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Microwave dielectric properties of SiC(B) solid solution powder prepared by combustion synthesis

X. SU[a,b,*], W. ZHOU[b], J. XU[a], Z. LI[c], F. LUO[b], D. ZHU[b], J. WANG[a]
[a]*College of Mechanical & Electronic Engineering, Xi'an Polytechnic University, Xi'an shaanxi, 710048, PR China*
[b] *State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an shaanxi, 710072, PR China*
[c]*School of Technical Physics, Xidian University, Xi'an shaanxi, 710071, PR China*

B-doped SiC powders were synthesized via combustion reaction of the Si/C system in a 0.1MPa nitrogen atmosphere, using polytetrafluoroethylene as the chemical activator and boron oxide as the dopant. The prepared powders have fine spherical particles and narrow particle size distribution. The electric permittivities of β-SiC samples were determined in the frequency range of 8.2-12.4 GHz. Results show that the β-SiC doped with 5% B_2O_3 has the highest real part ε' and imaginary part ε" of permittivity. The mechanism of dielectric loss by doping has been discussed.

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1. Introduction

The electromagnetic pollution by electronic and telecommunication systems and military stealthy techniques have recently increased the investigation of the microwave absorbing materials [1-3]. The SiC is often considered as the most important carbide, which has wide applications from structural materials to electric devices at elevated temperatures due to excellent properties, e.g. high strength and hardness, good corrosion resistance, and high thermal stability and thermal conductivity [4-6]. Furthermore, it was studied widely as one of the important microwave absorbing materials due to its good dielectric loss of microwave [7,8]. It is well known that the dielectric properties of SiC can be improved through *n*- or *p*-type doping [9-10]. Zhao and Jiao et al. [9,11] prepared nano SiC/N solid solution powders by laser induce method and chemical vapor deposition (CVD) method, respectively, which showed good microwave dielectric loss in the frequency range of 8.2-12.4 GHz (X-band) due to the *n*-type doping of N.

Compared with the conventional synthesis techniques of SiC powder, the combustion synthesis (CS) has many advantages: (1) easy generation of higher purity products; (2) relatively simple and energy efficient; (3) synthesis of novel materials with unique properties [12]. It is interesting that the CS process can produce novel phases with unique properties in materials due to high thermal gradient and rapid cooling rate [13]. So, in our previous work, [14] Al-doped SiC powder was prepared by combustion synthesis, using polytetrafluoroethylene (PTFE) as the chemical activator and Al powder as the dopant, and showed better microwave dielectric property than pure SiC powder. In accord with Al doping, boron atoms can substitute preferably the silicon atoms of SiC lattice, forming shallow acceptor doping [15-17]. Synchronously, the active B atoms were prepared by the reaction of solid carbon and boron oxide [18]. So it is possible that the prepared B atoms have entered the SiC lattice and formed the SiC(B) solid solution easilier to improve dielectric property of silicon carbide. But till now, to our knowledge, the preparation and dielectric properties of B-doped SiC powders by combustion synthesis have not been well investigated.

In this study, B-doped SiC powders were synthesized from the Si/C system in a N_2 atmosphere, using PTFE as the chemical activator and boron oxide powder as the dopant by CS technique. The phase compositions and microstructures of the as-prepared products were investigated. Finally, the electric permittivity and mechanism of dielectric loss of the products were discussed in the frequency range of 8.2-12.4 GHz.

2. Experimental

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. Boron oxide (B_2O_3, 99% pure, mean particle size of 20 μm; Shanpu Chemical Co. Ltd, Shanghai, China) and the PTFE powder (99% pure, mean particle size of 75 μm; Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as doping source and chemical activator, respectively. The reactant powders of B_2O_3, Si and C were weighed out in molar rations of 0:1:1, 0.025:0.975:1 and 0.05:0.95:1, respectively, with PTFE mass fraction of 15%. Namely, the molar rations of B, Si and C were 0:1:1, 0.05:0.95:1 and 0.1:0.9:1, respectively. The powder batches were mixed in ethanol for 20 h and then dried at 60 ^{0}C. The mixed powders were poured into a graphite crucible and initiated by preheating at 1250 ^{0}C with the heating rate of 40 ^{0}C /min in a 0.1 MPa N_2 atmosphere inside a resistance heating graphite furnace (Northwestern Polytechnical University, Xi'an, China). Additionally, because the excess carbon in CS products will affect the accuracy of Raman spectra and dielectric property, the prepared powders were fired in air at 650 ^{0}C for 0.5h to remove excess carbon.

