

Frequency-temperature compensation mechanism for bismuth based dielectric/PTFE microwave composites

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Abstract The dielectric property and thermal expansion property of Bi₂O₃-ZnO-Nb₂O₃-based (BZN) ceramics filler reinforced composites have been investigated as a function of temperature range from -50 to 175 °C. The composites with adjustable temperature coefficient of frequency (τ_f) and dielectric temperature coefficient (α_ϵ) are achieved by filling the ceramic filler with different α_ϵ into polymer matrix. A series of polytetrafluoroethylene (PTFE) based composites blended with different amount of ceramic filler with different α_ϵ have been studied in this paper. The results indicated that with the amount of ceramic filler increasing, both of the relative permittivity and dissipation factor of composites increased. Composite filled with positive α_ϵ (245 ppm/°C) BZN ceramic filler (40 vol.%) has low α_ϵ (22 ppm/°C), while filled with near-zero α_ϵ (10 ppm/°C) BZN ceramic filler (40 vol.%) have low τ_f (-5 ppm/°C).

Keywords Composite · Dielectric property · Thermal expansion property · Temperature compensation

With the development of electronic information technology, the miniaturization and high-speed operation have become the predominant trend for electronic components, which requires the microwave dielectric materials with reasonable

relative permittivity, low dissipation factor, good frequency and temperature stability in a wide spectrum range, and good mechanical and thermal stability [1, 2]. In these properties, temperature coefficient of frequency (τ_f) has received intensive attention for reducing temperature-induced drift. The τ_f depends both on the coefficient of thermal expansion (CTE) and the dielectric constant of temperature coefficient (α_ϵ) [3–5]. However, polymer, widely used in packaging and substrates, has the main disadvantages of its high linear CTE and large negative α_ϵ . A mechanism for the temperature compensation of τ_f in polymer composites has been obtained by introducing ceramic filler with a different α_ϵ into polymer matrix [3]. For efficient filling of polymers by ceramics filler with different dielectric properties, high dielectric constant microwave composites with near-zero τ_f can be achieved and it would be an effective way to reduce CTE and α_ϵ [6].

In this paper, high dielectric constant microwave composites with adjustable τ_f are achieved by introducing two ceramic fillers with different α_ϵ into polymer matrix, one with a positive α_ϵ and the other with near-zero α_ϵ to match the negative α_ϵ of polymer. Polytetrafluoroethylene (PTFE) is selected as the polymer matrix. Bismuth-based pyrochlore dielectric ceramics (BZN) is selected as the ceramic filler. Due to its excellent dielectric and chemical properties, PTFE has been extensively applied to microwave devices. Bismuth-based pyrochlore dielectric ceramics (BZN) have attracted attention in microwave dielectric areas because of their low sintering temperature, high relative permittivity, and wide adjustable α_ϵ range [7]. BZN/PTFE microwave composites were prepared by using the filler processing technology. The effect of ceramic filler with different α_ϵ on thermal expansion property and dielectric property for BZN/PTFE microwave composites was investigated in detail. According to the experimental

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Table 1 Properties of BZN and PTFE^a.

	Volumetric density ($\rho/g\text{ cm}^{-3}$)	ϵ_r (900 MHz)	Tan δ (900 MHz)	ρ (Ω/cm)	α_ϵ (900 MHz; 25–85 °C; ppm/°C)	CTE (25–85 °C; ppm/°C)	Average particle size (μm)
N-BZN	6.98	94.0	5×10^{-3}	$\geq 10^{13}$	-10	1.2	0.5
P-BZN	7.02	165	1×10^{-2}	$\geq 10^{13}$	+245	1.2	0.5
PTFE	2.35	2.1	1×10^{-4}	$\geq 10^{14}$	-198	124	4

^a Measured at 25 °C

results, the theoretical model for calculating τ_f of BZN/PTFE composites was also discussed.

1 Experimental

Two kinds of BZN ceramic with different α_ϵ were synthesized from Bi_2O_3 , ZnO and Nb_2O_5 using oxide mixing method, one with a positive α_ϵ (abbreviated to P-BZN), and the other with near-zero α_ϵ (abbreviated to N-BZN). The ceramic samples were sintered in muffle furnace at 980 °C for 4 h. After the thermal treatment, the samples were grinded by mechanical and ball grind methods to obtain the BZN powder. Some properties of BZN fillers and PTFE powder are listed in Table 1.

