Effect of boron doping on microwave dielectric properties of SiC powder synthesized by combustion synthesis

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ABSTRACT

Boron-doped SiC powders were synthesized from the Si/C/B system in a nitrogen atmosphere by combustion synthesis. Results showed that boron benefited the crystallization of β-SiC, and that SiC solid solution with B acceptor doping was generated in combustion process. In the frequency range of 8.2–12.4 GHz, it was found that both real part ε' and imaginary part ε'' of complex permittivity of SiC samples decreased firstly, and then increased with increasing B content.

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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 because of their applications in civil and military fields [3–5]. However, in these materials, most absorbers like ferrite and carbon series are unable to be employed at higher temperatures due to lower Curie temperatures and oxidation problem, respectively [6,7]. It is necessary to develop the microwave absorbers satisfying the requirements of higher structural strength, and chemical and temperature resistances in higher temperature environments.

SiC has many excellent properties, e.g. high strength and hardness, good resistance oxidation, and high thermal stability [8], which has been considered to be one of the important microwave absorbing materials used in higher temperature environments [9]. However, pure SiC hardly has the property of dielectric loss in microwave range, which can be greatly improved by n- or p-type doping [9–12]. Su et al. [11] prepared SiC/N solid solution powder by combustion synthesis (CS), indicating that the microwave dielectric properties of SiC were improved by n-type doping of N. Zhao et al. [12] also reported SiC/N solid solution powders with

good dielectric loss in the frequency range of 8.2–12.4 GHz. Additionally, we synthesized Al-doped SiC solid solution powders by CS technique from Si/C/Al system [13], and results showed that Al doping as well as N doping could improve the microwave dielectric properties of SiC. Subsequently, Jin et al. [14] employed microwave synthesis to produce SiC powder doped with Al, further showing the availability of doping on the microwave dielectric properties of SiC.

Besides the p-type doping by Al, boron atoms can substitute preferably silicon atoms of SiC lattice to form shallow acceptor doping [15]. Thus, the microwave dielectric properties of SiC may be improved by B doping. In our previous study [16], the effects of B doping on the synthesis and dielectric properties of SiC were investigated by CS technique from Si/C/B system in Ar atmosphere. Nevertheless, the permittivity of the as-prepared SiC decreased with increasing B content. So how B doping improves the dielectric properties of SiC has not been solved yet. Because nitrogen atmosphere can promote the combustion reaction of Si/C system with the highly exothermic reaction of Si_3N_4 formation (737 kJ/mol) in CS process [17], the aim of this paper is to investigate further the effect of B doping on the dielectric properties of SiC synthesized by CS technique from Si/C/B system in N_2 atmosphere, and to discuss the mechanism of dielectric loss by doping in the frequency range of 8.2–12.4 GHz.

2. Experimental procedures

Silicon powder (99% pure, mean particle size of 20 μm; Tianjin Kermel Chemical Reagents Development Centre, Tianjin, China) and carbon black (99% pure,

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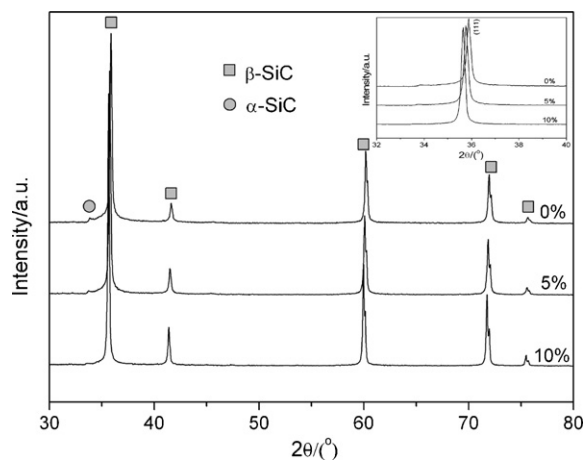E-mail address: lizhmin@163.com (Z. Li).

Fig. 1. XRD patterns of the CS products synthesized with different B contents.

