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Preparation and microwave absorption properties of Fe-doped SiC powder obtained by combustion synthesis

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Abstract

Fe-doped SiC powders were synthesized via combustion reaction of the Si and C system in a 0.1 MPa nitrogen atmosphere using iron as the dopant. The prepared powders have fine spherical particles and narrow particle size distribution. The electric permittivities of SiC samples were determined in the frequency range of 8.2–12.4 GHz. Results show that the permittivity of SiC increases with the increasing iron contents. The 5% Fe-doped SiC powder with 2 mm or 2.5 mm thickness exhibits the best microwave absorption over the frequencies ranging from 8.2 to 12.4 GHz.

Keywords: Silicon carbide; Combustion synthesis; Microwave absorption property

1. Introduction

Microwave absorbing materials are the materials to dissipate the electromagnetic energy of incident microwave into heat by magnetic or dielectric loss [1,2]. In recent years, they have been increasingly investigated due to their applications in civil and military fields [3,4]. But a large amount of microwave absorbing materials is not used at the higher temperature because of the low Curie temperature [5]. So the microwave absorbing absorbers with high structure strength, and chemical and temperature resistances in the high temperature environments have been focused in recent years.

Silicon carbide has many excellent properties, for example, high strength and hardness, good corrosion resistance, high thermal stability and high thermal conductivity, which has been considered to be one of the important microwave absorbing materials used in the higher temperature environments. However, the pure SiC material presents the poor absorbing ability in the gigahertz (GHz) band range. According to related studies, the dielectric property or microwave absorption property has been improved by the pure *n*-type or *p*-type doping. For example, Zhao et al. and Huan et al. have prepared the N-doped (*n*-type doping) SiC powder by laser synthesis and chemical vapor deposition, respectively, which presents a better dielectric property in the frequency range of 8.2–12.4 GHz [6,7]. Li et al., Luo et al. and Jin et al. have obtained the Al-doped (*p*-type doping) SiC powders using the combustion synthesis method, thermal diffusion and microwave method, respectively, which also showed a better dielectric property than the undoped SiC powder in the X-band range (8.2–12.4 GHz) [8–10]. Li et al. synthesized the B-doped SiC (*p*-type doping) nanopowder by the *sol–gel* and carbothermal reduction method and also gave the better dielectric property in the frequency range of 8.2–12.4 GHz [11]. Li et al. have prepared Ni-doped SiC powder by the mechanically activated self propagating high-temperature synthesis method and also presents the better dielectric property in the same frequency range [12]. Therefore, because the Fe element belongs to the VIII group, it presents the same effect on SiC powder as the Ni element possibly. However, little research has been focused on the effect of Fe-doping on the microstructure, dielectric property and microwave absorption property of SiC powder.

So in the paper, the Fe-doped SiC powders have been prepared by the CS method using silicon and carbon as raw materials, Fe as the dopant and PTFE as the chemical

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activator. The effects of Fe-doping on microstructure, dielectric property and microwave absorption property of SiC powder have been studied systematically. The sample with the best microwave absorption property has been presented.

2. Experimental procedure

Silicon powder (99% pure, mean particle size of 20 μm; Tianjin Kermel Chemical Reagents Development Centre, China) and carbon black (99% pure, particle size of 20–40 nm; Jiaozuo Chemical Co. Ltd., China) were used as reactant materials. Iron powder (Fe, 99% pure, mean particle size of 30μm; Shanpu Chemical Co. Ltd., Shanghai, China) and the PTFE powder (99% pure, mean particle size of 75μm; Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as doping source and chemical activator, respectively. The molar ratios of Fe, Si and C (n_{Fe}:n_{Si}:n_C) are 0:1:1, 0.05:0.95:1 and 0.1:0.9:1, respectively. Synchronously, the 15 wt% PTFE has been added to the powder. The powder batches were dry-mixed for 20 h using planetary milling with agate ball media, and then poured into a graphite crucible; the graphite crucibles were transferred into the cold chamber of CS reactor, which is shown in Fig. 1. When the temperature of the hot chamber of CS reactor reached the 1200 °C, the graphite crucibles were transferred into the hot chamber from the cold chamber quickly and kept for 15 min in 0.1 MPa N_2 atmosphere. Additionally, because the excess carbon and unreacted silicon in CS products will affect the accuracy of dielectric property, the products were calcined in air at 650 °C for 0.5 h to remove excess carbon, and then dipped into the hydrofluoric acid (HF) for 24 h to remove the unreacted silicon and then dried at 120 °C.

