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Thermoelectric properties of silicon hexaboride prepared by spark plasma sintering method

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Silicon hexaboride is attractive for various industrial applications because of its high temperature capability, high hardness and excellent electrical conductivity, in particular it is a promising material for use as a thermoelectric semiconductor at high temperature. We have used a spark plasma sintering technique to produce silicon hexaboride ceramics. The Seebeck coefficient, electrical conductivity and thermal conductivity were measured and the effect of additives, phase composition and microstructure on the thermoelectric properties were discussed. The approximate value of Z (figure of merit value) of the SPS specimen reached about 9.6×10^{-6}/K at 1273 K. The thermoelectric properties (Z) of the SPS specimen are improved in comparison with the specimen by hot-pressing. The effect of the addition of lanthanum and boron on thermoelectric properties of SiB_6 were also evaluated.

Key words: spark plasma sintering(SPS), silicon hexaboride(SiB_6), thermoelectric, Seebeck Coefficient.

Introduction

Silicon borides (Si_XB_Y) are attractive in various industrial application because of their high temperature properties, high hardness and excellent electrical conductivity. Of several Si_XB_Y phases which were previously reported, SiB_6 phase is a promising material for use as a thermoelectric semiconductor at high temperature [1] because it has a large Seebeck coefficient, low thermal conductivity, excellent electrical conductivity, high hardness [1, 2]. However, the application of SiB_6 has been limited by the poor sinterability using conventional sintering technique.

Spark plasma sintering (SPS) is one of the best candidates to fully densify materials that are otherwise poorly sinterable materials. The SPS technique is a newly developed sintering process that can heat the material several to tens of thousands of degrees Celsius by spark discharges between the particles. The spark discharges are generated by a pulsed direct current applied through electrodes. Due to these discharges, acceleration of mass-transfer occurs by the evaporation or melting on the particle surface and the densification can be achieved rapidly at lower overall temperatures. Therefore, the SPS process can control the grain growth by using a shorter sintering time than that of the conventional process, such as hot-pressing and hot-isostatic pressing [3-5]. The thermoelectric of figure of merit, Z is mostly influenced by the thermoelectric power through the S^2 term in $Z=S^2\sigma T/\kappa$ (S: Seebeck coefficient; σ: electrical conductivity; κ: thermal conductivity). This work presents the mechanism for sintering of SiB_6 by spark plasma sintering to improve the microstructure for thermoelectric applications at high temperature. We report the thermoelectric property changes after addition of lanthanum or boron.

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Experimental Procedure

Commercially available SiB_6 powder was used as starting material. Densification was performed by the spark plasma sintering system (Sumitomo Coal Mining: SPS-515S). The processing was carried out in a vacuum at 1200-1600°C for 5minutes in a 10 mm diameter graphite die. The phases of the initial powders and sintered bodies were identified using a X-ray diffraction (XRD). The particle size distribution was measured by a particle size analyzer (Microtrac-x100). The relative density of sintered bodies was determined using the Archimedes method and scanning electron microscope (JEOL: JSM-5900LV). The mixing of lanthanum or boron were carried out in glove box for 6 hours. Firstly weights of SiB_6 powder and additive were measured accurately, then it was stirred in a mortar under Ar-atmosphere. Microstructure and phase distribution were observed by a electron probe X-ray micro analyzer (EPMA) (JEOL: JXA-8900R). SiB_6 specimens were cut out for the electrical conductivity and Seebeck coefficient measurements. Electrical conductivity was measured using a D.C. four-probe method

under Ar-5%H_2 atmosphere. The Seebeck coefficient was measured from 573 K to 1273 K. Specimens were heated over a small temperature range by a substrate-heater and the electro-motive force was measured using a digital multimeter.

Results and Discussion

The powders are typically irregular and plate-like in shape and have a bimodal size distribution. Their average size is about 2.3 μm.

Figure 1 shows the typical X-ray diffraction pattern of sintered bodies of pure SiB_6(a) and 3 wt% La-doped SiB_6(b). The pure SiB_6 sintered body consists mainly of SiB_6 with a small amount of SiB_4 and Si_XB_Y phases detected. In the case of the La-doped specimen, most of the peaks became sharper, indicating that the addition of lanthanum improves the crystallinity of the sintered body.

