Microstructure Control and Performance Enhancement of Thermoelectric Materials

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Introduction

SUSTAINABLE DEVELOPMENT GOALS
17 GOALS TO TRANSFORM OUR WORLD

The 17 Sustainable Development Goals (SDGs) of the 2030 Agenda for Sustainable Development adopted by world leaders at a UN Sustainable Development Summit in September 2015.

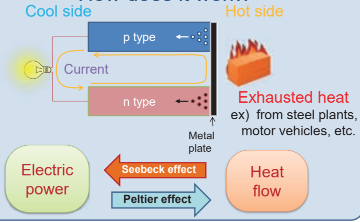
focused

https://www.un.org/sustainabledevelopment/development-agenda/

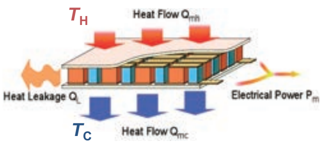
Possible solutions :
(e.g.)
- Energy saving technology
- Earth-friendly energies
- Green sustainable technology
- etc.

Thermoelectric generation!

A thermoelectric module: How does it work?



A typical thermoelectric module



How is the efficiency, η determined ?

$$\eta = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\dfrac{T_C}{T_H}}$$

Carnot efficiency (≤1)

> The higher *ZT* is the more favorable

How to improve the *ZT* value

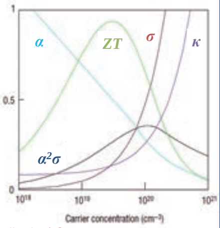
$$ZT = \frac{\alpha^2 T}{\rho\kappa} = \frac{\alpha^2\sigma T}{\kappa}$$ (Dimensionless figure-of-merit)

$$\alpha = -\frac{\pi^2}{3}\frac{k_B^{\,2}}{e}T\frac{1}{N(E_F)}\left\{\frac{\partial N(E_F)}{\partial E}\right\}_{E=E_F}$$ (Mott formula)

$$\sigma = ne\mu = \frac{e^2}{3}\Lambda_F v_F N(E_F)$$

$$\kappa = \kappa_{el} + \kappa_{ph}$$

$$\kappa_{el} = L\sigma T = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \sigma T$$ (Wiedemann-Franz Law)



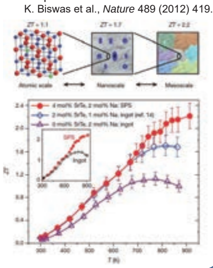
What about the κ_{ph} (phonon contribution) ?

Strategies to improve the *ZT* value

- To reduce the lattice thermal conduction without large degradation in the thermoelectric properties
- Effective sources for phonon scattering induced by
  - Grain boundary
  - Inclusions
  - Lattice defects
  - Crystal structure

Microstructure controls
- ➢ Grain refinement
- ➢ Composite
- ➢ Precipitation, etc.

Example:
K. Biswas et al., *Nature* 489 (2012) 419.

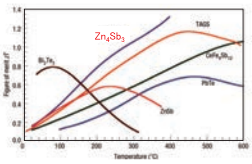


Case-1 *Zinc antimonide*

Zn_4Sb_3 compound

- A promising thermoelectric material
  High figure of merit in 200-400 °C
  ZT=1.3 at 400 °C
  Ref. T. Caillat *et al.*, *J. Phys. Chem. Solids*, (1997)

Potential applications:
- Power generation from waste heat at factories

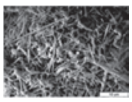


Temperature dependence of thermoelectric figure of merit (*ZT*) of Zn_4Sb_3 compared with other materials [G.J. Snyder *et al.*, *Nature Materials*, (2004)]

$$ZT = \frac{\alpha^2 T}{\rho\kappa} = \frac{\theta T}{\kappa}$$

α : Seebeck coefficient,
ρ: electrical resistivity,
κ : thermal conductivity,
T : absolute temperature,
θ : power factor

SiC whisker (SiCw)



SEM image of SiC whiskers used in this study

- high strength
- high stability
- high thermal conductivity (~360 W/mK)
- dimensions:
  diameter: 0.1 ~ 2μm
  lengths: 5 ~ 50μm

Drawback :
⊕ Extremely low fracture toughness

Strategy for improvement :
⊕ Incorporation of SiCw into matrix as reinforcements in order to introduce toughening mechanisms

