Synthetization and Characterization of Mo-doped Mn_{4}Si_{7} by High Energy Ball Mill

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Mn_{4}Si_{7} is a non-degenerating semiconductor with an indirect band gap of 0.77eV having multi-domain applications. The Mn_{4}Si_{7} and Mo-doped Mn_{4}Si_{7} were synthesized by high-energy ball milling at 600 RPM for 50H. From the X-ray diffraction (XRD), the tetragonal phase was observed. The average crystalline size was estimated by the Debye-Scherrer equation which lies below ~25 nm. The morphology studies reveal different shapes and sizes were observed by scanning electron microscopy (SEM).

Keywords: Phase purification; Ball milling; Manganese silicide; Earth-abundant; Doping

1 Introduction

Manganese silicide is an environment-friendly, earth-abundant, non-toxic material\(^1\) and has many applications such as thermoelectric, lithium-ion batteries\(^2\), electrical\(^3\), photodiodes\(^4\), optical\(^5\), etc. Manganese silicides are known as Higher Manganese silicides (HMS) because it exists in different phases such as Mn_{4}Si_{7}, Mn_{5}Si_{3}, Mn_{7}Si_{12}, Mn_{11}Si_{19}, Mn_{15}Si_{26}, Mn_{19}Si_{33}, Mn_{24}Si_{45}, Mn_{27}Si_{47}, and Mn_{30}Si_{48}\(^1,6,7\). Among the HMS family, Mn_{4}Si_{7} has non-degenerating semiconductor properties with an indirect band gap of 0.77 eV, while all other phases have degenerate semiconductors properties\(^8,9\). Mn_{4}Si_{7} is a Nowotny chimney-ladder (NCL) tetragonal crystal structure that consists of manganese (Mn) atoms from chimney frame walls and silicon (Si) atoms from spiral ladders\(^9\) (as shown in Fig. 1) and belongs to \(P-4c2\) space group with lattice parameters \(a=b=5.525\ \text{Å} \) and \(c=17.463\ \text{Å}\(^10\).

The challenge in the synthesis of single phase Mn_{4}Si_{7} is the multiple phases formation of HMS. As per the literature survey, Mn_{4}Si_{7} has been synthesized by different methods and different dopants (such as La\(^11\), Ce\(^11\), Cr\(^12\), etc.) to understand their properties. One of the transport properties thermal conductivity \(\kappa\), which is very high for thermoelectric material. One needs to be optimized the \(\kappa\), which may be selecting the suitable dopant at the Mn site. If the \(\kappa\) will be low, this system may be a good candidate for thermoelectric applications. In this paper, we doped Molybdenum (Mo) at the Mn site in Mn_{4}Si_{7} to understand their transport mechanism, may be Mo-doping will reduce the lattice thermal conductivity by creating large mass fluctuations and lattice distortion owing to their size differences compared with the matrix element Mn. In this paper, we present the synthesis of the tetragonal phase of Mn_{4}Si_{7} and Mo-doped Mn_{4}Si_{7} at the Mn site by high energy ball milling technique, a simple, fast, scalable, and environmentally friendly.

Fig. 1 — The Nowotny chimney-ladder tetragonal crystal structure of Mn_{4}Si_{7} composed of Mn (chimney frame wall) atoms and superimposed Si (spiral ladder) atoms.

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Experimental

The Mn₄Si₇ and Mo-doped (0.1% and 0.6%) Mn₄Si₇, were synthesized via high-energy ball milling at room temperature. The high-purity manganese pieces (99.9% Mn, Alfa Aesar), silicon lump (99.999% Si, Alfa Aesar), and molybdenum powder (99.9% Mo, Alfa Aesar), were homogenously mixed in a tungsten carbide jar and balls. Subsequently, the phase and crystallinity study were examined by X-ray diffraction (XRD) PANalytical X-pert diffractometer with Cu Kα-rays (λ = 1.54 Å). The morphology of samples was evaluated by scanning electron microscope (SEM, ZEISS EVO/18).

