Fabrication, characterisation and dielectric properties of KH550 modified BST/PVDF nanocomposites with high dielectric strength

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Abstract: Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST)/poly(vinylidene fluoride) (PVDF) 0–3 nanocomposites with BST nanoparticle contents of 10–40 vol% were prepared by tape casting method. The BST nanoperlaticles with ~60 nm crystal size and accurate atomic ratio were synthesised by sol–gel method. The effect of the BST nanoparticle contents on the microstructure and dielectric properties of BST/PVDF nanocomposites were investigated. The BST/PVDF nanocomposites system declares that feasibility of applying low contents nanoparticles to form a homogeneous distribution in polymer matrix, higher dense interface connectivity, thereby providing a significant improvement to the dielectric strength and energy storage density; meanwhile, the nanocomposites possess high dielectric tunability. In this study, the maximum dielectric strength ~287.12 kV/mm and energy storage density ~5.15 J/cm$^3$ were obtained in 10 vol% BST/PVDF nanocomposites, respectively. Moreover, the nanocomposite possesses high dielectric tunability ~62.6% at 58 kV/mm, which proposed the nanocomposites suitable for tunable microwave devices, supercapacitors and energy storage device applications at high-voltage environment.

1 Introduction

Recently, remarkable dielectric tunability has been reported in Ba$_{1-x}$Sr$_x$TiO$_3$-based ceramics, which possess extremely high dielectric constant, low dielectric loss, outstanding dielectric tunability under applied direct current (DC) electric field and well-controlled Curie temperature via adjusting barium/striontium (Ba/Sr) ratio [1–3]. Actually, though the dielectric ceramics possess excellent dielectric properties, they also have inconvenience such as lack flexibility and high sintering temperature [4–6]. On the other hand, from the practical perspective, low dielectric strength is not conducive to dielectric tunability device applications in high-voltage environment [7–9]. Furthermore, to meet the impedance matching, the dielectric properties for tunable microwave devices should have relatively low dielectric constant [10, 11]. Thus, the ceramics are not satisfied with the fabrication of tunable microwave and energy storage devices. By contrast with the ferroelectric Ba$_{1-x}$Sr$_x$TiO$_3$-based ceramics, ferroelectric poly(vinylidene fluoride) (PVDF) has received more attention among dielectric polymers because of their excellent dielectric strength, low dielectric loss, simple processing and low cost [12]. However, PVDF cannot be used for tunable microwave and energy storage devices individually because of its poor dielectric tunability and extremely low dielectric constant (~10 at room temperature), respectively. Therefore, one method has been carried out to fabricate ceramic–polymer composites via introducing Ba$_{1-x}$Sr$_x$TiO$_3$ particle fillers into PVDF matrix. At the beginning, most of research focus on energy storage density of the composites [13–15]. Only Zhang et al. reported the dielectric tunability of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST) PVDF composites. It turned out that the dielectric constant, dielectric tunability and energy storage density of the polymer can be enhanced by increasing the concentration of Ba$_{1-x}$Sr$_x$TiO$_3$ particle fillers. Unfortunately, the increasing of the particle fillers always results in dielectric strength decreases quickly. Moreover, it has been demonstrated that the disadvantage can be improved via advanced preparation technology of composites or modification of particle fillers. The results shown that these methods also can contribute to the enhancement of dielectric tunability [16–18].

However, the rise of dielectric strength of the composites is not particularly evident. A large number of studies have been reported that the dielectric strength of ceramic–polymer nanocomposites can be severely enhanced owing to the increased blocking effects of the interfaces [19–23]. The increased blocking effects are result of high interfacial area which derived from the high surface area of nanoparticle fillers, whereas the effect of nanoparticle filler contents on the dielectric tunability of Ba$_{1-x}$Sr$_x$TiO$_3$/PVDF nanocomposites has scarcely been reported.

In this paper, flexible nanocomposites were prepared by a tape casting with PVDF as the polymer matrix and modified BST nano-powder as fillers. The BST nanoparticles were fabricated by a sol–gel method, the surface was modified via silane coupling agent, aminopropyl triethoxy saline (KH550), to improve the interfacial adhesion between BST nanoparticles fillers and PVDF polymer matrix. The effects of modified BST nanoparticle filler contents on microstructure, dielectric properties and energy storage density of the BST/PVDF nanocomposites were investigated.

