

THERMOELECTRIC PROPERTIES OF β -FeSi₂ PREPARED BY THE MECHANICAL ALLOYING TECHNIQUE AND PRESSURELESS SINTERING

Kiatgamolchai S.¹, Parinyataramas J.¹, Nilpairach S.², Thueploy A.², Wanichsampan J.², Min G.³

¹Department of Physics, Faculty of Science, Chulalongkorn University,

Bangkok 10330 Thailand; e-mail: somchai.k@chula.ac.th

²Metallurgy and Materials Science Research Institute, Chulalongkorn University,

Bangkok 10330 Thailand

³Cardiff School of Engineering, Cardiff University, Newport Road, Cardiff CF24 0YF,

Wales, United Kingdom

TERMOELEKTRICKÉ VLASTNOSTI POLOVODIČA β -FeSi₂ PRIPRAVENÉHO MECHANICKÝM LEGOVANÍM A SPEKANÍM BEZ POUŽITIA TLAKU

Kiatgamolchai S.¹, Parinyataramas J.¹, Nilpairach S.², Thueploy A.², Wanichsampan J.², Min G.³

¹Department of Physics, Faculty of Science, Chulalongkorn University,

Bangkok 10330 Thailand; e-mail: somchai.k@chula.ac.th

²Metallurgy and Materials Science Research Institute, Chulalongkorn University,

Bangkok 10330 Thailand

³Cardiff School of Engineering, Cardiff University, Newport Road, Cardiff CF24 0YF,

Wales, United Kingdom

Abstrakt

Polovodič FeSi₂ je jedným zo sľubných termoelektrických materiálov určených pre vysokoteplotné termoelektrické generátory. Hlavnou výhodou použitia FeSi₂ oproti iným termoelektrickým materiálom je to, že základný materiál je relatívne lacnejší. Okrem toho má FeSi₂ dobrú odolnosť voči teplotnej oxidácii v prostredí bežného vzduchu a nie je toxický. V tomto príspevku je študovaná zliatina typu Fe_{1-x}Co_xSi₂ majúca modifikáciu β , pričom $x = 0, 0,01, 0,03$ a $0,05$. Zliatina bola pripravená mechanickým legovaním využitím kovov vo forme prášku, následne bola lisovaná za studena a spekaná bez použitia tlaku pri teplote 900°C pri rôzne dlhých časoch. Pre identifikáciu štruktúrálnej fázy Fe_{1-x}Co_xSi₂ bola použitá metóda rtg. difrakcie, pričom na hodnotenie termoelektrických a elektrických vlastností bola meraná odolnosť materiálu a Seebeckov koeficient. Bolo zistené, že spekanie po dobu desiatich minút zlepšilo tvorbu β fázy. Predĺženie doby spekania spôsobilo, že β fáza zanikla a namiesto toho došlo k tvorbe fáz ϵ a α . Hustota všetkých vzoriek dosahovala hodnotu asi 2,1 g.cm⁻³, čo je asi o 50 % menej než je dokumentované v literárnych prameňoch a tým je možné očakávať prítomnosť dutín v študovanom materiáli. Hlavným nosičom elektrického náboja bol v prípade nedopovaného polovodiča FeSi₂ typ p, pričom po dopovaní materiálu kobaltom sa zmenil na typ n. Odolnosť všetkých vzoriek klesá s nárastom teploty, čo je pre polovodiče typické. Pri experimente bol získaný Seebeckov koeficient pri izbovej teplote v rozsahu od 130 do -80 $\mu\text{V.K}^{-1}$. Najvyššia absolútna hodnota Seebeckovho koeficientu mala hodnotu 383 $\mu\text{V.K}^{-1}$ a bola dosiahnutá pri teplote asi 250°C v prípade nedopovaného polovodiča FeSi₂. Pridaním kobaltu došlo k poklesu Seebeckovho koeficientu, ale na druhej strane narástla elektrická vodivosť študovaného polovodiča. Získaný výsledok je dobrým signálom pre potenciálne použitie FeSi₂ pre termoelektrické aplikácie, obzvlášť za vysokých teplôt.

