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Abstract of Thesis

Name (KIM JUNGMIN)	
Title	Optimization of Chemical Composition of *p*-type Filled-Skutterudites for Enhancement of Thermoelectric Properties (熱電特性向上のための*p*型充填スクッテルダイトの化学組成最適化)

Abstract of Thesis

Thermoelectric power generation (TEG) is essential in new/renewable energy conversion technology to solve the global environmental pollution and energy crisis. They have been used in high end applications such as spacecraft and also have been recently applied in a variety of fields such as car engine or watch. The performance of thermoelectric (TE) device depends on the type of materials used and properties such as their electrical conductivity, Seebeck coefficient, thermal conductivity and thermal stability etc. Among the various TE materials, skutterudite compounds have considered as promising TE material due to the high TE performance and good mechanical properties. However, *p*-type skutterudites show lower TE performance than the *n*-type ones, therefore to improve high efficiency of TEG device, higher performance of *p*-type ones are required.

The purpose of this study is to enhance TE properties of *p*-type $CoSb_3$-based skutterudites. The another one is to confirm that behavior of introduced and substituted various elements (In, Ce, Ga, Fe) in the skutterudite main phase.

In the chapter I and II, I introduced the background of thermoelectric with essentially theoretical concepts and summarizes the experimental methods and characterize the material investigated used in this thesis. Especially, in the chapter II, I described the the sintering techniques and measurement techniques applied to confirm the material properties.

In the chapter III, thermoelectric properties of In single-filled *p*-type $In_xFeCo_3Sb_{12}$ were investigated. All the samples showed positive values of Seebeck coefficient as *p*-type ones. The filling fraction of $In_xFeCo_3Sb_{12}$ was revealed to extend to the value of $x = 0.43$. I confirmed that the increase of the In content led to the reduction hole concentration, because In provided the system with conduction electrons through the results of Hall measurement. As a result, the small lattice thermal conductivity caused by the rattling mode of filled In and the enhanced PF with an appropriate hole concentration led to large magnitude of zT.

In the chapter IV, I focus on Ce-filled Fe-substituted $CoSb_3$ as *p*-type skutterudites, where Fe will act as a hole dopant. The samples with nominal composition of $Ce_xFe_yCo_{4-y}Sb_{12}$ are synthesized and their TE properties are investigated. All the samples show the *p*-type conduction. I confirmed that the carrier concentration was optimized by tuning the Fe/Co ratio and the Ce filling fraction. As a result, this study revealed that Fe/Co substitution is more predominant than the Ce filling for the reduction of lattice thermal conductivity.

In the chapter V, I try to enhance the TE properties of Ce-filled (Co, Fe)Sb_3 by co-filling of Ga. The samples $Ga_xCeFe_{3.5}Co_{0.5}Sb_{12-x/3}$ in the nominal composition are synthesized and their TE properties are examined. It is revealed that the Ga contributed to optimize the carrier concentration as well as to reduce the lattice thermal conductivity. In addition, I confirmed that the Ga occupy not only the void site but also the Sb site. Owing to these Ga contributions, the material's TE properties are enhanced.

In summary, the effect of various filler atoms (In, Ce, Ga) and substituted Fe on the TE properties was compared experimentally. I confirmed that it is possible to optimize the carrier concentration tuning the filler/substituted atoms. Furthermore, in case of (Fe, Co)Sb_3, Fe/Co substitution is more predominant than the filling for the reduction of lattice thermal conductivity. As a result, I could enhance the TE properties of *p*-type skutterudites through the optimization of chemical composition.

The results in each of the studies discussed will provide valuable insight into the role of enhancement of TE properties in their respective applications and can apply to environmental, thermoelectric designs for the development of high-performance TEG materials.

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論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

The purpose of this thesis is to enhance TE properties of *p*-type $CoSb_3$-based skutterudites. The another one is to confirm that behavior of introduced and substituted various elements (In, Ce, Ga, and Fe) in the skutterudite main phase.

In the chapter Ⅰ and Ⅱ, the background of thermoelectric with essentially theoretical concepts and summarizes the experimental methods were introduced. Especially, in the chapter Ⅱ, the sintering techniques and measurement techniques applied to confirm the material properties were described.

In the chapter Ⅲ, the thermoelectric properties of In single-filled *p*-type $In_xFeCo_3Sb_{12}$ were examined. All the synthesized samples showed *p*-type conduction of Seebeck coefficient. The filling fraction of obtained samples was indicated that is extended to the value of $x = 0.43$. As a result, the reduced lattice thermal conductivity caused by the rattling effect of filled In and the enhanced *PF* with an appropriate hole concentration led to large magnitude values of *zT*.

In the chapter Ⅳ, Ce-filled (Co, Fe)Sb_3 as *p*-type $Ce_xFe_yCo_{4-y}Sb_{12}$ were investigated. The samples (x = 0.8, 0.9, 1.0 and y = 3.0, 3.5) are synthesized and their TE properties are examined, which obtained all samples indicate the *p*-type conduction. Consequently, it was revealed that the carrier concentration can be control by optimization of substituted Fe and filled Ce. Especially, results of this study mean that the substituted Fe is more effective than the filled Ce for the reduction of thermal conductivity.

In the chapter Ⅴ, to improve the TE properties of Ce-filled (Co, Fe)Sb_3, the co-filling method of Ga was used. The samples $Ga_xCeFe_{3.5}Co_{0.5}Sb_{12-x/3}$ in the nominal composition are synthesized and their TE properties are examined. It is revealed that the Ga contributed to optimize the carrier concentration as well as to decrease the lattice thermal conductivity. Owing to these Ga contributions, the material's TE properties are enhanced.

In summary, the effect of various filler atoms (In, Ce, Ga) and substituted Fe on the TE properties was compared experimentally. In case of (Fe, Co)Sb_3, substituted Fe/Co is more effective than the filled atom for the reduction of lattice thermal conductivity. Consequentially, it was possible to enhance the TE properties of *p*-type skutterudites through the optimization of chemical composition.

The results in each of the studies discussed will provide valuable insight into the role of enhancement of TE properties in their various applications and can apply to environmental, thermoelectric designs for the development of high-performance TEG materials.