Coupled Long- and Short-Period Dynamics in Bi^{3+}-Doped BCZT/Cellulose Nanogenerators for Optimized Output and High-Temperature Stability

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Supplementary Information

1. Experimental section

1.1 Materials

Natural cotton (-$(C_6H_{10}O_5)_n$-, DP=632, Hubei Jinhuan New Materials Co., Ltd.); N, N -dimethylacetamide (CH_3C (O) N $(CH_3))_2$, AR, Aladdin Reagent Co., Ltd. in Shanghai); anhydrous lithium chloride (LiCl, AR, Shanghai Aladdin Reagent Co., Ltd.); polyvinylidene fluoride (-$(CH_2$-$CF_2)_n$-, Mw=534,000, McLean & Company); barium chloride ($BaCl_2 \cdot H_2O$, AR, Shanghai Aladdin Reagent Co., Ltd.); sodium hydroxide (NaOH, CP, Shanghai Aladdin Reagent Co., Ltd.); Barium carbonate ($BaCO_3$, AR, Shanghai Aladdin Reagent Co., Ltd.); titanium oxide (TiO_2, AR, Shanghai Aladdin Reagent Co., Ltd.); sodium chloride (NaCl, AR, Shanghai Aladdin Reagent Co., Ltd.); anhydrous ethanol (C_2H_6O, LR, Shanghai Aladdin Reagent Co., Ltd.); phosphorus pentoxide (P_2O_5, CP, Tianjin Damao Chemical Reagent Factory); bismuth nitrate decahydrate (BCZT-*x*Bi ceramic fillers and precursor solutions were prepared, with BCZT-*x*Bi abbreviated as *x*BCZTB).

1.2 Synthesis of xBCZTB Ceramic Fillers

Barium calcium zirconate titanate ($Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$, BCZT), a ceramic filler, was prepared using the solid phase reaction method. The raw materials were weighed according to the stoichiometric ratio and equally divided into six groups, which were doped with different contents of Bi^{3+} (0.010 g, 0.020 g, 0.025 g, 0.030 g, 0.035 g, and 0.040 g of $Bi(NO_3)_3$-$10H_2O$, denoted as *x*Bi). The mixture was ball milled with anhydrous ethanol and ball milling media to induce solid-phase reaction of the raw materials to form the *x*BCZTB precursor. The precooked powder was again ball-milled

and refined, and the temperature was adjusted to 1250°C. The precooked powder was roasted at high and low temperatures for 6 h at a temperature increase rate of 3°C /min, respectively, and then milled to prepare the BCZT ceramic filler, and the flow is shown in Fig. 1(a).

1.3 Preparation of Cast Precursor Solution

Based on our previous work,[1] a cellulose/PVDF mixed solution with a mass ratio of 8:2, hereafter referred to as C8P2, was prepared. The *x*BCZTB nanoparticles (2% of the total volume) were sequentially subjected to 30 min of ultrasonication and 30 min of mechanical stirring for several cycles, followed by 12 h of continuous stirring at room temperature, and finally 30 min of vigorous stirring at 60°C, to obtain a homogeneous suspension, which was then coated onto the glass substrate by doctor blade calendering to form a monolayer composite film.

1.4 Fabrication of Piezoelectric Nanogenerators (PENGs)

The composite film was laser cut into circular electrodes (3 cm in diameter), and copper tape electrode contacts were fixed. To improve the operational stability, a Polyimide (PI) encapsulation layer was used for protection. The PENGs prepared based on different films were named as 0.010BCZTB@C8P2 PENGs, 0.020BCZTB@C8P2 PENGs, 0.025BCZTB@C8P2 PENGs, 0.030BCZTB@C8P2 PENGs, 0.010BCZTB@C8P2 PENGs, and 0.010BCZTB@C8P2 PENGs, respectively.

All experiments involving human participants were conducted in accordance with the relevant guidelines and regulations. Informed consent was obtained from all participants involved in the human motion sensing tests.

