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# PTFE/$Sr_2Ce_2Ti_5O_{16}$ polymer ceramic composites for electronic packaging applications

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## Abstract

$Sr_2Ce_2Ti_5O_{16}$ ceramics filled PTFE composites were prepared by powder processing technique. The structure and microstructure of the composites were investigated by X-ray diffraction and scanning electron microscopic methods. The effect of $Sr_2Ce_2Ti_5O_{16}$ ceramic content (0–0.6 volume fraction) on the dielectric properties of the composites was studied at 1 MHz and 7 GHz. The dielectric constant and dielectric loss increased with the increase of $Sr_2Ce_2Ti_5O_{16}$ content. The measured dielectric constant ($\varepsilon_r$) is compared with the effective dielectric constant calculated by Lichtenecker, Maxwell-Garnet, Jayasundere, Poon-Shin formulae and Effective Medium Theory. The observed dielectric constants are reasonably in good agreement with that calculated using Effective Medium Theory.

*Keywords:* Composites; Dielectric properties; Inclusions and microstructure-final

## 1. Introduction

Electronic industries are responding to the increasing consumer demand in telecommunication devices and computers for cost effective product miniaturization.[1,2] The requirement for denser and faster microelectronic circuits limits the use of conventional packaging materials.[3] Polymers and ceramics have extreme electrical, mechanical and thermal properties for the packaging materials.[4] The electrical properties of microelectronic devices such as signal attenuation, propagation velocity and cross talk are influenced by the dielectric properties of packaging materials.[1,2,4] The dielectric constant of the composites cannot be increased beyond a certain value as it reduces the signal speed. Hence, for a composite material to be used in packaging and substrate applications there must be a compromise between signal speed and $\varepsilon_r$.[1–3] So for practical applications packaging materials must posses optimum dielectric constant, low dielectric loss, high thermal conductivity to dissipate heat and thermal expansion should be matching to that of silicon.[1–4] Hence, polymers filled with low loss ceramics are suitable for electronic packaging for device encapsulation and substrates.

Polytetrafluoroethylene (PTFE) has been extensively used in electronic substrates and packaging applications because of its excellent dielectric properties ($\varepsilon_r = 2.1$ and $\tan\delta = 10^{-4}$ at 800 MHz) and chemical resistances.[5,6] However, applications are limited as the polymer has low dielectric constant and high coefficient of thermal expansion. Recently, Chen et al.[7] reported the dielectric properties of PTFE/$SiO_2$ composites. But the dielectric constant of the composites was low as $SiO_2$ has $\varepsilon_r$ of 4 only; hence, the miniaturization of microwave devices by the use of PTFE/$SiO_2$ composites is limited. In a similar investigation Wang et al.[8] reported the dielectric properties of $Ba_2Ti_9O_{20}$/PTFE composites. More recently, Xiang et al.[6] investigated the dielectric properties of composites involving PTFE and low loss, high $\varepsilon_r$ ($\varepsilon_r = 94$ at 800 MHz) $Bi_2O_3$–ZnO–$Nb_2O_5$ ceramics. However, incorporation of high amount of ceramics leads to poor process ability of the composites. Therefore, to improve the process ability of the composites, low loss ceramics with high dielectric constant are preferred, since addition of small amount of such ceramics can increase the dielectric constant significantly.

The precise prediction of effective dielectric constant of a composite material is very important for the design of packaging materials and substrates. Several quantitative rules[9–13] and simulation techniques[14–16] had been proposed for the prediction of dielectric constant. However, very little experimental evidence was provided to support the rule of mixtures.[17] Another

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problem in predicting dielectric constant is the non-availability of $\varepsilon_r$ values of ceramic powders. So in calculations $\varepsilon_r$ values of the bulk ceramics are used instead of the powders.[17] $Sr_2Ce_2Ti_5O_{16}$ is a high dielectric constant low loss ceramic material ($\varepsilon_r = 112$ and $\tan\delta = 10^{-4}$ at 7 GHz).[18] In the present paper, we report the dielectric properties of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites for the first time. Also the experimental dielectric constants are compared with that predicted by Lichtenecker, Maxwell-Garnet, Jayasundere, Poon-Shin formulae and Effective Medium Theory.[19]

