Chemistry of Metals and Alloys

Chem. Met. Alloys 15 (2022) 22-25
Ivan Franko National University of Lviv
http://publications.lnu.edu.ua/chemetal

Crystal structure of $EuGa_{1.68}Sn_{0.32}$

Yaroslav TOKAYCHUK[1]*, Illia OHONOVSKYI[1], Olha KULINYCH[1], Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
* *Corresponding author. E-mail: yaroslav.tokaychuk@lnu.edu.ua*

Received April 13, 2022; accepted June 29, 2022
https://doi.org/10.30970/cma16.0425

The new ternary intermetallic compound $EuGa_{1.682(18)}Sn_{0.318(18)}$ was synthesized and its crystal structure was determined by X-ray powder diffraction (structure type AlB_2, Pearson symbol *hP*3, space group *P*6/*mmm*, *a* = 4.3863(2), *c* = 4.5762(2) Å, *Z* = 1). The structure is characterized by a statistical distribution of Ga and Sn atoms, which form planar graphite-like 6^3 nets stacked in the crystallographic direction [001].

Europium / Gallium / Tin / X-ray powder diffraction / Ternary compound / Crystal structure

Introduction

The phase diagram of the ternary system Eu–Ga–Sn has not yet been studied systematically. The formation and crystal structure of a ternary compound, EuGaSn, have been reported: structure type YPtAs, Pearson symbol *hP*12, space group $P6_3/mmc$, *a* = 4.5243, *c* = 18.067 Å [1]. Among related ternary systems *R*–Ga–Sn (*R* = rare-earth metal), an isothermal section has been constructed only for the system Sm–Ga–Sn at 900°C [2]. Some other systems have been investigated for the existence of ternary compounds. In total, the crystal structures of 7 ternary compounds have been reported in the systems *R*–Ga–Sn [3]. Two YPtAs-type phases, the abovementioned compound EuGaSn and YbGaSn, are known to exist in the vertical sections with 33.3 at.% *R*.

In the related Eu–Ga–*M* systems with germanium and silicon, the phase relations in the cross-section $EuGa_2$–EuM_2 have been investigated [4]. In both systems, ternary phases of variable compositions with AlB_2-type structure (*hP*3, *P*6/*mmm*) were identified: $EuGa_{1.64-0.50}Si_{0.36-1.50}$ (*a* = 4.2640-4.0821, *c* = 4.6000-4.5538 Å) and $EuGa_{1.50-1.10}Ge_{0.50-0.90}$ (*a* = 4.2905-4.241, *c* = 4.6077-4.555 Å). Besides the AlB_2-type phase, three other ternary compounds with different crystal structures were characterized in the system with Ge: EuGaGe (YPtAs, *a* = 4.2655, *c* = 18.034 Å), $EuGa_{0.9}Ge_{1.1}$ (own type, *hP*27, *P*-3*m*1, *a* = 4.2537, *c* = 40.889 Å), and $EuGa_{0.8}Ge_{1.2}$ (own type, *hP*16, *P*-6*m*2, *a* = 4.2320, *c* = 22.974 Å). All the ternary $EuGa_{2-x}M_x$ (*M* = Si, Ge) compounds have related crystal structures derived from the structure type AlB_2 and can be described in terms of the Zintl concept.

The aim of the present work was to study the evolution of the crystal structure along the section $EuGa_{2-x}Sn_x$ (*x* = 0-1) at 400°C when Ga atoms are progressively replaced by Sn atoms. The section is delimited by two compounds, $EuGa_2$ and EuGaSn. No compound forms at the composition $EuSn_2$ [3]. The crystal structure of the stable room-temperature modification of the binary compound $EuGa_2$ belongs to the orthorhombic structure type KHg_2 (*oI*12, *Imma*, *a* = 4.6459, *b* = 7.6255, *c* = 7.6379 Å) [5]. A structure with hexagonal AlB_2 type (*hP*3, *P*6/*mmm*, *a* = 4.351, *c* = 4.506 Å) has also been reported [6]. However, it was later explained either as an off-stoichiometric phase [5], or as a high-temperature modification [7], or as stabilized by impurities [8].

