Highly dispersive $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ nanoparticles modified $\text{P(VDF-HFP)}/\text{PMMA}$ composite films with improved energy storage density and efficiency

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Abstract: Polymer composite films with high energy density as well as high efficiency are promising dielectric materials in pulsed power systems. In improving the energy discharged efficiency, poly vinylidene fluoride-hexafluoropropylene ($\text{P(VDF-HFP)}$) film blended with 20 vol.% poly(methylmethacrylate) (PMMA), which has a much slimmer ferroelectric hysteresis loop, is employed as the polymer matrix. Highly dispersive $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST) nanoparticles with an average particle size of 12.1 nm are utilised to improve the polarisation of the blend film without sacrificing the dielectric strength. Uniform nanocomposite films with high flexibility and excellent energy-storage performance are obtained. Especially, due to the optimisation of both polymer matrix and fillers, the BST modified $\text{P(VDF-HFP)/PMMA}$ blend films show improved breakdown strength and depressed energy loss, which leads to an enhanced energy density of 10.3 J/cm$^3$ at 378 kV/mm.

1 Introduction

All solid-state dielectric materials with a rather high charge-discharge rate and power density could be used as key materials for an energy storage component [1–3]. The energy density $U$, which is a determining parameter to access the potential of a material as an energy-storage dielectric, can be calculated by the integral $E = \int E dD$, Where $E$ is the electric field and $D$ is the electric displacement. Furthermore, with a high voltage resistance and long cycle life, dielectric materials with high energy density is eagerly desirable in advanced electronics and electric power systems, such as hybrid electric vehicles, aerospace power electronics, and pulsed power weapon systems [4–6].

In seeking high energy-density dielectrics, various material systems have been developed [7–10]. Among which the polymer–ceramic composite shows superior advantages because it can realise the high dielectric constant and breakdown strength simultaneously to achieve an excellent comprehensive performance [11, 12]. A polyvinylidene fluoride (PVDF)-based polymer combined with ferroelectric, dielectric, or even conductive fillers are one of the mostly studied composite materials [13–17]. As both the matrix and fillers are in the high-polarisation phase, the composite can achieve a relatively high displacement $D$, which is beneficial to improve the energy density. While at the same time, the fat ferroelectric hysteresis loop brings out undesirable energy dissipation during ferroelectric switching, which is rather large at the high electric field, resulting in the low discharge efficiency of the composite dielectrics. In the recent report from Niu et al., the discharged energy efficiency for fluorocarboxylic acid-modified barium titanate/PVDF composite drops sharply to $\sim50\%$ on an electric field higher than 100 MV/m [18]. This part of the loss is generally converted to heat, which can cause the temperature rise in the material and lead to early deterioration or even failure [19]. Therefore, developing high energy-density dielectrics with high discharge efficiency is quite important from the perspective of the practical application.

In theory, the discharge efficiency of a dielectric composite is mainly determined by the hysteresis loop, which means linear dielectrics can realise complete energy conversion without any ferroelectric loss. From this point of view, Luo et al. developed a blend polymer composite composed of poly vinylidene fluoride-hexafluoropropylene ($\text{P(VDF-HFP)}$) and poly(methylmethacrylate) (PMMA) [20]. Owing to a much slimmer hysteresis loop but only slightly decreased permittivity, the blend film has a maximal discharged energy density of 11.2 J/cm$^3$ with efficiency of 85.8%, which is much higher than the efficiency of 40% for pure $\text{P(VDF-HFP)}$ films. On the other hand, the filler phase also has a critical influence on the ferroelectric behaviour of the composite. It is well known that barium strontium titanate (BST) exhibits intrinsic high dielectric constant and breakdown strength, which also has a smaller hysteresis loop than the conventional used $\text{BaTiO}_3$ (BT) fillers [21]. Linear dielectrics such as $\text{TiO}_2$ and boron nitride have been reported as filler phases to improve the energy storage performance of the composite materials [13, 22–24]. Therefore, combining the more linear components is an effective way to improve the discharge efficiency of the polymer–ceramic composite. Previously, by investigating the size effect of BT fillers in the PVDF matrix, our group has verified that ultrafine ferroelectric fillers can significantly improve the dielectric strength as well as polarisation of the composite films [25, 26]. Based on this, highly dispersive BST nanoparticles modified $\text{P(VDF-HFP)/PMMA}$ composite films are developed to further improve the discharge efficiency towards future applications. The BST fillers used in this method, with an average particle size of 12.1 nm, are synthesised by a ‘TEG-sol’ method, with abundant active functional groups on the surfaces and thus show well combination and high dispersibility in the polymer matrix. This design takes advantage of the thin ferroelectric hysteresis loop of the two components as well as large interfaces induced by the ultrafine nanofillers, which is promising to improve the energy density and discharge efficiency at the same time. Microstructure, crystal phase, dielectric, and ferroelectric properties of the composite films are investigated in detail. The results show that dense and uniform nanocomposite films with a high content of $\beta$- and $\gamma$-phase $\text{P(VDF-HFP)}$ are obtained. The highly dispersive BST nanoparticles effectively improved the electric displacement and breakdown strength of the $\text{P(VDF-HFP)/PMMA}$ matrix. Meanwhile, compared with the BT-modified PVDF composite film, the energy efficiency is obviously improved. A maximal discharged energy density of 10.3 J/cm$^3$ at...
Furthermore, the composite films are moulded at 150°C for 15 min separately in DMAC solution at 40°C until totally dissolved, with the P(VDF-HFP) concentration kept at 0.1 g/ml. Then the two sols and BST suspension are mixed and stirred for 10 h to get a homogeneous and stable mixture. Finally, the blends are casted into films on clean glass plates and then dried at 150°C for 1 h. The prepared flexible films have film thicknesses in the range of 0.1–40 μm.

