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Thermoelectric Material Design in Pseudo Binary Systems of Mg_2Si–Mg_2Ge–Mg_2Sn on the Powder Metallurgy Route

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Abstract

New PM route via bulk mechanical alloying is developed to fabricate the solid solution semi-conductive materials with $Mg_2Si_{1-x}Ge_x$ and $Mg_2Si_{1-y}Sn_y$ for $0 < x, y < 1$ and to investigate their thermoelectric materials. Since Mg_2Si is n-type and both Mg_2Ge and Mg_2Sn are p-type, pn-transition takes place at the specified range of germanium content, x, and tin content, y. Through optimization of chemical composition, solid-solution type thermoelectric semi-conductive materials are designed both for n- and p-type materials.

Keywords : Solid state synthesis, Bulk mechanical alloying, $MgSi_{1-x}Ge_x$, $Mg_2Si_{1-y}Sn_y$, Bandgap, pn-transition

1. Introduction

Among various thermoelectric material candidates, magnesium base ternary and quaternary alloys and compounds are higlighted to be working in the middle temperature range instead of Pb-Te or TAGS systems [1]. In early 50's to 70's, fundametal studies of these alloys and compounds have been mainly done by physists [2]; since then, they were followed by very few researches, leaving many things un-accounted for [3]. Casting, or, melting and solidification methods were applied to fabricate these ternary thermoelectric compounds [4]; their success was limited to a narrowed range of contents in these ternary alloys. PM methods were also applied to fabrication of these alloys with less success [5]. The above limitation or failure of alloying originates from intrinsic features of magnesium: high vaporizing temperature, difference of melting points from Ge, Si, chemical reactivity with crucibles' and mechanical adhesion onto vials. New powder metallurgical route via bulk mechanical alloying (BMA) [6] is proposed to investigate the thermoelectric material design in the pseudo-binary system of Mg_2Si–Mg_2Ge–Mg_2Sn.

2. Experimental

For various germanium content, x, and tin content, y, the elemental powders of Mg (99.9 % in purity, 100 μm in diameter), Si (99.99 % in purity, 20 μm in diameter), Ge (99.99 % in purity, 20 μm in diameter) and Sn (99.99 % in purity, 20 μm in diameter) were prepared, blended and mixed with the specified molar ratio of $Mg_2Si_{1-x}Ge_x$ and $Mg_2Si_{1-y}Sn_y$. For solid-state synthesis, the bulk mechanical alloying (BMA) was utilized to synthesize the binary compounds and ternary solid solutions. The powder mixtures were blended homogeneously and then subjected to bulk mechanical alloying in a flowing argon atmosphere to prevent the powder compact from oxidation. The pass schedule with one forward extrusion mode and two compression modes was employed for cyclic loading in the laboratory-scaled BMA equipment. Hot pressing technique was employed for fabrication of brick-type and disc-shaped samples for measurement of thermoelectric properties. After pulverizing BMA compact and sieving by the mesh of #270, the BMA powders were sintered in a stainless steel die under an argon atmosphere.

X-ray diffraction (XRD) analysis with the mono-chromatic Cu k_α radiation was used to describe the solid solution formation by BMA. The differential thermal analysis (DTA) was carried out to explore the onset temperature of solid-state reaction during BMA process with the heating rate of 20 K/min up to 1073 K in an argon atmosphere. The samples for electrical measurement were cut out from the sintered pellets: a rectangular bar with the size of $2\times2\times8$ mm^3 for measurement of the Seebeck coefficient and the electrical conductivity, and, a circular disc with the diameter of 10mm and the thickness of 2 mm for measurement of thermal conductivity.