## 2. Experimental

$Sr_2Ce_2Ti_5O_{16}$ ceramics were prepared by the solid-state ceramic route. High purity $SrCO_3$ and $TiO_2$ (99.9+%, Aldrich chemical company Inc., Milwaukee, WI, USA) and $CeO_2$ (99.99%, Indian Rare Earth Ltd, Udyogamandal, India) were used as the starting materials. Stoichiometric amount of ceramic powders were ball milled in distilled water medium using yttria stabilized zirconia balls in a plastic container for 24 h. The slurry was dried and calcined at 1300 °C/5 h. The calcined material was ground in to fine powder. $Sr_2Ce_2Ti_5O_{16}$/PTFE (Hindustan Fluorocarbons, Hyderabad, India) composites were prepared by powder processing technology. In order to create an active surface for binding with polymer the fine powdered $Sr_2Ce_2Ti_5O_{16}$ was mixed with acrylic acid solution for 1 h and dried.[6] Acrylic acid is a well-known polymerizing agent. The dried powder was again treated with 2 wt.% tetra butyl titanate. The uses of titanate based coupling agents provide excellent mechanical and electrical properties compared to other organic functional coupling agents like silane. The evaporation of the solvent gives $Sr_2Ce_2Ti_5O_{16}$ powders cladded with coupling agents. Different volume fractions (0–0.6) of treated ceramics and PTFE powders were dispersed in ethyl alcohol using ultrasonic mixer for about 30 min. Then, the dry powder mixture was obtained by removing the solvent at 70 °C under stirring. The homogenously mixed PTFE/$Sr_2Ce_2Ti_5O_{16}$ powders were then compacted under uniaxial pressure of 50 MPa for 1 min. The cylindrical and rectangular pellets thus obtained were kept at 310 °C for 2 h.

The composites were characterized by X-ray diffraction technique using CuKα radiation (Philips X-Ray Diffractometer). The surface morphology of the composites was studied by scanning electron microscope (*JEOL-JSM* 5600 LV, Tokyo, Japan).

The low frequency dielectric properties were measured by LCR meter (Hioki 3532-50). Electroded samples having diameter of about 14 mm and thickness 1 mm were used for this measurement. HP 8510 Vector Network Analyzer was used to characterize the composite materials at microwave frequencies. For this purpose, rectangular samples of dimensions (40 mm × 3 mm × 2 mm) were made and the dielectric properties were measured using cavity perturbation technique.[20,21]

## 3. Results and discussion

Fig. 1 gives the XRD pattern of PTFE and its $Sr_2Ce_2Ti_5O_{16}$ filled composites. The pattern of PTFE (Fig. 1(a)) shows a strong crystalline peak superimposed over an amorphous halo as reported.[22] Fig. 1(b and c) show the XRD patterns of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites with ceramic volume fraction (vf) 0.3 vf and 0.6 vf, respectively. The XRD peaks corresponding to $Sr_2Ce_2Ti_5O_{16}$ are indexed based on JCPDS File No. 49–1554.

