

**SmAl<sub>2.64(4)</sub>Ge<sub>0.36(4)</sub>, with the hexagonal Ni<sub>3</sub>Sn structure type****Sheng-Qing Xia, Daniel Lins and Svilen Bobev\***Department of Chemistry and Biochemistry,  
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USACorrespondence e-mail:  
sbobev@chem.udel.edu**Key indicators**Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{Al}-\text{Al}) = 0.0004$  Å  
Disorder in main residue  
 $R$  factor = 0.020  
 $wR$  factor = 0.052  
Data-to-parameter ratio = 9.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

Single crystals of the title compound, samarium aluminium germanium, were synthesized from the corresponding elements using molten Al metal as a solvent. The structure is isotypic with GdAl<sub>2.90</sub>Ge<sub>0.10</sub>, crystallizing in the hexagonal Ni<sub>3</sub>Sn structure type (space group  $P6_3/mmc$ ), with two atoms in the asymmetric unit, namely Sm on Wyckoff site  $2c$  and a statistical mixture of Al and Ge on Wyckoff site  $6h$ . Structure refinement from single-crystal X-ray diffraction data result in the stoichiometry SmAl<sub>2.64(4)</sub>Ge<sub>0.36(4)</sub>.

**Comment**

The synthesis from Al flux and the properties of a number of ternary rare-earth aluminosilicides ( $RE\text{-Al-Si}$ ) have recently been reported (Bobev *et al.*, 2005; Bobev & Tobash, 2006). These studies demonstrate the suitability of elemental Al to serve as a solvent at high temperatures for the facile growth of large crystals of several general types, namely  $REAl_xSi_{2-x}$ , non-stoichiometric derivatives of the  $\alpha\text{-ThSi}_2$  structure type (Brauer & Mitius, 1942), formed predominantly by the early rare-earths ( $RE = \text{La, Ce, Pr, Nd, Sm or Gd}$ ), and stoichiometric  $RE_2Al_3Si_2$  compounds, formed by the late rare-earth metals Tb, Dy, Ho, Er or Tm, which crystallize in the  $Y_2Al_3Si_2$  structure type (Yanson *et al.*, 1994). Divalent Eu and Yb form  $REAl_2Si_2$  compounds with the trigonal  $CaAl_2Si_2$  structure type (Gladyshevskii *et al.*, 1967), and Tm and Lu form stoichiometric  $TmAlSi$  and  $LuAlSi$  compounds with the  $YAlGe$  structure type (Zhao & Parthé, 1990).

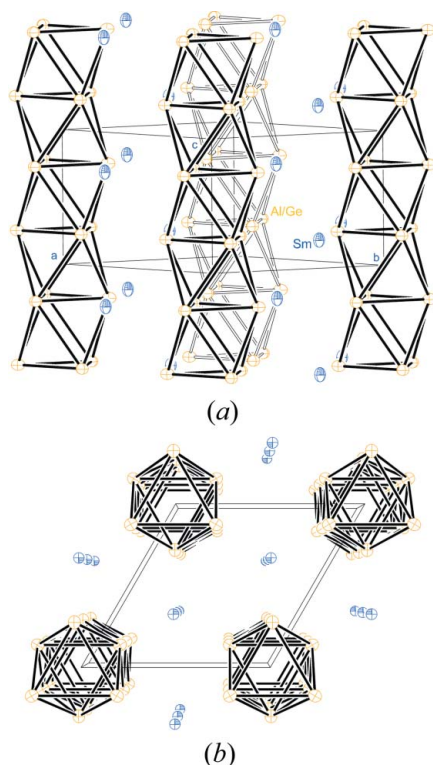
In our attempts to probe the field for new materials with interesting magnetic or electrical properties, we have embarked on thorough and systematic studies of the ternary  $RE\text{-Al-Ge}$  systems employing flux-growth techniques. Although these systems have already been explored to some extent (Zhao & Parthé, 1990; Johrendt *et al.*, 2000; Kranenberg *et al.*, 2002; Melnyk *et al.*, 2005), all syntheses reported therein involve arc-melting and annealing of the corresponding reaction mixtures. Recent work by Zhuravleva *et al.* (2001) reported three new  $REAl_{3-x}Ge_x$  phases ( $RE = \text{Gd, Tb or Ho}$ ) prepared from molten Al.