The products were identified by X-ray diffraction (XRD, X'Pert PRO MPD, Cu Kα) to detect the generated phases before the calcination, washing and drying of products. The 99.99% Si (a=5.43088 Å) was used as inner standard. The morphology of the CS powders was investigated by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Tokyo, Japan), and the compositions were analyzed by energy-dispersive spectroscopy (EDS, NORAN System SIX Model 300, Thermo Electron Corporation) after the calcination, washing and drying of products. The dielectric property of prepared powders has been determined in the frequency range of 8.2–12.4 GHz by the waveguide technique [8].

According to the transmission line theory, the reflection loss curves (RL) can be calculated from the complex permittivity and permeability at a given frequency as well as the thickness of microwave absorbing materials by the method, which is shown in reference [5]. In this study, because silicon carbide is the dielectric loss material, the real part μ' and imaginary part μ'' of permeability are 1 and 0, respectively.

3. Results and discussion

Fig. 2 shows XRD patterns of the CS powders synthesized with different Fe contents. It can be seen that the β-SiC is generated in all products. The reason is that when the graphite crucibles were transferred into the hot chamber from the cold chamber quickly the reaction (1) of PTFE and Si powder, which released high heat and promoted combustion synthesis reaction (2) between Si and C, took place due to the preheating (the temperature of the hot chamber is 1200 °C) [13].

$$Si(s)+2(-CF_2-)(s)\rightarrow SiF_4(g)+2C(s)+Q \quad (1)$$

$$Si(s)+C(s)\rightarrow SiC(s) \quad (2)$$

In addition, the unreacted Si phase was also observed, the peak intensity of Si phase decreases and the peak intensity of β-SiC phase increases with increasing Fe content. It is possible that the Fe-doping improves the reaction of Si and carbon black and leads to the formation of SiC easily [14]. Additionally, the Fe–Si compound phase was also detected in samples (b) and (c). The Fe–Si

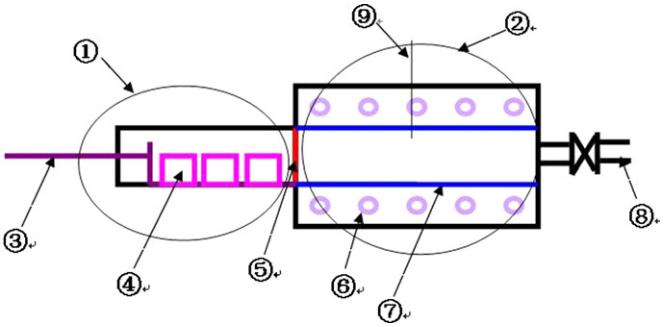

Fig. 1. Schematic diagram of CS reactor: 1—cold chamber; 2—hot chamber; 3—pushing rod; 4—graphite crucibles; 5—insulating plate; 6—heating resistance wire; 7—alumina tube; 8—pump; 9—thermocouple.

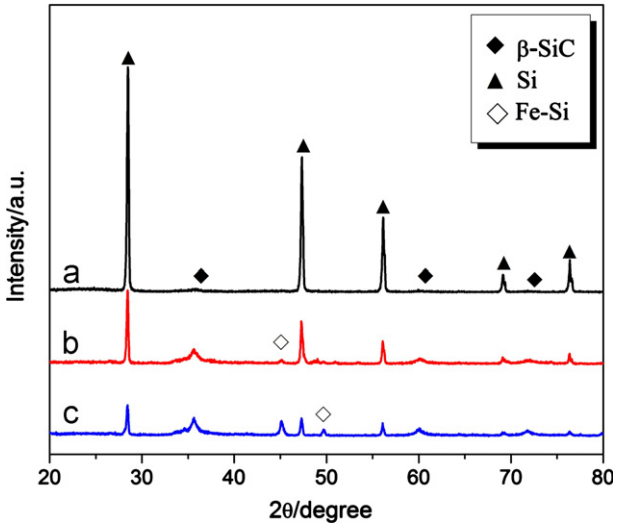

Fig. 2. XRD patterns of the CS powders synthesized with different Fe content: (a) n_{Fe}:n_{Si}:n_C=0:1:1; (b) n_{Fe}:n_{Si}:n_C=0.05:0.95:1 and (c) n_{Fe}:n_{Si}:n_C=0.1:0.9:1.

compound probably was formed through the reaction between Si and Fe at the initial stage of reaction. Since the compounds in the Fe–Si system have melting points ranging from 1207 °C to 1410 °C and temperature of CS reaction is above 1200 °C, they solidified to form Fe–Si compounds during cooling [14].

