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Short communication

Microwave dielectric properties of Ti_3SiC_2 powders synthesized by solid state reaction

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Abstract

Ti_3SiC_2 powders were synthesized by the solid state reaction in a vacuum using Ti/Si/TiC mixture powders as the starting materials. X-ray diffraction, scanning electron microscopy and energy-dispersive spectroscopy were utilized in analyzing phase, morphology, and chemical composition of the prepared powders, respectively. It was found that the powder synthesized at 1350 °C had the higher purity of Ti_3SiC_2. The dielectric permittivities of Ti_3SiC_2 samples were determined in the frequency range of 8.2–12.4 GHz. Results showed that the sample with higher purity of Ti_3SiC_2 had the greater real part of complex permittivity ε' and dielectric loss tan δ, indicating a good application prospect in microwave absorbing materials. The mechanism of microwave dielectric loss for Ti_3SiC_2 was discussed.

Keywords: A. Solid state reaction; C. Dielectric properties; D. Carbides; E. Functional applications

1. Introduction

Microwave absorbing materials have been paid much attention for their extensive use in commercial and military applications, which can dissipate incident electromagnetic energy into heat by electric conduction loss, dielectric polarization loss and magnetic hysteresis loss [1–3]. In general, microwave absorbing materials are categorized into two types: magnetic materials and dielectric materials. Magnetic absorbers, e.g. hexagonal ferrites and carbonyl iron powder, often have a relatively heavy density and will lose microwave absorbing characteristic in the environment at higher temperature because of their lower Curie temperatures [4–6]. Hence, dielectric absorbers with oxidation resistance such as Al or N-doped SiC [7], h-BN [8], and Sr-doped $LaMnO_3$ [9], etc. have been developed to satisfy the need of lightweight and employment at higher temperatures. Compared to microwave dielectric materials for resonator application [10], these dielectric absorbers are required to have higher microwave dielectric loss.

The ternary layered carbide Ti_3SiC_2 has been considered as a potential structure/functional material due to its combination of metallic and ceramic properties, such as good oxidation resistance, low density, high modulus, good thermal and electrical conductivity, excellent thermal shock resistance and high temperature strength, and easy machinability [11–15]. These properties possibly make Ti_3SiC_2 potential candidate for microwave absorbing application at higher temperature (e.g. >700 °C). However, the study on microwave dielectric properties of Ti_3SiC_2 has not been fully addressed.

In comparison to Ti_3SiC_2 bulk materials, it is difficult to prepare Ti_3SiC_2 powders with high purity [16]. To overcome this problem, various synthesis routes for preparing Ti_3SiC_2 powder have been reported, including solid state reaction at high temperature [17,18], mechanical-alloying- assisted synthesis [19,20], and carbothermal reduction method [21], etc. Among these methods, high purity Ti_3SiC_2 powder could be synthesized through heat treating Ti/Si/TiC mixture powders at high temperature in vacuum. In this study, Ti_3SiC_2 powders were synthesized by solid state reaction at high temperature using

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Ti/Si/TiC mixture powders as the starting materials. The phase purity, morphology and chemical component of prepared samples were investigated, and their complex permittivities in the frequency range of 8.2 − 12.4 GHz were determined.

2. Experimental

Titanium powder (99% in purity, < 325 mesh), silicon powder (99% in purity, < 200 mesh) and titanium carbide powder (99% in purity, < 400 mesh) were used as the starting materials, which were weighted out in the molar ratio of Ti:Si:TiC = 2:2:3 [18]. The powder batches were mixed in ethanol for 6 h using planetary milling with agate ball media and dried at 60 °C, then the mixtures were placed into the vacuum sintering furnace (ZRS-150, Sante, Jinzhou, China) and fired at temperatures of 1250–1400 °C for 2 h, with a heating rate of 10 °C/min and a vacuum degree of about 10^{-1} Pa.

The crystalline phases of the as-prepared powders were identified by X-ray diffraction (XRD, DX-1000, Fangyuan instrument Co. Ltd., Dandong, China) with Cu Kα radiation. The morphology of the powders was observed 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, Waltham, MA). Because of extremely low dielectric loss of paraffin, the samples for dielectric parameter measurements at room temperature were prepared by mixing the produced powders with paraffin in a mass ratio of 1:1. The mixtures were then molded into a brass flange to fabricate rectangular composite samples with the dimensions of 10.16 mm (width) × 22.86 mm (length) × 2 mm (thickness). The dielectric parameters of the samples were determined by the waveguide technique with mode TE10 in the frequency range of 8.2–12.4 GHz, with the prepared samples set in a brass holder in which filled the waveguide. After being calibrated with an intermediate of short circuit and blank holder, reflection and transmission coefficients were obtained using a PNA network analyzer (Agilent Technologies E8362B, Palo Alto, CA), and then both the real and imaginary parts of the permittivities were determined.