Fig. 2. Raman spectra of the CS products synthesized with different B contents.

mean particle size of 30 nm; Jiaozuo Chemical Co. Ltd., Jiaozuo, China) were used as reactant materials. Boron powder (99% pure, mean particle size of 20 μm; Shanpu Chemical Co. Ltd., Shanghai, China) and polytetrafluoroethylene (PTFE) powder (99% pure, mean particle size of 75 μm; Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as dopant and chemical activator, respectively. The reactant powders were weighed out in molar ratios of B:Si:C = 0:1:1, 0.05:0.95:1, and 0.1:0.9:1, with 15% PTFE in mass. Then the powder batches were mixed in ethanol for 6 h and dried at 60 °C. Finally, the mixed powders were poured into a graphite crucible and the CS reaction was initiated by preheating at 1350 °C with the heating rate of 1000 °C/h in a 0.1 MPa N_2 atmosphere inside a resistance heating graphite furnace (ZRS-150, Sante, Jinzhou, China).

The crystalline phases of the as-prepared powders were identified by X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical, Almelo, the Netherlands), using Cu Kα radiation. A Raman spectrometer (InVia, Renishaw, Old town, Gloucestershire, UK) was utilized, using the 514.5 nm line of an Ar ion laser as the excitation source for spectroscopic measurements. The morphologies of the CS powders were observed by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Tokyo, Japan). The real and imaginary parts of complex permittivity ε at room temperature were determined by the waveguide technique with mode TE10 in the frequency range of 8.2–12.4 GHz, using a PNA network analyzer (E8362B, Agilent Technologies, Palo Alto, CA). The samples for measuring permittivity were prepared by mixing the powders with molten paraffin, which has extremely low dielectric loss, in a mass ratio of 20:80, and then the mixtures were molded into a brass flange to fabricate rectangular composite samples with the dimension of 10.16 mm (width) × 22.86 mm (length) × 2 mm (thickness).

3. Results and discussion

The XRD patterns of the CS powders synthesized with 0%, 5% and 10% B are shown in Fig. 1. β-SiC was generated and no impurity peak of boron composites was observed in all the patterns. The additional weak peak at $2\theta = 33.6°$ was attributed to the generation of α-SiC with trace amount, which is believed to transform from β-SiC due to the presence of stacking faults in β-SiC crystal [18]. The peak intensity at $2\theta = 33.6°$ decreased and the peak intensity at $2\theta = 41.4°$ increased as the B content increased, suggesting that boron can benefit the crystallization of β-SiC. Additionally, all the characteristic peaks of doped β-SiC shifted to lower 2θ angle compared with that of undoped β-SiC, as shown in the inset in Fig. 1, which indicated the increase in the lattice constant a of doped β-SiC. The lattice constant of SiC doped with 0%, 5%, and 10% B were 4.344 Å, 4.351 Å and 4.359 Å, respectively, where the lattice constant a of 10% B-doped SiC was greater than the standard value 4.358 Å of perfect SiC crystal. Because the substitution amount of B atoms on C atoms in SiC lattice is extremely low [19], it is believed that the increase in lattice constant is attributed to the fact that B atoms enter the Si tetrahedral interstitial sites in SiC crystal to become interstitial atoms B_i through kick-out/kick-in mechanism, resulting in the lattice constant of 10% B-doped SiC greater than the standard value 4.358 Å. Meanwhile, some B_i atoms may substitute Si atoms in SiC lattice to form acceptor doping, as shown in Eq. (1)
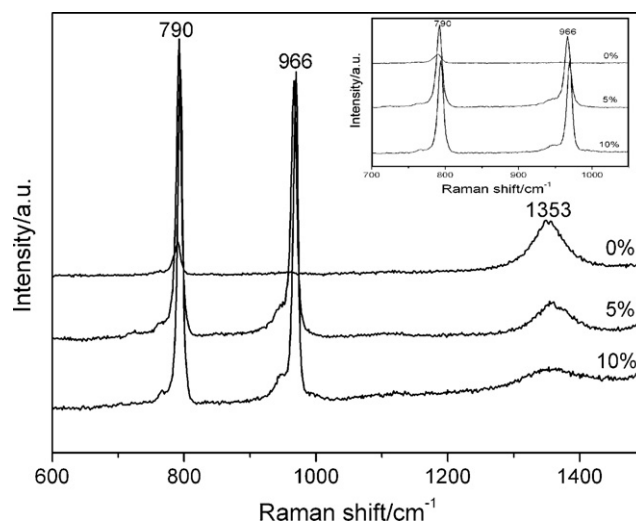
[20]:

$$B_i \rightarrow Si_i + B_{Si} \qquad (1)$$

Fig. 2 shows the Raman spectra of the CS products synthesized with different B contents in the 600–1500 cm^{-1} region. The Raman spectra showed the presence of sharp peaks at 790 cm^{-1} and 966 cm^{-1} which correspond to transverse optical (TO) phonon mode and longitudinal optical (LO) phonon mode peaks of β-SiC, respectively [21,22]. For doped products, the peak intensities at 790 cm^{-1} and 966 cm^{-1} increased significantly, which indicated that B doping was available on the crystallization of SiC, in agreement with the results of XRD. The peak at 1353 cm^{-1} was similar to the TO peak of diamond, which was indicative of the presence of C–C sp^3 bonds in β-SiC. Most probably the bonds were caused by carbon antisites C_{Si} in the SiC structure because of the lowest defect formation energy (1.1 eV) of C_{Si} in β-SiC [16]. Hence, the as-prepared SiC was C-enriched SiC which is a more suitable material for p-type doping [23].

