様　式　C－19、F－19－1、Z－19　(共通)

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研究課題名（和文）Improved cryogenic thermoelectric performance of MgAgSb-based materials by modulation doping of Cu

研究課題名（英文）Improved cryogenic thermoelectric performance of MgAgSb-based materials by modulation doping of Cu

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研究成果の概要（和文）：通常タイプの遊星ボールミリング法と放電プラズマ焼結法を用い、塊状のCu添加合金MgAgSb基熱電材料を合成できた。AgサイトにCu原子を置換することにより、MgAgSb基材料の電気特性を向上させた。複数パラメーターを最適化した結果、MgAg0.93Cu0.02Sb0.98試料のPFを2111 μW/mK-2 @ 523Kに向上させた。ドープしていないものより18%増加した。 更に、その内部構造を階層構造化することやミクロ孔を形成するなどよりκを低く抑え、MgAg0.935Cu0.015Sb0.98@ 60 MPaでは ZT ~ 1.08 @473 K のchampion data が得られた。

研究成果の学術的意義や社会的意義
熱電発電ではエントロピーの高い低品位の低中温熱源（LNGや石炭を燃料とする火力発電所や様々な産業プロセスからの100°C以下の大量廃熱、冷熱産業や人体を含めた様々な環境周囲からの200K-常温範囲の未利用熱など）から、高品質の電気エネルギーに変換できる技術で、通常のRankine サイクル利用の熱水蒸気発電システムに比較して、可動部分を少なくし単純化できる発電プラント構成にできる等の優位性から、省エネルギー・地球温暖化問題に寄与できるために大きな期待がかかる。今回研究した熱電素子は ZT ~ 1.08 @473 Kに達し、その学術的意義は高く、上記応用分野に充分適用可能で社会的意義も高い。

研究成果の概要（英文）：MgAgSb-based alloy was successfully prepared via ordinary planetary ball milling and spark plasma sintering. The element Cu successfully doped into MgAgSb to cooperatively optimize the electrical transport properties. The main parameters including nominal composition of raw powders Mg, Ag, Sb, Cu doping ratio, SPS pressure and heat treating conditions have been optimized. As a result, the maximum PF value of 2111 μW/mK-2 at 523K for MgAg0.93Cu0.02Sb0.98 was about 18% increased than 1788 μW/mK-2 for the initial sample MgAg0.95Sb0.98, and a peak ZT ~ 1.08 at 473 K were achieved for the sample MgAg0.935Cu0.015Sb0.98@ 60 MPa. In addition, we explored the phase composition and micro-pores effects and found that a large number of micro-pores can strengthen phonon scattering to reduce the lattice thermal conductivity. Thus, thermoelectric properties of MgAgSb-based alloys can be enhanced by Cu doping into Ag site and micro-pores structures.

研究分野：エネルギー材料

キーワード：MgAgSb熱電材料　廃熱発電　放電プラズマ焼結　電気特性　熱伝導率制御　ミクロ孔　Cuドープ

１．　　研究開始当初の背景

Natural gas, as a clean energy, has gradually become a main source in the energy market. The natural gas is cooled to 111 K to become liquefied natural gas (LNG) to facilitate transportation. During the gasification, about 840 MJ cold energy is released per ton of LNG. Thermoelectric materials provide a green, safe and reliable method for generating power or refrigeration, which plays a more and more important role in alleviating energy crisis, environmental pollution and climatic change. TE performance is usually assessed in terms of a figure of merit ZT = S2σT /κ, where T is absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity of the material. Due to the couple relation among S, σ and κ, how to optimize the three ones simultaneously is a nontrivial task.

Currently, most of the thermoelectric generators have the best performance at 100~300oC, but cryogenic cooling and power generation using thermoelectric materials remains challenging so far. Recently, α-MgAgSb has a large power factor (PF) like Half-Heusler, and ultralow thermal conductivity like glass. In addition, it has the advantages in rich elemental content and good mechanical performance. Our previous work demonstrates that MgAgSb-based materials are promising candidates for the development of TE devices, which can drive the MgAgSb-based TE applications towards to power generation and cooling system at near room-temperature or cryogenic temperature. The “key scientific question” is how to further improve TE properties at cryogenic temperature for MgAgSb-based materials through decoupling three parameters: S, σ and κ.

