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New ternary intermetallic compound SmRuSn₂

V A Pavlova¹, E V Murashova¹, A S Borodulin²

¹Lomonosov Moscow State University, Chemistry Department, Leninskie gory, GSP-1, str.3. 119991, Moscow, Russia

²Intersectoral Engineering Center «Composites of Russia» of Bauman Moscow State Technical University, FSAEI HE «Bauman Moscow State Technical University». 2-d Bauman str., 5. 105005, Moscow, Russia

E-mail: verapavlova@general.chem.msu.ru, asb@emtc.ru

Abstract. Ternary intermetallic compound SmRuSn₂ was synthesized in the system Sm-Ru-Sn by arc-melting and annealing at 600 °C in field with high content of Sn. Its crystal structure was determined from single crystal X-ray diffraction data (at 240 K) and then confirmed by the powder X-ray diffraction data (at 295 K). The compound crystallizes in with space group *Cmcm* (No. 63), unit cell unit cell parameters: $a=4.3954(19)$ Å, $b=10.3783(13)$ Å, $c=7.417(2)$ Å, $Z=4$. The intermetallic compound SmRuSn₂ belongs to the structure type MgCuAl₂.

Keywords: Intermetallics; Crystal structure, X-ray diffraction

1. Introduction

Intermetallic compounds in REE-PM-X systems (REE is a rare earth element, PM is a transition d-metal, X is a p-element of 13-15 groups) have been actively studied in the last 15 years. Interest in such IMCs is due to the fact that they demonstrate unique magnetic and electrical properties due to electronic correlations, hybridization between the 4f shell of REE atoms and electrons of s- and / or p-orbitals of neighboring atoms, as well as unusual interactions of itinerant conduction electrons with the atomic lattice [1]. In fundamental research, special attention is paid to triple IMCs with rare-earth elements Ce, Sm, Eu, and Yb, since the compounds of these particular REEs most often have interesting properties for research: strong Kondo effect, heavy-fermion state of current carriers, unusual heavy-fermionic superconductivity, fluctuation of atomic valence REE, quantum critical phenomena [2,3]. IMCs containing Ce and Ru can be distinguished into a special group, since in a number of such compounds the observed Ce-Ru interatomic distances are shortened (2.4-2.8 Å) or even anomalously short (up to 2.23 Å), while the sum of even covalent radii atoms of Ce and Ru is 2.89 Å [4]. Extremely short interatomic distances were observed in ternary indides and stannides Ce₃Ru₂In₃ (2.38 Å) [5], Ce₁₆Ru₈In₃₇ (2.37 Å) [6], Ce₃Ru₂In₂ (2.23 Å) [7], Ce₂Ru₂In₃ (2.32 and 2.37 Å) [7], CeRu (2.33 and 2.46 Å) [8, 9, 10], as well as in the aluminide Ce₅Ru₃Al₂ (2.4 Å) [11]. At present, the specific features of the chemical bond leading to the anomalous approach of the Ce and Ru atoms are not clear and require additional research. Undoubtedly, the formation of short distances REE-PM should affect the magnetic and transport properties of the substance [12].

The electronic configuration of the valence levels of the samarium atom is 6s²5d⁰4f⁶. Samarium is located near the middle of the lanthanide series and is characterized, like cerium, by two possible valence states of ions in compounds: Sm⁺² and Sm⁺³. The atomic ($R_{Ce} = 1.81$ Å / $R_{Sm} = 1.82$ Å) and covalent ($R_{Ce} = 1.62$ Å / $R_{Sm} = 1.65$ Å) radii of cerium and samarium are close in their values [4].