Experimental

Five alloys of nominal compositions $EuGa_{2-x}Sn_x$ (*x* = 0-1, $Eu_{33.3}Ga_{66.7-33.3}Sn_{0-33.4}$) were synthesized by arc melting from high-purity elements (Eu ≥ 99.95 mass%, Ga ≥ 99.99 mass%, Sn ≥ 99.99 mass%), on a water-cooled copper hearth using a tungsten electrode under a purified argon atmosphere, using Ti sponges as a getter. To achieve homogeneity the samples were melted twice. After cooling, the ingots were wrapped into tantalum foil to ensure their isolation, sealed under vacuum in quartz ampoules, and annealed at 400°C for 1450 h. Finally, the ampoules with the samples were quenched into cold water. The weight losses during the preparation of the samples were less than 0.5 mass%. The samples were stored under vaseline oil due to their sensitivity to components in the air.

Phase analysis was performed using the WinXPOW program package [9] on X-ray powder diffraction data collected at room temperature on a DRON-2.0M diffractometer (radiation Fe $K\alpha$, angular range $20° \le 2\theta \le 140°$, step 0.05°). The samples were ground into fine powders under vaseline oil to avoid contact with air. Results of the phase analysis are summarized in Table 1. The crystal structure of the ternary compound $EuGa_{1.68}Sn_{0.32}$ was refined by the Rietveld method, using the FullProf Suite program package [10], on X-ray powder diffraction data collected at room temperature from the single-phase sample $Eu_{33.3}Ga_{57}Sn_{10.7}$ on a STOE Stadi P diffractometer (radiation Cu $K\alpha_1$, angular range $6° \le 2\theta \le 110°$, step 0.015°). The atomic coordinates reported for the binary AlB_2-type compound $EuGa_2$ [6] were used as starting model for the refinement. The background was defined by a polynomial function using the Fourier filtering technique. The strongly anisotropic [00*l*] peak broadening was successfully modelled by an additional parameter describing general anisotropic strain of hexagonal symmetry during the Rietveld refinement. Experimental, calculated and difference X-ray powder diffraction patterns of the sample $Eu_{33.3}Ga_{57}Sn_{10.7}$ are shown on Fig. 1, experimental details and crystallographic data for the ternary compound $EuGa_{1.68}Sn_{0.32}$ are listed in Table 2.

The composition of the ternary compound was analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^{N}20. The obtained composition ($Eu_{0.98(2)}Ga_{1.71(3)}Sn_{0.31(2)}$) is in good agreement with the composition derived from the Rietveld refinement ($EuGa_{1.682(18)}Sn_{0.318(18)}$). On the photograph of the polished surface of the sample in a beam of secondary electrons (Fig. 1, inset) europium oxide is present as an admixture phase, which probably appeared during the polishing of the sample in the air.

Table 1 Crystallographic data for the phases of the system $EuGa_{2-x}Sn_x$ (x = 0-1).

Sample composition, at.%	x	Structure type	a, Å	b, Å	c, Å	V, Å
$Eu_{33.3}Ga_{66.7}$	0	KHg_2	4.6462(5)	7.6260(9)	7.6384(9)	270.64(6)
$Eu_{33.3}Ga_{60}Sn_{5.7}$	0.17	KHg_2	4.6544(6)	7.6352(10)	7.6502(10)	271.87(7)
		AlB_2	4.3831(7)	–	4.5706(7)	76.04(2)
$Eu_{33.3}Ga_{57}Sn_{10.7}$	0.32	AlB_2	4.3863(2)	–	4.5762(2)	76.250(7)
$Eu_{33.3}Ga_{47}Sn_{20.7}$	0.62	AlB_2	4.3874(5)	–	4.5780(4)	76.32(2)
		YPtAs	4.5248(5)	–	18.073(3)	320.45(4)
$Eu_{33.3}Ga_{33.3}Sn_{33.4}$	1	YPtAs	4.5251(4)	–	18.072(2)	320.47(3)

