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Synthesis of Nano-structured p-type Higher Manganese Silicide

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Abstract

The abundance and economic route synthesis materials are excellent potential thermoelectric material and such type of materials have much attention compared to other thermoelectric materials. The higher manganese silicide (HMS) is a best thermoelectric material in view of its abundance, non-toxic and chemical stability. To increase the figure-of-merit of such useful higher manganese silicide, we adopt nano-structuring approach which involves large interfaces between the nano-grained structures, significantly lower the thermal conductivity. High purity Mn (99.95 %) powders, Si (99.95 %) powders were weighed and mixed in high energy ball mill. The mixed powders were vacuum sealed in quartz tube and kept in furnace at 900 K for 48 hours. Then, the powders were milled in high energy ball mill with 15:1 ball to powder ratio for 50 hours. The stainless steel jars and bowl is used for this purpose and milling is carried out at argon atmosphere. The milled powders were synthesized via rapid sintering process employing spark plasma sintering (SPS). In the present study, we report the synthesis of nano-structured higher manganese silicide employing ball milling followed by SPS and its micro-structural features.

Keywords: Nanomaterials, Higher manganese silicide, Spark plasma sintering.

1. Introduction

Thermoelectric technology is a solid state energy conversion technology and best for both ways of, heat to be converted into electricity and electricity to be converted into refrigeration [1-7]. The efficiency of a thermoelectric material is determined by the dimensionless figure-of-merit, $ZT = \alpha^2\sigma/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the temperature. To maximize *ZT*, α & σ must be large and κ must be small. Maximizing *ZT* is a challenging task, as optimizing one of this physical parameter affects the other. Nanotechnology provides the solution of large phonon scattering without the interruption of carrier flow across the matrix. Spark plasma sintering (SPS) is the one of the most successful techniques for consolidation and sintering of nanostructured materials for obtaining near theoretical densification while retaining the nano-grained structure[8,9]. This technique works mainly based on the electric spark discharge, where a high energy pulse current momentarily generate spark plasma between the particles resulting in highly localized temperatures[10]. The rapid heating rates and shorter sintering cycles during SPS with simultaneous application of load avoids grain growth in nano-structured materials. In the present study, we report the synthesis of nano-structured p-type higher manganese silicide thermoelectric materials employing ball milling followed by spark plasma sintering technique.

2. Experiment Details

High purity Mn (99.95 %) powders, Si (99.95 %) powders were weighed and mixed in high energy ball mill. The stainless steel jars and bowl is used for this purpose and milling is carried out at argon atmosphere. The mixed powders were vacuum sealed in quartz tube and kept in furnace at 900 K for 48 hours. Then, the powders were milled in high energy ball mill with 15:1 ball to powder ratio for 50 hours. X-ray diffraction analysis was carried out using monochromatic Cu Kα radiation using RigaKu X-ray diffractometer. Crystallite size measurements were carried out using X-ray diffractometer and crystallite size was calculated using Debye-Scherrer's formula. The loading & unloading of powder materials handled in glove box (Mbraun Inert Gas System, GmBH, Germany) to minimize oxidation and other atmospheric contamination. The material is sintered by spark plasma sintering process, heated at 1173 K for 3 minutes at 60 MPa in a graphite die in vacuum. The surface morphology of sintered pellets was studied using field emission scanning electron microscope (SUPRA V40, Carl Zeiss, Germany).

3. Results & Discussions

Fig. 1a & b shows the XRD patterns of vacuum sealed followed by furnace reacted HMS powders and 50 hours milled HMS powders respectively. The XRD peak profile shown in Fig. 1(d) indicates an increase in peak broadening with a sharp decrease in peak intensity after 50 h of ball milling, due to the formation of nanostructure and the generation of crystalline defects created by impact and shear forces of stainless steel

jars & balls. The average crystallite size of 50 hours milled powder was found to be ~25 nm, from ~50 nm initial HMS powder. Ball milled powders were subsequently consolidated and sintered employing SPS technique (Fig. 2), which resulted nano-structured fully dense HMS pellet.