Samarium intermetallic Sm₂Ru₃Si₅ was reported earlier [13], it crystallizes in tetragonal unit cell with parameters $a = 10.747(6)$, $c = 5.695(3)$ Å, space group is *P4/mnc*. Structure relates to the type U₂Mn₃Si₅ (that also could be related to the Sc₂Fe₃Si₅ type). Samarium germanide Sm₂Ru₃Ge₅ was firstly described by Venturini [14] as isostructural to the U₂Co₃Si₅, it belongs to the space group *Ibam*. The unit cell parameters of Sm₂Ru₃Ge₅ was determined by powder X-ray diffraction data and equal to: $a = 9.867(8)$, $b = 12.44(1)$, $c = 5.790(4)$ Å. The transition metal atoms occupy two different crystallographic positions



and are enclosed in irregular octahedra. Gallide with samarium $\text{Sm}_2\text{Ru}_3\text{Ga}_5$ was considered [15], it crystallizes in tetragonal unit cell with space group $P4/mnc$ and corresponds to the structure type $\text{U}_2\text{Mn}_3\text{Si}_5$ ($\text{Sc}_2\text{Fe}_3\text{Si}_5$). Unit cell parameters of $\text{Sm}_2\text{Ru}_3\text{Ga}_5$ are $a = 11.3295(9)$, $c = 5.6271(6)$ Å. The exact composition of the samarium gallide was $\text{Sm}_2\text{Ru}_{2.73(2)}\text{Ga}_{5.27(2)}$. The compound $\text{Sm}_2\text{Rh}_3\text{Sn}_5$, which is characterized by van Vleck type behavior of Sm^{3+} and an antiferromagnetic ordering by temperature $T_N = 3.5$ (5) K. The unit cell parameters of $\text{Sm}_2\text{Rh}_3\text{Sn}_5$ with the orthorhombic $\text{Y}_2\text{Rh}_3\text{Sn}_5$ type structure, space group $Cmc21$, are $a = 4.4446(8)$, $b = 26.362(4)$, $c = 7.183(1)$ Å.

This arouses additional interest in comparing the displayed physical properties and gives grounds to assume the similarity of the crystal structures of compounds with the same stoichiometry. It is also important to search for new samarium stannides, to study their structure, and to determine the values of the Sm-Ru interatomic distances.

2. Experimental

2.1. Synthesis

The sample $\text{Sm}_{25}\text{Ru}_{25}\text{Sn}_{50}$ (at.%) was synthesized by arc-melting from the pure elements Sm (99.9 mass% Sm), Ru (99.99 mass% Ru), Sn (99.999 mass% Sn) in a purified argon atmosphere. To reach the homogeneity the fused mass was re-melted several times. After melting the alloy was annealed at 600 °C for 30 days. The annealing temperature was selected on the basis of the analysis of the phase diagram of binary systems Sm-Ru [16, 17], Ru-Sn [18] and Sm-Sn [19]. The total mass lost wasn't higher than 1% of weight.

2.2. X-ray single crystal diffraction (XRSCD)

The suitable single crystal for X-ray structure analysis was found at the surface of the annealed alloy $\text{Sm}_{20}\text{Ru}_{30}\text{Sn}_{50}$ (at.%). X-ray single crystal diffraction experiment was performed using a Bruker APEX-3 diffractometer employed monochromated CuK_α radiation ($\lambda = 1.5406$ Å). All obtained intensities were collected and derived using program Bruker SAINT [20]. Absorption correction was performed with SADABS program [21]. The structure was solved by direct methods and refined with the SHELX-2018 program package [22].

2.3. X-ray powder diffraction (XRD)

X-ray powder diffraction pattern was collected with using of STOE STADI P transmission diffractometer (monochromatized CuK_α – radiation ($\lambda = 1.54056$ Å), $10^\circ < 2\theta < 89.99^\circ$, linear position-sensitive detector, step scan 0.01° and counting time 10 s/point). Indexing the XRD pattern and lattice parameters determination were obtained using the STOE WinXpow package [23]. Quantitative refinement of the powder X-ray pattern by the Rietveld method was performed with the FULLPROF program [24, 25], employing internal tables for X-ray atomic form factors. Structure and atom polyhedra were visualized using program DIAMOND [26].

2.4. Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX analysis)

Microstructure and chemical composition of the prepared alloy was established by scanning electron microscopy and by energy dispersive X-ray spectroscopy using Carl Zeiss LEO EVO 50VXP microscope equipped with an INCA Energy 450 EDX-spectrometer (Oxford Instruments). Accelerating

voltage was 30 kV. As an internal standard, ternary compound SmRuSn_3 [27] was used. The measurement error did not exceed 1 at. %.