Abstract

A semiconducting iron disilicide FeSi_2 is one of the promising thermoelectric material for the high-temperature thermoelectric generator. The main advantage of using FeSi_2 over other thermoelectric materials are that the cost of raw materials are relatively cheaper. Moreover, FeSi_2 has good resistance to thermal oxidation in the normal air and is nontoxic. In this research, $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ alloy ($x = 0, 0.01, 0.03, 0.05$) in β -phase were prepared by the mechanical alloying of elemental powder, cold-press and pressureless sintering at 900°C for various times. XRD (X-Ray Diffraction) was employed to identify the structural phase of $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ while Seebeck coefficient and resistance were measured to evaluate the thermoelectric and electrical properties. It was found that 10 minute-sintering enhanced the formation of β -phase. Sintering for longer time resulted in the disappearance of β -phase but enhancement of ε -phase and α -phase instead. The density of all samples was approximately 2.1 g.cm^{-3} which is 50 % less than that reported in the literature, indicating the presence of voids. The majority carriers in our undoped- FeSi_2 was p-type but changed to n-type after doping with cobalt. The resistance of all samples decreased with increasing temperatures which is typical for semiconductor. The room temperature Seebeck coefficient in the range from 130 to $-80 \mu\text{V.K}^{-1}$ was obtained. The highest absolute value of $383 \mu\text{V.K}^{-1}$ was observed at around 250°C for undoped- FeSi_2 . The addition of cobalt reduced the Seebeck coefficient but increased the electrical conductivity. This result is of good sign for the potential use of FeSi_2 for the thermoelectric application, especially at high temperatures.

Keywords: β - FeSi_2 , iron disilicide, thermoelectric, Seebeck coefficient, mechanical alloying

1. Introduction

Thermoelectric generator has been a fascinating device because it can directly convert heat energy into electricity. In comparison with the conventional method of having produced electricity from the mechanical energy, i.e. from a diesel engine, the thermoelectric generator has no moving part to induce any vibration or noise. Moreover, it does not produce any exhaust gases that pollute our environment. The efficiency of thermoelectric generator is estimated to increase with temperature difference between heat source and sink; a concept from the Carnot's engine. Therefore, any thermoelectric generator of interest should bear the high-temperature operation..

A semiconducting iron disilicide (β - FeSi_2) is one of the potential candidates for practical use in the high temperature range up to 900°C because it has a good resistance to thermal oxidation in the air and is not toxic. The cost of starting materials, iron and silicon, are also relatively cheap due to their abundance on earth.

Iron-silicon alloy exists in three phases, which are β - FeSi_2 , ε - FeSi , and α - Fe_2Si_5 , but only β - and ε -phase are thermodynamically stable at room temperature. The β -phase is the most preferred because of its relatively higher Seebeck coefficient. Unfortunately this phase is not directly formed from the melt which consists of α - and ε -phases instead, according to the equilibrium phase diagram of the Fe-Si alloy system [1]. The isothermal sintering after solidification is required to induce the peritectoid reaction: $\varepsilon + \alpha \rightarrow \beta$. However, this reaction can take more than 4 days at 900°C for a complete β -phase formation [2]. The extrinsic FeSi_2 can be prepared by doping Mn or Al for p-type and Co for n-type. Preparing doped- FeSi_2 from the melt cannot produce a homogeneous dopant distribution in the matrix [3]. Deposition techniques such as rf-sputtering [4], thermal spraying [5] and Chemical Vapor Deposition (CVD) [6] has also been reported.

Mechanical alloying (MA) is a powder metallurgy technique that produces partially alloy in a fine powder form. A typical process starts from MA of either melted Fe-Si alloy, which has been initially crushed into sub-millimeter-size powder, or elemental powders. It is followed by a hot pressing and isothermal sintering at the temperature below 970°C [3, 7]. Recently, a cold pressing of flake melted- $\text{Fe}_{0.94}\text{Co}_{0.06}\text{Si}_2$ and $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with subsequent sintering at 800°C for 100 hours has been successful which results in porous n- and p-type compounds and a reasonably good thermoelectric modules [8]. In our work, we will use the MA of elemental powders, followed by a cold pressing and subsequent sintering. This process requires less energy during the pressing and therefore would help reduce the cost in mass-production of the thermoelectric generator from this material.

