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Syntheses and Crystal Structure of the Ternary Silicides RE_2Si_2Mg (RE = Y, La–Nd, Sm, Gd–Lu) and Structure Refinement of Dy_5Si_3

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Summary. The rare earth metal–magnesium–silicides RE_2Si_2Mg (RE = Y, La–Nd, Sm, Gd–Lu) were prepared by induction melting of the elements in sealed tantalum tubes in a water-cooled sample chamber of a high-frequency furnace. The silicides were investigated *via* X-ray powder diffraction. The structures of Sm_2Si_2Mg and Dy_2Si_2Mg were refined from X-ray single crystal diffractometer data: Mo_2FeB_2 type, $P4/mbm$, $a = 727.86(7)$, $c = 428.16(6)$ pm, $wR2 = 0.0194$, 206 F^2 values, 13 variable parameters for Sm_2Si_2Mg and $a = 713.85(7)$, $c = 419.07(6)$ pm, $wR2 = 0.0331$, 286 F^2 values, 12 variable parameters for Dy_2Si_2Mg. The samarium compound shows a small homogeneity range $Sm_{2+x}Si_2Mg_{1-x}$. The investigated single crystal had the refined composition $Sm_{2.022(3)}Si_2Mg_{0.978(3)}$. The RE_2Si_2Mg silicides are 1:1 intergrowth structures of CsCl and AlB_2 related slabs of compositions REMg and $RESi_2$. Crystals of the binary silicide Dy_5Si_3 were obtained as side product. The structure was refined from X-ray single crystal data: Mn_5Si_3 type, $P6_3/mcm$, $a = 841.0(2)$, $c = 631.3(1)$ pm, wR2 = 0.0661, 269 F^2 values, 12 variable parameters.

Keywords. Rare Earth Compounds; Silicides; Crystal Chemistry.

Introduction

The binary transition metal (T), rare earth metal (RE), and actinoid (An) silicides T_3Si_2 (T = Cr, Zr, Nb, Mo, Hf, W), RE_3Si_2 (RE = La, Ce, Pr), and An_3Si_2 (An = Th, U, Np, Pu) with tetragonal U_3Si_2 type are 1:1 intergrowth structures of distorted AlB_2- and W-like slabs of compositions TSi_2 ($RESi_2$, $AnSi_2$) and T_2 (RE_2, An_2). An overview on these compounds is given in a recent review [1]. The W-like slabs can also be occupied by two different metals in an ordered manner, leading to CsCl related slabs. With this ordering pattern, the ternary silicides RE_2Si_2Al

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(*RE* = Sc, Yb) [2, 3], RE_2Si_2Li (*RE* = Y, Nd) [4], Ce_2Si_2Mg [5], Dy_2Al_2Si [6], RE_2Si_2Sc (*RE* = Ce, Nd, Sm) [7–10], and RE_2Si_2Y (*RE* = La, Ce) [8] have been reported. In the germanium based systems, only the series of RE_2Ge_2Mg (*RE* = Y, La–Nd, Sm, Gd, Tb) germanides [11, 12] is known.

We have now started a more systematic investigation of the silicon based ternary systems with respect to U_3Si_2 type compounds. Herein we report on the synthesis and structural characterization of the ternary silicides RE_2Si_2Mg with *RE* = Y, La–Nd, Sm, Gd–Lu. So far, only lattice parameters of the 12 K antiferromagnet Ce_2Si_2Mg [5] have been reported. The existence of La_2Si_2Mg, Ce_2Si_2Mg, Nd_2Si_2Mg [13], and Yb_2Si_2Mg [14] has been announced, however, to the best of our knowledge, no basic crystallographic parameters have been reported.

During our phase analytical investigations we got also single crystals of the binary silicide Dy_5Si_3 with Mn_5Si_3 type structure. Up to now, only powder data are available for this 125 K antiferromagnet [15–19]. A single crystal structure refinement is reported herein.