3. Results and discussion

3.1. Sample characterization

EDX analysis revealed the sample SRN-50 contains two phases: $\text{SmRu}_{0.26(1)}\text{Sn}_2$ and new phase SmRuSn_2 , chemical composition of it to be close to $\text{Sm}_{23.2}\text{Ru}_{25.7}\text{Sn}_{51.1}$ (at.%). The microstructure of the as cast sample is presented on the Fig. 1a. After the heat treatment of the alloy the content of the $\text{SmRu}_{0.26(1)}\text{Sn}_2$ phase was so small that it is missing on the microstructure of the sample.

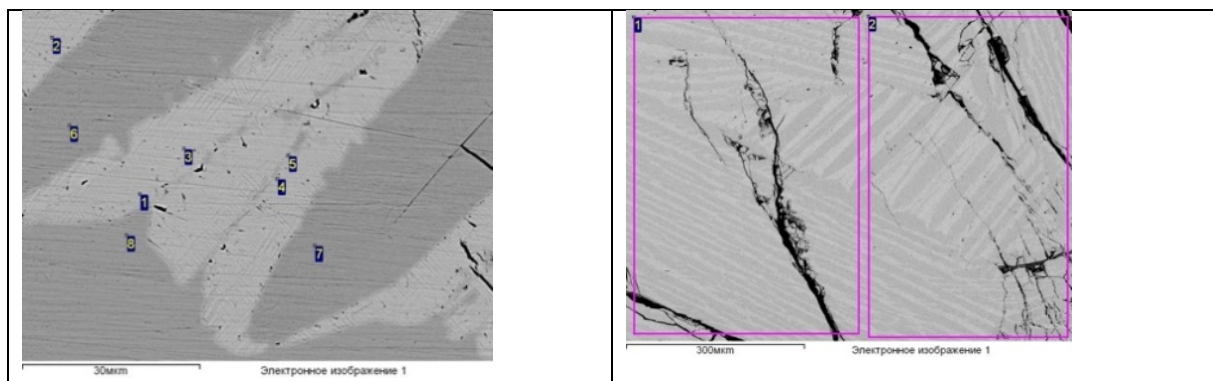


Figure 1. The microstructure of the alloy SRN-50: points 1-5 correspond to the phase SmRuSn_2 - $\text{Sm}_{23.2}\text{Ru}_{25.7}\text{Sn}_{51.1}$, points 6-8 (light-grey phase) correspond to the average composition of $\text{Sm}_{27.7}\text{Ru}_{11.6}\text{Sn}_{60.6}$ and considered to be the second phase $\text{SmRu}_{0.26(1)}\text{Sn}_2$.

3.2. Crystal structure

The initially synthesized sample labeled SRN-50 contained an impurity phase – $\text{SmRu}_{0.26(1)}\text{Sn}_2$, which was confirmed by X-ray phase analysis. However, crystals suitable for XRD were found on the sample surface. According to single-crystal data, the new compound crystallizes in an orthorhombic unit cell and corresponds to the structural type MgCuAl_2 [28], space group $Cmcm$, unit cell parameters: $a=4.3954(19)$ Å, $b=10.3783(13)$ Å, $c=7.417(2)$ Å, $Z=4$. The conditions for the X-ray diffraction experiment, atomic coordinates, and anisotropic parameters of atomic displacement are presented in the tables. 1-3 The image of the projections of the unit cell of the new SmRuSn_2 compound onto various coordinate planes, as well as the coordination environment of atoms, are shown in Figures 2 and 3, respectively.

Table 1. Crystallographic parameters and conditions of the X-ray diffraction experiment of SmRuSn_2 .

