

Title	第一原理電子状態計算による新奇硫化物熱電材料のマテリアルデザインと電子輸送現象の研究
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# 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<sub>2</sub>Te<sub>3</sub> 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<sub>1-x</sub>Co<sub>x</sub>SbS ( $x = 0, 0.10, 0.20, \text{ and } 0.40$ ) experimentally and theoretically. For mother phase NiSbS shows a metallic conduction, however, the NiSbS shows large thermopower  $S$  of  $-27 \mu\text{VK}^{-1}$  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,  $1.9 \text{ mWK}^{-2}\text{m}^{-1}$ , 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  $\mu$  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<sub>4</sub>GeS<sub>8</sub> and the substitution system V<sub>4-x</sub>Mn<sub>x</sub>GeS<sub>8</sub> ( $x = 0.02, 0.05$ ) was investigated experimentally and theoretically. For the mother phase V<sub>4</sub>GeS<sub>8</sub>, the electrical resistivity  $\rho$  decreases concomitantly with increasing temperature, and the estimated band gap  $E_g$  is 0.20(4) eV. The value  $S$  is  $330 \mu\text{VK}^{-1}$  at 300 K. The broad maximum of  $S$  is around 260 K. These results indicate V<sub>4</sub>GeS<sub>8</sub> 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<sub>4</sub>GeS<sub>8</sub> reproduces the experimental  $S$ - $T$  of V<sub>4</sub>GeS<sub>8</sub>, which denotes that the V<sub>4</sub>GeS<sub>8</sub> is a p-type narrow gap semiconductor experimentally and theoretically. The calculated  $ZT_{\text{DFT}}$  is enhanced by the hole doping of V<sub>4</sub>GeS<sub>8</sub> at 340 K. For the Mn substitution V<sub>4-x</sub>Mn<sub>x</sub>GeS<sub>8</sub> ( $x = 0.02, 0.05$ ), 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  $ZT_{\text{DFT}}$  of hole doped V<sub>4</sub>GeS<sub>8</sub>, denoting that the hole doping occurs by the substitution of V<sup>3+</sup> to Mn<sup>2+</sup>.

The wide gap sulfide ZnCr<sub>2</sub>S<sub>4</sub> and the substitution system Zn<sub>1-x</sub>Ga<sub>x</sub>Cr<sub>2</sub>S<sub>4</sub> ( $x = 0, 0.10, 0.25, 0.50, 0.75$ ) was investigated experimentally and theoretically. The experimental ZnCr<sub>2</sub>S<sub>4</sub> shows a non-conduction as an insulator, which is consistent with the DFT calculation result. For the Zn<sub>1-x</sub>Ga<sub>x</sub>Cr<sub>2</sub>S<sub>4</sub> ( $x = 0, 0.10, 0.25, 0.50, 0.75$ ), the  $\rho$  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<sub>2</sub>S<sub>4</sub> shows that the  $x \sim 0.2$  is suitable. According to this result, the author succeeded the enhancement of  $ZT$  for ZnCr<sub>2</sub>S<sub>4</sub>.

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  $\mu\text{VK}^{-1}$ , or the Lorentz number  $L$  is  $2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2}$ , or the  $B$  factor ( $= \kappa_{\text{el}} / (\kappa_{\text{el}} + \kappa_{\text{lat}})$ ) is 0.6. The suitable primitive cell volume is about 3000 bohr<sup>3</sup>.

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