Effect of SiC on the dielectric and microwave absorption performance of F-doped Si_3N_4 ceramics in X-band

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Abstract: In this study, silicon carbide reinforced silicon nitride (SiC/Si_3N_4) ceramics were fabricated by hot press (HP) sintering with the addition of fluorides (F= AlF_3, MgF_2). In order to investigate the dielectric and microwave (MW) absorption properties of SiC/Si_3N_4 ceramics in X-band, various concentrations of silicon carbide (SiC) have been used. The results demonstrate a complete phase transformation and the intergranular behavior of the SiC/Si_3N_4 ceramics with large and irregular grains of β-Si_3N_4. The relative complex permittivity and dielectric loss tangent increase significantly with the increasing fraction of SiC. The Cole-Cole semicircle analysis for SiC/Si_3N_4 ceramics shows a ternary dielectric behavior with the addition of SiC. Meanwhile, the reflection loss (R_L) decreases with the increase of SiC content and the lowest value of R_L was achieved -8.2 dB at 12.4 GHz, which reveal a favorable prospect as MW absorbers.

Keywords: SiC/Si_3N_4; ceramic composites; fluoride additives; dielectrics; MW absorption properties

1. Introduction

Si_3N_4 ceramic is one of the most favorable multi-functional structural material for numerous industrial applications because of its excellent mechanical, thermal, and electrical properties, with the additional characteristics of low permittivity and good MW absorption. [1, 2]. In recent years, MW absorbers have achieved huge attention due to the development of electronic and communication devices. Generally, the MW absorbers are comprised of absorption agent and matrix. In order to fabricate an excellent MW absorber, the dielectric constant should be ~1 and the dielectric loss should be greater, therefore to meet these requirements the MW absorbing agent is usually reinforced with a non-conductive matrix to prepare MW absorber [2]. The Si-based ceramics (such as SiC and SiCN) are usually preferred to fabricate the MW absorbers. A lot of investigations have been dedicated to develop the materials with exceptional MW absorption properties, such as carbon-based, ferromagnetic and SiC-based materials. The SiC possesses excellent MW absorption properties due to its wide band gape semi-conduction, good electrical and dielectric properties [3]. Furthermore, Li et al. [4] and Zheng et al. [5] synthesized the Si_3N_4-SiC ceramics and improved the dielectric and MW absorption performance of the ceramics. Therefore, SiC/Si_3N_4 ceramics can be a good MW absorber, which can be used in an open environment [6]. In this paper, the dielectric and MW absorption properties of F-doped SiC/Si_3N_4 ceramics have been investigated at various concentrations of SiC.

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2. Experimental

The starting materials were α-Si$_3$N$_4$ (0.5 µm, >93%, Beijing Ziguang Co.), SiC (Shanghai Haiyi Technology) and sintering additives (AlF$_3$ and MgF$_2$, Shanghai Macklin Biochemical technology). The detail of different compositions of raw materials is illustrated in **Table 1**. The mixed raw powders were wet milled with ethyl alcohol for 30 minutes, Resulted powders were dried in an oven at 70˚C, ground and sieved with a mesh size of 154 µm. Afterward, the as-prepared powders were densified in HP sintering furnace at 1700˚C for 1h in a high purity N$_2$ atmosphere at a pressure of 30 MPa (heating rate 10˚C min^{-1}). The synthesized materials were characterized by X-ray diffraction (XRD, D/MAX, Ultima-IV, Rigaku, Japan), scanning electron microscope (FE-SEM, JSM-7800F) and Raman analysis was performed at room temperature using Raman spectroscopy (RMS, Renishaw, UK). Furthermore, the bulk density of ceramics was measured by Archimedes' principle in distilled water. The dielectric and MW absorption parameters were analyzed by the transmission line and free space method with a vector analyzer (Agilent Technologies, N5222A) in the frequency range 8.2-12.4 GHz (X-band). The specimens for MW dielectric parameters test were prepared in a rectangular shape with the dimension of $22.88 \times 10.16 \times 3$ mm^3.