To prepare BZN powder with a modified surface, it was first dipped in crylic acid solution, and dried to remove solvent after 30 min. The filler was then fully mixed with 2 wt.% tetrabutyl titanate. After removing the solvent, the BZN powder clad by coupling agent were obtained.

The PTFE powder and treated BZN powder with various BZN volume fraction (0–60%) were put into a beaker with solvent added, and dispersed by ultrasonic mixer for 6 h. Then the mixture was put on a stirrer and heated to 75 °C to remove the solvent by evaporation, and hence the homogeneously mixed BZN/PTFE powder was obtained. The mixed BZN/PTFE powder was then pressed under 60 MPa pressure for 60 s, and the obtained disc was sintered in muffle furnace from room temperature to 350 °C with a heating rate of 1 °C/min and the soaking time of 4 h.

The relative permittivity and dissipation factor were measured by HP4291B impedance analyzer, in the frequency range of 1 M–1 GHz. For the measurement, the samples are discs with a diameter of 15 mm. Dielectric measurements as a function of temperature were carried out with the HP4291B impedance analyzer at 900 MHz between -50 and 175 °C, with a heating rate of 3 °C/min. Thermal expansion was measured by a thermal dilatometer (DIL 402C, Netzche) with temperature rising of 3 °C/min between -100 and 200 °C. The τ_f is calculated from the CTE and the α_ϵ .

2 Results and discussion

2.1 Dielectric properties

Figure 1 shows the BZN volume fraction dependence of the relative permittivity and the dissipation factor at the frequency of 900 MHz. The results show that both the relative permittivity and the dissipation factor increase with the filler volume fraction increasing. The increase of the relative permittivity is attributed to the high relative permittivity of the BZN filler, which are introduced to the PTFE matrix. The dissipation factor increases due to the increase of the interface phase between BZN and PTFE [8].

Temperature dependence of the relative permittivity and dissipation factor for PTFE in the temperature range from -50 to 180 °C at 900 MHz is shown in Fig. 2(a), in which a step-like decrease occurs at 15–35 °C. The characteristic structural first-order phase transition of PTFE has been extensively studied [9]. These phase transitions in PTFE cause step-like changes of the specific volume and hence the relative permittivity also shows a step-like decrease in the vicinity of phase transitions temperature.

The relative permittivity and dissipation factor as a function of temperature for composites fill with 40 vol.% of

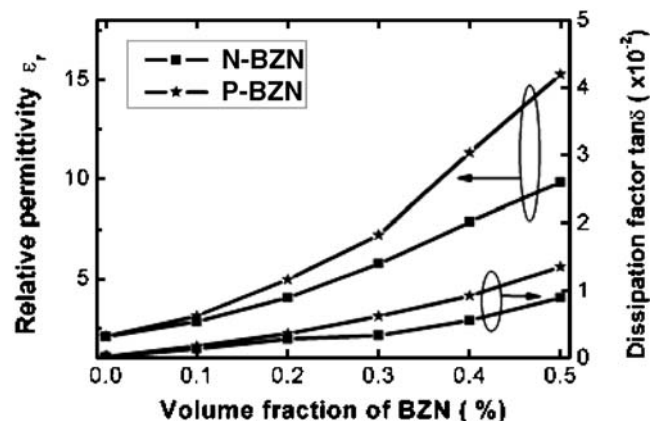
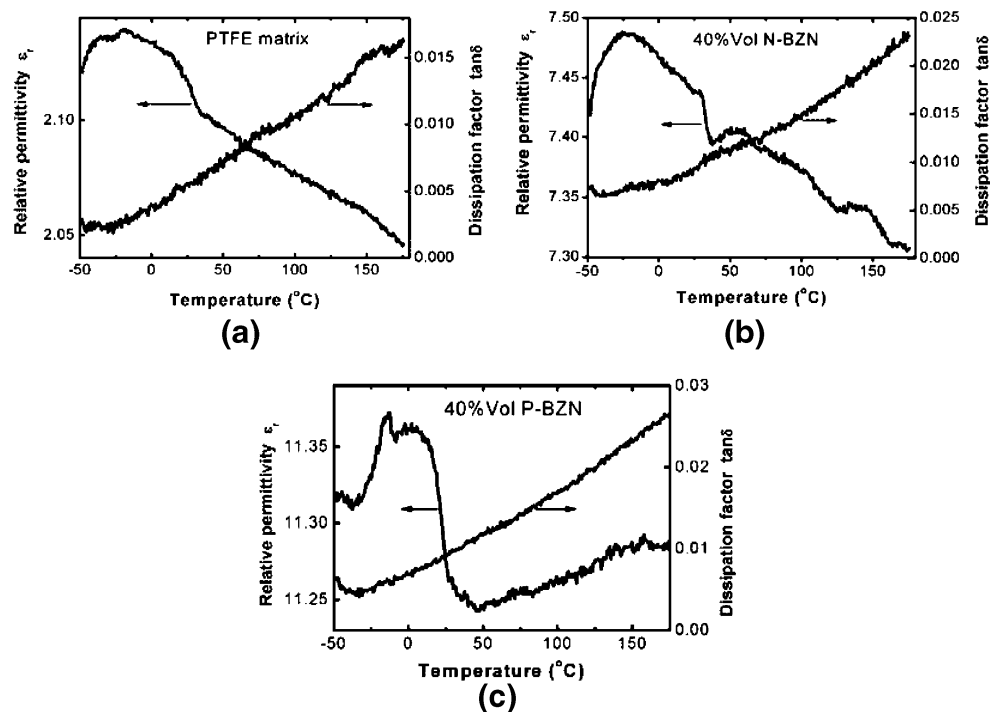


