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# $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)] with the tetragonal $\alpha$-$ThSi_2$ structure type

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(SiAg–Si/Ag) = 0.001 Å
Disorder in main residue
$R$ factor = 0.009
$wR$ factor = 0.020
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Single crystals of the title compound, ytterbium silver silicide, were synthesized from the corresponding elements using a eutectic Ag/Si mixture as a solvent. Structure determination suggested the composition of the product to be $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)], *i.e.* a new ternary derivative of the $\alpha$-$ThSi_2$ structure type, which crystallizes in the body-centered tetragonal space group $I4_1/amd$. The two atoms in the asymmetric unit lie on special positions with Wyckoff symbols 4$a$ (Yb), and 8$e$ (disordered Ag and Si).

## Comment

Binary rare-earth silicides and germanides are important materials, which have been extensively studied in the last two or three decades (Gschneider & Eyring, 1979). Of specific interest to us was the divalent oxidation state of Eu and the mixed valency of Yb in some silicides and germanides and their derivatives. The pronounced stability of the divalent $Eu^{2+}$ and $Yb^{2+}$ oxidation states can be explained by their half-filled and completely filled 4$f$-shells, respectively.

The purpose of the present work was to study the variations of the polyanionic network of such europium and ytterbium compounds as a function of electron count, electronegativity, and constituent size. Some results from the systematic investigation of the physical properties and chemical bonding in $REAl_xSi_{2-x}$ compounds (RE is a rare earth) adopting the $\alpha$-$ThSi_2$ structure type (Villars & Calvert, 1991) have already been published (Bobev *et al.*, 2005). Those studies confirmed wide homogeneity regions in both systems, which present a significant challenge for obtaining the phases as pure products and with defined composition. We report here the synthesis and structural characterization of a new member of the family, $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)], which also crystallizes in the body-centered tetragonal $\alpha$-$ThSi_2$ structure type. Detailed physical property studies of this new material will be reported in a forthcoming publication.

The $\alpha$-$ThSi_2$ type is a very common structure among such intermetallics. As described already, many of these are indeed non-stoichiometric phases with large stoichiometry ranges. This fact, together with the rather anisotropic physical properties one might expect from the crystal structure type, presents challenges for researchers in this field.

To circumvent these difficulties, we employed the flux-growth technique (Canfield & Fisk, 1992) to obtain high-quality single crystals of $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)]. The availability of sizeable single crystals in this and many other cases proved very important for unequivocal structure determination and precise property measurements. The title compound was successfully prepared in good yield from an Ag–Si low-melting eutectic mixture.

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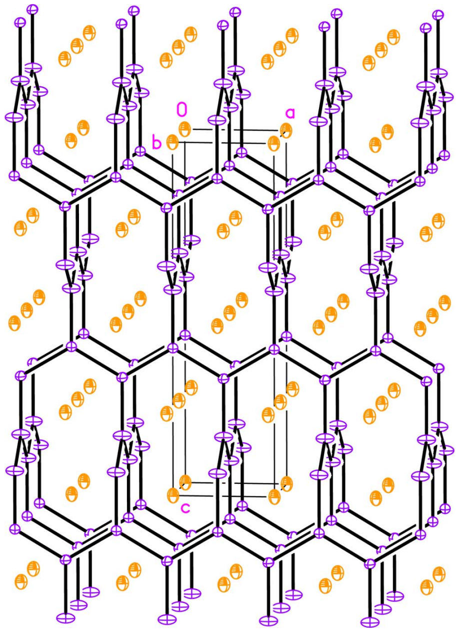

**Figure 1**
A view of the $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)] structure projected approximately along [010]. Displacement ellipsoids are drawn at the 98% probability level. Si/Ag are drawn as purple ellipsoids and Yb is shown as orange ellipsoids with octant shading. The unit cell is outlined.

The structure of $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)] is a new ternary derivative of the $\alpha$-$ThSi_2$ structure type (Villars & Calvert, 1991). Notably, the binary phase $YbSi_2$ is known, although it is also not fully stoichiometric and adopts the $AlB_2$ structure type (Villars & Calvert, 1991). $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)], therefore, is a rare example of a ternary phase, based on a structure type very common among the binary rare earth metals, but yet not realised in the Yb–Si system.

The lattice parameters $a$ = 4.0757 (7) Å and $c$ = 14.1965 (11) Å compare well with those for other $REAg_xSi_{2-x}$ phases, such as $CeAg_xSi_{2-x}$ (Cordruwisch *et al.*, 2001). Although $YbSi_2$ (or rather $YbSi_{2-x}$) with the $\alpha$-$ThSi_2$ structure type does not exist, an elongation of the crystal axes, especially the $c$ axis, is clearly seen for $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)] in comparison with those for other unsubstituted $RESi_{2-x}$ compounds. Such expansion of the unit cell is typical in other solid solutions $REM_xSi_{2-x}$ ($M$ = main-group or transition metal), and is due to the larger atomic size of Ag compared with that of Si. Thus, all interatomic Si—Si distances are slightly longer than those found in pure binary phases (Villars & Calvert, 1991).

$YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)] and its parent structure, $\alpha$-$ThSi_2$, can be viewed as polar intermetallics, *i.e.* compounds formed by electropositive and electronegative metals and semi-metals. The structure can be considered as made up of an Si-based polyanionic subnetwork, with the rare-earth cations occupying the voids and channels within it, as shown in Fig. 1. The Yb atom is situated on a site with $\bar{4}m2$ symmetry, whereas the Si site has $2mm$ symmetry. The Si—Si contacts fall within the narrow range 2.3463 (16)–2.3664 (8) Å, which agrees with the description above. The shortest Yb—Si contact is 3.1116 (3) Å, a distance normal for such a high coordination number (Fig. 2).

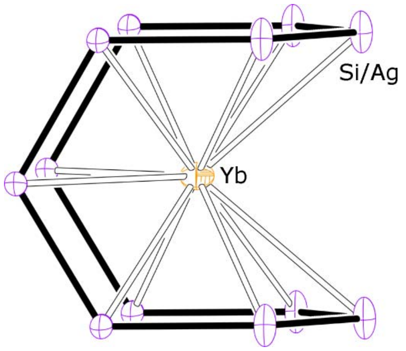

**Figure 2**
A view of the Yb coordination polyhedron in $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)]. Displacement ellipsoids are drawn at the 90% probability level.

## Experimental

All starting materials were used as received: Yb (Ames Laboratory, ingot, 99.99% metal basis), Ag (Alfa, foil, 99.999%) and Si (Alfa, pieces, 99.999%). A mixture of the elements in a ratio Yb:Ag:Si = 1:0.11:0.89 was loaded in an alumina crucible, which was subsequently enclosed in an evacuated fused silica jacket by flame-sealing. The reaction was carried out at a temperature of 1423 K for 2 h, followed by slow cooling (4 K $h^{-1}$) to 1148 K. At this point, the molten flux was removed by centrifugation. The product of the reaction were small crystals with silver metallic luster. These were later identified as $YbAg_xSi_{2-x}$ [$x$ = 0.28 (1)]. The crystals are stable in air and moisture over extended periods of time.

### *Crystal data*

$YbAg_{.28}Si_{1.72}$
$M_r$ = 251.76
Tetragonal, $I4_1/amd$
$a$ = 4.0757 (2) Å
$c$ = 14.1965 (11) Å
$V$ = 235.82 (2) Å$^3$
$Z$ = 4
$D_x$ = 7.091 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 796 reflections
$\theta$ = 5.2–30.9°
$\mu$ = 42.37 mm$^{-1}$
$T$ = 293 (2) K
Bar, grey
0.05 × 0.04 × 0.03 mm

### *Data collection*

Bruker SMART APEX diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min}$ = 0.155, $T_{max}$ = 0.280
796 measured reflections
118 independent reflections
107 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018
$\theta_{max}$ = 30.9°
$h = -5 \rightarrow 5$
$k = -5 \rightarrow 4$
$l = -20 \rightarrow 19$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.009$
$wR(F^2) = 0.020$
$S$ = 1.23
118 reflections
9 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0097P)^2 + 0.0681P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.66 e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0086 (6)

**Table 1**
Selected interatomic distances (Å).

| | | | |
|---|---|---|---|
| Yb—Si/Ag$^{i}$ | 3.1116 (3) | Si/Ag—Yb$^{i}$ | 3.1116 (3) |
| Si/Ag—Si/Ag$^{ii}$ | 2.3463 (16) | Si/Ag—Yb$^{iii}$ | 3.1302 (6) |
| Si/Ag—Si/Ag$^{i}$ | 2.3664 (8) | | |

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{3}{4}-z$; (iii) $x, y-1, z$.

Structure solution and refinement were performed with origin choice 2 of the space group $I4_1/amd$. The structure refinement based on a composition '$YbSi_2$' converged at poor residuals and two crystallographically unique sites (Yb and Si) exhibited unusually anisotropic displacement parameters. By freeing the site-occupation factor for an individual atom, while other remaining parameters were kept fixed, it became evident that the Si site is statistically occupied by Si and Ag atoms. The Si/Ag site was found to be a nearly 85:15 statistical mixture of Si and Ag, whereas the Yb site is fully occupied with deviations from full occupancy within less than $3\sigma$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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