Composition, at. %	$\text{Sm}_{23.14}\text{Ru}_{26.36}\text{Sn}_{50.5}$
Crystal size, mm	$0.3 \times 0.03 \times 0.05$
Radiation, λ , Å	$\text{CuK}\alpha$; 1.5406

Space group	<i>Cmcm</i> (No.63)
Unit cell parameters, Å	Single crystal data
	$a=4.3954(19)$ $b=10.783(13)$ $c=7.417(2)$
Volume, Å ³ , Z	348.19(7), 4
Molar mass, g/mol	448.80
Calculated density, g/cm ³	9.325
Adsorbition coefficient, mm ⁻¹	268.64
F (000)	824
Angle range 2 θ , °	10.0 - 89.99
Range of indexes	$0 \leq h \leq 8$
	$0 \leq k \leq 3$
	$0 \leq l \leq 9$
Number of reflections	206
Number of independent reflections (Rint)	196 (0.084)
Reflections with $I > 2\sigma(I)$ (R σ)	135 (0.036)
Refined parameters	12
GOF на F ²	1.152
R1 / R1 (all reflections)	0.066 / 0.069
wR2 / wR2 (all reflections)	0.084 / 0.088

Table 2. Atomic coordinates and parameters of thermal displacement in structure of SmRuSn₂.

Atom	Wp	x/a	y/b	z/c	$U_{eq}, \text{\AA}^2$
Sm	$4c$	0	0.07118(8)	0.75	0.0087(2)
Sn	$4c$	0	0.35802(8)	0.54734(10)	0.0083(2)
Ru	$4c$	0	0.20953(16)	0.25	0.0083(3)

Table 3. Anisotropic displacement parameters in the structure SmRuSn₂ (* $U_{23} = U_{13} = U_{12}$).

Atom	U_{11}	U_{22}	U_{33}
Sm1	0.0067(4)	0.0132(4)	0.0061(4)
Sn1	0.0063(3)	0.0140(4)	0.0045(3)
Sn2	0.0057(7)	0.0130(7)	0.0060(6)
Ru1	0.0067(4)	0.0132(4)	0.0061(4)

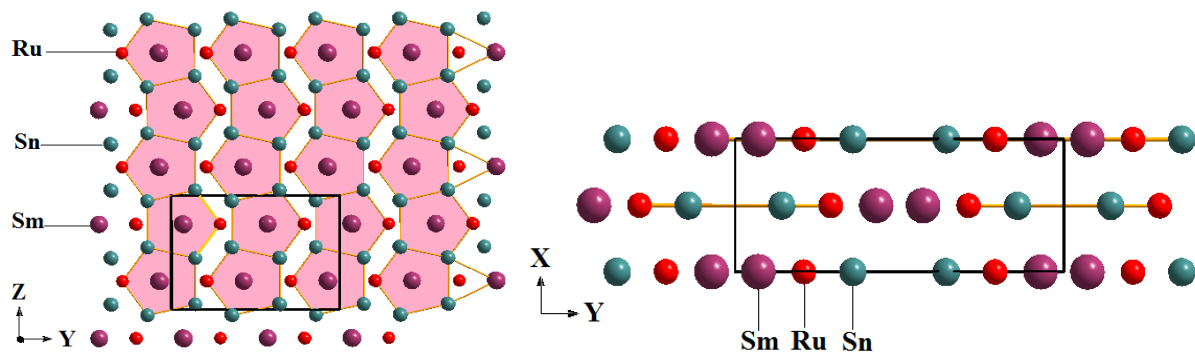


Figure 2. Projection of the SmRuSn_2 unit cell onto the YZ plane and the projection of the SmRuSn_2 unit cell onto the XY plane.

Table 4. Some values of interatomic distances (Å) in the SmRuSn_2 compound.

Atom 1,	Atom 2	Distance, Å
CN		
Sm 13	Ru	3.027(2)
	4Sn	3.1882(10)
	2Ru	3.2107(17)
	4Sn	3.4389(14)
	2Sn	3.5015(12)
Ru 9	1Sn2	2.7254(14)
	3Sn	2.7400(10)
	Sm	3.027(2)
	2Sm	3.2107(16)
Sn1 12	Ru	2.7254(14)
	2Ru	2.7400(10)
	2Sn	3.0064(18)
	Sn	3.1415(19)
	2Sm	3.1882(10)
	2Sn	3.2615(15)
	2Sm	3.5014(12)

The new compound is a structure built of samarium polyhedra condensed along common lateral faces (Fig. 2). Samarium atoms in the structure occupy one independent crystallographic position and are located inside distorted pentagonal prisms, with ruthenium and tin atoms at the vertices. Coordination polyhedra constructed from the obtained crystallographic data are shown in Figure 3.

