

W. Liu et al.: Preparation of silicon boride SiB_x ($x = 3, 4, 5, 6$) powders by chemical oven self-propagating combustion

Weisheng Liu^{a,b}, Peizhong Feng^a, Xuanru Ren^a, Lu Zhu^a

^aSchool of Materials Science and Physics, China University of Mining and Technology, Xuzhou, P.R. China

^bSchool of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, P.R. China

Preparation of silicon boride SiB_x ($x = 3, 4, 5, 6$) powders by chemical oven self-propagating combustion synthesis

A new method was developed for quickly preparing a high-emissivity silicon boride compound of SiB_x ($x = 3, 4, 5, 6$) by highly exothermic Ti–TiO₂–Si–Al chemical oven pre-heating. The SiB_x combustion synthesis process and adiabatic combustion temperature were investigated. A large exothermic reaction occurred at the combustion temperature of 1700 K. X-ray diffraction results indicate that an SiB_x phase and a substantial amount of unreacted Si were identified in the products. By increasing the boron content until the Si–B ratio reached to 1:6, the diffraction peaks primarily indicated SiB_6 , SiB_4 , and $\text{Si}_{11}\text{B}_{33}$ in the final product. According to the spectra and quantitative results, the atomic chemical composition ratio of Si and B was close to the nominal composition. Thus, this method offers an efficient way to produce Si–B compounds with less time and energy consumption than current methods.

Keywords: Chemical oven; Silicon boride; Combustion synthesis; Self-propagating

1. Introduction

With the continuous development of new hypersonic flight vehicles and hypersonic strike weapons, it has been universally acknowledged that frictional heat inevitably occurs on the surface of the vehicle and the surrounding air, causing the surface temperature to reach 1600–3000 K during the vehicle roundtrip [1]. The primary method to address

this problem is to use a high radiation-resistant coating to prepare the aircraft surface with an oxidation protective film, as this technology helps radiate heat when the base material is heated rapidly, reducing the influence of heat on the aircraft surface. Currently, common highly rated radiation additives include SiB_4 , SiB_6 , and MoSi_2 [2, 3]. Silicon boride has the characteristics of a high melting point (2776 K) and good oxidation resistance. When it is in the boron silicate glass phase on the base surface at temperatures greater than 823 K, these attributes endow the compound with the capability to fill gaps through self-healing when micro-cracks appear in extreme environments in civil, military, and industrial applications [4]. Currently, silicon boride, as one of these radiation additives, is promising as a thermoelectric material for reaction-cured glass coatings (RCG), toughened uni-piece fibrous insulation (TUFI), and high efficiency tantalum-based ceramic (HETC) composite coatings under high temperatures because of its high melting point, excellent heat resistance, low density, and relatively large Seebeck coefficient [5].

The compounds of SiB_3 , SiB_4 , SiB_6 , and SiB_x have been identified as the main products in the Si–B binary system [6–8]. However, SiB_3 is unstable above 1473–1673 K, so it could be erroneously identified as SiB_4 [9]. The commonly applied method of synthesizing Si–B components includes arc-melting, spark plasma sintering, and solid-state reactions from silicon and boron powder mixtures at high temperatures in argon [10]. Roger et al. [11] obtained boron-enriched SiB_n ($13 < n < 32$) compo-

nents by melting the samples in an arc furnace under a Ti/Zr-getter argon atmosphere and re-melting them several times at 1273 K for 1 month. Wu et al. [12] mixed the initial atomic composition of $\text{Si/B} = 9/1$, melted the mixture at 1723 K for 10 h, and then quenched it at 1573 K, obtaining the SiB_4 phase and residual Si in the final product. Makarenko et al. [5] used amorphous 99.8% pure boron and nano-crystalline silicon in a vacuum (10^{-3} Pa) furnace in the temperature range of 1173–1623 K for 1 to 8 h to synthesize SiB_4 and SiB_6 , and some residual Si was found in the final product. Takashi et al. [13] prepared SiB_6 powders by spark plasma sintering at 1973 K and the powder compact disk specimens were composed of SiB_6 , SiB_{14} , and residual Si phases.

Previous scholars synthesizing Si–B compounds only focused on high temperatures with heat preservation for long periods to prompt a solid solution reaction between Si and B. However, these methods require long heating times and huge energy consumption and are unable to achieve industrialized mass production. Self-propagating high-temperature synthesis has been widely used due to its unique characteristics under extreme conditions, such as extremely fast heating rates (up to 10^6 K s^{-1}), high temperatures (up to 3500 K), and short reaction times (on the order of seconds) [14–16]. Recently, over one thousand different compounds, including carbides, borides, silicides, nitrides, and intermetallics, as well as their composites, have been synthesized [17]. However, the adiabatic temperature of the reaction system needs to be higher than 1800 K to maintain self-propagating high-temperature synthesis. Therefore, the silicon boron self-propagating high-temperature synthesis cannot be maintained. The adiabatic temperature of the reaction of the Si–B compounds is approximately 1700 K, so outside energy, such as preheating materials, heat explosion, and chemical furnaces, must be provided to maintain the reaction [18]. Kurbatkina et al. [19] used a highly exothermic Ti–B–C mixture (combustion temperature 3200 K) as a chemical oven to preheat boride ceramic samples (Zr, Ta) B_2 , allowing the ignition of these samples, which could not be ignited otherwise. Levashov et al. [20] applied a two-layer chemical oven (Ti, B, and C powders) surrounding the central layer of the principal reaction mixture to successfully synthesize an Mo_5SiB_2 compound.