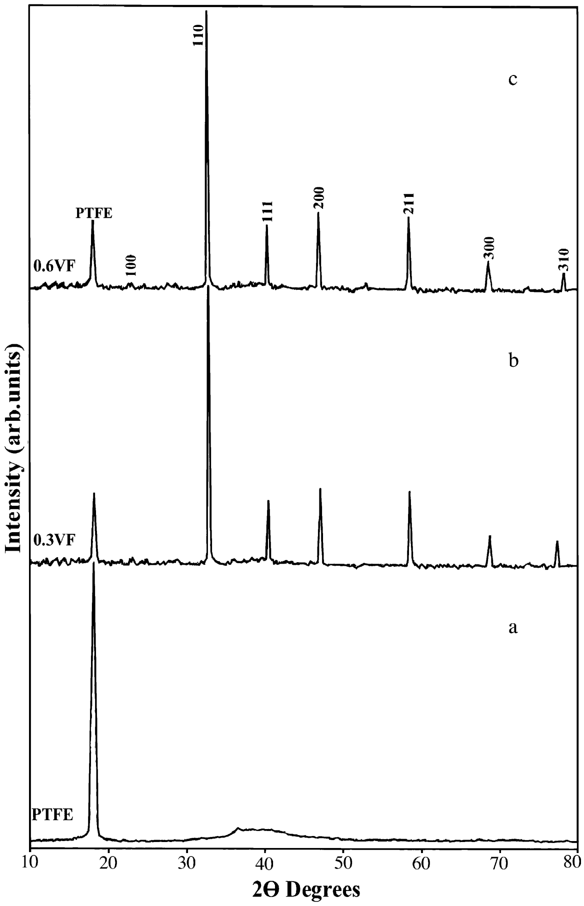

Fig. 1. XRD pattern of (a) PTFE (b) PTFE + 0.3 vf of $Sr_2Ce_2Ti_5O_{16}$ and (c) PTFE +0.6 vf of $Sr_2Ce_2Ti_5O_{16}$ composites.

Fig. 2 shows the SEM pictures of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites with different volume fractions. It can be seen that $Sr_2Ce_2Ti_5O_{16}$ particles are well dispersed in the PTFE matrix, however, at higher mixing ratios crowding of ceramic particles were observed (Fig. 2(c)). Hence, for higher mixing ratios the connectivity among the ceramic particles increases. The surface energy of PTFE is relatively low and so it is difficult for PTFE to have good adhesion with ceramics.[7] In such cases, the use of coupling agents will improve filler matrix inter facial strength. Fig. 3 shows the fractogarph of 0.1 vf PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. The presence of PTFE fibrils in the fractured surface is an indication of better adhesion between ceramics and PTFE.[7]

Figs. 4 and 5 show the variation of dielectric constant and dielectric loss at 1 MHz and 7 GHz, respectively. The dielectric constant and dielectric loss of the composites increase with the increase in $Sr_2Ce_2Ti_5O_{16}$ content. The increase in dielectric constant is expected as the ceramic have high dielectric constant compared to that of PTFE matrix. Also at higher mixing ratios, the connectivity (see Fig. 2(c)) among the ceramic particles increases which in turn increases the dielectric constant.

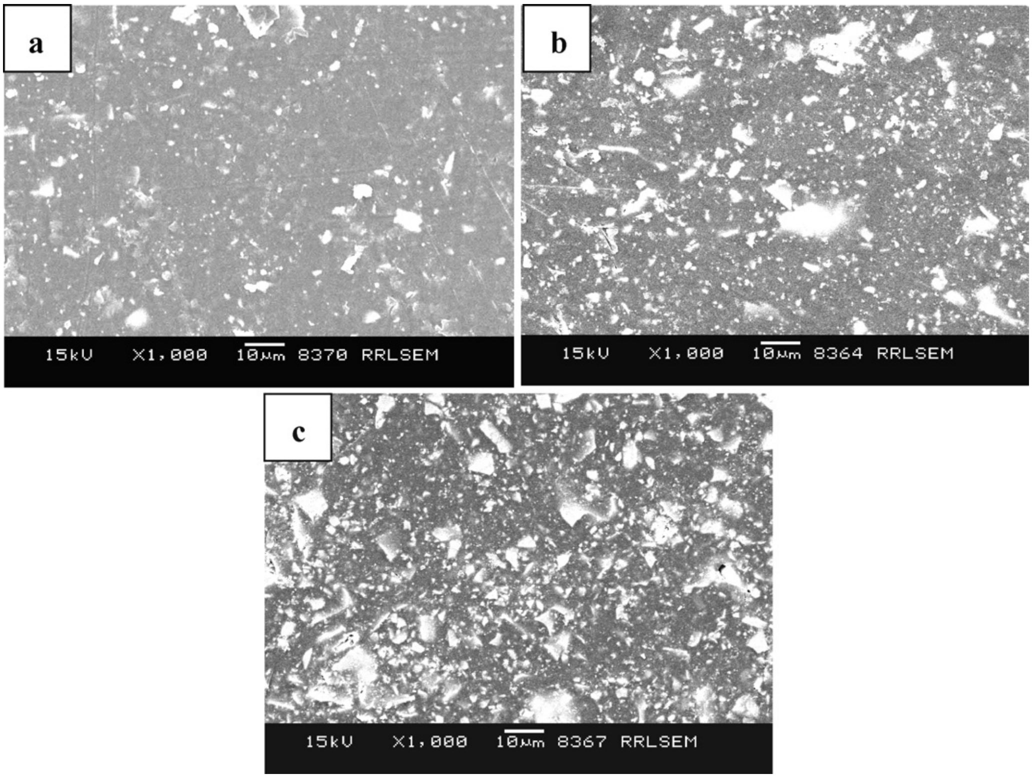

Fig. 2. SEM micrographs of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites containing (a) 0.1 vf, (b) 0.3 vf and (c) 0.6 vf of ceramics.