2. Experimental Method

Iron powder (Goodfellow CAS No. 7439-89-6, 98+ % purity, size < 149 μm) silicon powder (Sigma Aldrich No. 215619, 99 % purity, size < 44 μm), and cobalt powder (Sigma Aldrich No. 266647, 99.9+ % purity, size < 149 μm) were used as the starting materials to prepare for FeSi_2 and $\text{Fe}_x\text{Co}_{1-x}\text{Si}_2$ ($x = 0.01, 0.03, 0.05$). The mixture of powders were milled in a planetary ball mill (Fritsch model pulverisette) to reduce the particle size, and to some extent producing the Fe-Si alloy, under the argon-gas ambience. The weight ratio of stainless-steel balls to the mixture was 20:1 with the ball diameter of 10 mm. The ball mill rotated at the speed of 295 rpm. It was experimentally found that a good recipe of milling to lessen the mixture from sticking to the inner wall of vial was to mill at low speeds initially and gradually increase the speed. The mixture inside the vial was scratched off the vial's inner wall regularly at 12 hours interval. All processes always were under the argon atmosphere in order to reduce the oxidation of iron or silicon with the oxygen in the atmosphere. During the milling, small amount of mixture was sampled and analyzed by the X-ray diffraction (XRD, Phillips model PW3710) and a Laser particle-size-distribution analyzer (Malvern model mastersizer S) as to determine the state of mixture and predict the appropriate milling time. For the particle-size-distribution analyzer, the aggregated mixture was ultrasonically dissolved in water before the measurement.

After milling, the mixture was sieved to the size less than 177 μm and hydraulic-pressed in the room-temperature air with the gauge pressure of 400 MPa into a rectangular bar of the size $15 \times 32 \times 1.5 \text{ mm}^3$. Samples were then put on a silicon wafer which was inside a furnace. Samples were sintered at 900°C under the argon ambience at the pressure of 7.6×10^4 - 8.1×10^4 Pa. This temperature was chosen because it was near but below 970°C where the transformation from $\beta\text{-FeSi}_2$ to $\alpha\text{-FeSi}$ would occur [3]. After sintering, the morphology of samples were examined by the Scanning Tunneling Microscope (SEM, Jeol model JSM5410LV). The phases of alloy were also determined by the XRD. The Seebeck coefficient, the ratio of potential difference to the temperature difference, was determined by the hot-probe technique. The high-temperature Seebeck coefficient and resistance measurements in the temperature range 30 - 500°C were carried out under the vacuum at 5×10^{-2} Pa.

3. Result and Discussion

The effect of milling-time to the particle size is shown in Fig. 1. It can be seen that with increasing milling time, two groups of particle size can be identified. The first one has peaks around 10 - 100 μm range and the second one is around 1 μm range. This could be explained in term of breaking-down and recombination of material. Silicon is brittle while iron

is ductile. This means that silicon will be broken down into smaller-size particle while iron behave like glue, combining small particle into a bigger one.