Additionally, one can find that the peak at 966 cm^{-1} of 10% B-doped product shifted to higher wavenumber by 4 cm^{-1}, compared with that of 5% B-doped product (see the inset in Fig. 2). It is known that the LO peak will shift to higher wavenumber as the carrier concentration of the product increases [24]. So the peak shift of CS product was due to the fact that the B atoms substituted Si atoms in SiC lattice to form B acceptor doping and result in the increase in the carrier concentration of holes. Because of the better crystallization of SiC with B doping, the peak intensity at 1353 cm^{-1} decreased as the B content increased, which suggested the decrease in the amount of C_{Si} defects in SiC crystallite.

Fig. 3 shows the SEM photographs of the combustion products synthesized with 0%, 5%, and 10% B. The undoped β-SiC powder had fine spherical particles with a mean size of 0.5 μm and narrow particle size distribution. For doped β-SiC powder, the particle size decreased with increasing B content. Martin et al. [8] reported that boron additive could give rise to the increase of synthesis temperature and cause the particle size to decrease during the synthesis of SiC. Furthermore, the incorporation of B atoms into SiC lattice would retard the growth of SiC crystal in the CS process, which also resulted in the decrease in the particle size of doped SiC.

Figs. 4 and 5 show the real part ε' and imaginary part ε'' of complex permittivity ε as a function of frequency in the range of 8.2–12.4 GHz for the combustion powders, respectively. One can find that both ε' and ε'' decreased firstly, and then increased with

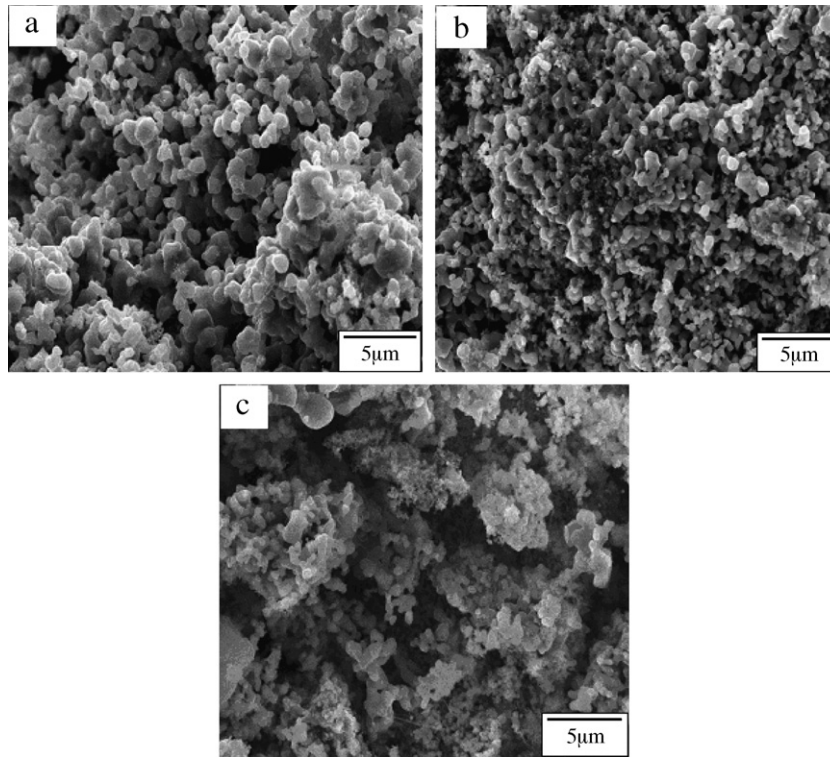**Fig. 3.** SEM photographs of the CS products synthesized with different B contents: (a) 0%, (b) 5% and (c) 10%.