2 Experimental procedure

2.1 Materials

The following materials are used to prepare the BST/PVDF nanocomposites. Acetic acid glacial (C$_2$H$_4$O$_2$, AR, ≥99.5%) and ethanol (C$_2$H$_5$O, AR, ≥99.7%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Sr acetate [Sr(C$_2$H$_3$O$_2$)$_2$, AR, ≥99.0%], Ba acetate [(BaC$_2$H$_5$O$_2$)$_2$, AR, ≥99.9.0%] and tetrabutyl titanate (Ti [OCH(CH$_3$)$_2$)$_4$, chemically pure reagent (CP), ≥98.0%)] were supplied by Sinopharm Chemical Reagent Co., Ltd. N,N-dimethyl formamide (DMF) (AR, ≥99.5%) was provided by Guangdong Guanghua Sci-Tech Co., Ltd. PVDF polymer was obtained from Shanghai 3F New Materials Co., Ltd.

2.2 Preparation of KH550 modified BST nano-powders

The BST nano-powder were prepared by sol–gel method. Stoichiometric amount of Ba(C$_2$H$_5$O$_2$)$_2$, Sr(C$_2$H$_5$O$_2$)$_2$ and Ti[OCH
(CH$_3$)$_2$J$_4$ were used as reagents, as well as C$_3$COOH and C$_2$H$_6$O were used as solvent. First, Ba(C$_2$H$_3$O$_2$)$_2$ and Sr(C$_2$H$_3$O$_2$)$_2$ were taken in the molar proportion of 3:2 and dissolved in C$_3$COOH at 60°C with continuous stirring until the reagents completely dissolved, which is called A solution. Second, Ti[OCH(CH$_3$)$_2$]$_4$ was dissolved in C$_2$H$_6$O with continuous stirring for 15 min, which is called B solution. Finally, the B solution was slowly added into the A solution, and then moderate deionised water was added to form uniform mixture solution; meanwhile, appropriate C$_3$COOH was added to adjust the pH value to 5–6. Subsequently, the mixture solution was stirred at 60°C for complex formation and to obtain homogeneous sol and the sol was evaporated at 100°C with continuous stirring to form gel. After that, the gel was further dried in a vacuum oven at 120°C for 24 h. The fine powder was heated at 800°C for 2 h with intermediate repeated grinding.

To modify the surface of BST nanoparticles, BST nanoparticles were dispersed in an aqueous solution of hydrogen peroxide in a magnetic stirrer at 80°C for 2 h, and then 4 wt% KH550 was added to form uniform mixture solution; meanwhile, appropriate C$_3$COOH was added to adjust the pH value to 5–6. Subsequently, the mixture solution was stirred at 60°C for complex formation and to obtain homogeneous sol and the sol was evaporated at 100°C with continuous stirring to form gel. After that, the gel was further dried in a vacuum oven at 120°C for 24 h. The fine powder was heated at 800°C for 2 h with intermediate repeated grinding.

2.3 Preparation of BST/PVDF nanocomposites

PVDF and BST nano-powder were mixed in DMF solvent with various volume fraction ratio. The mixtures were dispersed by using ultrasonic for 1 h, stir for 2 h and ball-milling for 12 h, successively. Next, the mixtures were tape cast on glass substrates and the films were kept in a vacuum oven overnight at 60°C in order to evaporate the DMF solvent. Finally, the BST/PVDF films were peeled off from the glass substrate. For dielectric measurements, the surfaces of the specimens were coated electrode with silver paste. The films obtained were 0.02–0.1 mm thick.