Relative densities of the sintered specimens as a function of temperature are represented in Fig. 2. The sintered density increases with increasing sintering

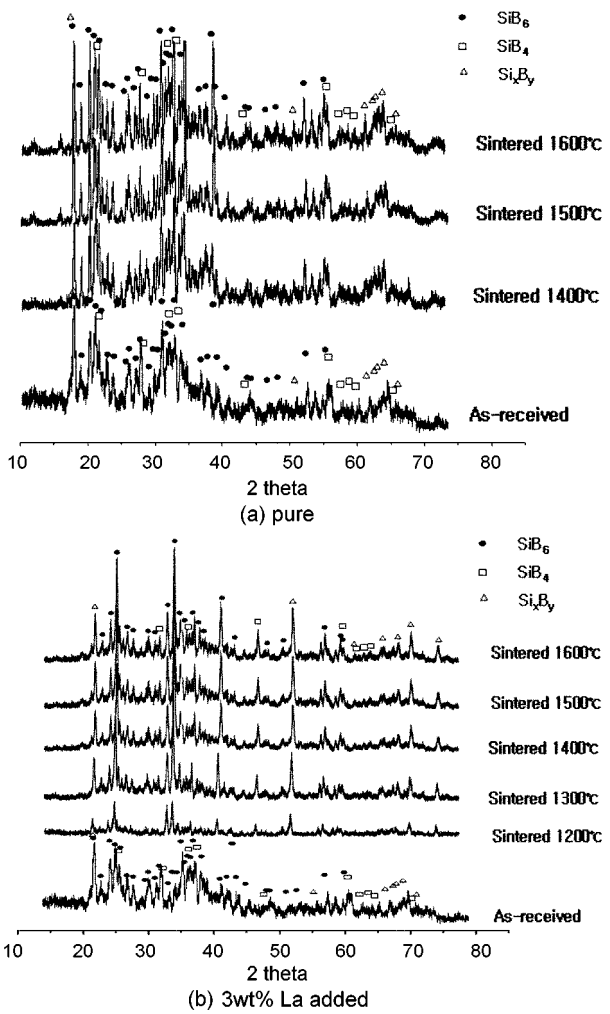


Fig. 1. X-ray diffraction patterns of the SiB_6 powder and sintered bodies.

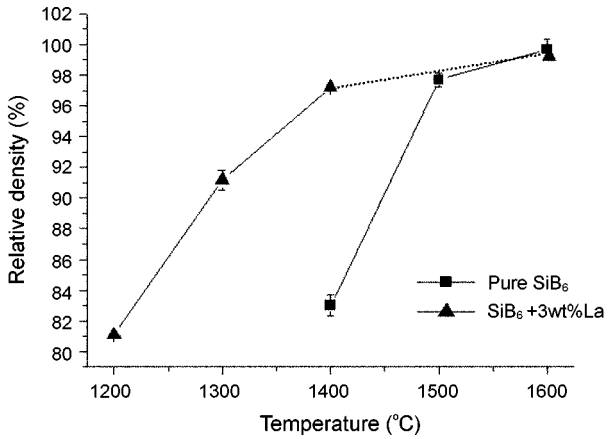
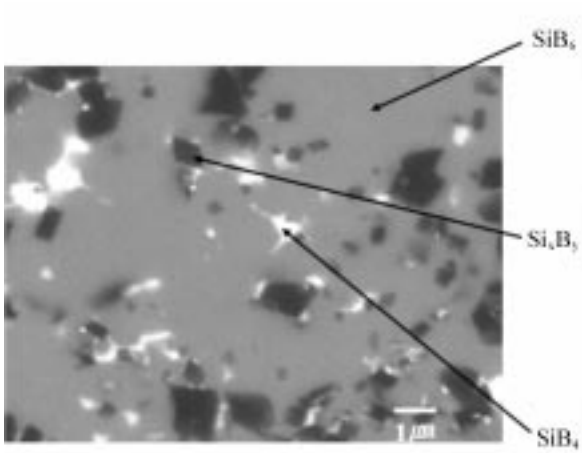


Fig. 2. Variation of the relative densities with temperature.

temperature. In the case of pure SiB_6 powder, the sintered body reached 98% relative density even at 1500°C and was fully densified at 1600°C. In the case of 3 wt% La doped SiB_6, the sintered body reached 97% theoretical density at 1400°C and completed the densification at 1500°C. However, some melting in the disc specimen was observed over 1600°C, indicating the proof of localized melting during the SPS process.

