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A phase width for CaGaSn. Crystal structure of mixed intermetallic $Ca_4Ga_{4+x}Sn_{4-x}$ and $SmGa_xSn_{3-x}$, stability, geometry and electronic structure

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ABSTRACT

X-ray single-crystal structure has been established for new compositions in intermetallic systems of tin and gallium. Crystals were successfully obtained in alloys prepared from elements. The structure of $SmGaSn_2$ (cubic $Pm\bar{3}m$, a=4.5778(8) Å, Z=1, R1=0.012) is described with atomic disorder at all Sn/Ga positions and the structure of $Ca_4Ga_{4.9}Sn_{3.1}$ (hexagonal, $P6_3/mmc$, a=4.2233(9), c=17.601(7) Å, Z=1, R1=0.062) raises an interesting question about existence of a composition domain for CaGaSn. Finally, $Ca_4Ga_{4.9}Sn_{3.1}$ should be considered as a particular composition of $Ca_4Ga_{4+x}Sn_{4-x}$, a compound assumed to exist in the range $x \sim 0-1$. Partial atomic ordering characterizes the Sn/Ga puckered layers of hexagons whose geometries are analyzed and discussed comparatively with analogous arrangements in AlB_2 related hexagonal compounds. The study is supported by rigid band model and DFT calculations performed for different experimental and hypothetic arrangements.

1. Introduction

Numerous ternary combinations that involve tin and gallium are known and structurally characterized. Among the reports listed in the Pearson crystal database, a great number of compositions mainly includes Ba and adopts the famous clathrate type structures. In these ternary compounds, Sn and Ga atoms are 4-bonded within tridimensional networks composed by large cages that enclose Ba atoms. These arrangements are affected by some atomic disorder since Sn and Ga at cage vertices are statistically mixed at metal atoms positions. Various structures are described for the remaining compounds that contain p-block or transition elements. The M^V–Sn–Ga compounds have been subject of interest for their superconducting behavior [1–5] and the Sn/Ga atom distribution in structures would play a role in their properties. Combinations that involve electropositive elements display more or less complicated intermetallic frameworks, as for example, layers in SrGaSn [6], double layers in Li_5Ga_4 [7], infinite chains of clusters in $Na_{10}Ga_6Sn_3$ [8] or complex 3D network in $Na_3Ga_8Sn_3$ in which coexist clusters and waved layers [9]. In most cases, Sn and Ga atoms are 4-bonded within networks and Sn/Ga atom disorder is often reported.

Only two compounds with very simple stoichiometries contrast with this general trend, SrGaSn and CaGaSn [6]. The structure of SrGaSn is described without atomic mixing and was solved from single-crystal diffraction while CaGaSn was stated isostructural on the basis of its similar powder pattern. Their hexagonal structure is related to the AlB_2 structure-type in which alkaline-earth atoms occupy Al positions while Sn and Ga alternately fill the boron sites. Each metal atom on the hexagon network is then linked to three neighbors different in nature, it results in a waving of the layers which remain without any bonding interactions, as attested by shortest interlayer distances of 3.30 and 3.98 Å at Ga-Ga pairs in SrGaSn and CaGaSn, respectively.

These structures fairly remind those of Li_3Ga_2 [10] and Li_5Ga_4 [7] Zintl compounds also deriving from the AlB_2 structure. Layers therein are puckered and composed of 3-bonded Ga atoms (partially reduced by Li) at two independent crystallographic sites. Beyond the atom nature, the structural arrangements in Li_3Ga_2 and Li_5Ga_4 differ from that in SrGaSn by the staggered position of consecutive layers. Since layers are shifted against each other, interlinking is prevented in Li_3Ga_2. Instead, the shift two-by-two of the layers in Li_5Ga_4 allows association into double layers through Ga-Ga bonding of 2.68 Å.

The present work reports on two ternary intermetallic compounds of tin and gallium for which single crystal structures are determined. The compound $SmGaSn_2$ displays an original network for a ternary composition and the hexagonal structure of $Ca_4Ga_{4.9}Sn_{3.1}$ raises questions about the existence of a phase width

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for CaGaSn. Structural descriptions, network and bonding analyses are supported by DFT calculations.

2. Experimental section

The elements Ga (Rhone Poulenc, 6 N), lumps of Sn and Sm (Alfa Aesar, 99.9%), Ca (Merck, 99%) were taken without further purification. Stoichiometric amounts were weighed to prepare alloys at compositions $SmGa_3Sn_2$ and $Ca_5Ga_9Sn_4$, they were inserted in Ta tubes weld-sealed under argon atmosphere and protected from oxidation in Ar-filled sealed stainless steel jackets. Samples were heated to 900 °C for 16 h in a classical tubular furnace and then submitted to slow cooling at 10°/h. The well crystallized products were handled under argon atmosphere, several crystals could be selected using a microscope placed in the glove box and then sealed into capillaries to be checked for crystallinity. The best diffracting single crystals that display the required quality were used for X-ray diffraction data collection and were further analyzed to establish their composition. EDX measurements were performed using an Oxford Instrument Environmental Scanning Electron Microscope, equipped with an X-Max large area SDD sensor that allows excellent sensitivity/precision/resolution. The EDX analysis led to Sm: Ga:Sn and Ca: Ga:Sn ratios of 26.4:24.1:49.5 and 33.5:37.9:29.1, respectively. Crystal structures were solved [11] and refined [12] using SHELX programs. Details on single crystal data collection and structural refinements are given in Table 1. Atom disorder Sn/Ga was considered for the two compounds and site occupation factors were refined together with atom positions and anisotropic displacement parameters. Within the standard deviation limits, site occupation at all positions does not deviate from full site occupancy. The final refined compositions from X-ray study are $SmGaSn_2$ and $Ca_4Ga_{4.9}Sn_{3.1}$, respectively. They quite well agree with atom proportions found from the EDX analysis of the single crystals previously used for diffracted intensity recording. It is noteworthy that Ga content is fairly lower in compounds than in the prepared alloys, this may underline the role of a Ga excess in the crystallization processes. The final refined atom positions and equivalent displacement parameters are given in Table 2. Further details on crystal structures may be obtained from FIZ Karlsruhe (crysdata@fiz-karlsruhe.de) on quoting the CSD deposition numbers 431519 ($Ca_4Ga_{4.9}Sn_{3.1}$) and 431520 ($SmGaSn_2$).