The connectivity of the individual components has maximum importance as it controls the electric flux pattern as well as mechanical and thermal properties.[23] The dielectric constant and the dielectric loss of the composites are affected by a number of factors such as porosity, water content and interface between the two components in the composite. The dielectric loss of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites increases with increase in ceramic content. As the volume fraction of ceramic increases the interface between PTFE and $Sr_2Ce_2Ti_5O_{16}$ increases. Hence, the increase in dielectric loss with mixing ratio is attributed to the increased interfacial polarization at higher volume fractions of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites.

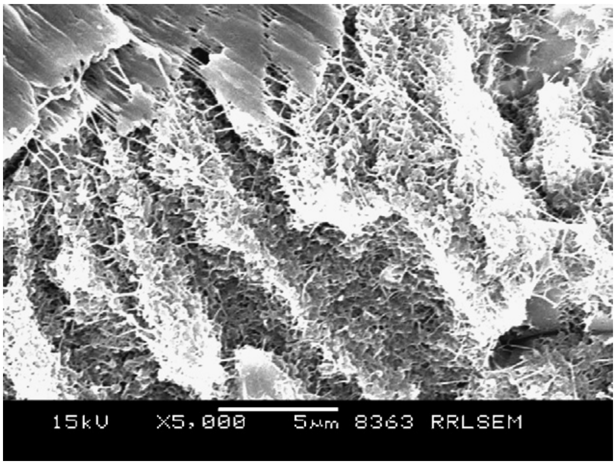

Fig. 3. SEM fractograph of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites containing 0.1 vf of ceramics.

A number of numerical relations have been put forward by researchers to predict the effective dielectric constant of the composites. In the present study, the following equations were used to calculate the effective dielectric constant of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites.[10,12]

$$\ln\ \varepsilon_{\mathrm{eff}} = f\ \ln\ \varepsilon_i + (1-f)\ \ln\ \varepsilon_m \quad \text{(Lichtenecker equation)} \tag{1}$$

$$\frac{\varepsilon_{\mathrm{eff}} - \varepsilon_m}{\varepsilon_{\mathrm{eff}} + 2\varepsilon_m} = f\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \quad \text{(Maxwell Garnet equation)} \tag{2}$$

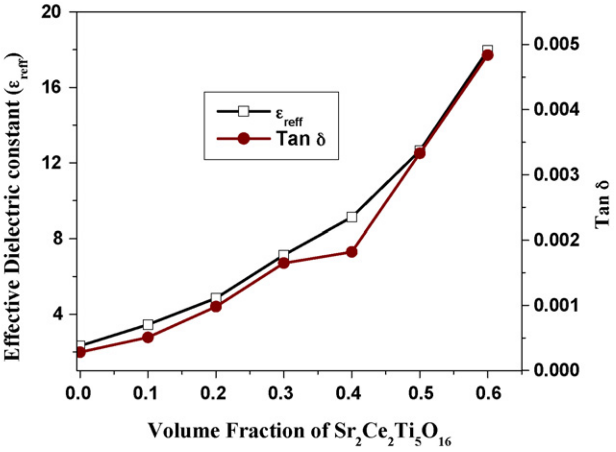

Fig. 4. Variation in dielectric constant and loss tangent of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites at 1 MHz.