In addition, compared with the undoped β-SiC the peak (111) of doped SiC shifts in the direction of the lower 2θ, suggesting the increase of lattice constant a of β-SiC due to the increase of interplanar distance d according to the Bragg formula. The lattice constants corresponding to β-SiC doped with 0%, 5% and 10% Fe are a=4.352 Å, 4.362 Å, and 4.368 Å, respectively. It can be seen that the lattice constant of undoped SiC powder is less than the standard value (4.358 Å) of β-SiC, which results from the generation of C antisites (C_{Si}). So the undoped SiC powder is the C enriched SiC powder, which is suitable for the p-type doping [8]. In addition, for the doped SiC, because the covalent radius of Fe (1.17 Å) is larger than that of Si (1.46 Å), the increase of lattice constant is caused by the Fe substitution on Si of SiC lattice in CS products.

Fig. 3 shows the SEM photographs of the prepared SiC powders synthesized with different Fe contents. It can be seen that the powder size of undoped sample is about 20 nm and presents the narrow size distribution. The SiC whisker has been observed in the SEM photographs of samples (b) and (c) and the amounts of SiC whisker increases with increasing Fe content. The reason is that owing to the existence of the Fe–Si liquid phase in the processing of Si and C at the reaction temperature, SiC seems to be formed easily by the dissolution–precipitation. Especially, the Fe is a catalytic additive to improve the generation of SiC whisker [14]. So when the Fe content is 10%, a large amount of SiC whisker was observed.

In addition, to examine in more detail the chemical composition of prepared powders with different Fe contents, the EDS analysis was performed, as shown in Fig. 4. For undoped product only C, Si and O are observed. However, for the doped products the Fe element has been also observed besides C, Si, and O. In addition, the Fe content increases and Si content decreases with increasing Fe-doped content, as shown in Table 1. It indicates that more Si atoms are substituted by more Fe atoms, thus resulting in the increase of lattice constant of SiC, which is in agreement with results in Fig. 2. Additionally, the O element may be then adsorbed on the surface of prepared powder.

Fig. 5 shows the real part ε' and imaginary part ε'' of complex permittivity as a function of frequency in the frequency range of 8.2–12.4 GHz for the CS powders. It can be seen that the ε' and ε'' of samples (a), (b) and (c) are 7.7–7.4 and 2.2–0.8, 12.5–10.5 and 5.0–3.0, and 19.5–18.6 and 8.9–8.0, respectively, which shows that the dielectric properties increased with increasing Fe-doped contents. The higher ε'' suggests a better capacity of dielectric loss in the microwave range. Because the Fe atoms present trivalent state usually have three electrons bonded with the other element. So when the Fe atoms enter the SiC lattice and substitute the Si atoms, the p-type material, Fe-doped SiC, is synthesized and there exists bound holes around Fe_{Si} defects in the SiC crystal. Under the alternating electromagnetic field, these bound holes will migrate to and fro to form relaxation polarization and loss, thus leading to the higher ε', ε'' and tan δ, respectively.