Here, we report the structure of a new intermetallic compound SmAl<sub>2.64(4)</sub>Ge<sub>0.36(4)</sub> (SmAl<sub>2.64</sub>Ge<sub>0.36</sub> hereinafter), grown from Al flux. To date, several ternary compounds in the Sm-Al-Ge system have been structurally characterized, namely SmAl<sub>2</sub>Ge<sub>2</sub> with the  $CaAl_2Si_2$  structure type (Johrendt *et al.*, 2000), Sm<sub>2</sub>Al<sub>3</sub>Ge<sub>4</sub> with the  $Hf_2Ni_3Si_4$  structure type (Zhao & Parthé, 1991), Sm<sub>2</sub>AlGe<sub>6</sub> with the  $La_2AlGe_6$  structure type (Zhao *et al.*, 1991), SmAlGe with the  $LaPtSi$  structure type (Zhao, 1997), and Sm<sub>2</sub>AlGe<sub>3</sub> with the  $Y_2AlGe_3$  structure type (Melnyk *et al.*, 2005). SmAl<sub>2.64</sub>Ge<sub>0.36</sub> is a new non-stoichiometric phase in this system, which appears to

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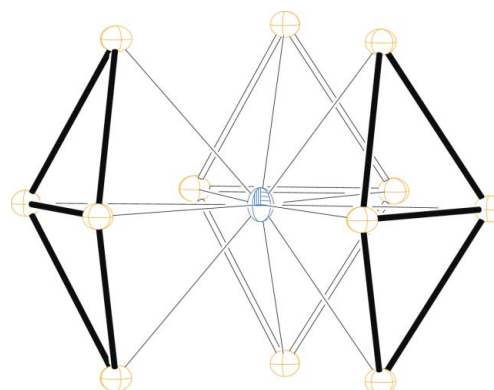
**Figure 1**

A view of the  $\text{SmAl}_{2.64}\text{Ge}_{0.36}$  structure, (a) projected approximately along  $[110]$  and (b) projected approximately along  $[001]$ . Displacement ellipsoids are drawn at the 90% probability level. Sm atoms are shown as full blue ellipsoids, and Al/Ge atoms are represented with yellow crossed ellipsoids. The unit cell is outlined in both diagrams.

form readily in an excess of Al. The phase crystallizes with the hexagonal  $\text{Ni}_3\text{Sn}$  structure type, space group  $P6_3/mmc$ , No. 194 (Lihl & Kirnbauer, 1955), and can be viewed as a substitution derivative of the binary compound  $\text{SmAl}_3$  with the same structure (Buschow & van Vucht, 1965).

There are two unique sites in the asymmetric unit of this structure, *viz.* Sm at Wyckoff site  $2c$  ( $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ ) and Al at  $6h$  ( $x, 2x, \frac{1}{4}$ ). Thus, the Al atoms form one-dimensional chains of face-shared Al octahedra, running along the direction of the  $c$  axis, as shown in Fig. 1. The octahedra are slightly distorted and there are two sets of Al–Al contacts, which are normal for Al–Al bonding and compare well with the distances observed in other Al-rich intermetallics (Zhao & Parthé, 1990; Johrendt *et al.*, 2000; Kranenberg *et al.*, 2002; Melnyk *et al.*, 2005).

Almost one in every ten Al atoms in the structure is randomly substituted by Ge, according to the refinement of the single-crystal X-ray diffraction data. This can also be seen from the slightly different unit-cell parameters of the pure binary compound  $\text{SmAl}_3$  and the substituted compound  $\text{SmAl}_{2.64}\text{Ge}_{0.36}$ :  $a = 6.380$  (3) and  $c = 4.597$  (4) Å for the former (Buschow & van Vucht, 1965), and  $a = 6.318$  (3) and  $c = 4.583$  (5) Å for the latter. This is in agreement with the covalent radii of Al and Ge, which differ by nearly 1% (Pauling, 1960). It should be noted here that the cell measurements in both cases were taken at different



**Figure 2**

A view of the Sm coordination polyhedron in  $\text{SmAl}_{2.64}\text{Ge}_{0.36}$ . Displacement ellipsoids are drawn at the 90% probability level. Sm atoms are shown as full blue ellipsoids and Al/Ge atoms are represented with yellow crossed ellipsoids.

temperatures, which may make the difference in the cell constants larger than expected. Nonetheless, the Al/Ge disorder is clearly seen from the structure refinement (below). Similar Al–Ge solid solutions have already been reported for the analogous compounds  $\text{REAl}_{3-x}\text{Ge}_x$  ( $\text{RE} = \text{Gd}, \text{Tb}, \text{Ho}$ ), where  $x$  ranges from 0.1 to 0.3 (Zhuravleva *et al.*, 2001).