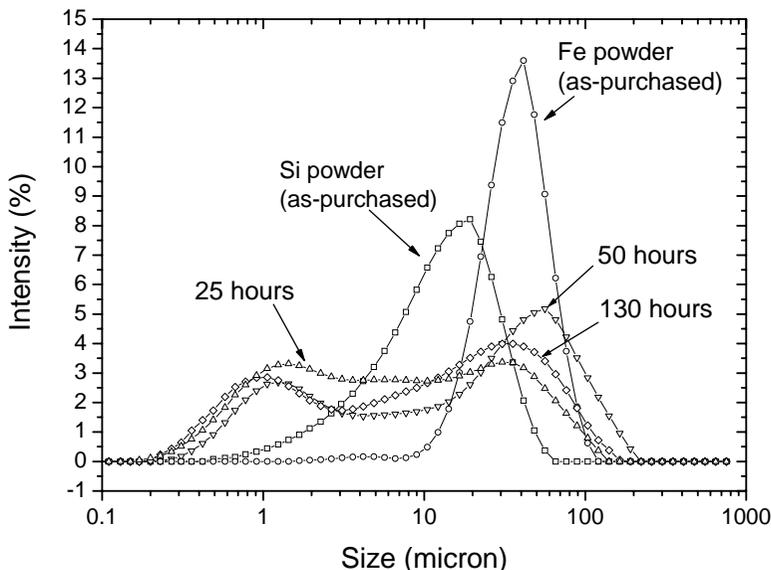


Fig.1 The particle-size distribution of as-purchased Fe and Si, and of mixture Fe-Si after various milling times

Figure 2 shows the SEM micrographs of as-purchased iron and silicon powder, and the mixture after milling for 72 hours. The aggregation of small silicon particle into a bigger one is clearly seen.

The XRD patterns of milled-powder as a function of milling time are shown in Fig. 3 which are similar to those reported in literature [3]. It can be seen that the elemental peaks totally disappear after 130 hours while the Fe-Si alloy in three forms (α -Fe₂Si₅, β -FeSi₂, ϵ -FeSi) are observed instead. These milled powders were believed to be in a meta-stable state because the rate of phase transformation is slow. The formation of β -FeSi₂ by the mechanical alloying requires at least 500 hours of milling [9] but we can see a slight β -peak after 130 hours of milling.

The density of cold-pressed sample before and after sintering were approximately the same of 2.1 g.cm⁻³ which is nearly 50 % less than the density of FeSi₂ single crystal of 4.93 g/cm³ [10]. This could be implied that there exist voids between powder particles or our sample has the porosity of about 50 %. This means that the thermal energy was not sufficient to enhance the merging of small-grain particle to form a bigger one. This is supported by the image of surface of FeSi₂ sample, sintered at 1100°C for 3 hours, as shown in Fig. 4. It reveals that in some area (at the center of the picture), the powder granules remain clearly seen. So, the cold-press after mechanically alloying of elemental powders and subsequent heating are not sufficient to produce a dense and sound FeSi₂ sample.

Figure 5 shows the silicon and iron atom distribution on the surface of the sample which is reasonably uniform. It should be noted that the smallest size of milled powder particle is around 0.1 μ m (see Fig. 1).