The transmission electron microscopy (TEM) image, energy dispersive spectrum (EDS) and selected area electron diffraction (SAED) of the BST nanoparticles are characterised by a TEM (JEM-2010, JEOL Ltd, Tokyo, Japan) at an accelerating voltage of 200 kV. The cross-sectional microstructure of the composite films and EDS mapping are obtained by scanning electron microscopy (SEM; MERLIN VP Compact, Zeiss Ltd, Germany) at 15 kV. X-ray diffraction (XRD) patterns are performed on a Bruker D8 Advance A25 X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm) at 40 kV and 200 mA. Fourier-transform infrared (FTIR) spectra are recorded in the 600–4000 cm⁻¹ range with a Nicolet 6700 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are performed using a TA Instruments thermal analyser (New Castle, DE, USA) with a heating rate of 10°C/min in air and nitrogen, respectively. Before the electrical test, circular gold electrodes with 1 mm radius are prepared on both sides of the films by using an ion sputtering equipment (SBC-12, KYKY Technology Co. Ltd, China). Frequency-dependent dielectric constant and loss of the composite films are determined using a precision impedance analyser (4980A; Agilent, Palo Alto, CA) at a frequency range of 1 kHz to 2 MHz. Ferroelectric hysteresis loops and electric breakdown strength of the nanocomposite films are measured on a ferroelectric test module (TF2000 analyser; axi ACCT, Germany) at a constant frequency of 100 Hz and gradually increased voltages.

### 2 Experimental procedure

**Ba₀.₆Sr₀.₄TiO₃** (BST) nanoparticles with an atomic ratio of Ba/Sr = 6:4 are prepared by a ‘TEG-sol’ method, which has been reported earlier [27]. PVDF-HFP wafers (Sigma Aldrich Co., Ltd) with an average molecular weight of 455,000, PMMA (YuanYe Biological Technology Co., Ltd), and N,N-dimethylacetamide (DMAC; Sinopharm Chemical Reagent Co., Ltd) are used as raw materials to fabricate the blend films. The BST nanoparticles modified P(VDF-HFP)/PMMA composite films are fabricated by simple blending, mechanical stirring, casting and hot-moulding method. Firstly, P(VDF-HFP) pellets and PMMA powders are dissolved separately in DMAC solution at 40°C until totally dissolved, with the PVDF-HFP concentration kept at 0.1 g/ml. Then the two sols are blended with a volume ratio of V_P(VDF-HFP):V_PMMA = 4:1, following the procedure of the literature. To obtain the BST modified P(VDF-HFP)/PMMA composite films, 0–60 vol.% BST nanoparticles were accurately weighed and ultrasonically dispersed in DMAC solvent to form a uniform suspension. Then the polymer sol and BST suspension are mixed and stirred for 10 h to get a homogeneous and stable mixture. Finally, the blends are casted into films on clean glass plates and then dried at 120°C for 3 h. Furthermore, the composite films are moulded at 150°C for 15 min under a pressure of 8 MPa. The prepared flexible films have film thicknesses in the range of 20–40 μm.

