Surface-modified Zn0.5Ti0.5NbO4 particles filled polytetrafluoroethylene composite with extremely low dielectric loss and stable temperature dependence

Hao WANG
School of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

Fuming ZHOU
School of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

Jianming GUO
School of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

Yuanyuan ZHANG
Jiaxing Glead Electronics Co., Ltd., Jiaxing 314003, China

Hui YANG
School of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

Recommended Citation
Hao WANG, Fuming ZHOU, Jianming GUO et al. Surface-modified Zn0.5Ti0.5NbO4 particles filled polytetrafluoroethylene composite with extremely low dielectric loss and stable temperature dependence. Journal of Advanced Ceramics 2020, 9(6): 726-738.

This Research Article is brought to you for free and open access by Tsinghua University Press: Journals Publishing. It has been accepted for inclusion in Journal of Advanced Ceramics by an authorized editor of Tsinghua University Press: Journals Publishing.
Surface-modified Zn0.5Ti0.5NbO4 particles filled polytetrafluoroethylene composite with extremely low dielectric loss and stable temperature dependence

Authors
Hao WANG, Fuming ZHOU, Jianming GUO, Yuanyuan ZHANG, Hui YANG, and Qilong ZHANG

This research article is available in Journal of Advanced Ceramics: https://dc.tsinghuajournals.com/journal-of-advanced-ceramics/vol9/iss6/7
Surface-modified Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ particles filled polytetrafluoroethylene composite with extremely low dielectric loss and stable temperature dependence

Hao WANG$^a$, Fuming ZHOU$^a$, Jianming GUO$^a$, Yuanyuan ZHANG$^b$, Hui YANG$^a$, Qilong ZHANG$^a$,*

$^a$School of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

$^b$Jiaxing Glead Electronics Co., Ltd., Jiaxing 314003, China

Received: April 16, 2020; Revised: June 19, 2020; Accepted: July 13, 2020

© The Author(s) 2020.

Abstract: Polymer-ceramic composites are widely applied in microwave substrate materials due to the excellent dielectric properties and simple preparation process recently. Polytetrafluoroethylene-based (PTFE) composites filled with Zn$_{0.5}$Ti$_{0.5}$NbO$_4$ (ZTN) ceramic particles were fabricated by hot-pressing. The particles were modified by C$_{14}$H$_{19}$F$_{13}$O$_3$Si to enhance the interface compatibility between PTFE and ZTN powders, which was characterized by X-ray photoelectron spectroscopy (XPS) and contact angle. The surface characteristic of particles transformed into hydrophobicity and tight microstructure as well as better dielectric properties were obtained after the surface modification. The microstructure, dielectric, thermal, mechanical properties, and water absorption of the composites concerning ZTN content were investigated. Modified ZTN/PTFE composites with 50 vol% ZTN particles exhibit excellent dielectric properties with a high dielectric constant of 8.3, an extremely low dielectric loss of 0.00055 at 7 GHz, and a stable temperature coefficient of the dielectric constant of $-12.2$ ppm/°C. All the properties show modified ZTN particles filled PTFE composite is the potential material for microwave substrate application.

Keywords: composites; dielectric properties; niobium; substrate

1 Introduction

Recently, the 5th-generation communication system, integrated circuit, satellite base station, auto anti-collision system, radar systems, and electronic navigation technology are developing rapidly, which puts forward the higher requirement for advanced substrate materials, peculiarly guaranteeing the signal transmit with high speed and high frequency [1–3]. Because of the perfect combination properties and easy fabrication processing, ceramic particles filled polymer composite substrates have always been paid close attention. In all kinds of polymer, PTFE exhibits huge advantages for advanced substrate materials due to the low dielectric constant ($\varepsilon$), low dielectric loss ($\tan\delta$), and perfect chemical and thermal stability. However, the high coefficient of thermal expansion (CTE) and poor temperature coefficient of dielectric constant ($\tau_\varepsilon$) limit application for substrate
material. Therefore, various particles had been filled in PTFE to fabricate composites for microwave substrate application [4,5].

PTFE-based substrate material with high $\varepsilon$ has attracted increasing attention due to the specific application in recent years. In previous studies, PTFE/0.55ZrTi$_2$O$_6$–0.45ZnNb$_2$O$_6$ composites exhibited the best dielectric properties: $\varepsilon = 7.32$, $\tan\delta = 0.0015$, and $\tau_\varepsilon = -84$ ppm/$^\circ$C (10 GHz) at the powder content of 46 vol% [6]. The (Na$_{0.6}$Li$_{0.4}$)$_{0.5}$Nd$_{0.5}$TiO$_3$ and glass fiber were filled into PTFE matrix to fabricate composite substrate, and the composites showed the best dielectric properties: $\varepsilon = 10.4$, $\tan\delta = 0.0026$ (10 GHz), and excellent $\tau_\varepsilon = -0.9$ ppm/$^\circ$C when the weight fraction of fillers was 60 wt% [7]. PTFE/Ca$_{0.55}$Nd$_{0.3}$TiO$_3$ (CNT) composites possessed the best dielectric properties: $\varepsilon = 12$, and low $\tan\delta = 0.00085$ (10 GHz) at 50 vol% filler contents; the PTFE/Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ composite exhibited the dielectric properties: $\varepsilon = 6.7$, $\tan\delta = 0.003$ (X-band) when the weight fraction of particles was 76 wt%, but the $\tau_\varepsilon$ of both composites were not studied [8,9]. The $\varepsilon$, $\tan\delta$, and $\tau_\varepsilon$ have always been the key properties for substrate materials. The $\varepsilon$ determines the application fields of substrates, $\tan\delta$ influences the signal transmission loss, and the $\tau_\varepsilon$ affects the temperature dependence of dielectric property and the application outdoors. The $\varepsilon$, $\tan\delta$, and $\tau_\varepsilon$ can be adjusted by changing the volume fraction of fillers. However, according to the previous studies, the fabrication of substrate materials with high $\varepsilon$, extremely low $\tan\delta$ (< 0.001), and stable $\tau_\varepsilon$ simultaneously, is still very tough, which primarily ascribes the hardness of manufacture of appropriate particles with advanced dielectric properties.