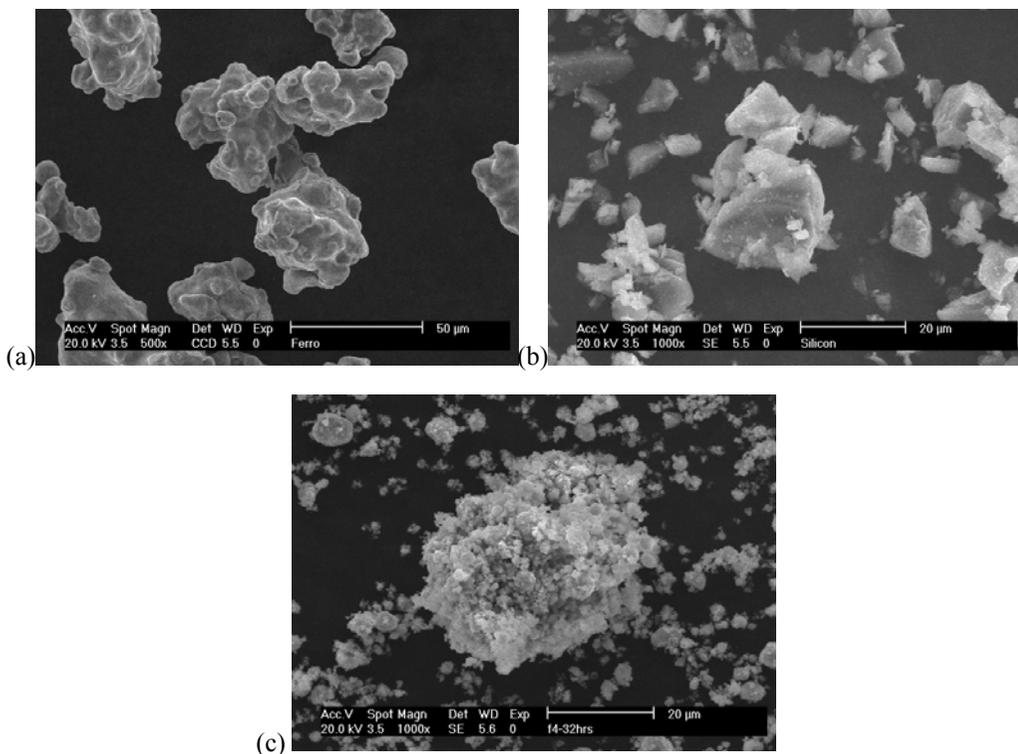


Fig.2 The SEM micrographs of (a) as-purchased iron powder, (b) as-purchased silicon powder, and (c) mixture of Fe and Si after 72 hour of milling

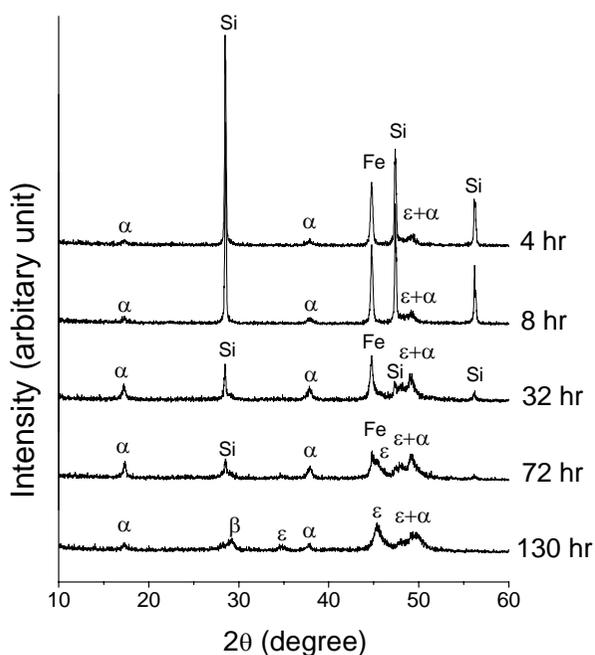


Fig.3 The XRD patterns of milled FeSi_2 powder for various milling times

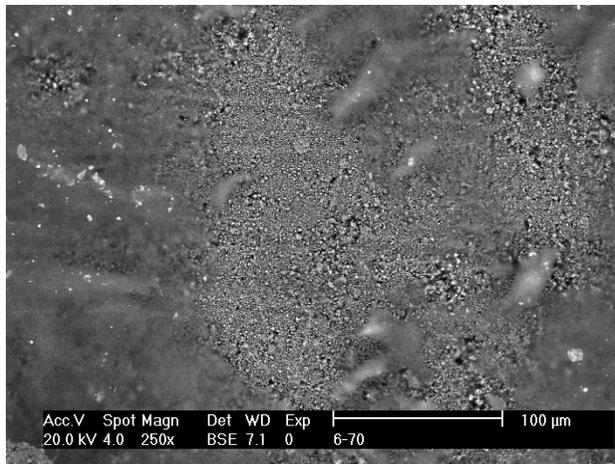


Fig.4 The SEM micrograph of 70 hour-milling, cold pressing and sintering at 1100 °C for 3 hours

