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Polyvinylidene fluoride-modified $BaTiO_3$ composites with high dielectric constant and temperature stability

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Abstract

Polyvinylidene fluoride (PVDF)-modified X7R-type $BaTiO_3$ (BTO) composites were prepared by hot pressing, and the dielectric properties were investigated. The dielectric constant of the PVDF–BTO composites at 1 kHz increased significantly with increasing the volume fraction of BTO up to 0.5, and good temperature stability of dielectric constant was obtained for the composites, which benefited from the temperature-stable dielectric constant of the modified $BaTiO_3$. Two significant dielectric relaxations were observed for the PVDF–BTO composites, and they fit the Vogel–Fulcher and Arrhenius fittings, respectively.
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Keywords: A. Hot pressing; B. Composites; C. Dielectric properties

1. Introduction

In the recent years, polymer–ceramic dielectric composites have attracted much attention due to their good comprehensive properties and potential applications in embedded circuits [1–3]. $BaTiO_3$ has been adopted as the ceramic material in the polymer–ceramic composites most frequently because of its high dielectric constant, non-toxicity and low cost [4–6]. There are three peaks for the dielectric constant of $BaTiO_3$ in the temperature range between 170 and 420 K, which corresponds to the ferroelectric phase transitions [7]. A sharp peak can be observed near room temperature [7], which will finally deteriorate the temperature stability of the polymer–ceramic composites. On the other hand, the peaks of dielectric constant are weakened significantly for some modified $BaTiO_3$ ceramics, and they have been widely used in the commercial multilayered ceramic capacitors (MLCC) [8,9]. Improved temperature stability of dielectric constant is desired for the polymer–ceramic composites, by adopting suitably modified $BaTiO_3$.

So in the present work, a modified X7R-type $BaTiO_3$ powder is used as the ceramic material of the composites, which has a high dielectric constant of about 2,400 at 1 kHz and good temperature stability. Polyvinylidene fluoride is adopted as the polymer matrix, which is a ferroelectric polymer with relatively high dielectric constant.

2. Experimental procedure

High-purity polyvinylidene fluoride (PVDF, Alfa Aesar Company, USA) and modified X7R-type $BaTiO_3$ (BTO, FH-2XL302A, Fenghua Advanced Technology Holding Co., Ltd., China) powders were used as the raw materials of the composites, respectively. PVDF and BTO powders were mixed with the volume fraction of BTO varying from 0.1 to 0.6 by ball milling with ZrO_2media in ethanol for 24 h, then dried and sieved. The well mixed powder was hot pressed at 140 °C for 10 min with a uniaxial pressure of 100 MPa. The cylindrical samples of the PVDF–BTO composites with the diameter of about 12.5 mm and thickness of about 2 mm were used for measurement.

The density of the composites was measured by the volume method. Gold was sputtered as the electrodes, and the dielectric properties were measured by a broadband dielectric spectrometer (Turnkey Concept 50, Novocontrol Technologies, Germany) in the temperature range of 213–403 K and frequency range of 10^2–10^5 Hz.

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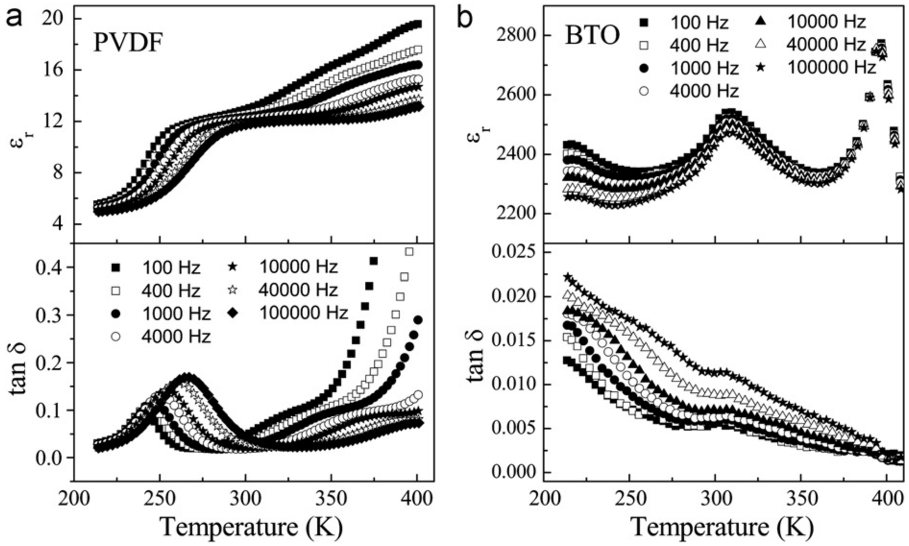

Fig. 1. Dielectric constant and dielectric loss of (a) PVDF and (b) BTO at different frequencies as functions of temperature.

