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$Ce_5Au_xGe_{4-x}$ [x = 0.43 (2)] with the orthorhombic Sm_5Ge_4 structure type

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Single crystals of the title compound, pentacerium gold tetragermanium, were synthesized from the corresponding elements using a eutectic Au/Ge mixture as solvent. Structure determination of a crystal from that reaction revealed the composition $Ce_5Au_xGe_{4-x}$ (x = 0.43). The compound is a new ternary derivative of the Sm_5Ge_4 structure type that crystallizes in the space group *Pnma* of the orthorhombic system. There are six atoms in the asymmetric unit, one Ce in Wyckoff site 4c, two Ce in 8d, two Ge in 4c and one Ge in 8d. Two of the Ge sites are statistically occupied by Ge and Au atoms, with a lack of long-range ordering. The results are consistent with an earlier report on the structure of the fully stoichiometric analog Ce_5Ge_4.

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(Ce–Ce) = 0.003 Å
Disorder in main residue
R factor = 0.028
wR factor = 0.056
Data-to-parameter ratio = 20.8

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

Comment

Binary rare earth silicides and germanides are important materials, which have been extensively studied in the last two to three decades. Of specific interest to us was the mixed-valent Kondo material $CeSi_2$ (Kohgi *et al.*, 1990) and its Ge analog $CeGe_2$. Both compounds crystallize in the body-centered tetragonal α-$ThSi_2$ structure type (Villars & Calvert, 1991). However, there are certain homogeneity regions in both systems, which present a significant challenge to

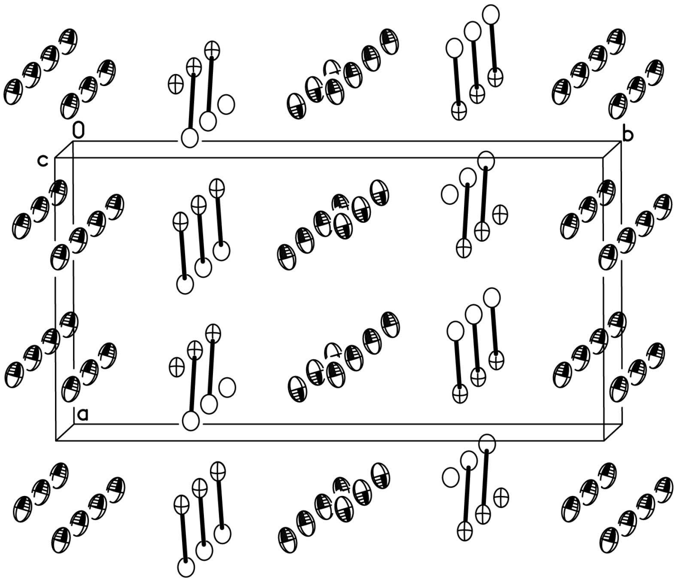

Figure 1
A view of the $Ce_5Au_xGe_{4-x}$ structure projected approximately along [001]. Displacement ellipsoids are drawn at the 95% probability level. Ge1/Au1 are drawn as crossed circles, Ge2 is shown with open circles, and Ge3/Au3 are shown with full ellipsoids. Ce atoms have been omitted for clarity.

obtaining the phases as pure products and with defined composition. Moreover, from the crystal structure, one might expect rather anisotropic physical properties, and the availability of sizeable single crystals becomes very important for precise property measurements.

To circumvent these synthetic challenges, we employed the flux-growth technique (Canfield & Fisk, 1992) to obtain high-quality single crystals from $CeSi_2$ and $CeGe_2$. Various low-melting metals have been tried with differing degrees of success. In all cases, the resulting compounds were found to be solid solutions, CeM_xSi_{2-x} and CeM_xGe_{2-x} (M = metal employed in the flux), or ternary Ce–*M*–Si and Ce–*M*–Ge intermetallics with different structure types. Here, we report the synthesis and structure of a new ternary Ce–Au–Ge compound. Detailed studies of the physical properties of this new material will be reported in a forthcoming publication.

The structure of $Ce_5Au_xGe_{4-x}$ (x = 0.43) is a new ternary derivative of the Sm_5Ge_4 structure type (Villars & Calvert, 1991). The fully stoichiometric analog Ce_5Ge_4 (Smith *et al.*, 1967) exhibits slightly different lattice parameters, a = 7.86 Å, b = 15.21 Å, and c = 8.04 Å, from those of the title compound. Although the cell dimensions for the latter were determined at 120 K, whereas for the unsubstituted compound the measurements were carried out at room temperature, the systematic elongation of all crystal axes of $Ce_5Au_xGe_{4-x}$ (x = 0.43) is clearly seen. This is due to the nearly 18% larger atomic size of Au compared with that of Ge. Therefore, all interatomic distances are slightly longer than those in the binary phase Ce_5Ge_4.

$Ce_5Au_xGe_{4-x}$ (x = 0.43) and its parent Ce_5Ge_{4-x} compounds can be viewed as polar intermetallics, *i.e.* compounds formed by electropositive and electronegative metals and semi-metals, following the Zintl concept (Zintl, 1939). There are six atoms in the asymmetric unit: Ce1 in Wyckoff site 4*c*, Ce2 in 8*d*, Ce3 in 8*d*, Ge1 in 4*c*, Ge2 in 4*c* and Ge3 in 8*d*. The structure can be considered as made up of Ge_2 dumbbells and isolated Ge atoms, as shown in Fig. 1. Ge—Ge contacts with the dumbbells of 2.665 (2) Å compare well with Ge—Ge contacts found in other alkaline earth and rare earth germanides. The isolated Ge anions are coordinated by Ce2 cations only, and the shortest Ce—Ge contact is 2.9588 (15) Å, which agrees with the description above.