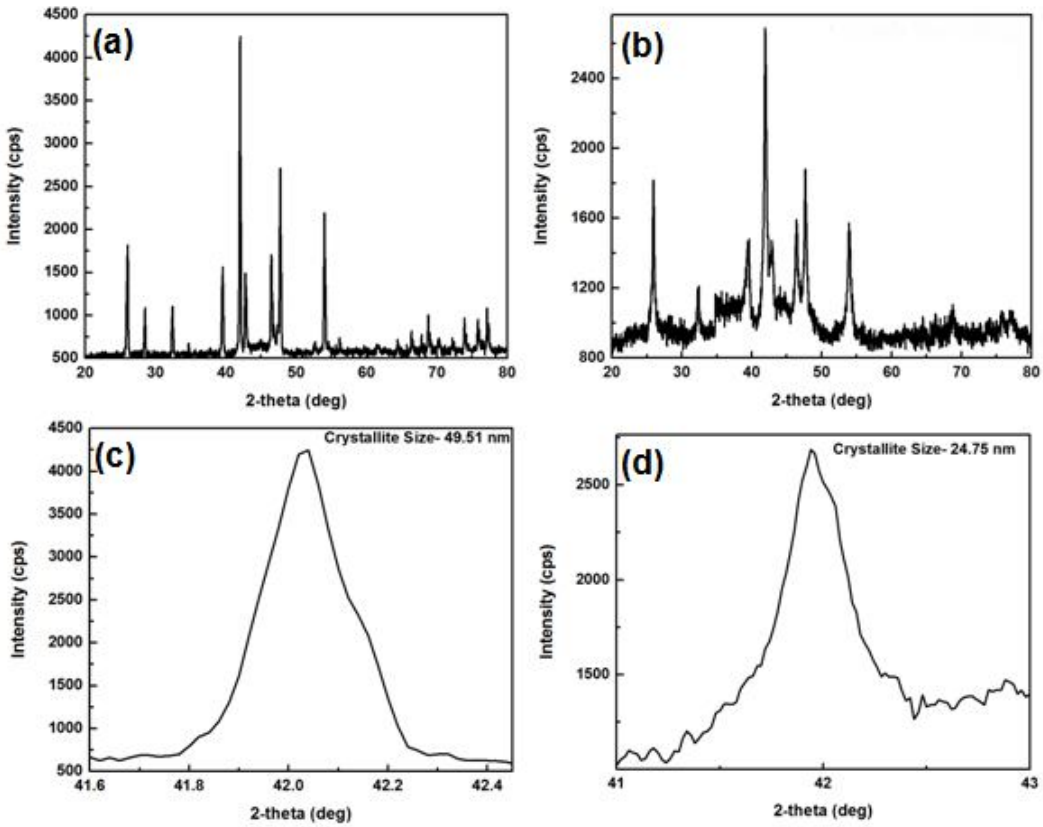

Fig. 1: XRD patterns of HMS: (a) & (c) Vacuum sealed followed by furnace reaction, (b) & (d) ball milled after 50 hours

Fig. 2: Spark Plasma Sintering Machine.

Fig. 3 shows the electron microscopy images of spark plasma sintered HMS pellets (a) after Vacuum sealed followed by furnace reaction, (b) after 50 hours of ball milled. The surface morphology of the balled milled HMS pellets shows evidence of sub-grains and nano-grains with non uniform grain boundaries. The microstructure of vaccum sealed followed by furnace reacted HMS pellet has no evidence of distinct grains with grain boundaries.

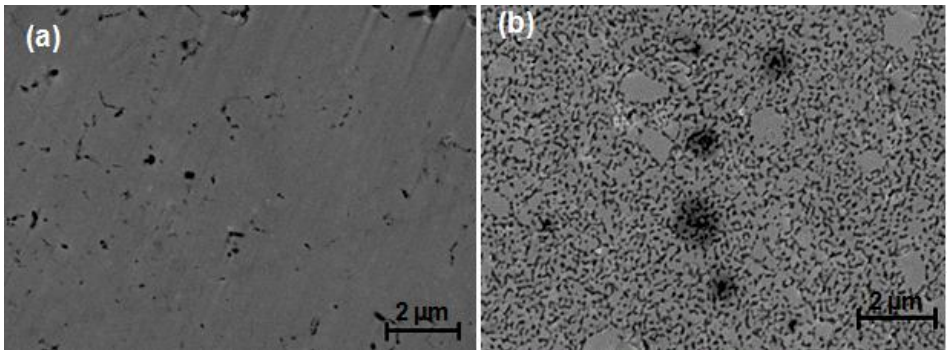

Fig. 3: SEM images of SPSed HMS pellet (a) Vacuum sealed followed by furnace reaction, (b) ball milled after 50 hours.

However, furnace reacted SPSed HMS pellet shows the evidence of second phases at sub-micron level. The present study revealed that ball milled followed by SPS technique promoted the formation of ultra-fine grains accompanied with non-uniform grain boundaries. From the micro-structural analysis (Fig. 3b), it can be inferred that SPS technique retain the nanoscale features of the p-type higher manganese silicides with near theoretical density. The anticipated lower thermal conductivity could be achieved by these types of microstructures. However, the obstacle of carrier/hole movement around the grain boundaries should be tuned for practical applications.

4. Conclusions

To summarize, we synthesized the nano-structured p-type higher manganese silicide thermoelectric material employing ball milling followed by spark plasma sintering technique. The average crystallite size ~ 25 nm has been achieved after 50 hours of ball milling. SPS synthesized Higher Manganese Silicide material shows the evidence of sub-grains and nano-grains with non uniform grain boundaries. These micro-structural features would enhance the thermoelectric properties of p-type TE material. The transport properties measurement of these nano-structured HMS pellet are the future avenues.

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