As reported in Ref. [10], Zn$_{0.5}$Ti$_{0.5}$Nb$_2$O$_6$ (ZTN) microwave dielectric ceramic exhibited dielectric properties with high $\varepsilon$ of 37.4, ultrahigh $Q\times f$ of 194,000 GHz and negative temperature coefficient of resonant frequency ($\tau_\varepsilon$) of -58 ppm/$^\circ$C, which is theoretically the potential fillers for the exploitation of substrate materials with high $\varepsilon$, low $\tan\delta$, and can compensate the poor $\tau_\varepsilon$ of PTFE to obtain composites with appropriate $\tau_\varepsilon$. Meanwhile, PTFE and ZTN ceramic particles own different surface properties, which would cause the usual problem (antipathic interface) in polymer-ceramic composites [11]. The surface modification of ceramic powders through coupling agents is an effective approach to solve the problem. KH550, PTMS, TEOS, TBT, and C$_{14}$H$_{30}$F$_{13}$SiO$_3$Si, etc. have been applied in various polymer-ceramic systems according to the component of the polymer matrix [12–15]. Recently, C$_{14}$H$_{10}$F$_{13}$Si has been used in PTFE-based composites due to the special function groups of –OCH$_3$CH$_3$ which can be hydrolyzed and –(CF$_2$)$_2$CF$_3$ similar to the structure of PTFE matrix [3]. Because of the two functional groups, C$_{14}$H$_{10}$F$_{13}$SiO$_3$Si can act as the “bridge” between the PTFE matrix and ZTN powders, which could enhance the interface compatibility and improve consistency. In this study, ZTN ceramic particles were treated using C$_{14}$H$_{10}$F$_{13}$SiO$_3$Si, and then filled in PTFE to fabricate ZTN/PTFE composites. The effects of ZTN loading on morphology, dielectric, thermal, mechanical properties, as well as moisture absorption and the microstructure, dielectric properties of untreated ZTN/PTFE composites, had been investigated systematically.

2 Experimental

2.1 Fabrication of ZTN ceramic powders

ZTN ceramic powders were synthesized according to the solid-state method. ZnO, TiO$_2$, and Nb$_2$O$_5$ powders (all with 99.99% purity) were purchased from Aladdin Biochemical Technology Co., Ltd., China, and weighed following the ZTN stoichiometric ratio. All the powders were mixed with ethyl alcohol and underwent a ball-milling process for 12 h. After drying at 80 $^\circ$C for 24 h removing ethanol, the mixture was calcined for 4 h at 1100 $^\circ$C. The powders went through the ball-milling process again for 24 h and dried at 80 $^\circ$C to acquire homogeneous particle size.

2.2 Surface modification of ZTN ceramic powders

As shown in Fig. S1 in the Electronic Supplementary Material (ESM), the content of C$_{14}$H$_{10}$F$_{13}$SiO$_3$Si (TCI Corporation, Japan) should be fixed at 2 wt% of ZTN powders. C$_{14}$H$_{10}$F$_{13}$SiO$_3$Si and deionized water were added into ethanol and mixed at 55 $^\circ$C for 1 h. Afterwards, all the solution was mixed with the suspension of ZTN powders and ethanol at 60 $^\circ$C for 6 h. The surface-treated ZTN powders were acquired after the heat treatment for 24 h at 120 $^\circ$C.

2.3 Fabrication of ZTN/PTFE composites

The volume fractions of ZTN particles in the composites changed from 20 vol% to 60 vol%. PTFE suspension and ZTN powders were weighed and mixed using magnetic-stirring for 12 h. Afterwards, the above

www.springer.com/journal/40145
mixture was heated to 100 °C for 24 h to wipe off the absorbed water and ethanol, and then dried at 280 °C for 6 h to remove the surfactant in suspension. ZTN/PTFE composites were synthesized through hot-pressing sintering at 25 MPa and 360 °C for 2 h. The diagram illustrating the fabrication of modified ZTN/PTFE composites is shown in Fig. 1.

2.4 Characterization

The morphology of untreated ZTN powders, modified ZTN powders, surface, and cross-sectional images of ZTN/PTFE composites were characterized by the field emission scanning electron microscopy (FESEM; SU8010, Hitachi Ltd., Japan). Untreated and modified ZTN powders were added into ethanol and the uniform suspension was obtained by ultrasonic treatment for 30 min. Then, the suspension was poured onto the surface of alumina tape and dried to fabricate samples for SEM. The composites were put in liquid nitrogen and fractured to obtain the SEM samples for cross-sectional images. The porosity and density of all samples were measured by Archimedes’ method. The surface modification of ZTN powders was characterized by X-ray photoelectron (XPS; Al Kα, AXIS SUPRA, UK) and Fourier transform infrared spectrometer (FTIR, Nicolet 5700, Thermo Nicolet, USA). X-ray powder diffraction (XRD, EMPYREAN, PANalytical Co., the Netherlands) with Cu Kα radiation was employed to characterize the crystal phase of ZTN powders and ZTN/PTFE composites. The video-based contact angle measuring device (OCA 20, Dataphysics, Germany) was used to reveal the variation of the contact angle on the surface of ZTN powders. The laser particle analyzer (Beckman Coulter LS13320, USA) was employed to study the particle size distribution of ZTN powders. The dielectric properties were measured by Agilent E5071C network analyzer according to the Hakki and Coleman method in the TE011 mode at about 7 GHz. The flexure strength was tested by the universal materials testing machine (CMT5205) according to IPC-TM-650 2.4.4B. TMA SS7300 was utilized to measure the coefficient of thermal expansion (CTE) according to IPC-TM-650 2.4.41. The moisture absorption was studied on the basis of IPC-TM-650 2.6.2. Hot Disk TPS 2500S was employed to measure the thermal conductivity and thermal diffusivity with the isotropous model.