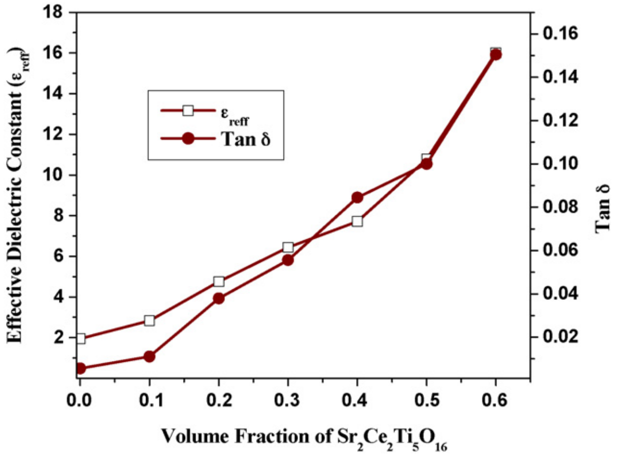

Fig. 5. Variation in dielectric constant and loss tangent of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites at 7 GHz.

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_m(1-f)+\varepsilon_i f[3\varepsilon_m/(\varepsilon_i+2\varepsilon_m)][1+(3f(\varepsilon_i-\varepsilon_m)/(\varepsilon_i+2\varepsilon_m))]}{1-f+f[3\varepsilon_m/(\varepsilon_i+2\varepsilon_m)][1+(3f(\varepsilon_i-\varepsilon_m)/(\varepsilon_i+2\varepsilon_m))]} \quad \text{(Jayasundere equation)} \tag{3}$$

$$\varepsilon_{\text{eff}} = \varepsilon_m\left[1+\frac{f((\varepsilon_i/\varepsilon_m)-1)}{f+(1-f/3)[(\varepsilon_i/\varepsilon_m)(1-f)+f+2]}\right] \quad \text{(Poon-Shin equation)} \tag{4}$$

where $\varepsilon_{\text{eff}}$, $\varepsilon_i$, and $\varepsilon_m$ are the dielectric constants of the composites, $Sr_2Ce_2Ti_5O_{16}$ and the PTFE matrix, respectively and $f$ is the volume fraction of the $Sr_2Ce_2Ti_5O_{16}$ ceramics.

Figs. 6 and 7 depict the comparison of effective dielectric constants of the composites with the values predicted by the above equations at 1 MHz and 7 GHz. Lichtenecker's and Jayasundere's mixing rules fit well with the experimental data at lower mixing ratios (up to 0.3 vf). At higher mixing ratios the predicted $\varepsilon_r$ values are much higher than the experimental. Maxwell-Garnet relation predicts lower $\varepsilon_r$ compared to the experimental data. Hence, Lichtenecker's, Jayasundere's and Maxwell-Garnet relations cannot be used to predict the $\varepsilon_r$ of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. However, the effective dielectric constant predicted by Poon-Shin equation nearly fits with the experimental dielectric constant at 1 MHz and 7 GHz. The dielectric constant of the composites is not only depending on the individual dielectric properties of the components but also on the shape and size of the ceramic particle, porosity, interface between components and on the homogeneity of distribution.[6] It will be difficult to include all these parameters in calculations.

In order to predict the dielectric constant of the composites precisely, the Effective Medium Theory (EMT) model developed by Rao et al.[19] is used. In the EMT model, composites can be treated as an effective medium whose dielectric constant is obtained by averaging over the dielectric constants of the constituents.[19] The schematic representation of the microstructure of polymer ceramic composites is shown in Fig. 8(a) which is in agreement with the SEM microstructures shown in Fig. 2. In order to account for the major features of a composite microstructure, a random unit cell is defined as core of $\varepsilon_i$ surrounded by a shell of host matrix $\varepsilon_m$ as shown in Fig. 8(b) (where $\varepsilon_i$, $\varepsilon_m$ and $\varepsilon_{\text{eff}}$ are dielectric constant of ceramics, matrix and composites, respectively). The basic concept of effective medium is that when a random unit cell is embedded in an effective medium it cannot be detected in the electromagnetic experiment.[19] Otherwise, the random unit cell can be replaced by a material characterized by $\varepsilon_{\text{eff}}$. The EMT model leads to the following equation to predict the effective dielectric constant of ceramic polymer composites.

$$\varepsilon_{\text{eff}} = \varepsilon_m\left[1+\frac{f(\varepsilon_i-\varepsilon_m)}{\varepsilon_m+n(1-f)(\varepsilon_i-\varepsilon_m)}\right] \tag{5}$$