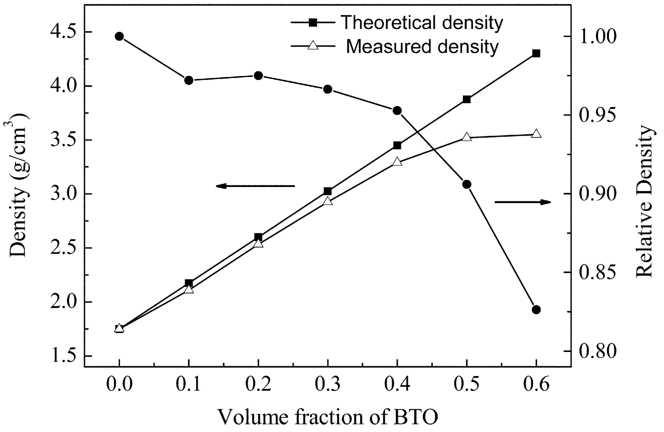

Fig. 2. Density and relative density of PVDF–BTO composites as functions of volume fraction of BTO.

3. Results and discussion

Fig. 1 shows the dielectric constant and dielectric loss of PVDF and BTO at different frequencies as functions of temperature. With increasing temperature from 213 K, the dielectric constant of PVDF first increases significantly, and then a plateau with the dielectric constant of about 12 is observed. Correspondingly, the peaks of dielectric loss around 250 K are observed, and the temperature where the dielectric loss reaches the peak value (peak temperature) is significantly dependent on the frequency. This indicates a typical dielectric relaxation, which corresponds to the glass transition of the amorphous fraction of PVDF (transition) [10,11]. Another dielectric relaxation has also been observed at higher temperatures, which results from the rotational and translational motions of molecules in the crystalline regions (transition) [10,11]. As shown in Fig. 1(a), this dielectric relaxation cannot be identified clearly in the present work because of the rapid increase in dielectric loss at high temperature, which may be due to the relatively high leakage conductivity of the present sample. As shown in Fig. 1(b), the three peaks of dielectric constant of BTO are much suppressed compared with those for the pure $BaTiO_3$ [7]. The dielectric constant of BTO is around 2,400 at 1 kHz, and a dielectric constant

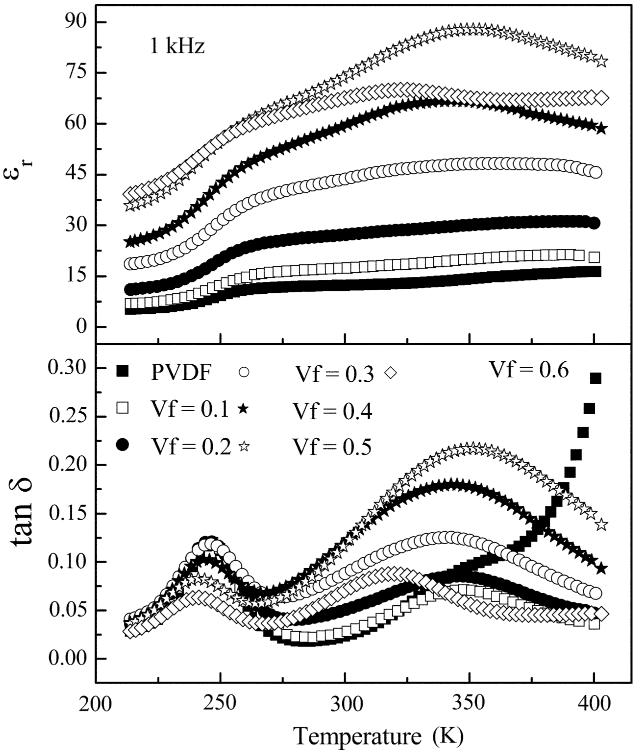

Fig. 3. Dielectric constant and dielectric loss of PVDF–BTO composites at 1 kHz as functions of temperature.

variation less than 6% over a wide temperature range between 210 and 380 K is observed, which indicates good temperature stability.

