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Improving the microwave dielectric properties of Ti_3SiC_2 powders by Al doping

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ABSTRACT

Al-doped Ti_3SiC_2 powders were synthesized by solid state reaction under a vacuum atmosphere. Results showed that Al doping effectively improved the purity of the as-prepared Ti_3SiC_2 powders which had a narrow particle size distribution. The complex permittivities and reflection loss of Ti_3SiC_2 samples were determined in the frequency range of 8.2–12.4 GHz. It was found that 20% Al-doped sample showed the greatest values in the real part ε' and imaginary part ε'' of complex permittivity and the better reflection loss with an absorbing thickness of 2.1 mm. The mechanism of dielectric loss by Al doping was discussed.

1. Introduction

Microwave absorbing materials have been increasingly investigated to protect electronic devices and human being from electromagnetic wave irradiation or to prevent the military equipments from being detected by radar waves, and they can dissipate the incident electromagnetic energy into heat by magnetic or dielectric loss [1–3]. Among microwave absorbing materials, the ferrites and carbonyl iron are important magnetic absorbers that show better magnetic dissipation properties at GHz frequency range and enable to realize readily electromagnetic matching [4,5]. However, these magnetic absorbers are unsuitable for employing at a higher temperature environment due to their lower Curie temperature [6,7]. Also, the permeabilities of the spinel and hexagonal ferrites will decrease sharply with the increasing frequency within the GHz range because of the Snoek's limit [8]. In order to overcome these problems, dielectric microwave absorbers, especially ceramic absorbers, have been developed [9,10].

The layered ternary carbide Ti_3SiC_2 has been well known as one of the remarkable ceramics because of its combined properties of both metals and ceramics [11], including low density, high modulus, good thermal and electrical conductivity, excellent thermal shock resistance and oxidation resistance, and easy machinability [12–14]. For these unique properties, Ti_3SiC_2 can be considered for many applications, one of which is to be a promising candidate of high temperature materials [15]. Especially, it possesses the electrical conductivity twice as high as that of Ti metal at room temperature, which is interested in applying to microwave absorbing materials. Our recent investigation showed that Ti_3SiC_2 revealed better dielectric loss tangent in X band, and that the microwave dielectric properties of Ti_3SiC_2 were closely relevant to its purity [16].

Zhou et al. [17] reported that Al addition to Ti/Si/2TiC starting powders could promote the synthesis of Ti_3SiC_2, which also lowered the synthesis temperature. Zhang et al. [18] found that the oxidation resistance of Ti_3SiC_2 bulk material was improved by forming a $Ti_3Si_{0.9}Al_{0.1}C_2$ solid solution. Apparently, the effect of Al doping on Ti_3SiC_2 is favorable on its application to microwave absorbing materials at higher temperature. Nevertheless, the microwave dielectric properties of Ti_3SiC_2 powders doped with Al have not been fully addressed. In this study, the effect of Al doping on the synthesis and microwave dielectric properties of Ti_3SiC_2 powders was investigated, and the mechanism of dielectric loss by Al doping was discussed.

2. Experimental procedures

Titanium powder (99% in purity, mean particle size of 75 μm), silicon powder (99% in purity, mean particle size of 40 μm) and titanium carbide powder (99% in purity, mean particle size of 75 μm) were used as starting materials, and aluminium powder (99% in purity, mean particle size of 40 μm) was used as dopant to synthesize Al-doped Ti_3SiC_2 powders. The molar ratios of reactant powders are shown in Table 1, and the nominal Al doping contents are 0%, 10%, 20% and 50% for listed Ti_3SiC_2 samples, respectively. The powder batches were mixed in ethanol using planetary milling with agate ball media for 6 h and dried at 60 °C. Then the mixtures

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Table 1
Molar ratios of reactant powders.

Samples	Molar ratios			
	Ti	Si	TiC	Al
Ti_3SiC_2	2	2	3	0
10% Al-doped Ti_3SiC_2	2	1.8	3	0.2
20% Al-doped Ti_3SiC_2	2	1.6	3	0.4
50% Al-doped Ti_3SiC_2	2	1	3	1

were placed into a vacuum sintering furnace and fired at 1300 °C for 2 h to prepare Al-doped Ti_3SiC_2 powders, 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., China) with Cu Kα radiation. The morphologies of the powders were observed by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Japan), and the compositions were analyzed by energy-dispersive spectroscopy (EDS, NORAN System SIX Model 300, Thermo Electron Corporation, USA).

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 molten paraffin in a mass ratio of 1:1. Then the mixtures were molded into a brass flange to fabricate rectangular composite samples with the dimensions of 10.24 mm (width) × 22.86 mm (length) × 2.46 mm (thickness). The dielectric parameters of the samples were determined by PNA vector network analyzer (Agilent Technologies E8362B, Palo Alto, CA) with waveguide technique in the frequency range of 8.2–12.4 GHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Ti_3SiC_2 powders synthesized with different Al contents at 1300 °C. As can be seen, the peaks of Ti_3SiC_2 are dominant in all the patterns of the prepared powders, and TiC peaks are relatively obvious in the powders synthesized with 0% and 50% Al contents, but they almost disappear in the powders synthesized with 10% and 20% Al contents, demonstrating that Al doping with appropriate levels can improve Ti_3SiC_2 purity in the product. It is noted that there do not appear any peaks of Al compounds in all the Al-doped samples, and Al element can be found by EDS analysis in the case of Al doping, e.g. 20% Al-doped Ti_3SiC_2 as shown in Fig. 2. Apparently, in the synthesis process, Al atoms possibly incorporate Ti_3SiC_2 crystal structure to generate $Ti_3Si_{1-x}Al_xC_2$ solid solution due to the close atomic radius and electronegativity between Si and Al atoms for Al-doped samples [19].

