Refinement of the crystal structure of barium hexasilicide, BaSi₆

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Abstract
BaSi₆, orthorhombic, Cmcm (no. 63), a = 4.4789(2) Å, b = 10.3679(5) Å, c = 11.9634(8) Å, V = 555.5 Å³, Z = 4, Rg(F) = 0.040, wR²(F²) = 0.073, T = 293 K.

Source of material
BaSi₆ was prepared by addition of silicon to BaSi₂ (Alpha Aesar, 99.9 %) which had been synthesized as a precursor by reaction of barium (Alpha Aesar, 99.999 %) with semiconductor-grade silicon (Alpha Aesar, 99.999 %). The pre-reaction was realized in an arc furnace followed by treatment at 12(2) GPa and 1200 - 1600(150) K for typically one hour. Although BaSi₆ reguli do not show any visible reaction with air or moisture within weeks, precursor preparation, sample loading and product recovery after high-pressure synthesis were performed in argon-filled glove boxes (MBraun; H₂O, O₂ < 0.1 ppm).

Pressures were generated with a Walker-type multi-anvil assembly [1] in combination with a hydraulic press for force generation. For pressure redistribution, we used octahedra manufactured from MgO with 5 % O₂O₃ and an edge lengths of 14 mm. Prior to the experiments, temperatures were calibrated with type-C thermocouples; pressures were determined using the resistivity changes of Bi and Pb at room temperature.

Experimental details
Lattice parameters were obtained by a least-square refinement with 97 reflections using LaBe as internal standard (a = 4.15692 Å) (Huber Image Plate Guinier camera G670, Cu Ka radiation, λ = 1.54056 Å, 5° < 2θ < 100°). The obtained values were used for the calculation of interatomic distances.

Discussion
The synthesis of BaSi₆ was reported by Demchyna et al. [2]. Crystal structure data based on a Rietveld refinement were published independently by Yamanaka et al. [3]. The crystal structure is isotypic to the binary compounds MSi₆ (M = Eu [4]; Ca [5], Sr [6]) and isopointal to ternary EuGa₂Ge₄ [7]. The atomic arrangement consists of a 3D network formed by four-bonded silicon atoms with large voids being occupied by barium atoms. The alkaline-earth metal is coordinated by 18 silicon atoms. The main difference with respect to the earlier determination is an improved accuracy by about one order of magnitude. The resistivity measurements show a metal-type behavior similar to the isotypic compounds with Ca, Sr or Eu. The determined resistivity differs by three orders of magnitude from earlier determined data [3]. The findings of the crystal structure determination as well as the measurements of the physical properties are in accordance with a description of the compound as polyanionic according to Ba²⁺(4Si°)Si₆⁻·2e⁻.

Table 1. Data collection and handling.

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<th>Atom</th>
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<th>x</th>
<th>y</th>
<th>z</th>
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<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
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References