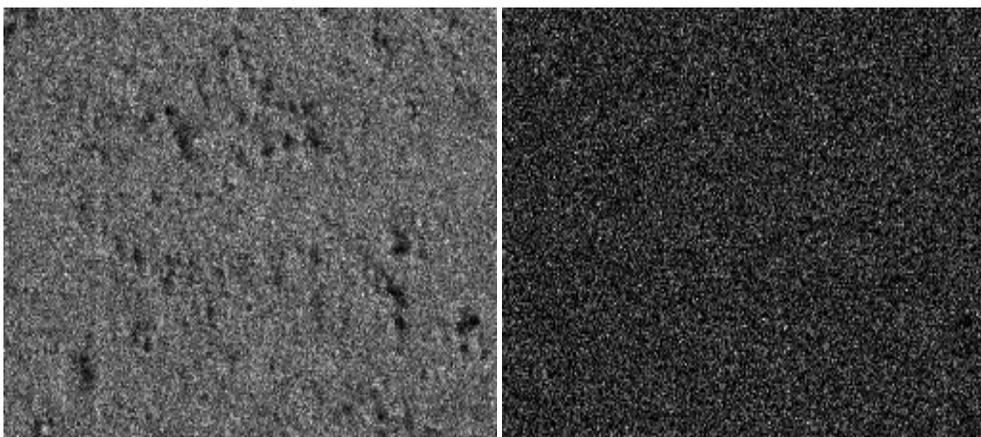


Fig.5 The EDX mapping image of (left) Si atom and (right) Fe atom, shown as white dots, of FeSi₂ sintered at 900°C for 1 hour. Each image represents an area of 200 μm × 200 μm.

The effect of heat energy to the phase transformation in FeSi₂ and Fe_{0.95}Co_{0.05}Si₂ is shown in Fig. 6. In both samples, β-FeSi₂ can be achieved by sintering at 900°C for 10 minutes (Figs. 6b, 6c). However, sintering for longer time results in the disappearance of β-FeSi₂ but enhancing the formation of ε-FeSi. Sintering at 1100°C for 3 hours also additionally produces α-Fe₂Si₅ which is typical for such high temperature sintering. It is well known that β-FeSi₂ is stable below 970°C and peritectoidally decomposes into nonstoichiometric α-Fe₂Si₅ and ε-FeSi above 970°C. Sintering below this temperature yields more β-FeSi₂ through the peritectoid reaction ($\alpha + \epsilon \rightarrow \beta$) and the eutectoid reaction ($\alpha \rightarrow \beta + \text{Si}$). So, it is still questionable for such a contradiction.

In Figure 7, several FeSi₂ samples ($x = 0$), sintering at 900°C for 10 minutes, exhibit different room-temperature Seebeck coefficient, ranging from -10 to 47 μV.K⁻¹ and are mostly p-type. Different values in coefficient can be partly explained in term of different amount of β-, ε-, α- phases presented in the sample. It has been reported that the Seebeck coefficient of β-FeSi₂,

α -Fe₂Si₅ and ε -FeSi are 250, 10, and 2.6 $\mu\text{V}\cdot\text{K}^{-1}$, respectively [8]. This indicates that our processing system still need further improvement for the consistency in production. In addition, our undoped-FeSi₂ is a p-type semiconductor which is in contradiction with most reports which is an n-type [7] and this indicates an unknown source of impurity. It was found experimentally that a single crystal β -FeSi₂ could be either p- or n-type depending on the iron purity. Reducing an impurity, the type can change from p- to n-type [6].

The temperature dependence of resistance and Seebeck coefficient of undoped-FeSi₂, Fe_{0.97}Co_{0.03}Si₂, and Fe_{0.95}Co_{0.05}Si₂ are shown in Fig. 8. The resistance of all samples decreases with increasing temperatures which is a typical characteristic of a semiconductor material. With Co as the dopant, it will supply more carriers and consequently less resistance. Our Seebeck coefficient results have similar characteristics as those reported by S.W. Kim [7] as follows. Firstly, the Seebeck coefficient decreases with increasing Co contents. Secondly, from room temperature, the absolute Seebeck coefficient initially increases with increasing temperatures but reaches the maximum and then decreases. The maxima Seebeck coefficient occur at higher temperatures with higher Co doping. Our Seebeck coefficient is about twice less than that reported in Ref. 7. This may indicate that our sample, as prepared by MA of elemental powders and subsequent cold pressing, has poorer quality. In Reference 7 they used the melted-Fe-Si alloy as the starting material for the MA and subsequent hot pressing.

