JOURNAL OF MATERIALS SCIENCE **38** (2003) 3553–3558

Mechanical alloying and thermoelectric properties of Zn_4Sb_3

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Thermoelectric Zn_4Sb_3 bulk specimens were produced by mechanical alloying of elemental powders and consolidated by hot pressing. Single phase Zn_4Sb_3 was not obtained using a nominal stoichiometric composition, but near single phase Zn_4Sb_3 with remnant elemental Zn having a relatively high density was produced using a nominally 11.7 at.% Zn rich powders. Phase transformations during mechanical alloying were systematically investigated using XRD and SEM. Thermoelectric and transport properties were evaluated for the hot pressed specimens and compared with results of analogous studies.

1. Introduction

Zn_4Sb_3 material has emerged as one of the most promising thermoelectric materials, since it shows a high figure of merit value in an intermediate temperature range (450–650 K) [1, 2]. It is relatively low cost and it can potentially substitute for high performance lead tellurides, which contain toxic lead [2, 3]. Zn_4Sb_3 shows an intrinsic *p*-type behavior and high value of the figure of merit, ZT = 1.3 at 673 K [1, 2]. The figure of merit is defined as $ZT = \alpha^2\sigma T/\lambda = \theta T/\lambda$, where α is the Seebeck coefficient, σ is the electrical conductivity, λ is the thermal conductivity, θ is the thermoelectric power factor and T is the temperature in Kelvin.

Several processing methods for Zn_4Sb_3 have been introduced such as melting in evacuated quartz ampoule followed by granulation and hot consolidation process [1, 3], vacuum melting process [2], mechanical alloying (MA) [4] and bulk mechanical alloying (BMA) process followed by hot pressing [5]. However, the preparation of polycrystalline ε-Zn_4Sb_3 involves rather complicated processes which are not suitable for industrial application and frequently involves the formation of undesirable metallic phases such as orthorhombic β-ZnSb and high temperature phase of orthorhombic δ-Zn_4Sb_3 [1–3]. In addition, in case of high temperature preparation processes such as melting or crystal growth, it is very common that a large number of macroscopic and microscopic cracks as well as occasional bubbles were found due to the volumetric changes during the phase transition between ε and δ at 765 K. Other difficulties in preparation process are compositional changes and poor tendency to form Zn_4Sb_3 [3] since it decomposes into ZnSb and Zn at high temperature due to the relatively poor stability of the compound [5, 6]. It is well established that intermetallic phases can be prepared by means of synthesis in solid state reactions produced by mechanical alloying [7, 8], bulk mechanical alloying [5], and repeated cold rolling plus annealing [9].

MA is known as a unique technique for solid state alloying process [7, 8], by which alloying proceeds with consecutive cold welding and fracturing, resulting in fine grain size and phase homogenization. Non-equilibrium phases such as supersaturated solid solution, metastable intermetallic compound, and amorphous phase can be synthesized by MA. It is also reported that MA materials having a fine grain size may improve thermoelectric conversion efficiency by the reduction in lattice thermal conductivity [10]. In an effort to produce fine grain size, which might provide short diffusion path to enhance phase transformation and phase homogenization, mechanical alloying of elemental Sb and Zn powders followed by hot pressing is considered in this study. However, when the starting materials are exposed to high temperature processing, some compositional changes are expected due to the evaporation of Zn [5]. Thus, as starting materials,

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stoichiometric compositions as well as Zn rich compositions to compensate for Zn evaporation are considered for each process. The effect of milling time, Zn addition and hot pressing conditions on the formation of ε-Zn_4Sb_3 phase was investigated in this study. The physical and thermoelectric properties were measured and compared with the results of analogous studies.

