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Dielectric loss behavior and microwaves absorption properties of TiB₂ ceramic

Zhuoran Song¹, Mengxiao Sun¹, Lipeng Wu¹,², Fan Wu¹,² * and Aming Xie¹,² *

¹ School of Mechanical Engineering, Nanjing University of Science & Technology, Nanjing 210094, People’s Republic of China
² School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, People’s Republic of China

E-mail: wufan@njust.edu.cn and xieaming@njust.edu.cn

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Abstract

Searching for microwaves absorption (MA) with outstanding resistance to harsh condition shows great potential in various special applications. As a typical high-temperature and conducting ceramic, TiB₂ can meet this requirement, but its high electrical conductivity will lead to high reflection of electromagnetic waves. In this paper, we find that TiB₂ ceramic can exhibit excellent MA performance after doping by C/N elements. The chemical structures, dielectric properties and MA performance of ZrB₂ ceramic are systematically measured and analyzed. The MA performance of TiB₂ ceramic reaches −21 dB at 8.00 GHz under a thickness of 2 mm. The results indicate that the MA performance of ZrB₂ can be ascribed to the multiple nonlinear dielectric resonance and polarization relaxation mechanism. This research significantly expands the application scope of TiB₂ ceramic to MA area.

1. Introduction

During the past decade, much effort has focused on the development of high-performance materials for microwaves absorption (MA) [1–3]. Conventionally developed MA materials are usually metal/metal oxides including ZnO nanorods [4], Ag nanofibers [5, 6], NiCu alloy [7], and complex nanostructures; [8–12] conducting polymers including polyaniline(PANI) [13], poly (3, 4-ethylenedioxythiophene)(PEDOT) [14], and polypyrrole (PPy); [15–18] carbonaceous materials including reduced graphene oxide (RGO) [19, 20], and carbon-nanotube (CNT); [21] and their hybrids including metal oxide/sulfide complexes [22, 23], polymer complexes [24–27], RGO complexes [28–30], and CNT complex [31–33]. However, most of these reported MA materials cannot be considered to be used under harsh conditions, such as high temperature, high corrosion, high stress, and etc Therefore, searching for a MA material with excellent tolerance under harsh condition is highly desirable, but still a challenge up to date.

Recently, there are several reports on the development of high-temperature materials for microwaves applications. For example, ferromagnetic Ferroferric/cobalt /nickel have been extensively applied to prepare MA materials with high thermal stability, but are still limited to below the Curie temperature [34–36]. Reduced graphene oxide (RGO) exhibits an enhanced dielectric loss ability toward microwaves at elevated temperature, but is easily oxidized at atmosphere [20]. It is widely considered that silicon carbide (SiC) is a good candidate for design of MA materials with high thermostability, high strength, as well as high oxidation and corrosion resistance [37, 38]. However, the application of SiC in MA area is greatly limited on account of its low electrical conductivity [39]. In short, a high-temperature MA material should need not only high stability under extreme condition, but also appropriate electrical conductivity.

Ultrahigh temperature ceramics are a kind of conductive materials that can suffer from harsh thermal and corrosive environments [40]. Titanium diboride (TiB₂), as a representative ultrahigh temperature ceramic, shows high melting-point, metallic electrical conductivity, excellent thermal stability and outstanding resistance to harsh condition [40–43]. It is rationally considered that the high electrical conductivity makes TiB₂ have great potential in applications of electromagnetic interference shielding which rely heavily on the reflection rather
than absorption [44]. As a result, the MA properties of TiB₂ ceramic still remains to be investigated. In this work, we find that TiB₂ ceramic can exhibit great MA performance if doping TiB₂ with a bit of C/N elementals. The dielectric properties and MA mechanism of TiB₂ ceramic are systematically discussed. The research provides a possibility for the design and applications of ultrahigh temperature ceramics in MA area.

2. Experimental section

Partially doped TiB₂ (4.52 g cm⁻³) powder was custom-made from commercial company. The microtopography was observed on a scanning electron microscope (SEM, S4800, Hitachi) and a transmission electron microscope (TEM, Tecnai G2 F20, FEI). The XRD pattern was measured via an instrument (X’ Pert Pro, Philips). The thermogravimetric analysis was performed on TA SDT Q600 analyzer. X-ray photoelectron spectroscopy (XPS) was measured from ESCALABTM 250Xi instrument (Thermo Fisher Scientific). The complex permissivity was obtained from a VNA analyzer (N5242A PNA-X, Agilent), where the samples for test were prepared by pressing the mixture of TiB₂ ceramics/paraffin into coaxial ring (inner diameter: 3.0 mm, outer diameter: 7.03 mm). The reflection loss values were calculated by the following equations (1) and (2), according to the classical theory [3, 28],

\[
RL \text{ (dB)} = 20\log \left| \frac{Z - 1}{Z + 1} \right|
\]

\[
Z = \frac{Z_{in}}{Z_0} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tan h \left( \frac{2\pi fd}{c} \sqrt{\varepsilon_r \mu_r} \right)
\]

Where \(Z_0\) and \(c\) stand for the impedance and light speed in free space, respectively, \(f\) represents the test frequency, and \(d\) represents sample thickness.