The present study has determined an innovative alternative method to prepare Si–B compounds using the chemical oven support. Using this method, several SiB_x ($x = 3–6$) compounds were produced by combustion synthesis. The microstructure and elemental composition of the prepared compounds were then analyzed. The proposed method may offer a more efficient way to produce Si–B compounds with less time and energy consumption.

2. Experimental procedure

2.1. Materials and preparation process

Raw materials employed for combustion synthesis were silicon powder (purity > 99.9%, grain size 200 mesh) and boron powder (purity > 99.9%, grain size 1–3 μm). Four different stoichiometric ratios, $\text{Si:B} = 1:3, 1:4, 1:5, 1:6$, were prepared. The powder was mixed in a high-energy ball milling device, with the weight ratio of grinding balls to mixed powder of 5:1, for 3 h to achieve a well-milled mixture. The entire process of loading and unloading the powder was conducted in a glove box under an atmosphere of high purity argon (99.99%) to prevent oxidation of the mixed powder. After the high-energy ball milling, each mixture was then uniaxial cold-pressed into cylindrical compacts with a diameter of 10 mm and a height of 4 mm under a pressure of 200 MPa. The green density of the sample compact varied from 50–60% of the theoretical maximum density of the powder mixture.

A chemical oven was prepared using a highly exothermic Ti– TiO_2 –Si–Al mixture for preheating each mixed SiB_x ($x = 3, 4, 5, 6$) compound; elemental Ti (purity 99.6%, grain size 325 mesh), Al (purity 99.9%, grain size 200–400 mesh), TiO_2 (purity 99.9%, grain size 60 nm), and Si (purity > 99.9%, grain size 200 mesh) were used for the chemical oven. The adiabatic temperature of the Ti– TiO_2 –Si–Al chemical oven could reach 3200 K, and the use of the chemical oven allowed the low adiabatic temperature of the Si–B compound reaction, which could not proceed otherwise. This chemical oven system for preheating is more effective than the pure Ti–Si system due to the thermite reaction in the system. The experimental process of the chemical oven supporting the Si–B compound reaction is described in Fig. 1. The Ti– TiO_2 –Si–Al mix-

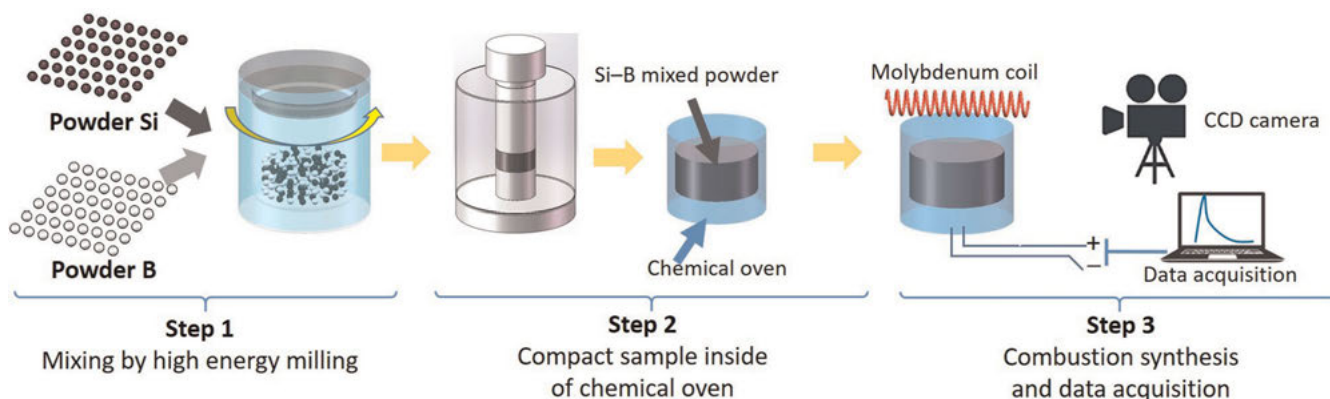


Fig. 1. Illustration of the experimental process of preparing SiB_x compounds.

ture powder was put into the bottom of the mold, and then the SiB_x sample, which was covered with graphite paper, was placed in the mold. After that, additional chemical oven powder was added, and the entire Si–B reaction sample was pressed into the cylindrical compact. The necessary quantity of the SiB_x was far less than that of the Ti– TiO_2 –Si–Al mixed powder to ensure that the SiB_x system would be able to obtain enough energy.

