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Thermoelectric Properties of Bulk Yttrium Silicide (YSi2) Fabricated by Arc Melting and Spark Plasma Sintering

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Yttrium silicide (YSi_2) nanoparticles in SiGe are reported to enhance the thermoelectric figure-of-merit (*ZT*) to the recorded value (≈1.81). However, the thermoelectric properties of bulk YSi_2 has never been reported. In this work, the thermoelectric properties of YSi_2 is studied for the first time. The bulk YSi_2 is fabricated by arc melting highly pure Si and Y raw materials. The ingot is crushed to powder and compacted to form a highly dense pellet by spark plasma sintering. By optimizing the processing parameters, the single phase with the AlB_2-type structure (*P6/mmm*) is formed. The Hall measurements show that YSi_2 exhibit a metallic-like behavior with a very high electron concentration. This result in the thermoelectric properties with a very large electrical conductivity ($\approx 18 \times 10^5\ \Omega^{-1}\ m^{-1}$) but a small Seebeck coefficient ($-26\ \mu V\ K^{-1}$) at room temperature, and decrease with temperature. The thermal conductivity is around 14–19 $W\ m^{-1}\ K^{-1}$ for all temperature range. The maximum *ZT* value is 0.026 at 423 K.

1. Introduction

Thermoelectric (TE) materials can directly convert wastes heat into electrical power.[1–3] The performance of TE materials is determined by the dimensionless figure-of-merit, $ZT = (S^2\sigma/\kappa)T$, where S, σ, κ, and T are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. The present state-of-the-art TE materials around room temperature and mid-range temperature are Bi_2Te_3 and PbTe.[1,2] However, these materials have a certain draw back from their thermal instability and consisting of toxic and rare elements.

Metal silicides are a class of materials which has been considered as candidates for TE materials. In recent review papers, several types of silicides for TE applications were summarized, including Mg_2Si, $MnSi_x$, $CrSi_2$, β-$FeSi_2$.[4–6] With proper doping, these silicides showed promising TE performances with a relatively large *ZT* (>0.5).

TE properties of silicide nanoparticles in Si or SiGe matrix was theoretically calculated by Mingo et al.[7] In their work, several types of silicide nanoparticles were incorporated in the matrix and a fivefold increase in the *ZT* values were observed as a consequence of a significant suppression in thermal conductivity. This work has stimulated many experimental works in exploiting silicide nanoparticles as phonon scattering sources. For instance, Mg_2Si and $FeSi_2$ nanoinclusions in SiGe matrix showed the reduced thermal conductivity compared to the single-phase SiGe alloy, and hence the maximum *ZT* of 1.3.[8] Furthermore, the Si/WSi_2 nanocomposites showed 40% reduction in lattice thermal conductivity and the *ZT* enhancement of 30%.[9]

The most promising experiment was demonstrated by Ahmad et al.[10] who incorporated yttrium silicide (YSi_2) nanoparticles in SiGe matrix and obtained the recorded *ZT* (≈1.81) for the *p*-type SiGe alloy. The enormous improvement in TE performance was attributed to the coherent interfaces between YSi_2 nanoparticles and SiGe grains which strongly scattered phonon but have a minimum effect on the power factor. This work has not only emphasized the nanoparticle-in-alloy concept but also shed the light on YSi_2 as a promising TE material. Nevertheless, YSi_2 was not included in the reviews on silicides,[4,5] or in the calculation by Mingo et al.[7] Moreover, research on bulk YSi_2 were rarely reported.

Consequently, in this work, the bulk YSi_2 was fabricated and the TE properties were investigated for the first time.

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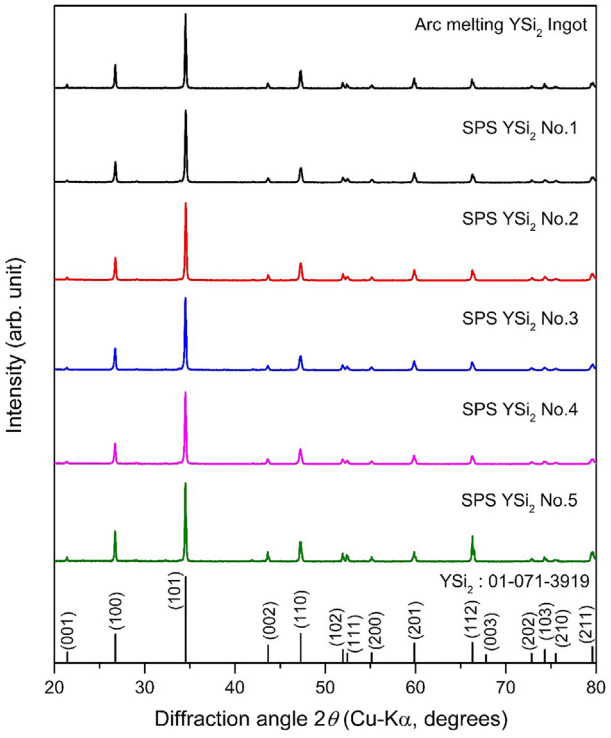