3. Experimental Results

Band gap is a design parameter for semi-conducting materials. Since Mg-Si-Ge system or pseudo Mg_2Si-Mg_2Ge

system has complete solid-solubility, the bandgap is thought to vary continuously with the germanium content, x. In fact, as shown in Fig, 1, the band gap decreases monotonically with x from 0.71 eV for Mg_2Si to 0.54 eV for Mg_2Ge. In Mg-Si-Sn system, since the lattice parameter increases monotonically with the tin content, y, the band gap is expected to decrease also monotonically with y. Figure 2 compares the variation of measured band gap with y. Reference samples were prepared by direct melting and annealed in Ar-filled ampoules [3]. Since $Mg_2Si_{1-y}Sn_y$ in the equilibrium state for $0.4 < y < 0.6$ has two phase or Mg_2Si + Mg_2Sn, the bandgap has a kink point in this range. On the other hand, every sample by the present method remains a solid solution in the whole range of y; bandgap decreases monotonically with y without a kink. Since Mg_2Si has n-type semi-conductivity, these solid solutions of $Mg_2Si_{1-x}Ge_x$ and $Mg_2Si_{1-y}Sn_y$ for $x < 0.35$ and $x < 0.2$ are also n-type. At the critical content where $x = 0.35$ and $y = 0.2$, n-type conductivity abrupt changes to p-type one. This p-n transition is intrinsic to these Mg-base alloying systems.

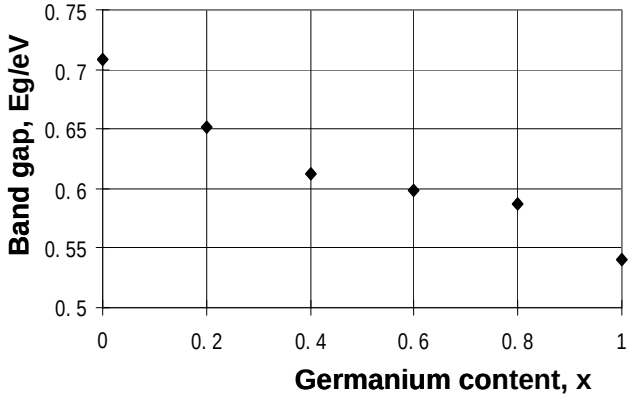

Fig. 1. Variation of bandgap with the germanium content, x in the peudo binary system of Mg_2Si–Mg_2Ge.

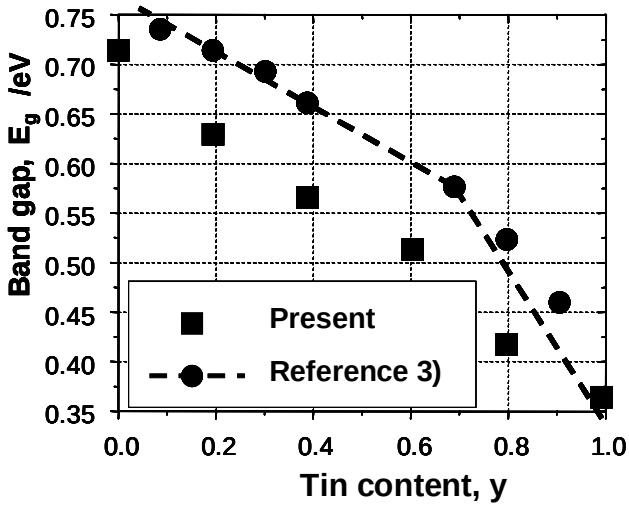

Fig. 2. Variation of bandgap with the tin content, y in the peudo binary system of Mg_2Si and Mg_2Sn.

4. Summary

The present solid-state synthesis via bulk mechanical alloying fabricates any solid solution type thermoelectric semi-conducting materials for any contents of germanium and tin. This highly accurate control of chemical composition in solid solution is preferable to control of fundamental properties for semi-conductivity. In both $Mg_2Si_{1-x}Ge_x$ and $Mg_2Si_{1-y}Sn_y$, pn-transition is observed at $x = 0.35$ and $y = 0.2$ where the Seebeck coefficient abruptly changes itself. Design of doping content must stand on this pn-transition behavior for improvement of thermoelectricity.

5. References

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