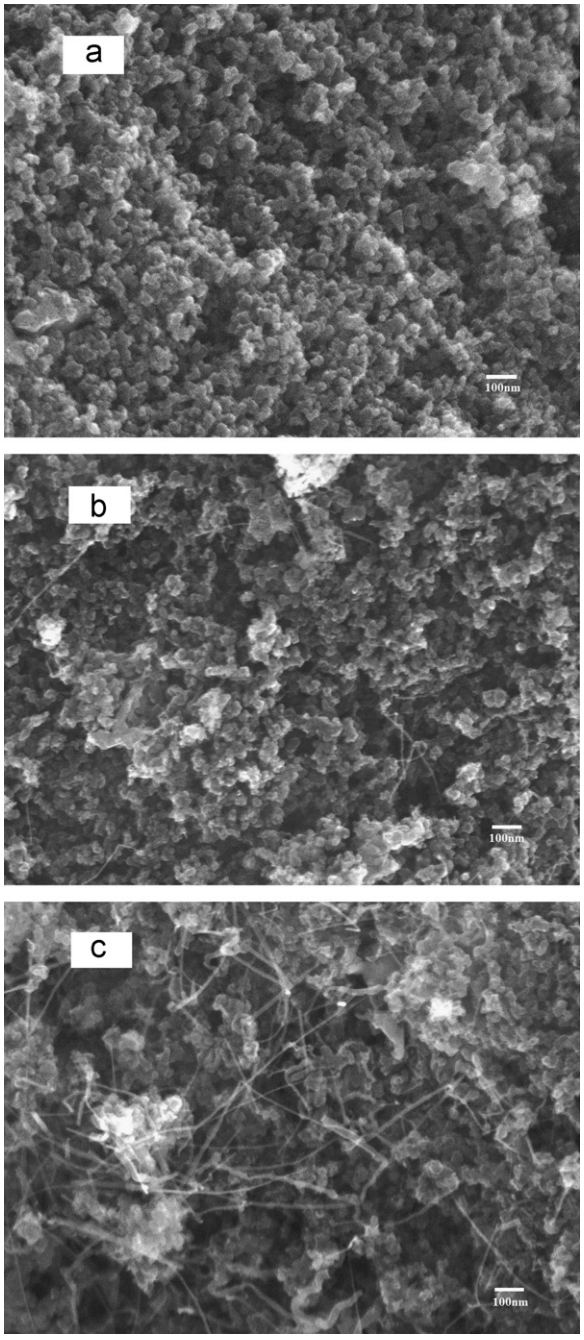

Fig. 3. SEM photographs of the prepared SiC powders synthesized with different Fe content: (a) n_{Fe}:n_{Si}:n_C=0:1:1; (b) n_{Fe}:n_{Si}:n_C=0.05:0.95:1 and (c) n_{Fe}:n_{Si}:n_C=0.1:0.9:1.

Fig. 6 presents frequency dependence of RL of CS powders with thickness from 1 mm to 4 mm in X-band. Because when the reflection coefficient is smaller than

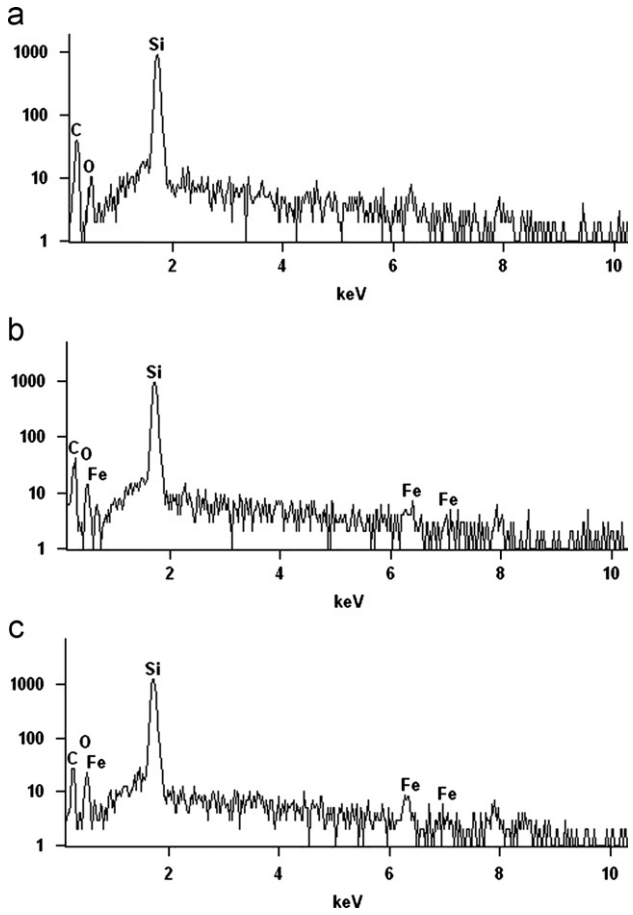

Fig. 4. EDS spectra of prepared powders with different Fe contents: (a) n_{Fe}:n_{Si}:n_C=0:1:1; (b) n_{Fe}:n_{Si}:n_C=0.05:0.95:1 and (c) n_{Fe}:n_{Si}:n_C=0.1:0.9:1.