Experimental

All starting materials were used as received [Ce (Ames Laboratory, ingot, 99.99% metal basis), Au (Alfa, foil, 99.999%), and Ge (Alfa, pieces, 99.999%)]. A mixture of the elements in the ratio Ce:Au:Ge = 1:0.72:0.28 was loaded into 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 1373 K for 6 h, followed by slow cooling (3.5 K h^{-1}) down to 823 K. At this point, the molten flux was removed by centrifugation. The products of the reaction were small crystals with a silver metallic luster. These were later identified as $Ce_5Au_xGe_{4-x}$ (x = 0.43). The crystals are stable in air and moisture, but decompose quickly in solutions of mineral acids.

Crystal data

$Ce_5Au_{0.43}Ge_{3.57}$
M_r = 1043.82
Orthorhombic, *Pnma*
a = 7.868 (5) Å
b = 15.258 (7) Å
c = 8.052 (6) Å
V = 966.6 (11) $Å^3$
Z = 4
D_x = 7.173 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3569 reflections
θ = 2.7–26.4°
μ = 40.31 mm^{-1}
T = 120 (2) K
Irregular fragment, metallic silver
0.07 × 0.06 × 0.05 mm

Data collection

Bruker APEX SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.083, T_{max} = 0.139
3569 measured reflections
1021 independent reflections
953 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 26.4°
$h = -9 \rightarrow 9$
$k = -19 \rightarrow 0$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.056
S = 1.10
1021 reflections
49 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 12.3954P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.46 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.77 e $Å^{-3}$
Extinction correction: *SHELXTL* (Sheldrick, 2001)
Extinction coefficient: 0.00019 (4)

Table 1
Selected geometric parameters (Å).

Ce1—Ge1/Au1$^{\rm i}$	3.064 (2)	Ce2—Ge2	3.1592 (19)
Ce1—Ge2$^{\rm ii}$	3.103 (3)	Ce2—Ge1/Au1$^{\rm i}$	3.2191 (15)
Ce1—Ge3/Au3$^{\rm iii}$	3.1657 (16)	Ce2—Ce1$^{\rm vi}$	3.5410 (16)
Ce1—Ge3/Au3$^{\rm iv}$	3.1658 (16)	Ce3—Ge3/Au3$^{\rm x}$	3.0884 (17)
Ce1—Ge2$^{\rm v}$	3.261 (2)	Ce3—Ge2$^{\rm xi}$	3.1738 (15)
Ce1—Ge1/Au1$^{\rm vi}$	3.299 (3)	Ce3—Ge3/Au3$^{\rm xii}$	3.2898 (15)
Ce1—Ce2$^{\rm vii}$	3.5409 (16)	Ce3—Ge2$^{\rm xiii}$	3.3082 (17)
Ce1—Ce2$^{\rm v}$	3.5410 (16)	Ce3—Ge1/Au1$^{\rm xiv}$	3.3133 (17)
Ce2—Ge3/Au3$^{\rm viii}$	2.9588 (15)	Ce3—Ge3/Au3$^{\rm xv}$	3.334 (2)
Ce2—Ge3/Au3$^{\rm iii}$	2.9791 (19)	Ce3—Ce2$^{\rm xvi}$	3.6211 (15)
Ce2—Ge3/Au3$^{\rm ix}$	3.0528 (18)	Ge1/Au1—Ge2$^{\rm v}$	2.665 (2)
Ce2—Ge1/Au1$^{\rm vi}$	3.1259 (15)		

Symmetry codes: (i) $x-1, y, z$; (ii) $x, y, z-1$; (iii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (v) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (vi) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (vii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x, y-1, z$; (ix) $-x, -y+1, -z+1$; (x) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$; (xi) $x+1, y, z$; (xii) $x+\frac{1}{2}, y-1, -z+\frac{3}{2}$; (xiii) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (xiv) $x, y, z+1$; (xv) $-x+1, -y+1, -z+1$; (xvi) $-x+1, -y, -z+1$.

The structure refinement, assuming a composition Ce_5Ge_4, converged to poor residuals and two of the three crystallographically unique Ge sites (Ge1, Ge3) exhibited unusually large anisotropic displacement parameters. By freeing the site occupation factor for each individual atom, while the remaining parameters were kept fixed, it became evident that those two sites are statistically occupied by Ge and Au atoms. The third Ge site (Ge2), along with the three Ce sites, proved to be fully occupied, with corresponding deviations from full occupancy within 3σ. This is consistent with the slightly larger unit-cell parameters for $Ce_5Au_xGe_{4-x}$ compared with those for Ce_5Ge_4 (Smith *et al.*, 1967). The Ge1/Au1 site was found to be a nearly 75:25 statistical mixture of Ce and Au, whereas the Ce3/Au3 site is close to 90:10, leading to an x value of 0.43 (2). The highest peak and the deepest hole in the final difference Fourier map are 0.91 and 1.40 Å, respectively, from the Ce1/Au1 site.

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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