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Partial Sn-atom ordering in $\text{Sm}_3\text{Ga}_{0.80-2.48}\text{Sn}_{4.20-2.52}$

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Trisamarium digallide tristannide crystallizes with a partially ordered Pu_3Pd_5 -type structure in space group $Cmcm$. In a single crystal of $\text{Sm}_3\text{Ga}_{1.89(4)}\text{Sn}_{3.11(4)}$, the 8g position is mostly occupied by Sn atoms (93% Sn and 7% Ga), while the 4c and 8f positions are occupied by a Ga/Sn statistical mixture. The evolution of the structure as a function of the Ga content has been studied by X-ray powder diffraction on ten $\text{Sm}_3\text{Ga}_{5-x}\text{Sn}_x$ samples. It is shown that the 8g position remains occupied essentially exclusively by Sn atoms within the whole homogeneity range, with x ranging from 2.52 to 4.20.

Comment

Among numerous intermetallic compounds crystallizing with a Pu_3Pd_5 structure type (Cromer, 1976), only one ternary compound, $\text{Er}_3\text{Ga}_2\text{Ge}_3$, has been reported to date (Welter & Venturini, 1999). In spite of the negligible contrast between Ga and Ge atoms in their non-resonant X-ray diffraction experiment, Welter & Venturini assumed a partially ordered Ga/Ge distribution, though admitting that 'the evolution of the structure as a function of the Ga content is not well understood'. We present here the structure of an $\text{Sm}_3\text{Ga}_{5-x}\text{Sn}_x$ compound that crystallizes with the Pu_3Pd_5 structure across a wide compositional range. The considerable difference between the atomic scattering factors for Ga and Sn enables an accurate refinement of the Ga/Sn distribution over three main-group atom positions.

In a single crystal of $\text{Sm}_3\text{Ga}_{1.89}\text{Sn}_{3.11}$, extracted from an alloy of composition close to $\text{Sm}_3\text{Ga}_2\text{Sn}_3$, the 8g position (labelled Sn1 in Fig. 1) was found to be mostly occupied by Sn atoms (93% Sn and 7% Ga), while the 4c and 8f positions (Ga3/Sn3 and Ga2/Sn2, respectively) are occupied by a Ga/Sn statistical mixture, with a strong preference of Ga atoms for the 8f position (Table 1).

A powder diffraction study of ten $\text{Sm}_3\text{Ga}_{5-x}\text{Sn}_x$ samples has shown that the structure is preserved within 10–31 at. % of Ga.

Cell parameters and nominal compositions for the eight single-phase samples are listed in Table 2. For all eight samples, the atomic positional and occupancy parameters were refined by the Rietveld method, in order to clarify the evolution of Ga/Sn site occupancies as a function of Ga content. As can be seen from Fig. 2, within the limits of three standard uncertainties, the 8g position remains exclusively occupied by Sn atoms over the whole concentration range. In contrast, Sn atoms in the 4c and 8f positions are gradually substituted by Ga, as the nominal Ga content increases.

The structure of the title compound can be described by the stacking along the c axis of two different layers (Fig. 1*a*). Layer