Table 1. Compositions of the composites, density and relative density.

Composites name	Compositions				Density (g/cm^3)	Relative density (%)
	Si$_2$N$_4$ wt%	SiC wt%	AlF$_3$ wt%	MgF$_2$ wt%		
S1	95	0	2.5	2.5	3.10	97.3
S2	90	5	2.5	2.5	3.08	96.7
S3	85	10	2.5	2.5	3.04	95.3
S4	80	15	2.5	2.5	3.05	95.4

3. Results and discussion

XRD patterns of hot pressed F-doped SiC/Si$_3$N$_4$ ceramics can be observed in **Fig. 1a**. A complete phase transformation from α to β-Si$_3$N$_4$ have been detected with few extra peaks of MgSiN$_2$ and SiC. The presence of MgSiN$_2$ relates to the reaction of doping materials with Si, present on the surface of Si$_3$N$_4$ due to the liquid phase sintering phenomenon, which is beneficial for the interfacial interaction between grain boundaries. The Raman spectra for all the composites can be seen in **Fig. 1b**. The Raman spectra for S2, S3 and S4 show two peaks of SiC (at ~787 and 972 cm^{-1}) [7]. Furthermore, the S2, S3, and S4 also showed D (~1400 cm^{-1}) and G (~1519 cm^{-1}) bands with a low intensity suggesting a very less content of free carbon [8]. The intensity of the G band increases slightly with the increase of SiC content attributing to the graphitization degree. SEM images (**Fig. 1c-d**) shows the intergranular behavior of the SiC/Si$_3$N$_4$ ceramics with large and uneven grains of β-Si$_3$N$_4$ and SiC. Furthermore, the presence of SiC contents within the grain boundaries shows a strong interfacial interaction, as well as promoted the β-Si$_3$N$_4$ grains and helps to reduce its grain size. The bulk and relative densities (**Table 1)** of the ceramics decreases with the increasing contents of SiC, attributing to the more significant interaction of grains rearrangements and volumetric retraction of ceramic composites. Previously reported that the presence of fluoride additives decrease the oxygen contents and help to improve the density of a material, therefore the overall improvement in the composites can also be attributed to the presence of fluoride additives [9]. The dielectric properties of SiC/Si$_3$N$_4$ ceramics with various SiC content were examined at the frequency range of 8.2-12.4 GHz. The relative complex permittivity ($\varepsilon_r = \acute{\varepsilon} - j\breve{\varepsilon}$) and magnetic permeability ($\mu_r = \mu' - j\mu''$) are the key parameters to characterize the dielectric and MW absorption performance. The $\acute{\varepsilon}$ and $\breve{\varepsilon}$ are related to polarization and capability of dielectric loss, also correspond to the ability to store and dissipate electromagnetic (EM) wave energy, respectively. Although, the high $\breve{\varepsilon}$ implies good MW absorption properties, whereas the too high value of $\breve{\varepsilon}$ can affect the impedance match and absorption capacity