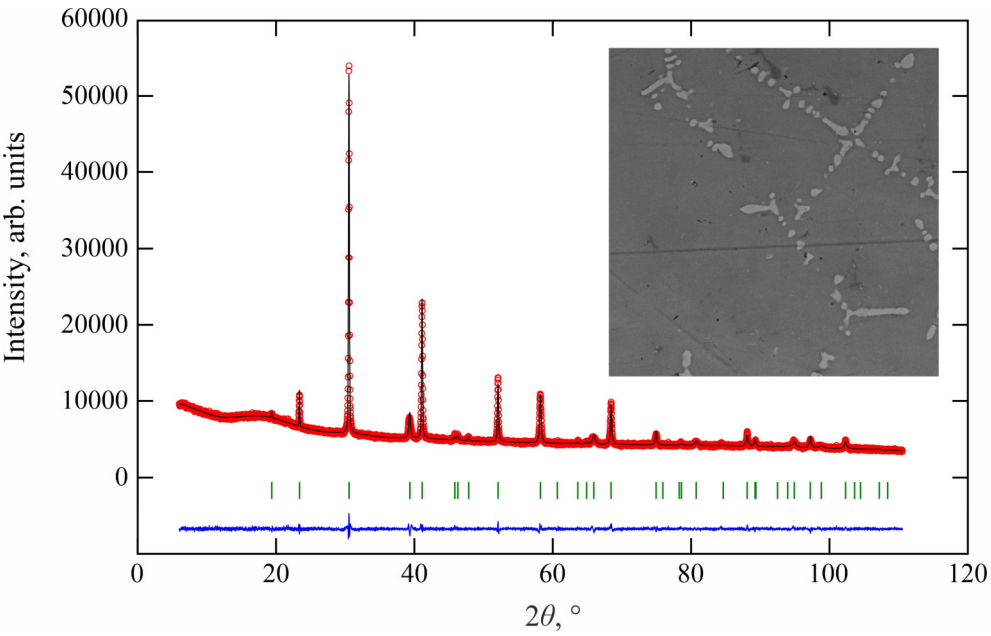


Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction pattern of the samples $Eu_{33.3}Ga_{57}Sn_{10.7}$ (radiation Cu $K\alpha_1$). Vertical bars indicate the positions of reflections of the ternary compound $EuGa_{1.68}Sn_{0.32}$. Inset: photograph of a polished surface of the sample $Eu_{33.3}Ga_{57}Sn_{10.7}$ in a beam of secondary electrons; light sections correspond to europium oxide.

Results and discussion

According to the phase analysis by X-ray diffraction, three phases, crystallizing with the structure types KHg_2, AlB_2, and YPtAs, form along the section $EuGa_{2-x}Sn_x$ (x = 0-1) at 400°C (Table 1). Different unit-cell parameters for the KHg_2- and AlB_2-type phases in different samples indicate possible formation of solid solutions based on the binary compound $EuGa_2$ and the ternary compound $EuGa_{1.68}Sn_{0.32}$, respectively. The AlB_2-type phase is a new ternary compound, not yet reported in the literature. The three-component alloy of the nominal composition $Eu_{33.3}Ga_{57}Sn_{10.7}$ was found to be single-phase and was used for the crystal structure determination.

The Rietveld refinement confirmed that the crystal structure of the ternary compound with the refined composition $EuGa_{1.682(18)}Sn_{0.318(18)}$ belongs to the hexagonal structure type AlB_2. Atom coordinates, isotropic displacement parameters, and site occupancies are given in Table 3. The structure is characterized by one site (Wyckoff position 1*a*) occupied by Eu atoms and one site (2*d*) occupied by a statistical mixture of Ga and Sn atoms. The coordination polyhedra of the Eu atoms are twenty-vertex pseudo Frank-Kasper polyhedra $\underline{Eu}M_{12}Eu_8$, which can be described as hexagonal prisms M_{12} with all faces capped by Eu atoms. The site *M*, occupied by the statistical mixture of Ga and Sn atoms, centers trigonal prisms Eu_6 with three additional *M* atoms above the rectangular faces, forming polyhedra of composition $\underline{M}Eu_6M_3$. The shortest interatomic distances in the structure are δ_{M-M} = 2.532 Å, δ_{Eu-M} = 3.413 Å, δ_{Eu-Eu} = 4.386 Å.