Results and Discussion

The ternary silicides RE_2Si_2Mg (*RE* = Y, La–Nd, Sm, Gd–Lu) have been prepared and characterized by X-ray diffraction. They crystallize with a ternary ordered version of the U_3Si_2 type [1] and are isotypic with the recently reported germanides RE_2Ge_2Mg (*RE* = Y, La–Nd, Sm, Gd, Tb) [12]. The cell volumes are plotted in Fig. 1 as a function of the rare earth element. As expected from the lanthanoid contraction, the cell volume decreases from the lanthanum to the lutetium compound. Similar to the germanide series, also the Y_2Si_2Mg cell volume fits between the terbium and the dysprosium compound. The volumes of the silicides are between 2–3% smaller than those of the germanides. The cerium and ytterbium compounds show no anomaly in the cell volume. We can thus expect stable trivalent cerium and ytterbium in Ce_2Si_2Mg and Yb_2Si_2Mg. For Ce_2Si_2Mg, the trivalent state was evident from the magnetic data (2.47 μ_B/Ce atom) [5].

As is evident from Fig. 2, the RE_2Si_2Mg silicides are intergrowth structures of distorted CsCl and AlB_2 related slabs of compositions *RE*Mg and $RESi_2$. The Si–Si

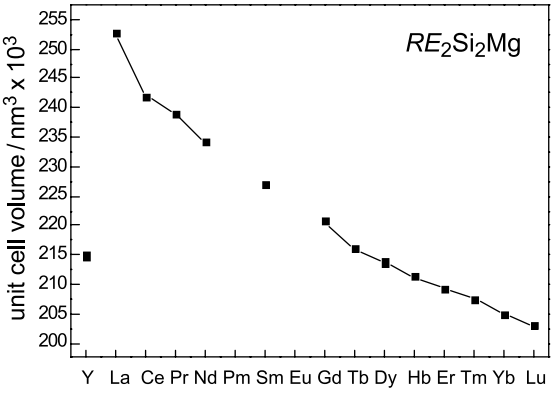

Fig. 1. Plot of the cell volumes of the RE_2Si_2Mg silicides

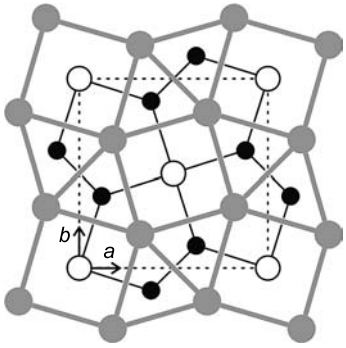

Fig. 2. Projection of the Dy_2Si_2Mg structure onto the *xy* plane; all atoms lie on mirror planes at $z = 0$ (Si, Mg) and $z = 1/2$ (Dy); dysprosium, silicon, and magnesium atoms are drawn as grey, filled, and open circles, respectively; the CsCl and AlB_2 related slabs and the $[Si_2Mg]$ network are emphasized

distances of 239 pm in Sm_2Si_2Mg and Dy_2Si_2Mg are close to the Si–Si single bond distance of 235 pm in elemental silicon [25]. The crystal chemistry of Mo_2FeB_2 type intermetallics has recently been reviewed [1]. For more details we refer to this article. Chemical bonding in the RE_2Si_2Mg intermetallics can safely be described within a rigid band model in comparison with Ce_2Ge_2In [26] and Gd_2Ge_2Mg [11]. The electronic structure calculations for these germanides revealed strong Ge–Ge bonding within the Ge_2 dumb-bells.