2. Experimental procedure

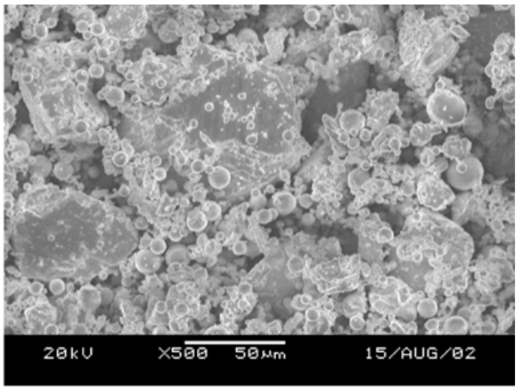
Appropriate elemental powder mixtures of −325 mesh Sb (99.9%) and −325 mesh Zn (99.9%) for stoichiometric ε-Zn_4Sb_3 and 2.3–11.7 at.% Zn rich mixtures to compensate for possible Zn loss during MA and hot consolidation were prepared as presented in Table I. The premixed powders were mechanically alloyed in a Szegavari type attritor mill for 48 h with maximum speed of 400 rpm under an Ar atmosphere. Each charge consisted of 50 g powder mixtures and 5 mm diameter stainless steel balls with a weight ratio of balls to powder of about 20 to 1. The oxygen content of the atmosphere was kept below 50 ppm throughout the process. As-milled powders were sieved to −325 mesh and hot pressed in a cylindrical high strength graphite die with an internal diameter of 31.75 mm at 673 K with a stress of 70 MPa for 2 h under Ar atmosphere. In order to investigate the degree of alloying during each processing step, X-ray diffraction (XRD) analyses were carried out for the powders as well as hot pressed samples. In order to observe microstructures and to identify phases, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were employed. Densities after hot consolidation were measured using a helium pycnometer. Microhardness was also measured to characterize general mechanical properties and correlated with microstructures. Thermoelectric properties were evaluated for the hot consolidated compacts at room temperature. Electrical conductivity (σ) was measured by the 4-point probe method. The electrical leads were taken from the indium contacts and gold wires. Seebeck coefficient (α) was determined by the constant temperature gradient method in which one end of the specimen was kept at a constant low temperature by a heat sink and the other end was heated by a small heater. The developed thermal emf (electromotive force) was measured with respect to the temperature gradient. Copper-constantan thermocouples were used to measure the temperatures of the hot and cold ends, and the thermal emf of the specimen with respect to copper was recorded. Thermoelectric power factor ($\theta = \alpha^2\sigma$) was obtained from the Seebeck coefficient and electrical conductivity. Thermoelectric properties as a function of temperature were also investigated from room temperature to 600 K. Electronic transport parameters were evaluated. Hall coefficient (R_H), carrier concentration (p) and mobility (μ) were measured by the Van der Pauw method (1.64T, 100 mA).

TABLE I Sample designations and nominal compositions used in MA process

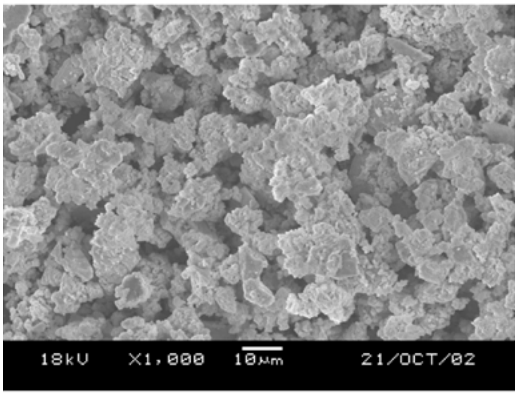
Sample	Zn (at.%)	Sb (at.%)	Excess Zn (at.%)
MAHP0	57.1429	42.8571	0
MAHP1	58.1429	41.8571	2.3
MAHP3	60.1429	39.8571	7.0
MAHP4	61.1429	38.8571	9.3
MAHP5	62.1429	37.8571	11.7

3. Results and discussion

MA powder size was typically less than 10 μm and Fig. 1 represents the progressive morphology variation during MA process. In Fig. 1a, large irregular particles are Sb and spherical particles are Zn. XRD analysis as a function of milling time is presented in Fig. 2. The appearance of superlattice lines with decreasing elemental powder peaks were shown as in typical MA process [8]. Alloy development of Zn_4Sb_3 and ZnSb phases appeared after 4 h of milling, and proceeded further as milling time increased. Elemental Sb and Zn peaks were no longer distinguishable after 48 h of milling. It was reported that ZnSb appeared first after 5 h, and Zn_4Sb_3 phase come out after then, and resultant phases were Zn_4Sb_3, and ZnSb with residual Zn and Sb after 48 h of milling in a small scale planetary milling [6]. It is hard to compare directly the phase transitions during processes when using different types of equipment, since alloy development during milling strongly depends on process parameters such as equipment type, speed, ball to powder ratio, and atmosphere. Nevertheless, alloying seemed to be complete after 48 h of milling, but single phase Zn_4Sb_3 powders could not be obtained



(a)



(b)

Figure 1 SEM micrograph of stoichiometric powders: (a) as-mixed and (b) mechanically alloyed for 48 h.