3. Results and discussion

Under electron microscope, it is observed that TiB₂ ceramic shows a broad size distribution from tens nanometer to tens micrometer (figures 1a–d). The element of Ti distributes in accordance with TiB₂ in SEM image (figures 1e and f). But the signal of B element is very weak. Two reasons can be used to explain this phenomenon. One is the much lower sensitivity of B element under energy dispersive spectrometer than that of Ti element. The other is that the Ti/B atomic ratio in ceramic may be higher than pure TiB₂. Figure 2a displays the XRD pattern of TiB₂. The intense peaks at 27.4, 34.2, 44.5, 57.1, 61.2, 68.1, 78.5 and 88.4 degree can be well assigned to the (001), (100), (101), (002), (110), (102), (201), and (112) crystal face (PDF 65-1073), indicating the crystal nature of TiB₂ ceramic.

XPS was employed to explore the composition of TiB₂. As exhibited in figure 2b, TiB₂ ceramic is composed of O, Ti, N, C, and B elements. The peak of Ti 2p at 459 eV can be divided into three peaks with the binding energy of 464, 458 and 454 eV (figure 2c). The band of B 1 s with the binding energy around 190 eV can be separated into three peaks at 192, 190 and 187 eV (figure 2d). The atomic ratio of Ti and B elements is determined to be 22.61: 77.39, near to 1: 7, which is much higher than that of 1 : 2. It indicates that some of the B atoms in TiB₂ ceramic should be bonded to N or C atoms. The core-level spectrum of C 1 s was provided to indicate the existence of B-C bonding moieties. The presence of N 1s peak with the binding energy of 397.8 eV in full XPS spectrum indicates the existence of B–N bonding in TiB₂ ceramic (figure 2b). The O element should be made up of adsorbed oxygen, and carbon bonded oxygen such as O=C=O/C–O=C=O which is evidenced by C1s spectrum (figure 2e). In short, the TiB₂ can be deemed as a kind of C/N-doped ceramic. Figure 2f shows the weight loss curve of TiB₂ during a heating process (TG analysis under air). It is found that TiB₂ ceramic keeps stable at least 800 °C, indicating that this ceramic can be used as a high-temperature material.

Figure 3 exhibits the frequency dependent complex permittivity of TiB₂ ceramic with different filler loading ratio. It is observed that the permittivity presents a frequency interval, where the real part (\(\varepsilon'\)) gets the maximal value at 14.5 GHz then drops to the minimum at 15.9 GHz, and the image part (\(\varepsilon''\)) exhibits a peak at 15.3 GHz (figure 3a). This phenomenon is the typical characteristic of nonlinear resonant behavior [45, 46]. When the filler loading ratio increases to 35 vol%, dual nonlinear resonant peaks around 14.9 GHz and 17.0 GHz are observed in the permittivity (figure 3b). It is noteworthy to point out that the \(\varepsilon''\) curve shows negative values from 15.7 to 18 GHz. One intense resonance around 12.1 GHz and two weak peaks at 7.1 GHz and 15.9 GHz appear at filler loading ratio of 45 vol% (figure 3c). Under 60 vol%, the permittivity exhibits two intense resonant peaks around 5.3 GHz and 11.3 GHz (figure 3d), indicating that the maximal dielectric loss may take place in the
Figure 1. The (a), (b) SEM images, (c), (d) TEM images, and (e)–(g) elemental mapping analysis of TiB$_2$ ceramic.

Figure 2. The (a) XRD pattern, (b) XPS survey curve, core-level spectra of (c) Ti 2p, (d) B 1 s, and (e) C 1 s, and (f) TG analysis of TiB$_2$ ceramic.
frequency area. It is found that the resonance intensity of TiB₂ ceramic enhances remarkably with the increasing of filler loading ratio.