Questions

- Difficulties in achieving high density and homogeneous dispersion of reinforcements
- How does the performance of products depend on forming processes? (e.g. hot-pressing, hot-extrusion)
- **How does the reinforcement influence on thermoelectric properties?**

Objective: To clarify the effect of SiCw addition on microstructure, mechanical properties, and thermoelectric properties of the Zn_4Sb_3 bulk materials

Experimental procedure

Mechanochemical Milling → Mixing → Forming → Characterization

- Zn, Sb powders
- Powder mixture
- SiC whisker
- Hot pressing
- Hot extrusion
- Microstructure
- TE performance
- Hardness
- Fracture toughness

Sample preparation

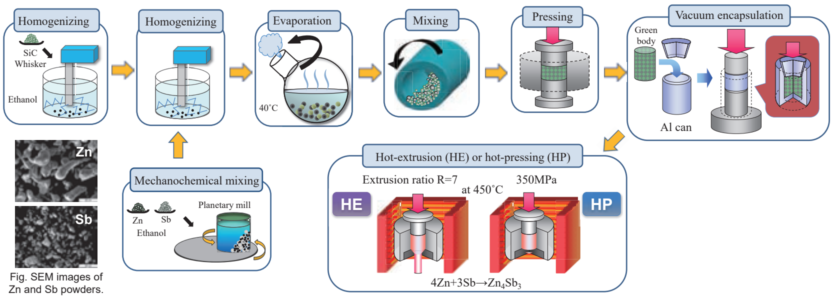
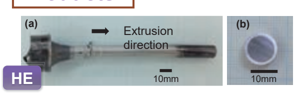
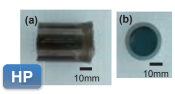


Fig. SEM images of Zn and Sb powders.

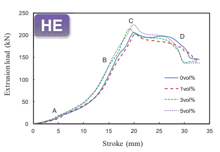
Products



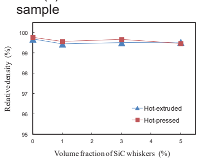
Typical pictures of (a) appearance and (b) cross-section of the HEed sample



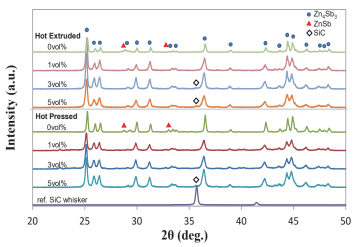
Typical pictures of (a) appearance and (b) cross-section of the HPed sample



Extrusion load vs. stroke curves under the conditions of *R*=7 at 450°C

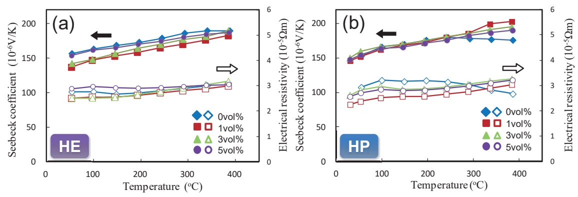


Relative density of HEed and HPed bulk samples

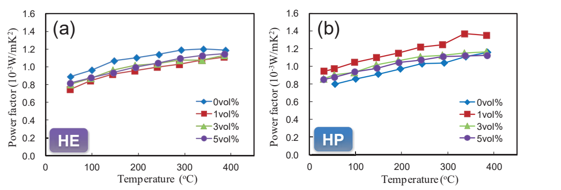


XRD patterns of the HEed and HPed samples with addition of various amounts of SiC

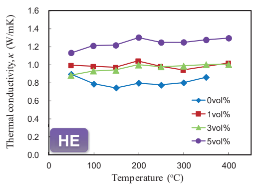
Thermoelectric properties



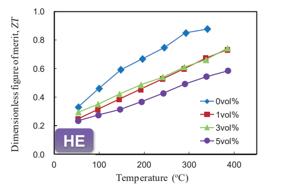
Temperature dependence of the Seebeck coefficient and electrical resistivity of (a) HEed and (b) HPed Zn_4Sb_3 samples. The filled and unfilled symbols indicate the Seebeck coefficient and electrical resistivity, respectively