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### 3 Results and discussion

Fig. 1a shows the TEM image of the as-obtained BST nanoparticles, in which no severe aggregation is observed on a large-scale. The uniform morphology and high dispersibility of the nanoparticles is the basis for the formation of a dense composite microstructure. The particle size distribution of the sample is calculated based on the TEM images. As shown in the inset in Fig. 1a, the prepared BST particles have a size range of 5–20 nm and an average diameter of 12.1 nm. In Fig. 1b, most of the particles show the quasi-hexagon shape and the small crystallites are nearly spherical owing to the Ostwald ripening process. The well-ordered lattice fringes in Fig. 1c confirm the single crystallinity of the BST nanoparticles. Furthermore, EDS in Fig. 1d indicates that except the Cu peak introduced by the copper network, the particles are composed of O, Sr, Ba, and Ti elements, which is in accordance with the designed chemical formula. The XRD pattern in Fig. 1e and the inserted SAED pattern reveal a well-crystallised perovskite structure of the nanoparticles. Except for a small peak at 2θ = 24° that is caused by the BaCO₃ impurity phase, all the diffraction peaks at 2θ corresponding to 22.4° (100), 31.9° (110), 39.3° (111), 45.7° (200), 51.5° (210), 56.8° (211), 66.6° (220), 71.3° (221), and 75.8° (310) can be indexed to the cubic Ba₀.₆Sr₀.₄TiO₃ (JCPDS no. 34-0411). Besides, the diffraction peaks are obviously broadened, which confirms the small crystal size of the particles.

Ultrafine and highly dispersive nanoparticles have unique advantages in fabricating uniform composite structures [28]. Figs. 2a–g show the cross-sectional SEM images of the BST modified P(VDF-HFP)/PMMA composite films with different...
The composite films with 0–γ₀ vol.% BST loadings are dense and uniform. As the polymer is a major phase, EDS mapping of Ba element is conducted and illustrated in the inset of Fig. 2b, which confirms the uniform distribution of the filler phase. Due to the small crystal size and high flexibility, the composite films are similar to typical polymers, showing high flexibility. Especially, the macroscopic photograph in Fig. 2h displays that the blend film with 10 vol.% BST is comparatively transparent, which is quite different from the previously reported ones and offers new potential for the application of oxide-based optoelectronic devices [11, 29, 30]. With a BST loading >γ₀ vol.% porous structures with polymer frameworks and BST particle aggregations are obtained, shown in Figs. 2e and f. Here ceramic fillers turn into the major phase, which dominates the mechanical and electrical properties of the composite films. EDS mapping of F element in the inset of Fig. 2e also confirms the non-uniform distribution of the polymer framework. When the BST loading is as high as 60 vol.% the composite film becomes very fragile. The cross-sectional image in Fig. 2g is smoother than the films with 40 and 50 vol.% BST, showing typical features of the porous inorganic film. Therefore, dense and uniform composite films with high flexibility and transparency can be obtained in the P(VDF-HFP)/PMMA blend films with BST volume fractions <30%. The PVDF-based polymer is widely used in high-κ dielectric composites owing to its high relative permittivity (6–14), which is mainly contributed by the high-polarisation ferroelectric phase of P(VDF-HFP) and PMMA = 4:1–considering both the energy storage performance and mechanical flexibility. It is observed that the composite films with 0–30 vol.% BST loadings are dense and uniform. As the polymer is a major phase, EDS mapping of Ba element is conducted and illustrated in the inset of Fig. 2b, which confirms the uniform distribution of the filler phase. Due to the small crystal size and high dispersibility, the composite films are similar to typical polymers, showing high flexibility. Especially, the macroscopic photograph in Fig. 2h displays that the blend film with 10 vol.% BST is comparatively transparent, which is quite different from the previously reported ones and offers new potential for the application of oxide-based optoelectronic devices [11, 29, 30]. With a BST loading >γ₀ vol.% porous structures with polymer frameworks and BST particle aggregations are obtained, shown in Figs. 2e and f. Here ceramic fillers turn into the major phase, which dominates the mechanical and electrical properties of the composite films. EDS mapping of F element in the inset of Fig. 2e also confirms the non-uniform distribution of the polymer framework. When the BST loading is as high as 60 vol.% the composite film becomes very fragile. The cross-sectional image in Fig. 2g is smoother than the films with 40 and 50 vol.% BST, showing typical features of the porous inorganic film. Therefore, dense and uniform composite films with high flexibility and transparency can be obtained in the P(VDF-HFP)/PMMA blend films with BST volume fractions <30%.