2.4 Characterisation

The X-ray diffraction (XRD, X’pert Pro, Holland) are used to show the as-prepared BST nanoparticles phase structure and calculated crystal size by using Scherrer equation. The particles size of BST nanoparticles were measured using a laser diffraction particle size analyser (BI-90Plus, Brookhaven Instruments, USA). The crystallinity and chemical composition of the BST nanoparticles were studied by the transmission electron microscope image (TEM, Philips Tecnia) coupled with an energy dispersive spectroscopy (EDS, Oxford Instruments, UK). The microstructure and the morphology of the BST/PVDF nanocomposite samples were characterised via scanning electron microscopy (SEM; TESCAN VEGA3). In addition, the dielectric properties were measured using Agilent E4980A LCR meter (Palo Alto, CA). The dielectric tunability of the nanocomposites was measured at 1 kHz with a DC bias voltage source. Moreover, dielectric strength was tested by a dielectric withstand voltage test (CJ2671S, Nanjing Changjiang Electronic Co., Ltd.).

3 Results and discussion

3.1 Microstructure of BST nano-powders

Fig. 1a shows the XRD pattern of the as-prepared BST nano-powder sintered at 800°C for 2 h. All diffraction peaks can be labelled and assigned to the pure cubic perovskite structure corresponding to JCPDS No. 34-0411. No visible signal from any other impurities are observed. The results confirm the pure BST and its polycrystalline nature. The grain size of about 60 nm was calculated from the XRD data by using Scherrer equation. The detailed size distribution of BST nanoparticles is plotted in Fig. 1b. From the quantitative data, it is easy to see that the average nanoparticles size is 55.89 nm, which is consistent with the previous result.

Fig. 2a shows the TEM micrograph of the as-prepared BST nanoparticles. The nanoparticles are in an agglomerated form having the average size distribution in the vicinity of 60 nm, in a good agreement with the XRD data and size distribution result. To certify the crystalline nature of the as-prepared BST nanoparticles, selected area electron diffraction (SAED) pattern (as shown in Fig. 2b) was taken from the region surrounded by a circle (as shown in Fig. 2a). Concentric rings in the SAED pattern demonstrate the polycrystalline nature of the as-prepared BST nanoparticles which has been proved by XRD data analysis. In the meantime, energy dispersive spectrometer (EDS) analysis was carried out in the same region (as shown in Fig. 2a) and the corresponding EDS spectrum is exhibited in Fig. 2c, which demonstrate the presence of Ba, Sr, Ti and O, as well as its atomic percent and barium/(barium+strontium) ratio (R) (as shown in the inset of Fig. 2c). The result illustrates that the pure BST nanoparticles can be obtained by using sol–gel method.

3.2 Microstructure of BST/PVDF nanocomposites

The SEM micrographs (fracture cross-sections) of BST/PVDF nanocomposite thick films with different volume fractions of BST nano-powders (i.e. 10–40 vol%) are shown in Fig. 3. The nanocomposites filled with BST nanoparticles all show good distributions of the fillers in the PVDF matrix without obvious agglomeration via using ball-milling technology. Fig. 3a clearly shows that the BST nanoparticles are well compatible with PVDF matrix and the nanocomposite shows dense structure. However, the pores, cracks and other defects gradually increase and net distribution of PVDF slowly disappears with increasing the contents of BST nanoparticles, which lead to the poor compatibility between the nano-fillers and the matrix. Although
there are a certain amount of KH550 bonded on the BST nanoparticles surface, their effectiveness is limited when the contents of BST nano-powders exceed 20 vol%. A large amount of BST nanoparticles are still to be free from PVDF matrix. The main reason lies in that the surface of BST nanoparticles cannot be fully coated on account of inappropriate content of KH550, which results in incompatibility between the BST nanoparticles and the PVDF matrix [18].

3.3 Dielectric properties of BST/PVDF nanocomposites

The frequency dependency of dielectric constant and dielectric loss of the nanocomposites with different volume fractions of BST nanoparticles in frequency range 100 Hz–1 MHz at room temperature are shown in Fig. 4. First, Fig. 4a reveals that the dielectric constant increases from 14.11 to 29.67, at room temperature and 1 kHz, with increasing volume fractions of BST nanoparticles, which should be attributed to the high dielectric constant of BST nano-ceramics. Nevertheless, the dielectric constant of all the nanocomposites decreases with increasing frequency, which results from the polarisation relaxation including interface polarisation and dipole orientation relaxation polarisation generating from the inner structure of the nanocomposites [24]. Second, the tendency that dielectric constant decreases faster and faster at low frequency with increasing volume fraction of BST nanoparticles is discovered. The results demonstrate that the leakage conductance is improved with increasing volume fractions of BST nanoparticles. The reason comes from two aspects: on the one hand, the gradual deteriorative interface connectivity and increased defects can result in high conductivity; on the other hand, the increased BST nanoparticle contents with high conductivity were introduced.