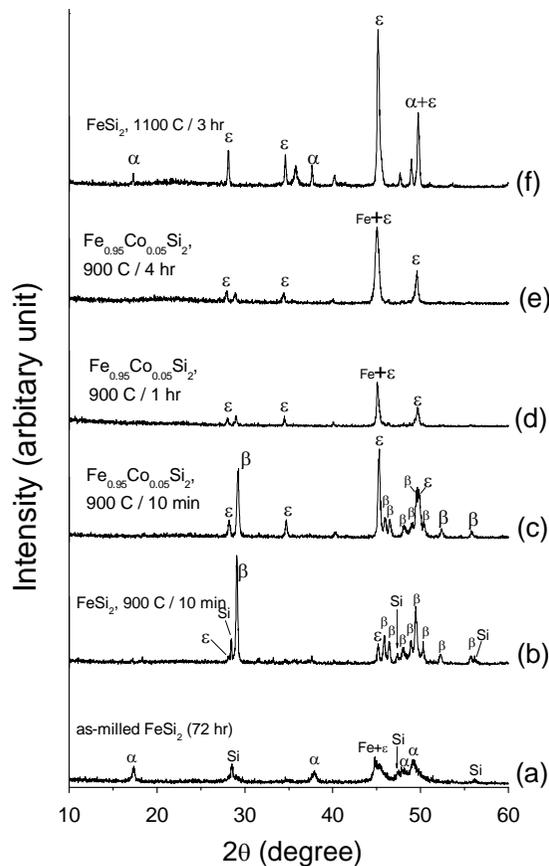


Fig.6 The XRD patterns of FeSi₂ and Fe_{0.95}Co_{0.05}Si₂ samples for various sintering times

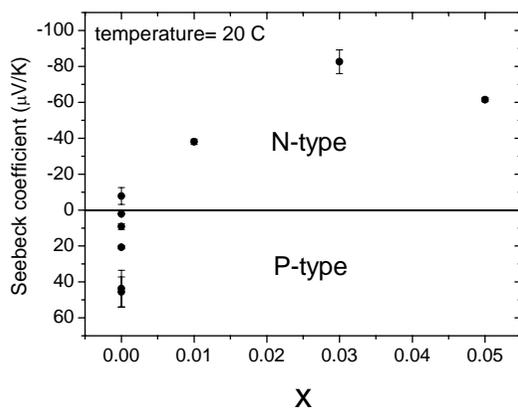


Fig.7 Seebeck coefficient of $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ for $x = 0, 0.01, 0.03$ and 0.05 at temperature of 20 °C

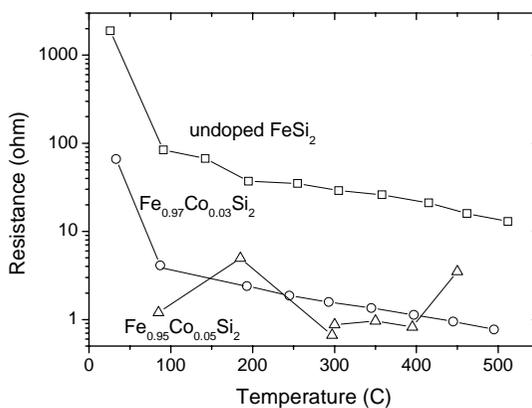
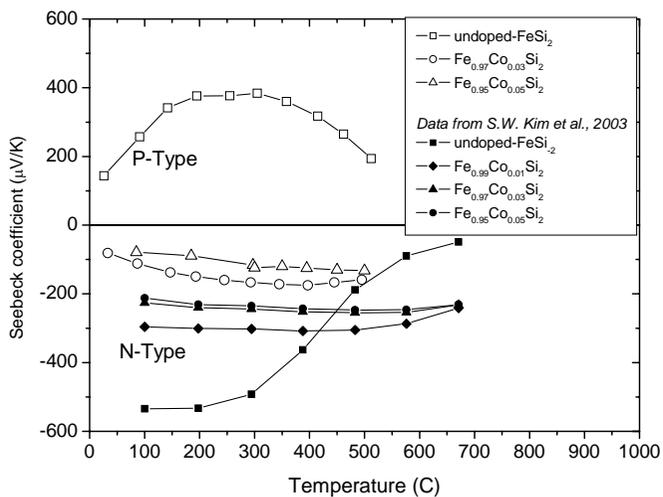


