

The dielectric properties and dielectric mechanism of perovskite ceramic CLST/PTFE composites

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Abstract Polytetrafluorethylene (PTFE) composites filled with perovskite (Ca,Li,Sm)TiO₃ (CLST) dielectric ceramic of various volume fractions filler up to 60% were prepared. The effects of volume fraction of ceramic filler on the microstructure and dielectric properties of the composites have been investigated. A comparative study of dielectric properties of experiment and modeling analysis has been carried out at high frequencies for the CLST/PTFE composites. The results indicate that both the dielectric constant and the dielectric loss increase with the filler. The CLST/PTFE composite with 40% ceramic has exhibited good dielectric properties: $\epsilon_r = 7.92$ (~10 GHz), $\tan \delta = 1.2 \times 10^{-3}$ (~10 GHz), and $\tau_f = -45$ ppm/°C. The dielectric properties are obviously better than most composites reported previously at high frequencies in the aspects of dielectric loss and thermal stability. The dielectric constant and dielectric loss of composites predicted by the Rother–Lichtenecker equation and the general mixing model are in good agreement with the experiment data when the volume fraction

of ceramic is less than 40%. When the volume fraction of the ceramic is more than 40%, the deviation occurs. By introducing the correction factor, the theoretical values of the dielectric constant agrees well with the experimental values.

1 Introduction

Nowadays, with the rapid advances of electromagnetic devices in electronic industry, such as the telecommunication systems and high speed digital devices and so on, there is a vast demand of high-performance dielectric materials for the requirements of developing trend of high-speed of signal delivering, miniaturization, good signal quality and stability of temperature of electron components. The dielectric materials should have tuneable dielectric constant (ϵ_r), low dielectric loss ($\tan \delta$) and near to zero temperature coefficient of resonance frequency (τ_f). Temperature coefficient of dielectric constant (τ_{ϵ_r}) is also a kind of parameters of the thermal stability. These two parameters are related by $\tau_f = -1/2\tau_{\epsilon_r} - \alpha$, where “ α ” is the linear coefficient of thermal expansion (CTE).

To meet these requirements, organic–inorganic composite materials have been widely used for the advantages of good processing ability, flexibility, controllable dielectric properties. There is a lot of work about different polymers. For example, polytetrafluorethylene (PTFE), polyethylene (PE), polystyrene (PS), polyimide (PI), polyvinylidene difluoride (PVDF) and epoxy resin (EPR) have been extensively used as matrix [1–3]. Among them, PTFE is ideal dielectric material due to its superior dielectric properties of a low dielectric constant (ϵ_r) of about 2.1 and extremely low dielectric loss ($\tan \delta$) which is constant over a wide

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range of frequencies and excellent chemical inertness for solvents and chemicals.

Many studies were conducted to prepare PTFE based dielectric composite materials by filling ceramic fillers. You et al. reported a dielectric response of 0.55 ZrTi₂O₆–0.45 ZnNb₂O₆/PTFE composites. The ϵ_r is 7.32 with $\tan\delta$ of 1.5×10^{-3} and τ_f is 24.5 ppm/°C when volume fraction (VF) is 46% at 10 GHz [4]. Rajesh et al. prepared a rutile/PTFE composite with dielectric properties with 67 wt% rutile at X-band frequency region: $\epsilon_r=10.2$, $\tan\delta=2.2 \times 10^{-3}$, $\tau_{\epsilon_r} \approx -427$ ppm/°C [5]. Rajesh et al. also prepared BaSm₂Ti₄O₁₂/PTFE composites with $\epsilon_r=7.6$, $\tan\delta \approx 7.9 \times 10^{-3}$ at 67 wt% at X-band frequency region [6]. And Rajesh et al. also prepared CaTiO₃/PTFE composites and had ϵ_r of 11.8, $\tan\delta$ of 3.6×10^{-3} and τ_{ϵ_r} of 427 ppm/°C with optimum filler loading of 61 wt% at X-band frequency region [7]. Murali et al. had prepared cordierite (2MgO–2Al₂O₃–5SiO₂)/PTFE composites with ϵ_r of 3.17, $\tan\delta$ of 3.4×10^{-3} with filler loading of 60 wt% at X-band frequency region [8]. From these studies we could know that filling ceramic in PTFE could acquire improved dielectric properties but still exist some problems like high $\tan\delta$, high τ_{ϵ_r} or low ϵ_r . So we consider solving the problem by introducing a kind of ceramic with high performance of high ϵ_r , low $\tan\delta$ and near to zero τ_f to apply in this PTFE based systems to acquire comprehensive excellent dielectric composites.