Table 1
Crystal data and structure refinement.

Compound	$SmGaSn_2$	$Ca_4Ga_{4.9}Sn_{3.1}$
Initial composition (alloy)	$SmGa_3Sn_2$	$Ca_5Ga_9Sn_4$
Refined composition	$SmGa_3Sn_{2.00(1)}$	$Ca_4Ga_{4.91(3)}Sn_{3.09(3)}$
Crystal system	Cubic	Hexagonal
Space group	$Pm\bar{3}m$	$P6_3/mmc$
Lattice parameters (Å)	4.5778(8)	4.4233(9), 17.601(7)
Volume (Å^3)	95.93(5)	298.24(17)
Crystal size (mm)	0.05 × 0.06 × 0.10	0.05 × 0.10 × 0.10
F(000)	193	387
Absorption coefficient (mm^{-1})	34.63	18.9
θ range (deg)	4.45–45.35	2.31–29.88
Diffractometer	Oxford Xcalibur CCD	Nonius CAD4
Extinction coefficient (× 10^{-4})	0.011(1)	
Independent reflections	114 [R(int)=0.0470]	204 [R(int)=0.0475]
Goodness-of-fit on F^2	1.074	1.191
Final R1/wR2 indices [I > 2σ(I)]	0.0084/0.0207	0.0418/0.1042
R1/wR2 indices (all data)	0.0118/0.0212	0.0673/0.1142
Residual densities (e. Å^{-3})	0.95/−0.74	3.60/−2.46

Table 2
Positional and atomic equivalent displacement parameters. U_{eq} is defined as one third of the trace of orthogonalized U_{ij} tensor.

$SmGaSn_2$

	Position	Occupation	x	y	z	U_{eq} (Å^2)
Ga	*3c*	0.334(4)	0	1/2	1/2	0.0180(1)
Sn		0.666(4)				
Sm	*1a*	1	0	0	0	0.01296(7)

$Ca_4Ga_{4.9}Sn_{3.1}$

		Position	occupation	x	y	z	U_{eq} (Å^2)
M1	Sn	*4f*	0.773(2)	1/3	2/3	0.38497(6)	0.0077(4)
	Ga		0.227(2)				
M2	Ga	*4f*	1	2/3	1/3	0.3414(2)	0.0250(7)
Ca1		*2a*	1	0	0	0	0.0135(9)
Ca2		*2b*	1	0	0	0.25	0.0146(9)

3. Calculation method

Calculations at the DFT level have been performed with the code CASTEP [13] using the gradient-corrected GGA-PW91 exchange and correlation functional [14]. CASTEP uses plane-wave basis sets to treat valence electrons and pseudo potentials to approximate the potential field of ion cores. Ultra-soft pseudo potentials (USPP) generated for each element according to the Vanderbilt [15] scheme were chosen. Tin was taken with four $5s^2\ 5p^2$ valence states and calcium with ten $3s^2\ 3p^6\ 4s^2$ valence states. The inner 3*d* and 4*f* levels were respectively considered for Ga $3d^{10}\ 4s^2\ 4p^1$ and Sm $4f^6\ 5s^2\ 5p^6\ 6s^2$. Kinetic cut-off energies were set at ultrafine qualities (330 and 420 eV) and a Monkhorst-Pack grid of automatically generated *k*-points was used for numerical integration in the Brillouin zone [16].

All along this work, both atom positions and unit cell dimensions were fully relaxed in the geometry optimizations performed at the DFT level by minimizing the total energy. Calculations were carried out within the experimental cubic $Pm\bar{3}m$ symmetry for Sm compounds, instead the *P*3*m*1 symmetry (which is common to all arrangements) was used for the hexagonal models in cells containing four layers.

Density of states DOS and crystal overlap populations COOP have also been calculated for CaGaSn using a rigid band model within the tight binding extended Hückel method provided in CAESAR2 package [17].

4. Results and discussion

The structural representation of compounds $SmGaSn_2$ and $Ca_4Ga_{4.9}Sn_{3.1}$ given in Fig. 1 highlights the differences in p-block sub-lattices yet characterized with a common feature, namely the occurrence of Sn/Ga atomic mixing.

4.1. $SmGaSn_2$ structure

Compound $SmGaSn_2$ crystallizes within cubic $Pm\bar{3}m$ symmetry with a =4.5778(8) Å. Its structure is easily visualized as a 3D network of octahedral units sharing all vertices. Sn and Ga are statistically mixed on octahedra at the unique *3c* (0,½,½) position and separated by 3.267 Å (octahedra edges) from alike neighbors. At origin of the cell, Sm atom is located at the center of a cuboctahedron formed by 12 Sn/Ga atoms. The Sn to Ga atomic proportion, freely refined in the structural refinement, converges to 2 and then the compound can be formulated $Sm[GaSn_2]$. Its structure belongs to the $AuCu_3$-type and is so far not observed for