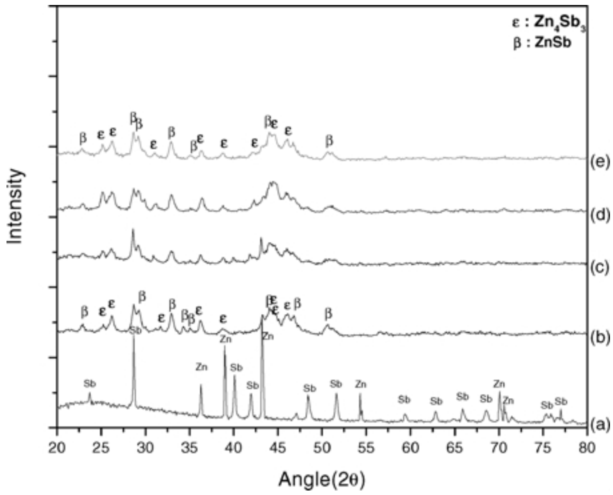


Figure 2 XRD patterns of powders with nominal stoichiometric composition during MA: (a) as-mixed, (b) MA for 4 h, (c) MA for 16 h, (d) MA for 24 h, and (e) MA for 48 h.

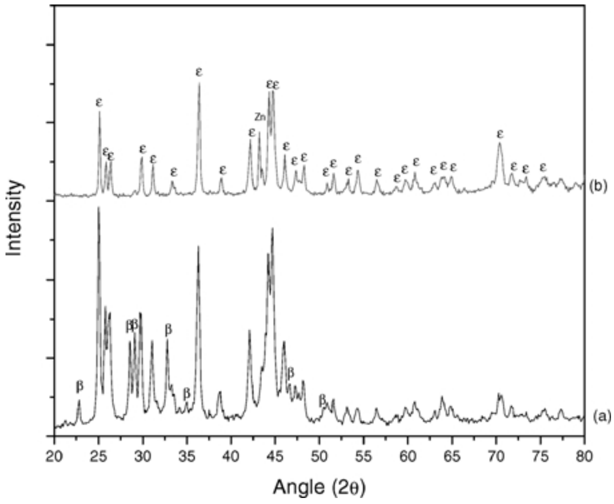
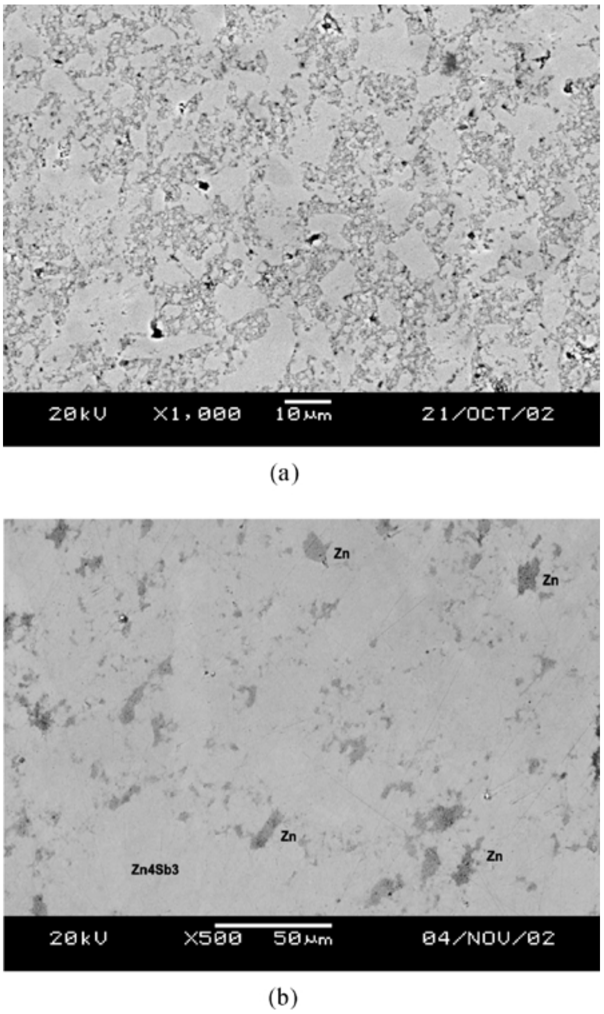


Figure 3 XRD patterns of compacts processed by hot pressing for 2 h at 673 K after 48 h of mechanical alloying: (a) nominally stiochiometric composition and (b) nominally 11.7 at.% Zn rich composition.



