High-pressure synthesis of the electron-excess compound CaSi$_6$

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Abstract

The binary phase CaSi$_6$ is prepared at a pressure of 10(1) GPa and a temperature of 1520(150) K. X-ray single-crystal structure refinements and powder diffraction data of quenched samples reveal that the compound crystallizes in the orthorhombic crystal system (space group $Cmcm$, $a = 4.4953(5)$ Å, $b = 10.078(1)$ Å, $c = 11.469(1)$ Å). At ambient pressure, exothermic decomposition into CaSi$_2$ and Si at 737(5) K indicates that the compound is a metastable high-pressure phase. Physical property measurements reveal that the new hexasilicide is diamagnetic and a bad metallic conductor, with resistivity $\rho \approx 900 \mu \Omega \cdot \text{cm}$ at 300 K.

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1. Introduction

A large number of semiconducting valence compounds comprise sub-structures in which the electron count and the number of covalent bonds of post-transition main group elements is related by the $8-N$ rule. In a large fraction thereof, chemical bonding can be described in accordance with the Zintl–Klemm concept. In phases of electropositive metals with germanium like $K_8Ge_{44}$ or $A_8M_{16}Ge_{30}$ ($A = Sr, Ba; M = Al, Ga$), group 14 elements form polyanions in electron-precise compounds by the formation of electron pairs around defects [1,2] or by substitution of group 14 elements with group 13 atoms [3,4]. In phases $MGe_{6-x}Ga_x$, ($M = Eu, Sr$) the electron-precise composition with $x = y = 2$ can be synthesized for $M = Eu$ [5] and the corresponding binary strontium germanide with $M = Sr$, $x \approx 0.5$ and $y = 0$ ($SrGe_{6-x}$) comprises vacancies [6], which indicates that it can fulfill the $8-N$ rule.

In sharp contrast, binary silicon-rich high-pressure phases like EuSi$_6$ [7], SrSi$_6$ [8] or BaSi$_6$ [9,10] comprise solely four-bonded silicon atoms. The metal-type temperature dependence of the electrical conductivity is in agreement with a description as $\text{Eu}[[4b]Si^6]_6 \cdot 2e^-$. Investigating the ternary-substituted variety $\text{EuGa}_x\text{Si}_{6-x}$ reveals a homogeneity range from $x = 0$ to 0.6. The finding indicates that the phase requires a significant excess of electrons since a composition $\text{Eu}[[4b]Si^6]_6 \cdot [4b]Ga^-$, with $x = y = 2$, which would be in accordance with the $8-N$ rule, cannot be realized experimentally. As a borderline case, the binary EuSi$_6$ ($x = y = 0$) exhibits a surplus of two electrons per formula unit. Here, we study phase formation upon compression in the silicon-rich part of the binary Ca–Si system and report on high-pressure synthesis, crystal structure, magnetic and electrical properties of the new binary compound CaSi$_6$.

2. Experimental section

Preparation of the precursors and sample handling including the assembly of the octahedral high-pressure set-up is performed in glove boxes with a purified argon atmosphere (MBraun, $H_2O < 1$ ppm; $O_2 < 1$ ppm). The synthesis of CaSi$_2$ by melting calcium (Alfa Aesar 99.98% metal basis) and silicon (Alfa 99.9999%) in a high-frequency induction furnace using sealed tantalum crucibles precedes the high-pressure reaction of disilicide with various amounts of silicon in order to realize ratios Ca:Si between 1:3.5 and 1:8. Aiming to avoid chemical reactions of the educts with oxygen or water, the octahedral assembly is transferred to the high-pressure
equipment just before pressurizing. After the pressure and heating cycle, the arrangement is instantaneously removed and transferred into a glove box where the sample is isolated from the crucible.

