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BaGe₅: An intermetallic clathrate with a new structure type

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Intermetallic clathrates constitute a class of cage compounds in which electropositive metal atoms are encapsulated in covalently bonded frameworks of mainly Group 14 elements (Si, Ge, Sn). The growing research interest on clathrates is mainly due to their potential as thermoelectric materials.¹ The crystal structures commonly found are related to the type I and type II gas hydrates.² By increasing the content of electropositive elements, related structures as the clathrate *cP124* can be formed, which have no corresponding gas hydrate structure.³ In the binary system Ba-Ge, two clathrate types have been reported, namely the clathrate *cP124* Ba₆Ge₂₅ and the clathrate-I Ba₈Ge₄₃□₃.⁴ Here we report on the synthesis, crystal structure and physical properties of BaGe₅. The crystal structure (Figure 1) constitutes a new prototype clathrate *oP60* of the orthorhombic space group *Pmna*. BaGe₅ is a diamagnetic and semiconducting Zintl phase and might represent a structure type of new prospective thermoelectric materials.

In the Ge-rich part of the Ba – Ge system, Ba₆Ge₂₅ and Ba₈Ge₄₃□₃ are the only clathrate phases found to be in thermal equilibrium with α -Ge.^{4a} Ba₆Ge₂₅ decomposes peritectically at 815 °C to BaGe₂ and melt. Ba₈Ge₄₃□₃ forms at 770 °C from the reaction of Ba₆Ge₂₅ and α -Ge and decomposes peritectically at 810 °C to α -Ge and melt. No other phase was proposed to be thermodynamically stable between Ba₆Ge₂₅ and α -Ge below 770 °C. On the other hand, a phase with composition BaGe₅ was found by electron microscopy investigations in a heterogeneous mixture of Ba₆Ge₂₅, Ba₈Ge₄₃□₃ and α -Ge. From thermal analyses, BaGe₅ was concluded to be metastable.^{4a} Our further investigations showed that this heterogeneous mixture containing BaGe₅ is only formed from a stoichiometric melt by cooling to room temperature within few minutes. Fast quenching of the melt led to the formation of Ba₆Ge₂₅ and Ba₈Ge₄₃□₃, lower cooling rates to Ba₆Ge₂₅ and α -Ge. In agreement with the reported phase diagram, mixture of Ba₆Ge₂₅ and Ba₈Ge₄₃□₃ were found to be thermodynamically stable between 770 °C and 808 °C.^{4a} By annealing slightly below 770 °C, Ba₈Ge₄₃□₃ decomposes rapidly to Ba₆Ge₂₅ and α -Ge. All our attempts to react Ba₆Ge₂₅ and α -Ge to BaGe₅ failed. These results indicate that BaGe₅ originates from the decomposition of Ba₈Ge₄₃□₃ at temperatures within its thermal stability range. The preparation of phase pure Ba₈Ge₄₃□₃ was recently achieved by rapid quenching,^{4b,5} thus allowing for detailed investigation of its decomposition along with the formation of BaGe₅. Bulk pieces of Ba₈Ge₄₃□₃ were annealed in glassy carbon crucibles under Ar atmosphere at various temperatures between 300 °C and 700 °C. In agreement with former results, Ba₈Ge₄₃□₃ is metastable up to ~300 °C.⁵ Annealing at 400 °C for 12h resulted in a complete decomposition into a microcrystalline product of BaGe₅ and α -Ge (~5 wt-%)(Figure S1)

