Improved dielectric permittivity of NBCTO/epoxy composite films with low dielectric loss

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Abstract

In this paper, NBCTO/epoxy composite films with different contents of NBCTO were prepared by solution mixing and casting method. The structure, morphology, thermostability and dielectric properties of the composite films were studied by X-ray diffraction, scanning electron microscopy, thermo-gravimetric analysis and broadband dielectric spectrometer. The composite film showed a homogeneous structure and better thermostability, and the dielectric permittivity was almost independent of the frequency range from 10 to 10^6 Hz at room temperature. The dielectric permittivity and dielectric loss of NBCTO/epoxy composite film increased with increasing in NBCTO content, and the dielectric permittivity was as high as 37.10 whereas the dielectric loss was only 0.019 at 1 kHz when the NBCTO volume fraction reached 50 vol%. Theoretical analysis indicated that the dielectric permittivity calculated by the EMT model was close to the experimental data. The results showed that NBCTO/epoxy composite might have potential applications in the electronic devices.

Keywords $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ · Composites · Thermostability · Dielectric properties

1 Introduction

High dielectric permittivity polymeric composites have been attracted great attentions of many researchers due to their great potential applications in many fields, such as electronics, energy conversion and storage materials [1, 2]. The development trend of miniaturization and multifunctionality of electron components requires dielectric materials have dielectric permittivity as high as possible. Ceramic–polymer composite, combining the processability and flexibility of polymer and high dielectric permittivity of ceramic, is a promising candidate material in electrical engineering and electronic industry fields.

Up to now, many dielectric ceramics such as BaTiO_3 [3–10], BaSrTiO_3 [11], $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 [12] and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) [13–18] have been used as fillers in polymer matrix due to the high dielectric permittivity. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (NBCTO), similar to CCTO, is a lead-free material with pseudo-perovskite structure and no

piezoelectric effect, which also exhibits a colossal dielectric permittivity of about 10^4 and dielectric loss as low as 0.1 at room temperature [19, 20]. However, compared with CCTO, there are few reports about NBCTO. Studies on NBCTO were mainly focused on the dielectric properties of NBCTO ceramic [21–25] or NBCTO/PVDF composites [26, 27]. To our knowledge, there has been no report on the effect of incorporating NBCTO fillers in epoxy matrix on their dielectric properties.

In the present work, NBCTO/epoxy composite films with high dielectric permittivity and low dielectric loss were prepared by using NBCTO powders as filler and epoxy as polymer matrix. Epoxy has many excellent properties such as superior electrical insulating, high dielectric breakdown strength and electrothermal stability, which has been recognized as a good candidate for its practical application in the manufacturing of electrical equipments. It is novel to combine NBCTO with epoxy to achieve high dielectric material for the embedded capacitor. In this paper, the

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effects of NBCTO volume fractions on the structure, thermostability and dielectric properties of the composite films were discussed in detail. The theoretical dielectric permittivity of the NBCTO/epoxy composite films was also predicted using various theoretical models.

2 Materials and methods

2.1 Materials

The bisphenol A epoxy resin (E-51) was purchased from Guangzhou Suixin Chemical Co., Ltd. 2-Ethyl-4-methylimidazole (serving as the curing agent) was purchased from Adamas reagent Co., Ltd. Acetone was obtained from Jiangsu Qiangsheng Functional Chemical Co., Ltd. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. NBCTO powder was fabricated by the solid state reaction method [26]. SEM result showed the average particle size of the synthesized NBCTO powder was 2–5 μm (Fig. 1).

2.2 Preparation of NBCTO/epoxy composite films

The NBCTO/epoxy composite films with different NBCTO volume fractions (0, 10, 20, 30, 40 and 50 vol%) were prepared as follows. Firstly, NBCTO powders were mixed with acetone using ultrasonic dispersion for 40 min. Secondly, the NBCTO solution mixed with acetone was added to a certain amount of epoxy resin. Then the mixture mixed with NBCTO and epoxy was mechanically stirred for 4 h at 50 °C. After that, 2-ethyl-4-methylimidazole was added to the above mixture and kept stirring for 20 min. Finally, the mixed solution was casted onto a pretreated copper sheet using a scraper, followed by degassing under vacuum at

60 °C for 30 min. The composite films were obtained after curing at a procedure of 80 °C/2 h + 110 °C/2 h and post-curing at 140 °C for 4 h.

2.3 Characterization

The phase structure of epoxy, NBCTO and NBCTO/epoxy composite films was identified by X-ray diffraction (XRD, Cu LFF X-ray tube Pw3373/10). The cross-section microstructure of the composite films was observed by scanning electron microscope (SEM, FEI Quanta FRG 200F). The thermal behavior of the different samples was detected by thermo-gravimetric analyzer (TGA, TA Discovery TGA) at a heating rate of 10 °C/min in nitrogen atmosphere. The dielectric properties were measured using a broadband dielectric spectrometer (Novocontrol Concept 80) at the frequency range of 1–10⁶ Hz at room temperature. For dielectric measurements, silver paste was applied to the upper side of the film as one electrode and another side electrode was used as Cu substrate. The composite films were cut into 2 cm × 2 cm and the thickness of the composite films was about 500–800 μm . The theoretical dielectric permittivity of the composite films was also predicted using various models.