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0 vol.% BST. For the curves of TGA, a total weight loss of 7.5 wt.% is observed for the BST nanoparticles, which confirms the existence of active functional groups on the surface of the nanoparticles. These organic groups not only increase the dispersibility of the BST nanoparticles in the polymer matrix but also can interact with the polymer and form hydrogen bonding at the interface [8], therefore promote the generation of uniform and compact microstructures of the composite films. For the blend films with and without BST, two weight loss steps starting from \(~260°C\) and \(~40°C\) are observed, which corresponds well with the decomposition temperature of PMMA and P(VDF-HFP), respectively. As is known, the glass transition temperature of PMMA is around 100°C. The crystallisation temperature of P(VDF-HFP) is \(~173°C\) for \(\alpha\) phase and \(~166°C\) for \(\beta\) phase. From the DSC curves, the crystallisation temperature of P(VDF-HFP) in the blend films is measured as \(117°C\), which is much lower than the crystallisation temperature of pure P(VDF-HFP). Furthermore, two melting peaks located at 150 and 162°C are observed in the blend film without BST, which corresponds to the melting temperature of \(\alpha\)- and \(\beta\)-phase P(VDF-HFP), respectively. While in the P(VDF-HFP)/PMMA blend film with 20 vol.% BST, only one melting peak at 152°C can be distinguished, which coincides with the FTIR spectra and further confirms that the highly dispersive BST nanoparticles can promote the generation of \(\beta\)-phase in the composite film.

Frequency-dependent dielectric constant and loss of the P(VDF-HFP)/PMMA composite films with different volume fractions of BST are shown in Figs. 4a and b, respectively. The dielectric constant for P(VDF-HFP)/PMMA blend film with 20 vol.% BST addition is 8.64 at 1 kHz, which is slightly lower than that of the pure P(VDF-HFP) due to the linear component of PMMA [20]. Although having a dielectric constant lower than BST, BT is still a well-known high permittivity dielectric material that is widely used in the integrated circuit, energy storage devices, field-effect transistors etc. [39]. With the increase of the BST content, the relative permittivity of the composite films is effectively improved. As shown in Fig. 4a, the dielectric constant firstly increases to a maximum value of 27.3 at 1 kHz and then decreases with the increase of the BST volume fraction. Combining with the microstructure in the SEM images, the uniform distribution of BST nanoparticles and dense combination between the polymer and filler phase are the basis for the enhancement of the dielectric properties. When the BST volume fraction is too high, a porous structure with a polymer network and particle aggregation is formed, which would involve a third air phase and severely suppress the dielectric constant. Fig. 4c displays the experimental value and the fitted dielectric constant at 1 kHz using a modified Kerner model, which considers the interactions between adjacent fillers in a binary composite [40, 41]. As is shown, the experimental value coincides well with the fitted one at volume fractions <40%, then decreases sharply at high volume fraction and shows large discrepancy with the modelling, which clearly reflects the influence of pores in the composites. PVDF-based polymers usually possess a high dissipation at the frequency >100 kHz [40]. The dielectric loss in Fig. 4b confirms that the introduction of BST nanoparticles can also effectively lower the loss tangent of the composite films. With a proper amount of BST addition, tan \(\delta\) \(\leq 0.05\) can be obtained in the frequency range of 1–100 kHz.

