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# Synthesis, flux crystal growth, structure and properties of the new rare-earth compounds $EuAl_{4-x}Si_x$ ($x \sim 1$), TmAlSi and LuAlSi

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**Abstract**

Reported are the crystal growth and properties of two new stoichiometric TmAlSi and LuAlSi compounds, crystallizing with the *C*-centered orthorhombic YAlGe-type, and of the non-stoichiometric $EuAl_{4-x}Si_x$ ($x \sim 1$), a ternary derivative of the body-centered tetragonal $BaAl_4$-type. All three compounds were synthesized from reactions of the corresponding metals, and using an excess of elemental aluminum as a flux. Their crystal structures were determined by single-crystal X-ray crystallography: space group *Cmcm* (No. 63) with cell parameters $a = 3.9638(7)$ Å, $b = 10.116(2)$ Å and $c = 5.6314(10)$ Å for TmAlSi, and $a = 3.964(2)$ Å, $b = 10.034(4)$ Å and $c = 5.598(3)$ Å for LuAlSi, respectively, and space group *I*4/*mmm* (No. 139) with $a = 4.3826(11)$ Å and $c = 10.785(6)$ Å for $EuAl_{2.96(2)}Si_{1.04(2)}$, respectively. Magnetization measurements carried out as a function of the temperature suggest the Eu- and the Tm-compounds to order magnetically below ~17 K and ~6 K, respectively.

*Keywords:* Rare-earth intermetallics; Crystal structure; Magnetic measurements; $EuAl_{4-x}Si_x$; TmAlSi; LuAlSi

## 1. Introduction

A number of ternary rare-earth alumo-silicides (RE–Al–Si) have recently been synthesized from pure elements by high temperature reactions, carried out in aluminum flux [1]. Under these experimental conditions, large single crystals of three general structure types can be easily grown: (1) $REAl_xSi_{2-x}$, $0.8 < x < 1.2$, non-stoichiometric ternary derivatives of the body-centered tetragonal α-$ThSi_2$-type [2], formed by the early rare-earths (RE = La, Ce, Pr, Nd, Sm and Gd); (2) stoichiometric $RE_2Al_3Si_2$ compounds, formed when RE = Tb, Dy, Ho, Er and Tm, i.e. the late rare-earths, which crystallize in the *C*-centered monoclinic $Y_2Al_3Si_2$-type [3]; (3) $EuAl_2Si_2$ and $YbAl_2Si_2$ with the trigonal $CaAl_2Si_2$-type [4], formed by the divalent Eu and Yb.

Herein, we discuss the continuation of these systematic studies, and report on the crystal growth and properties of two new stoichiometric TmAlSi and LuAlSi compounds, crystallizing with the *C*-centered orthorhombic YAlGe-type [5], and of the non-stoichiometric $EuAl_{4-x}Si_x$, a ternary derivative of the body-centered tetragonal $BaAl_4$-type [6]. The formation of TmAlSi and LuAlSi, along with the inability to synthesize other analogs, are peculiarities with regard to the late lanthanide elements, Tm and Lu, which are most certainly due to their almost completely and completely filled f-shells, and the corresponding small ionic sizes, respectively. On the other hand, the fact that non-stoichiometric $EuAl_{4-x}Si_x$ ($x \sim 1$, i.e. $EuAl_{2.96}Si_{1.04}$ hereafter) can be made only with Eu is another example of deviation from the general structural trends across the lanthanide family, and it is ascribed to the tendency of Eu to form more stable compounds when in $f^7$ configuration, i.e. $Eu^{2+}$.