3 Results and discussion

Figure 2 displays the XRD patterns of epoxy, NBCTO powder and NBCTO/epoxy composite films. As seen from Fig. 2, there is a broad peak around at 2θ value of 17.2° for epoxy, and the main diffraction peaks of NBCTO powder are indexed according to the JCPDS #75-2188 [26]. There is no impurity phase for the synthesized NBCTO powder.

Fig. 1 SEM micrograph of the synthesized NBCTO powder

Fig. 2 XRD patterns for epoxy, synthesized NBCTO powder and NBCTO/epoxy composite films

With increasing in NBCTO content, the diffraction peak of epoxy decreases gradually until it disappears when the NBCTO content is above 40 vol%. This is mainly due to the fact that the diffraction peaks of NBCTO in the composite become stronger and stronger with the increase of NBCTO content, which covers the diffraction peak of epoxy. It is also observed that there is no significant change for the XRD diffraction peaks of NBCTO, indicating that the NBCTO crystal structure is stable during the preparation of NBCTO/epoxy composite films.

The thermal behavior of epoxy matrix and composite films was investigated. TGA curves of epoxy and NBCTO/epoxy composite films are shown in Fig. 3. In the temperature range of 50–900 °C, the degradation behavior of all the samples has a similar trend. It is indicated that the structure of epoxy did not change when NBCTO was added to the epoxy matrix. It can be seen from the TGA curves that epoxy starts to decompose at about 400 °C, whereas the decomposition temperature of the composites is about 430 °C, which shows that the composites exhibit better stability than epoxy matrix. The increase in decomposition temperature is due to the enhancement of interaction between NBCTO and epoxy matrix, which hinders the movement of polymer chains in epoxy. In addition, the theoretical weight loss of the samples is also calculated in Table 1. There is a little deviation between the experimental and theoretical values, but the deviation is almost within 5%, which indicates that NBCTO powder has good dispersion in the epoxy matrix.

Figure 4a–c show the SEM micrographs of the fresh cross-section of NBCTO/epoxy composite films containing with 10 vol%, 30 vol% and 50 vol % NBCTO, respectively. SEM results show that NBCTO particles are distributed uniformly in the epoxy matrix and there are no obvious voids and agglomerations. With the increase of NBCTO volume

Table 1 Comparison of theoretical weight loss and experimental weight loss of NBCTO/epoxy composite films

Sample	Theoretical weight loss (%)	Experimental weight loss (%)
10 vol% NBCTO-90 vol% epoxy	66.55	64.80
20 vol% NBCTO-80 vol% epoxy	46.95	49.28
30 vol% NBCTO-70 vol% epoxy	34.07	34.37
40 vol% NBCTO-60 vol% epoxy	24.92	24.10
50 vol% NBCTO-50 vol% epoxy	18.12	19.40

fraction, the structure of the composite film becomes more compact. It will help the samples maintain stable dielectric properties in the measuring frequency range.

The dielectric properties of epoxy and NBCTO/epoxy composite films were measured at the frequency of $1\text{--}10^6$ Hz and room temperature. Figure 5a, b show the frequency dependence of dielectric permittivity and dielectric loss of samples, and Fig. 5c shows the dielectric permittivity and dielectric loss varying with the volume fraction of NBCTO at 1 kHz. As shown in Fig. 5, the dielectric permittivity and dielectric loss of the composite films decrease with increasing the frequency, which could be interpreted by interfacial polarization inside the composites in applied alternating field. From the obtained data shown in Fig. 5a, the dielectric permittivity of the composite films decreases in all the measuring frequency range due to the relaxation process type Debye [28]. However, the dielectric permittivity decreases slightly with increasing the frequency, and the stable dielectric permittivity may be attributed to the uniform distribution of NBCTO particles in the epoxy matrix. With increasing in NBCTO volume fraction, the dielectric permittivity increases from 8.92 to 37.10 at 1 kHz when the NBCTO volume fraction increases from 10 to 50 vol%. Compared with epoxy matrix ($\epsilon = 8.07$, $f = 1$ kHz), the dielectric permittivity of the composite film with 50 vol% NBCTO is more than three times higher than that of epoxy. As seen from Fig. 5b, the dielectric loss is more dependent on the frequency. The dielectric loss decreases in a low-frequency due to dc conductance effect and then increases due to the relaxation polarization in the polymer in higher frequencies, but the dielectric loss is almost below 0.03 from 10^2 to 10^5 Hz. In addition, the dielectric loss is only 0.019 at 1 kHz when NBCTO content is 50 vol% (shown in Fig. 5c). In this case, the slow mobility of epoxy chain under electric field plays an important role in the stable dielectric loss.