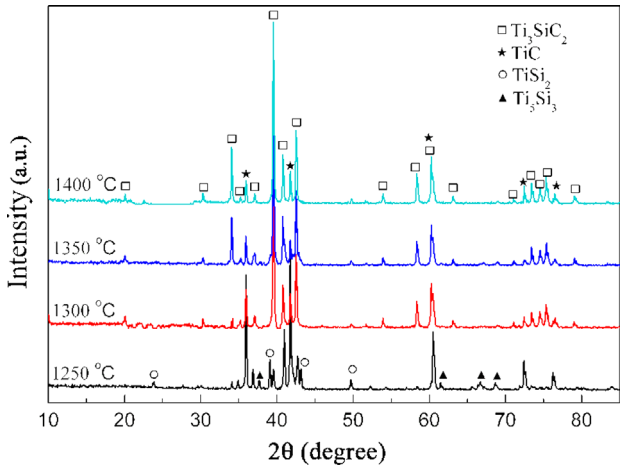

Fig. 1. XRD patterns of the powders synthesized at different temperatures.

3. Results and discussion

Fig. 1 shows the XRD patterns scanned at $2\theta = 10–85$ ° of the powders synthesized at 1250–1400 °C. As can be seen, the intensities of Ti_3SiC_2 peaks are quite weak and TiC is the main

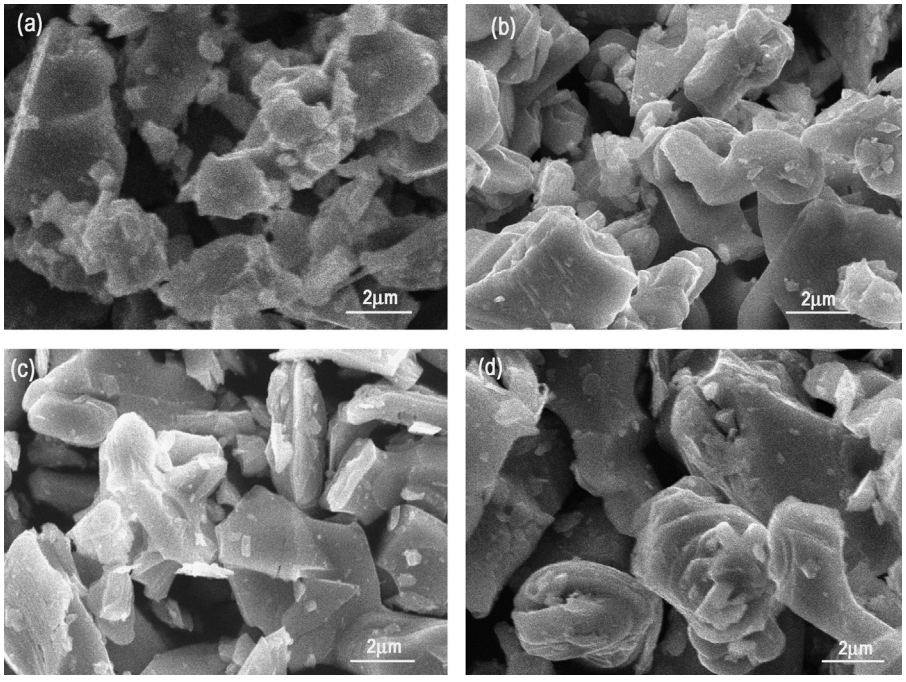

Fig. 2. SEM photos of the powders synthesized at different temperatures: (a)1250 °C; (b)1300 °C; (c)1350 °C; and (d)1400 °C.

phase for the powder synthesized at 1250 °C, including $TiSi_2$ and Ti_5Si_3 as well. When the temperature is above 1300 °C, Ti_3SiC_2 becomes the dominant phase with minor phase of TiC. The weight fractions of Ti_3SiC_2 phase in the powders were calculated, according to the ratio of the integrated diffraction peak intensity of Ti_3SiC_2 (104) to TiC (200) from X-ray diffractogram [14,22], which were 90.8%, 92.4% and 90.7% for the powders synthesized at 1300 °C, 1350 °C and 1400 °C, respectively.

In the synthesis process of Ti_3SiC_2 from Ti/Si/TiC mixture, the following reactions took place possibly. Ti_5Si_3 and $TiSi_2$ were firstly formed, and Ti_5Si_3 could react with the surrounding Si and TiC to generate slight Ti_3SiC_2 at relatively lower temperature by the reaction (3) [23]. Then, the eutectic liquid appeared for the Si and Ti compositions near the eutectic point (1330 °C) to accelerate the process of reactions (3)–(5), leading to higher purity of Ti_3SiC_2 in the powder synthesized at 1350 °C [22]. Additionally, the amount of a decrease of Ti_3SiC_2 in the powder synthesized at 1400 °C possibly contributed to the accompanying decomposition of Ti_3SiC_2 in a vacuum atmosphere responding to reaction (6) [24].

