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論文題目	Synthesis and Characterization of Nanoparticles and Nanostructured Materials for Thermoelectric Applications (熱電ナノ粒子の化学合成とナノ構造熱電材料の創製)
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論文の内容の要旨

conversion such as cooling devices, power generation or energy harvesting materials. Recently, in an attempt to improve our overall energy production efficiency, TE materials have developed into a strong potential candidate which can enable the direct alternative conversion between poor-quality thermal energy and high-quality electric energy. The reuse of waste heat will be significant with the renewal of these materials to become a next generation technology. TE materials with phonon-glass electron-crystal (PGEC) property have been recognized as one of the most promising approaches to improve the TE efficiency for practical applications and introducing desired nanostructure into TE materials is one way to create PGEC materials. Because of the capability of well controlled morphology and nanostructure, chemical synthesis is interesting for producing nanoparticles (NP)s with tailorable characteristics for TE applications. Furthermore, the chemical synthesis can be scaled up to obtain bulk amounts of NPs for creating nanostructured thermoelectric materials.

The purpose of this research is to develop the chemical synthesis approaches towards nanoparticles and nanostructured materials for TE applications. With this purpose, my research will be designed to address the issues regarding NPs synthesized *via* chemical methods in order to offer scalable and economic comparative syntheses with capability of creating compounds and alloys with tailorable characteristics in the nanoscale regime. The NPs which I focus on include Bi-Sb-Te based ternary alloys and Zn-Sb alloys which can be applied in a broad temperature range (room temperature to 400 oC) and are challenging for chemical synthesis.

(1) Chemical synthesis and formation mechanism of BiSbTe NPs

The modified polyol method was utilized to synthesized BiSbTe containing NPs *via* a one-pot chemical reaction. The resulting NPs show various morphologies (nanowires, nanodiscs, nanodiscs grew on NWs) associated with the capping ligands (oleylamine (OAM) and oleic acid, decanethiol (DT), and oleic acid and decanethiol respectively) used in the synthesis. The particles also possess a well-defined phase segregation based structure in each case. Because of the complicated interactions between metal precursors and capping ligands as well as the metal interaction in the one-pot reaction, a systematic investigation of the synthesis of monometallic, bimetallic and trimetallic NPs was conducted to elucidate the NP's formation mechanism. The results of the investigation indicate that when using DT as capping ligand, Te can act as a catalyst for the formation of Bi2Te3 and Sb2Te3 and the strong interaction between Te and Bi and/or Sb precursor complex results in phase segregation of the resulting BiSbTe containing NPs. On the other hand, when using OAM as the capping species, BiSb NPs (alloy) can be formed, and the interaction between BiSb and Te NPs in the solution can result in the formation of ternary BiSbTe NPs. Based on the NP's formation mechanism, the one-pot synthesis is performed with tri-molecular precursors in OAM to achieve ternary BiSbTe NWs. To further control the morphology and composition of the ternary BiSbTe NPs, we modified the chemical synthesis in which BiSb alloy NPs with tailorable composition were first prepared in the presence of OAM and were then used as seeds for the growth of BiSbTe NPs. The resulting NPs are a ternary alloy of Bi, Sb and Te and the ratios of Bi:Sb and the morphology of the seeds were maintained in the final BiSbTe NPs. The results of these studies offer the fundamental understanding of the NPs' formation mechanism and basic knowledge to synthesize NPs with controllable morphology and composition.

(2) ZnSb NPs: chemical synthesis and large scale reaction to create nanostructured ZnSb materials.

I designed a one-pot chemical synthesis reaction with multiple steps to create the target ZnSb NPs. The NP formation was achieved by using Sb NPs as a seed followed by the reduction of Zn on the surface of Sb NPs and subsequent alloying to form ZnSb NPs. Careful investigation using TEM, XRD, EDS, XPS, STEM-HAADF reveals the complex structure of the Zn-Sb NPs with core-shell like morphology and an inverted composition distribution of Zn and Sb from the core to the shell of single NPs. The enhancement in oxidation stability of the ZnSb NPs was observed to be associated with the alloy formation.

Nanostructured ZnSb materials were prepared from ZnSb NPs obtained in the large scale synthesis (after surface treatment) *via* hot-pressing. The ZnSb pellet still possesses the nanograin-boundaries arising from the building block constituents and the resulting TE properties of the pellet were investigated. The results indicated that the pellet has semiconducting properties with good electrical conductivity, low thermal conductivity and Seebeck coefficient similar to Sb which arises from the existence of a mixture of Sb and ZnSb phases together within a ZnO shell. Even though the TE efficiency is not significant, the research exhibits the capability of utilizing NPs as building blocks for creating nanostructured TE materials. Further study on the reaction and pressing conditions can help to improve the TE efficiency.

論文審査の結果の要旨

本博士学位論文は、環境・エネルギー分野での応用が期待される熱電変換素子のエネルギー変換効率を高めることを目的として、ナノ構造制御された熱電材料をボトムアップ式に創製するためのビルディングブロックとなる熱電材料ナノ粒子の化学合成法の確立とその評価を行なったものであり、以下の 3 つの研究成果から構成される。第一に、低温領域で高い ZT 値を示す Bi-Te 系及び Bi-Sb 系のナノ粒子の合成法を確立し、粒子生成機構を明らかにした。粒子生成機構の理解をもとに三元系の Bi-Sb-Te ナノ粒子の合成にも成功している。第二に、Bi-Sb ナノ粒子を種粒子とし、組成を任意に制御しながら Bi-Sb-Te ナノ粒子を合成する手法を確立した。第三に、Zn-Sb 系のナノ粒子をワンポットで合成する手法を開発し、さらに反応をスケールアップすることでグラムスケールの Zn-Sb ナノ粒子を合成することを可能とした。これにより、ホットプレスでナノ構造を有した Zn-Sb ペレットの作製が可能になった。Zn-Sb ペレットを用いて熱電性能の精密測定を行い、得られた物性値（ゼーベック係数、電気伝導率、熱伝導率）とペレットの微細構造との関係の考察から、ナノ構造制御された熱電材料創製への指針を与えた。

熱電変換材料は、環境・エネルギー問題を緩和するための脱フロン冷却装置や廃熱利用発電等のエネルギー変換素子の材料として近年特に注目されている。しかし 60 年以上も熱電変換効率の向上が進まず、熱電材料の応用範囲は限られてきた。熱電変換効率の向上のためには、電気伝導度を低下させずに熱伝導率を低下させる必要があり、このトレードオフを解消することは通常の材料では困難であったためである。最近のナノテクノロジーの進歩によって、材料の組成、構造および形状をナノメートルオーダーで制御することが可能となり、トレードオフを解消できる可能性が出てきた。熱電ナノ粒子は、高効率の熱電変換素子を実現する材料として極めて有望な材料の一つであり、本論文の成果は、熱電変換素子によるエネルギーハーベスティングの実現に向けて新たな可能性を示すと同時に、様々な多元系ナノ粒子の化学合成を行なう際に有用な知見を与えるものである。

以上、本論文は、廃熱を利用した熱電発電のためのナノ構造熱電材料の創製を目指し、熱電ナノ粒子の化学合成とその構造および物性について新たな知見と可能性を提示したものであり、当該分野に限らず幅広い関連分野において学術的に貢献するところが大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。