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Dielectric and energy storage properties of the (1-x)$BaTiO_3$-xBi($Li_{1/3}Hf_{2/3}$)O_3 ($0.08 \leq \times \leq 0.14$) ceramics

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ABSTRACT

In the present work, a series of (1-x)$BaTiO_3$-xBi($Li_{1/3}Hf_{2/3}$)O_3 ($0.08 \leq \times \leq 0.14$) ceramics were prepared via solid state reaction method. All the compositions were found to belong to a perovskite phase by X-ray diffraction. As x value increased from 0.08 to 0.12, the breakdown strength increased from 175 kV/cm to 240 kV/cm, resulting maximum values of both charge and discharge energy densities, ~ 1.71 J·cm^{-3} and ~ 1.65 J·cm^{-3} respectively, in the 0.88$BaTiO_3$-0.12Bi($Li_{1/3}Hf_{2/3}$)O_3 ceramic with a high efficiency about ~ 95.6%. The low dielectric loss, high breakdown strength makes this system a good candidate for high power pulse devices applications.

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1. Introduction

Energy has been the biggest problem and challenge nowadays. Hence there is an urgent need to develop effective electric energy storage technologies. Dielectric capacitors not only have the highest power density, but also have the advantages of wide working temperature range, fast charge and discharge rates, and long service cycle [1–5]. The energy storage density (U) refers to the energy stored per unit volume of the dielectric [1–10]. For non-linear dielectric materials, due to the existence of electric domains, the polarization intensity and the electric field exhibit hysteresis loop characteristics, so that the dielectric constant changes with the change of the electric field. The calculation and derivation of the charge energy density (U), discharge energy density (U_e) and energy storage efficiency (η) of the non-linear dielectric capacitor during charge and discharge were introduced in previous work [8–12]. The energy storage performance of the dielectric material is usually determined by the three main dielectric parameters: breakdown field strength (E_b), dielectric constant and dielectric loss [2–4]. Previous studies [5–13] have shown that the dielectric constant and breakdown strength of single-phase dielectric materials are mutually limited, and this contradiction between the two parameters is inevitable. $BaTiO_3$-based ceramic, glass–ceramic, and film samples have always attracted much attention due to their large dielectric permittivity and environmental non-toxicity [3,8–12]. Recently, in the (1-x)$BaTiO_3$–x$BiScO_3$ (x = 0–0.5) system, it was found that the dielectric constant is high and relatively stable from 0 to 300 °C [3] for the 0.7$BaTiO_3$–0.3$BiScO_3$ compared with the classical relaxor ferroelectrics such as $PbMg_{1/3}Nb_{2/3}O_3$, making this composition attractive for high-energy density capacitor applications. Moreover, a high-energy density, on the order of 13–18 J/cm^3 for a bias field of about 1.3–2.0 MV/cm at room temperature, was calculated from the hysteresis loop in 0.6$BaTiO_3$-0.4$BiScO_3$ thin films. This high value is partly due to the high breakdown strength of the film, but suggests that bulk ceramics might also have high-energy densities. Followed the above study, a series of Bi-based perovskite structured ceramics were explored for high energy density capacitor applications, such as $BaTiO_3$-Bi[$(Zn,Mg)_{2/3}Nb_{1/3}$]O_3, $BaTiO_3$-Bi[$Li_{1/2}(Nb,Ta)_{1/2}$]O_3, $BaTiO_3$-Bi[$(Zn,Mg)_{1/2}Zr_{1/2}$]O_3 [8–13]. Bi additions accelerated the change from ferroelectric to relaxor and improved the energy storage properties. In the present work, a novel series of (1-x)$BaTiO_3$-xBi($Li_{1/3}Hf_{2/3}$)O_3 ($0.08 \leq \times \leq 0.14$) ceramics were designed and their dielectric, energy storage properties were studied in detail.