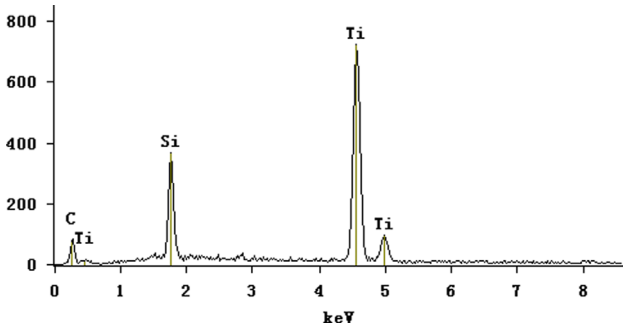

Fig. 3. EDS of the powder synthesized at 1350 °C.

$$5Ti+3Si \rightarrow Ti_5Si_3 \quad (1)$$

$$Ti+2Si \rightarrow TiSi_2 \quad (2)$$

$$Ti_5Si_3+2Si+10TiC \rightarrow 5T_3SiC_2 \quad (3)$$

$$7TiC+2TiSi_2 \rightarrow 3Ti_3SiC_2+SiC \quad (4)$$

$$TiC+SiC+2Ti \rightarrow Ti_3SiC_2 \quad (5)$$

$$Ti_3SiC_2 \rightarrow 3TiC_x+Si(g) \quad (6)$$

The SEM photos of the powders synthesized at different temperatures are shown in Fig. 2. For the powder synthesized at 1300 °C, the average size of Ti_3SiC_2 particles was about 4 μm with laminated appearance, which enlarged with increasing temperature. As mentioned above, the presence of eutectic liquid phase at higher temperature enabled rapider atom

