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Bipolar fatigue-resistant behavior in ternary $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$–$SrTiO_3$ solid solutions

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A ternary solid solution (0.935–x)$Bi_{0.5}Na_{0.5}TiO_3$–0.065$BaTiO_3$–$x$$SrTiO_3$ (BNBST, BNBSTx), reported in our previous work, that exhibits a large strain response at a critical composition, was investigated with the emphasis on its bipolar fatigue behavior. The results indicated that BNBST with a high $SrTiO_3$ content owning an ergodic relaxor state exhibited fatigue-free behavior after 10^6 cycles. Furthermore, unexpected almost fatigue-free behavior was also observed in BNBST with a low $SrTiO_3$ concentration which has a typical ferroelectric long-range order. The excellent fatigue properties are quite favorable for practical applications.

Keywords: Ferroelectric ceramics; Fatigue; Piezoelectricity; Lead-free; Electrical conductivity

Ferroelectric fatigue, which generally refers to the degradation of ferroelectric properties upon repeated reversal of polarization, is significant for the long-term reliability of ferroelectric devices. To date, $Pb(Zr_xTi_{1-x})O_3$ (PZT) is still the dominant ferroelectric and piezoelectric material due to its excellent overall electrical properties for compositions around the morphotropic phase boundary (MPB) [1]. The fatigue behavior of PZT systems under various loading scenarios has been studied extensively in previous works [2–5] and significant degradation of the ferroelectric and piezoelectric properties was observed after 10^5 bipolar cycles [4,5]. Several mechanisms have been proposed to elucidate the fatigue behavior [2–6]. On the other hand, PZT systems face global restrictions due to environmental concerns. Therefore, the search for high-performance lead-free material and minimizing degradation to ensure reliable performance is not only scientifically interesting but also technologically important for practical applications [7–10].

Recently progress has been made with regard to developing lead-free counterparts with superior piezoelectric response. Ren et al. reported an exciting lead-free system with an ultrahigh d_{33} of ~620 pC N^{-1} [7]. Large strain response was reported in $(Bi_{0.5}Na_{0.5})TiO_3$-based solid solutions such as $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$–$(K_{0.5}Na_{0.5})NbO_3$ (BNT–BT–KNN), $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$–$SrTiO_3$, and $(Bi_{0.5}Na_{0.5})TiO_3$–$(Bi_{0.5}K_{0.5})TiO_3$–$SrTiO_3$ (BNT–BKT–ST) with normalized strains (S_{max}/E_{max}) of up to 560, 490 and 585 pm V^{-1}, respectively, which is entirely comparable to the PZT system [8–10]. Nevertheless, fatigue study on lead-free piezoelectric systems is still at an early stage with quite limited publications. Luo et al. investigated the fatigue behavior of 0.94$Bi_{0.5}Na_{0.5}TiO_3$–0.06$BaTiO_3$ (BNT–6BT) and observed severe degradation after 10^6 cycles [11]. The addition of 1 mol.% CuO was found to stabilize the fatigue-resistant phase and retain the electromechanical

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properties of BNT–6BT [12]. In addition, fatigue-resistant behavior was observed in specific compositions of BNT–BT–KNN, $Bi(Mg_{0.5}Ti_{0.5})O_3$–$(Bi_{0.5}K_{0.5})TiO_3$–$(Bi_{0.5}Na_{0.5})TiO_3$ (BMT–BKT–BNT) and $Bi(Zn_{0.5}Ti_{0.5})O_3$–$(Bi_{0.5}K_{0.5})TiO_3$–$(Bi_{0.5}Na_{0.5})TiO_3$ (BZT–BKT–BNT) solid solutions with relaxor pseudocubic phase [13–15]. Regarding to the mechanism responsible for the fatigue-free behavior, Ehmke et al. attributed the improved fatigue property in CuO-doped BNT–6BT to the combined effects of symmetry variation and a decrease in the local charges instead of the microcracks proposed in BNT–6BT [11,12]. The improved fatigue property in BNT–BT–KNN, BMT–BKT–BNT and BZT–BKT–BNT [13–15] was attributed to the reversible field-induced phase transition between the ergodic relaxor pseudocubic and ferroelectric phase along with the low concentration of defects.

However, it should be mentioned that for the CuO-doped BNT–6BT, only 100 cycles were performed and the long-term reliability remains uncertain [12]. For the BNT–BT–KNN, BMT–BKT–BNT and BZT–BKT–BNT systems, although fatigue behavior was improved, which is favorable for actuator applications, the dominant state was ergodic relaxor pseudocubic with short-range coherence [13–15], and ferroelectric memories and sensors require a ferroelectric long-range order system with fatigue-free response. Therefore, developing environmentally friendly fatigue-resistant lead-free systems with different ferroelectric order states is essential for practical applications.