Fig. 4b shows that the dielectric loss of the nanocomposites decreases first and then increases when the volume fractions of BST nanoparticles are no more than 20 vol%. It is well known that there are two different dielectric behaviours play a part in dielectric loss. One is the conductivity loss at low frequency which results from the weakened interface polarisation, increased defects of BST/PVDF nanocomposites and high conductivity of BST nano-ceramics, the other is the Debye relaxation loss at high frequency which derived from the C–F dipole orientation polarisation of PVDF matrix. The phenomenon at high frequency, dielectric loss peak will become very smooth or even suppressed, is mainly because the conductivity loss significantly increases with increasing volume fractions of BST nanoparticles.

The Cole–cole plots of the dielectric behaviour of the nanocomposites at room temperature are shown in Fig. 5. The deviation from semi-circle of Cole–cole plots at high frequency illustrates that there are several kinds of polarisation relaxation mechanisms of asymmetric distribution relaxation time in the inhomogeneous structure of the BST/PVDF nanocomposites. The relaxation time are mainly affected by the C–F dipoles in the relaxor ferroelectric PVDF polymer. Meanwhile, a unique dielectric behaviour (the ends of plots upturn at low frequency) is observed, which results from the conductivity. Moreover, the degree of upturn becomes much more evident with increasing the volume fraction of BST nanoparticles. The result demonstrates that the leakage conductivities of the nanocomposites are gradually increased due to the weakened interface polarisation, increased defects and high volume fractions of BST nanoparticles, in a good consistency with the dielectric frequency spectra.

Fig. 6 shows the dielectric constant and dielectric loss of BST/PVDF micro and nanocomposites with the addition of micro and nanometer BST particles, as well as its error bars with different BST contents at 1 kHz and room temperature [18]. The dielectric constants of the nanocomposites are lower than those of the micro-composites (as shown in Fig. 6a). It is mainly because the ferroelectric domain walls in a single BST nanocrystal size will be reduced or even disappear, so the effect of domain wall vibration

![Figure 2: TEM micrograph of the as-prepared BST nanoparticles](image)

*Fig. 2 TEM micrograph of the as-prepared BST nanoparticles*

a TEM micrograph of as-prepared BST nanoparticles in an agglomerated form

b SAED pattern taken from the region as shown in image (a)

c EDS spectrum taken from the same region
which make a contribution to dielectric constant of BST nano-ceramic will be attenuated [25, 26]. The dielectric losses of the nanocomposites are higher than those of the micro-composites (as shown in Fig. 6b). It is due to the more interface in nanocomposites on account of the high surface area of nanoparticle fillers. In addition, a great amount of pores, cracks and other defects and weakened interface connectivity can also cause low dielectric constant and high dielectric loss.

Fig. 7 shows the temperature dependence of the dielectric constant and dielectric loss of BST/PVDF nanocomposites at 1 kHz. Fig. 7a shows that the dielectric constant increases with temperature increasing from 35 to 175°C because of the lifting dipole orientation polarisation level. It is found carefully that the Curie temperature \( T_c \) of BST/PVDF nanocomposites shifts to lower temperature with increasing the volume fraction of BST nanoparticles, owing to the low Curie temperature of BST \( (T_c \approx 5°C) \) [16]. In addition, the Curie temperature of PVDF \( (T_c \approx 155°C) \) was first improved to 165°C and then suppressed with increasing the volume fraction of BST nanoparticles. The maximum dielectric constants of BST/PVDF nanocomposites with 10, 20, 30 and 40 vol% BST nanoparticles were 49.4, 71.5, 88.1 and 82.0, respectively, measured in the range of 170–180°C. Fig. 7b shows that the dielectric loss of BST/PVDF nanocomposites first slowly increases and then sharply increases with increasing temperature from 35 to 175°C and reaches maximum in the range of 170–180°C. It is mainly because that the orientations of dipoles

**Fig. 3**  SEM images of BST/PVDF nanocomposites with different contents of BST nanoparticles

- a 10 vol%
- b 20 vol%
- c 30 vol%
- d 40 vol%

**Fig. 4**  Frequency dependence of BST/PVDF nanocomposites at room temperature

- a Dielectric constant
- b Dielectric loss
(C–F) are accelerated due to the molecules thermal motion. Moreover, it has been observed that the dielectric loss peak is less narrow and sharp-pointed with increasing volume fractions of BST nanoparticles. The result indicates that statistical thermal motions of PVDF polar groups are hindered on account of the connectivity between BST nanoparticles and PVDF matrix.