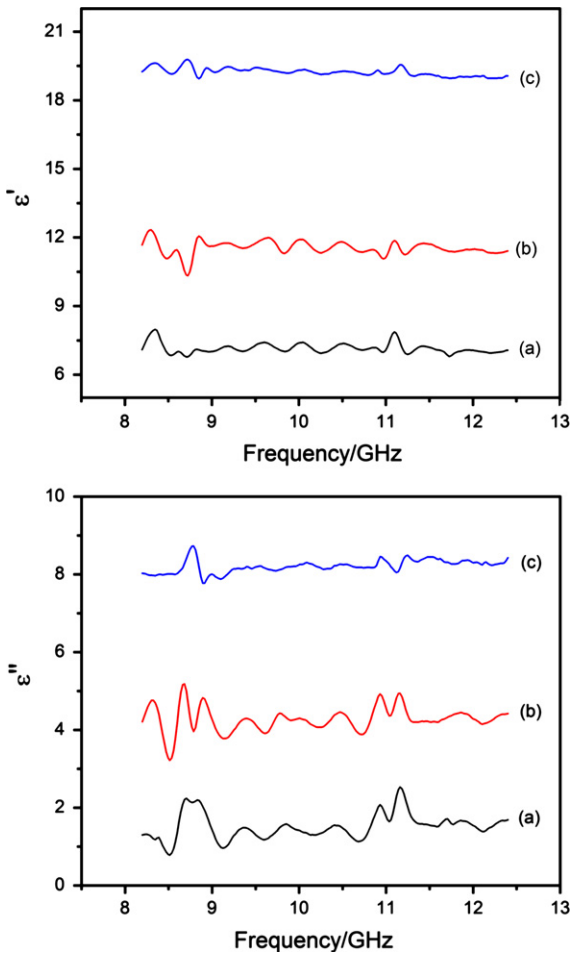

Fig. 5. Real part ε' and Imaginary part ε'' of complex permittivity as a function of frequency in the frequency range of 8.2–12.4 GHz for the CS powders with different Fe content: (a) n_{Fe}:n_{Si}:n_C=0:1:1; (b) n_{Fe}:n_{Si}:n_C=0.05:0.95:1 and (c) n_{Fe}:n_{Si}:n_C=0.1:0.9:1.

Table 1
Elements content of prepared powders: (a) n_{Fe}:n_{Si}:n_C=0:1:1; (b) n_{Fe}:n_{Si}:n_C=0.05:0.95:1 and (c) n_{Fe}:n_{Si}:n_C=0.1:0.9:1.

Samples	Elements content (at%)			
	C	Si	Fe	O
(a)	49.81	40.50	–	9.69
(b)	56.45	36.65	0.17	6.73
(c)	59.99	33.35	0.25	6.41

−10 dB, only 10% of the microwave energy is reflected and 90% of the microwave energy is absorbed. The corresponding frequency range over which reflection coefficient is smaller than −10 dB, is defined as the effective absorption bandwidth. It can be seen that for sample (a) the RL is below −10 dB with a thickness of 2.5 mm from 11.07 GHz to 11.29 GHz and with a thickness of 3.5 mm from 8.62 GHz to 8.96 GHz, which have the effective absorption bandwidths of 0.22 GHz and 0.34 GHz, respectively. It shows the narrow effective absorption bandwidth in X-band for the undoped SiC powder.

However, for sample (b) when the RL value is less than −10 dB, the effective absorption bandwidths are 2.48 GHz (from 9.92 GHz to 12.40 GHz) with a thickness of 2 mm and 2.14 GHz (from 8.20 GHz to 10.34 GHz) with a thickness of 2.5 mm. Compared with sample (a) the effective absorption bandwidth becomes broader and the thickness is lower. Especially, when the frequency is 11.08 GHz and from 11.25 GHz to 11.35 GHz with a thickness of 2 mm and 8.83 GHz and from 8.96 GHz to 9.04 GHz with a thickness of 2.5 mm, respectively, the RL values are less than −30 dB. Because the RL is smaller than −30 dB, only 0.1% of the microwave energy is reflected and 99.9% is absorbed [15], the 5% Fe-doped SiC powder shows better absorption ability. However, for the 10% Fe-doped SiC powder, sample (c), when the RL is smaller than −10 dB the effective absorption bandwidths are only 1.99 GHz (from 10.41 GHz to 12.40 GHz) with a thickness of 1.5 mm and 1.2 GHz (from 8.20 GHz to 9.40 GHz) with a thickness of 2 mm. It can be seen that although the thickness becomes thinner the absorption ability is a little worse than that of sample (b).

