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Synthesis, structure and properties of the new rare-earth Zintl phase $Yb_{11}GaSb_9$

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Abstract

A new rare-earth rich Zintl phase $Yb_{11}GaSb_9$ was synthesized by direct fusion of the corresponding elements, and large single crystals of the compound were obtained from high temperature flux synthesis. Its crystal structure was determined by single-crystal X-ray diffraction to be orthorhombic in the non-centrosymmetric space group *Iba*2 (No. 45), $Z = 4$ ($R_1 = 3.24\%$, $wR_2 = 6.40\%$) with $a = 11.7257(12)$ Å, $b = 12.3204(13)$ Å, $c = 16.633(2)$ Å measured at 90(3) K. The structure belongs to the $Ca_{11}InSb_9$-type and can be viewed as built of isolated Sb_4-tetrahedra centered by Ga, Sb-dimers and isolated Sb anions, which are separated by Yb^{2+} cations. Electron count according to the Zintl formalism suggests that the phase is electron-precise and charge-balanced, which is supported by the virtually temperature-independent magnetization for $Yb_{11}GaSb_9$. Electrical resistivity data from 2 to 400 K confirm that $Yb_{11}GaSb_9$ is a small band-gap semiconductor with room temperature resistivity $\rho_{298} = 45.1\,\mathrm{m\Omega\,cm}$, and low-temperature resistivity at 2 K $\rho_2 = 1.9\,\Omega\,\mathrm{cm}$. As such, $Yb_{11}GaSb_9$ and related compounds might be promising materials for thermoelectric applications, and currently, efforts to synthesize new members of this family and test their thermoelectric performance are under way.

Keywords: Rare-earth intermetallics; Crystal structure; Magnetic measurements; $Yb_{11}GaSb_9$; Heat capacity; DFT-calculations; Zintl phase

1. Introduction

In the past decade, polar intermetallic compounds formed between the electropositive alkaline-earth (Ca, Sr, Ba) and divalent rare-earth metals (Eu, Yb) with the early post-transition elements from group 13 (Al, Ga, In) and the pnicogens, i.e., group 15 (P, As, Sb, Bi) have been extensively studied [1–4]. In many of these compounds, in spite of the inherent structural complexity and diversity, simple electron counting rules such as the classic octet (8-N) rule have been found highly effective for rationalization of their structures and bonding [1–5]. This is done assuming complete transfer of valence electrons from the electropositive elements to the electronegative ones, and hence, the electropositive atoms could be viewed simply as spectator cations, while the electronegative atoms rearrange to form partial anionic sub-lattices with varying degrees of localized and/or delocalized bonding—widely known as Zintl concept [6].

Nevertheless, this simple-minded idea for rationalization of the formal electronic structure should be used very carefully—there are instances where interesting magnetic and electronic properties abound in seemingly closed-shell systems. For example, just the series of compounds $AE_{14}(M)Pn_{11}$ and $RE_{14}(M)Pn_{11}$ ($AE =$ Ca, Sr, Ba; $RE =$ Eu, Yb; $M =$ Al, Ga, In, Zn, Mn; $Pn =$ P,

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As, Sb, Bi) offers a wide range of properties ranging from semiconducting behavior, to large and/or colossal magnetoresistance, ferro-magnetism, mixed-valency, non-stoichimetry, etc. [7]. Using the classical Zintl approach, these structures can be viewed as built of discrete tetrahedral *M*-centered units, linear *Pn* trimers and isolated *Pn* ions, surrounded by divalent *AE* or *RE* cations. However, it has been demonstrated that this electron-counting scheme is overly simplistic in evaluating the complex physical properties of at least some of these phases (e.g., $Yb_{14}MnSb_{11}$) [8].

This remarkably rich and structurally diverse chemistry provided us with the motivation to continue studying similar materials and led us to the discovery of several novel compounds such as $Eu_{10}Mn_6Sb_{13}$ [9], $AE_{21}Mn_4Sb_{18}$ ($AE =$ Ca, Sr) [10], $Yb_9Zn_{4+x}Sb_9$ and $Yb_9Mn_{4+x}Sb_9$ [11]. These novel Zintl phases, analogously to the "14-1-11"-compounds [7], also contain isolated antimony anions and/or polyanions, that are arranged in a comparable manner in respect to both the anionic and the cationic sub-structure. In all these new polar intermetallics, Zintl concept can be applied in a straightforward manner, although their properties are not necessarily consistent with the idealized charge-balanced compositions [7–11].

