Journal of ELECTRONIC MATERIALS, Vol. 42, No. 7, 2013
DOI: 10.1007/s11664-012-2415-9

Thermoelectric Properties of Higher Manganese Silicides Prepared by Mechanical Alloying and Hot Pressing

DONG-KIL SHIN,[1] KYUNG-WOOK JANG,[2] SOON-CHUL UR,[1] and IL-HO KIM[1,3]

1.—Department of Materials Science and Engineering, Korea National University of Transportation, Chungju, Chungbuk 380-702, South Korea. 2.—Department of Advanced Materials Engineering, Hanseo University, Seosan, Chungnam 356-706, South Korea. 3.—e-mail: ihkim@ut.ac.kr

Higher manganese silicides (HMS), $MnSi_{1.75-\delta}$, were synthesized by mechanical alloying and consolidated by hot pressing. The optimum condition of mechanical alloying was ball milling at 400 rpm for 6 h, and sound sintered compacts could be obtained by hot pressing at temperature higher than 1073 K. The phase fraction of HMS showed no significant difference with compositional (δ) variation, but the $MnSi_{1.75}$ specimen had the lowest fraction of MnSi of approximately 3%. The lattice constants of HMS with compositional variation were similar to values reported in the literature. All specimens showed Nowotny phase with tetragonal structure, and exhibited i-type conduction at measuring temperatures between 323 K and 823 K. HMS behaved as degenerate semiconductors in that the absolute values of the Seebeck coefficient increased and the electrical conductivity slightly decreased with increasing temperature. $MnSi_{1.73}$ showed the highest figure of merit of 0.28 at 823 K.

Key words: Thermoelectric, higher manganese silicide, mechanical alloying, hot pressing

INTRODUCTION

Higher manganese silicides (HMS, $MnSi_{1.72-1.75}$) are regarded as candidate *p*-type thermoelectric materials because of the low cost and abundance of their constituent elements, environmental friendliness, and high-temperature oxidation resistance.[1–3] Four kinds of HMS have been reported: $Mn_{11}Si_{19}$ ($MnSi_{1.72}$),[4] $Mn_{15}Si_{26}$ ($MnSi_{1.73}$),[5] $Mn_{27}Si_{47}$ ($MnSi_{1.74}$),[6] and Mn_4Si_7 ($MnSi_{1.75}$).[7] These phases are referred to as Nowotny chimney–ladder phases which possess the tetragonal crystal structure with almost equal a-axis and unusually long c-axis.[8] For thermoelectric applications of HMS, knowledge on the crystal structure, composition, phase transformation, and stability is required. However, the stability range of HMS phases has not been determined so far, and there are difficulties in precise composition control because of Si loss during processing.

In general, HMS have been prepared by melting and solidification, or various crystal growth methods. Groβ et al.[9] evaluated the thermoelectric properties of $MnSi_{1.73}$ prepared by melting, annealing, and hot pressing. However, these fabrication methods need high synthesis temperature and long-time annealing for homogenization. In addition, mechanically brittle ingots with inhomogeneous composition are not appropriate for thermoelectric modules. On the other hand, mechanical alloying followed by hot pressing via powder metallurgy is a good process to obtain sufficient mechanical strength and precise composition control. Umemoto et al.[10] reported $MnSi_{1.73}$ prepared by mechanical alloying and pulse discharge sintering. In this study, four kinds of HMS with compositions of $MnSi_{1.72-1.75}$ were prepared by mechanical alloying and hot pressing. Crystal structure, phase fraction, microstructure, and thermoelectric properties were examined.

(Received June 28, 2012; accepted December 26, 2012; published online January 29, 2013)