Title	化学合成したI-III-IV-VI族四元化合物ナノ結晶を用いたナノ構造熱電材料の作製
Author(s)	DWIVEDI, PRATIBHA
Citation	
Issue Date	2020-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/17008
Rights	
Description	Supervisor:前之園　信也，先端科学技術研究科，博士

Abstract

Thermoelectric (TE) technology has acquired a lot of attention due to the ever-growing demand for energy conversion. The research finding on TE materials is hot topic. However, majority of the high efficiency TE materials contains toxic and rare elements such as Se and Te that are not feasible for real application. To investigate the sustainable TE materials with high efficiency, quaternary copper-metal-tin-sulfide based compounds emerged as promising TE material was selected because it consists of environmental friendly, earth abundant and relatively low-cost elements. This dissertation surrounds on the research work of quaternary copper sulfide-based nanocrystals as building block for TE materials, synthesized by chemical methods. The nanobulk material fabrication approaches, characterizations and TE properties in combination with the methodology to improve the TE figure of merit are all presented in this research work.

Chapter 1 provides the general introduction of the TE materials. This chapter includes the basic concepts of TE's, conventional TE materials, synthesis, effective methodologies to enhance the thermoelectric efficiency, background about the quaternary copper-sulfide based material and its potential as well as challenges for being selected as TE materials. In this research we decided to counter the high lattice thermal conductivity (κ_{lat}) through not only all-scale hierarchical architechuring but also introducing the copper-aluminium-tin-sulfide based material for the first time in thermoelectrics due to predictions of these system to possess very low κ_{lat}. High power factor (*PF*) and low κ_{lat} was not sufficient for Cu_3AlSnS_5 (CATS) system to acquire high *ZT* value. The shortcomings of the CATS system were systematically countered with the gradual substitution of Al by Ga, and by introducing nanoinclusions of Cu_2SnS_3 (CTS). We are the first to investigate the I_3-II/III-IV-VI_{5-y} (I=Cu; II=Zn; III=Al/Ga; IV=Sn; VI=S; *y* is to maintain electrical neutrality of the system) based TE materials. Various methodologies available for the nanocrystals synthesis have been discussed and out of all the one pot chemical method was shortlisted for this research due to their unprecedented control on the reaction reproducibility as well as scalability. In other words, this chapter represents the challenges associated with present TE materials have been postulated in combination with a brief outlook about the scope of this research, as one of the plausible solutions.

Chapter 2 describes the synthesis of Cu-Zn-Sn-S nanocrystals using one pot chemical method. After ligand exchange, the nanocrystals were pelletized using pulse electric current sintering (PECS) technique to yield Cu_3ZnSnS_{5-y} nanobulk material. To lower the κ_{lat}, a gradual substitution of Zn with Al was performed in the Cu_3ZnSnS_{5-y} system to yield $Cu_3Zn_{1-x}Al_xSnS_{5-y}$ (x = 0.25, 0.5, 0.75, and 1). Complete substitution of Zn by Al substantially decreased the κ_{lat} and dramatically increased σ of the material. *ZT* value of 0.39 at 658 K was achieved for the Cu_3ZnSnS_{5-y} material. However, the *ZT* value could not be significantly enhanced with complete Al substitution, which

could be primarily attributed to the κ_{car}. These results highlight the production of $Cu_3Zn_{1-x}Al_xSnS_{5-y}$ TE materials and unveil the scope for improvement of *ZT* values by altering transport properties.

The Chapter 3 demonstrate a methodology for curtailing the κ_{car} of the CATS nanobulk TE materials without compromising the already suppressed κ_{lat}. This chapter presents the effect of Ga substitution in $Cu_3Al_{1-x}Ga_xSnS_5$ nanobulk materials on the transport properties of the materials has been systematically examined. The *ZT* value of the $Cu_3Al_{1-x}Ga_xSnS_5$ nanobulk at $x = 0.5$ was found to be more than twice ($ZT = 0.26$) than the pristine CATS nanobulk at 665 K, primarily because of the significant reduction in κ_{car}. Correlation among transport parameters and material structural characteristics of the $Cu_3Al_{1-x}Ga_xSnS_5$ nanobulks ($0.25 \leq x \leq 1$) revealed that a larger fraction of zincblende (ZB) phase leads to a higher *PF*.

The Chapter 4 examines the ability of CTS nanocrystals as nanoinclusions in the CATS system for reducing the κ_{car} without negatively impacting the κ_{lat}. The doping content of CTS gradually varied from 0.1 wt%, 1 wt%, 3 wt%, 5 wt% and 10 wt% in CATS. The fabricated nanobulk TE material shows, interestingly, wurtzite (WZ) as a major crystalline phase from 1 wt% CTS content onwards; which increases with the increase in CTS nanoinclusions. A correlation has been observed between the type and content of major crystallographic phase and the thermoelectric performance of the fabricated nanobulk TE materials. Greater content of WZ phase has been associated with the lower *ZT* value. The results direct the attention towards the role of interface between the nanoinclusion and primary matrix in deciding the fate of, especially, σ. The 0.1 wt% CTS nanoinclusions leads provided better trade-off between σ and S without compromising κ and thus improved the *ZT* value 3× than neat CATS system. The 0.1 wt% CTS containing sample possess greater ZB phase content than any other pellets under consideration and prevail the importance of symmetric crystal structure content in deciding the fate of TE properties.

Chapter 5 disseminates the general summary and conclusions followed by the future prospects of the research presented in this dissertation. The results highlight the importance of co-ordination between the material crystalline structural traits and *ZT* value of I_3-III-IV-VI_5 based TE materials without using rare and/or highly toxic elements. This research provides an important insight in understanding the behavior of ZB-/WZ-rich nanobulk TE materials. The correlation observed among material structural traits that apart from nanostructuring, the greater content of more-ordered crystalline phase plays an important in regulating the transport characteristics. On the other hand, the mechanistic details for understanding the reasons which affects inherently the content and the distribution of ZB/WZ phase fraction in the material in association with their respective electrical and thermal transport properties represents a challenging yet interesting future outlook.

Keywords: Thermoelectric, Quaternary Copper Sulfides, Crystallographic Phases, One Pot Chemical Synthesis, Nanocrystals