Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Strontium tetragallide

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(Ga–Ga) = 0.001 Å
R factor = 0.017
wR factor = 0.042
Data-to-parameter ratio = 11.1

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

Received 8 July 2005
Accepted 12 July 2005
Online 16 July 2005

Single crystals of the title compound, $SrGa_4$, were synthesized from the corresponding elements using molten Sn metal as a solvent. The structure determination suggested the product to be a binary phase with composition $SrGa_4$, which crystallizes with the $BaAl_4$ type in the body-centered tetragonal space group $I4/mmm$ (No. 139). The three atoms in the asymmetric unit lie on special positions with Wyckoff symbols 2*a* (Sr), 4*d* and 4*e* for the Ga atoms.

Comment

The published binary phase diagram for the system Sr–Ga (Massalski, 1990) suggests the existence of three intermetallic compounds: (i) Sr_8Ga_7 with the cubic Sr_8Al_7 type; (ii) $SrGa_2$ with the hexagonal AlB_2 type; (iii) $SrGa_4$ with the tetragonal $BaAl_4$ type. Among these, only $SrGa_2$ melts congruently, whereas Sr_8Ga_7 and $SrGa_4$ are reportedly formed by peritectic reactions. No additional binary phases in the system have been identified (Villars & Calvert, 1991).

Additionally, the crystal structure of Sr_8Ga_7 has been confirmed and refined from single-crystal work (Fornasini, 1983), whereas the structures of $SrGa_2$ (Bruzzone, 1966), and of $SrGa_4$ (Bruzzone, 1965; Kripyakevich *et al.*, 1965) have been identified only from the corresponding X-ray powder patterns. Variations in the lattice parameters for different $SrGa_2$ samples have led to the conclusion that $SrGa_2$ has a homogeneity range from *ca* 60–66.7% Ga, and that the formulation

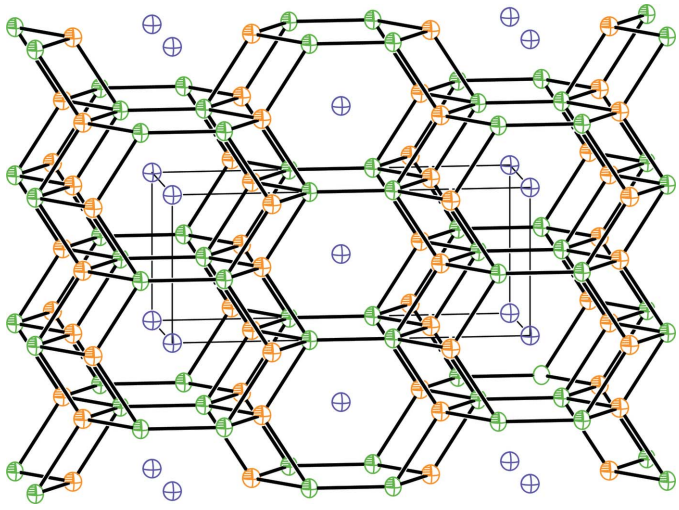

Figure 1
A view of the $SrGa_4$ structure projected approximately along [100]. Displacement ellipsoids are drawn at the 98% probability level. Sr atoms are drawn as purple unshaded ellipsoids, and Ga1 and Ga2 are shown with orange and green shaded ellipsoids, respectively. The unit cell is outlined.

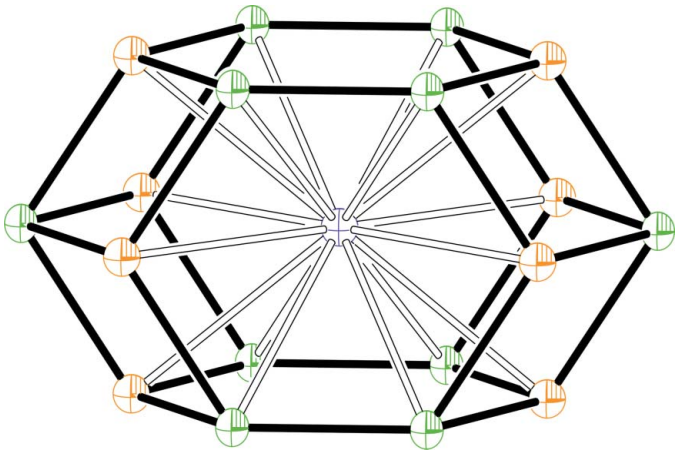

Figure 2
A view of the Sr coordination polyhedron in $SrGa_4$. Displacement ellipsoids are drawn at the 95% probability level. Ellipsoid styles and colors are as in Fig. 1.

$SrGa_{2-x}$ better describes the nature of this compound (Bruzzone, 1966). Studies of annealed $SrGa_4$ have been performed and have suggested that it is indeed a line compound (Häussermann *et al.*, 2002). Our crystals were grown from Sn flux, and this motivated us to undertake the refinement of the structure in order to confirm the composition and compare with the earlier reports.

Small and shiny crystals of $SrGa_4$ with a silver metallic luster were serendipitously discovered from a reaction of Sr, Ga, and Sn, which was intended to produce $Sr_8Ga_{16}Sn_{30}$ clathrate from an 'on stoichiometry' reaction of the pure elements. These synthetic efforts were part of a broad study of the variations of the polyanionic network of binary and ternary open-framework intermetallic compounds, clathrates in particular, as a function of electron count, electronegativity, and constituent sizes. Our particular focus in this case was on the systematic investigation of the physical properties and chemical bonding in $Ba_8Ga_{16}Sn_{30}$ and the existence of two allotropic forms of that compound, clathrate-I and clathrate-VIII, with reactions in the Sr—Ga—Sn system aimed at establishing the possible formation of Sr counterparts.

