Study of novel sulfide thermoelectric materials and electron transport phenomena using first-principles electronic structure calculation

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Industrial waste heat of 60% represents a huge unused but available energy resource worldwide. Notably, thermoelectric (TE) conversion, a technology of mutual conversion between thermal energy and electrical energy from the viewpoint of resolving waste heat recovery difficulties. For example, many tellurides such as Bi_2Te_3 or PbTe are well known as good TE materials for applications. They include tellurium, which is present in smaller amounts in the Earth's crust. In recent times, sulfides are attracting attention as alternatives to tellurides because sulfur is an abundant and cheap group 16 element.

The author has investigated the electronic and thermoelectric properties of high power factor sulfide $Ni_{1-x}Co_xSbS$ (x = 0, 0.10, 0.20, and 0.40) experimentally and theoretically. For mother phase NiSbS shows a metallic conduction, however, the NiSbS shows large thermopower S of -27 μVK^{-1} at 300 K, indicating that the NiSbS is n-type TE material. The power factor PF ($= S^2 \cdot \rho^{-1}$) for NiSbS is extremely high, 1.9 $mWK^{-2}m^{-1}$, at 300 K compared to that of high performance TE sulfide materials such as tetrahedrites or colusites. For the DFT calculation result, the chemical potential μ for NiSbS is located near the peak of PF, which results from the pseudo-gap electronic structure. High PF for NiSbS results from the pseudo-gap electronic structure. The pseudo-gap and the filling control of electron are effective to change TE properties.

The electronic and TE properties of V_4GeS_8 and the substitution system $V_{4-x}Mn_xGeS_8$ (x = 0.02, 0.05) was investigated experimentally and theoretically. For the mother phase V_4GeS_8, the electrical resistivity ρ decreases concomitantly with increasing temperature, and the estimated band gap E_g is 0.20(4) eV. The value S is 330 μVK^{-1} at 300 K. The broad maximum of S is around 260 K. These results indicate V_4GeS_8 as a p-type narrow gap semiconductor. For density functional theory (DFT) calculation, the E_g is expanded from 30 to 165 meV under the rigid band approximation. The calculated S-T curve of V_4GeS_8 reproduces the experimental S-T of V_4GeS_8, which denotes that the V_4GeS_8 is a p-type narrow gap semiconductor experimentally and theoretically. The calculated ZT_{DFT} is enhanced by the hole doping of V_4GeS_8 at 340 K. For the Mn substitution $V_{4-x}Mn_xGeS_8$ (x = 0.02, 0.05), the S decrease, and the temperature of maximum S is shifted to higher temperature region with increasing x. The ZT enhances with increasing x. These results correspond with the calculated S-T and ZT_{DFT} of hole doped V_4GeS_8, denoting that the hole doping occurs by the substitution of V^{3+} to Mn^{2+}.

The wide gap sulfide $ZnCr_2S_4$ and the substitution system $Zn_{1-x}Ga_xCr_2S_4$ (x = 0, 0.10, 0.25, 0.50, 0.75) was investigated experimentally and theoretically. The experimental $ZnCr_2S_4$ shows a non-conduction as an insulator, which is consistent with the DFT calculation result. For the $Zn_{1-x}Ga_xCr_2S_4$ (x = 0, 0.10, 0.25, 0.50, 0.75), the ρ of decreases with increasing temperature as a semiconductor behavior. The S shows a large negative value, indicating that these samples were a n-type TE materials. The absolute value of S and slope of S decreases with increasing x, denoting that the electron doping was occurred with the Ga substitution. The calculated x dependence of ZT for $ZnCr_2S_4$ shows that the $x \sim 0.2$ is suitable. According to this result, the author succeeded the enhancement of ZT for $ZnCr_2S_4$.

The author performed the electron transport calculation of 809 sulfides using OpenMX and BoltzTraP and handmade programs. The guideline of the material design for the high performance TE materials was established. The suitable condition of the high ZT materials is that thermopower S is between 140 and 170 μVK^{-1}, or the Lorentz number L is 2.45×10^{-8} V^2K^{-2}, or the B factor ($= \kappa_{el} / \kappa_{el} + \kappa_{lat}$) is 0.6. The suitable primitive cell volume is about 3000 $bohr^3$.

Keywords: thermoelectric conversion, sulfides, first-principle calculation, electron transport calculation, 3d transition metal, high-throughput screening