Temperature dependence of power factor of (a) HEed and (b) HPed Zn_4Sb_3 samples



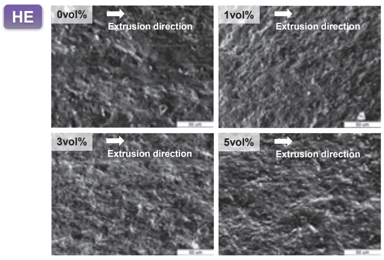
Temperature dependence of thermal conductivity of the HEed Zn_4Sb_3 samples with various SiCw contents



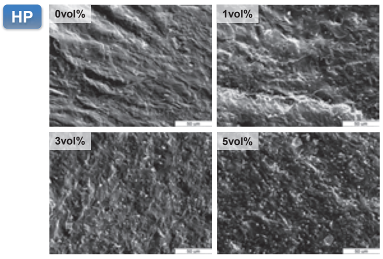
Temperature dependence of dimensionless figure of merit of the HEed Zn_4Sb_3 samples with various SiCw contents

Microstructures

SEM images of Zn_4Sb_3 bulk samples; (a) cross-section of the HPed sample without SiCw addition, (b) cross-section of the HPed sample with 3vol% SiCw, and (c) and (d) cross-section and longitudinal-section of the HEed sample with 3vol% SiCw, respectively.

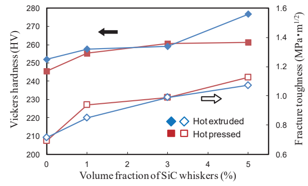


SEM images of the fracture surfaces of HEed Zn_4Sb_3 samples with addition of SiCw

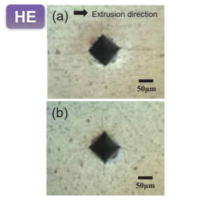


SEM images of the fracture surfaces of HPed Zn_4Sb_3 samples with addition of SiCw

Mechanical properties



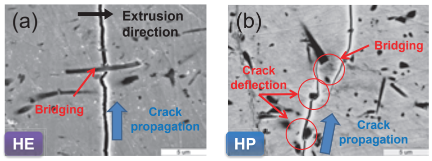
Vickers hardness and fracture toughness of the HEed and HPed Zn_4Sb_3 samples as a function of volume fraction of SiCw



Typical Vickers indentation on (a) longitudinal-section and (b) cross-section of the HEed sample

Toughening mechanisms

SEM image of a fracture surface of the HPed sample with 3vol% SiCw, exhibiting a typical trace of whisker pullout



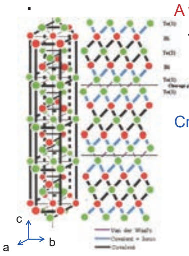
Crack deflection and crack bridging seen in (a) HEed and (b) HPed samples

Summary – Zinc antimonide

(1) Dense and sound Zn_4Sb_3 bulk materials have been fabricated by both hot pressing and hot extrusion techniques.
(2) Mechanical properties, especially toughness, were enhanced due to crack deflection, bridging and pullout mechanisms.
(3) The thermoelectric performance was suppressed by addition of large amount of SiC whiskers.

Case-2 Bismuth telluride

Bi_2Te_3 compound



Crystal structure of Bi_2Te_3

A well-established thermoelectric material

-> High figure of merit, ZT ~1 at 300 K

$$ZT = \frac{\alpha^2 T}{\rho \kappa}$$

α : Seebeck coefficient,
ρ: electrical resistivity,
κ : thermal conductivity,
T : temperature

Crystal structure:
Rhombohedral (R-$3m$), a layered structure

-> Large anisotropy

$\alpha_{\perp c} / \alpha_{//c} \leq 1.10$

$\rho_{\perp c} / \rho_{//c} = 4.2 \sim 6.67$

$\kappa_{\perp c} / \kappa_{//c} = 0.4 \sim 0.5$

$\Rightarrow ZT_{//c} \sim 2\, ZT_{\perp c}$

-> Cleavage at (0001) basal plane

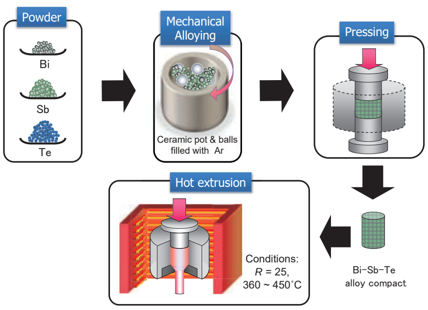
Strategies for fabrication of high-performance $Bi_{0.4}Sb_{1.6}Te_3$ bulk material