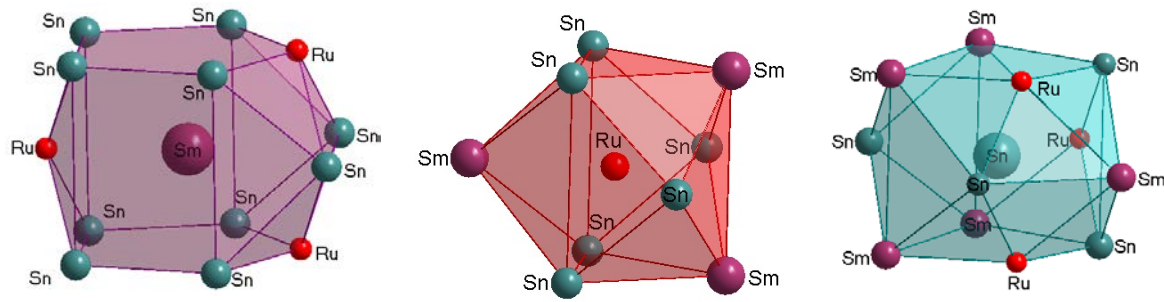


Figure 3. Coordination polyhedra in the SmRuSn_2 structure (Interatomic distances up to 3.6 Å).

When comparing the new intermetallic SmRuSn_2 with the previously known compound $\text{CeRu}_{0.88}\text{In}_2$ [29], one can note a close composition and a significant discrepancy in the value of the parameter a : $a(\text{CeRu}_{0.88}\text{In}_2) = 4.5449(11)$ Å, $a(\text{SmRuSn}_2) = 4.3954(19)$ Å.

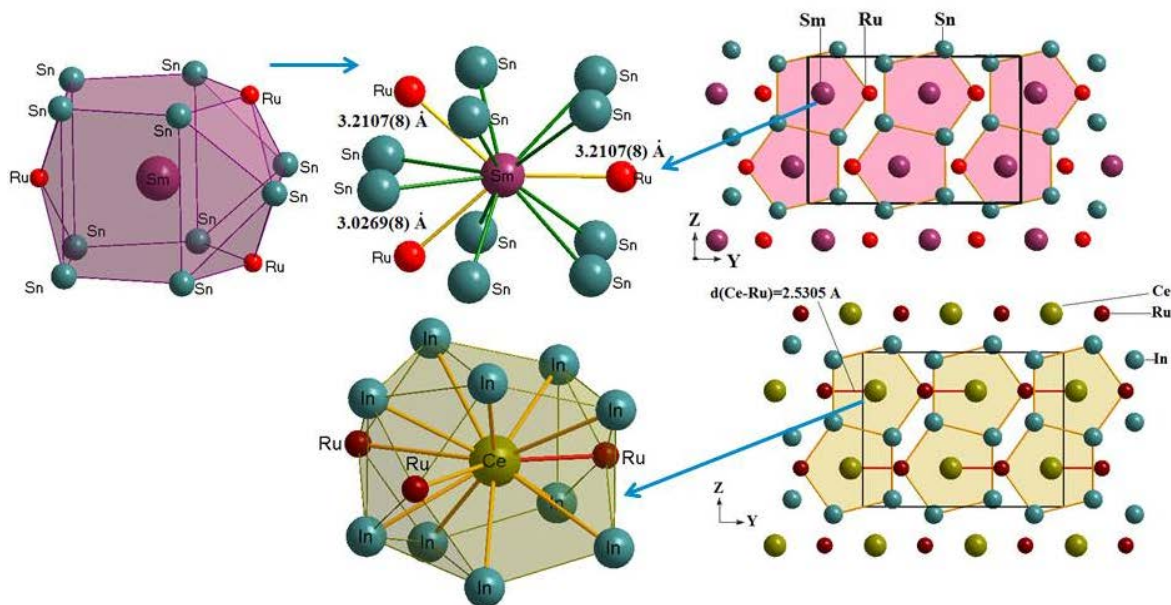


Figure 4. Comparison of the crystal structures of SmRuSn_2 and $\text{CeRu}_{0.88}\text{In}_2$: coordination environment of REE atoms with indication of the values of REE – Ru bonds, projections of unit cells onto the ZY plane.