Figure 4a shows variation curves of tanδ values versus frequency, which is used to evaluate the dielectric loss ability of a material. It is observed that the dielectric loss of microwaves by TiB₂ ceramic under a lower filler loading ratio than 35 vol% is very weak (Blue and red lines in figure 4a). This is most probably ascribed to ε″ values and weak nonlinear resonance intensity, evidenced by figures 3a and b. The curve of tanδ presents an intense dielectric loss peak centered at 12.2 GHz (Green line in figure 4a), which can be attributed to the intense
nonlinear resonance around that frequency. Besides, two moderate resonances could also cause obvious dielectric loss peaks. For TiB$_2$ with a filler loading ratio of 60 vol.%, the value of dielectric loss increases sharply which corresponds well to the resonant frequency (Yellow line in figure 4a), indicating high potential of this material in application in MA. Figure 4b displays the MA performance of TiB$_2$ ceramic under different filler loading ratio. As is well known, it is normally that a material with high electrical conductivity should be designed for electromagnetic shielding that considers reflection rather than electromagnetic absorption [44]. Therefore, TiB$_2$ ceramic should not be deemed as microwaves absorbent, on account of its high conductivity [40, 41]. But here TiB$_2$ ceramic exhibits good MA performance especially at the frequency lower than 10 GHz, where the maximal reflection loss gets to $-21$ dB (figure 4b). It is also observed in figure 4b that the maximal absorption shift from high to low frequency with the increasing of filler loading ratio. This good absorption performance most probably originates from predominant resonance loss on microwaves. Besides, the C/N doping of TiB$_2$ ceramic that causes interfacial attenuation may contribute to the MA.

Debye theory was adopted to determine the polarization relaxation loss by heterogeneous interfaces, which the $\varepsilon'$ and $\varepsilon''$ meet the relationship as formula (3) [47],

$$
\left(\frac{\varepsilon' - \varepsilon_s + \varepsilon_\infty}{2}\right)^2 + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2
$$

Where $\varepsilon_s$ is static permittivity, $\varepsilon_\infty$ represents complex permittivity at high-frequency limit.

The Debye theory indicates that one circle centered at $((\varepsilon_s + \varepsilon_\infty)/2, 0)$ corresponds one Debye relaxation process. But under complicated practical condition, Debye relaxation often appears as irregular semicircles, where one semicircle may imply more than one relaxation processes [47, 48]. The cole-cole curves of TiB$_2$ ceramic were plotted as shown in figure 5. According to the previous research [39, 49], the relaxation of permittivity is attributed to polarization by defect dipoles. It is found that TiB$_2$ ceramic with low filler loading ratios shows one circle or semicircle (figures 5a and b). When the loading ratio increases to 45 vol.%, multi-semicircles can be clearly observed (figure 5c), indicating the polarization relaxation enhances obviously. More importantly, a large irregular circle accompanying with multi-semicircles appear when loading ratio reaches 60 vol.%, which corresponds well to the resonant frequency (Yellow line in figure 4a), indicating high potential of this material in application in MA.

![Figure 5. Cole-cole plots of TiB$_2$ ceramic with filler loading ratios of (a) 20 vol%, (b) 35 vol%, (c) 45 vol%, and (d) 60 vol%](image)
vol% (figure 5d), further demonstrating the enhancing polarization relaxation with increasing of filler loading ratio. It is indicated by the above results that the polarization relaxation exists in ceramic and contributes to the MA. The existence of heterogeneous interfaces in TiB₂ ceramic should be, most probably, originated from the C/N doping, evidenced by the XPS results.

4. Conclusion
In summary, we report the chemical structures, dielectric properties and MA performance of TiB₂ ceramic. The structural characterization demonstrates that the TiB₂ ceramic is doped by a bit of C/N elements, but shows good crystallinity. It is inferred that heterogenous interfaces should exist in TiB₂ ceramic on account of the C/N doping. As expected, TiB₂ ceramic exhibits excellent high-temperature stability, evidenced by TG analysis. The complex permittivity of TiB₂ were measured, and show multiple nonlinear resonance feature at microwaves band. It is found that the resonance intensity increases apparently with the increasing of filler loading ratio. It is these nonlinear resonances that leads to high MA performance of TiB₂ ceramic. In addition, the polarization relaxation in TiB₂ ceramic contributes to MA performance. Under 2 mm, the TiB₂ shows a filler-loading dependent MA performance, and reaches ~21 dB at 8.00 GHz. This research greatly promotes the development and progress of heat-resisting MA materials.

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Data availability statement
The data that supports the findings of this study are available within the article.

ORCID iDs
Fan Wu https://orcid.org/0000-0002-0468-2868
Aming Xie https://orcid.org/0000-0001-5381-0689

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