Synthesis and Infrared Performance of SiB₆ Powder through “Chemical Oven” Self-Propagating Combustion

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SiB₆ powders were prepared by the “chemical oven” method from Si and B powders. Here combustion with acid pickling “two-step” mode replaces the traditional synthesis method which helps to avoid severe condition of high temperature and high pressure. It could realize maximum reaction temperature to about 2000°C, and the whole process just needs ∼30 s. The averaged diameter of products is ∼10 μm. And the raw material Si and B are ∼3 μm and ∼20 μm, respectively. The infrared emissivity of products was evaluated by UV-vis spectrum with absorption band around 250 ∼2500 nm. All five samples show higher emissivity over UV-visible light range with lower emissivity over near-infrared range. Typically, the sample’s Si/B ratio of 1:1 shows highest integral intensity for about 0.85 compared with other molar ratios. It can be used as a more simple and effective method to obtain infrared ceramic SiB₆ with high emissivity.

1. Introduction

Infrared radiation coating could improve the emissivity of coating surface effectively [1, 2], enhancing the radiation heat transfer and achieving the purpose of energy saving. Thus, it shows a broad application prospect on the energy conservation of industrial kiln. High-emissivity infrared ceramic powders are the key to determine the properties of infrared radiation coatings. Nowadays, high-emissivity infrared ceramic powder under O₂ atmosphere is mainly the spinel oxide system. However, its service temperature is lower than 1300°C which is difficult to be used in high-temperature kiln. Also, SiB₆ is a good candidate as radiation substrate, which can be applied to infrared radiation coatings above 1300°C [3].

SiB₆ was first discovered in 1900 [4], when a mixture of silicon and boron was melted. The crystal structure of SiB₆ was initially reported to be cubic; however, it was later confirmed to be orthorhombic Pmm [5]. Until now, there is no efficient method for synthesis of bulk SiB₆ samples. Generally, the polycrystalline samples of SiB₆ should be prepared under high temperature and hot pressing. Si and B powders are usually weighed and mixed according to the measurement ratio and loaded into graphite mold lined with boron nitride (BN) to be hot-pressed into crystalline state at ∼1600°C and ∼4.0 × 10⁶ Pa. According to complex Si-B phase diagram, we know that the product is not always a single SiB₆ phase, and when hot-pressing was chosen, the elemental carbon solubility in SiB₆ could reach to about 2% (carbon in graphite mode will contaminate the sample). Thus, polycrystalline block composition and purity often do not meet the requirements.

Here the “chemical oven” method has attracted great attention due to its simple process, convenient operation, high yield, and easy industrialization, which has become a hot research topic for powder materials [6]. One recent work reported that Wang et al. have developed an ultrafast high-temperature sintering process for the fabrication of ceramic materials by radiative heating under an inert atmosphere. This kind of synthesis also belongs to a kind of “chemical
oven” [7]. Thus, inspired by this work, we propose to use a similar method for SiB₆ synthesis. The external reactant on the surface is ignited by high-energy heat input, and combustion occurs in a certain internal wave propagation rate of reactant particles. Then the inner reactant was also lit by external reaction heat. Transient superhigh temperature reduces reaction synthesis time. Jianguang Xu et al. have prepared a high pure molybdenum disilicide. And the product by “chemical oven” self-propagating high-temperature synthesis (SHS) method is more homogeneous than the normal SHS method. The whole process can be reacted in just a few seconds by the application of an electric field [6].

This method has been widely used to prepare high-temperature materials such as ceramics and intermetallic compounds [8–10]. Here we propose to use the high exothermic effect of reaction between reactants (Si and B powders) to make the chemical reaction maintain itself, so as to synthesize new materials.

2. Materials and Methods

The raw powders were mixed according to different stoichiometric ratios of Si/B. Here silicon’s particle size is ~3 microns whose purity is 99.99% (Shanghai Aladdin Biochemical Technology Co. Ltd.). Also, boron’s particle size is ≤20 microns with the purity of 99% (Shanghai Aladdin Biochemical Technology Co. Ltd.). Ball milling was adopted to mix the materials to ensure a homogeneous mixture, and ethanol was also added to wet grinding for 1 hour. The sample was dried in an oven over 110°C after taking out. Then were then pressed into (10 MPa, maintaining 3 min) cylindrical pellets with a diameter of 15 mm.