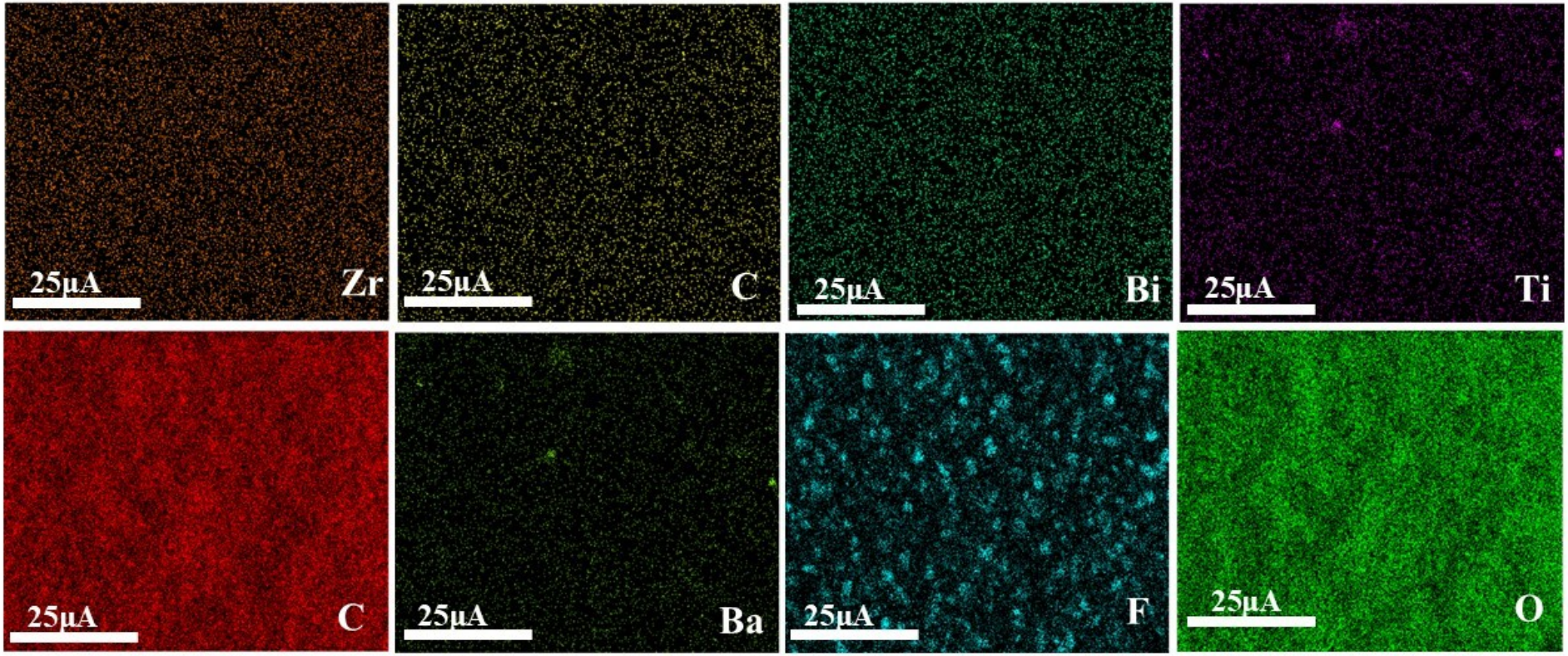

Figure S1: *The energy dispersive spectroscopy (EDS) plot in Figure 2(d).*

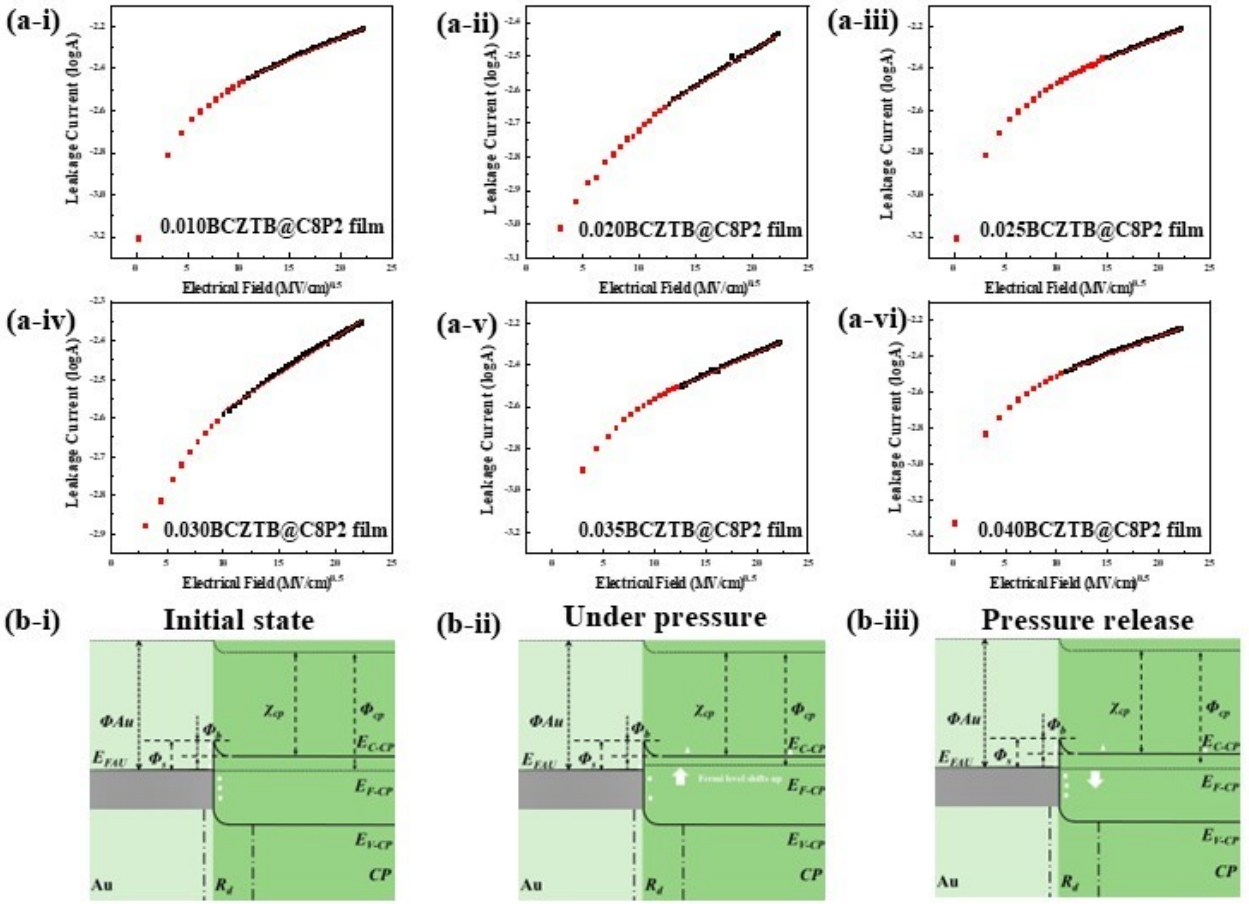

Figure S2: *(a-i)–(a-vi) Fitting results of J-E curves of the BCZTB@C8P2 PENGs with different Bi^{3+} doping amounts;(b1)-(b3) is the band diagram of the interface between the Au electrode and the BCZTB@C8P2 film.*

1. The physical meaning of the abbreviations in the band diagram analysis

$\boldsymbol{E_{FAu}}$: the Fermi energy level of Au.

$\boldsymbol{\Phi S}$: the Schottky barrier height.

$\mathbf{\Phi_b}$: the built-in potential.

$\mathbf{\Phi_{CP}}$: the work function of the BCZTB@C8P2 film.

$\boldsymbol{\chi_{CP}}$: the electron affinity of the BCZTB@C8P2 film.

$\boldsymbol{E_{C\text{-}CP}}$: the conducting band of the BCZTB@C8P2 film.

$\boldsymbol{E_{F\text{-}CP}}$: the Fermi level of the BCZTB@C8P2 film.