For the properties of ceramic and the interface have a big influence to the dielectric properties of ceramic/PTFE composites, in this paper, perovskite (Ca,Li,Sm)TiO₃ (CLST) dielectric ceramic was chosen for this work as it exhibits high ϵ_r , low $\tan\delta$, low τ_f and excellent stability over a wide range of applicable frequency and temperature. Various influencing factors including volume fractions, phase structure, microstructure, thermal properties, and dielectric properties of CLST/PTFE composites are investigated. The ϵ_r and $\tan\delta$ are fitted to related theoretical models and the fitting results are discussed. The impact factors of the dielectric properties of composites and the method to acquire improved dielectric properties of the CLST/PTFE composites have been discussed.

2 Experiments and experimental aspects

The perovskite CLST ceramics were synthesized by with raw materials of CaCO₃, Li₂CO₃, Sm₂O₃ and TiO₂ by using solid state sintering route at 1200 °C. The dielectric properties of the perovskite ceramic CLST are $\epsilon_r \sim 94$ and $\tan\delta \sim 2 \times 10^{-3}$ at ~ 10 GHz. The obtained ceramic was milled by jet milling to desirable particle size and modified by 1 wt% silane coupling agent of PTMS. The PTFE powder was used from Chenguang Research Institute

of Chemical Industry, China. Various volume fraction ceramics (0–60%) were loaded and mixed with PTFE powders by a three-dimensional mixing machine. The mixing powder was compressed and heated at 400 °C for 2 h and perovskite CLST/PTFE composite with dimension suitable for dielectric property measurement were obtained.

The phase structure of composites was analyzed by X-ray powder diffraction (XRD) (Philips, X'PertProMPD, Netherlands). The XRD patterns were obtained at room temperature by step scanning from 10° to 80°. The fracture morphology of composites was examined by a scanning electron microscope (SEM) (JEOL, JSM-5610LV, Japan) with an accelerating voltage of 25 kV. The thermal properties of the composites were performed by a differential scanning calorimeter (TG-DSC) (NETZSCH, STA449c/3/G, Germany) from 40 to 700 °C with a heating rate of 10 °C/min under air atmosphere. The dielectric constant and dielectric loss of the CLST/PTFE composites were measured by using a vector network analyzer (Agilent, HP8722ET, America) at 10 GHz. In this study, the thermal stability was measured by τ_f which was also tested by the vector network analyzer (Agilent, HP8722ET, America). The resonant frequencies for samples were found in the range of 8–12 GHz. The test cavity was placed over a thermostat and temperature applied in the range of 25–80 °C. The bulk densities of composites samples were measured by the Archimedes method. The porosity of the composites $w_{Porosity}$ was calculated by using the following Eq. 1.

$$w_{Porosity} = \frac{\rho_{cal} - \rho_{exp}}{\rho_{cal}} \times 100\% \quad (1)$$

where the ρ_{cal} and ρ_{exp} is the theoretical density and experimental density of composites respectively.

3 Results and discussion

3.1 Phase structure

Figure 1 shows the XRD patterns of CLST/PTFE composites. It can be seen that the (100) reflection (at $2\theta=18^\circ$) as a qualitative measure of the crystalline order of PTFE appears in all samples. The rest diffractions are corresponding to the CLST ceramic. As the volume fraction of the ceramic fillers increases, the crystalline intensity of PTFE reduces and the full width at half maximum increases. This is possibly due to the aggregation and crystallization of PTFE hindered by the increasing ceramic.