In our previous works, a ternary lead-free solid solution $(0.935-x)Bi_{0.5}Na_{0.5}TiO_3$–$0.065BaTiO_3$–$xSrTiO_3$ (BNBST, BNBSTx) was proposed and a schematic phase diagram was established [9]. The aim of present work is to investigate the fatigue behavior in this system, focusing on bipolar fatigue which could induce more severe degradation compared to unipolar fatigue [16]. Three representative compositions were considered based on the phase diagram and excellent fatigue response was observed. The underlying mechanisms corresponding to these findings are discussed.

The details for fabricating the BNBST system have been shown in our previous works [9]. The obtained samples were carefully polished and the root mean square (RMS) roughness was ~1–2 nm (see online Supplementary information). Silver paste was applied to both sides of the polished sintered samples, which were then fired at 650 °C for 0.5 h.

The crystal structures were characterized by X-ray diffractometry (D8 Focus, Bruker AXS, Karlsruhe, Germany). The fatigue test was performed on annealed unpoled samples under bipolar triangular fields of $4\ kV\ mm^{-1}$ at 10 Hz. The ferroelectric hysteresis P–E loops and bipolar S–E curves were measured under the same electric field and frequency after 1, 10, 10^2, 10^3, 10^4, 10^5 and 10^6 cycles using a ferroelectric analyzer (TF2000, Aixacct, Aachen, Germany) along with a laser interferometer. During the fatigue test, in order to ensure the reliability of the fatigue data obtained, two separate sets of samples for each composition were performed. The temperature-dependent electrical conductivity was measured using an impedance analyzer (Agilent HP4294A, Santa Clara, CA) in the range of 550–650 °C from 40 Hz to 1 MHz.

The fatigue behavior before and after 10^6 bipolar cycles for the three representative compositions is shown in Figure 1. For BNBST0.02 with typical ferroelectric long-range order, following the completion of 10^6 cycles of fatigue at $4\ kV\ mm^{-1}$, a typical ferroelectric response could still be observed as shown in Figure 1a. The coercive field E_c was found to decrease from ~2.1 to ~$1.7\ kV\ mm^{-1}$ with a decrease of ~20%. The maximum polarization P_m exhibited a small increase of ~$0.1\ \mu C\ cm^{-2}$. This amounts to a ~0.4% increase from the initial cycle. In the case of the remnant polarization P_r, a slightly larger decrease ~5.4% was observed. For the BNBST0.18, the P_m also kept almost constant while the P_r exhibited a relative large decrease in the first 10^5 cycles from 18.7 to $15.1\ \mu C\ cm^{-2}$, but further increased slightly up to $15.7\ \mu C\ cm^{-2}$. The E_c value decreased by ~35% compared to the initial one. The effects of fatigue on the ferroelectric properties in BNBST0.22 were minimal with a fatigue-free process. The average values of the P_m and P_r of two separate sets of samples for each composition are shown in Figure 1g–i with increasing number of cycles along with the error bars. Even though a slight difference in P_m and P_r could be observed for two separate sets of samples, the fatigue behavior was very similar for both. To quantify the change in strain response for the three compositions, the average strain amplitude ΔS between positive and negative maximum strain under bipolar electric field was also summarized in Figure 1g–i. The change in the amplitude of the right and left wings of the "butterfly curves" represents ΔS^+ and ΔS^-, respectively. From the figures no obvious strain variation could be observed for all the compositions. It is also important to note that the strain loops maintained a high degree of symmetry after 10^6 cycles. Compared to the pure BNT–6BT ceramic [11] and BNT–BT–KNN with ferroelectric long-range order [13], substantially enhanced fatigue properties were obtained after a small amount of $SrTiO_3$ substitution (BNBST0.02) while keeping the ferroelectric long-range order structure. A comparison of the fatigue data for the present BNBST and other lead-free systems is summarized in Table 1 (see online Supplementary information).

Based on the bipolar fatigue results on three BNBST compositions, a significant improvement in the fatigue response was found compared to traditional PZT and pure $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ (BNT–BT) solid solution. The fatigue models for the traditional PZT ceramics [2–6] appeared to be quite weak for the BNBST system. Regarding to the intrinsic mechanism responsible for the observed fatigue-free behavior, several mechanisms such as the combined effects of the symmetry variation and decrease in the local charges, and a reversible field-induced phase transition have been proposed [11–15]. These explanations could indeed account to some extent for the ferroelectric fatigue-free behavior of lead-free solid solutions with a specific order state. Nevertheless, for the present BNBST system, a fatigue-free response was clearly observed in all the compositions with different ferroelectric order states. Such a phenomenon has not been reported before and it is therefore necessary for us to clarify the intrinsic underlying reason for this.

It is well known that defects play an important role in the fatigue behavior of the perovskite ferroelectric sys-