２．研究の目的

This project intends to challenge new regulation method in MgAgSb materials for the conversion of low-quality cold energy during LNG transportation and gasification into electricity. New strategy concerned here is modulation doping of Cu as a foreign atom introduction to achieve high ZT value by two steps.

1.Developing a low-cost preparation method for Cu doped MgAgSb -based TE materials with high thermoelectric conversion efficiency for large scale LNG cold energy utilization;

2. Analyzing the TE generation characteristics at cryogenic temperature working conditions and exploring the mechanism for improving ZT value.

３．研究の方法

Synthesis

The Cu-MgAgSbmaterials were fabricated by an ordinary planetary ball-milling (WXQM-1L) and a spark plasma sintering system (SPS, LABOX-225, SINTER LAND INC.). Mg (99.5%, Aladdin), Ag (99.9%, Macklin), Cu (99.9%, Macklin) and Sb (99.5%, Aladdin) were weighed with the nominal composition MgAg0.95Sb0.99 and then loaded into a stainless-steel jar with balls inside an argon-filled glove box, followed by ball milling at 600 rpm for 18 hours under argon atmosphere. The final powders were sintered by SPS at 573 K for 10 min in vacuum under a compressive pressure of 20 MPa, 40 MPa, 50 MPa, 60 MPa, 80 MPa and 100 MPa, respectively. The obtained samples were further heated to 573 K at 3 K min−1 in a tubular furnace (OTF-1200 X, Kejing) under the atmosphere with 5% H2 and 95% Ar and held for 10 days.

4．研究成果

1. Effect of Cu doping on MgAgSb based thermoelectric materials

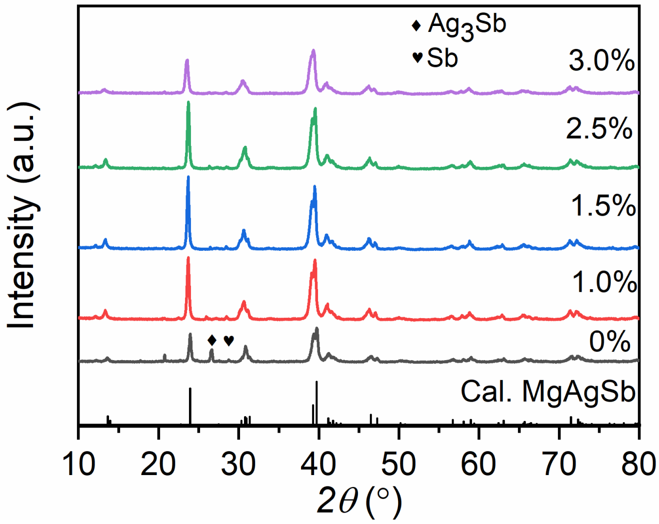

Fig. 1. (a)XRD patterns for $MgAg_{0.95-x}Cu_xSb_{0.98}$ (x=0,0.005,0.01,0.015) samples.

Table1

Samples	Mg (%)	Ag (%)	Sb (%)	Cu (%)
$MgAgSb_{0.98}$	30.6	34.7	34.6	
$MgAg_{0.935}Cu_{0.015}Sb_{0.98}$	33	33.1	33.7	0.1

Fig.1 presents the X-ray powder diffraction (XRD) patterns of $MgAg_{0.95-x}Cu_xSb_{0.98}$ (x=0,0.01，0.015,0.025,0.03) samples. The XRD results indicate that the diffraction peaks of the samples are consistent with the calculated results for MgAgSb with $I\bar{4}c2$ space group. We clearly found that the samples have a few impurity phases of Sb and Ag_3Sb. As expect, the ratios of atoms the pristine sample $MgAg_{0.95}Sb_{0.98}$ and $MgAg_{0.935}Cu_{0.015}Sb_{0.98}$ are listed in table 1. We can see that the content of Ag and Sb in the original sample is higher than Mg, which is a good explanation for the presence of Ag_3Sb in the pristine sample.