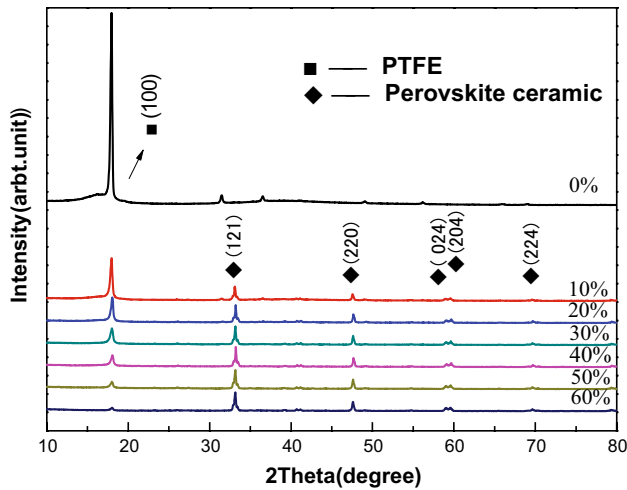


Fig. 1 XRD patterns of 0–60% perovskite ceramic filled PTFE composites

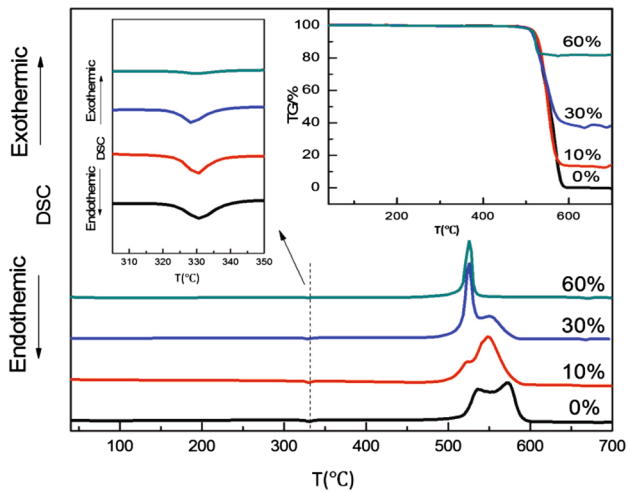


Fig. 2 DSC and TG curves of the pure PTFE and PTFE composites with 10, 30 and 60% of CLST ceramic

3.2 Thermal properties

Figure 2 depicts the weight loss and the endothermic and exothermic changes of the pure PTFE and the composites with 10, 30, and 60% of CLST ceramic measured by DSC/TG from 40 to 700 °C, respectively. The thermal weight loss below 500 °C is very little. When the temperature is higher than 600 °C, there is only ceramic left.

As the content of ceramic increases, the thermal degradation onset temperature and the area of the exothermic peak decrease obviously and the peaks become narrower. The exothermic peak of composites decreases from 2915 J/g for pure PTFE to 947.2 J/g for the composite with 60% ceramics. This is because as the increasing of ceramic and decreasing of PTFE, the high VF composites

need less heat and time to degrade. On the other hand, for the low thermal conductivity and specific heat capacity of the ceramic, the temperature of PTFE matrix around the ceramic increases faster in the heating process. At the same heating conditions, a sample with more ceramic would acquire enough heat for organics decomposing at a lower temperature, so the thermal degradation onset temperature is lower for a sample with more ceramic.

The feeble endothermic peak near 330 °C is referring to the softening temperature of PTFE. The endothermic peak moves slightly to the low temperature direction as ceramic contents increase. One reason is similar to the thermal degradation onset temperature above. The other reason may be because of the thermal interface resistance between the matrix and filler.

As the ceramic VF increases, the double exothermic peaks change to a single peak. The heating curve change from double peaks to a single peak which is caused by chain scission of PTFE in the linear segments. The double peaks in DSC heating curve are attributed to that the folded-ribbon structures of pure PTFE denotes linear segments. While in high VF composites, crystallites consist only of the extended-chain crystals with many defects formed by chain ends, and are smaller in size, especially in the lateral direction, and more defective than crystallites in pure PTFE [9].