Figure 6 gives the frequency dependence of conductivity of epoxy and composite films. The conductivity exhibits a good linear behavior as a function of frequency, and the conductivity increases sharply as the frequency is increased. This phenomenon is mainly caused by the free

Fig. 3 TGA curves for epoxy and NBCTO/epoxy composite films

Fig. 4 SEM micrographs of different samples **a** 10 vol% NBCTO-90 vol% epoxy; **b** 30 vol% NBCTO-70 vol% epoxy; **c** 50 vol% NBCTO-50 vol% epoxy

charges available in a low-frequency whereas the trapped charges are activated at higher frequencies, which leads to increase of the conductivity [29]. As shown in Fig. 6, the conductivity increases slightly with the increase of NBCTO volume fraction. Even when the NBCTO content is up to 50 vol%, the conductivity is only 2.2×10^{-10} S/cm at 10 Hz and 1.8×10^{-5} S/cm at 10^6 Hz and room temperature, which confirms that a conductive network is still not formed. Thus the composite with insulation structure has a low dielectric loss, and this is consistent with the results of Fig. 5b.

Until now, some models have been put forward to predict the dielectric permittivity of ceramic–polymer composites. In this work, the following equations are used to calculate the effective dielectric permittivity of NBCTO/epoxy composites:

$$\ln \varepsilon = (1 - f) \ln \varepsilon_1 + f \ln \varepsilon_2 \quad (1)$$

$$\varepsilon = \varepsilon_1 \left[1 + \frac{3f(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - f(\varepsilon_2 - \varepsilon_1)} \right] \quad (2)$$

$$\varepsilon = \varepsilon_1 \left[1 + \frac{nf(\varepsilon_2 - \varepsilon_1)}{n\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1 - f)} \right] \quad (3)$$

$$\varepsilon = \varepsilon_1 \left[1 + \frac{f(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + n(1 - f)(\varepsilon_2 - \varepsilon_1)} \right] \quad (4)$$

In the above four equations, Eqs. (1)–(4) correspond to Logarithmic model, Maxwell–Garnet model, Yamada model and EMT model, respectively [30–32], where ε , ε_1 and ε_2 are the dielectric permittivity of the composite, epoxy matrix and NBCTO powder, respectively, and f is the NBCTO volume fraction and n is the ceramic morphology fitting factor. The dielectric permittivity of epoxy and NBCTO used in this work is 8.07 and 13,510, respectively, measured at 1 kHz and room temperature.

Figure 7 gives a comparison between experimental and theoretical dielectric permittivity of NBCTO/epoxy composite films. As seen from Fig. 7, the experimental

Fig. 5 The frequency dependence of **a** dielectric permittivity and **b** dielectric loss, and **c** the dielectric permittivity and dielectric loss varying with the volume fraction of NBCTO

Fig. 6 The frequency dependence of conductivity of epoxy and NBCTO/epoxy composite films

Fig. 7 Comparison of experimental data and theoretical dielectric permittivity of NBCTO/epoxy composite films

values are in good agreement with the EMT model calculated using Eq. (4), where the derived n is 0.26. The value of n obtained is higher than those reported previously [14, 30], which indicates that the dielectric permittivity of the composite is more closely associated with the filler size and shape [16]. For Logarithmic model, there is a big deviation between experimental values and theoretical predictions. The Logarithmic model is not valid due to the great difference between the dielectric permittivity of NBCTO and epoxy matrix, which is only valid in the case of the filler and the matrix have close value of dielectric permittivity [4]. Similarly, the Yamada model predicts higher dielectric permittivity for all components of the composite films. Whereas, the experimental value is close to the calculated value using Maxwell–Garnet model when $f_{\text{NBCTO}} \leq 20$ vol%, but there have lower

predicted values with increasing in NBCTO content. Maxwell–Garnet model is applicable to those filler particles that are nearly spherical, uniformly distributed and non-interacting [18], whereas the NBCTO particles used in this work are non-spherical and would contact each other with the increase of NBCTO filler content, so there is a deviation between experimental and predicted values.

4 Conclusions

NBCTO/epoxy composite films with good thermal stability were successfully prepared by solution mixing and casting method. The dielectric permittivity increases with increasing in NBCTO content and reaches 37.10 at 1 kHz and room temperature when the NBCTO volume fraction is 50 vol%, while the composite film keeps a very low dielectric loss of 0.019. Compared with epoxy matrix, the dielectric permittivity of the composite film with 50 vol% NBCTO is more than three times higher than that of epoxy. Among the various theoretical models used to predict the dielectric permittivity, the EMT model can predict the dielectric permittivity of NBCTO/epoxy composite film very well, where the derived n is 0.26. The results showed in this study could provide a promising candidate dielectric material for the embedded capacitor.

Acknowledgements This work was supported by the Natural Science Foundation of Jiangsu Province (BK20130314) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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