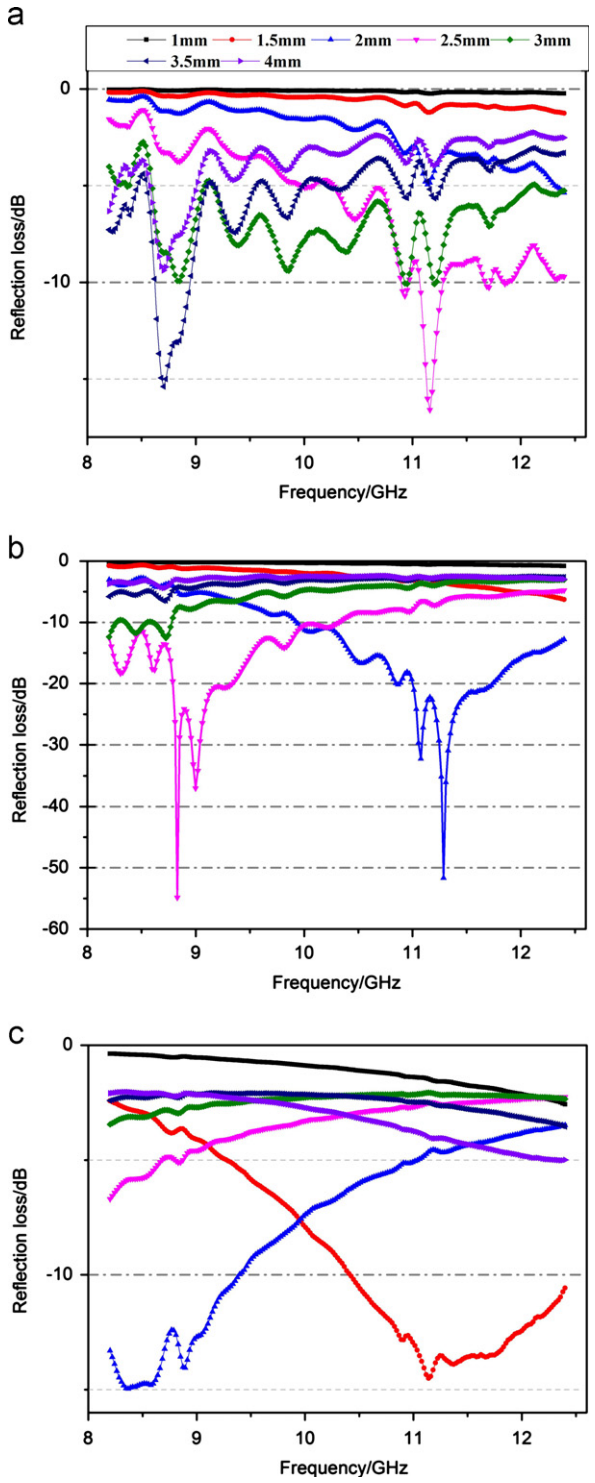

Fig. 6. Frequency dependence of RL of CS powders with thickness from 1 mm to 4 mm in X-band: (a) n_{Fe}:n_{Si}:n_C=0:1:1; (b) n_{Fe}:n_{Si}:n_C=0.05:0.95:1 and (c) n_{Fe}:n_{Si}:n_C=0.1:0.9:1.

4. Conclusions

Fe-doped SiC powders were synthesized successfully via combustion reaction of the Si and C system in a 0.1 MPa nitrogen atmosphere using iron as the dopant. XRD results show the formation of Fe–Si compound during CS processing. The prepared powders have fine spherical particles and narrow particle size distribution. When Fe content is 10% there is a little amount of SiC whiskers due to the generation of Fe–Si compound. Results show that the electric permittivity of SiC in the frequency range of 8.2–12.4 GHz increases with the increasing iron content due to the generation of the more Fe_{Si} defects. The 5% Fe-doped SiC powder with 2 mm or 2.5 mm thickness exhibit the best microwave absorption properties over the frequencies ranging from 8.2 to 12.4 GHz.

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