The compact was loaded in a graphite crucible and placed into a reaction chamber. A molybdenum coil was fixed above the top surface of the compact. The reaction chamber was first evacuated and then filled with Ar gas up to a pressure of 2 MPa. The reactant compact was ignited by passing an electric current of 10 A for 2 s through the coil and continued to self-sustain the burning until finally burning off after a few minutes. After the combustion reaction, the SiB_x was generated by the chemical oven.

2.2. Characterization technique

The entire combustion process was captured by a color CMOS video camera (HDR-CX900E, SONY) at a speed of 100

frames s^{-1} . A thermocouple (WRe3-WRe25) of 0.1 mm diameter was placed between the two samples to monitor their temperature. The sintered samples were ground into a fine powder, and the phase compositions were identified using X-ray diffraction (XRD) on a Bruker D8ADVANCE machine with a Cu target ($\lambda = 0.15406$ nm). A Quanta 250 scanning electron microscope (SEM) was used to characterize the microstructure, combined with energy dispersive X-ray spectrometry (EDS, Uantax 400) for elemental analysis.

3. Results and discussion

3.1. Combustion synthesis process and adiabatic combustion temperature analysis

According to the Si–B binary phase diagram, when the B molar ratio was greater than 60% in the original reactants to produce the B-rich solid phase after passing the 2100 K phase-transition temperature, SiB_x and residual Si could be acquired in the final product compositions.

Experimental observations in this study indicated that with the chemical oven, preheating affected the SiB_x ($x = 3, 4, 5, 6$) samples, and the Si–B compounds had carried

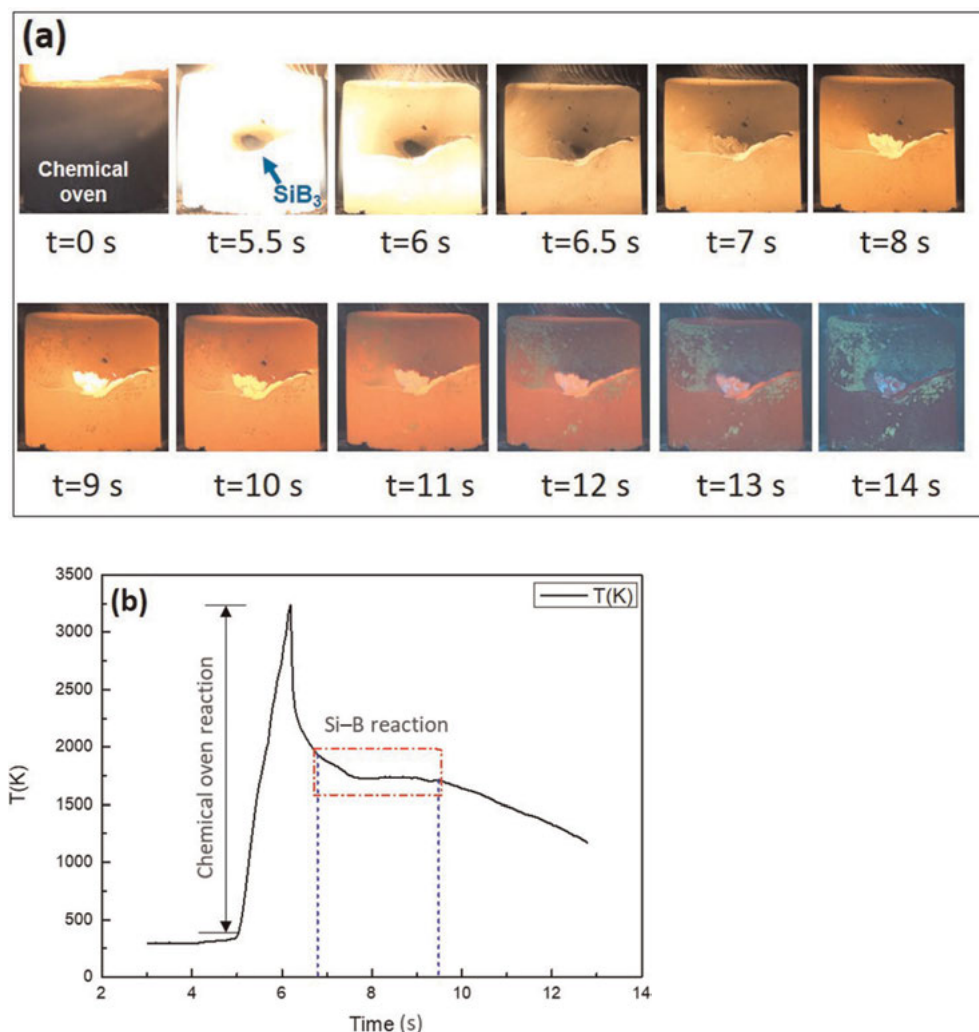


Fig. 2. (a) Typical SiB_3 synthesis process validation during chemical oven support. (b) Typical combustion temperature-time profile of SiB_3 reactant preheated by chemical oven.

