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Preparation of pure Higher Manganese Silicides through wet ball milling and reactive sintering with enhanced thermoelectric properties

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ABSTRACT

A simple and effective process is used to synthesize undoped Higher Manganese Silicides (HMS), involving ball milling under soft conditions to obtain homogeneous mixtures of constituting elements, and subsequent spark plasma sintering for a direct solid state reaction. For comparison purpose, the ball milling step is carried out under both dry and wet conditions using n-hexane as the liquid medium, Analysis of the granulometry demonstrates that the wet milling process in n-hexane results in finer particles, thus improving the reaction rate later on. According to X-ray diffraction and scanning microscopy, materials produced via wet milling and spark plasma sintering contain only HMS while dry milled samples contain MnSi impuritties. The Seebeck coefficient of the wet milling sample is 20% higher, while its electrical resistivity is 23% lower than those of the dry milling one over the whole temperature range. Moreover, the thermal conductivity was reduced up to 30% when using n-hexane as milling media. The maximum thermoelectric figure of merit obtained is 0.55 at 850 K, a high value for undoped HMS.
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1. Introduction

In recent years, Higher Manganese Silicides (HMS) have been considered as promising p-type thermoelectric materials for several reasons i) manganese and silicon are two of the most abundant elements of the Earth's crust; ii) being made of non toxic elements, HMS are ecologically benign; iii) they possess high mechanical strength and iv) they are stable in air up to 750 °C [1]. HMS exist as several incommensurate phases with chemical formulae of Mn_4Si_7, $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, and $Mn_{27}Si_{47}$, all crystallizing in the Nowotny chimney-ladder structures [2–4]. These structures are constructed by the two Mn and Si sublattices, where the Mn atoms form the chimneys in which the Si atoms spiral as ladders. The tetragonal unit cells of different HMS compounds have similar *a* parameter, and different *c* parameter, depending on the c_{Si}/c_{Mn} ratio of the two sublattices.

The techniques utilized for synthesizing bulk HMS can mainly be divided into two categories: melting process and solid state reaction. In the first approach, the high melting points of manganese (1263 °C) and silicon (1414 °C) are one of the big obstacles, especially in large scale synthesis. Additionally, the compositional control is a challenge at elevated temperature due to the high vapor pressure of manganese. Moreover, HMS produced by melting method always contain secondary phases of manganese monosilicided MnSi and of elemental Si because HMS melt incongruently. The striations of the monosilicided phase MnSi were reported by many authors for the as-grown ingots obtained from Bridgman, Czocharalski, and other techniques using the solidification of a melt [5–10]. The precipitates are observed as parallel thin planes, which usually grow perpendicularly to the c-axis of the HMS matrix. This metallic secondary phase is known to be detrimental to the thermoelectric performance as it generates electrical short-circuits in the matrix materials, which, consequently, degrades their thermopower and at the same time increases their thermal conductivity. Theoretically speaking, a high cooling rate is required to avoid the decomposition of the liquid phase into MnSi and Si, which is practically unachievable at the moment.

For industrial production, solid state techniques are often preferred due to lower energy consumption, homogeneity of the product. The driving force for the diffusion process is provided by either mechanical or thermal energy. On one hand, the mechanical

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alloying usually requires hard conditions for the formation of HMS, including high ball-to-powder ratio (BPR) [11–13], high rotation speed [13,14], and long milling duration [14–17]. The biggest problem encountered for applying hard ball milling conditions is the agglomeration of the powder around the balls and on the inside wall of the vials [18,19]. The agglomeration causes a loss of materials, but more importantly causes a departure from stoichiometry of the compounds. Aside from the low efficiency due to the material loss, the stoichiometric aspect is more essential for Higher Manganese Silicides due to the existence of various compounds with different transport properties in a very narrow compositional range (from 63 to 64 at-% of silicon). Furthermore, a loss of silicon during the processing has been recognized by several groups [11–13], which can be explained by its more adhesive characteristics than manganese, a softer element.

On the other hand, the typical solid state reaction usually requires several days or weeks with intermediate manual grindings to prepare HMS due to the slow diffusion rate of Si [20–23]. The ball-milling process is an alternative solution to achieve finer and more homogeneous mixtures, which helps to avoid the regrinding step during the heat treatment. The heat treating process can be done in conventional furnace [16,20–23], or during the consolidation such as in hot press [24], pulse discharge sintering, and spark plasma sintering apparatus [25]. We report here the thermoelectric performances of HMS materials prepared by ball milling in n-hexane, followed by heat treatment using spark plasma sintering. The improvement of solid state reaction rate by using small particle sizes is illustrated here through a comparative study between the wet milled and dry milled compounds.