High-pressure conditions are achieved by using a hydraulic uniaxial press. Force redistribution is accomplished by a Walker module and MgO octahedra with an edge length of 14 mm [11]. Elevated temperatures are realized by resistive heating of graphite tubes enclosing the sample crucibles. Pressure and temperature calibration is completed before the experiments by monitoring the resistance changes of bismuth [12] and measurements with a thermocouple, respectively. The crucibles girdling the sample mixtures are machined from hexagonal boron nitride. X-ray powder diffraction data and energy-dispersive X-ray analysis give no indication for a reaction of the containers with the samples. Consistent with these results, separation of reaction products and crucible material can be achieved easily. A typical high-pressure synthesis requires a heating time of 1 h. Small single crystals grow at a pressure of 10(1) GPa and a temperature of 1520(150) K. The samples are quenched to ambient temperature by disconnecting the heating current before decompression.

In order to investigate homogeneity and phase distribution of the reaction products by optical and electron microscopy, samples for metallographic studies are prepared in an inert gas atmosphere of a glove box using dried hexane as a lubricant. Spectra up to 25 keV are determined by energy-dispersive X-ray spectroscopy (EDXs) on an attached EDAX system and show for all investigated samples only the characteristic X-ray lines of Si and Ca. The composition of the 1:6 target phase is determined by wave-length dispersive X-ray spectroscopy (WDXS) with a microprobe (Camesc SX100). Pure silicon and the mineral andradite containing 23.84 wt% calcium are used as references. The intensities of both lines Si Kα (E = 1736 eV) and Ca Kα (E = 3693 eV) are used for calculating the composition of the phases. Counting rates of 10 000 cps (counts per seconds) on a spectrometer with a thallium acid phthalate (TAP) and a large pentaerythritol monochromator (PET) crystal are realized by using an excitation voltage of 15 keV for the electron beam with 5 and 20 nA, respectively. Averaging the results of measurements at 10 different spots yields recoveries in the range of 100.5(±0.5) wt%.

Differential scanning calorimetry (DSC) measurements at ambient pressure are performed with the Netzsch DSC 404c equipment using Al₂O₃ crucibles at temperatures between 298 and 1223 K and heating rates of 10 K/min.

X-ray powder diffraction data are collected in a transmission alignment using a Huber Image Plate Guinier Camera G670 and Cu Kα radiation (λ = 1.54056 Å). In order to avoid oxidation during powder preparation, samples are ground in a purified argon atmosphere. After adding LaB₆ as an internal standard (a = 4.15692 Å), the mixtures are placed between two polyimide foils. For lattice parameter refinements, sets of about 50 reflections are used. Profile fitting and lattice parameter calculations are performed with the program package WinCSD [13]. Structure refinements with single-crystal diffraction intensities are carried out with the computer program SHELXL-97 [14]. The parameters of data collection and refinement are shown in Table 1. Final least-squares calculations are performed using an anisotropic parameterization of the atomic displacement and weighting of the reflections by 1/σ².

Magnetization at various external fields between 20 Oe and 70 kOe (temperature range 1.8–400 K) is measured with a SQUID magnetometer (MPMS XL-7, Quantum Design) using a polycrystalline sample (mass 7.55 mg). On the same sample an electrical resistivity measurement is performed with a dc four-point method (4–320 K). The error of the resistance measurements corresponds to typically 10⁻⁴ of the measured signal; however, the resulting inaccuracy of the resistivity is estimated to be ±30% due to the small size of the investigated specimen and the inherent problems in determining the contact geometry.

### Table 1

| Data collection and crystallographic information for CaSi₆⁴ |
|------------------------------------------------------------|
| **Composition**        | CaSi₆                      |
| **Symmetry**           | Orthorhombic, Cmcm (no. 63) |
| **Pearson symbol**     | oC28                       |
| **Unit cell parameters** |                           |
| a, Å                   | 4.4953(5)                  |
| b, Å                   | 10.078(1)                  |
| c, Å                   | 11.469(1)                  |
| V, Å³                  | 519.59(9)                  |
| **Formula units/unit cell, Z** | 4                          |
| **Calculated density, g cm⁻³** | 2.67                      |
| **Size of the crystal, µm** | 15 x 20 x 40             |
| **Diffractions**       | Rigaku AFC 7              |
| **Detector**           | Mercury CCD                |
| **Wavelength, λ(Mo Kα), Å** | 0.71073         |
| **Scans, step/deg**    | φ, α, 0.6                  |
| **2θmax, deg**         | 62.94                      |
| **Range in h, k, l**   | -6 ≤ h ≤ 6, -11 ≤ k ≤ 14, -11 ≤ l ≤ 16 |
| **Transmission factors T_max / T_min** | 1.29                   |
| **Number of measured reflections** | 2049                 |
| **Number of unique reflections** | 458                   |
| **Averaging R(int)**   | 0.034                      |
| **Number of observed reflections** | 411                       |
| **Observation criterion** | P(bhkl) > 4σ(F)           |
| **Number of refined parameters** | 23                        |
| **R1 (P(bhkl) > 4σ(F))** | 0.036                     |
| **Residual density, eA⁻³** | -0.62/0.91               |