out combustion synthesis. The entire combustion behavior of the chemical oven with the Si–B compounds was recorded by the CMOS camera. Figure 2a is representative of a typical phenomenon of the chemical oven combustion synthesis of SiB_3 . In the production of SiB_3 , the reactions were initiated with the preheating, the temperature rapidly increased with the electrical molybdenum wire igniting the surface of the chemical oven, and then the entire chemical oven reacted downward and rapidly reached the bottom of the sample at approximately 5.5 s. Figure 2a shows that chemical oven remained incandescent, but the released energy was used to preheat the Si–B binary system to support the completed combustion synthesis. With the support of the chemical oven, another exothermic reaction observably occurred from 7 to 10 s in the center. The recorded combustion images show that Si–B binary system began to react in the center and released a dazzling lux, while the chemical oven began to lose heat and darkened. The entire reaction of the Si–B binary system lasted 10 s. These observations indicate that the Si–B compound self-propagation high temperature synthesis (SHS) process proceeded after the chemical oven had completed its reaction, representing a prolonged combustion period.

In addition to the combustion process, the typical combustion temperature profiles were recorded from the chemical oven reactant compacts. The temperature–time profile of the SiB_3 reactant sample preheated by the chemical oven is presented in Fig. 2b. With the completion of the self-propagating reaction of the Ti–TiO₂–Si–Al chemical oven after 6 s, the combustion temperature

was 3 200 K at $T_0 = 293$ K, and the temperature profile contains several small inflection points from 6.5 s to 9.5 s. This phenomenon reflects that another exothermic reaction occurred during this period, with the additional reaction temperature of approximately 1 700 K. This combustion temperature profile observation is in agreement with the findings during the combustion behavior. During the combustion synthesis of SiB_3 , which releases energy to maintain the reaction, the temperature curve appears flat, and this phenomenon further validated the feasibility of the Si–B compound synthesis using chemical-oven-assisted self-propagation. The combustion process presented the same characteristics when using the same method to prepare other silicon boride compounds (Si:B = 1:4, 1:5, 1:6).

3.2. Composition analysis of initial reaction material and combustion products

Figure 3 shows the XRD patterns of SiB_x ($x = 3, 4, 5, 6$). According to the results of XRD analysis of the burned sample after being removed from the chemical oven, composite products consisting of SiB_x phase and a substantial amount of unreacted Si were identified in the products. After the chemical oven reaction, the combustion temperature was nearly 3 000 K. The SiB_x ($x = 3, 4, 5, 6$) had experienced the highest temperatures based on the Si–B binary phase diagram, and the component was formed by the reaction of the liquid Si+ β boron solid solution of SiB_x . The residual silicon existed due to inadequate heat provided by the chemical oven, it is difficult support the Si(B) solid solution fully reflected by heat treatment, this phenomenon also exists in the methods of arc-melting, spark plasma sintering, and solid-state reactions [4, 11]. Mararenko et al. [21] found that increasing the temperature to 1 300–1 350 °C again leads to free silicon as SiB_4 , peritectic decomposed into SiB_6 , and residual Si.

In this study, the Rietveld method was used for the quantitative phase analysis. The absolute error was less than 0.5 %, and the fitting convergence factors were less than 11 %, with the final results listed in Table 1. The results show that with the boron content increasing, the residual Si diffraction peak decreased, with relative mass contents ranging from 13.3 % to 5.0 %. This situation was caused by the incomplete reaction due to the chemical oven providing lower energy during the SHS process. When the Si–B ratio reached 1:6, the main diffraction peak in the final product was SiB_6 , with the relative mass content accounting for more than 70 %. Furthermore, the diffraction peak of SiB_4 and $\text{Si}_{11}\text{B}_{33}$ was also captured in the final product.

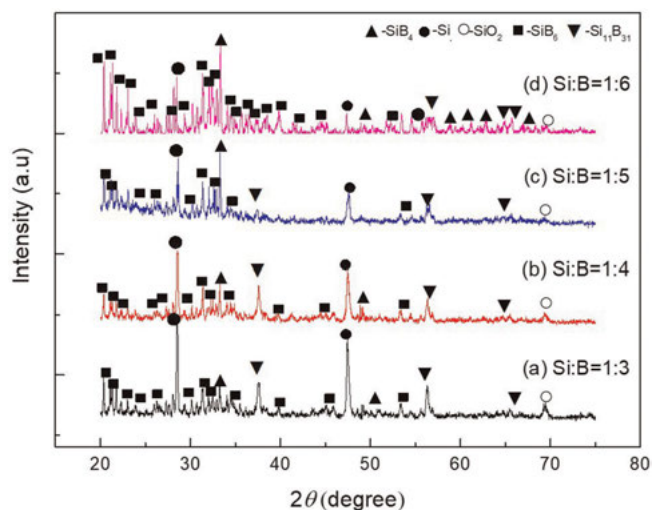


Fig. 3. XRD patterns of (a) SiB_3 , (b) SiB_4 , (c) SiB_5 , (d) SiB_6 .

