Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of the European Ceramic Society 26 (2006) 1999–2002
JECS
www.elsevier.com/locate/jeurceramsoc

Preparation and dielectric properties of bismuth-based dielectric/PTFE microwave composites

Feng Xiang, Hong Wang*, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Available online 25 October 2005

Abstract

PTFE-based microwave composites filled with bismuth-based pyrochlore dielectric ceramics were prepared by using the powder processing technology. The effect of ceramic powder content on dielectric properties was studied. The relative permittivity was also predicted using percolation theory. The results indicated that as the content of ceramic powder increased, both the relative permittivity and dielectric loss of composites increased, showing excellent frequency in a wide spectral range. The theoretical result predicted by percolation theory is in good agreement with the experimental data.

Keywords: Microwave dielectric property; Composite materials; Percolation; Ceramics

With the development of electronic information technology, the miniaturization and high-speed operation have become the predominant technology for electronic components, which requires better microwave dielectric materials with reasonable relative permittivity, low dielectric loss, good frequency and temperature stability in a wide spectral range, and good mechanical and thermal stability.[1] PTFE (Teflon), with excellent physical and chemical properties, has been extensively applied to microwave devices. But because of its low relative permittivity and poor thermal stability, further applications are limited. Recently, ceramic modified polymer microwave dielectric materials have been considered as the promising materials to overcome the limitation due to their excellent comprehensive properties.[2–4] Bismuth-based pyrochlore dielectric ceramics have attracted attention in microwave dielectric areas because of their low-sintering temperature, high-relative permittivity, and wide dielectric temperature coefficient range.[5,6] Therefore, PTFE filled with BZN (Bi_2O_3–ZnO–Nb_2O_5) ceramic powder would be an effective approach to improve the dielectric properties of microwave materials in order to satisfy the requirement of dielectric materials in microwave areas.

In this paper, BZN/PTFE microwave composites were prepared by using the powder processing technology. The influences of the amount of BZN ceramic on the relative permittivity and frequency properties of the composites were studied. According to the experimental results, the percolation theory for the theoretical model of the relative permittivity of BZN/PTFE composites was also discussed.

1. Experiment

BZN ceramic was synthesized from pure Bi_2O_3 ZnO and Nb_2O_5 by oxide mixing method. The samples were heated in muffle furnace at 980 °C for 4 h and then cooled to room temperature in the furnace. After the thermal treatment, the samples were ground by mechanical and ball grind methods and then the BZN powders were obtained. Some properties of BZN and PTFE are listed in Table 1.

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

The PTFE powder and treated BZN powder with various BZN volume fraction (0–60%) were transferred into a beaker containing alcohol 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 compacted under 60 MPa pressure for 60 s, and the

* Corresponding author.
E-mail address: hwang@mail.xjtu.edu.cn (H. Wang).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.09.048

Table 1
Properties of BZN and PTFE (measured at 25 °C)

	Volumetric density (ρ/g cm^{-3})	ε_r 800 MHz	tan δ 800 MHz	ρ (Ω/cm)	α_ε 25–85 °C (ppm/°C)	Average particle size (μm)
BZN	6.98	94.0	<5 × 10^{-3}	≥10^{13}	≤±30	0.5
PTFE	2.35	2.1	<1 × 10^{-4}	≥10^{14}	≤−1000	<4

obtained disc was heated in muffle furnace from room temperature to 350 °C with a heating rate of 1 °C/min. The dwell time was 4 h.

The relative permittivity and dielectric loss at 800 MHz were measured by a HP4291B impedance analyzer. For this measurement, the samples were discs with a diameter at 15 mm. By using coaxial transfer-reflection method, a HP8720ES network analyzer was used to measure the relative permittivity and dielectric loss at high frequencies, within the range of 500 M–15 GHz. For this measurement, the samples had a ring shape, with internal diameter of 3.018 mm, external diameter of 6.980 mm, and thickness of 3–5 mm. To get the electrical resistivity, a HP4140B PA meter was used for the leakage current measurements of the samples under 100 V dc voltage for 1 min.

2. Results and discussion

2.1. Dielectric properties

Fig. 1 presents frequency dependency of relative permittivity of the composites. Some small relative permittivity peaks occur near 7 GHz, increasing with the increasing of BZN amount. When the amount of BZN becomes larger, the relative permittivity declines with the increasing frequency after 7 GHz.

As shown in Fig. 2, dielectric loss of the composites is very small. The curve of dielectric loss closes to a flat and straight line in the whole measurement range. Even negative dielectric loss was measured due to the measurement error when the loss is very near to zero. As the BZN content increases, obvious loss peaks occur near 7GHz, corresponding to the change of relative permittivity.