3 Results and discussion

3.1 Microstructure analysis

The XRD pattern of ZTN ceramic powders and ZTN/PTFE composite is exhibited in Fig. 2. Peaks of ZTN powders are consistent with the result of Tseng’s work [10], which indicates that Zn₀.₅T₁₀.₅NbO₄ is
fabricated successfully and there are no impurity phases. XRD patterns of ZTN/PTFE composites are composed of the peaks of the PTFE matrix and ZTN ceramic. The peak at about 18° matches with PTFE (#JCPDS 00-054-1595) and PTFE peak height decreases persistently with the ZTN loading increases, which is attributed to the relation between the peak height and the content of components. Furthermore, there are no other phases that existed in the composites, which manifest that the uniform mixture is fabricated and the ZTN ceramic powders as well as PTFE show perfect chemical stability.

XPS, FTIR, and contact angle change are utilized to characterize surface modification of ZTN particles. The elements in both modified and untreated particles were detected by XPS full spectrum and the carbon fine spectrum was used to reveal carbon states in different organic groups that existed in C_{14}H_{19}F_{13}O_{3}Si. Due to the hydrophobicity caused by C_{14}H_{19}F_{13}O_{3}Si modification, the change of contact angle of untreated and modified ZTN powders was characterized. Figure 3 shows the XPS full spectra of untreated and modified ZTN powders. Zinc, oxygen, titanium, carbon, and niobium can be detected in both the spectra and every corresponding peak in the two spectra shows nearly the same position [16], which is attributed to the elemental composition of Zn_{0.5}Ti_{0.5}NbO_{4}. However, the obvious F_{1s} and F_{Auger} peaks appear in the modified ZTN powders, in the same energy position, no peak exists in untreated ZTN particles, which ascribes F in C_{14}H_{19}F_{13}O_{3}Si coated on the surface of modified ZTN powders. Meanwhile, there is only one obvious and strong carbon peak in the untreated powders, but in the modified ZTN powders, different carbon peaks appear, which confirms that there are different carbon states with various binding energy. The fine carbon spectrum was used to characterize the carbon states of modified powders. The spectra of raw data, fitting peak sum, and C–H, C–F, C 1s, C–F, C–F 3 with a binding energy of 283.6, 290.5, 284.8, 289.8, and 292.9 eV respectively are exhibited in Fig. 4. It is evident that fitting peak sum spectrum matches with raw data basically, which confirms that (CH_{2})_{2}-(CF_{2})_{5}-CF_{3} existed in C_{14}H_{19}F_{13}O_{3}Si would cause the appearance of different carbon states and the deviation of carbon binding energy. The untreated powders only show the C 1s peak, indicating that C_{14}H_{19}F_{13}O_{3}Si has been introduced into the modified ZTN powders. To highlight the huge improvement in the hydrophobic property of particles through modification of C_{14}H_{19}F_{13}O_{3}Si, the contact angle of untreated as well as modified particles is shown in Fig. 5. The untreated ZTN powders exhibit hygroscopicity with the contact angle of 16.6°, and after the modification, the contact angle is improved to 139°, which indicates

![Fig. 2](image1)

**Fig. 2** XRD patterns of ZTN powders and ZTN/PTFE composites.

![Fig. 3](image2)

**Fig. 3** XPS spectra of modified ZTN powders and untreated ZTN powders.

![Fig. 4](image3)

**Fig. 4** Carbon XPS spectra of modified ZTN powders.
the strong hydrophobicity of modified ZTN powders caused by long \(-\text{CF}_2\)- chain. Meanwhile, the FTIR spectrum was also used to show the surface modification of ZTN powders and explained whether \(\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}\) still exists on the surface of powders after the high-temperature treatment during the fabrication of composites. Figure S2 in the ESM shows the FTIR spectra of original, modified powders, and modified powders through \(380^\circ\text{C}\) heat treatment. All the spectra own the peak at 3435 cm\(^{-1}\), which is corresponding to the \(-\text{OH}\) on the surface of powders. Many complex peaks in the range of 1000–1500 cm\(^{-1}\) appear in the spectra of modified powders and modified powders through heat treatment, which may be the \(-\text{F}_2\) and \(-\text{F}_3\) groups because the infrared characteristic peaks of these groups are easily affected by other organic groups and specific peak positions can not be confirmed. However, in the same wavenumber range, no peaks appear in the FTIR spectrum of original ZTN powders, which demonstrates that the surface of ZTN powders has been modified successfully by \(\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}\) and the high-temperature heat treatment during the fabrication of composites would not destroy the modification effect drastically. All the results concluding XPS, FTIR, and contact angle can confirm that \(\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}\) has covered ZTN powders successfully. Due to special groups of \(-\text{C(F}_2)\text{C(F}_3\text{)}\) existed in \(\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}\), particularly \(-\text{CF}_2\) similar to the structure of PTFE matrix, the interface compatibility between ZTN ceramic and PTFE can be forecasted to be improved by the modification of silane coupling agent, which would influence the microstructure and properties of composites theoretically.

The property of particles filled polymer composite chiefly depends on the property of every component. Nevertheless, particle size, morphology features, uniformity, and interface compatibility between ceramic and polymer are also significant \([17,18]\). Figure 6 shows the SEM images of original, modified ZTN powders, and the particle size distribution of ZTN powders. It is evident that untreated particles are severely agglomerated and the surface is rough, which could impute that the raw ZTN powders own strong hygroscopicity and too many \(-\text{OH}\) groups on the surface cause strong interaction between the powders. The modified powders are well-dispersed and show a smooth surface, which is due to that the modification of \(\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_3\text{Si}\) can form the coated polymer layer on the surface of the powder to decrease the binding force between the powders. The particle size distribution of ZTN particles has been characterized and exhibited in Fig. 6(c). The particle size is distributed uniformly in the range of 0–4 \(\mu\text{m}\) and the mean size is about 1.3 \(\mu\text{m}\).