(a)

(b)

Figure 4 SEM micrograph of hot pressed MA compacts: (a) nominally stiochiometric composition and (b) nominally 11.7 at.% Zn rich composition.

in this process. No amorphous transition was observed during milling, but significant peak broadening was observed possibly resulting from particle refinement and cold work.

It can be considered that relatively ductile Zn is more preferable to cold welding on to balls and vials rather than fracturing, resulting in significant Zn deficiency in as-milled powders. MA powders were hot pressed at 673 K for 2 h, and resultant XRD patterns are presented in Fig. 3a. By comparing peak intensities for each phase, Zn_4Sb_3 seems to be the major phase but the amount of ZnSb phase is not negligible. The density of the hot pressed MA specimen is 89.1% of theoretical. SEM micrograph revealed no microcracks, but some voids and some zinc oxides were not unavoidable, as shown in Fig. 4a. In the figure, Zn_4Sb_3 and ZnSb phases were not distinguishable, presumably due to that two phase might coexist in form of fine lamellar structure as expected in mechanically alloyed powders [7, 8].

In order to compensate Zn deficiency, additional Zn up to 11.7 at.% were added to as-mixed powders and hot pressed with the same process conditions. MA powders after 48 h resulted in Zn_4Sb_3, ZnSb and Zn phases in XRD analysis. During XRD analyses, it was observed that relative peak intensities for Zn_4Sb_3 were generally increased as the amount of Zn was increased. Producing a single phase Zn_4Sb_3 seemed to be somewhat difficult in this MA process due to the Zn loss by cold welding during MA as well as evaporation during hot pressing. However, hot pressed Zn_4Sb_3 as a major phase with some remnant Zn phase was possible to produce by adding 11.7 at.% Zn to the as-mixed powder, as shown in Figs. 3b and 4b. This near single phase Zn_4Sb_3 shows a relative density of 98.8%. It was shown that ZnSb phase still appeared up to the 9.3 at.% Zn addition. This implies that single phase Zn_4Sb_3 might be produced with Zn between 9.3–11.7 at.% added to the stoichiometric alloy. Zn is not finely dispersed throughout the matrix as might be expected for the MA process. It is shown that Zn agglomerates in the prior boundary corners possibly due to the high temperature process near melting point and limited solubility.

Thermoelectric properties at room temperature were evaluated for the hot pressed MA specimens, and are presented in Fig. 5 and Table II. The properties of single phase Zn_4Sb_3 reported by Caillat *et al.* [1], where samples were prepared by melting in quartz ampoule,

TABLE II Properties of hot consolidated specimens processed by MA

Sample	α (μV/K)	σ (Ω^{-1} cm^{-1})	θ (μV/ cm K^2)	Relative density (%)	Hv	Phases
Ref. [1]	113	500	6.4	–	–	ε
MAHP0	74.4	219.3	1.2	89.1	174.3	$\varepsilon + \beta$
MAHP1	84.0	228.9	1.6	90.3	172.8	$\varepsilon + \beta$
MAHP3	113.8	23.1	0.3	86.2	113.7	$\varepsilon + \beta$
MAHP4	133.7	169.2	3.0	91.6	130.8	$\varepsilon + \beta$
MAHP5	86.8	621.2	4.7	98.8	243.6	ε + Zn