Fig. 2 shows the density and relative density of PVDF–BTO composites as functions of the volume fraction of BTO (*Vf*). The theoretical density increases linearly with increasing *Vf*. The same tendency is indicated for the measured density when *Vf* does not exceed 0.4, and the relative density higher than 95% can be achieved. Increasing *Vf* further, the relative density decreases rapidly, which is due to the increasing porosity for high ceramic volume fraction.

Fig. 3 shows the temperature dependence of dielectric properties of PVDF–BTO composites at 1 kHz. The dielectric constant of the composites increases significantly with increasing *Vf* up to 0.5, and this is due to the much higher dielectric constant of BTO than that of PVDF. A decrease in dielectric constant is observed for $Vf = 0.6$, which is results from the high porosity. With increasing temperature up to 260 K, the dielectric constant increases rapidly, and a peak in dielectric loss can be observed at about 250 K for all the composites, which corresponds to the transition of PVDF. Furthermore, another peak of dielectric loss is observed at higher temperature. Good temperature stability of dielectric constant can be achieved in the temperature range between 260 and 400 K for all the composites, especially when *Vf* does not exceed 0.3.

Fig. 4 shows the temperature dependence of dielectric properties at different frequencies for the PVDF–BTO composites with $Vf = 0.2$, 0.4 and 0.6. Two dielectric abnormities can be observed for all the composites, which are indicated by the peaks of dielectric loss. For the low-temperature peak, the peak temperature increases significantly with increasing frequency for the PVDF–BTO

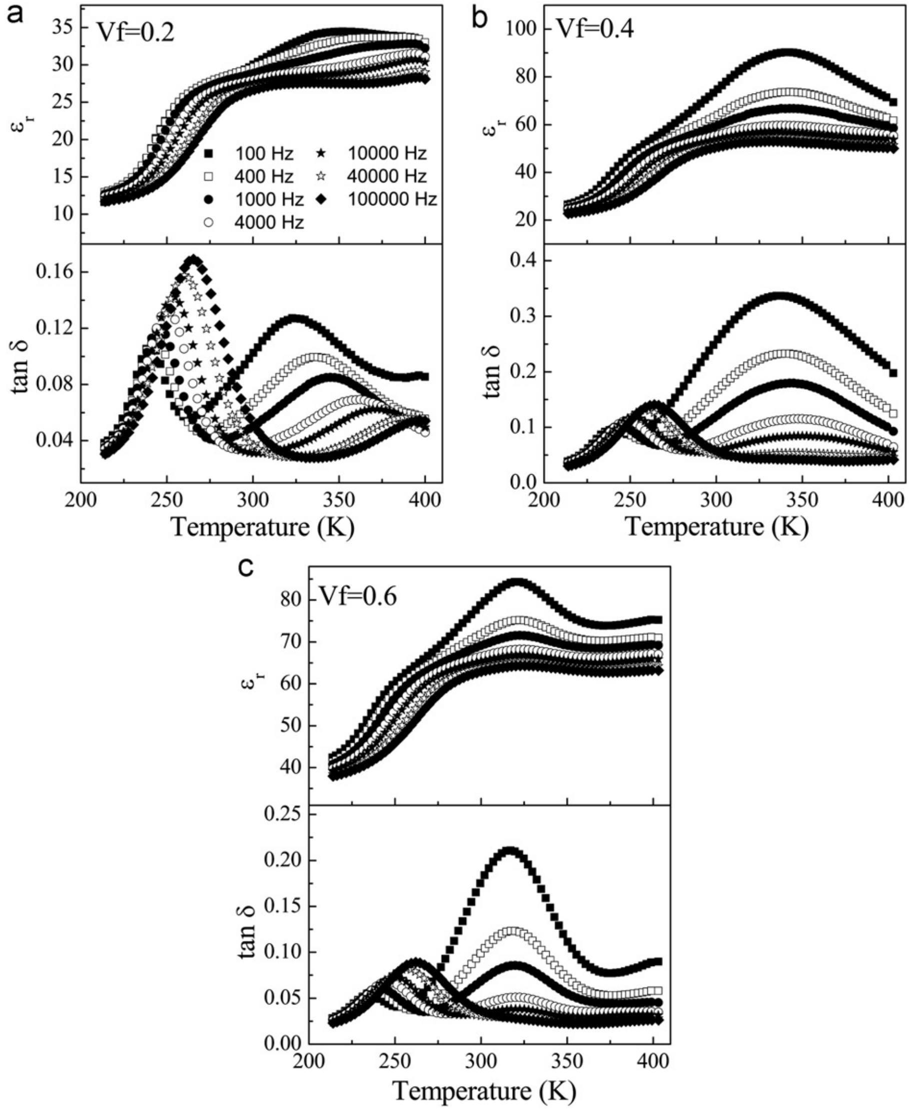

Fig. 4. Dielectric constant and dielectric loss of PVDF–BTO composites at different frequencies as functions of temperature, where the volume fraction of BTO is (a) 0.2, (b) 0.4, and (c) 0.6.