Fig. 2 show the SEM images of freshly fractured surface for $MgAg_{0.95-x}Cu_xSb_{0.98}$ (a) x = 0; (b) x = 0.01; (c) x = 0.015; (d) x = 0.025 samples. It can be seen that each bulk sample is comprised of the compacted grains, which is consistent with its high relative density. Notably, the size of the grains in the pristine sample $MgAg_{0.95}Sb_{0.98}$ (x = 0) is on nanometer scale (Fig. 2a). Notably, as the Cu amount increases to x=0.01 and 0.015, there appear a few micron-particles in the matrix (Fig. 2b-c), possibly conducive to reducing the lattice thermal conductivity of the materials. However, when Cu content is higher than 2.5, a large number of micron particles appear in the sample (Fig. 2d), which is unfavorable to the reduction of thermal conductivity.

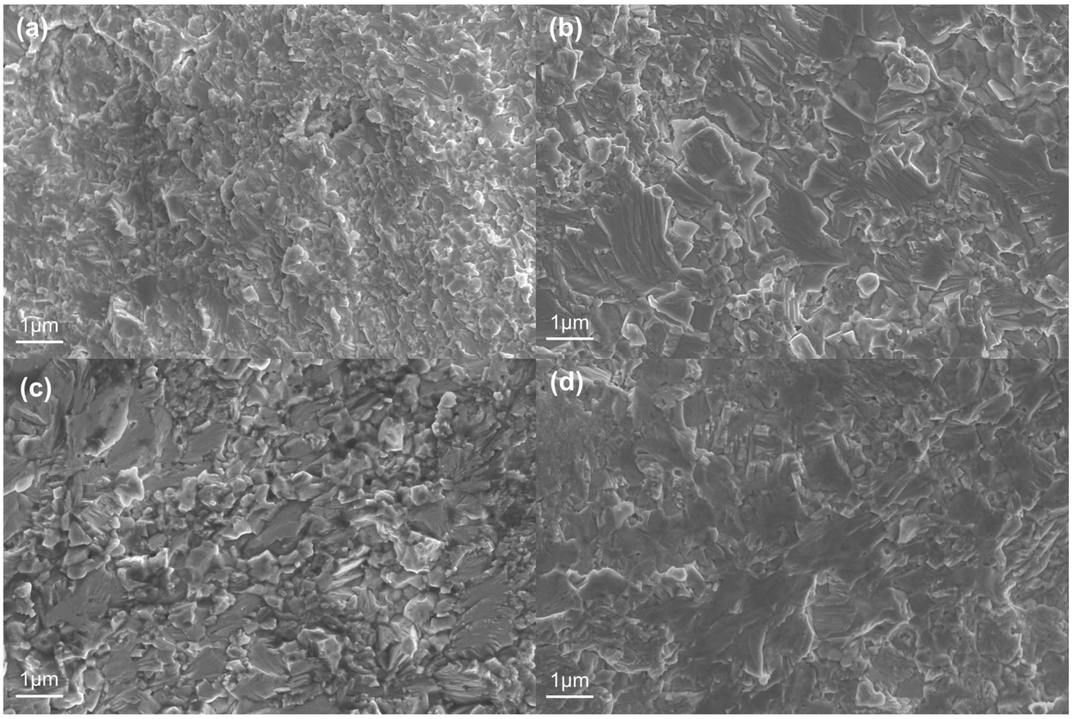

Fig.2 The SEM images of freshly fractured surface for $MgAg_{0.95-x}Cu_xSb_{0.98}$ samples: (a) $x = 0$; (b) $x = 0.01$; (c) $x = 0.015$; (d) $x = 0.025$.

Fig.3 shows the temperature dependent electrical transport properties for $MgAg_{0.95-x}Cu_xSb_{0.98}$ (x=0,0.01,0.015,0.025.0.03) samples. Fig.3(a) shows the Seebeck coefficient of the samples as functions of temperature, which displays a contrary trend with the electrical conductivity. With the increase of Cu content, the S of all samples showed a decreasing trend, which may be related to the influence of Cu introduction on conductivity. As shown in the Fig.3(b), it distinctly found that the electrical conductivity first decreases and then increases with rising temperature. Furthermore, compared to the initial sample $MgAg_{0.95}Sb_{0.98}$, the electrical conductivity of all samples increase with the increase of Cu content.