- Mechanical alloying (MA) for starting powders
  - -> To promote reaction between raw powders
  - -> To refine the sizes of the powders
- Hot-extrusion process
  - -> Introduction of a preferential orientation
  - -> Grain size reduction

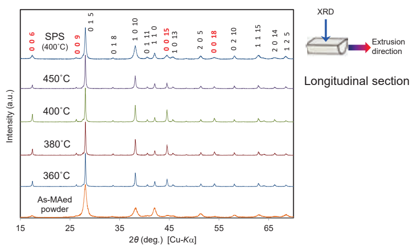
Objectives

To clarify the extrusion behavior as well as thermoelectric and mechanical properties of hot-extruded $Bi_{0.4}Sb_{1.6}Te_3$ (p-type) bulk materials

Hot-extrusion process for bulk $Bi_{0.4}Sb_{1.6}Te_3$ materials

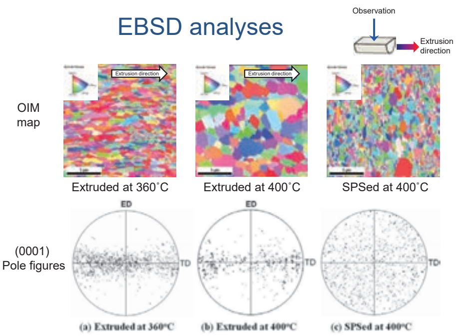


XRD patterns of the hot-extruded and SPSed $Bi_{0.4}Sb_{1.6}Te_3$ bulk samples

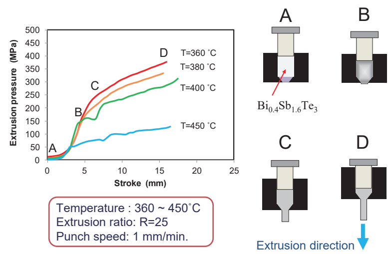


† The indices for peaks are reduced from (h k i l) to (h k l).

EBSD analyses

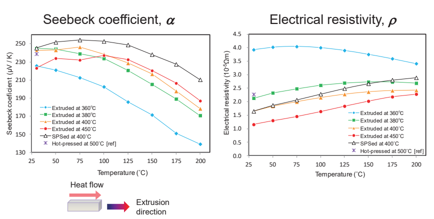


Extrusion pressure vs. stroke curves



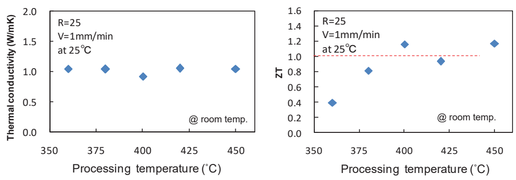
Temperature : 360 ~ 450˚C
Extrusion ratio: R=25
Punch speed: 1 mm/min.

Seebeck coefficient and electrical resistivity

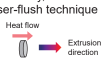


Ref. for the HPed sample: D. B. Hyun , J. S. Hwang , J. D. Shim, *J. Mater. Sci.*, **36** (2001) 1285-1291.

Thermal conductivity and dimensionless figure-of-merit at room temperature

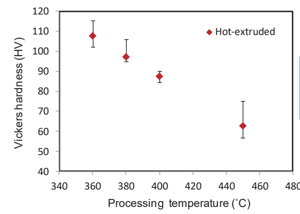


Thermal conductivity, κ was measured by laser-flush technique



$$ZT = \frac{\alpha^2 T}{\rho \kappa}$$

Vickers hardness



HV 108 (360˚C) : 2.5 times higher than the Hot-pressed sample

Summary – Bismuth telluride

(1) The $Bi_{0.4}Sb_{1.6}Te_3$ bulk materials have been successfully prepared by mechanical alloying and hot-extrusion techniques.
(2) The grain refinement and preferential orientation could be obtained simultaneously.
(3) The enhancement in hardness (HV108) and ZT value of 1.2 at room temperature were obtained.

Conclusions

The thermoelectric performance and the mechanical properties in Bi_2Te_3-alloys and Zn_4Sb_3 bulk materials are significantly improved by micro-structure control such as grain refinement and/or composite structure induced by the hot-extrusion technique.

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