[10]. As exhibited in **Fig. 2a** and **b**, both $\acute{\varepsilon}$ and $\breve{\varepsilon}$ decreased with the increase of frequency, which
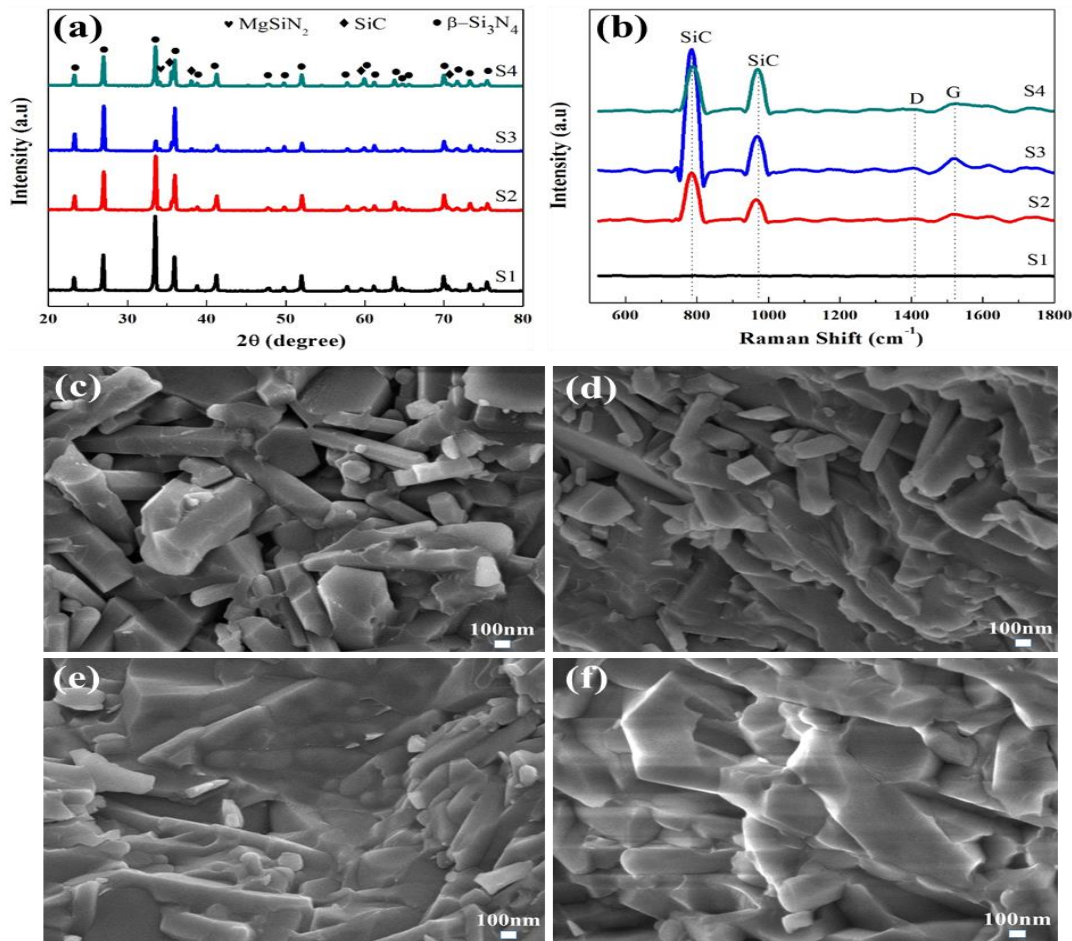

affect the complex permittivity of SiC/Si$_3$N$_4$ ceramics.

Fig. 1: XRD patterns (a) and Raman spectra (b), SEM images of S1 (c), S2 (d), S3 (e) and S4 (f) of SiC/Si$_3$N$_4$ ceramics.

The performance of the real part (μ') and imaginary part (μ'') of the permeability of SiC/Si$_3$N$_4$ ceramics are shown in **Fig. 2c** and **d**. The resonance peaks of both μ' and μ'' appeared for S3 and S4 composites at high frequency, however other composites showed no intense change. Generally, the MW absorption performance of ceramics can be improved with the reduction of complex permittivity. In this case, it can be observed that the complex permittivity and tangent loss decreases as the SiC content decreased to the lowest value and increased rapidly with the increase of SiC content.

