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Effects of ball milling on microstructures and thermoelectric properties of higher manganese silicides

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ABSTRACT

Bulk nanostructured higher manganese silicide (HMS) samples with different grain size are prepared by melting, subsequent ball milling (BM), and followed by spark plasma sintering (SPS). The effects of BM time on the microstructures and thermoelectric properties of these samples are investigated. It is found that BM effectively reduces the grain size to about 90 nm in the sample after SPS, which leads to a decrease in both the thermal conductivity and electrical conductivity. By prolonging the BM time, MnSi and tungsten/carbon-rich impurity phases are formed due to the impact-induced decomposition of HMS and contamination from the tungsten carbide jar and balls during the BM, respectively. These impurities result in a reduced Seebeck coefficient and increased thermal conductivity above room temperature. The measured size-dependent lattice thermal conductivities agree qualitatively with the reported calculation results based on a combined phonon and diffuson model. The size effects are found to be increasingly significant as temperature decreases. Because of the formation of the impurity phases and a relatively large grain size, the *ZT* values are not improved in the ball-milled HMS samples. These findings suggest the need of alternative approaches for the synthesis of pure HMS with further reduced grain size and controlled impurity doping in order to enhance the thermoelectric figure-of-merit of HMS via nanostructuring.

1. Introduction

Owing to the increased demand for energy and the negative environmental consequence of energy generation from fossil fuels, thermoelectric (TE) materials, which can be used to convert waste heat into electricity, have received renewed attention in the past decades [1,2]. The performance of TE materials is related to the dimensionless figure-of-merit $ZT = S^2\sigma T/(\kappa_E + \kappa_L)$, where S, σ, T, κ_E, and κ_L are the Seebeck coefficient, electrical conductivity, absolute temperature, electronic thermal conductivity, and lattice thermal conductivity, respectively. The numerator $S^2\sigma$ is called the power factor (*PF*). Recently, *ZT* improvement has been reported in some nanostructured TE materials [3,4]. The *ZT* of nanostructured materials can be enhanced only if grain boundary scattering can result in a larger reduction in the lattice thermal conductivity than in the power factor. It has been reported that this approach is effective in several TE materials such as $AgPb_mSbTe_{2+m}$ [5], Bi_2Te_3-based [6,7], and $Si_{80}Ge_{20}$ [8,9] bulk nanostructured materials.

Higher manganese silicides (HMS) with composition of $MnSi_{\sim 1.74}$ are regarded as attractive *p*-type TE materials owing to the abundance of the constituent elements in the earth's crust, environmental friendliness and good chemical stability at high temperatures. The crystal structure of HMS belongs to the Nowotny chimney ladder (NCL) phases, which are characterized by two interpenetrating sublattices with the tetragonal Mn sublattice forming chimneys and the helical Si sublattice forming ladders along the *c* axis. HMS single crystals prepared by the Bridgman method or Czochralski method possess anisotropic transport properties, which are related to the complex NCL structure and the layers of secondary MnSi phase precipitating perpendicular to the *c* axis [10]. For example, the κ_L along the *c* axis is approximately half of that along the *a* axis at room temperature. Polycrystalline HMS samples are usually prepared by solid-state reaction or melting, and show nearly isotropic transport properties [11,12].

The maximum *ZT* of pure HMS has been reported to be about 0.4 at 800 K [11–13], which is still not sufficient for efficient thermoelectric conversion. In order to improve the *ZT* of HMS, a number of works have been focused on optimization of TE

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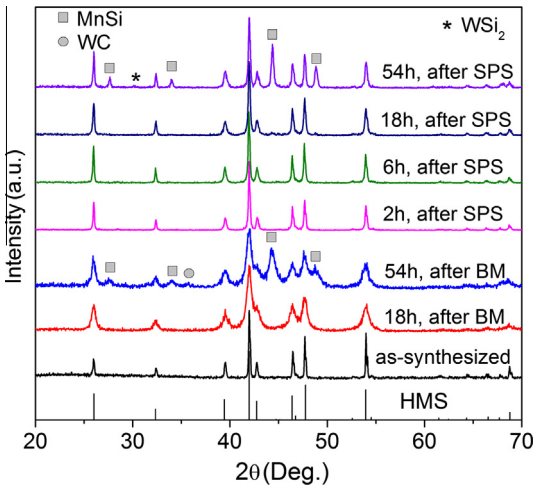

Fig. 1. XRD patterns of various HMS samples after melting, BM and SPS, respectively, with the BM time indicated as the number in the legend for each data.