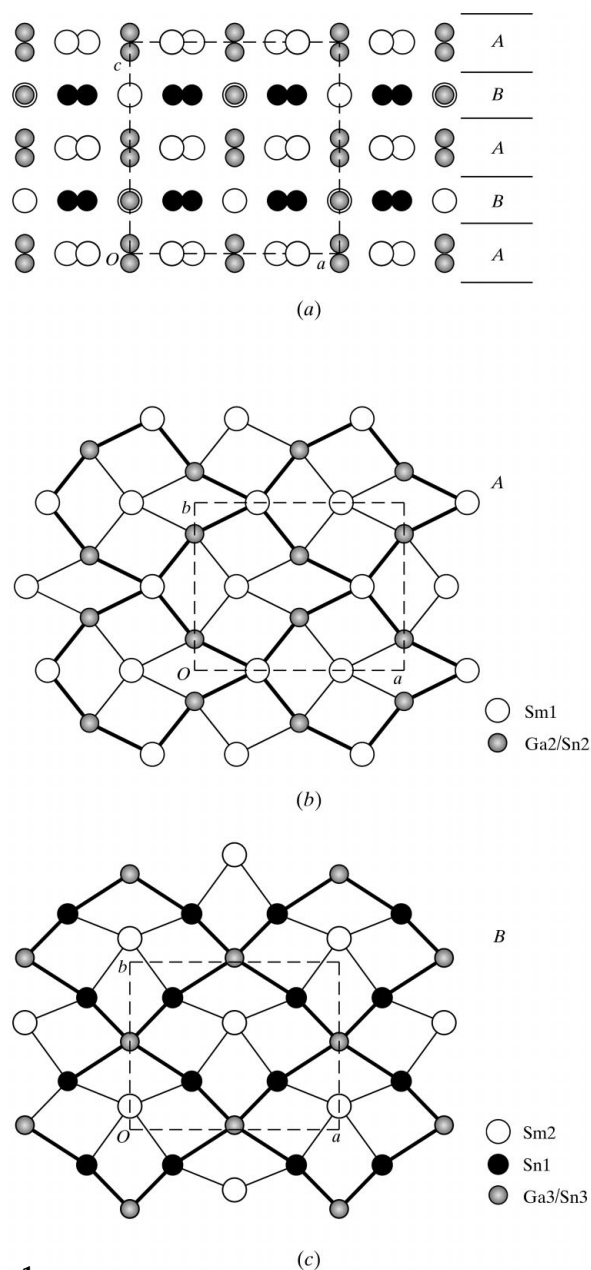


Figure 1
(*a*) The structure of $\text{Sm}_3\text{Ga}_{5-x}\text{Sn}_x$, represented by the stacking of two different layers, A and B. (*b*) The A layer, a distorted NaCl-type layer. (*c*) The B layer, a distorted layer of the tetragonal InLiO_2 -type structure (Hoppe & Schepers, 1958).

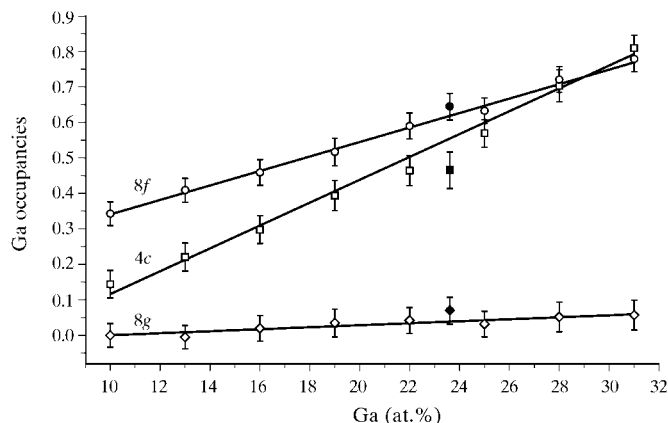


Figure 2
The variation of Ga content in three Ga/Sn positions plotted versus nominal Ga content. The single-crystal data are shown by the filled symbols. The three-standard-uncertainty limits are marked off with error bars.

A ($z = 0$ and $z = \frac{1}{2}$, mapped by a mirror plane) is built of Sm1 and Ga2/Sn2 atoms in a distorted NaCl manner (Fig. 1b). Layer B ($z = \frac{1}{4}$ and $z = \frac{3}{4}$, mapped by a 2_1 screw axis) is an ordered substitutional derivative of layer A (Fig. 1c); while the Ga/Sn position becomes fully occupied by Sn1 atoms, half of the Sm atoms are replaced with a Ga3/Sn3 statistical mixture. Thus, layer B corresponds to a distorted layer of the tetragonal InLiO₂ structure type (Hoppe & Schepers, 1958), an ordered derivative of the NaCl structure type.

The shortest distances between the Sm and main-group element atoms correlate with the corresponding Ga/Sn occupancies. For the ordered atom Sn1, the distance is 3.1718 (7) Å, for Ga3/Sn3, nearly equally occupied by Ga and Sn atoms, it is 3.0775 (14) Å, and for the Ga-rich Ga2/Sn2 position, the shortest distance to an Sm atom is 3.0003 (10) Å (Table 3).

Experimental

A single crystal of Sm₃Ga_{1.89}Sn_{3.11} was extracted from an arc-melted Sm₄₀Ga₂₀Sn₄₀ ingot annealed at 870 K for one month. To investigate an evolution of the structure as a function of the Ga content, ten alloys with nominal compositions Sm_{37.5}Ga₇₋₃₄Sn_{55.5-28.5} were additionally prepared, with each sample weighing 2 g and subjected to arc-melting (with weight losses of less than 0.5%) and subsequent annealing at 870 K for one month. The X-ray powder diffraction patterns were recorded at room temperature with a Bruker D8 Advance diffractometer (Cu K_{α1} radiation, $2\theta_{\min/\max} = 20\text{--}120^\circ$, increment in $2\theta = 0.0144^\circ$). One scale factor, ten profile and seven structural parameters were refined for each composition by the Rietveld method, using the *FULLPROF2002* program package (Rodríguez-Carvajal, 1990).