The dielectric loss ($\tan\delta_\varepsilon = \frac{\varepsilon''}{\varepsilon'}$) tangent and magnetic loss ($\tan\delta_\mu \frac{\mu''}{\mu'}$) tangent, represent to the MW attenuation capability of materials. The greater values of $\tan\delta_\varepsilon$ and $\tan\delta_\mu$ means good MW attenuation capability. The behaviour of $\tan\delta_\varepsilon$ and $\tan\delta_\mu$ can be observed in **Fig. 3a** and **b**, the MW attenuation capability of SiC/Si$_3$N$_4$ ceramics increase with the increase of SiC. The resonance peaks of $\tan\delta_\varepsilon$ were shifts towards high frequency with a maximum value of 0.36 at 12.4 GHz and the average value of $\tan\delta_\mu$ for composites, S1, S2, and S3 was ~ 0, whereas composite S4 shows a small resonance peak with a maximum value of 1.19 at 10.24 GHz. The overall behavior of $\tan\delta_\mu$ was closely related to μ'' at high frequency. The dielectric loss phenomenon is related to the Debye relaxation ($\acute{\varepsilon} - \breve{\varepsilon}$), generally examined by the Cole-Cole semicircle equation ($(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2 = (\varepsilon_s - \varepsilon_\infty)^2$, where ε_s and ε_∞ are the stationary and optical dielectric constants) in which each

semicircle relates to a Debye relaxation [11]. The Cole-Cole semicircles for SiC/Si$_3$N$_4$ ceramics can be observed in **Fig. 3c**, in which all composites with SiC show three semicircles for each, attributing to the ternary dielectric behavior, which could lead to a favorable perception for a MW absorber.
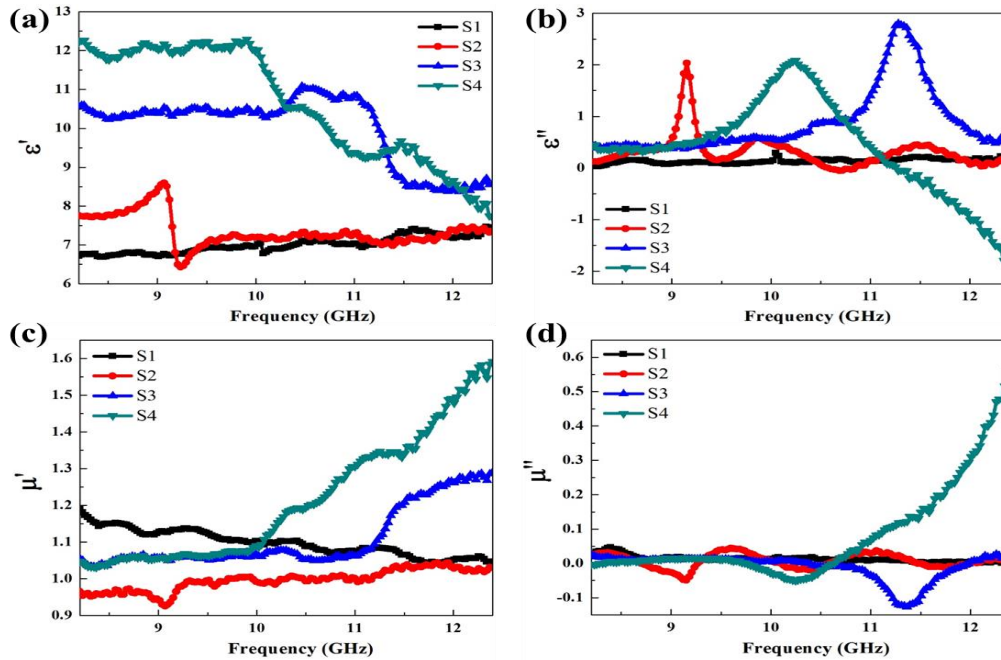
Fig. 2: Frequency dependence on the real part of permittivity (a), imaginary part of permittivity (b), real part of permeability (c) and imaginary part of permeability (d).
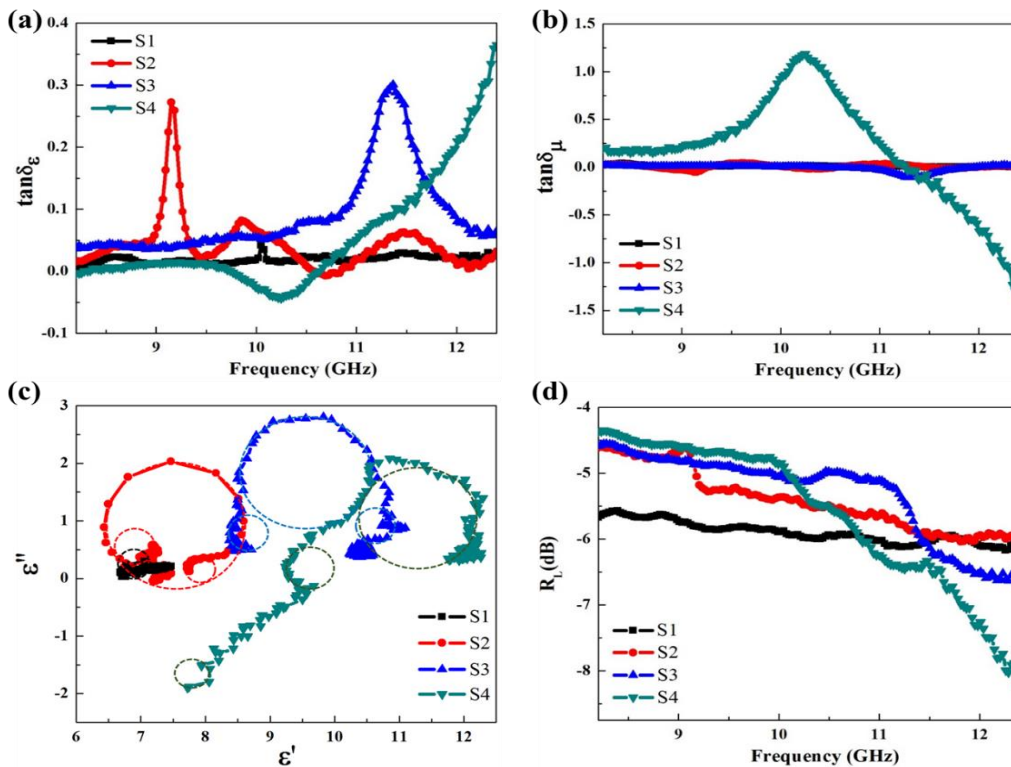
Fig. 3: Frequency dependence on the dielectric loss tangent (a) and magnetic loss tangent (b). The Cole-Cole analysis (c) and frequency dependence R$_L$ (d).