There are some defects such as air gap, water and the interface phase between BZN and PTFE in BZN/PTFE composites materials, which can influence the relative permittivity and the dielectric loss of the composites. The increase of the BZN content lowers the density of composite ring samples with the increased air gap and looser connection, leading to more air and water inside the composites. Like the polar liquid dielectric materials, water has both the electronic displacement polarization and dipolar orientation polarization at low frequency, and mainly has electronic displacement polarization at high frequency. At microwave range, there is large dielectric loss due to the large loss from the dipole relaxation of water.[7,8] In addition, the increase of the BZN amount also causes the increase of interface phase between BZN and PTFE; therefore, the influence of interface polarization on the dielectric loss becomes more significant.[9] All these factors can increase dielectric loss as a function of BZN amount. As shown in Figs. 1 and 2, BZN/PTFE has excellent dielectric properties at frequencies lower than 7 GHz, and hence it has promising applications in microwave frequency region.

Fig. 3 shows the BZN volume fraction dependence of the relative permittivity and the dielectric loss measured by HP4291B at the frequency of 800 MHz. The results show that both the relative permittivity and the dielectric loss increase as the BZN powder volume ratio increases. The increase of the relative permittivity attributed to the high relative permittivity of the BZN powders, which are introduced to the PTFE matrix. The dielectric loss increases due to the increase of the interface phase between BZN and PTFE. Furthermore, leakage current measurement showed that the BZN/PTFE

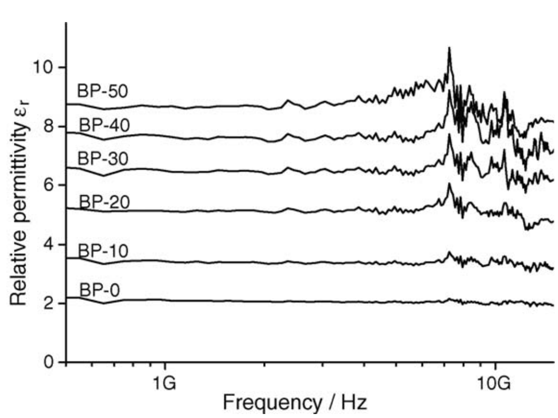

Fig. 1. Relation between relative permittivity and frequency of BZN/PTFE, denoted as BP with the amount of BZN in vol%.

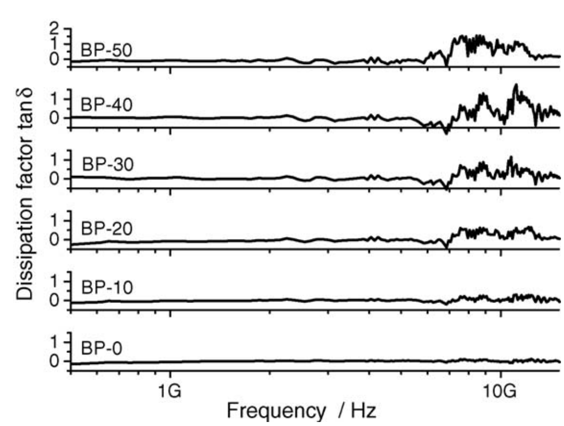

Fig. 2. Relation between dissipation factor and frequency of BZN/PTFE.

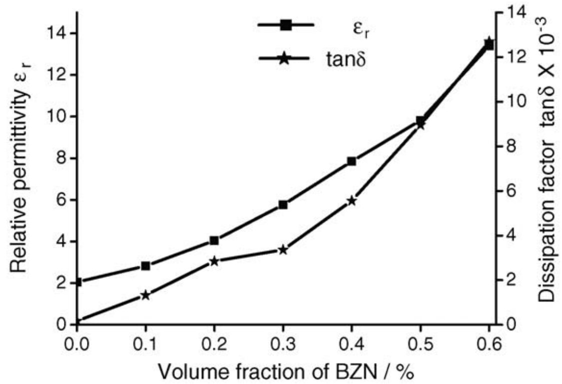

Fig. 3. Change of relative permittivity and dissipation factor with BZN content of BZN/PTFE composites (frequency $f = 800$ MHz).