Figure 1. Powder XRD patterns of the YSi_2 samples after arc melting and after SPS.

2. Experimental Section

YSi_2 ingots were prepared by arc melting (AM) under Ar atmosphere, by melting highly pure Si (11N), and Y chunks (99.9%). The ingot was crushed to powder and then loaded into a graphite die for fabricating the bulk samples by using spark plasma sintering (SPS). The SPS was carried out at 1273 K for 5 min in Ar atmosphere under a pressure of 100 MPa. To test the reproducibility, five samples under the same synthesis conditions were prepared.

Crystallinity and morphology of the samples were observed using the X-ray diffraction analysis (XRD; Ultima IV, Rigaku) and scanning electron microscopy (SEM, JSM-6500F, JEOL). The chemical composition was confirmed by energy dispersive X-ray spectrometry (EDS) equipped in the SEM. Seebeck coefficient and electrical conductivity were measured by ZEM-3 (Ulvac-Riko) from room temperature to 773 K. The mobility and carrier concentration at room temperature were measured by Hall measurement system (Toyo ResiTest8300). Thermal conductivity (κ) was calculated from $\kappa = DC_pd$, where D, C_p, and d are thermal diffusivity, heat capacity, and density, respectively. D was measured by laser flash technique (NETZSCH, LFA457). $C_p = 3nR$, where n and R are the number of atoms per formula unit and gas constant. D was calculated from the measured weight and dimensions of the samples.

3. Results and Discussion

Figure 1 shows the powder XRD patterns of the YSi_2 ingot and the bulk samples after SPS. The main peaks of all samples agree well with the $YSi_{1.67}$ standard pattern (JCPDS 01-071-3919), representing the single phase of the AlB_2-type structure ($P6/mmm$), without any secondary phases observed. Samples 1–5 show the identical peaks indicating the reproducibility of the fabrication technique. The lattice parameters calculated from the XRD patterns are shown in **Table 1**, which are almost same with the literature values.[11] The densities of the bulk samples are also presented in Table 1. All samples possess very high density between 93.3 and 94.5% of theoretical values which are the fundamental requirements for good TE materials.

The SEM micrographs alongside with the EDS mappings of the pressed surface of the bulk YSi_2 sample are shown in **Figure 2**. It is obviously seen the fully dense sample with homogenous distribution of the elements. Quantitative analysis showed that the chemical compositions of Y and Si were 37.14 and 62.86 at.%, respectively, which is equivalent to Y:Si = 1:1.69. This result showed that the nominal composition YSi_2 was in fact $YSi_{1.69}$, which is closely agreed with the literature value of $YSi_{1.67}$.[11,12] The elemental analysis of all five samples show nearly identical compositions as summarized in Table 1.

The TE properties of the bulk YSi_2 samples are shown in **Figure 3**. All five samples show almost the same TE characteristics. The Seebeck coefficients were negative throughout the temperature range, indicating the n-type charge carrier, which was confirmed by the Hall measurement (Table 1). The absolute S values decreased with temperature from 26 $\mu V K^{-1}$ at room temperature to 14 $\mu V K^{-1}$ at 773 K. These values are very low compared to other silicide materials (100–300 $\mu V K^{-1}$).[4,5] The reason for the low S values is attributed to the very large carrier concentration ($n_H \approx 6–7 \times 10^{22}$ cm^{-3}), Table 1, much higher than

Table 1. Density (d), relative density (%T.D.), lattice parameter (a and c), Hall carrier concentration (n_H), and Hall mobility (μ_H) at room temperature.