Figure 7 shows the surface morphology features of modified ZTN powders filled PTFE composites with the ceramic loading from 20 vol% to 60 vol% and the untreated ZTN/PTFE composites with ZTN loading of

---

**Fig. 5** Contact angles of water drop on (a) the modified ZTN powders and (b) untreated ZTN powders.

**Fig. 6** SEM images of (a) untreated ZTN powders and (b) modified ZTN powders; (c) particle size distribution of modified ZTN powders.
40 vol%. All the composites with the volume fraction of ZTN powders below 60 vol% exhibit smooth and compact surface, whereas many pores appear on the surface when the loading of powders reaches 60 vol%, which is due to that the PTFE matrix could encase the particles absolutely at relative low ZTN loading and the particles will contact with each other when the content of powders exceeds polymer matrix. Hence, there would be pores, defects, and powders that appeared on the composite’s surface. Untreated ZTN/PTFE composites with the loading of the ceramic powder of 40 vol% are also depicted in Fig. 7(f) to compare with the modified ZTN powders filled PTFE composites to show the influence of C14H19F13O3Si on the surface morphology. The surface of untreated ZTN/PTFE composite is rougher than the modified one and many pores appear, which is attributed to the improvement of dispersity and the interface compatibility between powders and the polymer caused by the modification. The cross-sectional micrographs of modified ZTN/PTFE composites with powder contents within 20–60 vol% and untreated ZTN powders filled PTFE composite with 60 vol% ceramic loading are exhibited in Fig. 8. When the volume fraction of ZTN powders stay between 20 vol% and 50 vol%, all the cross-sectional images of modified ZTN/PTFE composites exhibit relatively compact microstructure, and increasing pore amount and particles do not aggregate in the polymer matrix, which is owning

![Fig. 7](image1.png) Surface SEM micrographs of modified ZTN/PTFE composites: (a) 20 vol%, (b) 30 vol%, (c) 40 vol%, (d) 50 vol%, (e) 60 vol%, and (f) untreated ZTN/PTFE composite of 40 vol%.

![Fig. 8](image2.png) Cross-sectional SEM micrographs of modified ZTN/PTFE composites: (a) 20 vol%, (b) 30 vol%, (c) 40 vol%, (d) 50 vol%, (e) 60 vol%, and (f) untreated ZTN/PTFE composite of 60 vol%.

www.springer.com/journal/40145
to that the powders can be wrapped by PTFE completely at such low powder loading. Nevertheless, when the ZTN loading reaches 60 vol%, many pores and the agglomeration appear in the cross-section, which ascribes the less volume fraction of polymer than ZTN powders. Meanwhile, the cross-sectional image of untreated ZTN/PTFE composites with ceramic powder loading of 60 vol% is shown in Fig. 8(f). Compared to the modified ZTN/PTFE composites with the same loading, the untreated ZTN/PTFE composites exhibit more pores and detects as well as loose microstructure, which confirms that the interface compatibility between ZTN powders and PTFE matrix is feeble in untreated ZTN/PTFE composites. The feeble compatibility is on the account of the enormous discrepancy existed in the interface energy of untreated powders and PTFE due to the extremely low surface energy of the PTFE matrix. Modification of C_{14}H_{19}F_{13}O_{3}Si improves the dispersibility of ZTN powders and the interface compatibility between particles and PTFE as shown in Figs. 6–8. Finally, compact and uniform microstructure for ZTN/PTFE composite is acquired, which ensures excellent properties. Figure 9 depicts the element mapping and content of all elements in cross-section of modified ZTN/PTFE composite with ZTN loading of 50 vol%. All the elements are detected to be the same with the components of ZTN ceramic and PTFE, such as zinc, titanium, oxygen, niobium, carbon, and fluorine. Meanwhile, all the elements are well-dispersed which manifest the homogeneous microstructure has been formed. The content of all elements investigated by SEM–EDS shown in Fig. 9(g) is corresponding to the ratio of ZTN powders and PTFE matrix, which verifies the reliability of experimental data.

3.2 Density, porosity, and water absorption

The porosity and relative density are the significant properties for substrate materials, which is due to that the moisture absorption, dielectric, and mechanical properties are influenced by the porosity. Table 1 shows the bulk density, theoretical density, porosity, relative density, and moisture absorption of different composites. The densities of ZTN ceramic and PTFE polymer are 5.14 and 2.2 g/cm³, respectively. With the volume

| Element | (at%) |
|---------|-------|
| O       | 25.77 |
| F       | 30.78 |
| Ti      | 3.43  |
| Zn      | 4.71  |
| Nb      | 5.69  |

Fig. 9 Corresponding element mappings of (a–f) Zn, Ti, O, Nb, C, and F, respectively; (g) EDS spectra and element content of ZTN/PTFE composite with 50 vol% loading.
fraction of ZTN powders increasing, porosity and moisture absorption all exhibit the increase, whereas relative density decreases. The porosity of ceramic particles filled polymer composites mainly depends on the contact among the particles and the interface compatibility between the polymer and fillers. The probability of contact among particles would increase as ZTN particle loading increases, thus resulting in an increase of porosity as well as the decrease of relative density. Moisture absorption is influenced by the porosity and relatively high porosity would cause higher moisture absorption. However, the porosity as well as water absorption maintains low levels when ZTN volume fraction is below 60 vol%, which can ascribe that particles can be encased absolutely by polymer to form tight microstructure at a low loading of fillers. As ZTN particle content reaches 60 vol%, the porosity and water absorption become higher, which is mainly due to the relatively less proportion of PTFE and too much contact among the particles. Meanwhile, all the above results can be confirmed from the microstructure of all the composites shown in Fig. 8. Generally, the following equations are used to calculate the theoretical density (\( \rho_0 \)) and the water absorption (\( W \)):

