Exploration of the Na-Si Phase Diagram and Theoretical Structure Prediction of a Layered Sodium Zintl Phase Na_2Si_3

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Abstract

First-principles crystal structure prediction and density functional theory (DFT) calculations were employed to investigate the high-pressure behavior and electronic properties of the sodium silicide Na_2Si_3. Evolutionary structure searches identified a previously unknown tetragonal phase (space group *P*-42$_1$*m*, *Z* = 2) that becomes thermodynamically stable near 5 GPa and remains dynamically stable upon decompression to ambient pressure. The predicted structure consists of layered silicon slabs separated by sodium atoms and can be interpreted within the Zintl–Klemm framework through formal charge transfer from Na to the silicon network.

Electronic structure calculations indicate semiconducting behavior with an indirect band gap of approximately 1.14 eV at ambient pressure. Compression leads to a systematic increase in the band gap, demonstrating pressure-dependent electronic tunability. The calculated bonding characteristics and charge distribution support the ionic–covalent nature of the compound and the formation of a layered silicon framework. Analysis of the crystal topology highlights pentagonal motifs within the silicon sublattice, while lattice-dynamics and transport-related calculations suggest relatively low thermal conductivity. These computational results establish Na_2Si_3 as a pressure-stabilized Zintl phase with potentially attractive electronic and thermoelectric properties.

In addition to the Na_2Si_3 compound, the binary Na–Si phase diagram under pressure has been explored using a variable-composition evolutionary algorithm (XtalOpt) and *ab initio* random structure searching (AIRSS) combined with machine-learned interatomic potentials, such as EDDPs. New compositions and phases have been identified as not only dynamically stable but thermodynamically stable or metastable. Their structural and electronic properties will be presented and discussed.

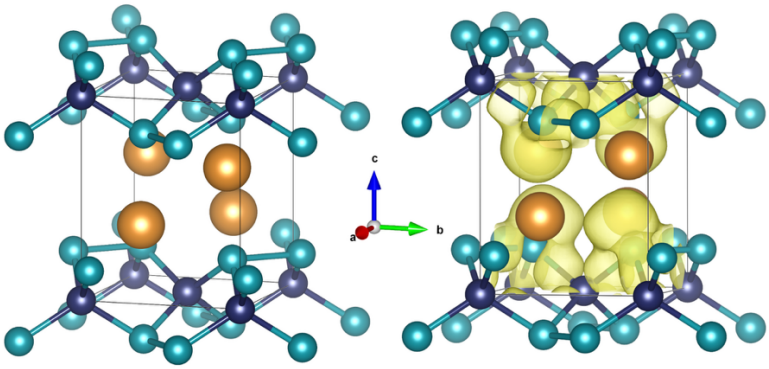

Figure 1. Crystal structure of tetragonal Na_2Si_3 at 5 GPa. The Na atoms are in orange, the four-coordinated Si1 atoms are in blue and the three-coordinated Si2 atoms are in cyan. The electron localization function (ELF) is shown in yellow with an isosurface value of 0.7.