Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Gallium–tin mixing in $BaGa_{4-x}Sn_x$ [x = 0.89 (2)] with the $BaAl_4$ structure type

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Received 20 December 2006
Accepted 4 January 2007

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ() = 0.000 Å
Disorder in main residue
R factor = 0.018
wR factor = 0.039
Data-to-parameter ratio = 10.3

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

Single crystals of the barium trigallium tin, $BaGa_{3.11\,(2)}Sn_{0.89\,(2)}$, have been obtained by a reaction of the elements in a sealed Nb tube. The title compound crystallizes with the $BaAl_4$-type (Pearson's code tI10), and some of the Ga atoms are replaced by Sn atoms. All atoms occupy special positions: Ba ($4/mmm$), Ga1/Sn1 ($\bar{4}m2$) and Ga2/Sn2 ($4mm$). The refined composition has also been confirmed by means of elemental microanalysis.

Comment

Single crystals of the title compound were serendipitously discovered as a side product of a reaction of the elements. This experiment was originally intended to produce $Ba_8Ga_{16}Sn_{30}$ with the clathrate-I structure (von Schnering *et al.*, 1998). Such studies were part of a broader program aimed at examination of the intricate equilibrium conditions in the Ba–Ga–Sn system, where three closely related ternary compounds are known. The first of these is the above-mentioned clathrate-I, $Ba_8Ga_{16}Sn_{30}$ (also known as the β-form), crystallizing in space

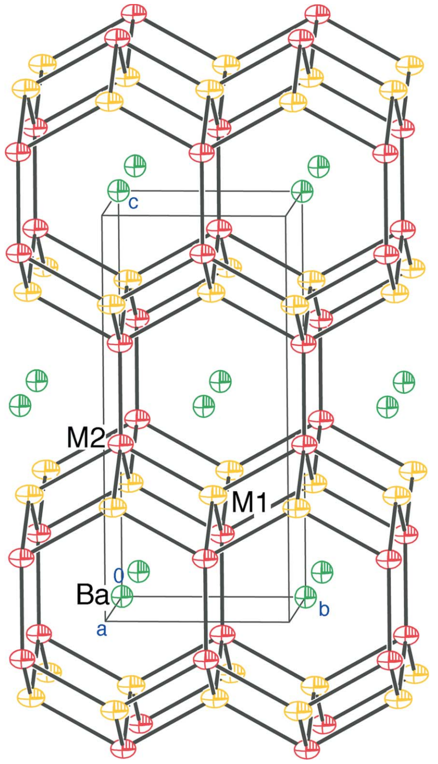

Figure 1

A view of $BaGa_{3.11\,(2)}Sn_{0.89\,(2)}$, projected approximately along [100]. Displacement ellipsoids are drawn at the 95% probability level. Ba atoms are shown as green octant-shaded ellipsoids, and Ga1/Sn1 atoms (denoted M1) and Ga2/Sn2 atoms (denoted M2) are drawn as red and yellow octant-shaded ellipsoids, respectively. The unit cell is outlined.

group $Pm\bar{3}n$, the second is its polymorphic α-form ($I\bar{4}3m$; Eisenmann *et al.*, 1986), and the third is the defect clathrate-II, $Ba_{16}Ga_{32}Sn_{104}$ ($Fd\bar{3}m$; Kröner *et al.*, 1998). Previous studies indicate that these are not line compounds and all three will have limited stoichiometry breadths, for example α-$Ba_8Ga_{17.2}Sn_{28.8}$ (Carrillo-Cabrera *et al.*, 2002).

The compound we report here is the first example of a ternary Ba–Ga–Sn compound which crystallizes in the ubiquitous tetragonal $BaAl_4$ type (Villars & Calvert, 1991). Fully stoichiometric $BaGa_4$ and $BaIn_4$ with the same structure are also known (Häussermann *et al.*, 2002; Wendorf & Röhr, 2005). Our earlier studies have confirmed the existence of the isostructural compounds $SrGa_4$ (Tobash *et al.*, 2005) and $EuGa_4$ (Bobev *et al.*, 2004). We also note the mention of a compound with the formula $BaGa_{4-x}Sn_x$ (Carrillo-Cabrera *et al.*, 2002), but no structure refinement and/or range for x have been reported to date.

Fig. 1 shows a view of the crystal structure of $BaGa_{3.11\,(2)}Sn_{0.89\,(2)}$, which can be described in terms of a polyanionic Ga/Sn framework with Ba cations occupying the channels within it. Relevant interatomic distances are listed in Table 1. The refinement indicates a limited phase width associated with random mixing of Ga and Sn on both anionic sites. The refined composition was further corroborated from scanning electron microscopy–energy-dispersive X-ray analysis.