Table 1. Atomic coordinates and isotropic displacement parameters (pm^2) for $Sm_{2.022(3)}Si_2Mg_{0.978(3)}$, Dy_2Si_2Mg (space group $P4/mbm$), and Dy_5Si_3 (space group $P6_3/mcm$); U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor; the positional parameters of Dy_5Si_3 derived from neutron powder data [19] are given in italics

Atom	*Wyckoff* site	*x*	*y*	*z*	U_{eq}
$Sm_{2.022(3)}Si_2Mg_{0.978(3)}$					
Sm	4*h*	0.17888(2)	$1/2+x$	1/2	63(1)
Si	4*g*	0.3837(1)	$1/2+x$	0	72(3)
Mg/Sm[a]	2*a*	0	0	0	104(8)
Dy_2Si_2Mg					
Dy	4*h*	0.17820(2)	$1/2+x$	1/2	56(1)
Si	4*g*	0.3816(2)	$1/2+x$	0	54(3)
Mg	2*a*	0	0	0	80(5)
Dy_5Si_3					
Dy1	6*g*	0.24375(10) *0.2370(3)*	0	1/4	93(3)
Dy2	4*d*	2/3	1/3	0	106(3)
Si	6*g*	0.6066(6) *0.6143(4)*	0	1/4	95(9)

[a] This site shows mixed occupancy: 97.8(3)% Mg and 2.2(3)% Sm

Single crystals of Dy_5Si_3 were obtained as a side product during the first synthesis attempts for Dy_2Si_2Mg. So far, this binary silicide was only characterized on the basis of X-ray and neutron powder data [15–19]. The single crystal data essentially confirm the structure refinement at 150 K based on neutron powder data [19], however, the positional parameters determined here from the single crystal X-ray data are slightly different (Table 1). This has a drastic effect especially of the Dy–Si interatomic distances which differ by up to 10 pm (Table 1). The difference in the positional parameters and thus the interatomic distances is most likely due to the different data collection temperatures (RT *vs.* 150 K). The crystal chemistry and chemical bonding of isotypic Lu_5Si_3 [24] has been discussed recently. For details and drawings we refer to this paper.

Experimental

Synthesis

Starting materials for the preparation of the silicides RE_2Si_2Mg and Dy_5Si_3 were ingots of the rare earth metals (Johnson Matthey, Chempur, or Kelpin, >99.9%), silicon lumps (Wacker, >99.9%), and a magnesium rod (Johnson Matthey, ∅ 16 mm, >99.5%). In a first step, the rare earth metal pieces were melted under 600 mbar argon to small buttons in an arc-melting furnace [20]. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The surface of the magnesium rod was then removed on a turning lathe in order to remove impurities and the rod was subsequently cut into thin plates. Pieces of the magnesium rod, the arc-melted rare earth metal buttons, and pieces of the silicon lumps were then weighed in the ideal 2*RE*:2Si:1Mg atomic ratios and sealed in small tantalum tubes (*ca.* 1 cm^3 volume) under an argon pressure of *ca.* 800 mbar.

The tantalum containers were put in a water-cooled sample chamber [21] of a high-frequency furnace (Hüttinger Elektronik, Freiburg, Typ TIG 5/300), heated for 15 minutes at *ca.* 1500 K and subsequently annealed for another 4 hours at ca. 1070 K. Finally the tube was quenched to room temperature by switching off the power of the generator. The temperature was controlled through a Sensor Therm Metis MS09 pyrometer with an accuracy of ±30 K.

The brittle products could easily be separated from the tantalum tubes. No reaction with the container material was observed. In some cases, small irregularly shaped single crystals with metallic lustre occurred directly after the inductive annealing process. During several preparations small amounts of volatile magnesium had distilled at the upper, colder parts of the tantalum tubes, leading to a lower magnesium content in the sample. This way the binary silicide Dy_5Si_3 formed. Compact pieces and powders of the silicides are stable in air over months.

Scanning Electron Microscopy

The single crystals investigated on the diffractometer have been analyzed by EDX measurements using a LEICA 420 I scanning electron microscope with the rare earth trifluorides, SiO_2, and MgO as standards. No impurity elements were detected. Various point analyses on the crystals revealed the compositions 45 ± 2 at.-% Sm:39 ± 2 at.-% Si:16 ± 2 at.-% Mg, 38 ± 2 at.-% Dy:40 ± 2 at.-% Si:22 ± 2 at.-% Mg, and 55 ± 3 at.-% Dy:45 ± 3 at.-% Si, close to the values obtained from the structure refinements. The EDX analyses nicely reflect the slightly higher samarium content observed for $Sm_{2.022(3)}Si_2Mg_{0.978(3)}$.