In the Si-B binary system, there are many compounds such as SiB_4 (rhombohedral), SiB_6 (orthorhombic) and SiB_n (hexagonal, n=14-49) [6, 8]. Among them, SiB_4 has a low thermal conductivity and high electrical conductivity but a low seebeck coefficient [9]. On the other hand, SiB_6 and SiB_n have large Seebeck coefficients, low thermal conductivities and a moderately low electrical conductivities. Therfore, control over the the phase distribution in material which is nominally SiB_6 will affect thermoelectric properties. The thermoelectric properties of spark plasma sintered B-doped SiB_6 specimen containing 90 at% B had the largest values [2]. Figure 3 shows the microstructure and phase distribution of an SPS-processed specimen. The EPMA results showed that the overall structure is mainly composed of SiB_6 phase (grey contrast) with a small amount of SiB_4 (white contrast) and Si_XB_Y (black contrast) phases homogeneously distributed. The overall boron content in the raw materials was 87%. Therefore, addition of boron provides some possibility of improving of thermoelectric property.

Figure 4(a) shows the temperature dependence of the Seebeck coefficients (S) of SiB_6. The S values increase with increasing temperature. The Seebeck coefficient of pure SiB_6 sintered at 1600°C changed from 8.7×10^{-5} to 240×10^{-6} V/K in the temperature range 300 K to 1273 K. The SPS specimens have higher Seebeck coefficients than the specimen prepared by hot-pressing. Figure 4(b) shows the Seebeck coefficients for La-doped SiB_6 and boron-doped SiB_6. The Seebeck coefficient of 3 wt% La-doped specimen was decreased. The B-doped specimen had an improved Seebeck



	B	Si
Atomic%	86.17	13.83

	B	Si
Atomic%	97.61	2.39

	B	Si
Atomic%	84.38	15.62

Fig. 3. Microstructure and chemical composition the body sintered at 1600°C.

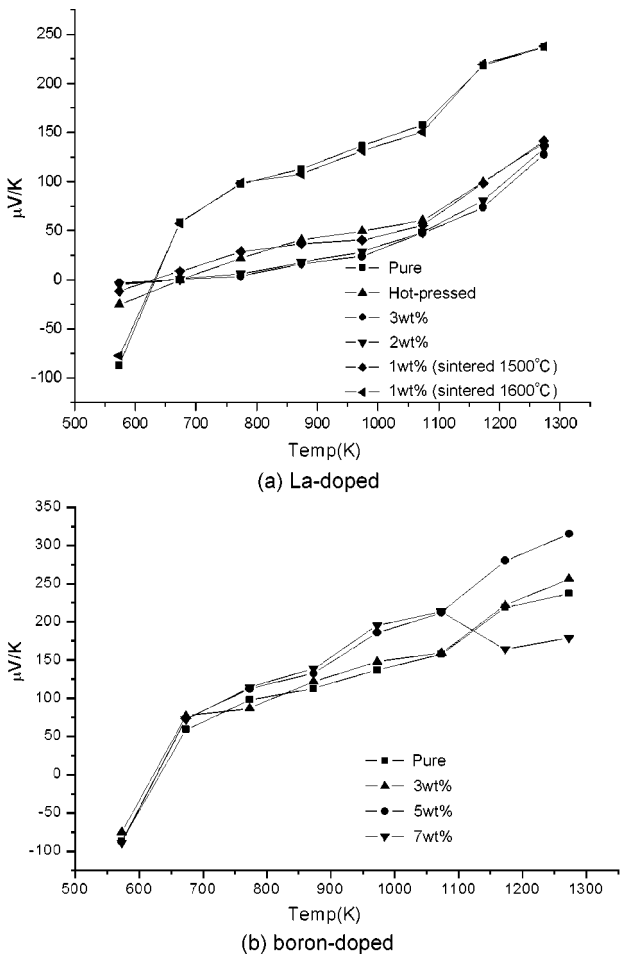


Fig. 4. Temperature dependence of Seebeck Coefficients of SiB_6.