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2. Experimental procedure

The (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics were prepared via traditional solid state reaction method as before [11,12]. Calcination and sintering temperatures were 1100 °C and 1300 °C, respectively. X-ray diffraction patterns (XRD) were recorded using a diffractometer to study the crystal structures. Microstructures of thermally etched (1250 °C for 10 min) surfaces of ceramics were observed using scanning electron microscope. Dielectric properties as a function of temperature were measured using an LCR with a homemade temperature chamber. Polarization–electric field (P–E) hysteresis loops were recorded using a TF Analyzer 2000 (aix ACCT) ferroelectric test system with a triangular wave at 10 Hz.

3. Results and discussions

Fig. 1 presents XRD patterns of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics sintered at 1300 °C. All the patterns were well indexed as pure perovskite phase without any secondary phases, which indicates that Bi^{3+}, $(Li_{1/3}Hf_{2/3})^{3+}$ occupied the A and B site of perovskite, respectively. In the perovskite structure, cations on A site are 12-cooridinated and Bi^{3+} (1.11 Å) is little bit smaller than that of Ba^{2+} (1.61 Å) [10–13]. Hf^{4+} has the same electrovalence but larger ionic radius (0.71 Å) than that of Ti^{4+} (0.605 Å) on B site in perovskite. Li^+ (0.76 Å) ions have also been proved to occupy the B site in many perovskite solid solutions. SEM images of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics sintered at 1300 °C were shown in Fig. 2. Dense and homogenous microstructures with clear grain boundaries and no pores were revealed from the SEM images, which are consistent with relative densities above 98.5%.

Dielectric properties of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics as a function of temperature 25 ~ 400 °C (at 1 MHz) and their P-E loops under different electric fields are shown in Fig. 3. With the increase in $Bi(Li_{1/3}Hf_{2/3})O_3$ contents, dielectric constant decreased from above 2000 for x = 0.08 to about 790 for x = 0.14, along with slight decrease in dielectric loss at 1 MHz, which indicates the change from ferroelectric to relaxor behaviors. With the increase in temperature, dielectric constant decreased sharply to below 500 at 400 °C. Meanwhile, dielectric loss decreased to below 0.001 and kept stable in a quite wide temperature range.

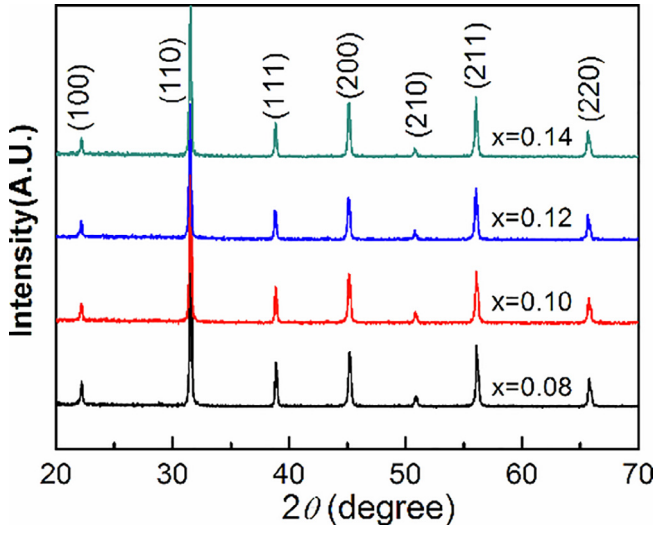

Fig. 1. XRD patterns of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \times \leq 0.14$) ceramics.

