ISSN : 0974 - 7486 Volume 10 Issue 7

Materials Science

An Indian Journal

Review

MSAIJ, 10(7), 2014 [295-298]

Thermoelectric properties of Zn_4Sb_3-ZnSb composites synthesized by microwave plasma and hot pressing combination

Sudarat Sitthichai[1], Titipun Thongtem[2,3], Somchai Thongtem[1,3]*, Tawat Suriwong[4]

[1]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, (THAILAND)

[2]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, (THAILAND)

[3]Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, (THAILAND)

[4] School of Renewable Energy Technology, Naresuan University, Phitsanulok 65000, (THAILAND)

E-mail : schthongtem@yahoo.com

ABSTRACT

Zn_4Sb_3-ZnSb composites were synthesized by a combination of 900 W microwave plasma in 4.3 kPa argon atmosphere and 550 °C hot pressing in argon of Zn and Sb powder mixture. Phases, internal texture and constituents were detected using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopic mapping. Thermoelectric properties of the composites were also studied and discussed in this research.

KEYWORDS

Zn_4Sb_3-ZnSb composites;
X-ray diffraction;
Scanning electron microscopy;
Energy dispersive X-ray spectroscopy;
Thermoelectric properties.

INTRODUCTION

Recently, thermoelectric properties have received much attention due to the conversion of energy caused by temperature difference of thermoelectric couples. Materials, such as TAGS (Te-Ag-Ge-Sb), Zn_4Sb_3 and skutterudites, show high figure of merit (ZT), which have high potential for a number of applications. Among them, Zn_4Sb_3 has high ZT over the temperature range of 450-650 K[1]. There are two solid-solid and one solid-liquid phase transitions: $\alpha \rightarrow \beta$ over the temperature range of 253-263 K, $\beta \rightarrow \gamma$ at the temperature of ~763 K, and $\gamma \rightarrow$ melt at 857 K[2]. They can be used in a variety of applications, including waste heat recovery from power plants and automobile industries[3]. Zn_4Sb_3 was discovered to have high thermoelectric figure of merit, mostly influenced by its low thermal conductivity[2]. Different processes were used to synthesize Zn_4Sb_3 semiconductors: solid state synthesis of ε-Zn_4Sb_3 bulk specimens[1], semiconducting Zn_4Sb_3 samples processed by hot pressing[3], stoichiometric Zn_4Sb_3 mixture of Zn and Sb heated at 973 K in vacuum for 2 h[2] and β-Zn_4Sb_3 by hot pressing[4]. In this research, Zn_4Sb_3-ZnSb composites were synthesized by a combination of microwave plasma and hot pressing of Zn and Sb mixture in argon atmosphere. The final product was further characterized by different techniques.

EXPERIMENT

In this research, Zn and Sb powders (purum, analytical grade, Fluka) were used without further purification. A powder mixture with 4.5:3 molar ratio of Zn:Sb (total mass = 1 g) was loaded into silica tubes

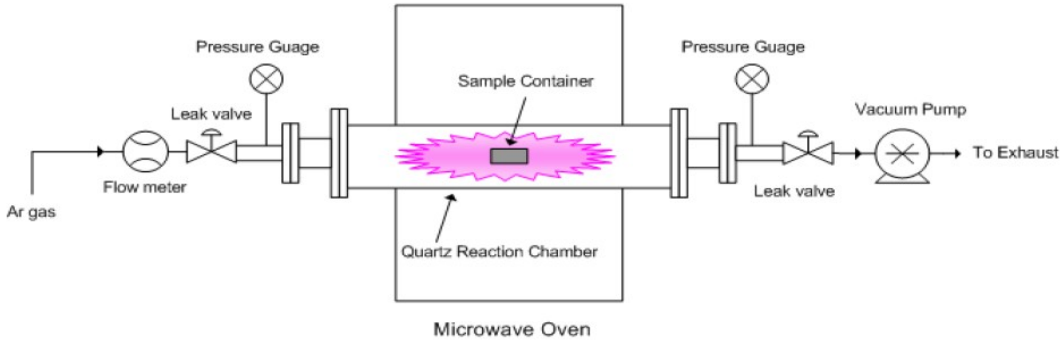

Figure 1 : Schematic diagram of the apparatus used for microwave plasma synthesis.

(11 mm I.D. x 100 mm long) which was placed in a horizontal (H) quartz tube, as shown in Figure 1.

The tube was tightly closed and evacuated to 4.3±1 kPa absolute pressure for removal of air. Following the evacuation, argon was concurrently fed into this H tube for 5 min. Subsequently, the solid mixture was heated by 900 W microwave plasma for 5 min, and left it cool down in the vacuum to room temperature. In the end, the product was hot pressed at 550 °C in argon atmosphere for 2 h for further characterization.

RESULTS AND DISCUSSION

Figure 2 shows XRD pattern of the Zn_4Sb_3-ZnSb composites synthesized from 4.5:3 molar ratio Zn and Sb, processed by 900 W microwave plasma for 5 min, and followed by 550 °C hot pressing for 2 h. In this research, spectrum of the composites was in consistence with those of the JCPDS nos 34-1013 for Zn_4Sb_3 and 05-0714 for ZnSb[5]. It should be noted that their peaks were very sharp showing that the product was composed of an array of atoms residing in normal crystal lattice.

