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$Nd_3Ge_{1.18}In_{0.82}$ and $Sm_3Ge_{1.33}In_{0.67}$ – New ternary indides with La_3GeIn type structure

Oksana Kravets [a], Galyna Nychyporuk [a], Ihor Muts [a], Viktor Hlukhyy [b], Rainer Pöttgen [c], Vasyl' Zaremba [a,*]

[a] Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla and Mefodiya Street 6, 79005 Lviv, Ukraine
[b] Department of Chemistry, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany
[c] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

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ABSTRACT

New indides, $Nd_3Ge_{1.18}In_{0.82}$ and $Sm_3Ge_{1.33}In_{0.67}$, were synthesized from the elements by arc-melting and subsequent annealing at 870 K. Single crystals were grown through special annealing procedures in sealed tantalum tubes in a resistance furnace. Both compounds were investigated on the basis of X-ray powder and single crystal data: La_3GeIn type structure, Pearson code tI80, space group *I*4/*mcm*; $a = 1200.1(1)$, $c = 1562.8(1)$ pm, $wR2 = 0.0781$, 716 F^2 values, 34 variables for $Nd_3Ge_{1.18}In_{0.82}$ and $a = 1184.7(2)$, $c = 1537.0(3)$ pm, $wR2 = 0.0305$, 911 F^2 values, 34 variables for $Sm_3Ge_{1.33}In_{0.67}$. The crystal chemistry in $Nd_3Ge_{1.18}In_{0.82}$ is discussed from a geometrical point of view and in terms of LMTO band structure calculations.

1. Introduction

Intense investigations of the ternary *RE*–Ge–In (*RE* – rare earth element) systems were started in recent years, aiming at determination of the character of interaction of the components in these systems, searching new ternary compounds and investigating their physical properties. Isothermal sections of phase diagrams at 870 K were investigated for systems with Y [1], La [2], Ce [3], Nd [4], Sm [5], Gd [6], Yb [7], and Lu [8]. These systems are quite complicated and they exhibit many ternary compounds.

Eight representative structure types with compositions RE_3GeIn (La_3GeIn type), $RE_{11}Ge_4In_6$ ($Sm_{11}Ge_4In_6$ type), $RE_{11}Ge_8In_2$ ($Gd_{11}Ge_8In_2$ type), La_5Ge_3In (Gd_5Si_4 type), $LuGe_{0.96}In_{0.04}$ (CrB type), RE_2Ge_2In (Mo_2FeB_2 type), RE_3GeIn_4 (La_3GeIn_4 type), and EuGeIn (EuGeIn type) exist in the *RE*–Ge–In systems (Table 1).

For some of these compounds physical properties were investigated. The RE_2Ge_2In (*RE* = Ce, Pr and Nd) compounds exhibit localized magnetism of the RE^{3+} ions with complex magnetic behavior hinting at canted antiferromagnetism or spin-glass freezing at the lowest temperatures [17]. The other RE_2Ge_2In compounds with Sm, Gd, Tb and Ho are antiferromagnets with Néel temperatures of 25, 42, 51 and 23 K, respectively, and Yb_2Ge_2In is a Pauli paramagnet [19]. Ce_3GeIn_4 is paramagnetic down to 1.72 K, whereas $Ce_{11}Ge_4In_6$ orders ferromagnetically at $T_C = 7.5$ K [12]. $RE_{11}Ge_8In_2$ (*RE* = Gd–Tm) order ferromagnetically at low temperatures and for the Gd, Tb and Tm containing phases a magnetocaloric effect was observed with the largest magnetic entropy change of $\Delta S_m = 10.6$ J/kg K in $Tm_{11}Ge_8In_2$ [11]. $Y_{11}Ge_4In_6$ is a Pauli paramagnet, whereas $Gd_{11}Ge_4In_6$ and $Tb_{11}Ge_4In_6$ order antiferromagnetically at low temperatures [14].