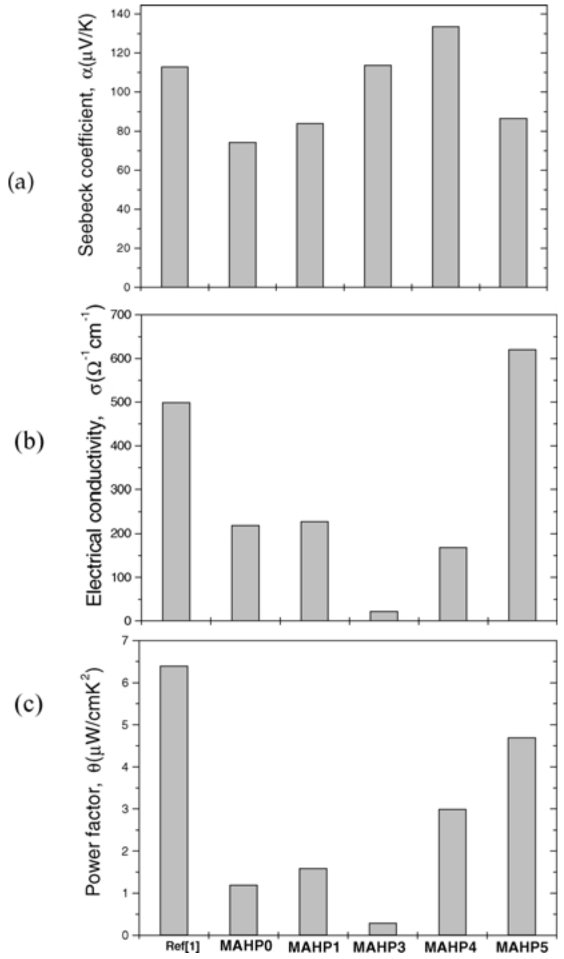


Figure 5 Thermoelectric properties of hot pressed MA specimens: (a) Seebeck coefficient, (b) electrical conductivity, and (c) thermoelectric power factor.

TABLE III Transport properties of hot pressed MA Zn_4Sb_3 (MAHP5)

Sample	Hall coefficient R_H (cm^3/C)	Hall mobility μ (cm^2/Vsec)	Carrier concentration p (cm^{-3})
Reference [1]	–	30	9×10^{19}
MAHP5	0.0483	30	1.29×10^{20}

granulation and hot pressing, are presented for comparison. In Table II, relative density and Vickers microhardness values are also presented with thermoelectric properties. Microhardness and relative density in hot pressed MA specimens were less than those in directly synthesized Zn_4Sb_3 by hot pressing at 673 K for 24 h [11], indicating that 2 h of hot pressing was insufficient for full densification.

Seebeck coefficients, $\alpha(\mu V/K)$, for all specimens show positive values, representing p-type conductivity. Seebeck coefficients in $\varepsilon + \beta$ phases showed an increase with increasing ε phase fraction. Electrical conductivities in $\varepsilon + \beta$ phases were relatively low compared to the reference values presumably due to the microstructural defects resulting from partial densification, and showed a decrease with increasing ε phase fraction. Seebeck coefficient in the near single phase Zn_4Sb_3 containing remnant Zn (MAHP5) is a little bit low possibly due to microstructural defects in this material. Electrical conductivity of MAHP5 is somewhat high compared to that of reference [1]. Electrical conductivity is generally expected to increase when containing metallic phases. On the other hand, it can also be speculated that electrical conductivity might be decreased in the presence of metallic phase in this p-type thermoelectric material, since holes are major charge carriers so that free electrons in metallic phases can couple with holes resulting in charge compensation. Our recent investigation on the effect of Zn addition on thermoelectric properties in this alloy system revealed that the parameters of α, σ and θ were generally decreased with increasing Zn contents. Here, the possible reason for high electrical conductivity in this material cannot be simply adopted, since it would be affected by several parameters such as carrier type, carrier concentration, carrier mobility, microstructural defects and so forth. Thus, in order to gain an insight into the fact, transport properties in the near single phase material were measured as presented in Table III. In the Table III, a positive value of Hall coefficient represents that major carriers are holes in this material indicating p-type. Hall mobility is about the same as the reference [1], but carrier concentration is higher compared to that of reference, indicating higher electrical conductivity and lower Seebeck coefficient.

Thermoelectric power factors ($\theta = \alpha^2\sigma$) obtained from the Seebeck coefficient and electrical conductivity in $\varepsilon + \beta$ phases were generally lower than those in reference material, due to the existence of ZnSb phase as well as partial densification. θ in MAHP5 showed 73.4% of the reference value [1], and the property is believed to increase by increasing hot pressing time and starting with appropriate powder composition to yield single phase material. Thermoelectric properties as a function of temperature were also investigated from room temperature to 600 K.

