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MgSrSi-Type Compounds as a Possible New Family of Thermoelectric Materials

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We calculated electronic structures and transport properties of 33 Zintl phase compounds M^1M^2X (M^1, M^2 = Li, Na, Mg, K, Ca, Rb, Sr, Ba; X = Si, Ge, As, Se, Sn, Sb, Te, Pb, Bi) having orthorhombic MgSrSi-type ($PbCl_2$-type) structure. These compounds were calculated to be narrow-gap semiconductors or semimetals. By comparison with known thermoelectric materials, our analysis showed that these compounds are promising candidate new thermoelectric materials, when heavily doped with holes or electrons. The weak chemical bonds and the variety in constituent elements indicate the possibility to achieve high thermoelectric figure of merit.

Key words: Thermoelectric materials, electronic structure calculation, Zintl phases, MgSrSi-type compounds

INTRODUCTION

Discovery of new high-efficiency thermoelectric materials composed of environmentally friendly elements has long been awaited for a breakthrough in thermoelectric technology. However, only a limited number of compound families have been intensively studied, as a consequence of the experimental difficulty in evaluating potential thermoelectric materials.

Thermoelectric figure of merit $ZT = S^2\sigma T/\kappa$ over 1 is widely used as a measure for application. To improve ZT, it is necessary to increase the Seebeck coefficient S, increase the electrical conductivity σ, decrease the thermal conductivity κ, and operate at high temperature T. However, S, σ, and κ are all strongly dependent on carrier density n, hence there is a strong dependence of ZT on n. This means that, unless investing tremendous efforts in carrier control experiments, one cannot evaluate the potential of a single compound as a thermoelectric material.

Thus, selection of the target compound before starting experiments is very important in the search for new thermoelectric materials. In contrast to experiments, carrier control is quite easy in first-principles calculations. The recent developments in density-functional calculation[1] and transport analysis software[2] allow us to calculate thermoelectric properties of compounds only from the atomic positions. Transport properties S, σ/τ, and electron thermal conductivity κ_{el}/τ can be calculated as solutions of the Boltzmann transport equation in forms containing the noncalculable relaxation time τ.

We applied an analysis proposed by Takeuchi[3] to decompose ZT into A and B, where A is a factor purely dependent on the electronic structure and B is a lattice-dependent factor containing the phonon thermal conductivity κ_{ph}. Since B is less than unity, A can be understood as the maximum possible ZT in the limit of $\kappa_{el} \gg \kappa_{ph}$.

$$ZT = \frac{S^2\sigma T}{\kappa_{el} + \kappa_{ph}} = AB, \quad A = \frac{S^2\sigma T}{\kappa_{el}}, \quad B = \frac{1}{1 + \kappa_{ph}/\kappa_{el}}.$$

Calculation of A eliminates τ from the calculation results as follows:

$$A = \frac{S^2(\sigma/\tau)T}{(\kappa_{el}/\tau)}.$$

As the first target for our calculation-based search, we selected compounds having MgSrSi-type

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