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Single-crystal investigation of the compound $\text{SmNi}_{5.2}\text{Mn}_{6.8}$

<https://doi.org/10.1515/znb-2019-0181>

Received October 23, 2019; accepted December 1, 2019

Abstract: The intermetallic compound $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ was synthesized by arc-melting and its crystal structure has been determined using single-crystal X-ray diffraction data. The compound adopts the tetragonal structure type ThMn_{12} ; space group $I4/mmm$, Pearson code $tI26$, $Z=2$; $a=8.6528(3)$, $c=4.8635(3)$ Å; $R1=0.0175$, $wR2=0.0372$, 171 F^2 values, 17 refined variables. The two crystallographic positions $8f$ and $8j$ in the structure of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ are occupied by a mixture of Mn and Ni atoms.

Keywords: crystal structure; rare earth intermetallics; X-ray diffraction.

1 Introduction

The structure type ThMn_{12} [1] is rather widespread among intermetallic compounds. The representatives of this type exist both in the binary systems $R\text{-Mn}$ ($R=\text{Y, Gd, Tb, Dy, Ho, Er, Tm}$) [2, 3] and in the ternary systems $R\text{-Mn-}T$ ($R=\text{Ce, Pr, Nd, Sm}$; $T=\text{Fe, Co, Ni}$) [4, 5]. The transition metals appear to stabilize the compounds with this structure type including the systems with light rare earth metals. The largest number of isotopic compounds have been found in $R\text{-T-Al}$ ($T=\text{Cr, Mn, Fe, Cu, Re}$) [6] and $R\text{-T-In}$ ($T=\text{Cu, Ag}$) systems [7], while fewer compounds have been reported for related systems with gallium and silicon [6]. The ThMn_{12} type is characterized by a low content of rare earth metal and high coordination numbers (CN) of all atoms (CN=20 for the Th atoms and CN=12–14 for the Mn atoms). This structure type is

closely related to the CaCu_5 structure type [8] and can be derived from it by substitution of one R atom by a pair of T component atoms in the unit cell following the scheme: $2RT_5 = R_2T_{10} \rightarrow RT'_2T_{10} \rightarrow RT_{12}$. In cases of strong differences in nature and size of the T component atoms, the atoms can be ordered with the formation of the superstructure type CeMn_4Al_8 [9]. In our earlier work we found the existence of compounds with the ThMn_{12} type in $R\text{-Mn-}\{\text{Fe, Co, Ni}\}$ systems, but only the values of the cell parameters have been determined for them using powder X-ray diffraction [4, 5]. These compounds can be considered as promising magnetic materials.

Therefore, in this paper we report on the synthesis of high-quality $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ single crystals and the determination of the crystal structure of this compound.

2 Experimental details

A sample of nominal composition $\text{Sm}_{7.7}\text{Ni}_{40}\text{Mn}_{52.3}$ was synthesized from the high-purity elements ($\text{Sm} \geq 99.9$ wt.%, $\text{Ni} \geq 99.92$ wt.%, and $\text{Mn} \geq 99.90$ wt.%) by arc-melting under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components, the sample was melted twice. The ingot was annealed at 600°C in an evacuated quartz ampoule for 720 h and subsequently quenched in cold water. The weight loss during the preparation of the sample was less than 1% of the total mass of 2 g.

Laue and rotation diffraction patterns of selected single crystals showed tetragonal symmetry with lattice parameters $a \sim 8.6$ and $c \sim 4.7$ Å. Integrated intensities measured at room temperature with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) on an Oxford Diffraction Xcalibur four-circle diffractometer equipped with a CCD camera confirmed the tetragonal lattice. Data collection and reduction were made using CRYSTALIS CCD and CRYSTALIS RED programs [10] taking into account a numerical absorption correction. The structure was solved by Direct Methods, and refined using the SHELX-2014 program package [11].

The chemical composition of the selected crystals was checked with a field-emission scanning electron microscope (FEINovaNanoSEM 230) equipped with an EDS

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analyzer (EDAX GenesisXM4, accelerating voltage 20 kV, exposure time 120 s).

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-1958794.

Table 1: Crystal data and structure refinement details for $\text{SmNi}_{5.2}\text{Mn}_{6.8}$.