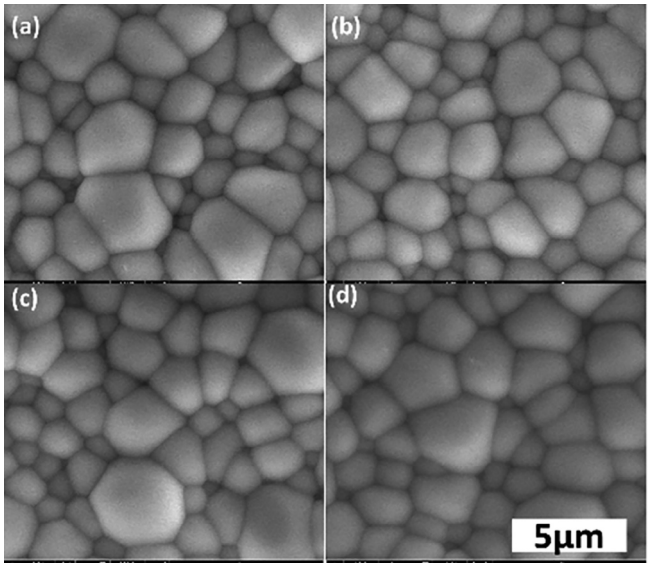

Fig. 2. SEM images of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics sintered at 1300 °C.

The P-E loops as shown in Fig. 3 (b), (c), (d) and (e) showed that with the increase in external electric field, the P-E loops of all the four compositions become fatter and fatter, which indicates that both the charge/discharge energy densities increased with electric field along with increasing dielectric loss. For x = 0.08 and 0.10 samples, P-E loops took on a parabola shape, which means that dielectric constant decreased with external bias [8–13]. As shown in Fig. 3(f), P-E loops became more like straight lines for x = 0.12 and 0.14 compositions, which is consistent with the relaxor behaviors. Especially in x = 0.12 sample, the dielectric breakdown strength reached a maximum value ~ 240 kV/cm, which is almost twice that pure $BaTiO_3$ ceramics.

Charge/discharge energy density and efficiency of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics as a function of electric fields and composition are shown in Fig. 4. As shown in Fig. 4 (a) and (b), both the U and U_e increased almost linearly with electric field, which was caused by the combined effect from decreasing dielectric constant and increasing E_b. The maximum value of E_b ~ 224 kV/cm achieved at x = 0.12 resulted in a maximum value of U ~ 1.71 J·cm^{-3} and U_e ~ 1.65 J·cm^{-3} with an efficiency ~ 95.6%. As seen from Fig. 4 (c), energy storage efficiencies of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq x \leq 0.14$) ceramics increased with x value due to the decreasing dielectric losses, which is consistent with the dielectric properties results shown in Fig. 3 (a). Meanwhile, energy storage efficiencies decreased with electric field slightly but kept above 95% even at 200 kV/cm for compositions with x value ≥ 0.10 as shown in Fig. 4 (d), which indicates that this system is a good candidate for high power pulse device.