The morphology of the CS powders was investigated by scanning electronic microscope (SEM, JSM-6360LV, JEOL, Tokyo, Japan). The products were identified by X-ray diffraction (XRD, X'Pert PRO MPD, Cu K_α). 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. Because of the no dielectric loss of paraffin, the samples for dielectric parameters measurement at room temperature were prepared by mixing the produced powders with paraffin in a mass ratio of 20:80, and then the mixtures were molded into a brass flange to fabricate rectangular composite samples with the dimensions of 10.16 mm (width) × 22.86 mm (length) × 2 ± 0.1 mm (thickness). The dielectric parameters were carried out by waveguide technique with mode TE_{10} in the frequency range of 8.2-12.4 GHz, with the prepared samples set in a brass holder in which fills the waveguide. After being calibrated with an intermediate of a short circuit and blank holder, reflection and transmission coefficients were obtained by PNA network analyzer (Agilent Technologies E8362B, Palo Alto, CA), and then both the real and imaginary parts of the permittivity were given.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CS powders synthesized with 0%, 2.5%, and 5%B_2O_3, respectively. β-SiC is generated in all products, which demonstrates that PTFE does promote the CS reaction of Si/C system due to the high heat released from the following reaction:

$$Si(s)+\text{-}(C_2F_4)\text{-}(s) \rightarrow SiF_4(g)+2C(s) \quad (1)$$

There are no impurity peaks of boron oxide or boron nitride when the B_2O_3 content are 2.5% and 5%, respectively. It suggests that the prepared products are pure β-SiC powders. Additionally, the additional peak observed at *d*=2.66Å is believed to be due to stacking faults in β-SiC [14].

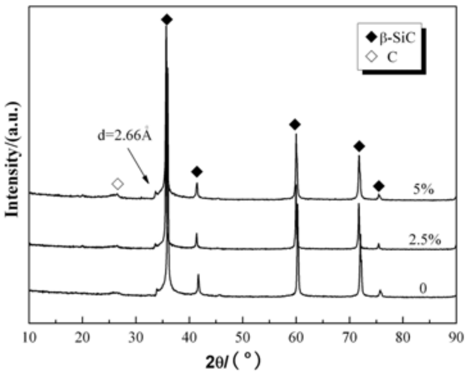


Fig. 1. XRD patterns of prepared powders with different B_2O_3 contents.

The Raman spectra of the CS products synthesized with different B_2O_3 contents are shown in Fig. 2. For the undoped product, the Raman spectrum shows the presence of a sharp peak at 790 cm^{-1} and a weak peak at 936 cm^{-1}, which correspond to the transverse optical (TO) and longitudinal optical (LO) phonon mode peaks of β-SiC, respectively. Any characteristic peaks corresponding to Si(520 cm^{-1}) or SiO_2(1000-1200 cm^{-1}) are not observed, which demonstrates that the combustion product is pure SiC. The peak at 1580 cm^{-1} is related to the graphite structure of carbon [19]. Finally, the peak at 1343 cm^{-1} is similar to the TO peak of diamond, which is indicative of the presence of C-C sp^3 bonds in β-SiC [20,21]. Most probably, the bonds are caused by carbon antisites because of the lowest defect formation energy (1.1eV) of C_{Si} in β-SiC [22]. Namely, the prepared SiC is C-enriched SiC which is a more suitable material for *p*-type doping, e.g. acceptor doping with B [23].

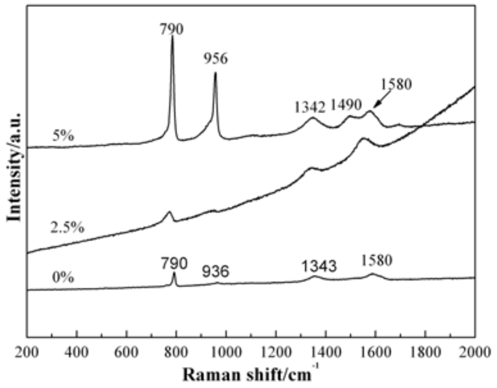
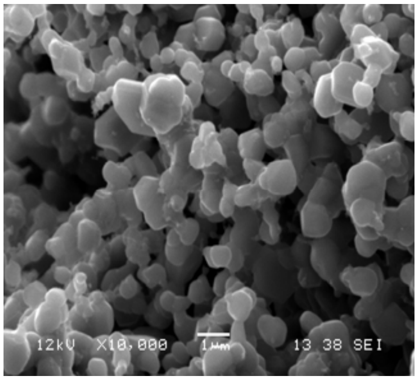


Fig. 2. Raman spectra of prepared powders with different B_2O_3 contents.

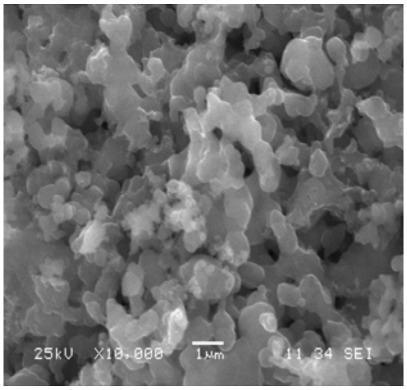
Compared with undoped product, one can find that when the B_2O_3 content is 5% the peak intensity at 790 cm^{-1} increases significantly and the peak at 936 cm^{-1} shifts to higher wavenumber by 20 cm^{-1}. The peak shift, peak broadening and relative intensities of the Raman spectra are closely related to crystal structures of the samples, and especially the LO peak will shift to higher wavenumber as the carrier concentration increases [24]. Synchronously, during the synthesis process of SiC powders the following reaction (2) takes place [18]:

