Title	熱電ナノ粒子の化学合成とナノ構造熱電材料の創製
Author(s)	Nguyen, Thanh Mai
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Description	Supervisor:前之園　信也，マテリアルサイエンス研究科，博士

Abstract

Thermoelectric (TE) materials are interesting research field for energy conversion applications such as cooling devices, power generation, energy harvesting materials. Because TE materials can enable the direct alternative conversion between poor-quality thermal energy and high-quality electric energy, the renewal of these materials can make them become potential candidate for a next generation technology of waste heat recovery. 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 control morphology and nanostructure, chemical synthesis is interesting for producing nanoparticles (NP)s with tailorable characteristics for TE applications. Furthermore, the chemical synthesis could be scaled up to obtain large amount of NPs for creating nanostructured TE 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 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 nanoscale regime. The NPs which I focus on include Bi-Sb-Te based ternary alloys and Zn-Sb alloys which can be applied for room temperature to 400 ºC and are challenging for chemical synthesis.

(1) Synthesis and formation mechanism to control the composition and morphology of solid solution 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 nature of the capping ligands used in the synthesis and the phase segregation occurs 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 using DT as capping ligand, Te can act as the catalyst for the formation of Bi_2Te_3 and Sb_2Te_3 and the strong interaction between Te and Bi and/or Sb precursor complex results in the phase segregation of the resulting BiSbTe containing NPs. On the other hand, 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 ternary BiSbTe NPs, the chemical synthesis was modified in which BiSb alloy NPs with tailorable composition first prepared in the presence of OAM and used as the seed to grow ternary solid solution BiSbTe NPs. The resulting NPs are ternary alloy of Bi, Sb and Te and the ratios of Bi:Sb and the morphology of the seeds were maintained in the BiSbTe NPs. The results of these studies offer the fundamental understanding of the NPs' formation mechanism and the basic knowledge to synthesize NPs with controllable morphology and composition.

(2) Zn-Sb NPs: chemical synthesis and large scale reaction to create the nanostructured Zn-Sb materials.

A chemical synthesis with multiple steps in one-pot reaction was designed via the formation of Sb NPs as the seed followed by the reduction of Zn on surface of Sb NPs and alloying to form Zn-Sb NPs. The careful investigation using TEM, XRD, EDS, XPS, STEM-HAADF reveals the complex structure of Zn-Sb NPs with core-shell like morphology and the opposite composition distribution of Zn and Sb from the core to the shell of single NP. The enhancement of oxidation stability of Zn-Sb NPs is associated with the alloy formation.

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

Key word: thermoelectric, nanoparticles, semiconductor, chemical synthesis, alloy