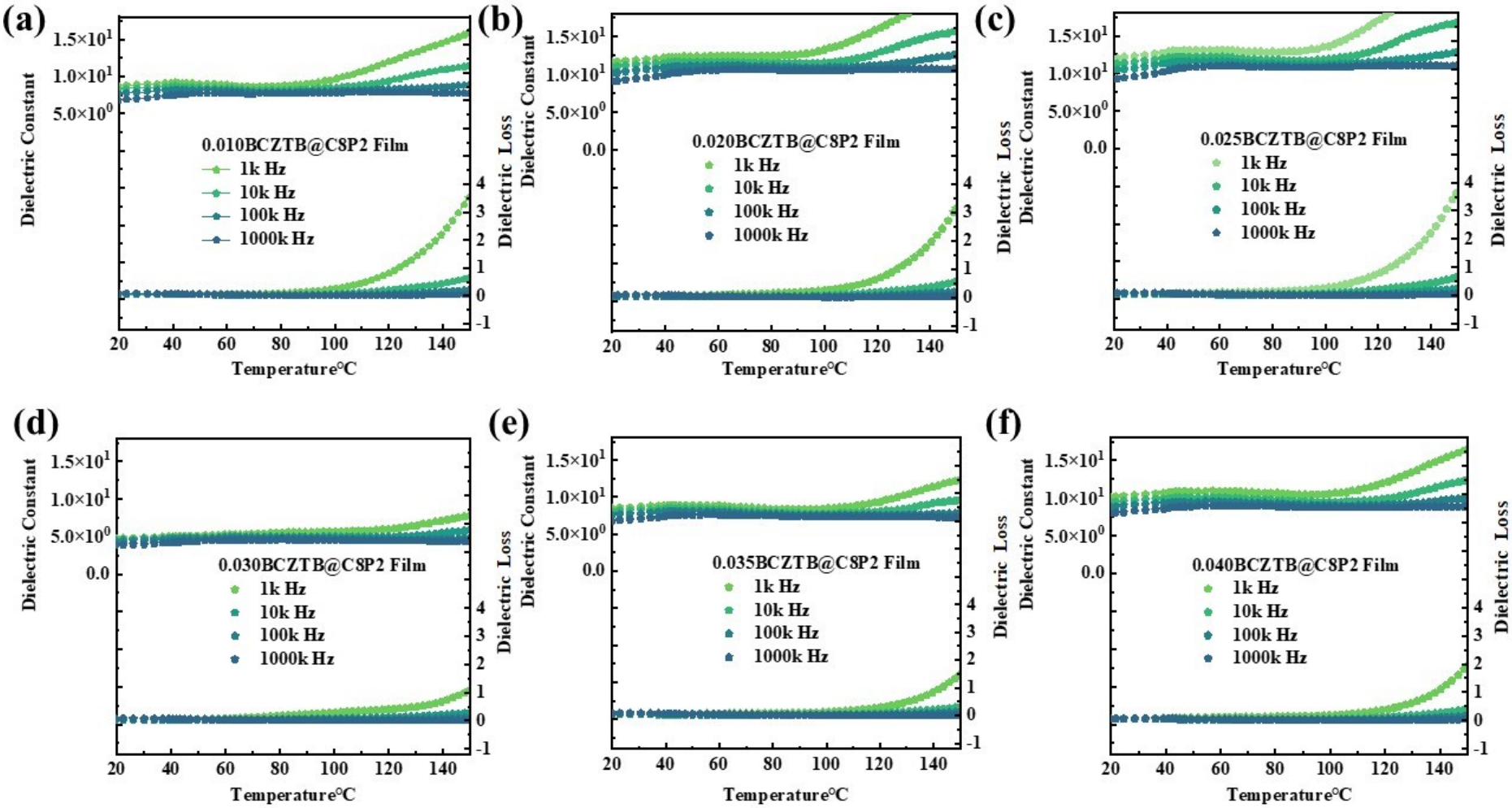

Figure S3: *The ε-T curves and tanσ-T curves for all the BCZTB@C8P2 films.*