\[
\rho_0 = \sum_a \rho_a V_a
\]

\[
V_a = \frac{m_a}{\sum_a \rho_a}
\]

\[
W = \frac{m - m_0}{m_0}
\]

\[
\rho_t = \frac{\rho}{\rho_0}
\]

\[
p = \left(1 - \frac{\rho}{\rho_0}\right) \times 100\%
\]

where \( \rho_a \), \( V_a \), \( m_a \) represent density, volume proportion, and the weight of filled particles and polymer, respectively, \( m \) and \( m_0 \) represent the weight of substrate materials after absorbing moisture and primary weight, respectively. \( \rho_t \) and \( p \) represent the relative density and the porosity of composite, respectively. \( \rho \) and \( \rho_0 \) are the experimental density and theoretical density, respectively.

### 3.3 Dielectric properties

The \( \varepsilon \), tan\( \delta \), and \( \tau_e \) are the pivotal properties for substrate materials applied in the microwave frequency band. Many factors are influencing the dielectric properties of substrate materials, especially the properties of the individual component. However, the pores and defects in the substrate materials are other significant elements. As depicted in Figs. 10(a) and 10(b), the \( \varepsilon \) and tan\( \delta \) of untreated and modified ZTN/PTFE composites are characterized. As the volume proportion of ZTN particles increases from 20 vol% to 60 vol%, the \( \varepsilon \) and tan\( \delta \) of both kinds of ZTN/PTFE composites all exhibit the increase. The \( \varepsilon \) in the microwave frequency band mainly depends on the electron displacement polarization and ionic displacement polarization of materials. In the usual microwave frequency band, \( \varepsilon \) is mainly related to the microstructure of the material and is not influenced obviously by the frequency. Hence, the dielectric constant of composites mainly depends on the dielectric constant of every component and ZTN ceramic possesses \( \varepsilon \) of 37.5 which is much higher than the \( \varepsilon \) of PTFE (Section 2.2). Hence, the growth of \( \varepsilon \) of ZTN/PTFE composites is attributed to the growing volume fraction of ZTN ceramic particles with higher \( \varepsilon \). The tan\( \delta \) of the PTFE matrix and ZTN ceramic particles are the main factors influencing the tan\( \delta \) of ZTN/PTFE composites. PTFE owns the dielectric loss of about 0.0001 at high frequencies and ZTN ceramic possesses extremely low dielectric loss of about 0.0002 at around 7 GHz, thus making the tan\( \delta \) of all composites with various
ZTN contents stay in low values (< 0.001) and even the tanδ of modified ZTN/PTFE composites with the particle loading of 60 vol% is just 0.0009. Nevertheless, the pores are increasing continually with the growth of ZTN loading, which could be confirmed by the results of porosity analysis and SEM images. As for substrate materials, pores are another significant factor affecting the tanδ, which can explain why tanδ is increasing persistently with the ZTN loading increasing [19]. When the volume fraction of ZTN stays between 20 vol% and 50 vol%, the porosity of all the composites maintains a low value, which would cause the minor fluctuation of tanδ. Meanwhile, it is worth noting that the untreated ZTN/PTFE composites own inferior dielectric properties with lower ε and higher tanδ compared with improved ZTN/PTFE composites, which is mainly attributed to porosity discrepancy through modification of C14H19F13O3Si. From an analysis of cross-sectional SEM micrographs of untreated and modified ZTN/PTFE composites, modified ZTN filled PTFE composites exhibit tighter microstructure and fewer pores. High porosity would cause the reduction of ε and growth of tanδ.

Meanwhile, to confirm that the experimental data of ε is credible and predictable, the famous model (effective medium theory (EMT)) for the theoretical ε of polymer-based composites filled with ceramic powders was listed and compared with experimental ε. The equation for EMT model is shown as follows [20]:

$$\varepsilon_{\text{eff}} = \varepsilon_m \left[1 + \frac{V_f (\varepsilon_f - \varepsilon_m)}{\varepsilon_m + m (1 - V_f) (\varepsilon_f - \varepsilon_m)} \right]$$  \hspace{1cm} (4)

where ε eff , ε m , and ε f represent the theoretical dielectric constant, dielectric constant of polymers as well as ceramic, respectively. V f is the volume fraction of ceramic particles. The value of m is 0.25, which depends on the morphology and microstructure of the composites. Figure 10(c) shows the EMT model matches the experimental dielectric constant well and the same conclusion was also obtained in Ref. [8].

Due to that the τ ε of PTFE matrix is about −400 ppm/℃, the application of PTFE-based substrates is limited immensely out of doors. The calculation equation for τ ε of ceramic filled composites is as follows:

$$\tau_{\varepsilon} = \varepsilon \left(\frac{1}{3} \frac{\partial \alpha}{\partial T} - 3\alpha_L \right)$$  \hspace{1cm} (5)

where ε is the dielectric constant of the composites, $\frac{1}{3} \frac{\partial \alpha}{\partial T}$ represents the variation in the polarization of composites, and α L is the coefficient of thermal expansion. As for ZTN filled PTFE composites, $\frac{1}{3} \frac{\partial \alpha}{\partial T}$ and α L exhibit positive values. The addition of ZTN ceramic particles can improve the polarization of composites due to the higher polarization ability of ZTN (higher dielectric constant) compared with the PTFE matrix and decrease α L simultaneously, which would cause the improvement of the value of $\left(\frac{1}{3} \frac{\partial \alpha}{\partial T} - 3\alpha_L \right)$ with the increase of ZTN volume fraction. Furthermore, as shown in Fig. 10, the ε of the composites also increases with increasing of ZTN loading. All the above variations can cause the improvement of the τ ε of the composites according to Eq. (5). Ref. [9] showed better properties were often acquired at high filler loadings, especially the appropriate τ ε and low CTE. Therefore, the modified ZTN/PTFE composites with 20 vol% and 30 vol% filler loading are not studied. It is shown in Fig. 10(d) that the τ ε (temperature range of 25–80 ℃) increases from −98.9 to 24.4 ppm/℃ when the volume fraction increases from 40 vol% to 60 vol%. The τ ε of ZTN/PTFE composites are regulated to −12.2 ppm/℃ at the volume fraction of 50 vol%, which is stable for the substrate materials with high ε and shows huge preponderance compared with the previous studies.

