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主 論 文 の 要 旨

論文題目　Effect of grain boundaries and partial substitution of transition metals on thermoelectric properties of higher manganese silicide

(結晶粒界と遷移金属の部分置換が高マンガンシリサイドの熱電特性に与える影響)

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論 文 内 容 の 要 旨

The non-renewable fossil fuels in the form of crude oil, coal, or natural gas are being used to fulfill the energy need of our modern society. The energy conversion efficiency has been limited and more than 60% of available energy is wasted in the form of heat. Here, thermoelectric generators (TEGs) are believed to play a key role to convert the waste form of heat energy into useful electrical energy. TEGs with efficiency 10% can save billions of dollars when they are operational on large scale worldwide.

Thermoelectric materials used for commercial TEGs are the compounds with Pb, Te, Ag, Ge, Sb, etc. Considering the European and Japanese norms for limiting hazardous elements for technological applications TEGs would be a harmful technology. So it's a need in thermoelectric research to reconsider developing this technology from start, by finding alternatives and designing new guiding principles. One of the most promising alternative material containing cheap and non-toxic elements, while possessing a large magnitude of *ZT* is higher manganese silicide (HMS) stabilized at $MnSi_\gamma$ ($1.73 \leq \gamma \leq 1.75$). Unfortunately, the *ZT*-value is not competitive with the commercially available thermoelectric materials. The need to improve the performance of higher manganese silicide has drawn our attention to investigate a new technique that can enhance the *ZT*.

In this study, we focused on preparing cheapest and most efficient higher manganese silicide compound for the thermoelectric generator by introducing two different strategies 1) energy filtering effect to improve the power factor and 2) partial substitution of transition metals on Mn site to tune the carrier concentration together with heavy atoms substitution to reduce lattice thermal conductivity. Here, we have tried to investigate the effect of carrier filtering due to secondary phases and grain boundaries. With the reference of Mn-Si binary phase diagram we synthesized different samples in silicon deficient and silicon rich regions, forming MnSi and Si precipitates, respectively. We employed a liquid quenching technique to obtain high density of grain boundary. The result suggests the energy filtering by grain boundaries could be an effective method to enhance performance by 30%.

The second strategy worked well to find out the optimal carrier concentration both for p-type and n-type by Cr and Fe substitution. The liquid quenching technique has helped us to improve the solubility for Cr, Fe, W and Re. We observed a reduction in grain size by a small amount of substitution. A large value of *ZT*~0.5 at 700K was obtained by simultaneous substitution of Fe and W, which was the highest *ZT* reported for n-type HMS. The Re substitution was very effective in reducing the lattice thermal conductivity to improve *ZT* more than unity above 900K. Hence, the strategy of implying energy filtering effect by grain boundaries in Re-HMS worked well to improve the power factor and could increase *ZT* by more than 20%. All the microstructural and physical property analyses has been systematically reported in this thesis.