Fig. 1 The relative permittivity and dissipation factor as a function of different filler volume fractions for composites with N-BZN (filled squares) filler and P-BZN (asterisks) filler at room temperature and 900 MHz

Fig. 2 (a) Temperature dependence of the relative permittivity and dissipation factor for PTFE at 900 MHz. (b) The relative permittivity and dissipation factor as a function of temperature for composites with 40 vol.% of N-BZN at 900 MHz. (c) The relative permittivity and dissipation factor as a function of temperature for composites with 40 vol.% of P-BZN at 900 MHz



N-BZN and 40 vol.% of P-BZN at 900 MHz are shown in Fig. 2(b) and (c), respectively. The step-like changes of the relative permittivity at 15–35 °C could be observed in both figures for all composites. Both transitions are native characteristics of PTFE, which have been inherited by the composites.

In the N-BZN/PTFE composites, the relative permittivity shows some temperature compensation, although the slope is negative over the temperature range due to the major contribution of PTFE matrix. In the P-BZN/PTFE composites, the relative permittivity shows slightly increase with temperature increases in the range from 35 to 200 °C. This can be attributed to the fact that the P-BZN filler have larger positive α_ϵ than the PTFE. However, the temperature compensation of α_ϵ shows less influence the temperature-dependent of the dissipation factor. As shown in Fig. 2, the dissipation factor is low, with only a slight increase with the increase of temperature.

2.2 Thermal expansion

The thermal expansion curve of BZN-reinforced PTFE in the temperature range from -100 to 200 °C is shown in Fig. 3. The CTE of composites with 40 vol.% of BZN is quite small, compared with the PTFE matrix as shown in Fig. 3. This result is quite expectable since the CTE for BZN is very small (1.2 ppm/°C) and the expansion of the matrix is constrained. Composites filled with P-type BZN show a lower CTE than those filled with N-type BZN, although the differences are very small.

2.3 Temperature coefficient of resonant frequency (τ_f)

The τ_f of composites has received comprehensive attention for reducing temperature-induced drift in microwave device [5, 10]. So, theoretical calculation of the τ_f of the composites from given data will provide the important reference for engineering applications.

The τ_f is defined by the following equation [5].

$$\tau_f = -\frac{1}{2}\alpha_\epsilon - \alpha_c \tag{1}$$

Where α_c is the linear CTE of the dielectric specimen.

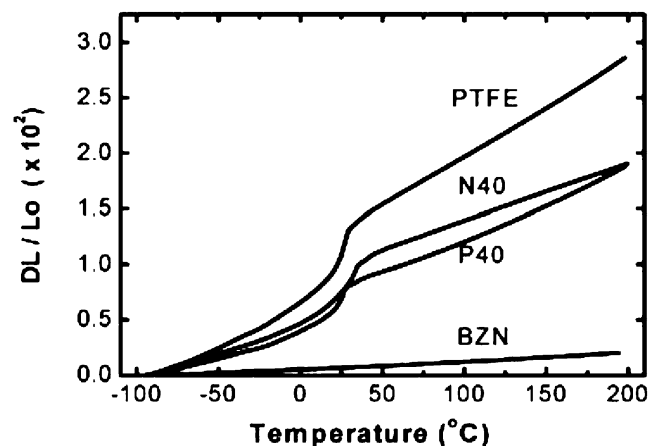


Fig. 3 Thermal expansions as a function of the temperature for composites with 40 vol.% of N-BZN and 40 vol.% of P-BZN, compared with the PTFE matrix and BZN ceramic

Table 2 Comparison of experimental data^a (CTE, α_ε and τ_f) and calculated data of BZN/PTFE composites.