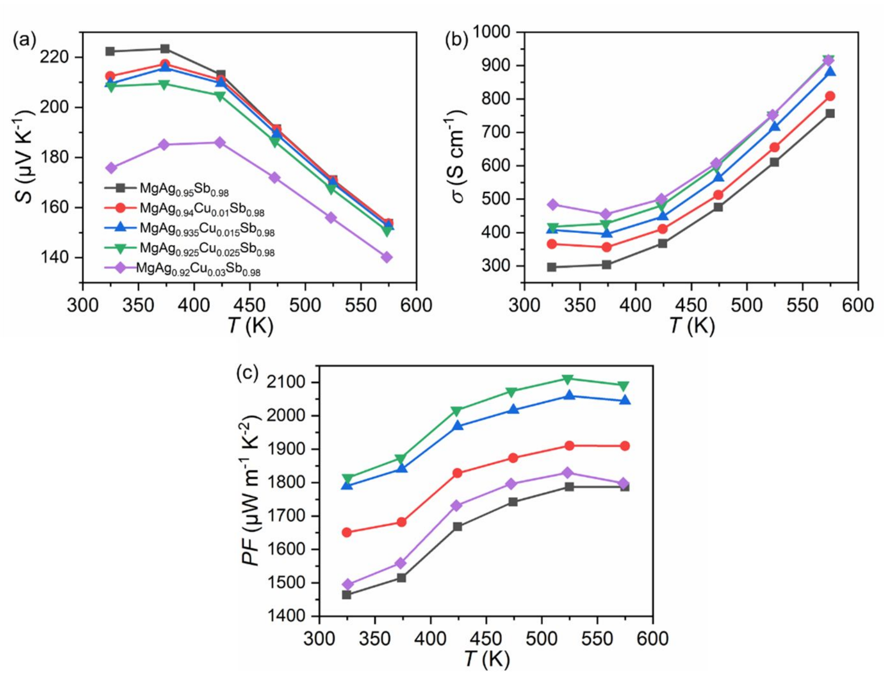

Fig. 3. Temperature dependencies of (a) Seebeck coefficient; (b) electrical conductivity and (c) power factor of $MgAg_{0.95-x}Cu_xSb_{0.95}$ (x=0, 0.01,0.015,0.025.0.03), respectively.

The temperature dependence of the power factor for $MgAg_{0.95-x}Cu_xSb_{0.95}$ (x=0, 0.01,0.015,0.025, 0.03) samples is shown in Fig. 3(c). Firstly, the PF of all samples present an increased trend with the temperature rising. At the same time, ,PF first increases and then decreases with the increase of Cu content, which is mainly caused by the sharp decrease of S when Cu content is too much. Finally, the maximum PF value of 2111 μW m^{-1} K^{-2} at 523K for $MgAg_{0.93}Cu_{0.02}Sb_{0.98}$ was about 18% increased than 1788 μW m^{-1} K^{-2} for the initial sample $MgAg_{0.95}Sb_{0.98}$.