In continuation of our systematic phase analytical work in the *RE*–Ge–In systems we obtained the new indides RE_3GeIn with neodymium and samarium. The synthesis, structure refinements and a detailed characterization of chemical bonding are reported herein.

2. Experimental section

2.1. Synthesis

Starting materials for the synthesis of the Nd_3GeIn and Sm_3GeIn samples were ingots of the rare earth elements (Johnson Matthey), germanium pieces (Alfa Aesar) and indium tear drops (Chempur), all with stated purities better than 99.9%.

In a first step, the neodymium and samarium ingots were cut into smaller pieces and arc-melted to small buttons (about 0.5 g)

* Corresponding author. Tel.: +380 32 2394483.
E-mail addresses: viktor.hlukhyy@lrz.tu-muenchen.de (V. Hlukhyy), pottgen@uni-muenster.de (R. Pöttgen), vazar@franko.lviv.ua (V. Zaremba).

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Table 1
The structure type of compounds in the RE–Ge–In systems.

Structure type	RE															
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	References
La_3GeIn	–	+	+	+	+	–	–	+	–	–	–	–	–	–	–	[1–4,9,10]
$Sm_{11}Ge_4In_6$[a]	+	+	+	–	+	+	–	+	+	–	+	+	–	–	–	[1,2,4–6,12–14]
$Gd_{11}Ge_8In_2$[a]	–	–	–	–	–	–	–	+	+	+	+	+	+	–	–	[11]
Gd_5Si_4	–	+	–	–	–	–	–	–	–	–	–	–	–	–	–	[15]
CrB	–	–	–	–	–	–	–	–	–	–	–	–	–	–	+	[8]
Mo_2FeB_2	+	+	+	+	+	+	–	+	+	+	+	–	–	+	–	[16–19]
La_3GeIn_4	–	+	+	+	+	–	–	–	–	–	–	–	–	–	–	[2–4,9,12]
EuGeIn	–	–	–	–	–	–	+	–	–	–	–	–	–	–	–	[20]

[a] $Sm_{11}Ge_4In_6$ and $Gd_{11}Ge_8In_2$ types are ordered versions of the $Ho_{11}Ge_{10}$ structure type with different occupation of the 16*m* position.

under argon atmosphere. Titanium sponge was used as a getter material. Subsequently the melted neodymium (or samarium) buttons were mixed with pieces of germanium and the indium tear drops in the ideal 3:1:1 atomic ratio and arc-melted under the same conditions. The product pellets were re-melted twice to ensure homogeneity. The total weight losses after the melting procedures were smaller than 0.5%. After the arc-melting procedure the RE_3GeIn indides were obtained only as polycrystalline material. Then the buttons were sealed in evacuated quartz tubes and annealed at 870 K for 720 h. Both samples are stable in moist air, also upon grinding to fine powder.

After the arc-melting procedure single crystals of good quality were not found. To obtain single crystals, a special thermal treatment was used which was similar for both compositions. First, the polycrystalline samples were powdered and cold-pressed into pellets. Next, the samples were put in small tantalum containers that have been sealed in evacuated silica tubes as an oxidation protection. The ampoules were first heated to 1325 K (for both samples) within 6 h and held at that temperature for another 4 h. Subsequently, the temperature was lowered at a rate of 3 K/h to 1075 K, then at a rate of 5 K/h to 875 K, and finally cooled to room temperature within 10 h. After cooling, the samples could easily be separated from the tantalum container. No reaction of the samples with tantalum could be detected. As result in both cases single crystals of irregular shape were obtained.

2.2. EDX data

The single crystals investigated on the diffractometer were studied by energy dispersive analyses of X-rays (EDX) using a Leica 420*i* scanning electron microscope with NdF_3, SmF_3, Ge and InAs as standards. No impurity elements heavier than sodium have been observed. For $Nd_3Ge_{1.18}In_{0.82}$ the composition determined by EDX (59 ± 2 at.% Nd : 22 ± 2 at.% Ge : 19 ± 2 at.% In) was in good agreement with the refined composition (60:23.6:16.4). For $Sm_3Ge_{1.33}In_{0.67}$ crystal the EDX data (61 ± 2 at.% Sm : 24 ± 2 at.% Ge : 15 ± 2 at.% In) are also close to the X-ray data (60:26.6:13.4).