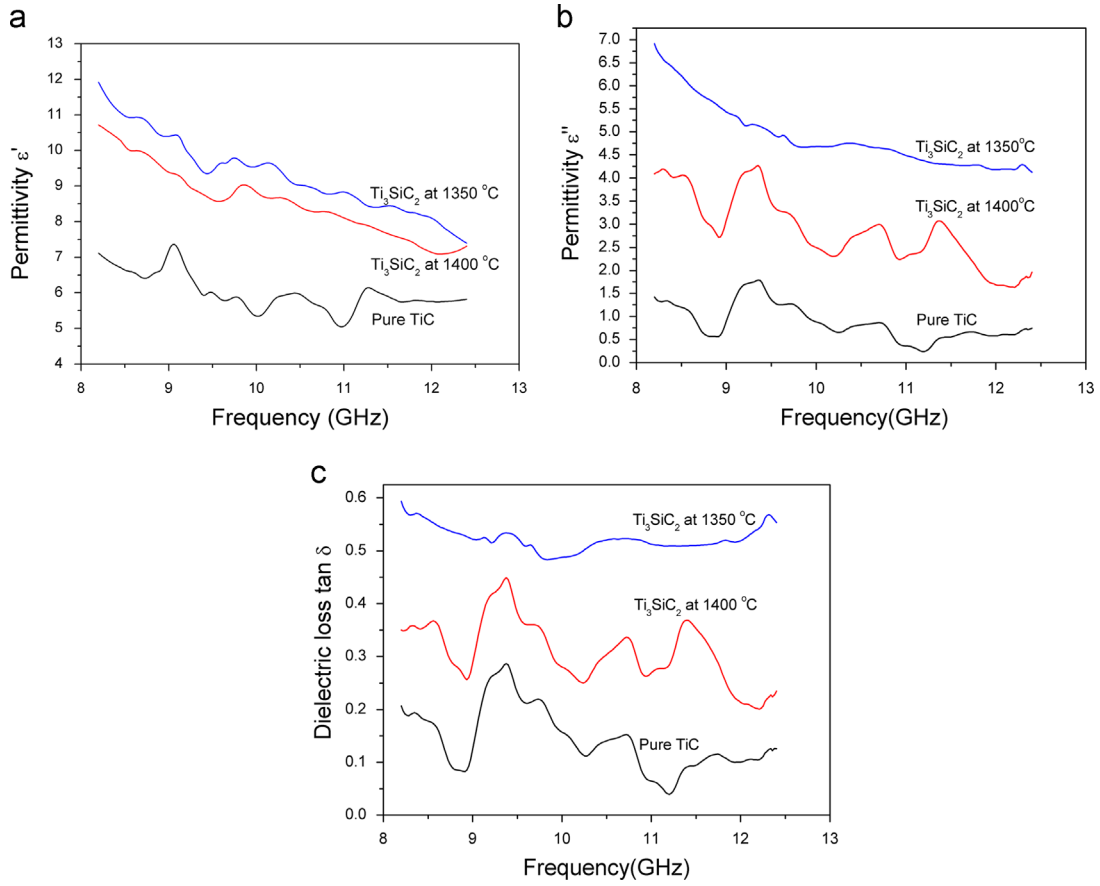

Fig. 4. Real part ε' (a) and imaginary part ε'' (b) of permittivity and dielectric loss tan δ (c) as a function of frequency for the Ti_3SiC_2 samples synthesized at different temperatures and pure TiC sample.

transport among the reactant particles, which made the synthesis reactions to occur readily and promoted the growth of Ti_3SiC_2 particles. Fig. 3 shows the analysis of EDS for the powder synthesized at 1350 °C. It was found that the sample contained Ti, Si and C elements which were 57.29%, 16.11%, and 26.60% in atomic molar percentage, respectively. The elemental stoichiometric ratio was close to nominal Ti_3SiC_2, further demonstrating the presence of Ti_3SiC_2 phase.

Considering the higher purity of Ti_3SiC_2 in the samples synthesized at 1350 °C and 1400 °C, the real part ε' and imaginary part ε'' of permittivity and dielectric loss $\tan\delta$ ($\tan\delta=\varepsilon''/\varepsilon'$) as a function of frequency in the range 8.2–12.4 GHz for both samples were determined, as shown in Fig. 4. The permittivity of pure TiC was also given for comparing the effect of minor phase TiC on dielectric property of Ti_3SiC_2 in prepared samples. As can be seen, all the values of ε', ε'' and $\tan\delta$ for pure TiC are much smaller than that for both Ti_3SiC_2 samples, or the microwave dielectric properties of the samples are mainly dependent on the weight fraction or purity of Ti_3SiC_2. Because of the greater purity of Ti_3SiC_2 (92.4%) for the sample synthesized at 1350 °C, the sample showed the greater values in ε', ε'' and $\tan\delta$ compared to the sample at 1400 °C, which were 9.33, 4.88 and 0.52 in average, respectively. Furthermore, the $\tan\delta$ of the sample at 1350 °C is higher than that of our previously prepared Al-doped SiC sample [25], suggesting a better capacity of dielectric loss in the microwave range. Additionally, the ε' and ε'' of pure paraffin employed in this study were 2.32 and 0.16 in average, respectively. Obviously, the dielectric loss $\tan\delta$ of paraffin was extremely low, and the paraffin hardly influenced the change tendency of dielectric loss of Ti_3SiC_2 in Ti_3SiC_2/paraffin composite samples. According to logarithmic mixing rule, an average value of about 8100 was obtained for ε' of Ti_3SiC_2 at 1350 °C in the frequency range of 8.2–12.4 GHz, with excluding paraffin.

Because Ti_3SiC_2 is a non-magnetic loss material (permeability $\mu'=1$ and $\mu''=0$), its power dissipation at high frequencies is determined only by dielectric loss. The microwave loss of dielectric materials is generally composed of electric conduction loss, dipole relaxation loss and electron or hole relaxation loss. For ternary layered Ti_3SiC_2 crystal, there is free charge density distribution in the interstitial of atoms on the Ti layers, especially on the Ti layers adjacent to Si layers, so Ti_3SiC_2 has a metal-like type of electrical conductivity (4.5×10^6 S/m at room temperature) [26–28]. It is concluded that there exists electric conduction loss with Ti_3SiC_2 samples under applied alternating field, which results in higher ε'' or $\tan\delta$ of the sample at 1350 °C.

4. Conclusions

Ti_3SiC_2 powders were synthesized by the solid state reaction at 1250–1400 °C under vacuum using Ti/Si/TiC mixture powders as the starting materials. Results showed that Ti_3SiC_2 became dominant phase in the as-prepared powders when the synthesized temperature was above 1300 °C, with a maximum Ti_3SiC_2 purity of 92.4% for the powder synthesized at 1350 °C. The particles prepared at 1300 °C had the average size of about 4 μm with laminated appearance which enlarged as the synthesized temperature increased. The complex permittivities of Ti_3SiC_2 samples were determined in the frequency range of 8.2–12.4 GHz. It was found that all the real part ε' and imaginary part ε'' of complex permittivity and dielectric loss $\tan\delta$ of the sample synthesized at 1350 °C were greater than that of the sample at 1400 °C due to the greater purity of Ti_3SiC_2. The better ε'' or $\tan\delta$ of the sample contributed to its electric conduction loss at GHz region.

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