

Structural Evolution of the Binary System Ba-Si under High-pressure and High-temperature Conditions

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A new silicon-rich binary compound BaSi_6 has been prepared by the treatment of the $\text{Ba}_8\text{Si}_{46}$ clathrate compound under a pressure of 15 GPa at 1000 °C, or from a stoichiometric mixture of BaSi_2 and Si by treatment under similar high-pressure and high-temperature conditions. The Rietveld refinements revealed that BaSi_6 is isomorphous with EuGa_2Ge_4 , and crystallizes with space group *Cmcm* and the lattice parameters $a = 4.485(1)$, $b = 10.375(2)$, and $c = 11.969(3)$ Å. Each Ba atom is surrounded by 18 Si atoms in an irregularly shaped polyhedron $@\text{Si}_{18}$. The polyhedra are connected by sharing faces to form Ba containing tunnels along the *a* axis. All of the Si-rich compounds so far with atomic ratios $\text{Si}/\text{Ba} > 2$ in the binary system have been prepared only under high-pressure and high-temperature conditions. There is a general tendency that the Si/Ba ratio of the compounds increases with an increase of the pressure in the preparation.

Key words: Ba-Si System, BaSi_6 , High-pressure Phase, Clathrate