3.4 Thermal properties

Figure 11 exhibits the thermal conductivity and thermal diffusivity of modified ZTN/PTFE composites containing various ceramic particles loading. When the volume fraction of ZTN varies from 20 vol% to 50 vol%, the thermal conductivity changes from 0.37 to 0.52 W/(m·K) and the thermal diffusivity shows the same increase with the variation from 0.13 to 0.25 mm2/s, which ascribes high thermal conductivity, high thermal diffusivity of ZTN ceramic powders compared with PTFE matrix, and the construction of thermal conductive path by ZTN particles. Nevertheless, the ZTN/PTFE composites with 60 vol% ceramic particles own inferior thermal conductivity and thermal diffusivity than 50 vol%, which may ascribe the higher porosity of ZTN/PTFE composites with 60 vol% powders. The pores possess very poor thermal conductivity and cause the separation between polymer and fillers, which may block heat transfer in the composites and result in low thermal
conductivity as well as low thermal diffusivity of the composites. Therefore, the best thermal conductivity and thermal diffusivity were obtained at the ZTN volume fraction of 50 vol% with 0.52 and 0.25 mm²/s, respectively.

The printed circuit board (PCB) is fabricated by adhering copper foil with substrate materials and for the sake of preventing delamination between copper foil and substrates during the drilling process, the CTE of substrates should match with copper foil. However, the PTFE matrix possesses a high CTE of about 109 ppm/℃, which is much larger than the copper foil (18 ppm/℃). The best way to adjust the CTE of substrates near to copper foil is filling modification. Figure 12 depicts the dynamic mechanical curves and CTE of ZTN/PTFE composites change within 96–25 ppm/℃ when the volume fraction of ZTN varies from 20 vol% to 60 vol%, which is mainly on account of the extremely low CTE of ZTN ceramic particles compared with PTFE. At last, at the ZTN volume fraction of 50 vol%, the substrate materials with acceptable CTE of 34 ppm/℃ are fabricated, which prevents the delamination to some extent.

3.5 Mechanical properties

The load-deflection curve, flexure strength of modified ZTN/PTFE composites including different ZTN loadings are shown in Fig. 13. The maximum force shown in Fig. 13(a) and the flexure strength shown in Fig. 13(b) all increase when the volume fraction changes from 20 vol% to 40 vol%. When the volume proportion of ZTN reaches 50 vol% and 60 vol%, the flexure strength decreases compared with the composites with 40 vol% ZTN powders. The polymer crosslink density, pore,
Fig. 12 (a) Dynamic mechanical curves and (b) CTE of ZTN/PTFE composites.

Fig. 13 (a) Variation of the load-deflection curve and (b) the flexure strength of ZTN/PTFE composites.

Table 2 Comparison of comprehensive properties of this study with other high dielectric constant PTFE-based composites

| Filler                     | Loading | $\varepsilon$ | $\tan\delta$ | $F$ (GHz) | $\tau_e$ (ppm/°C) | CTE (ppm/°C) | Moisture absorption (%) | Ref.   |
|----------------------------|---------|---------------|--------------|-----------|-------------------|--------------|------------------------|--------|
| TeO$_2$                    | 60 vol% | 5.6           | 0.006        | 7         | —                 | 32           | —                      | [23]   |
| (Ba,Mg$_{0.12}$)O$_3$      | 68 wt%  | 5.84          | 0.0015       | 10        | 10                | —            | —                      | [2]    |
| (Cu,Li,Sm)TiO$_3$          | 50 wt%  | 6.22          | 0.0012       | 10        | 10                | —            | —                      | [15]   |
| Ba (Mg$_{0.12}$)O$_3$       | 76 wt%  | 6.7           | 0.003        | X-band   | —                 | —            | 0.072                  | [9]    |
| 0.55ZrTi$_2$O$_4$·0.45ZnNb$_2$O$_6$ | 46 vol% | 7.32          | 0.0015       | 10        | −84               | 17.5         | —                      | [6]    |
| ZrTi$_2$O$_4$              | 46 vol% | 7.42          | 0.0022       | 10        | −89               | 20           | 0.15                   | [24]   |
| Li$_2$Mg$_2$TiO$_4$         | 70 wt%  | 6.17          | 0.0019       | 10        | 123               | —            | 0.16                   | [25]   |
| (Na$_{0.6}$Li$_{0.4}$)$_{0.5}$Nd$_{0.5}$TiO$_3$+glass fiber | 60 wt% | 10.4          | 0.0026       | 10        | −0.9              | —            | 0.34                   | [7]    |
| Ba$_{0.6}$Nd$_{0.4}$Ti$_2$O$_4$ | 70 wt% | 10.6          | 0.004        | 11.5      | 18                | —            | —                      | [26]   |
| Ca$_{0.12}$Nd$_{0.88}$TiO$_3$ | 50 vol% | 12            | 0.00085      | 10        | —                 | 35           | 0.27                   | [8]    |
| CaTiO$_3$                  | 40 vol% | 13            | 0.0053       | 5         | —                 | —            | —                      | [27]   |
| Zn$_{0.6}$Ti$_{0.4}$NbO$_4$ | 50 vol% | 8.3           | 0.00055      | 7         | −12.2             | 34           | 0.13                   | This study |

and defect would influence mechanical properties of composites [21]. When ZTN content ranges between 20 vol% and 40 vol%, all the composites own high specific density and low porosity. Hence, PTFE crosslink density is the main influence factor. The ZTN powders play a certain role as the nucleating agent for the PTFE matrix, which may improve the crosslink density and make the polymer matrix become uniform [21,22]. So, the flexure strength and maximum force are improved by ZTN powders at low filler loadings. However, when
the volume fraction increases to 50 vol% and 60 vol%, the high porosity and more defects cannot be ignored and become the primary affecting factors. The pores and defects would weaken the interaction force between the polymer and ZTN powders, which causes a decrease of flexure strength and the maximum force. Eventually, the appropriate flexure strength of 23 MPa for ZTN/PTFE composites is obtained when the loading of fillers is 50 vol%.