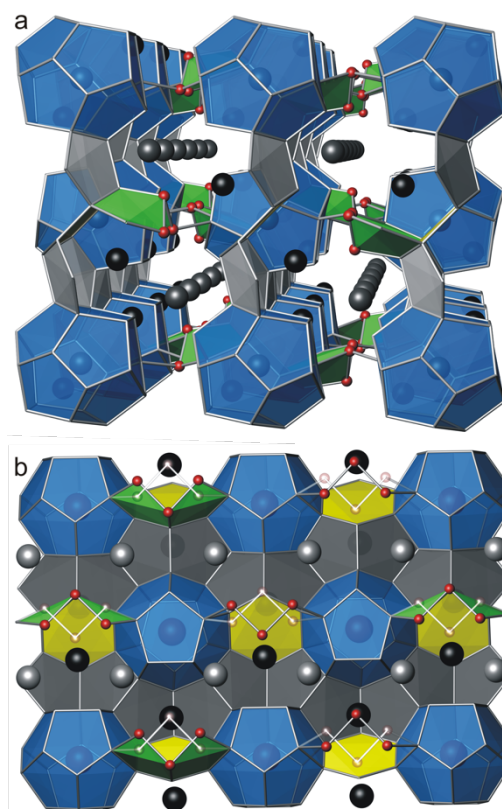
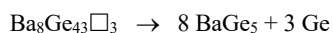


Figure 1. (a) Crystal structure of BaGe₅ along [100]. Ba1 are inside dodecahedral cages, Ba2 are drawn in gray and Ba3 in black. Half occupied Ge sites are drawn red. (b) Covalently bonded layers of Ge atoms perpendicular to [010]. Alternatively occupied Ge sites are drawn in red and white, respectively.

At 520 °C, the conversion is already complete within 1 h. No decomposition of BaGe₅ could be detected after further annealing for 6 weeks at 520 °C. However, after 1 week at 575 °C, only Ba₆Ge₂₅ and α -Ge were obtained. Therefore, BaGe₅ is thermodynamically stable up to 520 °C. For kinetic reasons, BaGe₅ cannot be obtained by annealing Ba₆Ge₂₅ and α -Ge below 520 °C. Mixtures of BaGe₂ and α -Ge, which yield phase pure Ba₆Ge₂₅ after 4d annealing at 700 °C, do not react at 500 °C as well. Therefore, the formation of α -Ge cannot be avoided by adding Ba to the starting material Ba₈Ge₄₃□₃. In this case, a mixture of Ba₆Ge₂₅ and Ba₈Ge₄₃□₃ is formed from the melt, the former remaining unreacted in the final product. The conversion of Ba₈Ge₄₃□₃ to BaGe₅ and α -Ge is reversible. Phase pure Ba₈Ge₄₃□₃ was retrieved after annealing BaGe₅ and α -Ge at 790 °C for 2 weeks.

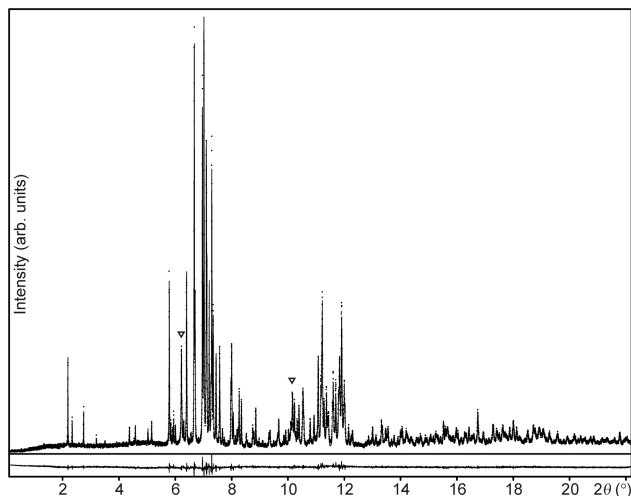


Figure 2. Synchrotron powder X-ray diffraction pattern of BaGe_5 ($\lambda = 0.35415 \text{ \AA}$). The two most intense α -Ge peaks are marked. The baseline corresponds to the residuals of a Rietveld refinement based on the structure model.^X

High-resolution synchrotron powder X-ray diffraction data were collected on a sample obtained at 400 °C (Figure 2, page S3).