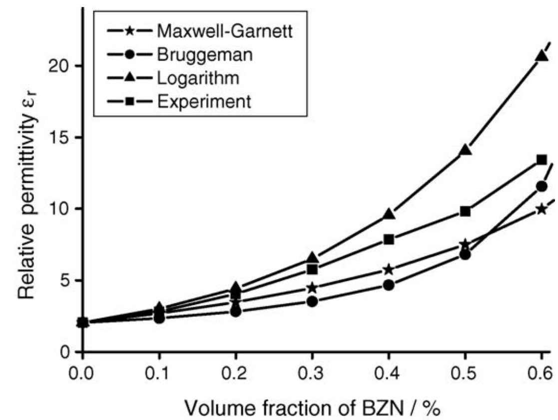

Fig. 4. The experiment and calculated values of BZN/PTFE composites.

composites have excellent electrical resistivity greater than 10^{13} Ω/cm.

2.2. *Theoretical fitting of the relative permittivity of BZN/PTFE composites*

Calculating effective relative permittivity of the composites from the relative permittivity of components and their volume ratios is very important for theoretical point of view and for engineering applications.[9–12] The following equations are often used to calculate the relative permittivity of insulator-insulator composites with low dopant phase content.[10]

$$\text{Logarithmic formula}: \quad \ln \varepsilon_{\text{eff}} = f \ln \varepsilon_{\text{i}} + (1 - f) \ln \varepsilon_{\text{m}} \qquad (1)$$

$$\text{Maxwell-Garnett formula}: \quad \frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{m}}}{\varepsilon_{\text{eff}} + 2\varepsilon_{\text{m}}} = f \frac{\varepsilon_{\text{i}} - \varepsilon_{\text{m}}}{\varepsilon_{\text{i}} + 2\varepsilon_{\text{m}}} \qquad (2)$$

$$\text{Bruggeman formula}: \quad f \frac{\varepsilon_{\text{i}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{i}} + 2\varepsilon_{\text{eff}}} + (1 - f) \frac{\varepsilon_{\text{m}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{m}} + 2\varepsilon_{\text{eff}}} = 0 \qquad (3)$$

where ε_{eff}, ε_{i} and ε_{m} are the relative permittivity of composites, dopant phase and matrix, respectively, and f is the volume ratio of dopant phase. According to the results of Table 1 and the Eqs. (1)–(3), the relative permittivity of BZN/PTFE composites was calculated, and the results are shown in Fig. 4. Compared with the experimental results, the calculated results obtained from the three equations have some error. This is because there are many factors influencing the relative permittivity, such as the homogeneity of component distribution, the shape and size of dopant particles, the inside defects of the composites, and the interface phase between the components. All these factors make the calculation very difficult.

All the above equations are based on the composites with low content of dopant phase. When there is large volume difference between two phases, the phase with larger volume ratio is considered as the matrix and the phase with less volume ratio is considered as the dopant phase, which has the random homogeneous distribution in the matrix. However, when the two phases have the similar volume, it is difficult to distinguish the matrix and the dopant phase. In this case, the same components tend to connect to networks, and percolation occurs.[12] Therefore, considering the influence of percolation, percolation theory[11] and Bruggeman equation were used to calculate the relative permittivity of BZN/PTFE composites.

For simplification, interface phase and micro pores were not considered here and BZN powders were considered as spherical particles with the same radii and random homogeneous distribution. According to the effective relative permittivity equation from classic electromagnetic theory by Sihvola and Kong,[13] the simplified equations are

$$\varepsilon_{\text{peff}} = \varepsilon_{\text{p}}(1 + f_{\text{peff}}) \qquad (4)$$

$$\varepsilon_{\text{beff}} = \varepsilon_{\text{b}}(1 - f_{\text{beff}}) \qquad (5)$$

where $\varepsilon_{\text{peff}}$ and $\varepsilon_{\text{beff}}$ are the effective relative permittivity of PTFE and BZN considering percolation; ε_{p} and ε_{b} are relative permittivity of PTFE and BZN; and f_{peff} f_{beff} are obtained from the following equations:

$$f_{\text{peff}} = \frac{P(1 - f(P))}{[P(1 - f(P)) + Bf(B)]} \qquad (6)$$

$$f_{\text{beff}} = \frac{B(1 - f(B))}{[B(1 - f(B)) + Pf(P)]} \qquad (7)$$

where P, B are the volume ratio of PTFE and BZN in the composites, and $f(P)$, $f(B)$ are the percolation probability of PTFE and BZN, respectively. $f(P)$ can be written as

$$f(P) = \begin{cases} 0, & 0 < P \le \alpha \\ \left(\dfrac{P - \alpha}{1 - \alpha}\right)^{\delta}, & \alpha < P \le \beta \\ 1 + \kappa(P - \beta), & \beta < P \le \gamma \\ 1, & \gamma < P \le 1 \end{cases} \qquad (8)$$

where $\alpha, \beta, \gamma, \delta$ and κ are 0.16, 0.6, 0.84, 0.4 and 0.9, respectively, from the percolation theory. The equation for $f(B)$ is similar to $f(P)$.