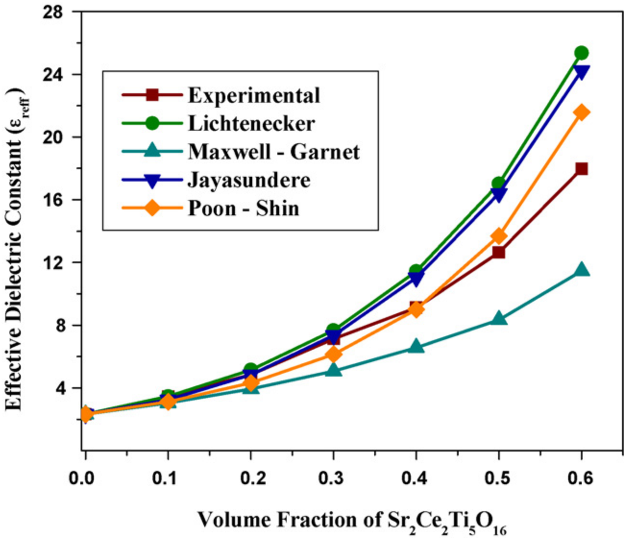

Fig. 6. Comparison of experimental and theoretical dielectric constants of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites at 1 MHz.

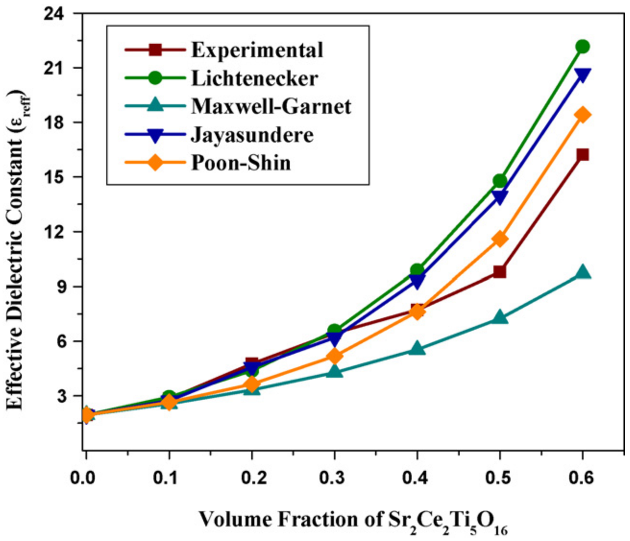

Fig. 7. Comparison of experimental and theoretical dielectric constants of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites at 7 GHz.

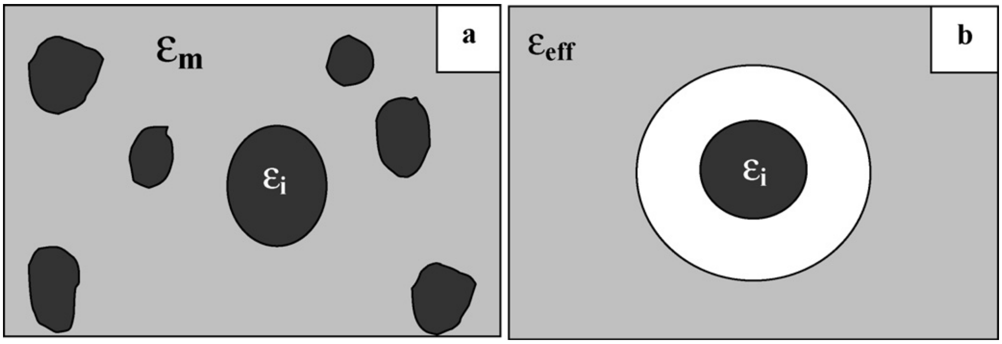

Fig. 8. Schematic diagrams of (a) microstructure of composite materials and (b) random unit cell embedded in the effective medium.