SEM image and EDX mapping are shown in Figure 3. In this research, the product was bulk composites with some dispersive cavities inside, including Zn and Sb detection as the constituents.

Figure 4 shows the thermal conductivity and figure of merit (ZT) of the composites at different temperatures. In this research, efficiency of the thermoelectric materials was controlled by figure of merit (ZT), where $Z = S^2\sigma/K$ (S, σ and K are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively), and temperature. ZT for the composites at 607 K is 0.51. A remarkable thermoelectric material has low thermal conductivity comparing to that of a glass, large %S% coefficient and high electrical conductivity. The total thermal conductivity (K) is caused by the lattice vibration (K_L) and electronic transport (K_e). The lattice thermal conductivity is influenced by crystalline structure. For complex structures composing of large unit cells, high atomic disorder and different atomic types are able to obstruct phonon transmission with effectively. Thus they have low thermal conductivities. Mean free path of phonon through amorphous materials can be as low as atomic range. These amorphous materials can reduce electronic mobility by obstructing the diffusion of electrons; therefore, electrical conductivity and power factor ($S^2\sigma T$)[6] are reduced accordingly[7]. In summary, the power factor is optimized in narrow gap semiconducting materials, controlled by carrier concentration to achieve at the highest ZT[6]. High mobility car-

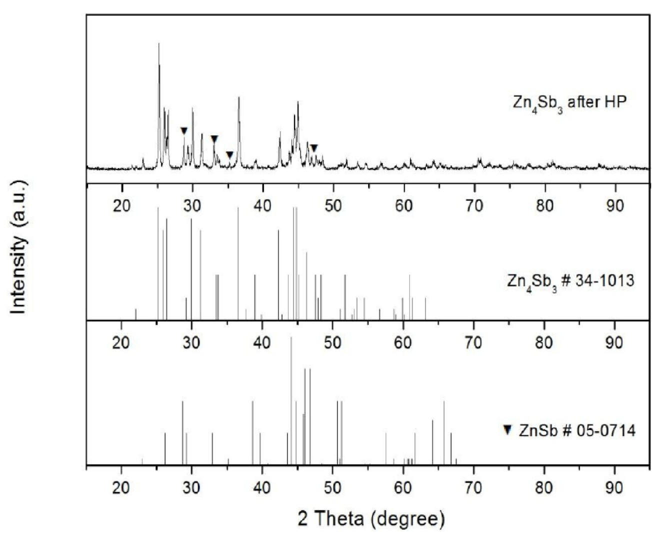

Figure 2 : XRD pattern of Zn_4Sb_3-ZnSb composites synthesized by a combination of microwave plasma and hot pressing processes, compared with those of the JCPDS database [5].