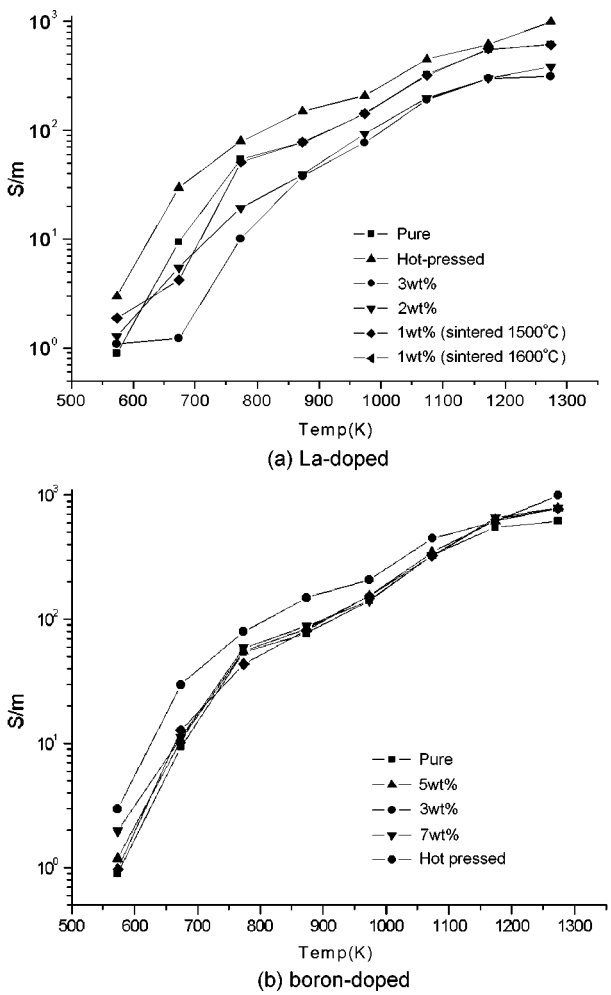


Fig. 5. Temperature dependence of electrical conductivity of SiB_6.

coefficient (about 315×10^{-6} V/K at 1273 K). In the case of 7 wt% Boron-doped specimens, the Seebeck coefficient value was decreased significantly at temperatures greater than 1000 K.

The temperature dependences of electrical conductivity in SiB_6 is shown in Fig 5. The electrical conductivity of SiB_6 sintered bodies increased with increasing temperature for all the specimens. The electrical conductivity of the pure SiB_6 specimen was 0.6×10^3 S/m at 1273 K. In the case of 3 wt% La-doped specimens, the electrical conductivity was lower, 0.4×10^3 S/m at 1273 K. On the contrary, in the case of 5 wt% boron-doped specimens, the electrical conductivity increased to

0.8×10^3 S/m at 1273 K.

Conclusion

Pure SiB_6 was successfully densified by a spark plasma sintering technique, reaching above 99% relative density at 1600°C. In case of 3 wt% La-doped SiB_6, the relative density reached about 97% at 1400°C and over 99% at 1500°C. The Seebeck coefficient of pure SiB_6 sintered at 1600°C, changed from -8.7×10^{-5} to 240×10^{-6}V/K in the temperature range 300 K to 1273 K. The electrical conductivity of the pure SiB_6 specimen was 0.6×10^3 S/m at 1273 K. The approximated figure of merit value, Z, of the SPS specimen reached about 9.6×10^{-6}/K at 1273 K. Therefore, the thermoelectric properties, ZT, of the SPS specimen were improved in comparison with the specimen prepared by hot-pressing. In the La-doped samples, the Seebeck coefficient and electrical conductivity were decreased. The thermoelectric properties of boron-doped specimens were improved. These thermoelectric properties are useful to evaluate the suitability of the thermoelectric materials.

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