No tendency towards ordering of the Ga and Sn atoms was observed. Two additional structural models, which would allow for partial ordering of Ga and Sn atoms, were tested: the structure type ZrBeSi (*hP*6, $P6_3/mmc$) [11] with a twice larger unit-cell parameter *c*, and LiBaSi (*hP*3, *P*-6*m*2) [12] with the same unit-cell parameters. The former model was excluded since no additional X-ray reflections suggesting a doubling of the *c*-parameter were observed. A structure refinement assuming the non-centrosymmetric LiBaSi-type, gave similar occupancy parameters for both sites containing *p*-element block atoms: 0.840(13)Ga + 0.160(13)Sn and 0.842(13)Ga + 0.158(13)Sn. The possibility of vacancies on the Eu site was also tested: the occupancy of Eu in position 1*a* of the space group *P*6/*mmm* (AlB_2-type) refined to 0.98(4) and was fixed to 1 in the final cycles of the refinements.

The structure of the intermetallic compound $EuGa_{1.68}Sn_{0.32}$ contains infinite planar graphite-like 6^3 nets formed by the *p*-element block atoms (statistical mixture 0.841(9)Ga + 0.159(9)Sn), interconnected by strong covalent bonds (δ = 2.532 Å). The layers are stacked in the crystallographic direction [001] with the interlayer distance δ = 4.576 Å. $EuGa_{1.68}Sn_{0.32}$ is a polar compound, combining the electropositive metal Eu and 2D polyanionic 6^3 nets of Ga and Sn atoms.

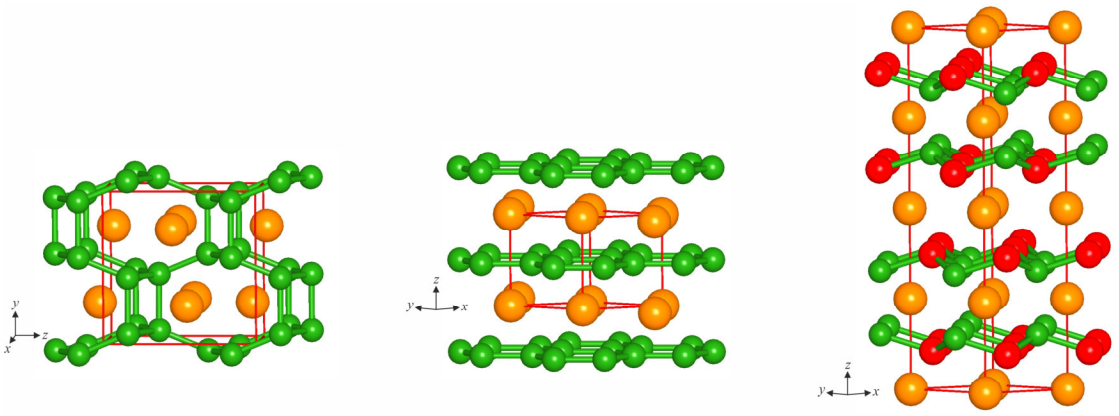
Substitution of Sn atoms for Ga atoms in $EuGa_2$ (structure type KHg_2) led to the formation of two ternary compounds, $EuGa_{1.68}Sn_{0.32}$ (AlB_2) and EuGaSn (YPtAs) [1]. All three closely related structures contain polyanionic structural fragments (Fig. 2). In the structure of the KHg_2-type binary gallide $EuGa_2$ the Ga atoms form slightly puckered hexagonal nets with Ga–Ga distances δ = 2.653 and 2.6921 Å. The nets are interconnected *via* δ_{Ga-Ga} distances of 2.811 Å [5]. The *p*-element atoms in the structure of the AlB_2-type ternary compound $EuGa_{1.68}Sn_{0.32}$ form planar graphite-like 6^3 nets, as described above. In the structure of the equiatomic YPtAs-type ternary compound EuGaSn the Ga and Sn atoms, which are ordered, occupying two different sites, form puckered 6^3 nets with δ_{Ga-Sn} = 2.737 Å within the layers, and with the shortest interlayer distances δ_{Ga-Ga} = 3.178 Å. The same sequence of structure transitions (types KHg_2, AlB_2, YPtAs) was also observed in the related system $EuGa_{2-x}Ge_x$ (x = 0-1) [4].