## 2. Experimental

### 2.1. Synthesis

All starting materials were used as received: Eu, Tm and Lu (Ames Laboratory, ingots, >99.99% metal basis), Al (shots, Alfa) and Si (lump, Alfa), both with purity greater than 99.999%. The metals were kept and handled in an argon-filled glove box (moisture and $O_2$ levels ~0.1 ppm). Mixtures of the pure elements in ratios RE:Si:Al = 1:1:20 were loaded in alumina containers, which were subsequently enclosed in evacuated fused silica jackets by flame-sealing. The reactions were carried out using the following temperature profile: (1) ramping rate 250 °C/h, reaction temperature 1175 °C; (2) dwell at that temperature for 2 h; (3) cooling to 750 °C at a rate of −30 °C/h. Aluminum flux was

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Table 1
Selected data collection and refinement parameters for $EuAl_{2.96(2)}Si_{1.04(2)}$, TmAlSi and LuAlSi

| | | | |
|---|---|---|---|
| Empirical formula | $EuAl_{2.96(2)}Si_{1.04(2)}$ | TmAlSi | LuAlSi |
| Formula weight | 261.03 | 224.00 | 230.04 |
| Space group, $Z$ | $I4/mmm$, 2 | $Cmcm$, 4 | |
| Radiation, λ (Å) | Mo Kα, 0.71073 | | |
| Temperature (°C) | −150(2) | −20(2) | |
| Unit cell parameters | | | |
| $a$ (Å) | 4.3826(11) | 3.9638(7) | 3.964(2) |
| $b$ (Å) | | 10.116(2) | 10.034(4) |
| $c$ (Å) | 10.785(6) | 5.6314(10) | 5.598(3) |
| $V$ (Å$^3$) | 207.15(14) | 225.80(7) | 222.6(2) |
| $\rho_{calc}$ (g/cm$^3$) | 4.185 | 6.589 | 6.863 |
| $\mu$ (cm$^{-1}$) | 158.3 | 397.5 | 448.1 |
| Data/parameter | 93/8 | 171/14 | 169/14 |
| Final $R_1$[a] ($I>2\sigma_I$) | 0.0202 | 0.0160 | 0.0166 |
| Final $wR_2$[b] ($I>2\sigma_I$) | 0.0375 | 0.0390 | 0.0405 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $wR_2 = [\sum[w\cdot(F_o^2 - F_c^2)^2]/\sum[w\cdot(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2\cdot F_o^2 + (A\cdot P)^2 + B\cdot P]$, $P = (F_o^2 + 2F_c^2)/3$, where $A$ and $B$ are the weight coefficients.

Table 2
Atomic coordinates, isotropic displacement parameters ($U_{eq}$[a]) in $EuAl_{2.96(2)}Si_{1.04(2)}$, TmAlSi and LuAlSi

| Atom | Site | $x$ | $y$ | $z$ | $U_{eq}$ [Å$^2$] |
|---|---|---|---|---|---|
| | | | $EuAl_{2.96(2)}Si_{1.04(2)}$ | | |
| Eu | $2a$ | 0 | 0 | 0 | 0.0066(3) |
| Al1 | $4d$ | 0 | 1/2 | 1/4 | 0.0121(8) |
| Al/Si2 | $4e$ | 0 | 0 | 0.3833(3) | 0.0105(7) |
| | | | TmAlSi | | |
| Tm | $4c$ | 0 | 0.30541(4) | 1/4 | 0.0058(3) |
| Al | $4a$ | 0 | 0 | 0 | 0.0075(6) |
| Si | $4c$ | 0 | 0.6022(3) | 1/4 | 0.0070(5) |
| | | | LuAlSi | | |
| Lu | $4c$ | 0 | 0.30533(4) | 1/4 | 0.0067(3) |
| Al | $4a$ | 0 | 0 | 0 | 0.0083(7) |
| Si | $4c$ | 0 | 0.6023(3) | 1/4 | 0.0090(7) |

[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

effectively removed by centrifugation at 750 °C. The crystals (plates or small rods, depending on the structure type) had silver-metallic luster and appeared stable in air.

### 2.2. X-ray diffraction studies

Phase purity was checked by taking X-ray powder diffraction patterns at room temperature. These were done using a Philips X'Pert powder diffractometer equipped with Cu Kα radiation. The recorded powder patterns were compared with the theoretically calculated ones, and both the peak positions and the intensities were in excellent agreement.