⁴Further details on the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, fax: +49 7247 808 666; e-mail: crydata@fiz.karlsruhe.de, on quoting the depository number CSD 418319.

³From powder diffraction data.
3. Results and discussion

The range of formation of CaSi₆ starts at about 6 GPa and extends to at least 12 GPa at 1500 K, which is the highest pressure investigated in this study. This field of stability is similar to that of SrSi₆ and EuSi₆, but the window for preparing nearly single-phase samples is quite narrow and extends only to 10(1) GPa. In order to achieve a higher yield of the target compound the thermal gradient within the crucible is reduced by using stepped graphite heaters. Despite these improvements single-phase samples could not be obtained according to WDXS and the recorded X-ray powder diffraction patterns. The powder diffraction data reveal lattice parameters for the 1:6 phase \( a = 4.4953(5) \text{ Å}, b = 10.078(1) \text{ Å} \) and \( c = 11.469(1) \text{ Å} \). In the investigated products, at least 5% impurities are detected so that for measurements of the physical properties one of the purest samples is selected.

In order to investigate the homogeneity range of CaSi₆, compositions between 78 and 89 at% silicon are prepared at the same conditions as the 1:6 compound, which corresponds to 85.7 at% Si. The lattice parameters of the silicon-poor sample \( a = 4.4939(5) \text{ Å}, b = 10.075(1) \text{ Å}, c = 11.466(1) \text{ Å} \) and the silicon-richer mixture \( a = 4.4948(5) \text{ Å}, b = 10.077(1) \text{ Å}, c = 11.464(1) \text{ Å} \) are equal within three standard deviations. Electron backscattering images of samples are shown in Fig. 1. In the investigated mixtures with Ca:Si \( \neq 1:6 \), elemental silicon is present as a minority phase. With respect to the composition of the hexasilicide, measurements by WDXS reveal an average of CaSi₅.₈(1) corresponding to CaSi₆ within experimental error. The present findings bear no evidence for a significant homogeneity range of the investigated phase.

The investigation of the thermal stability of CaSi₆ reveals a pronounced exothermic signal at 737(5) K (onset), which does not correspond to a thermal effect upon cooling or on repeated heating (Fig. 2). This observation is compatible with a monotropic (irreversible) phase transition. X-ray powder diffraction data of samples that are investigated after the heating cycle exhibit only diffraction lines of Si and CaSi₂. Thus, the experiments are consistent with a decomposition of CaSi₆ at 737(5) K and atmospheric conditions.

![Fig. 1](image1.png)

**Fig. 1.** Microstructures of samples in the silicon-rich part of the Ca–Si phase diagram after high-pressure treatment (see text). The pictures present backscattering electron images recorded with a scanning electron microscope, the display window width corresponds to approximately 0.5 mm. Black areas are attributed to cracks. In the pictures, beside the majority phase CaSi₆ (light grey), a silicon-rich solid solution (darker grey) is observed. This finding clearly proves that the sample is macroscopically inhomogeneous. In the sample with the nominal composition 1:3.5, elemental silicon is present as a minority phase. With respect to the composition of the hexasilicide, measurements by WDXS reveal an average of CaSi₅.₈(1) corresponding to CaSi₆ within experimental error. The present findings bear no evidence for a significant homogeneity range of the investigated phase.