Figure 1 shows inner structure of reaction oven. Here Ti, C, Al, and Fe₂O₃ were used as the thermite agents. The reaction was ignited in air through W coil in spiral shapes. Furthermore, we used tungsten-rhenium thermocouple to test inner reaction temperature curve, and here the sample was taken in a chemical oven with 65% test inner reaction temperature curve, and here the sample was 103.6 eV, 102.8 eV, and 102.0 eV that can be referred to Si 1s fine scan spectrum of Si/B=1:1 sample. The deconvolution peaks are displayed in Figure 3(b); O 1s spectrum was observed from 526.6 eV to 537.2 eV. The low binding energy (BE) component observed at ~531 eV corresponds to the main lattice oxygen (O lattice). The bands around ~533 eV can be assigned to adsorbed oxygen (O ads) while the peak between them (~532 eV) indicates the ionization of oxygen species that could allow compensation for some deficiencies (O def) connected in part to the variations in the concentration of oxygen vacancies in products [16]. The peak of Si at 99.1 eV is due to metallic Si⁹. The left peak can be divided into three peaks which are 103.6 eV, 102.8 eV, and 102.0 eV that can be referred to Si in (SiB₄), Si in (SiB₆), and SiOₓ [17]. The area ratio is 1:1:1.06:1.37. The B 1s spectrum indicates that there are B atoms at the surface or subsurface of SiB₆. In the B 1s spectrum, the peak at 187.5 eV is related to SiB₆, while the peak at 186.8 eV attributes to SiB₄ [18]. And the area ratio is 1.03:1.1:1.10:1.

Figures 4(a)–4(d) show different magnification time pictures of typical top-view SEM images for Si/B=1:1 sample’s cross section. The cylindrical sample was scraped for fresh cross profile. Here Figures 4(c) and 4(d) are enlarged views of white box in Figures 4(a) and 4(b). SiB₆ sintering piece shows brittle rupture from SEM. According to Figure 4(d), the average diameter of products is ~10 µm which is the between two raw materials’ diameter (Si (~3 µm) and B (~20 µm) powder). These might be due to ball milling before sintering. EDS results focusing on Si, B, and O elements are also characterized which are shown in Supplementary Information Figure 2.

The diffuse reflectance UV-vis spectra of products are shown in Figure 5. Five samples exhibit absorbance over 250–2500 nm. Also, they show higher absorption over UV-visible light range with lower absorption over near-infrared range. When Si/B ratio decreases, the emissivity...
Figure 1: (a) Inner structure of chemical oven and its (b) temperature combustion curve with time.

Table 1: Molar ratio of Si:B for different samples.

| Sample no. | Si (3 μm) | Reaction ratio | B (≤20 μm) |
|------------|-----------|----------------|------------|
| 1          | 2         | 1              | 1          |
| 2          | 1         | 1              | 1.5        |
| 3          | 1         | 2              | 2          |
| 4          | 1         | 3              | 3          |

Figure 2: XRD spectrum of all samples (a) with different thermite ratios and (b) different molar ratios of Si:B.

Figure 3: Continued.
over UV-visible part increases and over NIR part decreases. Herein, Si/B ratio 1:1 shows highest integral intensity for about 0.85.

The band gap energy ($E_g$) of semiconductor, following the equation: $\alpha E_{\text{photon}} = K (E_{\text{photon}} - E_g)^{1/2}$, where $K$, $\alpha$, $E_{\text{photon}}$ and $E_g$ are a constant; the absorption coefficient, the discrete photon energy, and the band gap energy are estimated by calculating the intercept of an extrapolated linear fit to the experimental date of a plot of $(\alpha E_{\text{photon}})^2$ versus $E_{\text{photon}}$ yielded $E_g$ for a direct transition. As shown in Figure 6, the band gaps of samples molar ratio from 2 to 1/3 are figured out to be 1.73, 1.62, 1.75, 1.91, and 1.84 eV, respectively.

**Figure 3:** X-ray photoelectron spectroscopy (XPS) spectra of all samples: (a) survey of products; (b) O 1s; (c) Si 2p; (d) B 1s.
4. Conclusions

SiB$_6$ powders were prepared by the “chemical oven” method from Si and B powders. The external reactant on the surface is ignited by high-energy heat input, and combustion occurs in a certain internal wave propagation rate of reactant particles. After acid pickling, the products are obtained. Here SiB$_6$ is a dominant phase. The UV-vis diffuse reflectance obtained at different B/Si molar ratios from 0.5 to 1.5 are investigated. All five samples show higher absorption on UV-visible light range with lower absorption on near-infrared range. What is more, when the ratio of Si/B decreases, the emissivity intense over UV-visible part increases and intense over NIR part decreases. Herein, Si/B ratio 1:1 shows highest integral intensity for about 0.85. So, this product is expected to be used in high-temperature infrared radiation, and this method can be used as a more simple and effective method to obtain infrared ceramic SiB$_6$.

Data Availability

The data used to support the findings of this study are included within the article and supplementary information file.
Conflicts of Interest
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials
Supplement Figure 1: XRD spectrum of products before acid pickling. Supplement Figure 2: EDS results of 1:1 molar ratio sample. (Supplementary Materials)

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