Caillat *et al.* reported that Seebeck coefficient increased and electrical conductivity decreased up to 623 K in single phase Zn_4Sb_3 [1]. As can be seen in Fig. 6, electrical conductivity decreases in the testing temperature range, and Seebeck coefficient shows an increase in general with some fluctuation at the medium temperature range. This fluctuation resulted in corresponding fluctuation in thermoelectric power factor as shown in Fig. 6c. The fluctuation is not generally expected in single phase Zn_4Sb_3 [1, 2]. During one cycle of heating excursion to measure the thermoelectric power factor up to 600 K, phase transition to ZnSb

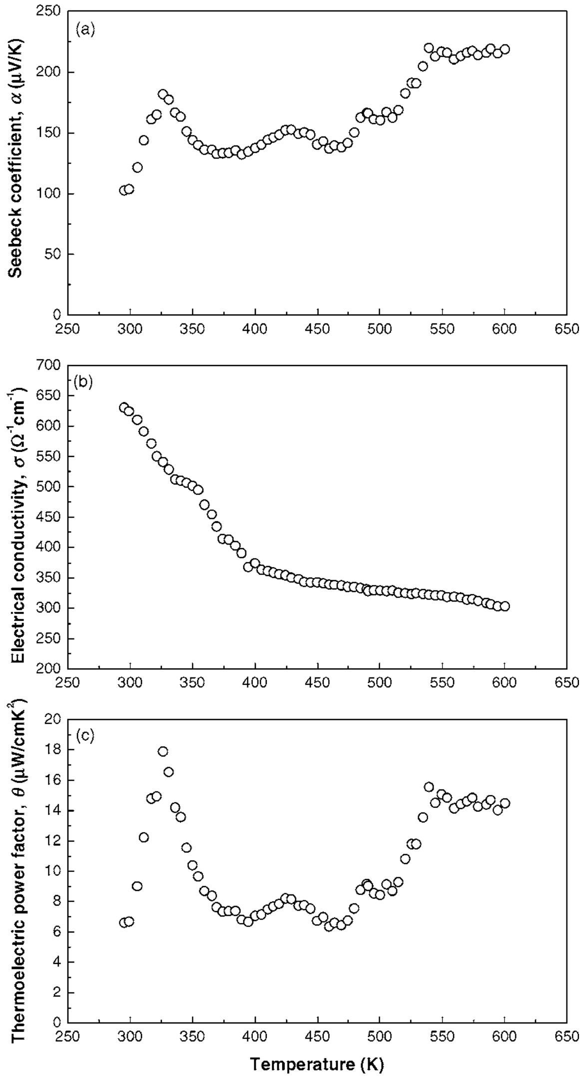


Figure 6 Thermoelectric properties as a function of temperature in hot pressed MAHP5 specimen: (a) Seebeck coefficient, (b) electrical conductivity, and (c) thermoelectric power factor.

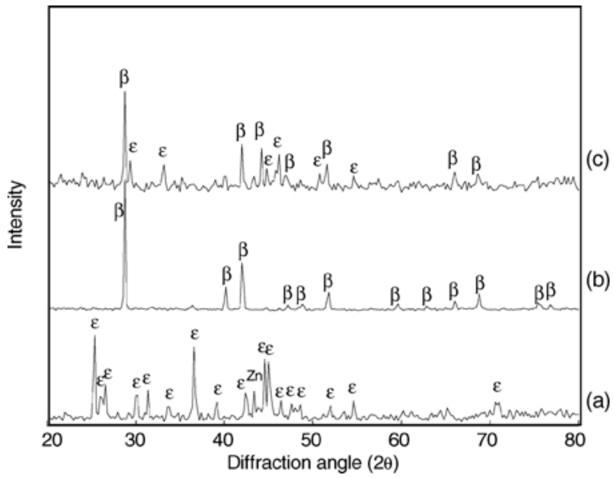


Figure 7 XRD patterns of MAHP5: (a) as-hot pressed, (b) after measurement of thermoelectric power factor up to 600 K (surface), and (c) after measurement of thermoelectric power factor up to 600 K (inside).

