# Composition-Driven Metal-to-Semiconductor Transition and Enhanced Phonon Transport in B→C-substituted Clathrate

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We have combined first-principles density functional theory (DFT) with advanced machine-learned interatomic potentials (MLIPs) and Boltzmann transport theory to elucidate the impact of minimal chemical substitution on the coupled electronic and thermal properties of these materials. We consider cubic $BaB_3C_3$ and subsequently perform a B→C substitution to form its tetragonal counterpart $BaB_2C_4$. We have found that a seemingly trivial single B→C substitution per formula unit fundamentally reconstructs the local bonding network, specifically triggering the formation of strong and short C–C bonds. This subtle chemical modification donates an extra valence electron to the framework, driving a striking metal-to-semiconductor transition and opening an indirect bandgap of 0.33 eV in the tetragonal $BaB_2C_4$. Intriguingly, the bonding reconstruction profoundly impacts the lattice dynamics and phonon thermal transport. The phonon spectrum hardens, and the lattice thermal conductivity surges from 7.6 in $BaB_3C_3$ to 18.7 $Wm^{-1}K^{-1}$ in the semiconducting tetragonal $BaB_2C_4$—a remarkable ~2.5-fold enhancement at room temperature. Furthermore, the thermal transport modifies from isotropic to highly anisotropic due to the lowered crystal symmetry.

To accurately and efficiently capture the complex harmonic and anharmonic phonon-phonon interactions governing this transport, we trained and deployed the Message Passing Atomic Cluster Expansion (MACE) MLIP. We rigorously benchmarked the MACE potential against explicit DFT calculations, demonstrating exceptional fidelity in reproducing energies, forces, phonon dispersions and lattice thermal conductivity. This highlights the outstanding physical transferability for predicting the lattice dynamics and phonon transport properties of other structurally and chemically similar compounds without the need for traditional computationally costly tools. Overall, the results provide comprehensive insights into how targeted chemical substitution can simultaneously co-engineer electronic structure and phonon thermal transport, underscoring their potential in advanced thermal management, thermoelectric and heat dissipation technologies.

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