Sample	d ($g\,cm^{-3}$)	%T.D.	Lattice parameter (nm)		EDS (at.%)		Carrier type	n_H ($\times 10^{20}$ cm^{-3})	μ_H ($cm^2 V^{-1} s^{-1}$)
			a	c	Y	Si			
No. 1	4.24	93.3	0.3843(4)	0.4143(2)	37.14	62.86	n	7.43 ± 0.7	17.9 ± 0.2
No. 2	4.29	94.5	0.3844(8)	0.4142(1)	37.11	62.89	n	6.11 ± 0.6	21.7 ± 0.2
No. 3	4.28	94.3	0.3845(4)	0.4147(5)	37.34	62.66	n	6.95 ± 0.7	19.1 ± 0.2
No. 4	4.25	93.6	0.3846(3)	0.4147(4)	37.26	62.74	n	6.84 ± 0.7	19.6 ± 0.2
No. 5	4.28	94.3	0.3844(9)	0.4143(2)	37.19	62.81	n	6.63 ± 0.7	18.7 ± 0.2
[11]	4.54	–	0.3843	0.4143	–	–	–	–	–

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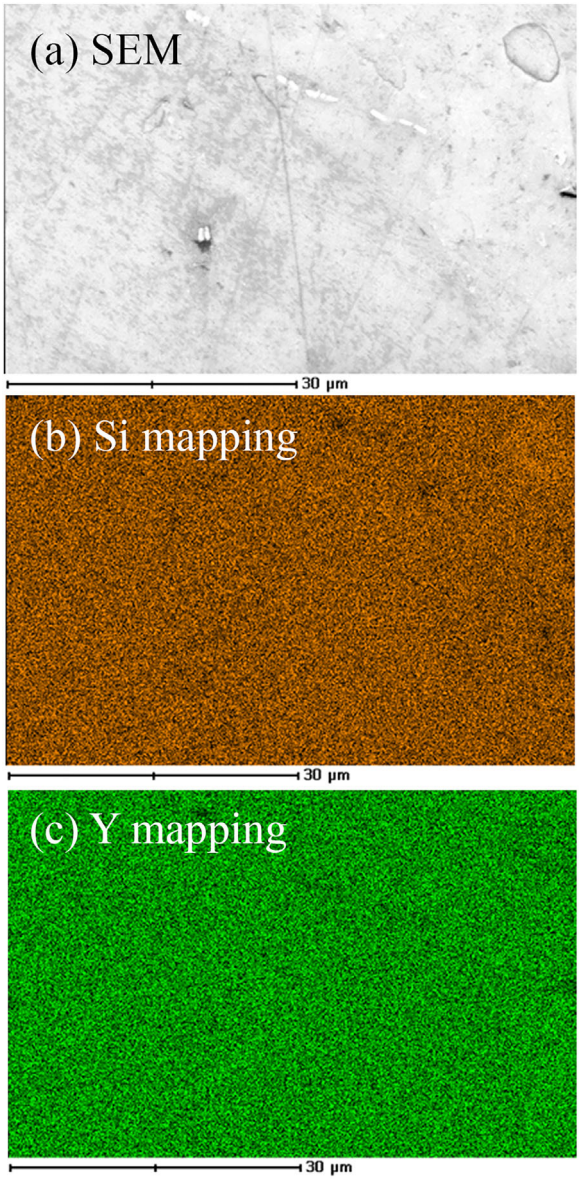

Figure 2. a) SEM images of the pressed surface of YiS_2 along with the elemental mapping (b) Y, (c) Si.