occurred as shown in Fig. 7. It was reported that Zn_4Sb_3 has a tendency to decompose into ZnSb and Zn at high temperature due to the relatively poor stability of the compound [3, 5]. However, stability in this material was reported up to 623 K [1], presumably due to their full density state. Since the specimen produced by MA has relatively large surface area introduced from microstructural defects in the specimen, phase dissociation through surface reaction is believed to occur. The transformed ZnSb is identified as a hexagonal phase differently from the orthorhombic ZnSb phase which usually forms in Zn deficient composition during MA process. The transformation to ZnSb phase showed to occur mostly at the surface during the heating excursion in Fig. 7b–c. However, elemental Zn was not identified after phase transition. It can be considered that the dissociation Zn_4Sb_3 into ZnSb + Zn have taken place and the dissociated Zn might be evaporated during heating. In addition, some portion of dissociated Zn might be possibly combined with oxygen to form ZnO, though the peak was not observed in XRD pattern. Thus, it is believed that the fluctuation in thermoelectric power factor attributed to the phase dissociation into metallic ZnSb + Zn phases and Zn evaporation. Producing a Zn_4Sb_3 by mechanical alloying process seems not to be appropriate due to the presence of microstructural defects leading to the phase dissociation and decreasing thermoelectric properties. However, it can be suggested that single phase Zn_4Sb_3 might be fabricated when appropriated amount of Zn is added and the phase dissociation might be suppressed when prolonged time of hot pressing is applied to reduce microstructural defects in mechanical alloying process.

4. Summary

1. Thermoelectric Zn_4Sb_3 bulk specimens were produced by mechanical alloying of elemental powders and consolidated by hot pressing. Single phase Zn_4Sb_3 was not obtained using a nominal stoichiometric composition, but near single phase Zn_4Sb_3 with remnant elemental Zn having a relatively high density was produced using a nominally 11.7 at.% Zn rich powders. Microhardness and relative density in hot pressed MA specimens are relatively low due to partial densification.

2. Thermoelectric and transport properties were evaluated for the hot pressed specimens. Thermoelectric power factors in $\varepsilon + \beta$ phases were generally low due to the existence of ZnSb phase as well as partial densification. Seebeck coefficient in the near single phase Zn_4Sb_3 containing remnant Zn is somewhat low possibly due to microstructural defects in this material. Higher carrier concentration in the near single phase Zn_4Sb_3 material was observed, resulting in relatively higher electrical conductivity and lower Seebeck coefficient. Thermoelectric power factors in the near single phase material containing remnant Zn are comparable to the published data for the single phase Zn_4Sb_3. Electrical conductivity decreases up to 600 K, and Seebeck coefficient shows an increase in general with some fluctuation at the medium temperature range, resulting in corresponding fluctuation in thermoelectric power factor, due to the phase dissociation into ZnSb + Zn.

References

1. T. CAILLAT, J.-P. FLEURIAL and A. BORSHCHEVSKY, *J. Phys. Chem. Solids* **58**(7) (1997) 1119.

2. T. J. ZHU, X. B. ZHAO, M. YAN, S. H. HU, T. LI and B. C. CHOU, *Mater. Lett.* **46**(1) (2000) 44.
3. M. TAPIERO, S. TARABICHI, J. G. GIES, C. NOGUET, J. P. ZIELINGER, M. JOUCLA, J. L. LOISON and M. ROBINO, *Solar Energy Mater.* **12** (1985) 257.
4. V. IZARD, M. C. RECORD and J. C. TEDENAC, *J. Alloys Comp.* **345** (2002) 257.
5. T. AIZAWA and Y. IWAISAKO, in Proceedings of the 18th International Conference on Thermoelectrics (Baltimore, USA, September 1999) IEEE, p. 173.
6. V. IZARD, M. C. RECORD, J. C. TEDENAC and S. G. FRIES, *Calphad* **25**(4) (2001) 567.
7. C. C. KOCH, *Annu. Rev. Mater. Sci.* (1989) 121.
8. S. C. UR, P. NASH and G. T. HIGGINS, *Scripta Mater.* **34**(1) (1996) 53.
9. L. BATTEZZATI, P. PAPPALEPORE, F. DUBIANO and I. GALLINO, *Acta Mater.* **47**(6) (1999) 1901.
10. D. M. ROWE and V. S. SCHUKA, *J. Appl. Phys.* **52**(12) (1981) 7421.
11. S. C. UR, P. NASH and I.-H. KIM, "Solid State Syntheses and Properties of Zn_4Sb_3 Thermoelectric Materials," submitted to *J. of Alloys and Compound* (2002).

Received 22 January
and accepted 6 March 2003