X-Ray Film Data and Structure Refinemens

All samples were studied through *Guinier* powder patterns using Cu $K\alpha_1$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The *Guinier* camera was equipped with an imaging plate system (Fujifilm BAS-1800). The lattice parameters (Table 2) were deduced from

Table 2. Lattice parameters of the tetragonal silicides RE_2Si_2Mg (space group $P4/mbm$, Mo_2FeB_2 type) and Dy_5Si_3 (space group $P6_3/mcm$, Mn_5Si_3 type)

Compound	a/pm	c/pm	V/nm^3
Y_2Si_2Mg	714.35(5)	420.72(2)	0.2147
La_2Si_2Mg	752.25(8)	446.26(6)	0.2525
Ce_2Si_2Mg	742.4(1)	438.90(9)	0.2419
Ce_2Si_2Mg [2]	743.0	439.1	0.2424
Pr_2Si_2Mg	740.09(6)	436.02(6)	0.2388
Nd_2Si_2Mg	734.62(7)	433.84(5)	0.2341
Sm_2Si_2Mg	727.86(7)	428.16(6)	0.2268
Gd_2Si_2Mg	720.33(9)	425.10(8)	0.2206
Tb_2Si_2Mg	716.51(9)	420.82(8)	0.2160
Dy_2Si_2Mg	713.85(7)	419.07(6)	0.2136
Ho_2Si_2Mg	711.27(8)	417.28(6)	0.2111
Er_2Si_2Mg	708.92(7)	416.12(6)	0.2091
Tm_2Si_2Mg	708.3(1)	413.33(7)	0.2074
Yb_2Si_2Mg	704.9(1)	412.24(8)	0.2048
Lu_2Si_2Mg	702.1(1)	411.41(9)	0.2028
Dy_5Si_3	841.0(2)	631.3(1)	0.3867
Dy_5Si_3 [16]	839	628	0.3828
Dy_5Si_3 [17]	837.9(3)	629.0(2)	0.3825
Dy_5Si_3 [19] (150 K data)	836.89(5)	629.60(4)	0.3819

least-squares fits of the powder data. The indexing of the powder patterns was facilitated through intensity calculations [22] using the atomic positions obtained from the structure refinements. The lattice parameters derived here for Ce_2Si_2Mg and Dy_5Si_3 are in good agreement with the literature data (see Table 2).

Small, irregularly shaped single crystals of Sm_2Si_2Mg, Dy_2Si_2Mg, and Dy_5Si_3 were selected from the annealed samples and examined by *Laue* photographs on a *Buerger* precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Intensity data were recorded at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized MoK_α radiation ($\lambda = 71.073$ pm) and a scintillation counter with pulse-height discrimination. The scans were taken in the $\omega/2\theta$ mode and empirical absorption corrections were applied on the basis of psi-scan data followed by spherical absorption corrections. All relevant crystallographic details for the data collections and evaluations are listed in Table 3.

The isotypy of the RE_2Si_2Mg silicides with the recently reported germanides was already evident from the *Guinier* data. The atomic positions of Ce_2Ge_2Mg [12] were taken as starting values and the structures of Sm_2Si_2Mg and Dy_2Si_2Mg were successfully refined using SHELXL-97 (full-matrix least-squares on F_o^2) [23] with anisotropic atomic displacement parameters for all sites.

Since the isotypic germanide $La_{2+x}Ge_2Mg_{1-x}$ showed a significant homogeneity range, the occupancy parameters of Sm_2Si_2Mg and Dy_2Si_2Mg were refined in separate series of least-squares cycles. While all sites of Dy_2Si_2Mg were fully occupied within one standard deviation, a small homogeneity range was observed for the samarium based crystal, leading to the composition $Sm_{2.022(3)}Si_2Mg_{0.978(3)}$ for the investigated crystal.