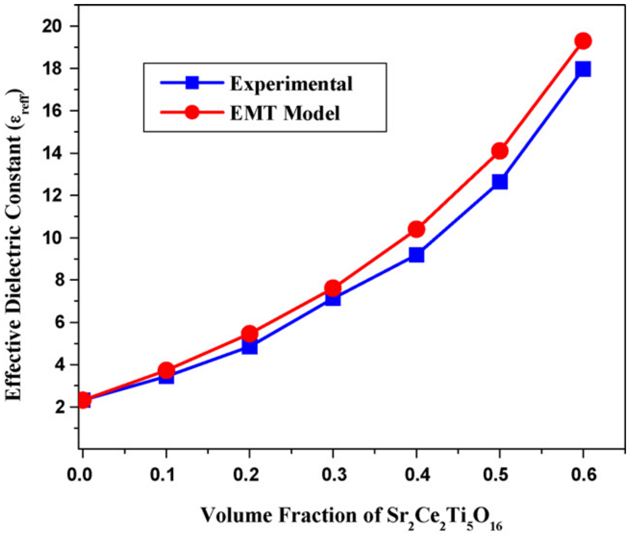

Fig. 9. The experimental and EMT model prediction of $\varepsilon_r$ of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites at 1 MHz.

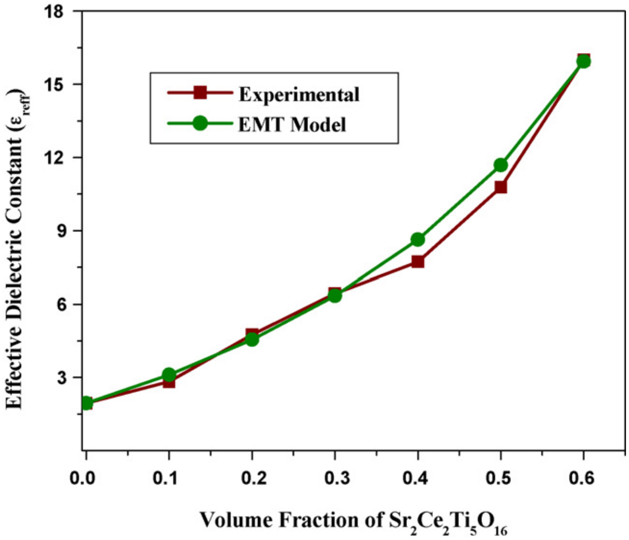

Fig. 10. The experimental and EMT model prediction of $\varepsilon_r$ of PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites at 7 GHz.

where $\varepsilon_{\text{eff}}$, $\varepsilon_i$, and $\varepsilon_m$ are the dielectric constant of the composites, $Sr_2Ce_2Ti_5O_{16}$ and the PTFE matrix, respectively, $f$ is the volume fraction of the $Sr_2Ce_2Ti_5O_{16}$ ceramics and $n$ is the correction factor to compensate for the shape of the fillers used in polymer ceramic composites. The value of $n$ is determined empirically which is found to be 0.165 for the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. A small value of $n$ shows that the filler particles have nearly spherical shape.[24] The comparison of experimental and theoretical dielectric constant calculated by EMT model at 1 MHz and 7 GHz are shown in Figs. 9 and 10, respectively. At 1 MHz measured and predicted $\varepsilon_r$ are nearly equal upto 0.3 vf of $Sr_2Ce_2Ti_5O_{16}$ ceramics. However, as volume fraction of the ceramics increases beyond 0.3 vf a slight deviation from the predicted value of $\varepsilon_r$ is observed in PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites. At 7 GHz the measured $\varepsilon_r$ is in good agreement with the EMT model. Hence, it can be concluded that EMT model can be used to predict the effective dielectric constant of the PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites.

## 4. Conclusions

PTFE/$Sr_2Ce_2Ti_5O_{16}$ composites are prepared by powder processing method. The dielectric properties of the composites were studied at 1 MHz and 7 GHz. As the volume fraction of $Sr_2Ce_2Ti_5O_{16}$ increases the dielectric constant and dielectric loss increases. The prediction of $\varepsilon_r$ using Effective Medium Theory is in good agreement with experimental results.

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## References

1. Pecht, M. G., Agarwal, R., McCluskey, P., Dishongh, T., Javadpour, S. and Mahajan, R., *Electronic packaging materials and there properties*. CRC Press, London, 1999, pp. 3–10.
2. Chung, D. L., *Materials for electronic packaging*. Butterworth, Heinemann, Washington, 1995, pp. 3–35.
3. Tummala, R. R., Ceramic and glass ceramic packaging in 1990’s. *J. Am. Ceram. Soc.*, 1991, **74**(5), 895–908.