2.3. X-ray powder and single crystal data

The polycrystalline samples were studied through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) using Cu$K\alpha_1$ radiation and α-quartz ($a = 491.30$ and $c = 540.46$ pm) as an internal standard. The X-ray phase analysis of the samples showed that they are two-phased and contain the main phase with the La_3GeIn structure type and an impurity phase with the $Sm_{11}Ge_4In_6$ structure type. It agrees well with the results obtained in Refs. [4,5]. The tetragonal lattice parameters were obtained from least-squares fits of the powder data. The correct indexing of the patterns was ensured through intensity calculations [21] taking the atomic positions from the structure refinements. Refined lattice parameters ($a = 1196.5(1)$, $c = 1558.1(1)$ for the Nd_3GeIn and $a = 1189.2(3)$, $c = 1544.2(5)$ pm for the Sm_3GeIn) are in good agreement with the lattice parameters derived from the single crystals (Table 2). The small discrepancies originate from the small homogeneity ranges (Ge/In mixing).

Irregularly shaped single crystals of both compounds were selected from the annealed samples by mechanical fragmentation. They were investigated by Laue photographs on an RKV-86 camera (white molybdenum radiation, photo technique) in order to check the quality for intensity data collection. Intensity data of $Sm_3Ge_{1.33}In_{0.67}$ and $Nd_3Ge_{1.18}In_{0.82}$ were collected at room temperature using a Stoe IPDS II image plate diffractometer and an Oxford Diffractions Xcalibur 3 diffractometer both with graphite monochromatized MoK_α ($\lambda = 71.073$ pm) radiation. The raw data were corrected for background, polarization and the Lorentz factor. The absorption correction for $Sm_3Ge_{1.33}In_{0.67}$ was numerical, whereas a semi-empirical absorption correction was performed for $Nd_3Ge_{1.18}In_{0.82}$. All relevant crystallographic data for the data collections and evaluations are listed in Table 2.

2.4. Electronic structure calculations

The electronic structures for the title compounds were calculated employing a linear muffin-tin orbital (LMTO) method in the

Table 2
Crystal data and structure refinement for $Nd_3Ge_{1.18}In_{0.82}$ and $Sm_3Ge_{1.33}In_{0.67}$ with La_3GeIn type structure.

Empirical formula	$Nd_3Ge_{1.18}In_{0.82}$	$Sm_3Ge_{1.33}In_{0.67}$
Molar mass	612.53 g/mol	624.68 g/mol
Space group, Z	*I*4/*mcm* (No. 140), 16	
Unit cell dimensions (single crystal data)	$a = 1200.1(1)$ pm $c = 1562.8(1)$ pm $V = 2.251$ nm^3	$a = 1184.7(2)$ pm $c = 1537.0(3)$ pm $V = 2.157$ nm^3
Calculated density	7.23 g/cm^3	7.69 g/cm^3
Crystal size	50 × 80 × 120 pm^3	10 × 40 × 70 pm^3
Absorption coefficient	36.3 mm^{-1}	41.1 mm^{-1}
F(000)	4127	4183
Total no. reflections	15185	6266
Independent reflections/ parameters	716/34	911/34
Goodness-of-fit on F^2	1.063	0.684
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0303$, $wR2 = 0.0757$	$R1 = 0.0269$, $wR2 = 0.0809$
R indices (all data)	$R1 = 0.0357$, $wR2 = 0.0781$	$R1 = 0.0244$, $wR2 = 0.0305$
Extinction coefficient	0.00006(2)	0.00005(1)
Largest diff. peak and hole	4.29 and −2.49	2.22 and −1.36