composites as well as PVDF (see Fig. 1(a)), and the frequency as a function of peak temperature is shown in Fig. 5 (a). It is observed that the low-temperature dielectric relaxation obeys the Vogel–Fulcher law well [12,13]:

$$f = f_0 \exp\left(\frac{-E_a}{k_B(T-T_f)}\right), \tag{1}$$

where f_0 is the Debye frequency, E_a is the activation energy, k_B is the Boltzmann constant and T_f is the static freezing temperature. The fitting parameters for the low-temperature dielectric relaxation of PVDF–BTO composites are shown in Table 1. With increasing Vf from 0 to 0.4, T_f increases, while E_a and f_0 decrease, and it is indicated that this dielectric relaxation is due to the β transition of PVDF. With further increasing Vf, abnornal trends of the fitting parameters are indicated, and this may be due to the increasing porosity of the composites. Quite different results are observed for the high-temperaturedielectric abnormity. The peak temperature decreases significantly with increasing frequency for PVDF–BTO composites with Vf =0.1, 0.2 and 0.3, and the relationship between frequency and temperature follows the Arrhenius equation well (see Fig. 5(b)) [14]:

$$f = f_0 \exp\left(\frac{-E_a}{k_B T}\right), \tag{2}$$

where f_0 is the relaxation frequency at an infinite temperature. The fitting parameters are shown in Table 2.

According to Ref. [15],the activation energy is of a similar value of 0.92 eV for the high-temperature dielectric relaxation of PVDF, and it is indicated that this dielectric relaxation of PVDF–BTO composites is due to the α transition of PVDF. The high-temperature dielectric relaxation is weakened significantly for the composites with Vf higher than 0.4 due to the non-relaxed dielectric properties of BTO, and the peak temperature shows little dependence on frequency, so that the fitting cannot be conducted.

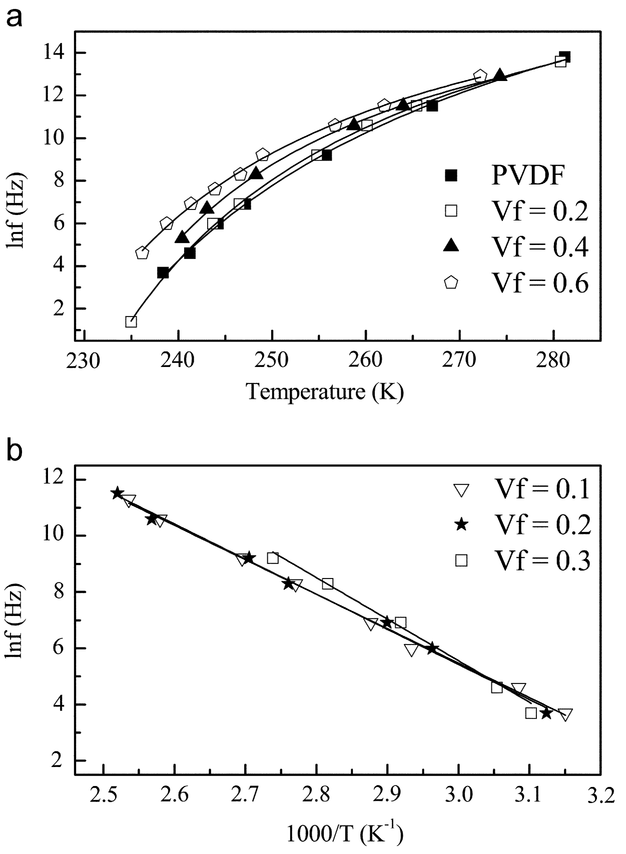

Fig. 5. Frequency as a function of peak temperature of dielectric loss for (a) low- and (b) high-temperature dielectric relaxations of the PVDF–BTO composites.

4. Conclusion

In conclusion, PVDF-modified BaTiO$_3$ dielectric composites have been prepared and characterized. The dielectric constant of the PVDF–BTO composites at 1 kHz increases significantly with increasing the volume fraction of BTO up to 0.5, while it decreases for higher volume fraction of BTO due to the low relative density. Good temperature stability of the dielectric constant is achieved for the composites, which benefits from the temperature-stable dielectric properties of the modified BaTiO$_3$. Two significant dielectric relaxations are observed for the composites, and they fit the Vogel–Fulcher and Arrhenius fittings, respectively.