Crystal data

Sm₃Ga_{1.89}Sn_{3.11}
 $M_r = 951.80$
 Orthorhombic, *Cmcm*
 $a = 9.9680$ (13) Å
 $b = 7.9720$ (17) Å
 $c = 10.056$ (2) Å
 $V = 799.1$ (3) Å³
 $Z = 4$
 $D_x = 7.911$ Mg m⁻³

Mo K_α radiation
 Cell parameters from 1823 reflections
 $\theta = 4.0\text{--}30.0^\circ$
 $\mu = 37.38$ mm⁻¹
 $T = 293$ (1) K
 Plate-like, metallic light grey
 $0.07 \times 0.06 \times 0.03$ mm

Data collection

Stoe IPDS diffractometer
 φ oscillation scans
 Absorption correction: analytical
 (*X-RED*; Stoe & Cie, 1999)
 $T_{\min} = 0.155$, $T_{\max} = 0.414$
 3252 measured reflections
 640 independent reflections
 556 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$
 $\theta_{\max} = 30.0^\circ$
 $h = -13 \rightarrow 14$
 $k = -11 \rightarrow 10$
 $l = -14 \rightarrow 14$
 200 standard reflections
 frequency: 10 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.053$
 $S = 0.99$
 640 reflections
 29 parameters

$w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.47$ e Å⁻³
 $\Delta\rho_{\min} = -2.61$ e Å⁻³

Table 1

Fractional atomic coordinates, occupancies and Wyckoff symbols for Sm₃Ga_{1.89}Sn_{3.11}.

Atom site	Wyckoff symbol	x	y	z	Occupancy
Sn1	8g	0.20466 (6)	0.28795 (8)	0.25	0.930 (12)
Ga1	8g	0.20466 (6)	0.28795 (8)	0.25	0.070 (12)
Sn2	8f	0	0.31416 (11)	0.04613 (8)	0.356 (12)
Ga2	8f	0	0.31416 (11)	0.04613 (8)	0.644 (12)
Sm1	8e	0.20025 (4)	0	0	1
Sn3	4c	0	0.02592 (13)	0.25	0.535 (17)
Ga3	4c	0	0.02592 (13)	0.25	0.465 (17)
Sm2	4c	0	0.63989 (8)	0.25	1

Table 2

Cell parameters for the eight Sm₃Ga_{0.80-2.48}Sn_{4.20-2.52} (Sm_{37.5}Ga₁₀₋₃₁Sn_{52.5-31.5}) single-phase samples.

Ga (at.%)	a (Å)	b (Å)	c (Å)	V (Å ³)
10	9.97522 (18)	8.02642 (16)	10.23304 (19)	819.31 (3)
13	9.96543 (17)	8.01286 (16)	10.1906 (2)	813.73 (3)
16	9.95661 (19)	7.99150 (18)	10.1297 (2)	806.00 (4)
19	9.9488 (2)	7.9686 (2)	10.0739 (3)	798.64 (4)
22	9.9402 (2)	7.9490 (2)	10.0367 (3)	793.04 (4)
25	9.9268 (3)	7.9255 (2)	9.9945 (3)	786.32 (4)
28	9.91021 (13)	7.89376 (11)	9.94854 (16)	778.26 (2)
31	9.89433 (18)	7.87246 (16)	9.91703 (19)	772.46 (2)

Table 3

Selected interatomic distances (Å) in Sm₃Ga_{1.89}Sn_{3.11}.

Sn1—Sn2	2.8997 (8)	Sn2—Sm1 ^{iv}	3.2360 (9)
Sn1—Sn3	2.9198 (10)	Sn2—Sm2	3.3085 (11)
Sn1—Sm2 ⁱ	3.1718 (7)	Sm1—Sn1 ^v	3.1743 (6)
Sn1—Sm1 ⁱⁱⁱ	3.1743 (6)	Sm1—Sn3	3.2167 (5)
Sn1—Sm1	3.4046 (7)	Sm1—Sn2 ^{iv}	3.2360 (9)
Sn1—Sm2	3.4689 (10)	Sn3—Sn1 ^{vi}	2.9198 (10)
Sn2—Sm2 ⁱⁱⁱ	3.0003 (10)	Sn3—Sm2 ^{vii}	3.0775 (14)
Sn2—Sn3	3.0794 (12)	Sn3—Sm1 ^{viii}	3.2167 (5)
Sn2—Ga2 ⁱⁱⁱ	3.1049 (18)		

Symmetry codes: (i) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $-x, 1 - y, -z$; (iv) $-x, -y, -z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $-x, y, \frac{1}{2} - z$; (vii) $x, y - 1, z$; (viii) $x, y, \frac{1}{2} - z$.

The atomic positions were standardized with the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). In the final difference Fourier map, all peaks greater than 1 e Å⁻³ (maximum 2.47 e Å⁻³) were located within 1 Å of the atomic positions.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1031). Services for accessing these data are described at the back of the journal.

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