When the prepared products only contain Ti_3SiC_2 and TiC phases, the relative weight percentage of Ti_3SiC_2 can be expressed as follow [20]:

$$W_{TSC} = 1.8/(1.8 + I_{TC}/I_{TSC}) \quad (1)$$

where I_{TC} and I_{TSC} represent the integrated diffraction peak intensities of TiC (200) at $2\theta = 41.705°$ and Ti_3SiC_2 (104) at $2\theta = 39.549°$,

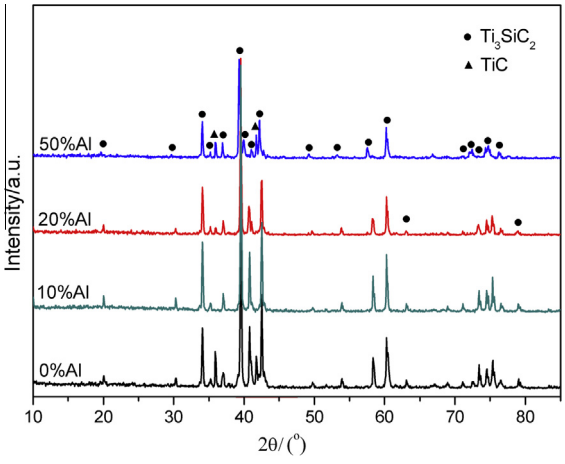

Fig. 1. XRD patterns of the Ti_3SiC_2 powders synthesized with different Al contents.

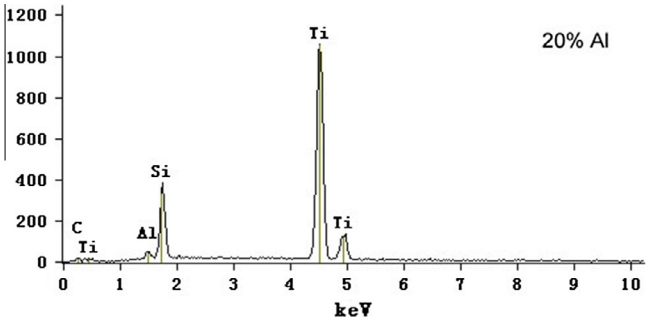

Fig. 2. EDS of the powder synthesized with 20% Al content.

respectively, and W_{TSC} represents the weight percentage of Ti_3SiC_2 in the products. According to Eq. (1), the weight percentages of Ti_3SiC_2 were 99.1% and 98.1% for 10% and 20% Al-doped powders, respectively, which had the higher purity of Ti_3SiC_2 compared to the Ti_3SiC_2 sample without Al doping. In the synthesis process, a liquid environment was provided by Al melting at 660 °C, which accelerated the migration of reactant particles. Also, small amounts of Al could dissolve into TiC crystal to form defects which were favorable on Si diffusion in TiC. Therefore, the synthesis reaction of Ti_3SiC_2 was promoted [21], leading to the higher purity of Ti_3SiC_2 products synthesized with 10% and 20% Al contents. When the content of Al increased to 50%, the decrease in the relative weight percentage of Ti_3SiC_2 for the prepared powder was possibly due to the fact that more volatilization of Al would cause the unreacted TiC residual in the synthesis process.

The SEM photos of the powders synthesized with different Al contents are shown in Fig. 3. For the powder undoped with Al, it can be seen in Fig. 3(a) that the particles size ranges from 1 to 10 μm with laminated appearance, which is clearly observed in the circle around by dotted line that is enlarged and marked by the arrow in the inset. The laminated appearance was apparently caused by the typical spiral growth, in which screw dislocations provided a continuous source of a new terrace in the synthesis process, as discussed by Li et al. [22]. When the Al content was 10%, the particles of as-prepared powder had a narrow size distribution, with an average size of about 4 μm. The average size of particles slightly increased as the Al content increased further.

Fig. 4 shows the variation tendency of the real part ε' and imaginary part ε'' of permittivities in the frequency range of 8.2–12.4 GHz for the samples synthesized with different Al contents. As can be seen, Both ε' and ε'' of Al-doped samples increase firstly, and then decrease with the increasing Al content, in which the sample with 20% Al content reveals the greatest values in ε' and ε'' that are 10.94 and 2.50 in average, respectively.

There exists free charge density distribution in the interstitial of atoms on the Ti layers, especially on the Ti layers adjacent to Si layers for Ti_3SiC_2 crystal. Thus, Ti_3SiC_2 shows a higher electrical conductivity of 4.5×10^6 S/m at room temperature [23], which will result in the electric conduction loss for Ti_3SiC_2 samples under applied alternating field. For 10% and 20% Al doped Ti_3SiC_2 samples, the higher purity of Ti_3SiC_2 would lead to the increase of ε'', which represents the loss capacity for incident electromagnetic wave. Additionally, the incorporation of Al atoms into Ti_3SiC_2 crystal structure or the substitution of Al atoms on Si atoms of Ti_3SiC_2 structure causes the difference of valence bond between Ti–Si atoms and Ti–Al atoms [24]. This will form reorientation polarization and energy dissipation due to enhanced ionic bonding character by Al doping. The more Al atoms contained in Ti_3SiC_2 contribute to the higher ε' and ε'', so 20% Al-doped sample has the greater values in ε' and ε'' than 10% Al-doped sample. While Al content was up to 50%, the corresponding sample had the low purity of Ti_3SiC_2 phase, resulting in the decrease in ε' and ε''.