Table 1. Rietveld quantitative phase analysis results of Si–B compounds in the final product.

Samples		Product phases	Relative content (wt.%)	Absolute error (wt.%)	Fitting convergence factor (R_{wp})
(a)	Si:B = 1:3	SiB_6 , SiB_4 , $\text{Si}_{11}\text{B}_{33}$, Si, SiO_2	23.5, 14.9, 42.1, 13.3, 6.1	0.15	9.06
(b)	Si:B = 1:4	SiB_6 , SiB_4 , $\text{Si}_{11}\text{B}_{33}$, Si, SiO_2	42.5, 11.8, 30.3, 10.8, 3.6	0.3	10.39
(c)	Si:B = 1:5	SiB_6 , SiB_4 , $\text{Si}_{11}\text{B}_{33}$, Si	63.1, 19.6, 6.9, 8.9	0.37	8.97
(d)	Si:B = 1:6	SiB_6 , SiB_4 , $\text{Si}_{11}\text{B}_{33}$, Si	70.1, 21.2, 3.3, 5.0	0.43	10.6

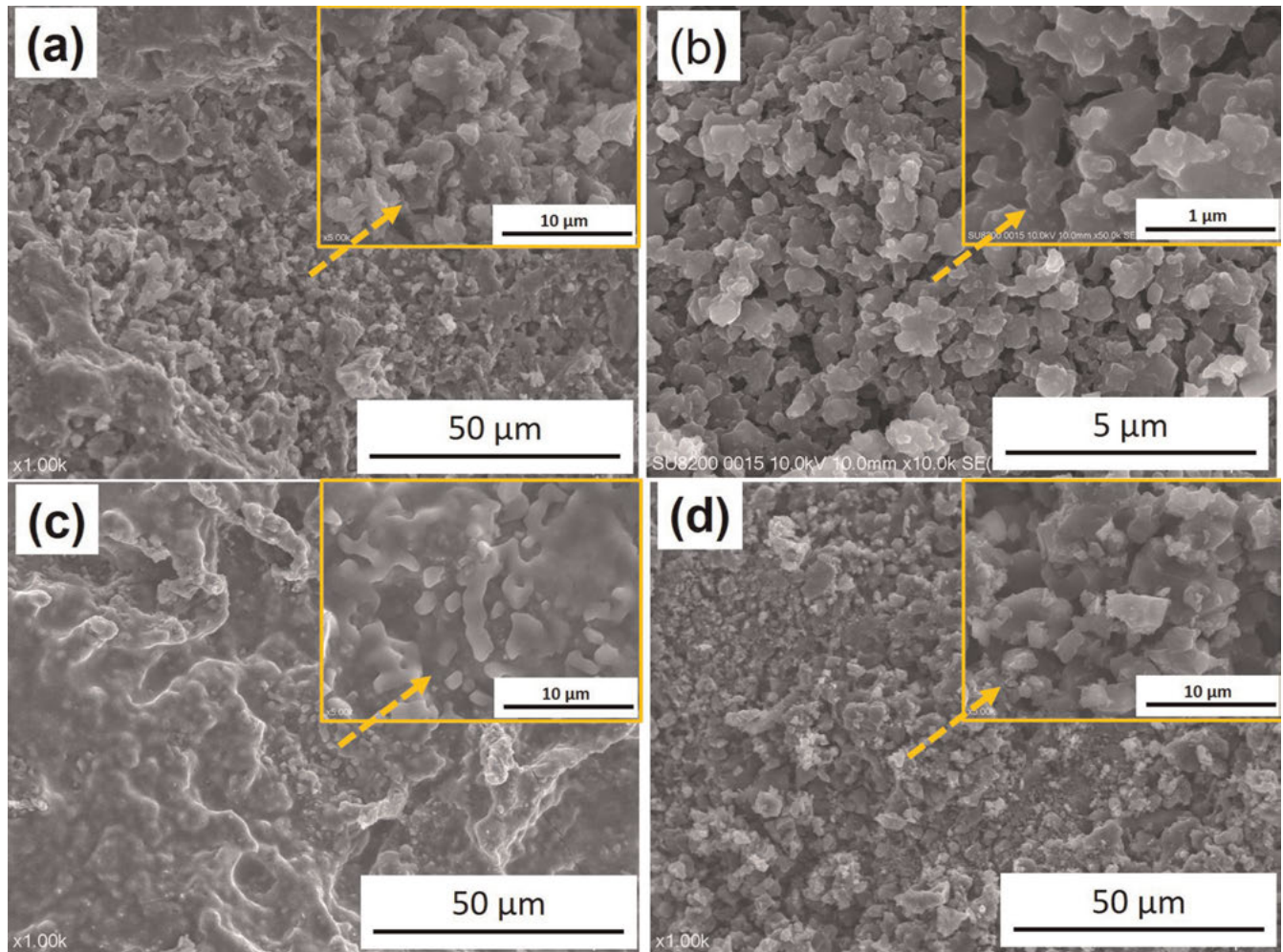


Fig. 4. SiB_3 , SiB_4 , SiB_5 , and SiB_6 SEM and local feature analysis.