In order to unequivocally determine the electronic properties of the recently discovered $Yb_9Zn_{4+x}Sb_9$ (non-stoichiometric phase existing in a narrow homogeneity range $0.2<x<0.5$), we attempted to produce large single crystals of it from molten Ga flux. Instead, this reaction produced large single crystals of the new rare-earth rich Zintl phase $Yb_{11}GaSb_9$ ($Ca_{11}InSb_9$-type) [12]. Herein, we report on the structural characterization, bonding and properties of this new material, whose structure is closely related to the "14-1-11" structure-type [7].

2. Experimental section

2.1. Synthesis

All manipulations were performed under vacuum or in an inert atmosphere. The starting materials (pure elements) were used as received. Yb (pieces, Ames 99.9%), Ga (ingot, Alfa, 99.999%), and Sb (ingot, Alfa 99.99%) were loaded with the desired stoichiometric ratios in either 5 or 2 cm^3 alumina crucibles, which were then put in fused silica ampoules. The ampoules were in turn closed under vacuum (or high purity Ar at 1/5 atm) by flame sealing.

Initially, single crystals of $Yb_{11}GaSb_9$ were obtained from a reaction loaded as $Yb_9Zn_{4.5}Sb_9Ga_x$ ($x>50$), which was intended to produce large single crystals of the non-stoichiometric $Yb_9Zn_{\sim 4.5}Sb_9$ from a molten Ga solution [11]. The reaction mixture was heated in a programmable muffle furnace using the following temperature profile: (1) quick ramping (150 °C/h) to 1000 °C, dwell at that temperature for 24 h, followed by slow cooling (–5 °C/h) to 600 °C. At that point, the excess Ga was removed by centrifugation. Details on the flux-growth synthetic procedures have been discussed in detail elsewhere [13].

After the structure and the composition were established from single crystal X-ray diffraction work, the synthesis of $Yb_{11}GaSb_9$ was successfully reproduced from pure elements in stoichiometric fashion. The mixtures were typically heated at 800–1000 °C and were always allowed to slowly cool down. The reactions were carried out in Al_2O_3-crucibles and/or sealed Ta-tubes, jacketed in evacuated fused-silica ampoules. Powder X-ray diffraction however indicated that the "on-stoichiometry" reaction outcomes contained trace amounts of impurity phases—$Yb_{11}Sb_{10}$ and Yb_4Sb_3 [14], below 5–10% by weight (est.).

Large single crystals of the title compound in quantitative yields were produced from reactions of Yb and Sb in Ga flux (reactions were loaded as $Yb_{11}Ga_xSb_9$ ($x\sim 70$) and the above-mentioned temperature profile for flux growth was employed). Irregularly shaped crystals with silver-metallic luster, some of them very large (up to ca. 7–9 mm) were isolated, cleaned from the excess Ga by sonification in warm water, and used for the precise structure determination and for the physical properties measurements. The crystals of $Yb_{11}GaSb_9$ appear stable in air, but dissolve readily in mineral acids. Despite the seeming stability, our property measurement data suggest the presence of trace amounts of Yb_2O_3, an indication for a slow sample oxidation (below).

2.2. Powder X-ray diffraction

X-ray powder diffraction patterns were used to monitor the reaction outcomes and were taken at room temperature on a Scintag XDS 2000 powder diffractometer equipped with monochromatized Cu $K\alpha$ radiation. The PXRD data analysis was carried out employing the MDI-JADE 6.5 software package [15]. The diffraction patterns were compared with those calculated from the single-crystal data using the Crystal Diffract 4.1 package [16]. Powder patterns of crushed crystals of $Yb_{11}GaSb_9$ before and after exposure to air showed no signs of decomposition products, indicating that the title compound is stable in dry air (*note: an indication for traces of impurity* Yb_2O_3 *in all our samples is evidenced from the calorimetry and magnetization data (below), but the estimated amount of* Yb_2O_3 *is* $\sim$*0.1%—well below the detectable limits*). The X-ray powder patterns were not used for determination of the unit cell parameters because of the relatively low symmetry and large cell constants (Table 1). The lattice parameters for different samples (determined from single-crystal X-ray