3.4 Dielectric tunability of BST/PVDF nanocomposites

The dielectric tunability ($T_u$) of the nanocomposites is evaluated according to

$$T_u = \frac{\varepsilon_r(E) - \varepsilon_r(0)}{\varepsilon_r(0)} \times 100\%$$

where $\varepsilon_r(0)$ and $\varepsilon_r(E)$ are the dielectric constant under zero and some given DC electric field, respectively. Some research results shown that ferroelectric domain walls vibration, interface polarisation and dipoles orientation polarisation have contributed to the dielectric tunability.

The applied DC electric field dependent dielectric constant of BST/PVDF nanocomposites with different volume fractions of BST nanoparticles is measured and it shows that the dielectric constant of the nanocomposites decreases with increasing applied DC electric field. The reason is that domain switching to generate large domain is promoted and the interface polarisation will be more weakened under applied DC electric field. The dielectric tunabilities of BST/PVDF nanocomposites with increasing applied DC electric field are shown in Fig. 8a. The result shows that the dielectric tunability increases slowly with increasing applied DC electric field below threshold electric field and then increases sharply after the electric field is larger than the threshold electric field. It is mainly because pores, creaks and other defects could lead to the concentration of the local electric charge and result in an inhomogeneous distribution of the local electric field below threshold electric field, which cause the reduction of the electric field on ceramic nanoparticles, so that the domain switching is suppressed; meanwhile, the ferroelectric domain walls reduce due to too small crystal size. In addition, the defects will lead to inferior interface connectivity which results in reduced interface polarisation. When the electric field exceeds threshold values, most defects in the nanocomposites will breakdown and become conducting state, which lead to a relatively homogeneous distribution of the electric field. Therefore, domain switching is enhanced and interface polarisation is further weakened, which make the dielectric tunability fast rise. Furthermore, the threshold electric field decreases with increasing the contents of BST nanoparticles, as shown in Fig. 8b, showing that the increased defects will make the nanocomposites easier to be local breakdown. In addition, it can be observed that the dielectric tunability always increases above threshold electric field with increasing contents of BST nanoparticles under the same applied DC electric field, which benefits from increased contents of BST nanoparticles with high dielectric tunability.

There are two parts in Fig. 8a separated by the threshold point, and the dielectric tunability of the two parts shows linear proportional relations to the applied DC electric field. The dielectric tunability ($T_{01}$ and $T_{02}$) under unit applied DC electric field of BST/PVDF nanocomposites with different contents of BST nanoparticles are shown in Fig. 8b and Table 1. It obviously indicates that the values of slope 1 are much smaller than that of slope 2. The results obviously demonstrate that the BST nanoparticle contents have hardly affected on the $T_{01}$ of the nanocomposites, while $T_{02}$ is enhanced tremendously.

3.5 Energy storage density of BST/PVDF nanocomposites

The energy storage density of dielectric materials can be described by the following equation

$$U = \frac{1}{2} \varepsilon_i E_r^2$$

where $\varepsilon_i$ is the relative dielectric constant, $\varepsilon_0$ is the vacuum dielectric constant.
constant (8.85 × 10^{-12} \text{ F/m}) and \( E_b \) is the applied electric field. Although the energy storage density is influenced by dielectric constant and dielectric strength according to (2), the breakdown strength plays a more important role compared with dielectric constant for improving the energy storage density because of its quadratic rise [27].