The MW absorption properties were calculated according to the transmission line theory, using R_L, which was calculated by using these equations;

$$R_L = 20 \log_{10} |(Z_{in} - 1)/(Z_{in} + 1)|$$

$$Z_{in} = \sqrt{\mu_r/\varepsilon_r} \tanh\left[j(2\pi fd/c)\sqrt{\mu_r\varepsilon_r}\right]$$

Where Z_{in} is input impedance, f is the frequency, d is the thickness of composite and c is the speed of light. Generally the values of μ_r affect the R_L, as the increase in μ_r shifts the reflection loss peak towards low frequency. The lower value of R_L means good MW absorption, μ_r for SiC is considered to be 1, because magnetic properties of SiC are poor. **Fig. 3d** shows the R_L for all the composites with a thickness of 3mm, where it can be seen that the R_L first increase with the increasing content of SiC and then start to decrease at high frequency. The lowest R_L peak was achieved -8.2 dB at 12.4 GHz (~ 90 % absorption) for S4 composite, which shows a good MW absorbance.

4. Conclusions

The F-doped SiC/Si$_3$N$_4$ ceramics were well prepared by HP sintering with different SiC content. The microstructural results confirmed a complete phase transformation from α to β-Si$_3$N$_4$ and revealed that the increasing content of SiC improved the dielectric properties of the SiC/Si$_3$N$_4$ ceramics. The complex permittivity and tangent loss was decreased at the low content of SiC and increased rapidly with the increase of SiC content. Furthermore, to investigate the MW absorption properties the lowest R_L was recorded -8.2 dB at 12.4 GHz (~ 90 % absorption). Hence, the as-synthesized F-doped SiC/Si$_3$N$_4$ ceramics can be a good candidate with the excellent characteristics of low permittivity and good MW absorption.

Acknowledgment

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