The Sm atoms form flat hexagonal layers (perpendicular to the  $c$  axis) and separate the chains of face-shared Al octahedra. Each Sm atom is enclosed between three such chains (Fig. 1b) and can be viewed as centering a highly symmetric dodecahedron, as shown in Fig. 2. There are two sets of Sm–Al (Sm–Ge) distances, which compare well with the contacts observed in  $\text{REAl}_{3-x}\text{Ge}_x$  (Zhuravleva *et al.*, 2001). More work on related RE–Al–Ge systems is currently underway.

## Experimental

Handling of the pure metals and of the reaction products was carried out either in an argon-filled glove box with controlled oxygen and moisture levels, or under a vacuum. All of the starting materials were used as received: Sm (lump, 99.9%+, Ames Laboratory), Al (shot, 99.999%+, Alfa), Ge (lump, 99.99%+, Alfa). Crystals of the title compound were obtained from the reaction of the elements in the ratio Sm:Al:Ge = 2:30:2. The mixture was loaded into an alumina crucible, which was subsequently sealed in a fused silica tube under high vacuum. The following temperature profile was used: heating from room temperature at a rate of  $300 \text{ K h}^{-1}$  to 1373 K, dwell for 7 h, and cooling at a rate of  $30 \text{ K h}^{-1}$  to 1023 K, at which point the excess of molten Al was removed by centrifugation. The reaction product consisted of irregularly shaped crystals with a silver-metallic lustre, which were later identified as  $\text{SmAl}_{2.64}\text{Ge}_{0.36}$ , elemental Al and Ge, as evidenced from X-ray powder diffraction patterns.

### Crystal data

$\text{SmAl}_{2.64}\text{Ge}_{0.36}$   
 $M_r = 247.5$   
 Hexagonal,  $P6_3/mmc$   
 $a = 6.318$  (3) Å  
 $c = 4.583$  (5) Å  
 $V = 158.42$  (19) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 5.183 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 605 reflections  
 $\theta = 3.7\text{--}27.0^\circ$   
 $\mu = 22.27 \text{ mm}^{-1}$   
 $T = 120$  (2) K  
 Irregular fragment, grey  
 $0.05 \times 0.05 \times 0.05 \text{ mm}$

Data collection

Bruker APEX SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.340$ ,  $T_{\max} = 0.368$   
 605 measured reflections

84 independent reflections  
 80 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$   
 $\theta_{\text{max}} = 27.0^\circ$   
 $h = -8 \rightarrow 5$   
 $k = -7 \rightarrow 7$   
 $l = -5 \rightarrow 4$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.052$   
 $S = 1.14$   
 84 reflections  
 9 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0365P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.76 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.27 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: SHELXTL (Sheldrick, 2001)  
 Extinction coefficient: 0.057 (8)

Table 1

Selected bond lengths (Å).

Sm—Al <sup>i</sup>	3.097 (3)	Al—Al <sup>iii</sup>	2.775 (3)
Al—Al <sup>iii</sup>	2.709 (6)		

Symmetry codes: (i)  $x - y, x, -z$ ; (ii)  $-y + 2, x - y + 1, z$ ; (iii)  $y, -x + y + 1, -z + 1$ .

After routine data collection, data reduction and absorption correction, the structure was refined using the coordinates from the parent hexagonal Ni<sub>3</sub>Sn structure (space group  $P6_3/mmc$ ), with Al on the Ni site (6*h*) and Sm on the Sn site (2*c*). Although the structure refinement converged at excellent residuals, the Al site exhibited an abnormal anisotropic displacement parameter. To check for potential partial occupation or substitution, structure refinements were undertaken with a free site occupation factor, while other remaining parameters were kept fixed. This resulted in significant deviations from full occupancy ( $>15\sigma$ ), which confirmed that Al and Ge are disordered on that site. Final refinement cycles were carried out with Al and Ge mixed on the 6*h* site [refined ratio Al:Ge = 0.88 (1):0.12 (1)], which resulted in better residuals and a better goodness-of-fit indicator. The anisotropic displacement parameters

also refined much better. The highest peak and deepest hole in the final difference Fourier map are 0.88 and 1.56 Å away from the Sm and Al sites, respectively.

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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