The atomic positions of Lu_5Si_3 [24] were taken as starting values for Dy_5Si_3. The refinement went smoothly to the residuals listed in Table 3. All sites were fully occupied within two standard deviations. Final difference *Fourier* synthesis revealed no significant residual peaks for all three data sets (see Table 3). The positional parameters and interatomic distances are listed in Tables 1 and 4. Further

Table 3. Crystal data and structure refinement for $Sm_{2.022(3)}Si_2Mg_{0.978(3)}$, Dy_2Si_2Mg (space group $P4/mbm$, Z = 2), and Dy_5Si_3 (space group $P6_3/mcm$, Z = 2)

Empirical formula	$Sm_{2.022(3)}Si_2Mg_{0.978(3)}$	Dy_2Si_2Mg	Dy_5Si_3
Molar mass	381.19 g/mol	405.49 g/mol	896.77 g/mol
Unit cell dimensions	Table 1	Table 1	Table 1
Calculated density	5.58 g/cm^3	6.31 g/cm^3	7.70 g/cm^3
Crystal size	$20 \times 30 \times 30$ μm^3	$15 \times 40 \times 60$ μm^3	$40 \times 60 \times 60$ μm^3
Transm. Ratio (max/min)	0.641/0.480	0.652/0.473	0.714/0.409
Absorption coefficient	26.1 mm^{-1}	35.2 mm^{-1}	48.1 mm^{-1}
$F(000)$	328	344	744
θ range	3° to 30°	4° to 35°	3° to 35°
Range in hkl	±10, ±10, ±6	±11, ±11, ±6	±13, ±13, +8
Total no. reflections	2436	3339	2654
Independent reflections	206 ($R_{int} = 0.0399$)	286 ($R_{int} = 0.0606$)	269 ($R_{int} = 0.1212$)
Reflections with $I > 2\sigma(I)$	192 ($R_{sigma} = 0.0155$)	264 ($R_{sigma} = 0.0217$)	204 ($R_{sigma} = 0.0424$)
Data/parameters	206/13	286/12	269/12
Goodness-of-fit on F^2	1.254	1.130	1.060
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0121$ $wR2 = 0.0192$	$R1 = 0.0162$ $wR2 = 0.0324$	$R1 = 0.0311$ $wR2 = 0.0603$
R indices (all data)	$R1 = 0.0142$ $wR2 = 0.0194$	$R1 = 0.0192$ $wR2 = 0.0331$	$R1 = 0.0515$ $wR2 = 0.0661$
Extinction coefficient	0.0153(6)	0.0148(9)	0.0113(9)
Largest diff. Peak and hole	0.61 and −0.69 e/Å^3	1.12 and −1.30 e/Å^3	3.06 and −1.66 e/Å^3

Table 4. Interatomic distances (pm) in the structures of $Sm_{2.022}Si_2Mg_{0.978}$, Dy_2Si_2Mg, and Dy_5Si_3 calculated with the lattice parameters taken from X-ray powder data; standard deviations are given in parenthesis; the 150 K neutron powder data from Ref. [19] are listed for comparison

$Sm_{2.022}Si_2Mg_{0.978}$				Dy_2Si_2Mg				Dy_5Si_3 (this work)				Dy_5Si_3 [19]
Sm:	2	Si	300.5(1)	Dy:	2	Si	293.4(1)	Dy1:	2	Si	289.3(4)	282.0
	4	Si	306.7(1)		4	Si	300.9(1)		1	Si	305.1(5)	315.8
	4	Mg	342.7(1)		4	Mg	335.9(1)		2	Si	339.8(2)	338.5
	1	Sm	368.3(1)		1	Dy	359.8(1)		2	Dy1	355.1(2)	343.5
	4	Sm	378.4(1)		4	Dy	371.4(1)		4	Dy2	361.0(1)	362.7
	2	Sm	428.2(1)		2	Dy	419.1(1)		4	Dy1	376.4(1)	372.1
Si:	1	Si	239.4(3)	Si:	1	Si	239.0(3)	Dy2:	6	Si	303.1(2)	303.8
	2	Mg	291.8(1)		2	Mg	285.2(1)		2	Dy2	315.7(1)	314.8
	2	Sm	300.5(1)		2	Dy	293.4(1)		6	Dy1	361.0(1)	362.7
	4	Sm	306.7(1)		4	Dy	300.9(1)	Si:	2	Dy1	289.3(4)	282.0
Mg:	4	Si	291.8(1)	Mg:	4	Si	285.2(1)		4	Dy2	303.1(2)	303.8
	8	Sm	342.7(1)		8	Sm	335.9(1)		1	Dy1	305.1(5)	315.8
									2	Dy1	339.8(2)	338.5