4. Bolt, J. D., Button, D. D. and Yost, B. A., Ceramic fiber polymer composites for electronic substrates. *Mater. Sci. Eng. A.*, 1989, **109**, 207–211.
5. Bur, J. A., Dielectric properties of polymers at microwave frequencies. *Polymer*, 1985, **26**, 963–977.
6. Xiang, F., Wang, H. and Xiyao, Preparation and dielectric properties of bismuth based dielectric/PTFE microwave composites. *J. Eur. Ceram. Soc.*, 2006, **26**(10/11), 1999–2002.
7. Chen, C. Y., Lin, C. H. and Lee, D. Y., Effect of filler content and size on properties of PTFE/$SiO_2$ composites. *J. Polym. Res.*, 2003, **10**(4), 247–258.
8. Wang, Y. M., Jia, D. C. and Zhou, Y., Preparation and properties of $Ba_2Ti_9O_{20}$/PTFE microwave dielectric composites. *Piezoelectrics Accoustooptics*, 2002, **24**(3), 225–229.
9. Sihvola, A. H., Effective permittivity of dielectric mixture. *IEEE Trans. Geosci. Remote Sens.*, 1988, **26**(4), 420–429.
10. Jayasundere, N. and Smith, B. V., Dielectric constant for binary piezoelectric 0–3 composites. *J. Appl. Phys.*, 1993, **73**(5), 2462–2466.
11. Wakino, K., A new equation for predicting dielectric constant of a mixture. *J. Am. Ceram. Soc.*, 1993, **76**(10), 2588–2594.
12. Poon, Y. M. and Shin, F. G., A simple explicit formula for effective dielectric constant of binary 0–3 composites. *J. Mater. Sci.*, 2004, **39**, 1277–1281.
13. Sihvola, A. H., Mixing rules with complex dielectric coefficient. *Surf. Sens. Technol. Appl.*, 2000, **1**(4), 393–415.
14. Sareni, B., Krahenubuh, L., Beroul, A. and Brosseau, C., Effective dielectric constant of random composite material. *J. Appl. Phys.*, 1997, **81**(5), 2375–2383.
15. Jylha, L. and Sihvola, A. H., Numerical modeling of disordered mixture using pseudo random simulations. *IEEE Trans. Geosci. Remote Sens.*, 2005, **43**(1), 59–64.
16. Jylha, L., Honkamo, J., Jantunen, H. and Sihvola, A. H., Microstructure based numerical modelling method for effective permitivity of ceramic polymer composites. *J. Appl. Phys.*, 2005, **97**, 104104–104110.
17. Cho, D. S., Lee, Y. S., Hyun, G. J. and Paik, W. K., Comparison of theoretical predictions and experimental values of dielectric constant of epoxy/$BaTiO_3$ composite embedded capacitor films. *J. Mater. Sci. Mater. Electron.*, 2005, **16**, 77–84.
18. Subodh, G. and Sebastian, M. T., Microwave dielectric properties of $Sr_2Ce_2Ti_5O_{16}$ ceramics, *Mater. Sci. Eng. B.*, in press.
19. Rao, Y., Qu, J., Marinis, T. and Wong, C. P., A precise numerical prediction of effective dielectric constant for polymer ceramic composites based on effective medium theory. *IEEE Trans. Compon. Packag. Technol.*, 2000, **23**(4), 680–683.
20. Prakash, A., Vaid, T. K. and Mansingh, A., Measurement of dielectric parameters at microwave frequencies by cavity perturbation technique. *IEEE Trans. Micro. Theory Tech.*, 1979, **27**, 791–794.
21. Chen, L., Ong, C. K. and Tan, B. T. G., Amendment of cavity perturbation method for permittivity measurement of extremely low loss dielectrics. *IEEE Trans. Instrum. Meas.*, 1999, **48**(6), 1031–1037.
22. Rae, P. J. and Datebaum, B. M., Properties of polytetraflouroethylene (PTFE) in compression. *Polymer*, 2004, **45**, 7615–7625.
23. Malachlan, S. D., Blaskiewicz, M. and Newham, R. E., Electrical resistivity of composites. *J. Am. Ceram. Soc.*, 1990, **73**(8), 2187–2203.
24. Todd, M. G. and Shi, G. F., Validation of a novel dielectric constant simulation model and determination of its physical parameters. *Micro. J.*, 2002, **33**, 627–632.