Composites	Experimental CTE ppm/°C	Theoretical CTE	Experimental α_ε	Theoretical α_ε	Experimental τ_f	Theoretical τ_f
N-BZN (40 vol.%)	69.5	74.7	-128	-115	-5.5	-18.6
P-BZN (40 vol.%)	63.2	74.7	-27.8	-22	-49.3	-65.1

^a The temperature range from 25 to 85 °C, at 900 MHz

The Logarithm formula is often used to calculate the relative permittivity of insulator–insulator composites [11].

$$\ln \varepsilon_{\text{eff}} = x \ln \varepsilon_i + (1 - x) \ln \varepsilon_m \quad (2)$$

Where ε_{eff} , ε_f , ε_m are the relative permittivity of composites, filler and matrix, respectively, and x is the volume fraction of the filler.

The α_ε was calculated by the following formula:

$$\alpha_\varepsilon = \frac{\varepsilon_{T_2} - \varepsilon_{T_1}}{\varepsilon_{T_1} \times (T_2 - T_1)} \quad (3)$$

where ε_{T_1} is the dielectric constant at T_1 (here T_1 is 25 °C), ε_{T_2} is the dielectric constant at T_2 (here T_1 is 85 °C).

Form Eqs. 2 and 3, the α_ε of the composites can be written as:

$$\alpha_{\varepsilon_{\text{eff}}} = \frac{(\alpha_{\varepsilon_m}(T_2 - T_1) + 1)^{1-x} (\alpha_{\varepsilon_i}(T_2 - T_1) + 1)^x - 1}{T_2 - T_1} \quad (4)$$

where $\alpha_{\varepsilon_{\text{eff}}}$, α_{ε_m} , α_{ε_i} are the dielectric temperature coefficient of composites, matrix and filler, respectively.

The rule of mixtures serves as the first-order approximation in the overall calculation of the CTE of the composites [6]. This can be expressed as

$$\alpha_c = \alpha_m + (\alpha_i - \alpha_m)x \quad (5)$$

where α_c , α_i , α_m is the CTE of the composite, the filler, and the matrix, respectively.

Thus the τ_f of the composites is

$$\tau_f = -\frac{1}{2} \frac{(\alpha_{\varepsilon_m}(T_2 - T_1) + 1)^{1-x} (\alpha_{\varepsilon_i}(T_2 - T_1) + 1)^x - 1}{T_2 - T_1} - (\alpha_m + (\alpha_i - \alpha_m)x) \quad (6)$$

According to the above equations, the CTE, α_ε and τ_f of BZN/PTFE composites was calculated. The result is shown in Table 2, which is in agreement with the experimental results.

The composites with 40 vol.% of N-BZN showed near-zero τ_f , effectively improving frequency stability. The composites with 40 vol.% of P-BZN showed near-zero α_ε and good temperature stability. The CTE in both composites have been effectively reduced. It was found that the Eqs. 4, 5 provided a good method to predict the α_ε and CTE of a two-

phase composite. The calculated τ_f are slightly higher than the experimental data, because the influences of microstructure, interface, processing technology and properties of material are not considered in the equation.

3 Conclusions

This paper described the mechanism of the temperature compensation of τ_f in polymer composites. The composites with adjustable τ_f are achieved by introducing the ceramic filler with a different α_ε into polymer matrix. Composite filled with positive α_ε (245 ppm/°C) BZN ceramic filler (40 vol.%) has low α_ε (22 ppm/°C); while filled with near-zero α_ε (10 ppm/°C) BZN ceramic filler (40 vol.%) have low τ_f (-5 ppm/°C). Theoretical equation were used to calculate the α_ε , CTE and τ_f of BZN/PTFE composites, and the calculated results show good agreement with the experimental.

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