Besides the reflections of α -Ge, all reflections could be indexed in a primitive, orthorhombic unit cell in agreement with former results obtained by transmission electron microscopy.⁶ The crystal structure was solved in the space group $Pmna$ (Tables S1 - S2).^{7,8} The Rietveld refinement resulted in the chemical composition BaGe_5 ($Z = 10$) which is in good agreement with the wavelength dispersive X-ray spectroscopy result of $\text{Ba}_{0.98(1)}\text{Ge}_{5.02(1)}$ (Page S3). The crystal structure is characterized by clathrate like Ge layers perpendicular to $[010]$, consisting of Ge_{20} dodecahedra connected by pentagons and hexagons. The layers are interconnected via $(3b)\text{Ge}^-$ anions by covalent bonds. The $(3b)\text{Ge}^-$ anions partially occupy two crystallographic sites ($SOF = 0.5$) leading to substantial disorder in the crystal structure (Figure 1b). An ordered arrangement of the $(3b)\text{Ge}^-$ anions in an isomorphic subgroup such as $Pmn2_1$ or $Pma2$ could not be verified from Rietveld refinements. Similar 2-D infinite layers, but fully separated by the cations, have been observed in the crystal structure of $A_3\text{Na}_{10}\text{Sn}_{23}$ ($A = \text{Cs, Rb, K}$).⁹ The Ba atoms in BaGe_5 occupy three crystallographic sites with distinctly different local environments. Ba1 atoms are enclosed within dodecahedral cages arranged on a B-centred orthorhombic lattice. Ba2 atoms are located in infinite channels running along $[100]$. The local environment of Ba3 depends on which of the alternative positions is occupied by the $(3b)\text{Ge}^-$ anions. Ba3 atoms are situated along the infinite channels in open cages formed by Ge_6 -hexagon and Ge_5 -pentagons. BaGe_5 constitutes a new structure type which can be considered as an intermediate between clathrate $cP124$ and clathrate I. The infinite channels are reminiscent to those of $\text{Ba}_6\text{Ge}_{25}$, while the arrangement of 5- and 6-rings resembles the polyhedral cages in clathrate I $\text{Ba}_8\text{Ge}_{43}\square_3$. 20 Ge atoms per unit cell are three bonded, leading to the electronic balance $[\text{Ba}^{2+}]_{10}[(3b)\text{Ge}]_{20}[(4b)\text{Ge}^0]_{30}$. Hence, BaGe_5 can be considered as a Zintl-phase as further corroborated by the physical property measurements (Page S4). BaGe_5 is diamagnetic in the whole investigated temperature range with $\chi \approx -210 \times 10^{-6} \text{ emu mol}^{-1}$ at 300 K (Figure 3a). A rough estimation of the diamagnetic contribution using tabulated values for closed-shell cations and anions gives $\chi_{\text{calc}} \approx -110.5 \times 10^{-6} \text{ emu mol}^{-1}$.¹⁰ The temperature dependence of the electrical resistivity indicates a semiconducting

behaviour (Figure 3b). The small hump observed around 170 K might point to a structural phase transition related to the ordering

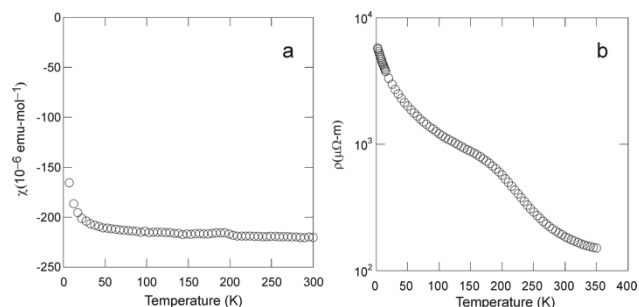


Figure 3. (a) Magnetic susceptibility $\chi(T)$ and (b) electrical resistivity $\rho(T)$ of BaGe_5 at low temperatures

of the $(3b)\text{Ge}^-$ anions. To understand this anomalous conduction behaviour, further investigations are required.

BaGe_5 is a Zintl phase crystallizing with the new clathrate type $oP60$. The compound results from the decomposition of $\text{Ba}_8\text{Ge}_{43}\square_3$ at temperatures between 350 °C and 520 °C. Its semiconducting behaviour together with a complex crystal structure may lead to interesting thermoelectric properties.

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Supporting Information Available: The supplementary materials concerning to crystallographic data, xx, of BaGe_5 is available free of charge at <http://pubs.acs.org>.

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