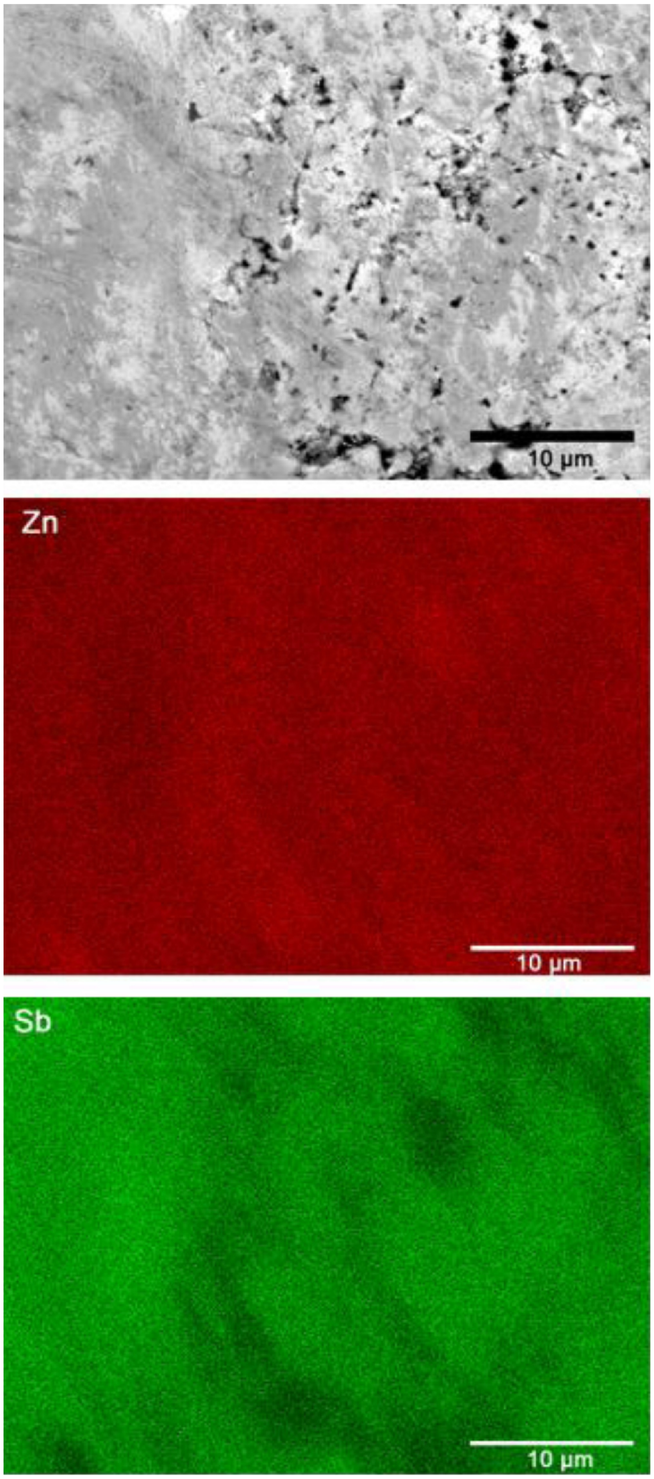

Figure 3 : SEM image and EDX mapping of the Zn_4Sb_3-ZnSb composites.

riers are the strongest desire to achieve at the largest electrical conductivity. The efficiency (η) of the thermoelectric materials is equivalent to the input power over the net heat flow rate[6]. Ideal thermoelectric materials are similar to phonon glasses and electronic crystals. Thermoelectric materials with the highest ZT are composed of heavy elements. Crystalline structures can be used to explain electronic properties by specifying the atomic sites and bond types, including valence states. Strong bonding can produce narrow band gap for semiconducting materials with high Seebeck coefficient[7]. The Seebeck coefficients for metals are very low. But for semiconducting materials, they become much larger. In addition, a related effect is known as Peltier coefficient (Π = ST)[6].

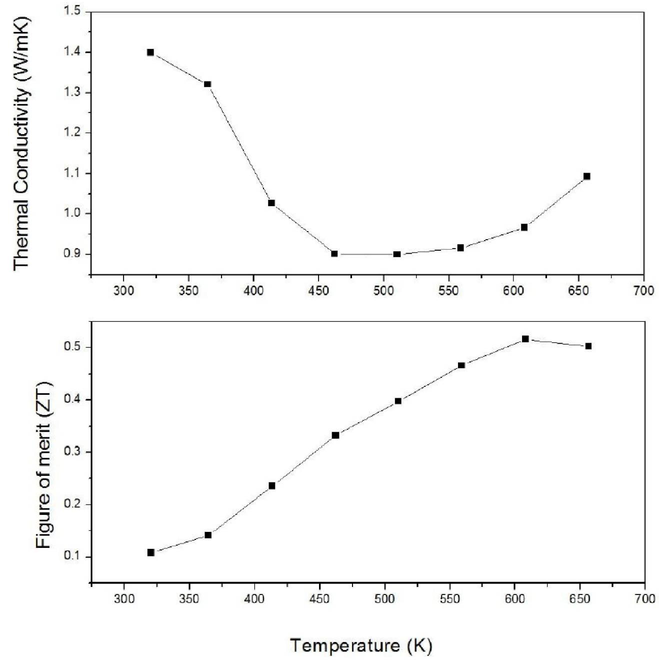

Figure 4 : (a) Thermal conductivity and (b) figure of merit (ZT) of the composites at different temperatures.

CONCLUSIONS

Zn_4Sb_3-ZnSb composites were successfully synthesized by an inexpensive solid-state synthesis using a combination of microwave plasma and hot pressing processes. At 607 K, the composites were found to have ZT of 0.51.

Acknowledgements: We wish to thank the Thailand's Office of the Higher Education Commission for providing financial support through the National Research University (NRU) Project for Chiang Mai University (CMU), and the National Research Council of Thailand for providing financial support for graduate research program, including the Graduate School of CMU for a general support. In addition, we would like to thank Professor Shinsuke YAMANAKA, Yamanaka Research Room: Future Resource, Energy and Eco-materials, Graduate School of Engineering, Osaka University, Japan, for assisting in the determination of thermoelectric properties.

REFERENCES

[1] S.C.Ur, P.Nash, I.H.Kim; J.Alloys Compd., **361**, 84–91 **(2003)**.

[2] Y.Mozharivskyj, A.O.Pecharsky, S.Bud'ko, G.J.Miller; Chem.Mater., **16**, 1580–1589 **(2004)**.

[3] M.Chitroub, F.Besse, H.Scherrer; J.Alloys Compd., **460**, 90–93 **(2008)**.

[4] T.Caillat, J.P.Fleurial, A.Borshchevsky; J.Phys.Chem.Solids, **58**, 1119–1125 **(1997)**.

[5] Powder Diffract.File, JCPDS-ICDD; 12 Campus Boulevard, Newtown Square, PA 19073-3273, U.S.A., **(2001)**.

[6] T.M.Tritt, M.A.Subramanian; MRS Bull., **31**, 188–198 **(2006)**.

[7] G.J.Snyder, M.Christensen, E.Nishibori, T.Caillat and B.B.Iversen; Nature Mater, **3**, 458–463 **(2004)**.