3.3 Microstructure

Figure 3 shows the SEM images of (a) pure PTFE, (b) 30%, (c) 60% perovskite ceramic CLST filled PTFE composites. The PTFE forms a continuous phase and the CLST ceramic particles are fillers in PTFE matrix. At lower volume fraction (30%, Fig. 3b), the CLST ceramic particles disperse homogeneously in PTFE, indicating that the ceramic fillers have good interface connection with PTFE matrix. At higher volume fraction (60%, Fig. 3c), some inhomogeneous dispersion of ceramic particles were observed by the partial agglomeration of ceramic filler and obvious pores in the composites.

Figure 4 shows the porosity expressed as volume fraction of composites loaded with different volume fraction of CLST ceramic. The porosity fraction of the composites increases with the volume fraction of ceramic fillers (porosity fraction increases three time from loading of 10–60%). This is mainly due to the increasing CLST ceramic results in the heterogeneous dispersion of ceramic and the incomplete coverage of PTFE over CLST ceramic particles. The results of porosity are in accordance with SEM images. While the porosity fraction is increased with CLST ceramic fillers amount, the increasing rate of porosity is reduced at the higher volume fraction possibly due to the higher pressure required for preparing the composites.

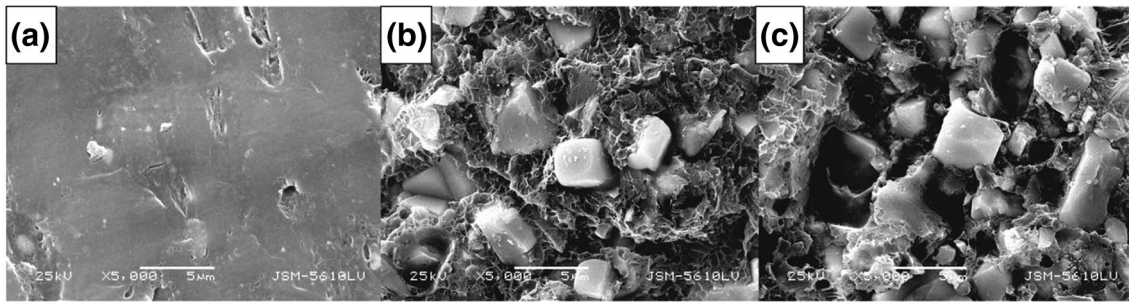


Fig. 3 SEM micrographs of **a** pure PTFE, **b** 30%, **c** 60% CLST ceramic filled PTFE composites

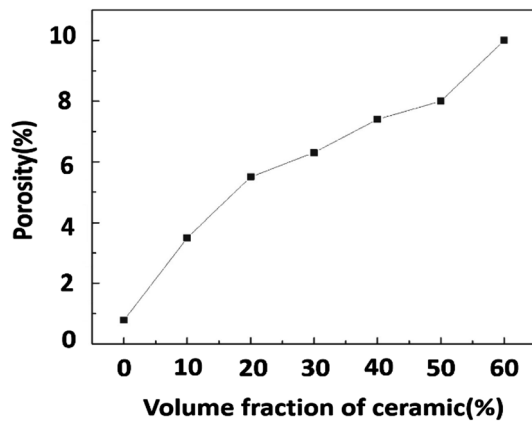


Fig. 4 The variation in porosity of composites with a function of ceramic filler content

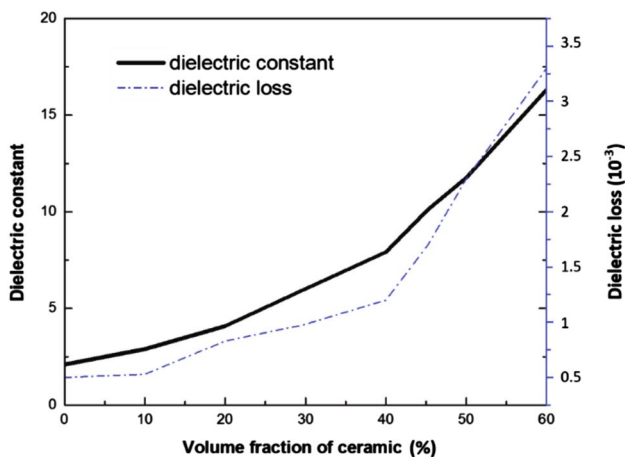


Fig. 5 Dielectric properties of 0–60% CLST ceramic filled PTFE composites at ~10 GHz