Traditional adopted ferroelectric fillers such as BT and BCZT \((\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3)\) inevitably deteriorate the high dielectric strength of the polymer matrix, thereby leading to the low energy density of the composite [11, 42]. Recently, we have confirmed that ultrafine ferroelectric nanocrystal fillers can simultaneously enhance the polarisation and breakdown strength of the composite in both spin-coated thin film [25] and casted thick film [26]. In this report, by employing more linear dielectrics in...
both fillers and matrices, the breakdown strength and efficiency can be significantly increased, which leads to a further improved energy density. By calculating the integral area of the hysteresis loop in the first quadrant, Figs. 5a–c show the charged energy density, discharge efficiency, and discharge energy density of the BST modified P(VDF-HFP)/PMMA composite films with 0–60 vol.% BST loadings. As the high-permittivity BST nanoparticles effectively improved the electric displacement of the nanocomposites, both the charged and discharged energy density increase with the increasing of the filler fraction. Moreover, it is obvious that the energy density is highly related to the applied electric field. Here the ultrafine and monocrystal BST nanoparticles, which have an intrinsic high breakdown strength, play a critical role in improving the overall dielectric strength of the composite films. As illustrated, both the breakdown strength and energy density of the composite films increase with the increase of the BST content at a filler fraction <β0%. With a uniform and dense microstructure, these highly dispersive BST nanoparticles show a significant strengthen effect on the breakdown strength of the composite films. As a result, a maximal charged and discharged energy density of 17.β and 10.γ J/cm γ is obtained on the composite film with β0 vol.% BST at γ78 kV/mm, respectively. Further increasing the BST content from γ0 to 60 vol.%, the breakdown strength and energy density drastically decline due to the inhomogeneous microstructure and increasing air phase. As depicted in Fig. 5d, the breakdown strength of the composite films firstly increases and then decreases with the increase of the BST content. It is worth noting that the breakdown strength of the composite films with 0–20 vol.% BST loadings is >300 kV/mm, which is quite unusual in the conventional polymer–ceramic structures. In the Weibull distribution inserted in Fig. 5d, the Weibull modulus β, which is obtained from the slope of the curve, is >3 for all the samples, indicating a highly concentrated data distribution and high reliability. This result confirms the superiority of the BST nanoparticles as fillers of the energy storage materials.

The energy discharged efficiency in Fig. 5b shows that the original P(VDF-HFP)/PMMA film without BST has an efficiency of 75% at 311 kV/mm, which is slightly lower than the referred literature but still much higher than pure P(VDF-HFP) [20]. The introduction of the high-polarisation BST phase lowers the discharge efficiency to some extent. For example, at the same applied electric field of 311 kV/mm, the efficiency for 10 and 20 vol.% BST modified P(VDF-HFP)/PMMA composite films are 67 and 65%, respectively. Also, the discharge efficiency decreases with further increasing of the BST content. Nevertheless, this value is still remarkable compared with the conventional 0–3 ceramic–polymer composites [13, 18, 22]. Fig. 6 compares the unipolar electric displacement–electric field (D–E) loops for the 20 vol.% BST/[P(VDF-HFP)–PMMA] and 20 vol.% BT/P(VDF-HFP) composite films. As is seen, with more linear filler and matrix dielectrics, the 20 vol.% BST/[P(VDF-HFP)–PMMA] composite film shows slimmer D–E loops. At an approximate applied electric field, the 20 vol.% BT/P(VDF-HFP) composite film only has a discharge efficiency of 56% at 194 kV/mm, while the 20 vol.% BST/[P(VDF-HFP)–PMMA] film has an efficiency of 70% at 238 kV/mm. With significantly increased breakdown strength, the 20 vol.% BST/[P(VDF-HFP)–PMMA] film can sustain a discharge efficiency of 60% at 378 kV/mm, which is still higher than the 20 vol.% BT/P(VDF-HFP) composite film, confirming the adoption of more linear dielectrics can effectively enhance the efficiency of the ceramic–polymer nanocomposite.

4 Conclusion
In summary, BST nanoparticles with intrinsic high breakdown strength and P(VDF-HFP)–PMMA blend film with a slimmer ferroelectric hysteresis loop are successfully utilised to fabricate polymer–ceramic nanocomposite films with high energy density.
and discharge efficiency. Owing to the small crystal size (5–20 nm, averaged at 12.1 nm) and high dispersibility, the BST modified P(VDF-HFP)–PMMA composite films are dense and uniform at the BST volume fraction of 0–20%. XRD patterns, FTIR spectra, and DSC curves confirm that the introduction of BST nanoparticles can promote the generation of the β-phase, thus the fabricated composite films possess a high β- and γ-phase content, which is beneficial to the high polarisation of the composite films. These BST nanoparticles not only effectively improved the electric displacement as revealed by the dielectric measurement but also have a significant strengthening effect on the dielectric strength of the composite films due to the monocrystal feature and intrinsic high breakdown strength. Moreover, the fabricated nanocomposite films show much slimmer hysteresis loops than the conventional BT modified PVDF-based composite. As a result, a maximal discharged energy density of 10.7 J/cm³ is obtained at 78 kV/mm on the 20 vol.% BST modified P(VDF-HFP)–PMMA composite film.

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