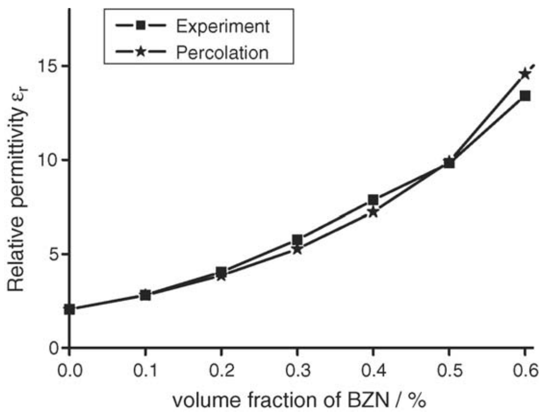

Fig. 5. The experiment and percolation theory calculated values of BZN/PTFE composites.

According to the above equations, the relative permittivity of BZN/PTFE composites was calculated. The result is shown in Fig. 5, which is in good agreement with the experimental result. Therefore, it is reasonable to consider the percolation when calculating the relative permittivity.

3. Conclusions

(1) When the frequency is lower than 7 GHz, the BZN/PTFE composites have excellent frequency stability, with the little change of relative permittivity and the dielectric loss is less than 5%.
(2) The relative permittivity and the dielectric loss increase when the amount of BZN increases. Furthermore the BZN/PTFE composites have excellent electrical resistivity greater than 10^{13} Ω/cm.
(3) Percolation theory was used to calculate the relative permittivity of BZN/PTFE composites, showing good agreement with the experimental result.

Acknowledgement

This work was supported by Ministry of Science and Technology of China through 973-project under grant 2002CB613302 and NSFC project of China under grant 50572085.

References

1. Tian, M. B., *Substrates for High Density Package Engineering*. Tsinghua University Press, Beijing, 2003, pp. 22–24.
2. Okhlopkova, A. A. and Shits, E. Y., Structure and properties of teflon composites with natural diamond powders. *Mech. Compos. Mater.*, 2004, **40**(2), 145–150.
3. Wang, Y. M., Jia, D. C. and Zhou, Y., Preparation and properties of $Ba_2Ti_9O_{20}$/PTFE microwave dielectric composite. *Piezoelectr. Acoustoopt.*, 2002, **24**(3), 225–229.
4. Chen, Y. C., Lin, H. C. and Lee, Y. D., The effects of filler content and size on the properties of PTFE/SiO_2 composites. *J. Polym. Res.-Taiwan*, 2003, **10**(4), 247–258.
5. Cann, D. P., Randall, C. A. and Shrout, T. R., Investigation of the dielectric properties of bismuth pyrochlore. *Solid State Commun.*, 1996, **100**(7), 529–534.
6. Wang, X. L., Wang, H. and Yao, X., Structure, phase transformations, and dielectric properties of pyrochlores containing bismuth. *J. Am. Ceram. Soc.*, 1997, **80**(10), 2745.
7. Zhang, L. Y. and Yao, X., *Dielectric Physics*. Xi'an Jiaotong University Press, Xi'an, 1991, p. 104.
8. Molla, J., Gonzalez, M. and Vila, R., Effect of humidity on microwave dielectric losses of porous alumina. *J. Appl. Phys.*, 1999, **85**(3), 1727–1730.
9. Zhao, X. H., Wu, Y. G. and Fan, Z. G., Three-dimensional simulations of the complex dielectric properties of random composites by finite element method. *J. Appl. Phys.*, 2004, **95**(12), 8110–8117.
10. Landauer, R., Electrical transport and optical properties of inhomogeneous media. *AIP Conf. Proc.*, 1978, 40.
11. Kirpatrick, S., Percolation and conduction. *Rev. Mod. Phys.*, 1973, **45**, 574.
12. Dai, X. and Liu, Z. L., The calculation or the effective permittivity of mixed medium by percolation theory. *Acta Electron. Sinica*, 1998, **26**(2), 36–41.
13. Sihvola, A. H. and Kong, J. A., Effective permittivity of dielectric mixtures. *IEEE Trans. Geosci. Remote Sens.*, 1988, **26**(4), 420–429.