To highlight the dedication of modified ZTN/PTFE composites for substrate materials, Table 2 exhibits the previous studies concerning high $\varepsilon$ PTFE-based substrate materials [23–27]. ZTN/PTFE composites with high $\varepsilon$ (8.3), extremely low tan$\delta$ (0.00055), and highly stable $\tau_e$ (−12.2 ppm/$\degree C$) show excellent dielectric properties in high $\varepsilon$ PTFE-based substrate materials. Simultaneously, the thermal conductivity, CTE, moisture absorption, and flexure strength are all appropriate for the substrate materials. Therefore, the $\text{Zn}_0.5\text{Ti}_0.5\text{NbO}_4$ ceramic particles are the perfect filler for PTFE-based substrate materials [28–35].

4 Conclusions

PTFE-based substrate materials filled with $\text{Zn}_0.5\text{Ti}_0.5\text{NbO}_4$ (ZTN) particles modified by $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_{3}\text{Si}$ were fabricated by hot-pressing. The results of XPS and contact angle showed the surface of particles had been modified successfully. Tight microstructure and superior dielectric properties were also obtained after the modification. The dielectric, thermal, mechanical, morphology, porosity, and water absorption of ZTN/PTFE composites were studied systematically. As ZTN ceramic particles content increases within 20–60 vol%, $\varepsilon$ and tan$\delta$ both exhibit the growth, whereas tan$\delta$ stays low value at various ZTN contents, which is on account of the extremely low tan$\delta$ of PTFE matrix and ZTN ceramic. The $\tau_e$ of PTFE was compensated by ZTN ceramic from about −400 to −12.2 ppm/$\degree C$. The ZTN/PTFE composite possesses excellent dielectric properties at 50 vol% filler content: high $\varepsilon$ of 8.3, extremely low tan$\delta$ of 0.00055 at 7 GHz, and stable $\tau_e$ of −12.2 ppm/$\degree C$ as well as other appropriate properties including water absorption of 0.13%, CTE of 34 ppm/$\degree C$, the thermal conductivity of 0.52 W/(m·K), and flexure strength of 23 MPa. Therefore, $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{O}_{3}\text{Si}$ modified ZTN ceramic particles filled PTFE composite is latent material for microwave substrates.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 51772267) and the Key R&D Program of Zhejiang Province (Grant No. 2019C05001).

Electronic Supplementary Material

Supplementary material is available in the online version of this article at https://doi.org/10.1007/s40145-020-0409-2.

References

[1] Guo J, Zhao XT, Herisson de Beauvoir T, et al. Recent progress in applications of the cold sintering process for ceramic-polymer composites. Adv Funct Mater 2018, 28: 1801724.
[2] Qi YY, Luo Q, Shen J, et al. Surface modification of BMN particles with silane coupling agent for composites with PTFE. Appl Surf Sci 2017, 414: 147–152.
[3] Luo FC, Tang B, Fang ZX, et al. Polytetrafluoroethylene based, F8261 modified realization of $\text{Li}_2\text{SnMg}_{0.5}\text{O}_{3.5}$ filled composites. Appl Surf Sci 2020, 503: 144088.
[4] Pan C, Kou KC, Jia Q, et al. Improved thermal conductivity and dielectric properties of hBN/PTFE composites via surface treatment by silane coupling agent. Compos Part B: Eng 2017, 111: 83–90.
[5] Pan C, Kou KC, Zhang Y, et al. Enhanced through-plane thermal conductivity of PTFE composites with hybrid fillers of hexagonal boron nitride platelets and aluminum nitride particles. Compos Part B: Eng 2018, 153: 1–8.
[6] You YY, Yuan Y, Wu KT, et al. The dielectric and thermal properties of Mn-doped (1−x)ZrTiO$_3$–xZnNb$_2$O$_6$ filled PTFE composites. J Mater Sci: Mater Electron 2014, 25: 3010–3015.
[7] Li ZT, Yuan Y, Yao MH, et al. Synthesis and characterization of PTFE/(Na$x$Li$_{1−x}$)Nd$_2$TiO$_3$ composites with high dielectric constant and high temperature stability for microwave substrate applications. Ceram Int 2019, 45: 22015–22021.
[8] Peng HY, Ren HS, Dang MZ, et al. Novel high dielectric constant and low loss PTFE/CNT composites. Ceram Int 2018, 44: 16556–16560.
[9] James NK, Jacob KS, Murali KP, et al. Ba($\text{Mg}_{0.6}\text{Ta}_{0.4}$)$_3\text{O}_5$ filled PTFE composites for microwave substrate applications. Mater Chem Phys 2010, 122: 507–511.
[10] Tseng CF. Microwave dielectric properties of low loss microwave dielectric ceramics: $\text{A}_{0.5}\text{Ti}_3\text{NbO}_4$ (A = Zn, Co). J Eur Ceram Soc 2014, 34: 3641–3648.
[11] Zhang XH, Ma YH, Zhao CW, et al. High dielectric constant and low dielectric loss hybrid nanocomposites fabricated with ferroelectric polymer matrix and BaTiO$_3$ nanofibers modified with perfluoroalkylsilane. Appl Surf
Thomas S, Raman S, Mohanan P, et al. Effect of coupling agent on the thermal and dielectric properties of PTFE/Sm$_2$Si$_2$O$_7$ composites. Compos Part A: Appl Sci Manuf 2010, 41: 1148–1155.