details on the structure refinements may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry Nos. CSD-415116 ($Sm_{2.022}Si_2Mg_{0.978}$), CSD-415117 (Dy_2Si_2Mg), and CSD-415118 (Dy_5Si_3).

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References

[1] Lukachuk M, Pöttgen R (2003) Z Kristallogr **218**: 767
[2] Tyvanchuk AT, Yanson TI, Kotur BYa, Zarechnyuk OS, Kharakterova ML (1988) Izv Akad Nauk SSSR Metally **4**: 187
[3] Krahnenberg C, Mewis A (2000) Z Anorg Allg Chem **626**: 1448
[4] Steinberg G, Schuster H-U (1979) Z Naturforsch **34b**: 1237
[5] Dhar SK, Manfrinetti P, Palenzona A (1997) J Alloys Compd **252**: 24
[6] Yanson TI, Zarechnyuk OS (1984) Vestn L'vov Univ Ser Khim **25**: 11
[7] Bodak OI, Mokra IR (1978) III Vsesoyizn Konf po Kristallokhimii Intermetallicheskikh Soedinenii (III All-Union Conf on Crystal Chemistry of Intermetallic Compounds), L'vov, p 66
[8] Dhar SK, Manfrinetti P, Palenzona A, Kimura Y, Kozaki M, Onuki Y, Takeuchi T (1999) Physica B **271**: 150
[9] Banakh OE, Kotur BYa (1998) J Alloys Compd **268**: L3
[10] Kotur BYu, Mokra IR, Toporinskii AYa (1991) Metally **5**: 204
[11] Choe W, Miller GJ, Levin EM (2001) J Alloys Compd **329**: 121
[12] Kraft R, Pöttgen R (2004) Monatsh Chem **135**: 1327
[13] Kubata C, Leoni S, Nesper R (2000) Chimia **54**: 415
[14] Merlo F, Pani M, Fornasini ML (1993) J Less-Common Met **196**: 145
[15] Gladyshevskii EI, Kripyakevich PI (1964) J Struct Chem **5**: 853
[16] Mayer I, Shidlovsky I (1969) Inorg Chem **8**: 1240
[17] Mayer I, Felner I (1972) J Less-Common Met **29**: 25
[18] Ganapathy EV, Kugimiya K, Steinfink H, Tchernev DI (1976) J Less-Common Met **44**: 245
[19] Semitelou JP, Yakinthos JK (2003) J Magn Magn Mater **265**: 152
[20] Pöttgen R, Gulden Th, Simon A (1999) GIT Labor Fachzeitschrift **43**: 133
[21] Kußmann D, Hoffmann R-D, Pöttgen R (1998) Z Anorg Allg Chem **624**: 1727
[22] Yvon K, Jeitschko W, Parthé E (1977) J Appl Crystallogr **10**: 73
[23] Sheldrick GM (1997) SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen
[24] Rodewald UCh, Heying B, Johrendt D, Pöttgen R (2004) Z Naturforsch **59b**: 969
[25] Donohue J (1974) The Structures of the Elements. Wiley, New York
[26] Zaremba VI, Johrendt D, Rodewald UCh, Pöttgen R (2005) Solid State Sci **7**: 998