Empirical formula	$\text{SmNi}_{5.2}\text{Mn}_{6.8}$
Formula weight	829.25
Crystal color	Black
Crystal size, mm ³	$0.069 \times 0.035 \times 0.026$
Space group	$I4/mmm$ (No. 139)
Pearson code	$tI26$
Unit cell dimensions	
a , Å	8.6528(3)
c , Å	4.8635(3)
Volume, Å ³	364.13(3)
Number of formula units per unit cell	2
Calculated density, g cm ⁻³	7.56
Absorption coefficient, mm ⁻¹	32.2
$F(000)$, e	755
θ range for data collection	$3.330\text{--}29.970$
Index ranges hkl	$\pm 11, \pm 11, \pm 6$
Reflections collected	1955
Independent reflections/ R_{int}	171/0.0277
Reflections with $I > 2\sigma(I)$	161
Refinement method	Full-matrix least-square on F^2
Data/ref. parameters	171/17
Goodness-of-fit on F^2	1.195
Final indices $R1/wR2$ [$I > 2\sigma(I)$]	0.0175/0.0372
Final indices $R1/wR2$ (all data)	0.0195/0.0387
Largest diff. peak/hole, e Å ⁻³	3.31/−0.91

3 Results and discussion

Analysis of the XRD data collected for $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ indicated that the compound crystallizes with a centrosymmetric structure, space group $I4/mmm$. The structure type ThMn_{12} was assigned and the structure was refined with anisotropic displacement parameters for all atoms. A final electron density difference map was flat and did not reveal any significant residual peaks. The crystal data and details of the data collection are given in Table 1, while the atomic coordinates and the displacement parameters are listed in Table 2. All crystallographic positions are fully occupied, but the atomic positions $8f$ and $8j$ are occupied by a mixture of manganese and nickel atoms with ratios of Mn to Ni of 0.24(3):0.76(3) and 0.46(3):0.54(3), respectively. The refined atomic positions for $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ are similar to the respective positions of atoms in the ThMn_{12} type [1]. The refined composition is in good agreement with the results of the EDX analyses (8 at% Sm: 52 at% Mn: 40 at% Ni).

A projection of the unit cell of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ onto the crystallographic ab plane and the coordination polyhedra of all atoms are shown on Fig. 1. The samarium atom is in the center of a 20-vertex polyhedron $[\text{SmMn}_4\text{T}_{16}]$ similar to the environment of the thorium atoms in the ThMn_{12} structure. The smallest atoms in $\text{SmNi}_{5.2}\text{Mn}_{6.8}$, i.e. the mixture of Mn/Ni atoms, are located inside the icosahedra $[\text{T}1\text{T}_6\text{Mn}_4\text{Sm}_2]$ and $[\text{T}2\text{T}_6\text{Mn}_4\text{Sm}_2]$ with CN=12, while the bigger manganese atoms have 14 neighbors $[\text{MnT}_8\text{Mn}_5\text{Sm}]$. Similar situations have been observed for the compounds $\text{ErCu}_{5.1}\text{In}_{6.9}$ [12] and $\text{YbAg}_{5.4}\text{In}_{6.6}$ [13], where the bigger In atoms, compared with the mixtures (Cu/In) or (Ag/In), also reside in 14-vertex polyhedra.

The main interatomic distances and their values of reductions orientated at the sum of atomic radii ($\Delta = 100(d - \Sigma r)/\Sigma r$, where Σr is the sum of the respective

Table 2: Atomic coordinates and displacement parameters for $\text{SmNi}_{5.2}\text{Mn}_{6.8}$.^a

Atom	WS	Occupation	x	y	z	U_{iso}
Sm	$2a$	1	0	0	0	0.0149(2)
T1	$8f$	0.24(3)Mn + 0.76(3)Ni	1/4	1/4	1/4	0.0080(3)
T2	$8j$	0.46(3)Mn + 0.54(3)Ni	0.22011(10)	1/2	0	0.0098(3)
Mn	$8i$	1	0.35615(10)	0	0	0.0097(2)
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm	0.0101(2)	U_{11}	0.0245(4)	0	0	0
T1	0.0090(3)	U_{11}	0.0058(4)	0.00087(19)	U_{23}	0.0005(3)
T2	0.0064(4)	0.0142(5)	0.0087(4)	0	0	0
Mn	0.0090(4)	0.0086(4)	0.0115(4)	0	0	0

^a U_{iso} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

Fig. 1: Projection of the unit cell of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ onto the crystallographic ab plane and coordination polyhedra of the atoms.