![Fig. 2](image2.png)

**Fig. 2.** Differential scanning calorimetry measurement of CaSi₆ at ambient pressure. With increasing temperature, the decomposition of the metastable high-pressure phase CaSi₆ into the products CaSi₂ and Si, which are thermodynamically stable at ambient pressure, is detected by the onset of an exothermic effect at 737(5) K. No signal is observed upon cooling (upper most line) or on reheating (middle, grey line). The heating rate in the experiments is selected to 10 K/min.
pressure, thus evidencing that the compound is a metastable high-pressure phase at ambient conditions.

The crystal structure of CaSi₆ is refined by means of X-ray single-crystal diffraction data. Atomic coordinates and displacement parameters are summarized in Table 2, and interatomic distances in Table 3. The atomic arrangement is isoeffective to EuGa₂Ge₄ [5] and isotypic to EuSi₆ [7], SrS₂ [8] and BaS₂ [9,10]. A 3D network of four-bonded Si atoms encloses large voids, which are occupied by calcium atoms (Fig. 3). According to the \( 8 - N \) rule, such a silicon species would be uncharged corresponding to \( (4b)Si \). If we assume in accordance with the Zintl–Klemm concept a full charge transfer from calcium to silicon, there would be an excess of one-third of the trace of the \( U_{ij} \) tensor, the total displacement is defined as \( \exp[-2\pi^2(U_{11}a^2 + \cdots + 2U_{23}kb^*c^*)] \).

For all positions \( U_{12} = U_{13} = 0 \).

### Table 2
Atomic coordinates and displacement parameters of CaSi₆ at 293 K

| Atom | Site | \( x \) | \( y \) | \( z \) | \( U_{eq} \) | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{23} \) |
|------|------|--------|--------|--------|--------|--------|--------|--------|--------|
| Ca   | 4c   | 0      | 0.27216(9) | \( \frac{1}{2} \) | 0.0159(5) | 0.150(4) | 0.0173(4) | 0      |
| Si1  | 8f   | 0      | 0.24736(7) | 0.53914(6) | 0.0126(2) | 0.0134(4) | 0.0120(4) | -0.0016(3) |
| Si2  | 8f   | 0      | 0.55652(8) | 0.35239(6) | 0.0112(2) | 0.0123(4) | 0.0125(4) | -0.0008(3) |
| Si3  | 8f   | 0      | 0.02466(8) | 0.60278(7) | 0.0143(2) | 0.0117(4) | 0.0124(5) | 0.0187(4) | 0.0026(3) |

*The \( U_{eq} \) values (in \( \text{A}^2 \)) are defined as one-third of the trace of the \( U_{ij} \) tensor.*

### Table 3
Selected interatomic distances in CaSi₆

| Atoms | \( d \) Å |
|-------|--------|
| Si1–Si2 | 2.336(1) |
| Si1–Si3 | 2.360(1) |
| Si1–Si1 (2 \( \times \)) | 2.420(9) |
| Si2–Si2 | 2.336(1) |
| Si2–Si2 | 2.349(2) |
| Si2–Si3 (2 \( \times \)) | 2.4466(5) |
| Si3–Si1 | 2.360(1) |
| Si3–Si3 | 2.409(2) |
| Si3–Si2 (2 \( \times \)) | 2.4466(5) |
| Ca–Si2 (2 \( \times \)) | 3.097(1) |
| Ca–Si–Si (4 \( \times \)) | 3.307(4) |
| Ca–Si (2 \( \times \)) | 3.325(6) |
| Ca–Si (2 \( \times \)) | 3.339(9) |
| Ca–Si3 (2 \( \times \)) | 3.435(1) |
| Ca–Si3 (4 \( \times \)) | 3.477(9) |
| Ca–Ca (2 \( \times \)) | 4.4953(5) |

*Fig. 3. Crystal structure of CaSi₆. The ellipsoids represent a probability density of 99%. The framework is formed by three crystallographically independent silicon atoms (dark grey), which are connected by covalent bonds. Voids of the 3D silicon network are occupied by calcium (light grey ellipsoids). The coordination polyhedron of the alkaline-earth metal with CN 18 is indicated by shading.*