Table 2 Experimental details and crystallographic data for $EuGa_{1.68}Sn_{0.32}$.

Refined composition	$EuGa_{1.682(18)}Sn_{0.318(18)}$
Structure type	AlB_2
Pearson symbol	*hP*3
Space group	*P*6/*mmm*
Unit-cell parameters: *a*, Å	4.3863(2)
c, Å	4.5762(2)
Cell volume *V*, Å^3	76.250(7)
Formula units per cell *Z*	1
Density D_X, g cm^{-3}	6.874
Preferred orientation: value / [direction]	0.915(4) / [110]
Reliability factor R_B	0.0158
Profile parameters *U*, *V*, *W*	-0.038(6), 0.093(5), 0.0035(11)
Asymmetry parameters	0.111(6), 0.0025(10)
Reliability factors R_p, R_{wp}	0.0170, 0.0226
χ^2	2.76

Table 3 Atom coordinates and isotropic displacement parameters for $EuGa_{1.682(18)}Sn_{0.318(18)}$ (structure type AlB_2, *hP*6, *P*6/*mmm*, *a* = 4.3863(2), *c* = 4.5762(2) Å).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Eu	1*a*	0	0	0	0.50(6)
M (0.841(9)Ga + 0.159(9)Sn)	2*d*	⅓	⅔	½	1.02(8)



$EuGa_2$
(structure type KHg_2,
*oI*12, *Imma*)

$EuGa_{1.68}Sn_{0.32}$
(structure type AlB_2,
*hP*3, *P*6/*mmm*)

EuGaSn
(structure type YPtAs,
*hP*12, $P6_3/mmc$)

Fig. 2 Crystal structures of $EuGa_2$, $EuGa_{1.68}Sn_{0.32}$, and EuGaSn. Eu atoms – large yellow, Ga and *M* – small green, Sn – medium-size red. The unit cells are drawn by thin red lines, Ga–Ga, *M*–*M*, and Ga–Sn contacts are highlighted in green.

Conclusions

The new ternary compound $EuGa_{1.682(18)}Sn_{0.318(18)}$ was synthesized and its crystal structure was refined by the Rietveld method from X-ray powder diffraction data. The structure belongs to the structure type AlB_2. Ga and Sn atoms statistically occupy one crystallographic site and form relatively strong bonds within planar graphite-like 6^3 nets.

Acknowledgement

This work was carried out under the grant of the Ministry of Education and Science of Ukraine No. 0121U109766.

References

[1] T.-S. You, Y. Grin, G.J. Miller, *Inorg. Chem.* 46 (2007) 8801-8811.
[2] Ya. Tokaychuk, *Chem. Met. Alloys* 8 (2015) 112-122.
[3] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2021/22.
[4] T.S. You, J.T. Zhao, R. Pöttgen, W. Schnelle, U. Burkhardt, Y. Grin, G.J. Miller, *J. Solid State Chem.* 182 (2009) 2430-2442.
[5] O.M. Sichevich, R.H. Cardoso Gil, Y. Grin, *Z. Kristallogr. – New Cryst. Struct.* 221 (2006) 261-262.
[6] A. Iandelli, *Z. Anorg. Allg. Chem.* 330 (1964) 221-232.
[7] K.H.J. Buschow, D.B Mooij, *J. Less-Common Met.* 97 (1984) L5-L8.
[8] V.Ya. Markiv, N.N. Belyavina, T.I. Zhunkovskaja, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* 2 (1982) 80-83.
[9] STOE WinXPow (Version 2.21), Darmstadt, Stoe & Cie (2005).
[10] J. Rodríguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.
[11] J.W. Nielsen, N.C. Baenziger, *Acta Crystallogr.* 7 (1954) 132-133.
[12] H. Axel, K.H. Janzon, H. Schäfer, A. Weiss, *Z. Naturforsch. B* 23 (1968) 108-109.