atomic radii) along with the coordination numbers of atoms for $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ are listed in Table 3 (values of the atomic radii are taken from ref. [14]: $r(\text{Sm})=1.80$, $r(\text{Ni})=1.24$, $r(\text{Mn})=1.27$, and calculated $r(T1)=1.24$ and $r(T2)=1.25$ Å). Most deviations of the interatomic distances from the sums of relevant atomic radii are very small (no more than 8%). Some Mn–Mn and $T1$ – $T1$ interatomic distances are slightly shorter compared to the sum of the respective atomic radii. Such shortening of

interatomic distances allows us to consider a pairing of the respective atoms. The manganese atoms form dumbbells, while the $T1$ atoms are combined to chains along the c direction. Two Sm atoms, four Mn atoms and 14 T atoms form the coordination sphere of the Mn_2 dumbbells in the $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ structure (Fig. 2). Such clusters $[\text{Mn}_2(\text{Sm}_2\text{Mn}_4T_{14})]$ are connected through common faces

Table 3: Interatomic distances (d , Å), Δ values ($\Delta=100(d-\Sigma r)/\Sigma r$, where Σr is the sum of the respective atomic radii [13]) and atomic coordination numbers (CN) for $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ ^a

Atom		d (Å)	Δ (%)	Atom	d (Å)	Δ (%)	
Sm	4 Mn	3.0817(1)	0.4	T_2	4 T_1	2.4949(1)	0.2
CN = 20	8 T_2	3.0888(1)	1.3	CN = 12	2 T_2	2.6935(9)	7.7
	8 T_1	3.2920(1)	8.3		2 Mn	2.7017(6)	7.2
					2 Mn	2.7230(11)	8.1
					2 Sm	3.0888(5)	1.37
T_1	2 T_1	2.4318(2)	−1.9	Mn	1 Mn	2.4894(12)	−2.0
CN = 12	4 T_2	2.4949(1)	0.2	CN = 14	4 T_1	2.6460(3)	5.4
	4 Mn	2.6460(3)	5.4		2 T_2	2.7017(6)	7.2
	2 Sm	3.2920(1)	8.3		2 T_2	2.7230(6)	8.1
					4 Mn	3.0020(5)	7.21
					1 Sm	3.0817(9)	0.38

^a $T1 = 0.76(3)\text{Ni} + 0.24(3)\text{Mn}$; $T2 = 0.54(3)\text{Ni} + 0.45(3)\text{Mn}$.

Fig. 2: The arrangement of the clusters $[\text{Mn}_2(\text{Sm}_2\text{Mn}_4T_{14})]$ in the crystal structure of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$.

and form grids perpendicular to the c direction, in the holes of which the Sm atoms are located. The coordination polyhedra of the T1 atoms are connected along the c direction to form tubes $[T_1(\text{Sm}_3\text{Mn}_6T_6)]$ in the middle of which there is the T1 atom chain (Fig. 3). Further, these tubes are connected through common faces and completely fill the space in the structure of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$.

The $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ structure can also be considered as a combination of simple fragments: tetragonal motifs of the CeMg_2Si_2 structure ($P4/mmm$, $a = 4.250$, $c = 5.765$ Å) [8] and slabs of a hypothetical substructure “ Mn_4T_4 ” (Fig. 4).

The results of our investigation together with all previous data [4, 5] indicate that $\text{Sm}(\text{Mn},\text{Ni})_{12}$ forms a homogeneity range with Mn/Ni substitutions. The formula of the compound can be described as $\text{SmNi}_{8.10-3.94}\text{Mn}_{3.90-8.06}$. The lattice parameters increase due to substitution of smaller Ni atoms with larger Mn atoms ($a = 8.465-8.693$, $c = 4.766-4.864$ Å).

Fig. 3: The $[T_1(\text{Sm}_3\text{Mn}_6T_6)]_\infty$ tube and the arrangement of these tubes in the crystal structure of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$.

Fig. 4: Packing of Mn_4T_4 and CeMg_2Si_2 slabs in the crystal structure of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$.

4 Conclusions

The crystal structure of $\text{SmNi}_{5.2}\text{Mn}_{6.8}$ has been investigated by using single crystal X-ray data. This compound forms a tetragonal ThMn_{12} -type unit cell (space group $I4/mmm$, $a = 8.6528(3)$, $c = 4.8635(3)$ Å), observed before for the binary phases RMn_{12} with $R = \text{Y, Gd, Tb, Dy, Ho, Er, Tm}$ [2, 3] and for the ternary systems $R\text{-Mn-T}$ with $R = \text{Ce, Pr, Nd, Sm}$ and $T = \text{Fe, Co, Ni}$ [4, 5]. Mixtures of Mn/Ni atoms occupy two crystallographic positions in the structure of this compound while the remaining two positions are occupied solely by Sm and Mn atoms.

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