The dielectric strength has been found to be most appropriate for the Weibull distribution [28, 29]

\[
X_i = \ln(E_i) \quad (3)
\]

\[
Y_i = \ln(-\ln(1 - p)) \quad (4)
\]

\[
p = i/(n + 1) \quad (5)
\]

where \( E_i \) is the specific breakdown electric field of each samples in the experiments, \( p \) is the probability, \( n \) is the sum of samples, in this work \( n = 4 \) and \( i \) is the serial number of samples. The dielectric strength values are arranged in ascending order of a composition in the Weibull distribution and the two parameters \( X_i \) and \( Y_i \) have linear relationship. The average dielectric strength can be obtained by extracting from point where the fitting lines intersect with horizontal line through \( Y_i = 0 \).

The Weibull dielectric strength of BST/PVDF nanocomposites with different contents of BST nanoparticles were measured under applied DC electric field using four samples of the same composition and the results are shown in Fig. 9. The average dielectric strengths of the nanocomposites with different contents of BST nanoparticles are shown in Fig. 9 and Table 1. Compared with the previously reported data [16–18], the results show that the dielectric strengths of the nanocomposites are enhanced greatly which derived from increased blocking effects of the interfaces. In addition, the dielectric strength rapid decreases from 287.12 to 158.2 kV/mm with increasing the contents of BST nanoparticles. As we all know that dielectric strength of composites is strongly influenced by particle filler contents, interface connectivity, agglomerations, polymer matrix phase (the \( \beta \)-phase generated has been proved by tape casting method in our previous work), defects and large difference of dielectric constant between particle fillers and polymer matrix. Thus, with regard to gradually reduced dielectric strength of BST/PVDF nanocomposites with increasing the contents of BST nanoparticles. One reason is the increased defects (including cracks, pores etc. which has been certified by SEM images) because of its low breakdown strength (~3 kV/mm). Another reason is the worsen interface connectivity which results from inappropriate coupling agent contents. The other reason is the large difference of dielectric constant between nanoparticle fillers and polymer matrix which will lead to a distortion in the distribution of the electric field. In this case, the electric field in PVDF matrix is much higher than the average electric field and increases with increasing the contents of BST nanoparticles.

Table 1 and Fig. 10 show the calculated energy storage density of BST/PVDF nanocomposites with different contents of BST nanoparticles. The results indicate that the energy storage density decreases with increasing contents of BST nanoparticles. It is mainly because of the slow increased dielectric constant and rapid decreased dielectric strength with increasing contents of BST nanoparticles. Although the dielectric constants of nanocomposites
are lower than those of micro-composites, the dielectric strengths of nanocomposites are greatly improved. Thus, the maximum energy storage density is up to 5.15 J/cm³ at 287.12 kV/mm in the BST/PVDF nanocomposites with the addition of 10 vol% BST nanoparticles, and 1.8 times as high as that of pure PVDF matrix (2.8 J/cm³). Thus, the nanocomposites may promise materials used as microwave tunable devices, supercapacitors and energy storage devices, which can be operated at high-voltage and non-disruptive electrical breakdown.

4 Conclusions

In summary, BST/PVDF nanocomposites with different volume fractions of BST nanoparticles were synthesised by tape casting methods. The ~60 nm BST nanoparticles can be obtained by sol-gel method. The SEM images of BST/PVDF nanocomposites with different contents of BST nanoparticles certify that the incompatibility between the BST nanoparticles and the PVDF matrix becomes more and more obvious with increasing volume fractions of the nanoparticles. The dielectric constant and loss tangent of the nanocomposites increased and decreased from 14.1 to 29.7 and 0.069 to 0.21, at 1 kHz and room temperature, with increasing contents of BST nanoparticles. The increased BST nanoparticle contents will improve the dielectric tunability from 62.6% to 86.7% and decrease the dielectric strength from 287.1 to 158.2 kV/mm. Moreover, the energy storage density decreased from 5.15 to 3.29 J/cm³ with increasing contents of BST nanoparticles. The BST/PVDF nanocomposite with 10 vol% BST nanoparticles shows the optimal dielectric properties such as high dielectric tunability (~62.6%), low dielectric loss (0.069), the highest dielectric strength (287.1 kV/mm) and energy storage density (5.15 J/cm³). The results suggest that ceramic–polymer nanocomposites with low contents of ceramic nanoparticles are a novel strategy to improve dielectric strength and energy storage density.

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6 References

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