Crystal structure of tristrontium octagallide, $Sr_{3-x}Ga_{8+3x}$ (x = 0.15)

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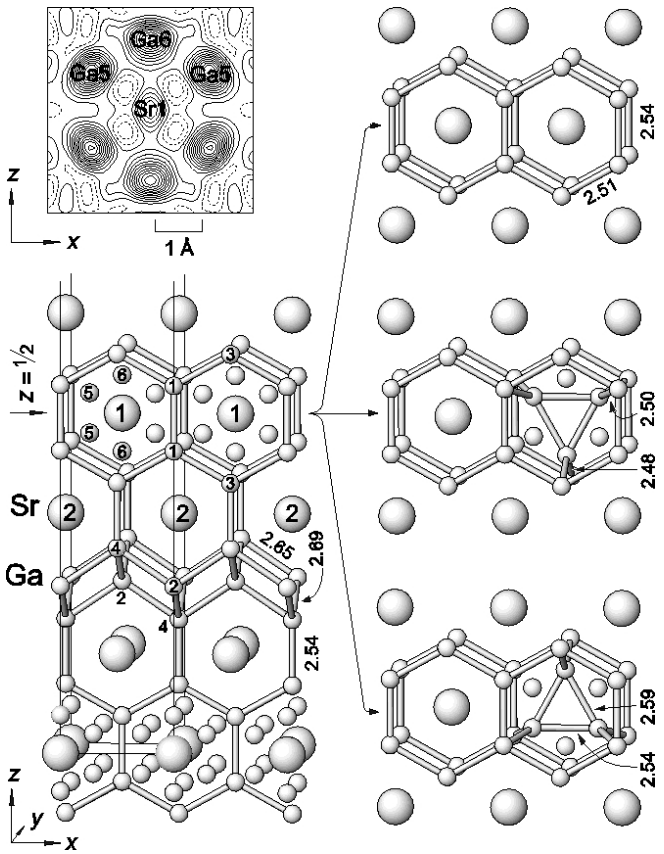

Abstract

$Ga_{8.45}Sr_{2.85}$, orthorhombic, *Immm* (no. 71), a = 4.3958(9) Å, b = 4.5298(6) Å, c = 26.002(4) Å, V = 517.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.091, T = 293 K.

Source of material

Three samples of $Sr_{3-x}Ga_{8+3x}$ with x = 0.07, 0.15 and 0.20 labeled as I, II and III, respectively, were prepared by melting of appropriate mixtures of the elements in welded Ta container in a high frequency furnace. After one week of thermal annealing at 800 °C they were quenched in ice water. According to the results of X-ray powder diffraction (Huber Guinier G670, Cu$K_{\alpha 1}$ radiation, λ = 1.540598 Å) and metallographic investigations sample II was single phase containing the title compound while samples I and III included admixtures of $Sr_{1-x}Ga_{2+3x}$ and $SrGa_4$, respectively. Single crystals for X-ray diffraction were isolated from sample II. The material is gray with metallic luster. Due to the sensitivity regarding oxidation the samples were handled under inert conditions.

Experimental details

As starting values for structure refinement we used the atomic positions observed in Eu_3Ga_8 [1,2] which realizes a binary variant of the $U_3Ni_4Si_4$ type [3]. In the advanced steps of the refinement some additional peaks in hexagon-like arrangement were observed on the difference Fourier maps in the vicinity of Sr1 atoms (figure, top left). These correspond to two crystallographically independent Ga positions with partial occupation. This structural feature is accompanied by a reduced occupation of the Sr1 site.

The lattice parameter of the compounds were determined with LaB_6 as internal standard (a = 4.15692 Å). They agree well for the different samples indicating the absence of a significant homogeneity range (sample I: a = 4.3983(7) Å, b = 4.5301(5) Å, c = 26.019(3) Å; sample II: a = 4.3958(9) Å, b = 4.5298(6) Å, c = 26.002(4) Å; sample III: a = 4.3964(4) Å, b = 4.5258(6) Å, c = 26.016(2) Å).

Discussion

The main motif of $Sr_{3-x}Ga_{8+3x}$ reproduces those of the $U_3Ni_4Si_4$ structure type [3]. It can be described as an intergrowth of AlB_2 [4] and $BaAl_4$ [5] type fragments being realized by the so far known neighboring phases $SrGa_2$ and $SrGa_4$ [6]. The Ga atoms form a regular 3D framework by four- and six-membered rings based on three- (Ga1 and Ga2) four- (Ga2) and five-fold (Ga4) coordinated Ga atoms. The Ga—Ga contacts within the framework are in the range of 2.5162(8) Å – 2.6902(8) Å being smaller than the average distances d(Ga—Ga) = 2.703 Å in α-Ga [7]. The Sr1 atoms in the AlB_2 like part of the crystal structure (figure, top right) are partially substituted by Ga atoms located at the Ga5 and Ga6 sites forming almost regular hexagons (figure, middle and bottom right). However, the distances of next neighboring positions of d(Ga5—Ga5) = 1.54(2) Å and d(Ga5—Ga6) = 1.46(1) Å are too short to be simultaneously occupied. A reasonable model can be obtained by occupation of every second position within the hexagons forming isosceles triangular Ga_3 groups with distances of d(Ga5—Ga5) = 2.54(2) Å and d(Ga5—Ga6) = 2.59(2) Å. Two orientations of the triangular Ga_3 units with respect to the unit cell are possible (figure, middle and bottom right). The distances d(Ga1—Ga5) = 2.498(5) Å and d(Ga3—Ga6) = 2.480(6) Å between the Ga1 and Ga3 atoms of the regular 3D framework and the positions Ga5 and Ga6 within the triangular units are comparable with the shortest contacts of 2.47 Å observed in α-Ga. The composition of the compound, the fractional occupation of the Sr1, Ga5 and Ga6 sites and the interatomic distances indicate a substitution of one Sr1 atom by three Ga atoms. This type of substitution of the cations by Ga_3 triangular units was also recently found in $Eu_{1-x}Ga_{2+3x}$ with x = 0.08 [8], in $Eu_{3-x}Ga_{8+3x}$ with x = 0.12 [9] and in $Sr_{1-x}Ga_{2+3x}$ with x up to 0.056 [10].

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Table 1. Data collection and handling.

Crystal:	metallic platelet, size 0.012 × 0.040 × 0.045 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	360.6 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, φ/ω
$2\theta_{max}$:	63.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2279, 554
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 431
$N(param)_{refined}$:	32
Programs:	SHELXL-97 [11], ATOMS [12]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
Ga(5)	8*m*	0.076(3)	0.289(3)	0	0.0297(4)	0.027(3)
Ga(6)	4*i*	0.074(5)	0	0	0.0572(6)	0.026(5)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr(1)	2*a*	0.846(5)	0	0	0	0.0086(7)	0.0109(7)	0.0149(6)	0	0	0
Sr(2)	4*j*		½	0	0.14871(3)	0.0082(4)	0.0118(4)	0.0167(4)	0	0	0
Ga(1)	4*i*		0	0	0.45114(4)	0.0067(5)	0.0224(6)	0.0138(4)	0	0	0
Ga(2)	4*i*		0	0	0.24947(4)	0.0086(5)	0.0166(5)	0.0149(4)	0	0	0
Ga(3)	4*j*		½	0	0.40403(4)	0.0056(5)	0.0251(6)	0.0131(4)	0	0	0
Ga(4)	4*j*		½	0	0.30635(3)	0.0078(5)	0.0154(5)	0.0142(4)	0	0	0

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