3.4 Dielectric behavior

Figure 5 depicts the dielectric properties of CLST/PTFE composites (~10 GHz). From Fig. 5 we know that the dielectric constant and dielectric loss increase with

the increasing VF of the ceramic filler respectively. It is observed that the dielectric constant and dielectric loss at ~10 GHz increases only moderately for the ceramic content up to 40% and beyond this loading both increase drastically. This indicates that composites of PTFE filled CLST ceramic $\leq 40\%$ may exhibit other suitable properties while it maintains desirable dielectric constant and low dielectric loss. Indeed the CLST/PTFE composite with 40% ceramic shows the dielectric properties as following: $\epsilon_r = 7.92$ (~10 GHz), $\tan \delta = 1.2 \times 10^{-3}$ (~10 GHz), $\tau_f = -45$ ppm/°C.

3.5 Dielectric fitting

Figure 6a compares the dielectric constants at about 10 GHz of CLST/PTFE composites obtained with the predicted by the Rother–Lichtenecker equation (Eq. 2).

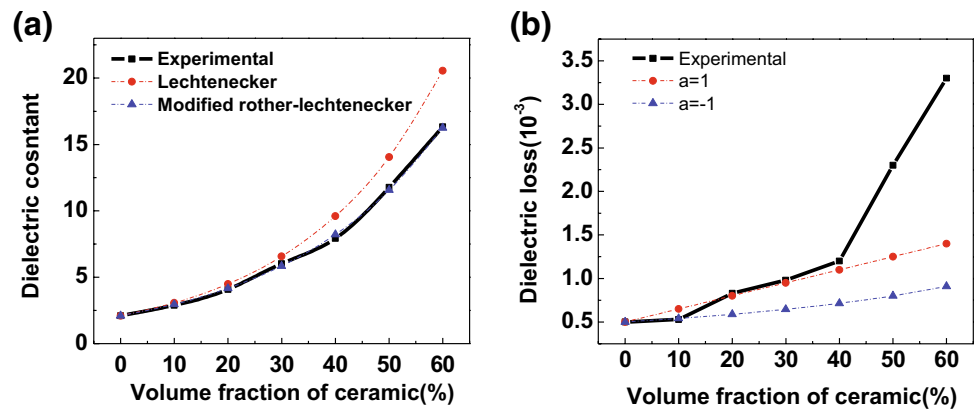
$$\ln \epsilon_{\text{eff}} = f \ln \epsilon_i + (1 - f) \ln \epsilon_m \quad (2)$$

where ϵ_{eff} , ϵ_i and ϵ_m are the dielectric constants of the composites, ceramic, and the PTFE matrix, and f is VF of a ceramic.

It can be seen that in low VF region (lower than 30%) the experimental data overlays very well the predicted curve given by Rother–Lichtenecker equation [10]. When VF increases to more than 30%, the predicted values deviate from the experimental data. Possibly Rother–Lichtenecker equation has just only taken into consideration of the ceramic fraction and PTFE phase, but effects of other structure characters, such as the interface, were ignored in the model. Furthermore, the model is only suitable for composites with near-spherical particles and good compatibility with PTFE. From the SEM images it is seen clearly that the ceramic in the perovskite ceramic/PTFE composites is deviated from the near-spherical model.

A modified Rother–Lichtenecker model is proposed to fit dielectric constants. The modified equation introduces a fitting parameter ' k ' [11], which is a shape-dependent parameter. The k is closely related to shapes and sizes of the ceramics, the interphase between the ceramic and polymer as well as the dispersion state of the composite

Fig. 6 Comparisons of theoretical and experimental of perovskite ceramic filled PTFE composites at ~10 GHz for **a** dielectric constants and **b** dielectric loss



[12]. The modified Rother–Lichtenecker equation was to show a good agreement with the experimental data of composite materials in a wide volume fraction range. Including the correcting parameter ‘*k*’ the modified Rother–Lichtenecker equation is written as:

$$\ln \epsilon_{\text{eff}} = \ln \epsilon_i + (1 - k) \ln \left(\frac{\epsilon_i}{\epsilon_m} \right) \quad (3)$$