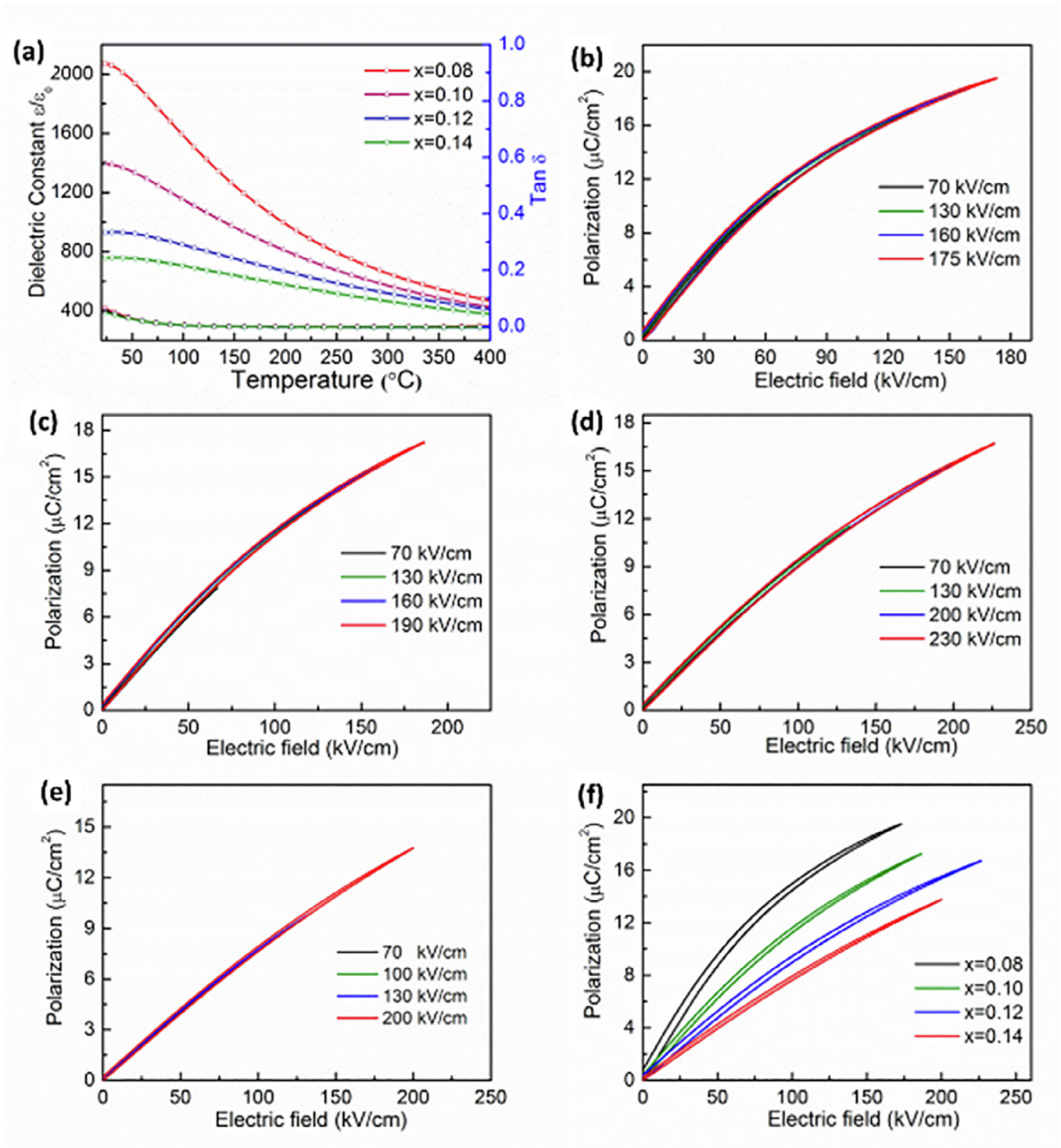

Fig. 3. Dielectric properties of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics as a function of temperature 25 ~ 400 °C at 1 MHz (a) and their P-E loops under different electric fields (b), (c), (d), (e) and (f).