Wu SY, Huang YL, Ma CCM, et al. Mechanical, thermal and electrical properties of aluminum nitride/polyetherimide composites. Compos Part A: Appl Sci Manuf 2011, 42: 1573–1583.

Shen YP, Gu AJ, Liang GZ, et al. High performance CaCu$_3$Ti$_5$O$_{16}$/cyanate ester composites with excellent dielectric properties and thermal resistance. Compos Part A: Appl Sci Manuf 2010, 41: 1668–1676.

Zheng L, Zhou J, Shen J, et al. TEOS surface modification of CLST ceramic particles for PTFE-based composites. J Mater Sci: Mater Electron 2018, 29: 17195–17200.

Park BH, Lee MH, Kim SB, et al. Evaluation of the surface properties of PTFE foam coating filter media using XPS and contact angle measurements. Surf Sci 2011, 257: 3769–3776.

Gu JW, Guo YQ, Lv Z, et al. Highly thermally conductive POSS-g-SiC$_6$P$_4$/UHMWPE composites with excellent dielectric properties and thermal stabilities. Compos Part A: Appl Sci Manuf 2015, 78: 95–101.

Liu LP, Lv F, Li PG, et al. Preparation of ultra-low dielectric constant silica/polyimide nanofiber membranes by electrospinning. Compos Part A: Appl Sci Manuf 2016, 84: 292–298.

Subodh G Pavithran C, Mohanan P, et al. PTFE/Sr$_2$Ce$_2$Ti$_5$O$_{16}$ polymer ceramic composites for electronic packaging applications. J Eur Ceram Soc 2007, 27: 3039–3044.

Sun YY, Zhang ZQ, Wong CP. Influence of interphase and moisture on the dielectric spectroscopy of epoxy/silica composites. Polymer 2005, 46: 2297–2305.

Varghese J, Nair DR, Mohanan P, et al. Dielectric, thermal and mechanical properties of zirconium silicate reinforced high density polyethylene composites for antenna applications. Phys Chem Chem Phys 2015, 17: 14943–14950.

Thomas S, Kavil J, Malayil AM. Dielectric properties of PTFE loaded with micro- and nano-Sm$_2$Si$_2$O$_7$ ceramics. J Mater Sci: Mater Electron 2016, 27: 9780–9788.

Subodh G, Joseph M, Mohanan P, et al. Low dielectric loss polytetrafluoroethylene/TeO$_2$ polymer composite materials. J Am Ceram Soc 2007, 90: 3507–3511.

Wu KT, Yuan Y, Zhang SR, et al. ZrTi$_2$O$_8$ filled PTFE composites for microwave substrate applications. J Polym Res 2013, 20: 223.

Luo FC, Tang B, Fang ZX, et al. Effects of coupling agent on the dielectric properties of PTFE based and Li$_2$Mg$_2$TiO$_6$ filled composites. Ceram Int 2019, 45: 20458–20464.

Jin SQ, Qu X, Huang BY, et al. Dielectric properties of modified BNT/PTFE composites for microwave RF antenna applications. J Mater Sci: Mater Electron 2016, 27: 8378–8383.

Hu YX, Zhang YM, Liu H, et al. Microwave dielectric properties of PTFE/CaTiO$_3$ polymer ceramic composites. Ceram Int 2011, 37: 1609–1613.

Manan A, Ullah Z, Ahmad S, et al. Phase microstructure evaluation and microwave dielectric properties of (1–x)Mg$_{0.95}$Ni$_{0.05}$TiO$_3$/Zn$_{0.02}$O$_{1-x}$/Ca$_{0.4}$La$_{0.6}$/TiO$_3$ ceramics. J Adv Ceram 2018, 7: 72–78.

Wu MJ, Zhang YC, Xiang MQ. Synthesis, characterization and dielectric properties of a novel temperature stable (1–x)CoTiNb$_2$O$_6$/ZnNb$_2$O$_6$ ceramic. J Adv Ceram 2019, 8: 228–237.

Hsiang HI, Chen CC, Yang SY. Microwave dielectric properties of Ca$_2$O–B$_2$O$_3$–SiO$_2$ glass for LTCC applications. J Adv Ceram 2019, 8: 345–351.

Cheng ZL, Ye F, Liu YS, et al. Mechanical and dielectric properties of porous and wave-transparent Si$_3$N$_4$/Si$_3$N$_4$ composite ceramics fabricated by 3D printing combined with chemical vapor infiltration. J Adv Ceram 2019, 8: 399–407.

Xu NX, Zhou JH, Yang H, et al. Structural evolution and microwave dielectric properties of MgO–LiF co-doped Li$_2$TiO$_3$ ceramics for LTCC applications. Ceram Int 2014, 40: 15191–15198.

Li ZH, Liu JS, Yuan Y, et al. Effects of surface fluoride-functionalizing of glass fiber on the properties of PTFE/glass fiber microwave composites. RSC Adv 2017, 7: 22810–22817.

Gorshkov N, Goffman V, Vikulova M, et al. Polytetrafluoroethylene-based high-k composites with low dielectric loss filled with priderite (K$_{1.46}$Ti$_{2.2}$Fe$_{0.3}$O$_{16}$). J Appl Polym Sci 2019, 137: 48762.

Yuan Y, Li ZT, Cao L, et al. Modification of Si$_3$N$_4$ ceramic powders and fabrication of Si$_3$N$_4$/PTFE composite substrate with high thermal conductivity. Ceram Int 2019, 45: 16569–16576.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.