3.3. SEM and EDS results of SiB_x compound

After removing the chemical oven powder from the surface of the SiB_x compounds, the SEM and EDS were used. The SEM images of Fig. 4a and b show that the samples of SiB_3 and SiB_4 have a heterogeneous microstructure composed of Si rich areas, especially for the SiB_4 SEM images, which present a special fluid shape throughout the structure. This illustrated that during the chemical oven pre-heating, the sample proceeded with the reaction of liquid Si+ β boron solid solution to form SiB_x compounds.

Figure 4b shows the micrograph of the sample SiB_4 . The sample consisted of a dark region corresponding to the pores, with dark gray and light gray phases dispersed around the bright core regions. EDS analysis shows that the composition of light gray is Si, which was identified as the Si(B) solid solution. Figure 5 shows the EDS analysis of the SiB_3 component prepared by the chemical oven self-propagating combustion synthesis. The EDS spectra and quantitative results of SiB_3 show an atomic chemical composition ratio of Si:B = 1:2.5, in which the average chemical composition of the overall sample is close to the nominal composition. Due to the disadvantageous effect of high-energy milling mechanical alloying (MA), the incorporation of a significant amount of impurities, especially oxygen, could not be prevented, even when milling

is performed under a protective atmosphere, causing the oxide found in the SiB_3 final production. Figure 6 shows the EDS analysis of the SiB_6 component prepared by chemical oven self-propagating combustion synthesis, with the chemical composition ratio of Si:B = 1:5.8, which was near the nominal composition of SiB_6 .

4. Conclusions

This paper reports a new method for the fast preparation of high-emissivity SiB_x compounds, supported by a highly exothermic Ti-TiO₂-Si-Al chemical oven.

1. The SiB_x combustion synthesis process and adiabatic combustion temperature analysis show that the Si-B compounds SHS process proceeded after the chemical oven had completed its reaction while during this period, the Si-B system released a dazzling lux. The combustion temperature of the chemical oven without significant plummeting reflected that the Si-B exothermic reaction occurred during this period, and the additional reaction temperature was approximately 1700 K.
2. The XRD results show that the SiB_x phase and a substantial amount of unreacted Si were identified in the products. With the boron percentage increasing, the residual Si diffraction peak decreased from 13.3% to 5%, until the Si-B ratio reach 1:6; the SiB_6 diffrac-