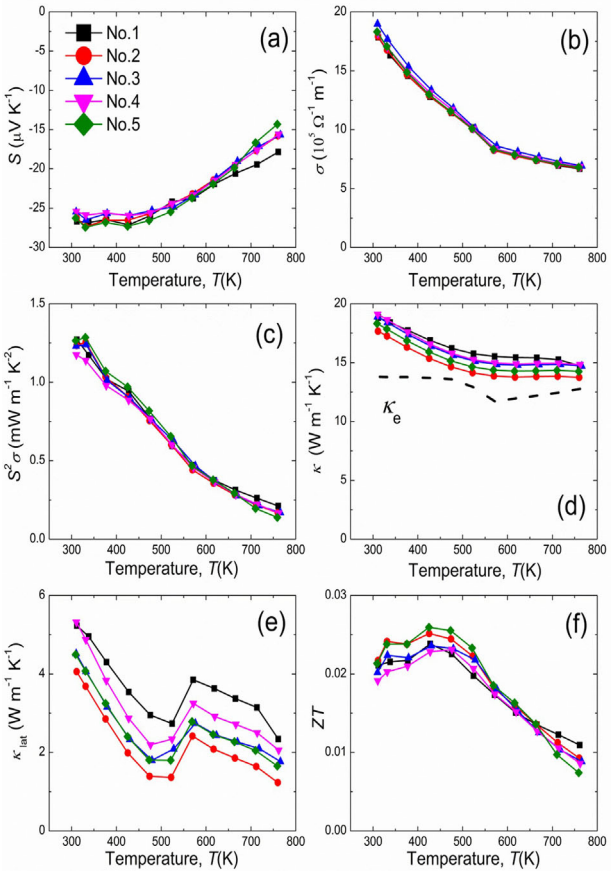

Figure 3. Temperature dependences of (a) S, (b) σ, (c) $S^2\sigma$, (d) κ, (e) κ_{lat}, and (f) ZT of YSi_2.

other silicide materials ($\approx 10^{20}$–$10^{21}\,cm^{-3}$).[4,5] Normally, for metals or degenerate semiconductors, the Seebeck coefficient is inversely proportional to the carrier concentration.[1,13] Therefore, the very large carrier concentration resulted in the reduced S values.

Figure 3b showed the decreasing electrical conductivity with increasing temperature, illustrating a metallic-like behavior. The observed σ values were very high throughout the measurement temperature ($18 \times 10^5\,\Omega^{-1}\,m^{-1}$ at RT), about an order of magnitude larger than other silicides ($\approx 10^4$–$10^{-5}\,\Omega^{-1}\,m^{-1}$).[4,5] The metallic-like behavior and large σ are consistent with the high n_H. The mobility of YSi_2 in the present study was nearly double of other silicides ($\approx 10\,cm^2\,V^{-1}\,s^{-1}$).[4,5] Though with very high σ, the small S led to relatively low power factor (1.28 mW $m^{-1}\,K^{-2}$ at RT), as shown in Figure 3c. It should be noted that the TE and Hall measurements in the present work are in consistence with the previous electronic structure calculations of which the Fermi energy was right in the middle of the conduction band,[14] representing the metallic characteristic of YSi_2.

Figure 3d shows the thermal conductivity of the bulk YSi_2 samples. The κ values slightly decreased with temperature and were approximately about $15\,Wm^{-1}\,K^{-1}$ above 500 K, several folds higher than other silicides.[4,5] Generally, $\kappa = \kappa_{lat} + \kappa_e$, where κ_{lat} is the lattice thermal conductivity and κ_e is the electronic thermal conductivity which can be estimated from Wiedemann–Franz's law, $\kappa_e = L\sigma T$, where L = Lorenze number $= 2.45 \times 10^{-8}\,V^2\,K^{-2}$.[1] The reason for the high thermal conductivity is due to the very large κ_e (dotted line). After subtracting κ_e, the κ_l is plotted as shown in Figure 3e. This implies that the thermal conductivity is mostly govern by the electronic part which could be justified from the very high carrier concentration. Figure 3f shows the temperature dependence of ZT which has the maximum of 0.026 at 423. This value is relatively low in comparison to other good TE silicides, i.e., Mg_2Si, $MnSi_x$, $CrSi_2$, $FeSi_2$, with $ZT > 0.5$. However, the ZT of YSi_2 in our case is comparable (or even better) to some inferior silicides, for example, URu_2Si_3, $Fe_{0.95}Cr_{0.05}Si_2$, $CeSi_2$, $SrSi_2$, $SrAl_2Si_2$, $BaSi_2$, $CaSi$.[5]

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4. Conclusion

In this work, the single phase of fully dense bulk YSi_2 was successfully fabricated using a combination of arc melting and SPS. The TE and Hall measurements of the bulk YSi_2 sample were carried out for the first time. From the results it was concluded that the bulk YSi_2 possessed the metallic characteristics. A large concentration of electrons above the Fermi level acts as the charge carrier. As a result, the very high electrical conductivity was found with the relatively small Seebeck coefficient. The thermal conductivity, dominated by the electronic contribution, was also large. Consequently, the *ZT* of this material is relatively low in comparison to other good TE silicides. Since the carrier concentration of YSi_2 was an order of magnitude larger than the optimum value for TE applications, it would be difficult to tune the carrier concentration by doping or other means. Therefore, even though the YSi_2 nanoparticles were successfully added in SiGe matrix to enhance the overall *ZT*, the stand-alone bulk YSi_2 might not be a promising TE material.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

silicides, spark plasma sintering, thermoelectric, YSi_2

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