properties by chemical doping or substitution [11,12,14–22]. For example, Re, Cr, Ge, and Al dopants have been employed to tune the transport properties of HMS. These approaches have resulted in the enhancement of the maximum *ZT* up to 0.6–0.7 at about 800 K. Recently, the effects of nanostructuring on HMS [23–34] have been investigated in an attempt to reduce the lattice thermal conductivity to enhance the *ZT* values. In one theoretical analysis based on a semi-classical two-band model and Debye approximation for calculating charge and phonon transport, respectively, it was estimated that the *ZT* of HMS can be enhanced somewhat by reducing the grain size to about 10 nm [27]. Recently, the full phonon dispersion of HMS crystals has been obtained through first principle calculation and inelastic neutron scattering measurements [35]. The obtained phonon dispersion has been used to establish a thermal conductivity model where the numerous optical vibration modes are treated as diffusons. This new model suggests that a glass-like thermal conductivity can be obtained in nanostructured HMS with the grain size reduced to the 10 nm level, which is still large compared to the previously estimated charge mean free path of 1–2 nm in HMS crystals [27]. Therefore, the impact on the power factor is not expected to be large. However, there is a lack of experimental results to verify whether the predicted size effects on the thermoelectric properties of nanostructured HMS can be achieved in experiments.

Here we report the results from an experimental study of the effects of ball milling (BM) time on the microstructures and thermoelectric transport properties of HMS samples, which were prepared by melting, subsequent BM, and followed by spark plasma sintering (SPS). We found that the grain size of HMS can be reduced to the 500–90 nm range without noticeable secondary phases in the as-synthesized nanostructured HMS samples. However, further increase of BM time leads to the formation of MnSi and tungsten/carbon-rich phases resulting from the decomposition of HMS and the contamination of tungsten carbide (WC) jars and balls, respectively. Moreover, not only the κ_L but also the σ and *PF* decrease with increasing BM time because of the increasing impurity concentrations and also likely defects. As a result, the *ZT* of HMS is not improved by BM. In addition, the measured grain size dependence of κ_L is used to verify the recent theoretical calculation [35] based on the phonon dispersion and a combined phonon and diffuson model. These results suggest the need of further reducing the grain size to ~10 nm while maintaining the phase purity in order to obtain enhanced *ZT* in nanostructured HMS samples.

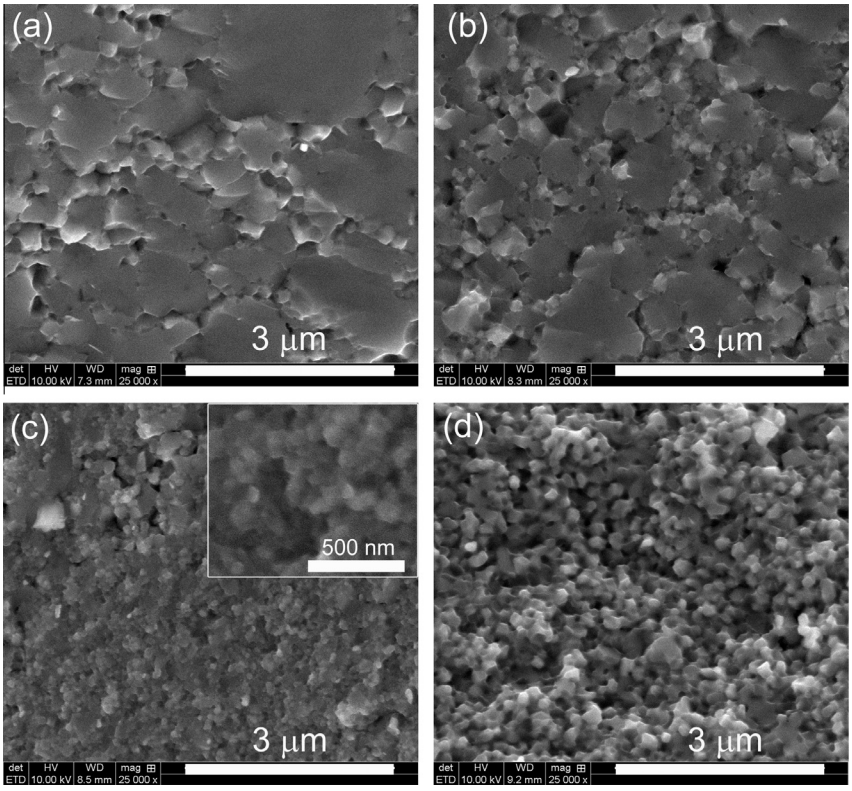

Fig. 2. SEM images of the fracture surface of various bulk HMS samples obtained by applying SPS to powders ball-milled for (a) 2 h, (b) 6 h, (c) 18 h and (d) 54 h. The inset of (c) is the magnified SEM image.