Results and Discussion

The environment-friendly and scalable, high-energy ball milling process was used to synthesize the pure phase of Mn₄Si₇ by optimizing various parameters such as RPM, milling time, on: off cycle and ball-to powder weight ratio. Based on the phase diagram, Mn₄Si₇ was synthesized at RPM 500 for 50H (M1), but no desired phase was observed, as shown in Fig. 2 (a). After multiple trials, the pure phase of Mn₄Si₇ was successfully synthesized at RPM 600 for 50H in a tungsten carbide jar and balls. The clear view can observe in Fig. 2 (a) and compared with a standard database (JCPDS# 01-072-2069) that only the Mn₄Si₇ phase was present, and no other phases were observed. After the successful synthesis of Mn₄Si₇, 0.1% Mo was doped at Mn-site in Mn₄Si₇ (synthesized at RPM 600 for 50H), as shown in Fig. 2 (b). Subsequently, increase the Mo-doping by 0.6% to eliminate the phase formation of MoSi₂, as shown in Fig. 2 (b). Fig. 2 (b) clearly show the polycrystalline nature of Mn₄Si₇ and Mo-doped Mn₄Si₇.

The crystalline size was estimated by Debye–Scherrer equation given:

\[ D = \frac{k \lambda}{β \cosθ} \]  \hspace{1cm} (1)

where k is Scherrer constant (k=0.9), \( λ \) the wavelength of the incident X-rays (1.5418 Å), θ the diffraction angle, and β stands for FWHM (full width at half maximum) for peaks. The average crystal size for the Mn₄Si₇ sample was ~18 nm which increased to ~25 nm with 0.6% Mo-doped in the Mn₄Si₇ sample. The FWHM for the peak (2 1 4) was slightly reduce on Mo-doping, may indicates successful replacement of Mo at Mn site. From the XRD pattern, the lattice parameters a and c and unit cell volume \( V \) of Mn₄Si₇ and Mo-doped Mn₄Si₇ were calculated by the Bragg equation given:

\[ nλ = 2d_{hkl} \sinθ \]  \hspace{1cm} (2)

where n is the order of diffraction (usually n = 1), \( λ \) refers wavelength of X-ray diffraction, h, k, and l variables represents Miller-Bravais Indices of crystallographic plane, \( d_{hkl} \) stands for inter planar spacing. In the Mn₄Si₇ tetragonal structure, the plane spacing d is related to the lattice constants a = b ≠ c and the Miller indices by the following relation,

\[ \frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \]  \hspace{1cm} (3)

\[ V = a^2c \]  \hspace{1cm} (4)

The lattice parameters of Mn₄Si₇, a = 5.514 Å, c= 17.545 Å and unit cell volume was ~533 Å³, which slightly increased on Mo doping 0.6% at the Mn site.
in Mn₄Si₇ a= 5.539 Å, c= 17.553 Å and unit cell volume was ~538 Å³. The calculated values of lattice parameters and unit cell volume for synthesized samples, are in good agreement with the standard database. Indicates that both the samples were successfully synthesized and exhibited tetragonal phase formation for both the samples.

The high-energy ball milling technique is a scalable process that enables the synthesis of Mn₄Si₇. Fig. 3 shows the morphology of Mn₄Si₇ (M), indicating the presence of non-uniform particles of different shapes and sizes with random aggregation. The minimum and maximum average particle size was ~0.18 µm and ~6.83 µm, respectively.

4 Conclusion

The tetragonal phase of Mn₄Si₇ and Mo-doped Mn₄Si₇ was successfully synthesized by the high-energy ball milling technique. The Mo was systemically replaced by Mn-site, which affects the particle size by decreasing the FWHM, which results in the increment in the crystallite size from ~18 nm to ~25 nm. FWHM change may indicates successful replacement of Mo may at Mn-site. The lattice parameters and unit cell volume were slightly increased, on Mo-doping 0.6% from a= 5.514 Å, c= 17.545 Å and unit cell volume = ~533 Å³ to a= 5.539 Å, c= 17.553 Å and unit cell volume= ~538 Å³ and are in good agreement with the standard database. A non-uniform, different size and shape morphology was observed from scanning electron microscopy.

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