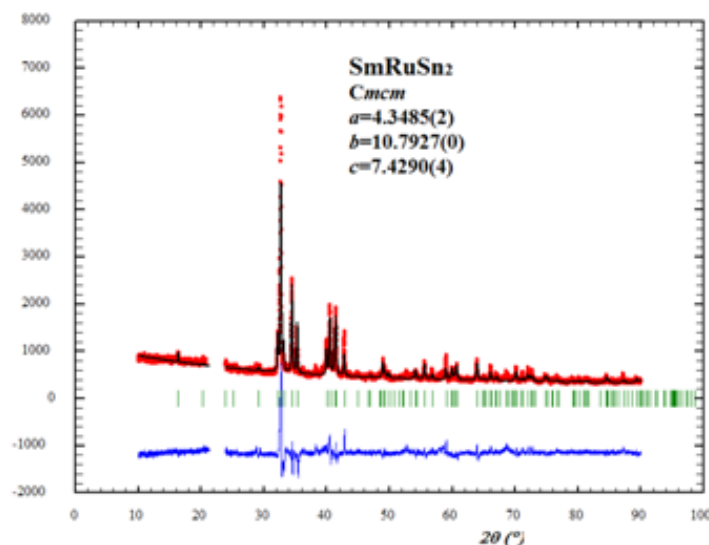


Figure 5. Rietveld refinement of the SmRuSn_2 structure based on the crystal model obtained in X-ray diffraction analysis, $R_p = 0.076$, $R_{wp} = 0.11$, $\chi^2 = 6.84$.

The structure of SmRuSn_2 and $\text{CeRu}_{0.88}\text{In}_2$ contains one independent position of REE, ruthenium, and tin (indium). In the SmRuSn_2 structure, the interatomic distances between the central atoms and neighboring atoms in the nearest coordination environment reach 3.59 Å, while the shortest distances between the ruthenium and tin atoms Sn_2 are $d(\text{Ru}-\text{Sn}_2) = 2.86$ Å. A characteristic feature of the structure under consideration in this class of ICs with REE is the absence of shortened REE-PM distances. The smallest value of Sm - Ru contacts in SmRuSn_2 reaches 3.02 Å, which is not close to the limiting value of the sum of covalent radii $r(\text{Sm}) + r(\text{Ru}) = 2.87$ Å. In comparison with the described compound $\text{SmRu}_{0.26(1)}\text{Sn}_2$, this is much less ($3.02 \text{ Å} < 3.34 \text{ Å}$), but this value is not evidence of electronic correlations in the structure and the possible appearance of special physical properties. On the contrary, the structure of $\text{CeRu}_{0.88}\text{In}_2$ contains short contacts $d(\text{Ce}-\text{Ru}) = 2.530(2)$ Å; this is reflected in the fact that inside the distorted pentagonal prisms the cerium atom is displaced from the center of the polyhedron towards ruthenium as compared to the samarium atoms in the structure of SmRuSn_2 .

4. Conclusion and outlook

A new samarium intermetallic compound SmRuSn_2 crystallizes in a structure of the MgCuAl_2 type with orthorhombic unit cell. The structure can be represented as a structure built of samarium polyhedra condensed along the common lateral faces where samarium atoms occupy one independent crystallographic position. Structure of SmRuSn_2 has a similar motif with a known compound $\text{CeRu}_{0.88}\text{In}_2$. It should be noted that the pair of compounds SmRuSn_2 and early known $\text{CeRu}_{0.88}\text{In}_2$ is the only example of isostructural ICs with cerium and samarium, one of which contains abnormally short REE-PM contacts, while the other does not. Based on a comparison of the properties of these two compounds, one can draw a conclusion about the reasons for the appearance of abnormally short contacts, the nature of the bond in the structure, as well as the relationship between short distances and the appearance of fluctuations in the valence of REE atoms, which is the main fundamental problem at present.

Acknowledgments

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