Fig.8 The resistance and Seebeck coefficient as a function of temperature

4. Conclusions

$\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ for $x = 0, 0.01, 0.03$ and 0.05 were prepared by the mechanical alloying of elemental powders under the argon ambience and followed by a cold pressing and subsequent sintering. It was found that $\beta\text{-FeSi}_2$ can be obtained from sintering at 900°C for 10 minutes. Sintering at 900°C for longer times or sintering at higher temperature resulted in the disappearance of β -phase but enhanced the formation of ε -phase and α -phase. The Seebeck coefficient in the range from 130 to $-80 \mu\text{V.K}^{-1}$ can be obtained at room temperature. Our unintentionally-doped FeSi_2 exhibited p-type semiconducting while Co-doped FeSi_2 was n-type. The absolute Seebeck coefficient increased with increasing temperature before reaching the maximum. With more Co doping, the maxima moved to higher temperature. The preparation process of MA of elemental powder, followed by the cold pressing and sintering seems to be insufficient to produce a good thermoelectric generator.

Acknowledgments

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Literature

- [1] Massalsky T.B.: Binary Alloy Phase Diagram, ASM, 1986, pp. 1108
- [2] Nishida I.: Study of semiconductor-to-metal transition in Mn-doped FeSi_2 , Physical Review, B7, 1973, pp. 2710 - 2713
- [3] Ur S.C., Kim I.H., Lee J.I., Cho K.W., Nash P.: Phase transformation in an n-type FeSi_2 processed by mechanical alloying, In: 21st International Conference on Thermoelectrics, IEEE, Longbeach, California, USA, 2002, pp. 114 - 117
- [4] Sorimachi Y., Honda K., Tsubata I., Ichinose Y., Wiyauchi S.: Structural and electrical properties of iron-silicide thin film resistor deposited by cosputtering, In: IEEE/ISHM'90 IEMT Symposium, IEEE, Italy, 1990, pp. 414 - 418
- [5] Tsutsumi A., Kuramoto K., Sawazaki J., Makita Y., Yoshida K., Ueno K., Sodeoka S., Suzuki M.: Structural design of large size thermoelectric module and thermoelectric properties of $\beta\text{-FeSi}_2$ prepared by thermal spraying. In: 17th International Conference on Thermoelectrics, IEEE, Nagoya, Japan, 1998, pp. 410 - 416
- [6] Behr G., Ivanenko L., Vinzelberg H., Heinrich A.: Single crystal growth of non-stoichiometric $\beta\text{-FeSi}_2$ by chemical transport reaction, Thin Solid Films, 381, 2001, pp. 276 - 281
- [7] Kim S.W., Cho M.K., Mishima Y., Choi D.C.: High temperature thermoelectric properties of p- and n-type $\beta\text{-FeSi}_2$ with some dopants, Intermetallics, 11, 2003, pp. 399 - 405
- [8] Cho W, Park K., Choi S., Yoon Y.: Thermoelectric properties of thermoelectric modules consisted of porous FeSi_2 based compounds fabricated by pressureless sintering, Materials Science and Engineering, B76, 2000, pp. 200 - 205
- [9] Uemoto M.: Preparation of thermoelectric $\beta\text{-FeSi}_2$ doped with Al and Mn by mechanical alloying, Materials Transaction JIM, 36, 1995, pp. 373 - 383
- [10] Maex K., van Rossum M.: Properties of metal silicides (emis datareviews series No.14), INSPEC publication, London, U.K., 1995