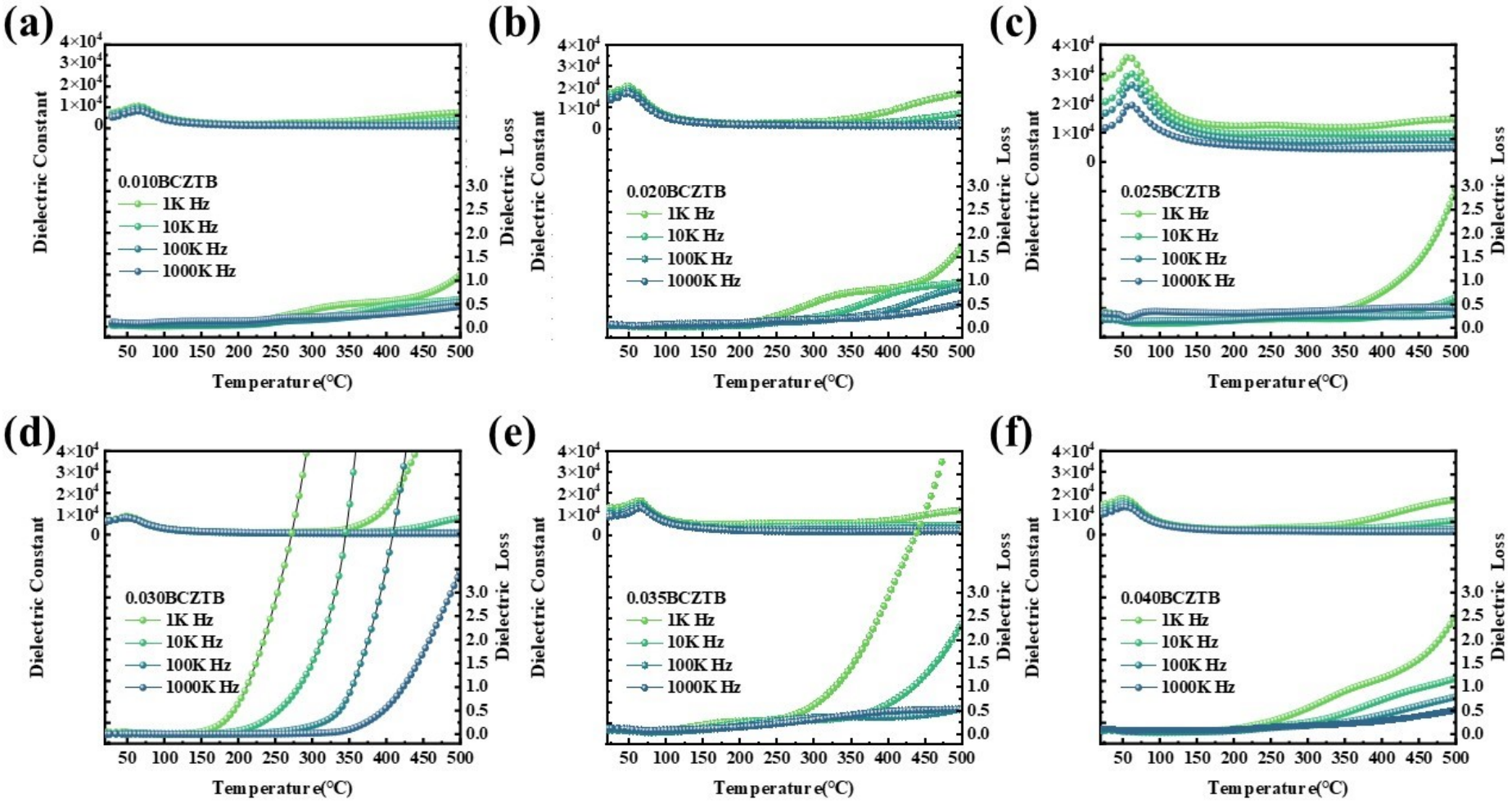

Figure S4: *The ε-T curves and tanσ-T curves for all the BCZT ceramics doped with varying* Bi^{3+} *contents.*