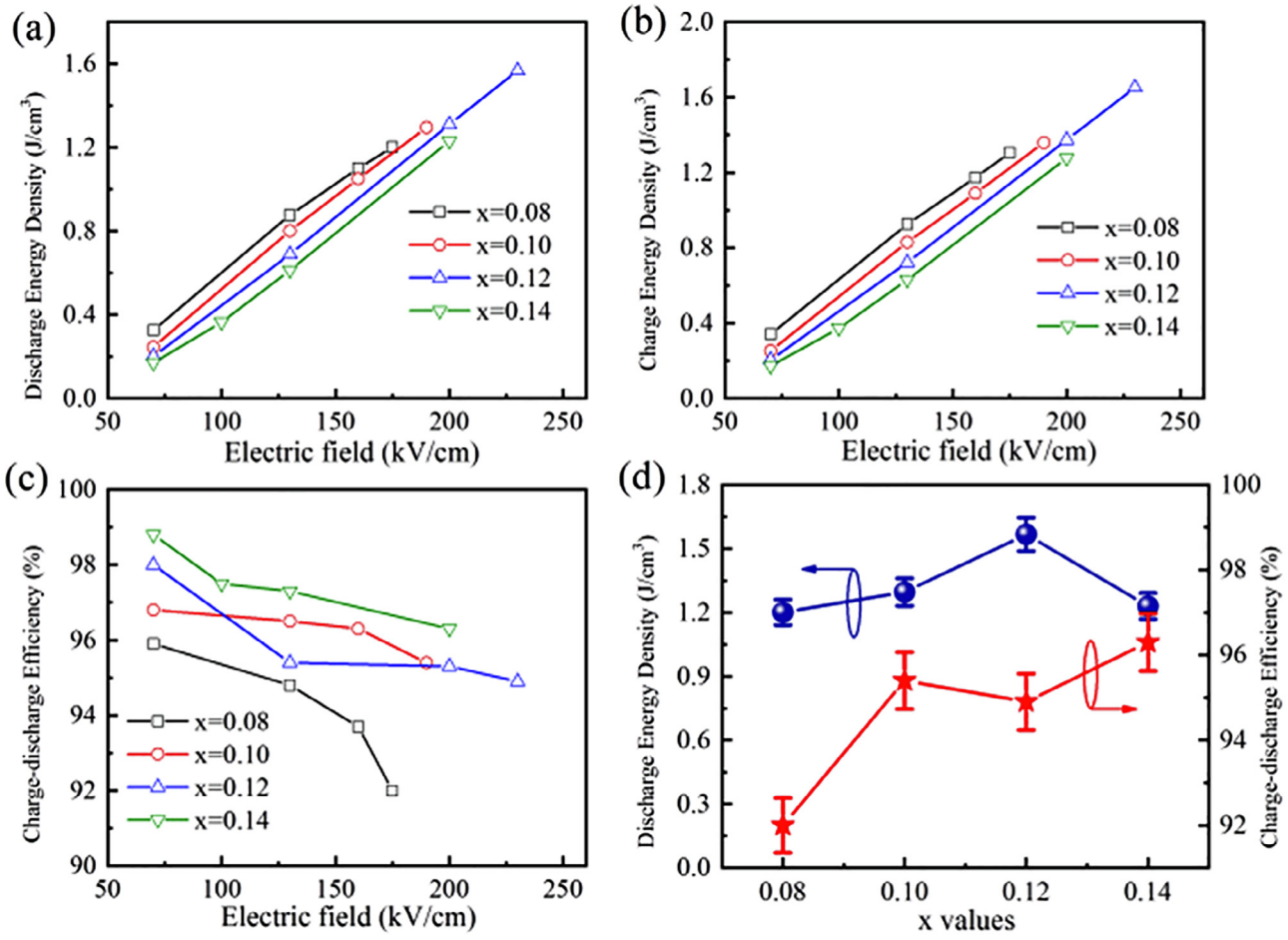

Fig. 4. Discharge and charge energy density (a), (b), efficiency (c) of the (1-x)$BaTiO_3$-x$Bi(Li_{1/3}Hf_{2/3})O_3$ ($0.08 \leq \times \leq 0.14$) ceramics as a function of electric fields and composition (d).

4. Conclusions

With the increase of x value, phase change from ferroelectric to relaxor increased the breakdown strength to 240 kV/cm at x = 0.12, which resulted in maximum values of $U \sim 1.71$ J·cm^{-3} and $U_e \sim 1.65$ J·cm^{-3} with an efficiency ~ 95.6% in the 0.88$BaTiO_3$-0.12Bi$(Li_{1/3}Hf_{2/3})O_3$ ceramic. High energy storage density and efficiency make this system a good candidate for high power pulse device.

CRediT authorship contribution statement

Li-Min Wang: Conceptualization, Software, Validation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. **Qing-Xiang Liu:** Conceptualization, Methodology, Writing - review & editing. **Di Zhou:** Resources, Funding acquisition, Validation, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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