Table 2
The parameters obtained from the Arrhenius fitting for the high-temperature dielectric relaxation of PVDF–BTO composites with Vf =0.1, 0.2 and 0.3.

Vf	0.1	0.2	0.3
E_a (eV)	1.06	1.08	1.27
f_0 (Hz)	2.26×10^{18}	4.26×10^{18}	4.7×10^{21}

Table 1
The parameters obtained from the Vogel–Fulcher fitting for the low-temperature dielectric relaxation of PVDF and PVDF–BTO composites.

Vf	0	0.1	0.2	0.3	0.4	0.5	0.6
T_f (K)	184	191	204	205	209	196	202
E_a (eV)	0.108	0.085	0.055	0.051	0.038	0.059	0.046
f_0 (Hz)	3.8×10^{11}	4.3×10^{10}	3.2×10^{9}	1.5×10^{9}	3.5×10^{8}	3.2×10^{9}	8.4×10^{8}

Acknowledgments

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References

[1] M. Akram, A.R. Javed, T.Z. Rizvi, Dielectric properties of industrial polymer composite materials, Turkish Journal of Physics 29 (2005) 355–362.

[2] T. Hu, J. Juuti, H. Jantunen, T. Vilkman, Dielectric properties of BST/polymer composite, Journal of the European Ceramic Society 27 (2007) 3997–4001.

[3] D.H. Kuo, C.C. Chang, T.Y. Su, W.K. Wang, B.Y. Lin, Dielectric properties of three ceramic/epoxy composites, Materials Chemistry and Physics 85 (2004) 201–206.

[4] D.H. Kuo, C.C. Chang, T.Y. Su, W.K. Wang, B.Y. Lin, Dielectric behaviours of multi-doped $BaTiO_3$/epoxy composites, Journal of the European Ceramic Society 21 (2001) 1171–1177.

[5] S.H. Xie, B.K. Zhu, X.Z. Wei, Z.K. Xu, Y.Y. Xu, Polyimide/$BaTiO_3$ composites with controllable dielectric properties, Composites Part A: Applied Science 36 (2005) 1152–1157.

[6] R. Popielarz, C.K. Chiang, R. Nozaki, J. Obrzut, Dielectric properties of polymer/ferroelectric ceramic composites from 100 Hz to 10 GHz, Macromolecules 34 (2001) 5910–5915.

[7] K. Kinoshita, A. Yamaji, Grain-size effects on dielectric properties in barium titanate ceramics, Journal of Applied Physics 47 (1976) 371–373.

[8] C. Pithan, D. Hennings, R. Waser, Progress in the synthesis of nanocrystalline $BaTiO_3$ powders for MLCC, International Journal of Applied Ceramic Technology 2 (2005) 1–14.

[9] C.H. Kim, K.J. Park, Y.J. Yoon, M.H. Hong, J.O. Hong, K.H. Hur, Role of yttrium and magnesium in the formation of core–shell structure of $BaTiO_3$ grains in MLCC, Journal of the European Ceramic Society 28 (2008) 1213–1219.

[10] G.A. Samara, Pressure-dependence of the beta-molecular relaxation process and dielectricproperties of polyvinylidene fluoride, Journal of Polymer Science Part B: Polymer Physics 30 (1992) 669–679.

[11] E. Ozkazanc, H.Y. Guney, T. Oskay, E. Tarcan, The effect of uniaxial orientation on the dielectric relaxation behavior of a-PVDF, Journal of Applied Polymer Science 109 (2008) 3878–3886.

[12] H. Vogel, The temperature dependence law of the viscosity of fluids, Zeitschrift für Physik 22 (1921) 645–646.

[13] G. Fulcher, Analysis of recent measurements of the viscosity of glasses, Journal of the American Ceramic Society 8 (1925) 339–355.

[14] E. Winkler, F. Rivadulla, J.S. Zhou, J.B. Goodenough, Evolution of polaron size in $La_{2-x}Sr_xNiO_4$, Physical Review B 66 (2002) 094418.

[15] H.Y. Guney, T. Oskay, H.S. Ozkan, Mechanical anisotropy in biaxially oriented polyvinyl-chloride, Journal of Polymer Science Part B: Polymer Physics 29 (1991) 897–906.