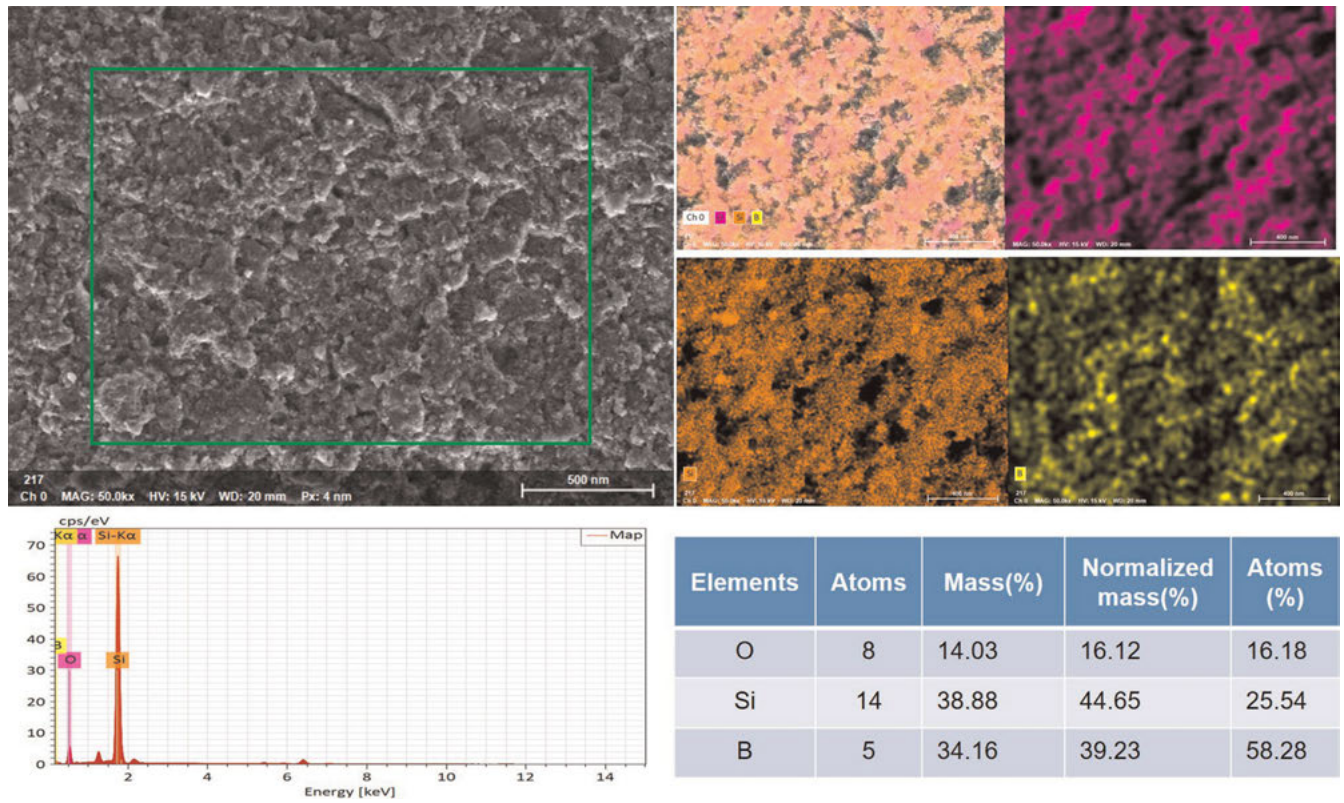


Fig. 5. EDS analysis of SiB_3 component prepared by chemical oven self-propagating combustion synthesis.

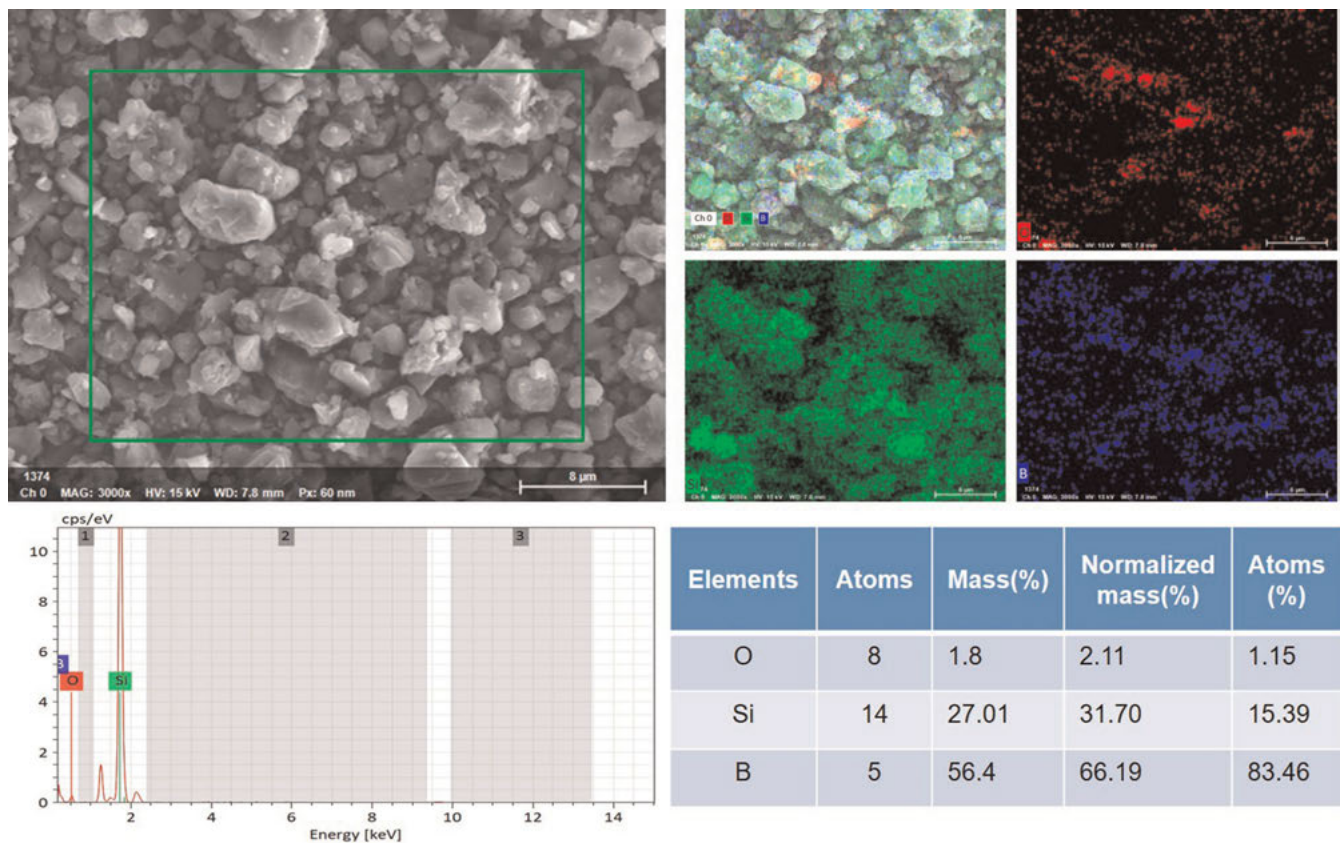


Fig. 6. EDS analysis of SiB_6 component prepared by chemical oven self-propagating combustion synthesis.

tion peak was the most substantial, and a small amount of SiB_4 and $\text{Si}_{11}\text{B}_{33}$ was observed in the final product.