Other binary compounds in the phase diagram calcium–silicon at ambient pressure are CaSi₃ (own structure type [15]), Ca₃Si₄ (own structure type [16]), Ca₁₄Si₁₉ (own structure type [17]), CaSi (CrB structure type [18]), Ca₃Si₃ (Cr₅B₃ type [19]) and Ca₃Si (PbCl₂ type [20]). At high pressures, CaSi₂ shows polymorphic behaviour and forms high-pressure modifications with crystal structures of the ThSi₂ type (4 GPa and 1270 K to 8.7 GPa and 1770 K [21–25]), with trigonal symmetry (9 GPa < \( P < 16 \) GPa at ambient temperature [26,27]) and with an AlB₂-like pattern (\( P > 16 \) GPa and ambient temperature [26,27]).

These binary compounds can be described in accordance with the Zintl–Klemm concept as phases with closed-shell configurations of metal atoms, i.e., formally a complete valence electron transfer from calcium to silicon takes place and the wealth of different anionic species fulfil the \( 8 - N \) rule. Thus, the hitherto characterized binary phases can be labelled as *silicides*, which are composed of Ca²⁺ and isolated Si⁴⁺ in Ca₂Si [20], isolated Si⁴⁺ and Si⁺⁺ dumbbells with (1b)Si³⁺ in Ca₅Si [19], (2b)Si²⁺ chains in CaSi [18], (2b)Si⁺⁺ and (3b)Si in the anion Si₂⁺ of Ca₅Si [19] and in the Si₁₂⁺ slabs of Ca₅Si [16,17], and finally (3b)Si⁺⁺ in the different anion networks of polymorphic CaSi₂ [15,21–27].
The unusual electron configuration of CaSi₆ motivated a characterization of some physical properties. The magnetic susceptibility χ(T) = M/H of CaSi₆ is diamagnetic in the whole temperature range. After taking into account minor para- and ferromagnetic impurities (by a Curie term and by Honda–Owen extrapolation, respectively) and subtraction of the sample-holder contribution, a χ₀ of −95(40) × 10⁻⁶ emu mol⁻¹ is estimated (Fig. 4). This value is significantly larger than the core contribution of −14 × 10⁻⁶ emu mol⁻¹ and, thus, the behaviour is in qualitative accordance with that of SrSi₆ (χ₀ = −50 × 10⁻⁶ emu mol⁻¹ [8]). In a broad step around T = 310 K the susceptibility rises to a value of −40(40) × 10⁻⁶ emu mol⁻¹ at 400 K. A diamagnetic signal below 4.9 K suggests that a superconducting phase is present in the sample. However, the flux expulsion (fc Meissner effect) is quite low (ca. 5%) and the shielding effect (measured in zfc) is also far from complete, 11% in a field of 20 Oe. Thus, the superconductivity is probably due to a secondary phase. On the basis of the observed superconducting transition temperature, tantalum metal (Tₜ(0) = 4.49 K), which is used as a crucible material for synthesis and which is frequently found in small quantities, can be ruled out as a possible contamination.

In the temperature range up to 300 K, the resistivity ρ(T) of CaSi₆ (Fig. 5) increases non-linearly with T. At 300 K a value of ≈900 μΩ cm (±30%) and at 4 K a residual resistivity of ≈50 μΩ cm (±30%) is observed. These findings indicate a conduction mechanism of a “bad metal”. Values of similar magnitude have been observed before for other silicides, e.g., Eu₃Si₄ ρ(300 K) = 5.5 mΩ cm [28] and the isotypic compounds EuSi₆ [7] and SrSi₆ [8]. At 310 K, however, a strong increase of ρ(T) is observed. Together with the anomaly observed in the magnetic susceptibility this indicates a transition, which is currently under investigation.

As a conclusion, within the Zintl–Klemm concept the chemical bonding in CaSi₆ can be represented by the charge balance [Ca²⁺] [(4b)Si⁶⁻·2e⁻], which indicates that the compound does not belong to the classical Zintl phases, but represents a member of the group of electron-excess intermetallic compounds [29,30].

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