problem in the synthesis of Heusler type compounds [8]. In spite of the Yb/Sn disorder on one of the sites, we believe that there is only a very narrow range of the Yb:Sn ratio for which the (Yb\textsubscript{1-x}Sn\textsubscript{x})Ru compound exists. This is based on the observation that in spite of employing different starting Yb concentrations, ranging from x=1 to 1.5 in the ratio of Yb:Ru:Sn:Pb = x:2:1:15, neither the lattice parameter nor the effective magnetic moment, calculated from magnetic susceptibility measurements, changes significantly in the different crystals obtained. A similar observation was reported for highly oxygen-deficient disordered perovskite BaBi\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{2.2}, which forms only in the range of 0.7 < x < 0.9. [9].
Acknowledgements

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References


Table 1

Data on the electron diffraction sets used for the structure refinement of Yb occupancy for (Yb0.24Sn0.76)Ru. The crystal misorientation is given as the position of the projection of the center of the Ewald sphere in Miller indices h,k,l.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Number of observed reflections</th>
<th>Thickness (nm)</th>
<th>Crystal misorientation</th>
<th>R-value (%)</th>
</tr>
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<tr>
<td>[1 0 0]</td>
<td>317</td>
<td>2.2(1)</td>
<td>0</td>
<td>2.0(1)</td>
</tr>
<tr>
<td>[1 0 0]</td>
<td>241</td>
<td>30.0(1)</td>
<td>0</td>
<td>−0.6(1)</td>
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<tr>
<td>[1 0 0]</td>
<td>504</td>
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<td>0</td>
<td>−0.7(1)</td>
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<tr>
<td>[1 1 0]</td>
<td>396</td>
<td>21.8(1)</td>
<td>0.6(1)</td>
<td>0.6(1)</td>
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<tr>
<td>[1 1 0]</td>
<td>279</td>
<td>11.3(1)</td>
<td>−1.0(1)</td>
<td>−1.0(1)</td>
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<tr>
<td>[1 1 0]</td>
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<td>4.3(1)</td>
<td>0.9(1)</td>
<td>0.9(1)</td>
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<tr>
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<td>−1.2(1)</td>
</tr>
<tr>
<td>[1 1 0]</td>
<td>547</td>
<td>4.8(1)</td>
<td>−1.2(1)</td>
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R = 2.8%, Yb occ. = 0.21, Sn occ. = 0.79.