It can be seen from Fig. 6a that the theoretical results from the modified Rother–Lichtenecker equation (Eq. 3) agree well with experimental results when *k* is set to 0.1. This value is different from the reported 0.3 which is maybe due to the different dispersion state. The modified Lichtenecker equation shows very good correspondence with the measurement results of the perovskite ceramic composite up to relatively high loadings. From this model, we could infer that the dielectric constant of the composites can be improved by choosing suitable ceramic with a high dielectric constant, a low dielectric loss, particle size and by increasing homogeneous dispersion of the CLST ceramic in PTFE matrix.

Figure 6b depicts a comparison of experimental dielectric loss of the composites with the values predicted by the general mixing model as shown in Eq. 4 [13].

$$(\tan \delta_c)^\alpha = \sum f_i (\tan \delta_i)^\alpha \quad (4)$$

where $\tan \delta_c$ and $\tan \delta_i$ are the dielectric loss tangents of the composite and the *i*th material, respectively. The f_i is the VF of the *i*th material. For this CLST/PTFE composite, the dielectric loss of the perovskite ceramic is $\sim 2 \times 10^{-3}$ while that of PTFE is 5×10^{-4} . The constant α is determined by the mixing state, where $\alpha = -1$ stands for serial mixing and $\alpha = 1$ stands for parallel mixing. It is reported that the dielectric loss of composites is not only influenced by the intrinsic factors as the interaction of the electric field with phonons, but also the extrinsic factors like size, shape of the ceramic and the defects, interface, holes etc. [14].

Shown in Fig. 6b, when VF is smaller than 10%, the mixing state of CLST ceramic and PTFE agrees well with serial mixing as indicated by the good overlap of theoretical dielectric loss values with the experimental values. When VF is between 10 and 40%, the mixing rule agrees well with parallel mixing. When VF is greater than 40%, the experimental dielectric loss increases dramatically and is not fit to both mixing models. When VF is very low (<10%), the dielectric properties of the composites are mainly determined by PTFE. When VF is 10–40%, the capacitor of the composites is the sum of the capacitor of kind components and the dielectric loss is mainly governed by the component with a greater dielectric loss. So the ceramic filler predominantly contributes to the dielectric loss of the composites. When VF is greater than 40%, the dielectric properties are tremendously influenced by the poor interface and defects, such as pores etc. as discussed in previous section.

Potential improvement of the dielectric properties may be achieved through tailoring of interphase and improving the interface compatibility. Further work on ceramic surface modification is underway and will be reported later.

There is significant meaning to study the effect rule of perovskite ceramic CLST on the dielectric properties of CLST/PTFE composites. The dielectric properties of perovskite ceramic CLST/PTFE composites are obviously better than most of the reported ones in high frequencies as shown in introduction which is a good candidate for dielectric industry application.

4 Conclusion

CLST/PTFE dielectric composites were prepared successfully and the effect rules of ceramic filler volume fraction on the properties of the composites have been investigated. As VF of the ceramic filler increases, the dielectric constant and dielectric loss increase. The CLST/PTFE

composite with 40% volume fraction ceramic has exhibited excellent dielectric properties among studied samples: $\epsilon_r = 7.92$ (~ 10 GHz), $\tan\delta = 1.2 \times 10^{-3}$ (~ 10 GHz), and $\tau_f = -45$ ppm/ $^{\circ}$ C. The curve fittings for the dielectric constant and dielectric loss of CLST/PTFE composites fit well Rother–Lichtenecker equation at $VF \leq 40\%$ but significant deviation is noted beyond this amount. Shape-dependent parameter “ k ” is introduced to the original Rother–Lichtenecker equation. The experimental data fit well by the modified Rother–Lichtenecker equation. The general mixing model is in good agreement with the experimental values of dielectric loss with parallel mixing when the volume fraction of CLST ceramic is between 10% and 40%. When the mixing rule agrees well when a VF is below 40%, the experimental values of dielectric loss increases dramatically which is mainly due to the interface defects.

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