Additionally, to check and unequivocally establish the structures, and to ascertain the crystals used in the property measurements, single crystals of $EuAl_{2.96}Si_{1.04}$ (platelet, 0.04 mm × 0.03 mm × 0.03 mm), TmAlSi (bar, 0.06 mm × 0.05 mm × 0.04 mm) and LuAlSi (bar, 0.07 mm × 0.05 mm × 0.03 mm) were selected from the reaction products and mounted on the top of glass fibers. Intensity data were collected on a Bruker SMART 1000 single-crystal diffractometer with monochromated Mo Kα radiation ($\omega$ scans, $2\theta_{max} \sim 58°$). Full spheres of diffraction data were collected using the SMART software [7], and were subsequently corrected for Lorentz and polarization effects and integrated with the SAINT package [8]. Empirical absorption correction was applied using SADABS [9]. The structures were refined on $F^2$ with the aid of the SHELXTL package [10]. List of important crystallographic parameters and details for the three refinements are summarized in Table 1. Final positional and isotropic thermal parameters and important distances are listed in Tables 2 and 3, respectively. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de), on quoting the depository numbers: CSD 415371 ($EuAl_{2.96(2)}Si_{1.04(2)}$); CSD 415372 (TmAlSi); CSD 415373 (LuAlSi).

### 2.3. Magnetic measurements

Temperature-dependent dc magnetization measurements for $EuAl_{2.96}Si_{1.04}$ and TmAlSi were performed in a Quantum Design MPMS magnetometer from 5 K to 300 K in a magnetic field $H = 0.05$ T. Different reaction batches were measured in order to provide reproducible results. In all cases the samples were prepared from carefully selected under a microscope single crystals. The samples, with a typical weight of approximately 10–15 mg, were loaded in plastic straws and secured with a low-signal diamagnetic tape. The raw data were corrected for the holder's contribution and converted to molar susceptibility.

### 2.4. Elemental analysis

Single crystals of $EuAl_{2.96}Si_{1.04}$ were mounted onto carbon tape, then placed in a JEOL 7400F electron microscope equipped with an INCA-Oxford energy-dispersive spectrometer. The microscope was operated at 10 μA beam current at 15 kV accelerating potential. The analysis was based on 15 spots (1 μm in

Table 3
Selected interatomic distances (Å) in $EuAl_{2.96(2)}Si_{1.04(2)}$, TmAlSi and LuAlSi

| $EuAl_{2.96(2)}Si_{1.04(2)}$ | | | |
|---|---|---|---|
| Eu | | | |
| 8 × Al/Si2 | 3.3448(13) | | |
| 8 × Al1 | 3.4744(12) | | |
| 4 × Eu | 4.3826(14) | | |
| Al1 | | | |
| 4 × Al/Si2 | 2.621(2) | | |
| 4 × Eu | 3.4744(12) | | |
| Al/Si2 | | | |
| Al/Si2 | 2.517(6) | | |
| 4 × Al1 | 2.621(2) | | |
| 4 × Eu | 3.3448(13) | | |
| TmAlSi | | LuAlSi | |
| Tm | | Lu | |
| 2 × Si | 2.855(2) | 2 × Si | 2.842(3) |
| 2 × Si | 2.9667(10) | 2 × Si | 2.948(2) |
| Si | 3.002(3) | Si | 2.980(4) |
| 4 × Al | 3.1280(4) | 4 × Al | 3.1148(9) |
| 2 × Al | 3.3951(6) | 2 × Al | 3.3681(13) |
| Tm | 3.6212(5) | Tm | 3.6048(13) |
| Si | | Si | |
| 4 × Al | 2.6418(11) | 4 × Al | 2.6345(15) |
| 2 × Tm | 2.855(2) | 2 × Tm | 2.842(3) |
| 2 × Tm | 2.9667(10) | 2 × Tm | 2.948(2) |
| Tm | 3.002(3) | Tm | 2.980(4) |
| Al | | Al | |
| 4 × Si | 2.6418(11) | 4 × Si | 2.6345(15) |
| 2 × Al | 2.8157(5) | 2 × Al | 2.7988(14) |
| 4 × Tm | 3.1280(4) | 4 × Tm | 3.1148(9) |
| 2 × Tm | 3.3951(6) | 2 × Tm | 3.3681(13) |