2. Experimental section

The stoichiometric amounts, corresponding to the $MnSi_{1.75}$ composition of the constituent elements including Mn powder, 99.95%, −325 mesh, and Si powder, crystalline, 99.9%, −100 mesh, all purchased from Alfa Aesar, were homogeneously mixed via planetary ball milling using vials and balls made of tungsten carbide. The milling process is carried out with a low ball-to-powder weight ratio of approximately 4:1, a slow rotation speed of 450 rpm, and a short duration of 20 min divided into two rotating periods in reverse directions. The obtained powders were then directly loaded into graphite die for spark plasma sintering (SPS) at 1050 °C for 45 min using a maximum pressure of 28 MPa. For the wet milling, n-hexane was directly added into the vials up to just immersing the powder. The mixtures obtained from the wet milling process were, then, dried under the fume hood.

The particle sizes were analyzed using a Malvern's Mastersizer 2000 equipment with deionized water used as the dispersant. Compositions of the samples were determined at each step of the process by using X-ray powder diffraction with a Phillips X-Pert Pro Panalytical diffractometer with a Cu $K_{\alpha1}/K_{\alpha2}$ radiation (λ = 1.540598 Å, 1.544426 Å). The microstructure and chemical analysis are studied by an energy dispersive X-ray scanning electron microscope (SEM/EDX) Carl ZEISS SUPRA 55. The density of the materials, d, is determined via the Archimedes' method. All the samples have densities higher than 95% of the theoretical density, which is satisfactory for subsequent physical property measurements considering the error range of the density determinations.

The obtained pellets were cut into bars of approximate sizes of $10 \times 3 \times 3$ mm^3 and square pieces of $6 \times 6 \times 1$ mm^3 for electrical and thermal property measurements, respectively. The electrical resistivity and Seebeck coefficient are simultaneously measured using a ZEM-3 system (ULVAC-RIKO) under partial pressure of helium. The thermal diffusivity, α, is obtained by using a laser flash diffusivity method with a Netzsch's LFA 457 Micro Flash measuring system. The thermal conductivity, κ, is then calculated by $\kappa = \alpha \times C_p \times d$, where C_p is the specific heat capacity calculated via the Dulong-Petit law.

3. Results and discussion

The use of a liquid medium during high energy ball milling is well known to prevent welding between particles during collisions, and decrease the final particle size, which is convenient for our purposes [18,19]. In this case, n-hexane is used as milling media due to its availability as well as low boiling point, which helps its removal after the ball milling process. From this point of view, alcohol can also be a good candidate for wet ball milling, which was used by Z. Wang et al. [26], except for the possibility to produce oxides during the process. The ball milling step is carried out under mild conditions (low ball-to-powder weight ratio, slow rotation speed and short milling duration) to avoid the formation of HMS compounds. Therefore, the obtained mixtures consist of elemental manganese and silicon only. On the contrary, M. Saleemi et al. [27] also used balls and vials made of tungsten carbide and obtained a mixture of HMS, MnSi, silicon, and manganese after milling for 8 h at 400 rpm with hexane as dispersion media.

The particle size distribution collected on these mixtures by the laser granulometer is presented in Fig. 1 together with the SEM images for the powders obtained after the milling process. The distribution curve of this sample is asymmetric with the peak situated at approximately 100 μm showing non-uniform size dispersion, which is in good agreement with the SEM image of the same powder. The results show that the particles are partly broken down by the ball milling under soft conditions. On the other hand, the wet-milled sample contains finer and more evenly distributed particles as seen in Fig. 1(b). For longer milling durations, E. Groβ et al. [28] obtained a mean grain diameter of 5 μm after 1 h with planetary steel ball mill, and M. Saleemi et al. [27] reached the sizes of 50–500 nm after 8 h with tungsten carbide vials and balls, both milled in hexane media. The distribution curve of the wet milling sample is divided into two peaks located at approximately 13 and 100 μm. It is remarkable that the sedimentation of the mixture happens in a short time, therefore, the measurements are repeated only twice which may bring extra errors to the measurements. It is difficult to propose any conclusions about the completion of the wet milling process due to the peaks at 100 μm that could be assigned to either single or multiple particles. The inhomogeneous morphology with agglomeration due to wet milling was also reported by other group [27]. However, it is clear that the smaller particle size is achieved by using wet milling as indicated by the presence of the peak at 13 μm.

The X-ray diffraction patterns of the ground powders after the sintering process, given in Fig. 2, identified the major phase of all samples to be HMS. The materials prepared by dry milling contain impurities of MnSi and Si, while no extra peaks are observed in the one synthesized by wet milling within the detection limit of X-ray analysis. As mentioned in the introduction, various compounds with the Nowotny chimney-ladder structure exist under the HMS appellation. The two subsystems (Si ladder and Mn chimney) have a common tetragonal an axis but different c axis lengths. Consequently, the XRD patterns of these compounds are very similar in both peak positions and intensities. Therefore, a specific compound, defined by the c-axis ratio γ, is rarely identified, hence the generic name of HMS is usually used in most of the reports. A profile matching refinement of the XRD data of wet-milled HMS is performed using FullProf software with the pattern of Mn_4Si_7 compound, which is equivalent to the nominal compositions. However, the peak positions between the pattern and the experimental data are not well-fitted, indicating that a different

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