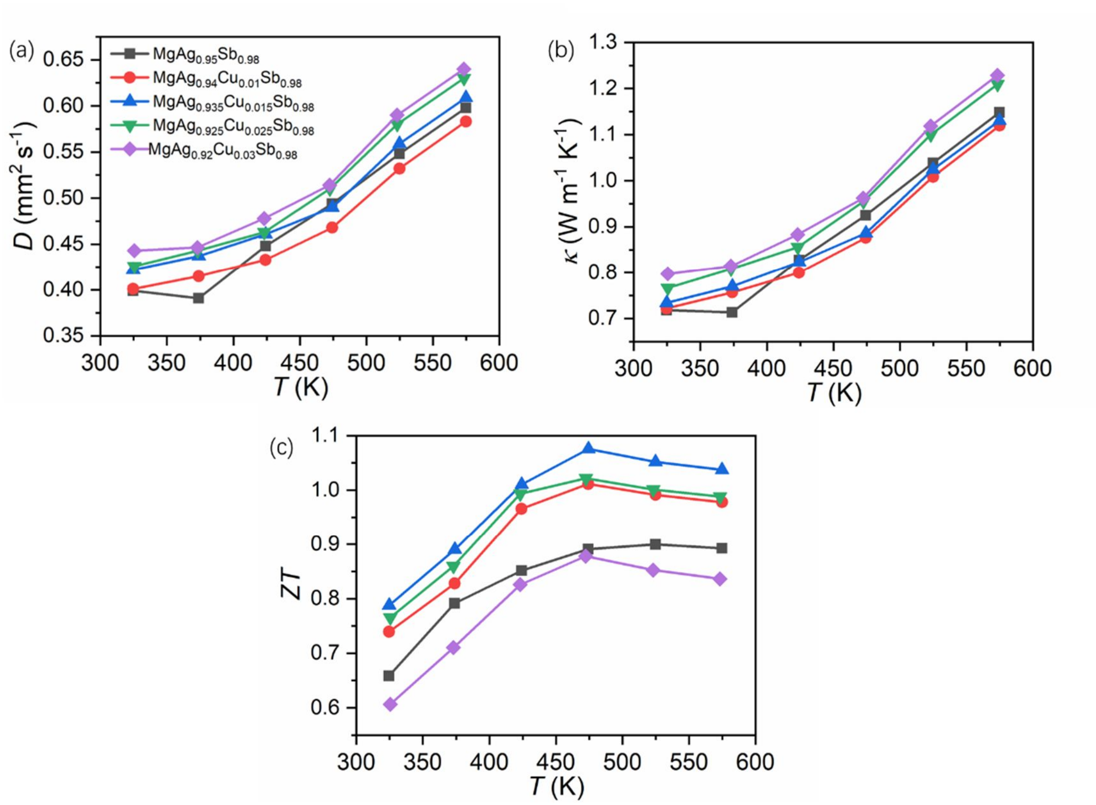

Fig. 4 Temperature dependencies of (a) thermal diffusion coefficient; (b) thermal conductivity and (c) ZT of $MgAg_{0.95-x}Cu_xSb_{0.95}$ (x=0, 0.01,0.015,0.025.0.03), respectively.

Fig.4 shows the temperature dependent thermal transport properties and ZT for $MgAg_{0.95-x}Cu_xSb_{0.98}$ (x=0,0.01,0.015,0.025.0.03) samples. Fig. 4(a) shows the thermal diffusion coefficient of the samples as functions of temperature. As can be seen from the figure, the thermal diffusion coefficient shows increasing trend with the increase of Cu content. As shown in the Fig. 4(b), it can be seen that the thermal conductivity increases with the increase of Cu content. This is consistent with the variation of thermal diffusivity. Fig. 4(c) shows the temperature-dependent ZT of the samples $MgAg_{0.95-x}Cu_xSb_{0.95}$ (x=0, 0.01,0.015,0.025, 0.03) over 323−573 K, which are greatly improved by Cu doping. The maximum ZT value of 1.07 at 473 K is achieved in $MgAg_{0.935}Cu_{0.015}Sb_{0.95}$, which improved 23%that value of the pristine sample.

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　1件）

１．著者名 Ying Peng, Lei Miao*, Chengyan Liu, Haili Song, Masashi Kurosawa, Osamu Nakatsuka, Song Yi Back, Jong Soo Rhyee, Masayuki Murata, Sakae Tanemura, Takahiro Baba, Tetsuya Baba, Takahiro Ishizaki, Takao Mori*	４．巻 12
２．論文標題 (1)Constructed Ge quantum dots and Sn precipitate SiGeSn hybrid film with high thermoelectric performance at low temperature region	５．発行年 2021年
３．雑誌名 Adv. Energy Mater	６．最初と最後の頁 2103191 (1-9)
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/aenm.202103191	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Yuntiao Liao, Jun-Liang Chen, Chengyan Liu, Jisheng Liang, Qi Zhou, Ping Wang and Lei Miao	４．巻 10
２．論文標題 (2)Sintering pressure as a “scalpel” to enhance the thermoelectric performance of MgAgSb	５．発行年 2022年
３．雑誌名 J.Mater Chem C	６．最初と最後の頁 3360-3367
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1TC05617D	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Pengfei Wang, Jiahong Zhang, Peng Ying, Xiulan Hu, Lei Miao*, Takahiro Ishizaki*.	４．巻 32
２．論文標題 (3)Recent progress of carbon-based electrocatalytic materials in Lithium-based Batteries	５．発行年 2022年
３．雑誌名 Sustainable Materials and Technologies	６．最初と最後の頁 e00384
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.susmat.2021.e00384	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計0件

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

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研究協力者	黒澤　昌志 (Kurosawa Masashi)		
研究協力者	森　孝雄 (Mori Takao)		
研究協力者	種村　栄 (Tanemura Sakae)		
研究協力者	村田　正行 (Murata Masayuki)		

７．科研費を使用して開催した国際研究集会

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８．本研究に関連して実施した国際共同研究の実施状況

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韓国	Kyung Hee University			