3. The EDS spectra and quantitative results of SiB_3 and SiB_6 show the chemical composition ratios of Si:B = 1 : 2.5, and Si:B = 1 : 5.8 separately, which are close to the nominal compositions. Similar results were obtained in the other samples.

References

- [1] Y.D. Ye: *Adv. Mech.* 39 (2009) 387–397. DOI:10.6052/1000-0992-2009-4-J2009-040
- [2] L. Xian, X. Tao, W. Dong, X.J. Xu: *Ceram. Int.* 44 (2018) 16333–16341. DOI:10.1016/j.ceramint.2018.06.037
- [3] G.F. Shao, X.D. Wu, S. Cui: *Ceram. Int.* 42 (2016) 8140–8150. DOI:10.1016/j.ceramint.2016.02.020
- [4] J. Matsushita, S. Komarneni: *Mater. Res. Bull.* 36 (2001) 1083–1089. DOI:10.1016/S0025-5408(01)00560-8
- [5] G.F. Shao, X.D. Shen, S. Cui: *Mater. Rep.* 28 (2014) 136–142. DOI:10.11896/j.issn.1005-023X.2014.21.026
- [6] A.I. Zaitsev, A.A. Kodentsov: *J. Phase Equilib.* 22 (2001) 126–135. DOI:10.1361/105497101770338987
- [7] S. Katrych, A. Grytsiv, A. Bondar, P. Rpgl: *J. Alloy Compd.* 347 (2002) 94–100. DOI:10.1016/S0925-8388(02)00676-X
- [8] J.J. Wu, W.H. Ma, D.Z. Tang: *Procedia Eng.* 31 (2012) 297–301. DOI:10.1016/j.proeng.2012.01.1027
- [9] J.C. Viala, J. Bouix: *J. LessCommon Met.* 71 (1980) 195–206. DOI:10.1016/0022-5088(80)90204-0
- [10] L.D. Chen, T. Goto, J.H. Li: *Transactions on Fundamentals and Materials.* 116 (1996) 248–252. DOI:10.1541/ieejfms1990.116.3_248
- [11] J. Roger, V. Babizhetskyy, J.F. Halet, R. Guérina: *J. Solid State Chem.* 177 (2004) 4167–4174. DOI:10.1016/j.jssc.2004.07.004
- [12] J. Wu, W. Ma, B. Yang: *Silicon.* 4 (2012) 289–295. DOI:10.1007/s12633-012-9134-y
- [13] T. Murakami, H. Inui: *TRIBOL. INT.* 92 (2015) 446–453. DOI:10.1016/j.triboint.2015.07.029
- [14] A. Varma, A.S. Mukasyan: *J. Chem. Eng.* 21 (2004) 527–536. DOI:10.1007/BF02705444
- [15] X. Li, B.Y. Liang, Z.X. Li: *Int. J. Mater. Res.* 104 (2013) 1038–1040. DOI:10.3139/146.110972
- [16] B. Akgün, N. Sevinç, H.E. Çamurlu, Y. Topkaya: *Int. J. Mater. Res.* 104 (2013) 403–407. DOI:10.3139/146.110868
- [17] I.V. Iatsyuka, Y.S. Pogozeva, E.A. Levashova: *J. Eur. Ceram. Soc.* 38 (2018) 2792–2801. DOI:10.1016/j.jeurceramsoc.2018.02.016

- [18] J.G. Xu, B.L. Zhang, G.J. Jiang, W.L. Li: *Ceram. Int.* 32 (2006) 633–636. DOI:10.1016/j.ceramint.2005.04.022
- [19] V.V. Kurbatkina, E.I. Patsera, E.A. Levashov, A.N. Timofeev: *J. Eur. Ceram. Soc.* 38 (2018) 1118–1127. DOI:10.1016/j.jeurceramsoc.2017.12.031
- [20] E.A. Levashov, Y.S. Pogozev: *Ceram. Int.* 40 (2014) 6541–6552. DOI:10.1016/j.ceramint.2013.11.107
- [21] G.N. Mararenko, V.B. Fedorus, I.A. Shaikevich: *Synthesis: Powder Metall. Met. C+.* 46 (2007) 3–4. DOI:10.1007/s11106-007-0023-7

(Received January 5, 2020; accepted June 24, 2020)

Correspondence address

Professor Peizhong Feng
School of Materials Science and Physics
China University of Mining and Technology
No. 1 Daxue Road
Xuzhou 221116
P. R. China
Tel.: +86-516-83592928
E-mail: fengroad@163.com

Weisheng Liu
School of Chemical Engineering and Technology
China University of Mining and Technology
No. 1 Daxue Road
Xuzhou 221116
P. R. China
Tel.: +86 18952209058
E-mail: 413643738@qq.com

Bibliography

DOI 10.3139/146.111949
Int. J. Mater. Res. (formerly Z. Metallkd.)
111 (2020) 10; page 792–798
© Carl Hanser Verlag GmbH & Co. KG
ISSN 1862-5282