increasing B content. The ε' and ε'' of undoped sample had the maximum values, which were 5.25–5.63 and 0.80–1.25, respectively, in all the samples. Though the as-prepared SiC structure contained C_{Si} defects, these defects cannot induce any additional energy levels into SiC energy band [23]. Namely, C_{Si} defects are not contributed to the changes of ε' and ε'' of SiC in the frequency range of 8.2–12.4 GHz. But it is concluded that there would exist silicon and carbon vacancies (V_{Si}, V_C) as well as C_{Si} in as-prepared SiC structure. The V_{Si} and V_C defects with opposite charges had a strong trend to form dipole pairs because of static electric attraction [16]. Under the alternating electromagnetic field, the reorientation of these dipole pairs would lead to polarization and energy dissipation, which made the undoped SiC sample show the mentioned

values of ε' and ε'' in GHz frequency range. Obviously, the more the dipoles, the higher the permittivity is. For doped SiC samples, the better crystallization resulted in the decrease in the amount of these dipoles, or leaded to the decrease in ε' and ε''. Nevertheless, the B_{Si} defects were generated in B-doped SiC structure and there would exist bound holes around B_{Si} defects. These holes would migrate to and fro to form relaxation polarization and loss under the alternating electromagnetic field [24]. Compared with 5% B-doped SiC sample, 10% B-doped SiC sample contained more bound holes, which resulted in greater values in ε' and ε''. But both ε' and ε'' of 10% B-doped SiC sample were still less than that of undoped sample due to the limitation of B substituting solubility in SiC crystal [19].
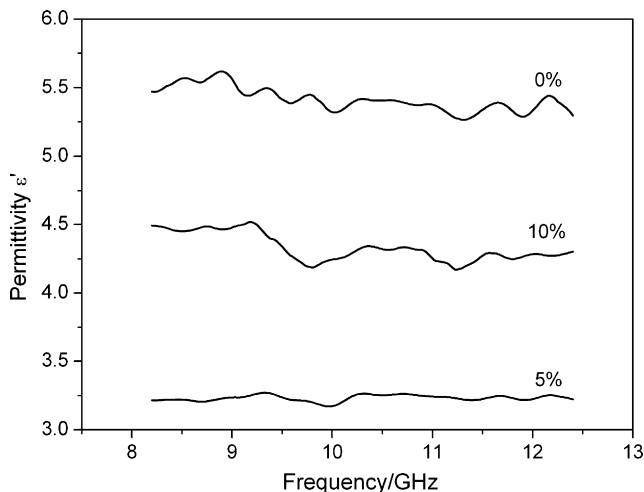

Fig. 4. Real part of permittivity ε' as a function of frequency for the powders synthesized with different B contents.
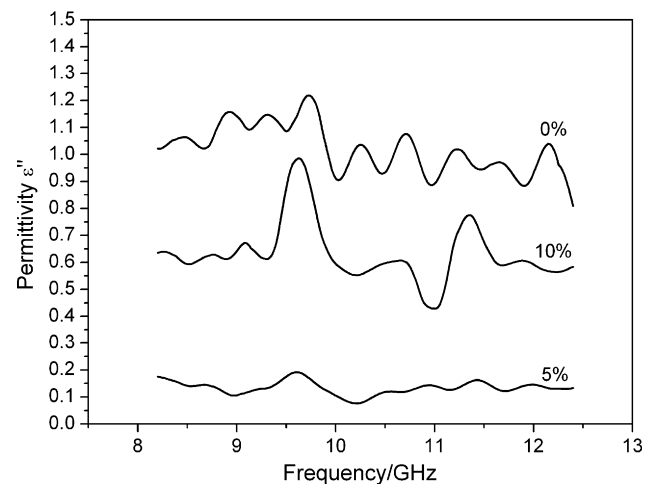

Fig. 5. Imaginary part of permittivity ε'' as a function of frequency for the powders synthesized with different B contents.

4. Conclusions

B-doped SiC powders were synthesized from the Si/C/B system in a nitrogen atmosphere by CS technique. In CS process, the presence of B benefited the crystallization of β-SiC, and B atoms could enter into SiC lattice to substitute Si atoms, forming the solid solution with B acceptor doping. B doping also leaded to the decrease in the particle size of SiC powders. The complex permittivity of SiC samples was determined in the frequency range of 8.2–12.4 GHz. Results showed that both real part ε' and imaginary part ε'' of permittivity of the samples decreased firstly, and then increased with increasing B content, which was attributed to the formation of better crystallization of SiC and B_{Si} defects arising from B doping.

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