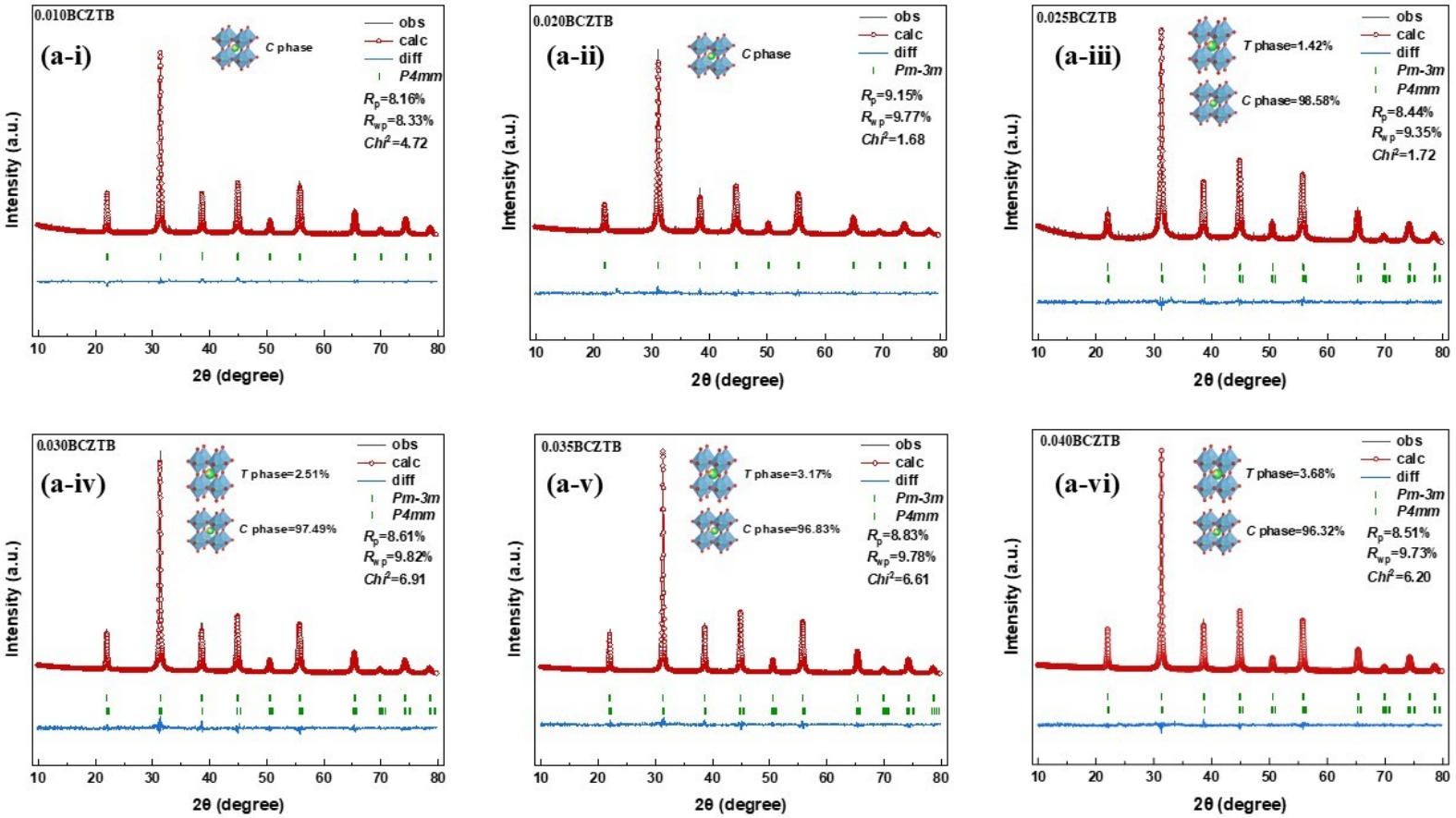

Figure S5: *(a-i)-(a-vi) shows the Rietveld refinement of the XRD data for BCZTB@C8P2 films.*

References

1. Z. Sun, S. Wang, S. Zhao, H. Wei, G. Shen, Y. Pu and S. Zhang, 2024, **12**, 859-867.