It is clear that the substitution of the smaller Ga with the larger Sn on the framework sites will not only be evident from the refined occupancies of Ga1 and Ga2, but will also result in substantial elongation of the unit-cell parameters. Indeed, the *a* lattice parameter of $BaGa_{3.11\,(2)}Sn_{0.89\,(2)}$ is almost 4.5% larger than the *a* lattice parameter of the isostructural $BaGa_4$ [a = 4.5645 (4) Å and c = 10.7757 (13) Å; Häussermann *et al.*, 2002]. However, the comparison of the *c* parameters does not seem to follow these arguments, and the reason for this is the change in the valence electron concentration, because Sn is one electron richer. The interplay of electronic and size effects in the structures of a series of $BaAl_4$ analogs has been thoroughly addressed by Häussermann *et al.* (2002). It should be mentioned here too that $BaGa_{3.11\,(2)}Sn_{0.89\,(2)}$ is the only tetragallide that forms solid solutions with the electron-richer group 14 elements. Our earlier work on $SrGa_4$ (Tobash *et al.*, 2005) and $EuGa_4$ (Bobev *et al.*, 2004) shows that these compounds have very rigid and stable structures.

Experimental

Handling of the pure metals and reaction products was carried out in an argon-filled glove-box with controlled oxygen and moisture levels or under vacuum. Starting materials (Ba rod, 99+%, Alfa; Ga, Sn >99.99%, Alfa) were used as received. A mixture of the reactants, in the stoichiometric ratio Ba:Ga:Sn = 8:16:30, was placed in a Nb tube within an evacuated fused-silica ampoule. The ampoule was heated slowly (10 K h^{-1}) to 1273 K and kept there for 5 h, then kept at 723 K for 12 h, and finally cooled at 20 K h^{-1} to room temperature. Two reaction products were identified from the corresponding X-ray diffraction patterns and their different crystal habits, namely plate-like crystals of $BaGa_{3.11}Sn_{0.89}$ and crystals with an irregular habit, which were identified as the type-I clathrate $Ba_8Ga_{16}Sn_{30}$ (von Schnering *et al.*, 1998). To ascertain the composition of the title compound, selected single crystals were mounted on to carbon tape and placed in a Jeol 7400 F electron microscope equipped with an INCA-Oxford energy-dispersive spectrometer. The microscope was operated at 10 µA beam current at 15 kV accelerating potential. Several crystals were analyzed and the values obtained correspond to a ratio (atomic %) of Ba:Ga:Sn = 19.5 (3):60.3 (3):20.1 (3), which is in very good agreement with the refined ratio of Ba:Ga:Sn = 20:62.2:17.8.

Crystal data

$BaGa_{3.11}Sn_{0.89}$
M_r = 459.80
Tetragonal, $I4/mmm$
a = 4.7455 (14) Å
c = 10.554 (6) Å
V = 237.68 (17) Å^3
Z = 2
D_x = 6.425 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 29.97 mm^{-1}
T = 120 (2) K
Plate, metallic grey
0.07 × 0.07 × 0.06 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.142, $T_{\max}$ = 0.165
651 measured reflections
103 independent reflections
92 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019
$\theta_{\max}$ = 27.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.039
S = 1.21
103 reflections
10 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2 + 0.0192P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.86 e Å^{-3}
$\Delta\rho_{\min}$ = −1.67 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ba—Ga1	3.5485 (13)	Ga2—Ga2$^{\rm i}$	2.631 (3)
Ga1—Ga2	2.7167 (9)		

Symmetry code: (i) $-x, -y, -z + 1$.

The initial refinement assuming fully stoichiometric $BaGa_4$ led to very poor residuals and abnormal displacement parameters, indicating a potential disorder or perhaps an unsuitable structure model. To check the former hypothesis, the occupancy of each Ga site was subsequently checked by freeing the site-occupation factor for an individual site, while keeping the others fixed. Freeing the Ga1 and Ga2 sites greatly improved the residuals and led to the conclusion that there was a mixing of Ga and Sn, since the site-occupation factors increased. When these two sites were refined as mixed, the refinements converged to excellent residuals and with reasonable displacement parameters. The final refinement gave Ga:Sn ratios of 82.4 (8):17.6 (8) on Wyckoff site 4*d* (Ga1), and 73.1 (9):26.9 (1) on Wyckoff site 4*e* (Ga2), leading to the formula $BaGa_{3.11\,(2)}Sn_{0.89\,(2)}$. The deepest hole is located 1.32 Å from Ga2/Sn2.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); 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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This work was funded by a University of Delaware start-up grant.

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