Title	化学合成したCu-Sn-S系ナノ粒子をビルディングブロックとして用いたナノ構造熱電材料の創製
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Abstract

Thermoelectric (TE) technique has attracted much attention due to the dramatical demand for energy conversion. The researches on TE materials is hotpot. However, most of the high efficiency TE materials contains toxicity and rare elements such as Te and Se that are not feasible for real application. To investigate the sustainable TE materials with high efficiency, copper tin sulfide (CTS), which emerged as promising TE material and has been widely studied for solar cells, was chosen as the target material because it contains environmentally friendly, earth abundance and low cost elements. However, it used as TE material is lack of understanding. The impacts of nanostructuring, Zn doping effect and grain size effect on the final TE performance of CTS material have been systematically investigated. This dissertation research surrounds on the work of CTS based nanoparticles (NPs) as building block for TE materials, which synthesized by chemical methods that can control over the size, shape, composition and structure of NPs. The fabrication approaches, characterizations and TE properties of the copper tin sulfide based materials are all presented in this work.

Chapter 1 gave a basic introduction of thermoelectricity and background about CTS material and its potential and challenges for being chosen as TE materials. A brief review of the chosen strategies to enhance the TE efficiency and current research work on CTS based TE materials have been given.

Chapter 2 demonstrated the chemically synthesized uniform hole-doped $Cu_2Sn_{1-x}Zn_xS_3$ (x=0-0.2) NPs and fabricated TE materials by sintering the NPs into dense bulk materials using pulse electric current sintering (PECS) technique after ligand exchange. Then, the structure and composition-property relationships in the $Cu_2Sn_{1-x}Zn_xS_3$ TE materials were analyzed. By

introducing Zn doping effect and nanostructuring, the highest *ZT* value of 0.37 at 670 K was achieved in both $Cu_2Sn_{0.95}Zn_{0.05}S_3$ and $Cu_2Sn_{0.85}Zn_{0.15}S_3$ nanostructured materials, which was comparable to the *ZT* value at the same temperature of the $Cu_2Sn_{0.9}Zn_{0.1}S_3$ non-nanostructured material.

Chapter 3 described the one pot chemical method and hot injection method synthesized copper tin sulfide materials with controllable size, shape and structure. The resulting particles after ligand exchange were pelletized by using PECS technique for further TE measurements. The grain size effect and composition-property relationships in the CTS TE materials have been analyzed. It was found that the lattice thermal conductivities decreased with grain sizes and could be strongly suppressed when the grain size of pellet decreased to around 30nm. In addition, the ratio of Sn/Cu in CTS materials has been found to have huge effect on the carrier concertation.

Chapter 4 studied the enhanced TE properties of blended $Cu_2Sn_{1-x}Zn_xS_3$ nanobulk materials, which fabricated by sintering a mixture of chemically synthesized $Cu_2Sn_{0.85}Zn_{0.15}S_3$ (high σ and high κ) and $Cu_2Sn_{0.9}Zn_{0.1}S_3$ (low σ and low κ) NPs with different weight ratios into dense bulk materials by PECS technique. $Cu_2Sn_{0.85}Zn_{0.15}S_3$ has been used as a host material and $Cu_2Sn_{0.9}Zn_{0.1}S_3$ used as nanoinclusions. By using different chemical mixing methods, these two heterogeneous (but nearly identical) NPs were blended in a weight fraction of 9:1 for making a nanobulk material, the pellet showed *ZT* = 0.64 at 670 K, which is 1.7 and 1.9 times higher than the *ZT* values of the pristine $Cu_2Sn_{0.85}Zn_{0.15}S_3$ and $Cu_2Sn_{0.9}Zn_{0.1}S_3$ nanobulk materials, respectively.

Chapter 5 gave the general conclusions, and future prospects of the overall research work.

Keywords: Thermoelectric, Copper Tin Sulfides, Chemical Method, Nanoparticles, Size effect