Until now, the only confirmed product of these syntheses was the title compound $SrGa_4$. It is a line compound as evidenced from the structure refinement, and crystallizes with the $BaAl_4$ type, which is a very common structure among such intermetallics (Villars & Calvert, 1991). The lattice parameters for $SrGa_4$ determined at 120 K compare well with the previously reported parameters at room tempetarture, a = 4.4474 (8) Å, and c = 10.730 (4) Å (Kripyakevich *et al.*, 1965), and a = 4.4454 (3) Å, and c = 10.7432 (12) Å (Häussermann *et al.*, 2002). This observation, along with the refinement of the site-occupation factors, confirms that $SrGa_4$ is a stoichiometric phase, and there are no Sn substitutions at detectable limits. Similar observations have been previously found for flux-grown single crystals of $EuGa_4$ (Bobev *et al.*, 2004).

$SrGa_4$ can be viewed as a polar intermetallic phase, *i.e.* compounds formed by the electropositive Sr and electronegative Ga metals. Its structure can thus be considered as made up of a Ga-based polyanionic sub-network, with the divalent Sr cations occupying the channels within it, as shown in Fig. 1. All Ga—Ga contacts (Table 1) agree with the description above. These compare well with the Ga—Ga distances in the annealed $SrGa_4$ (Häussermann *et al.*, 2002), as well as with the Ga—Ga distances in related flux-grown compounds, such as $EuGa_4$ (Bobev *et al.*, 2004). The divalent Sr cations occupy the highly symmetric 4/*mmm* sites and have 16 Ga neighbors with Sr—Ga contacts being normal for such high coordination number (Fig. 2). This confirms the bonding picture with 14 valence electrons as analyzed in greater detail elsewhere (Häussermann *et al.*, 2002).

Experimental

Handling of the pure metals and the reaction products was carried out in an argon-filled glove-box with controlled oxygen and moisture levels or under vacuum. All of the starting materials were used as received: Sr (Aldrich, pieces, distilled 99.99%), Ga and Sn both with purities greater than 99.99% were obtained from Alfa. The reaction was loaded with the nominal composition Sr:Ga:Sn = 8:16:30 and placed in a niobium tube. The tube was then sealed by arc-welding under argon, and subsequently flame-sealed in an evacuated fused silica jacket. The reaction mixture was slowly heated to 1273 K (rate 10 K h^{-1}) and kept there for 5 h, followed by quick cooling to 723 K (300 K), where the mixture was kept for 12 h. Finally, it was allowed to slowly cool to room temperature at a rate of 5 K h^{-1}. The products of the reaction consisted of irregularly shaped crystals with a silver metallic luster, which were later identified as $SrGa_4$, polycrystalline Sn and an amorphous Sr–Sn binary phase, as evidenced from the measured X-ray powder patterns.

Crystal data

$SrGa_4$
M_r = 366.50
Tetragonal, $I4/mmm$
a = 4.4474 (8) Å
c = 10.730 (4) Å
V = 212.23 (10) Å^3
Z = 2
D_x = 5.735 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 768 reflections
θ = 3.8–28.1°
μ = 37.32 mm^{-1}
T = 120 (2) K
Irregular fragment, silver
0.05 × 0.03 × 0.02 mm

Data collection

Bruker APEX SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.234, T_{max} = 0.475
768 measured reflections
100 independent reflections
94 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.1°
$h = -5 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -13 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.042
S = 1.03
100 reflections
9 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −1.16 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0043 (10)

Table 1
Selected bond lengths (Å).

Sr—Ga2	3.3861 (7)	Ga1—Ga2	2.6422 (7)
Sr—Ga1	3.4843 (8)	Ga2—Ga2^{i}	2.511 (2)

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

The structure refinement converged to excellent residuals, and three crystallographically unique sites (Sr, Ga1 and Ga2) exhibited regular anisotropic displacement parameters. To check for potential Sn substitutions on the Ga sites, structure refinements were undertaken by freeing the site-occupation factor for an individual atom, while other remaining parameters were kept fixed. No deviations from full occupancy larger than 3σ were observed, which confirmed the structure and composition of $SrGa_4$. The highest peak and the deepest hole in the final Fourier map are 0.96 and 0.66 Å, respectively, from the Sr 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* (Sheldrick, 2001); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded by a University of Delaware start-up grant.

References

Bobev, S., Bauer, E. D., Thompson, J. D. & Sarrao, J. L. (2004). *J. Magn. Magn. Mater.* **277**, 236–243.
Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruzzone, G. (1965). *Acta Cryst.* **18**, 1081–1082.
Bruzzone, G. (1966). *Boll. Sci. Fac. Chim. Industr. Bologna*, **24**, 113–132. (In Italian.)
Fornasini, M. L. (1983). *Acta Cryst.* C**39**, 943–946.
Häussermann, U., Amerioun, S., Eriksson, L., Lee, C.-S. & Miller, G. J. (2002). *J. Am. Chem. Soc.* **124**, 4371–4383.
Massalski, T. B. (1990). Editor. *Binary Alloy Phase Diagrams*. Materials Park, Ohio, USA: American Society for Metals.
Kripyakevich, P. I., Gladyshevskii, E. I. & Dzyana, D. I. (1965). *Kristallografiya*, **10**, 392-394. (In Russian.)
Sheldrick, G. M. (2001). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Villars, P. & Calvert, L. D. (1991). *Pearson's Handbook of Crystallographic Data for Intermetallic Compounds*, 2nd ed. Materials Park, Ohio, USA: American Society for Metals.