$$C(s)+B_2O_3(l)\rightarrow B(g)+CO(g) \qquad (2)$$

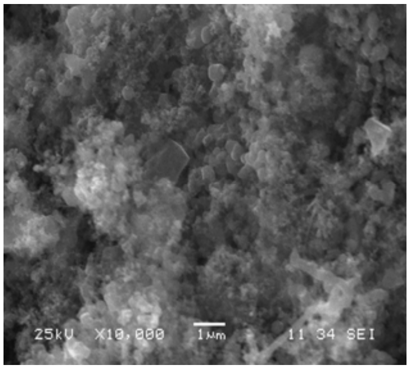
The active B atoms are generated by reaction of carbon and boron oxide. Meanwhile, because C-enriched SiC is a more suitable material for *p*-type doping, the B atoms easily substitute Si atoms of SiC lattice to form acceptor solid solution and contribute to the higher carrier concentration. Additionally, because boron doping results in the diamond transition of sp^3C, the peak at 1580 cm^{-1} shifts to the lower wavenumber 1490 cm^{-1}.



(a)0%



(b)2.5%



(c) 5%

Fig. 3. SEM photographs of prepared powders with different B_2O_3 contents.

Fig. 2 shows the SEM photographs of the combustion products of SiC synthesized with 0%, 2.5%, and 5% B_2O_3, respectively. It has been observed that all products have narrow particle size distribution and the particles size decreases with increasing B_2O_3 content. For the undoped β-SiC powder the mean size is only 0.5 μm. However, it decreases to 0.1 μm when the B_2O_3 content is 5%, which is due to the fact that the B doping will affect the crystallization of SiC and retard the crystalline growth.

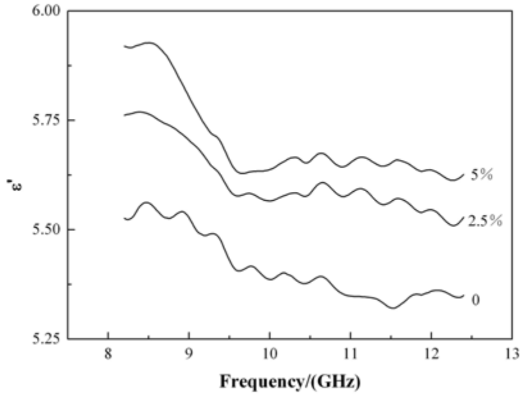


Fig. 4. Real part ε' of complex permittivity as a function of frequency in the frequency range of 8.2-12.4 GHz for the combustion powders.

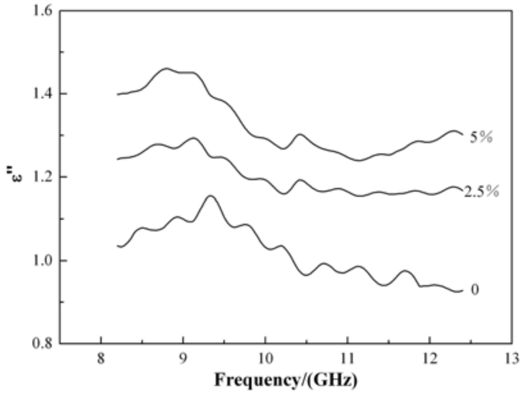


Fig. 5. Imaginary part ε" of complex permittivity as a function of frequency in the frequency range of 8.2-12.4 GHz for the combustion powders.

Fig. 4 and 5 show 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 combustion powders, respectively. The values of ε' and ε" increase with increasing B_2O_3 content. When the B_2O_3 content is 5%, ε' and ε" of the sample are 5.9-5.6 and 1.5-1.2, respectively, with the maximum values in all samples. Synchronously, the ε' and ε" show the better frequency dispersion behavior, which complex permittivity and loss tangents decrease with increasing frequency. Furthermore, the higher ε" suggests a better capacity of dielectric loss in the microwave range. Furthermore, the higher values of ε' and ε" of the B-doped sample illustrate that the SiC(B) solid solution is generated in CS products. In the work, the prepared B-SiC solid solution is a *p*-type SiC material, and there will exist bound holes around B_{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' and ε'', respectively.

4. Conclusions

B-doped SiC powders were synthesized from the Si/C system in a 0.1 MPa N_2 atmosphere using PTFE as the chemical activator and B_2O_3 as the dopant by CS technique. The undoped β-SiC powder produced in this process have fine particle size (0.5 μm) and narrow particle size distribution. When the B_2O_3 content is 5%, the particle size of sample synthesized decrease to 0.1 μm due to B doping from reaction of B_2O_3 and carbon. The results of dielectric parameters show that both real part ε' and imaginary part ε'' of permittivity of the samples increase with increasing B_2O_3 contents. The β-SiC doped with B has higher ε' and ε'' due to the relaxation polarization and loss of bound holes from B_{Si}, respectively.

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*Corresponding author: suxlei@163.com