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Ferroelectric, piezoelectric properties and magnetoelectric coupling behavior in aurivillius $Bi_5Ti_3FeO_{15}$ multiferroic nanofibers by electrospinning

Yuwei Zhao, Huiqing Fan*, Guocai Liu, Zhiyong Liu, Xiaohu Ren

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

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Aurivillius $Bi_5Ti_3FeO_{15}$ (BTF) multiferroic (MF) nanofibers (NFs) of about 400 nm were fabricated by electrospinning and calcination. The BTF NFs exhibit an effective micro–piezoelectric coefficient of 35 pm/V and benign micro-ferroelectricity. Macro-ferroelectric and magnetoelectric coupling behavior were investigated in detail by non-sintering and pressing for the first time, which is smaller than that of the BTF ceramic or film due to the adverse effects of filled air. A magnetoelectric (ME) voltage coefficient as large as 14 $mVcm^{-1}$ Oe^{-1} can be achieved. Weak ferromagnetism was also realized at RT. Although the sintering temperature was only 600 °C, MF BTF NFs as multiferroic materials were successfully obtained, which offers new insights into the design and application of promising lead-free MF materials for novel devices.

1. Introduction

Multiferroic (MF) materials with the coexistence of ferromagnetic (FM), ferroelectric (FE) and/or ferroelastic orderings recently have attracted ever-increasing interests and provoked a great number of researches driven by their significant potential for exploration of new multifunctional devices, including microwave phase shifters, resonance devices, various sensors, multi-state memory devices, spintronics devices and even photovoltaic devices [1–6]. Among them, $BiFeO_3$ with both the high magnetic-transition temperature ($T_N = 640$ K) and Curie point (1100 K) as the best candidate for the application of multiferroics at room temperature (RT), has been limited by the large leakage current and poor fatigue-resistant characteristics [7–9]. Moreover, Aurivillius ferroelectrics (bismuth layer structure ferroelectrics, BLSFs) have wide applied perspective in high-temperature piezoelectric applications, optical devices and nonvolatile FE random access memories (NvFRAMs) owing to the high FE phase transition temperature (T_C), strong FE polarization and resistant to polarization fatigue [10–13]. After inserting one perovskite layer of multiferroic $BiFeO_3$ phase into the isostructural $Bi_4Ti_3O_{12}$ BLSFs, both FM and FE for RT exploitation of the obtained bismuth titanium iron ($Bi_5Ti_3FeO_{15}$, abbreviated as BTF) have been significantly enhanced [14–16]. Up to now, electrical, magnetic, and optical properties such as refractive index *n*, extinction coefficient *k*, the fundamental bang-gap energy, photocatalytic property etc. of BTF have been substantially reported [17–19]. As a typical MF material, the polarization, magnetization, and strain of BTF can be facilely manipulated by its conjugate electric-, magnetic-, thermal-, optic- and elastic-fields, thus BTF significantly broadens the scope of functional material research and sheds light on the innovation of novel multifunctional devices designed as illustrated schematically in Fig. 1 [20–22]. The phase control in BTF is briefly shown as five-pointed star indicating the five physical quantities interact with each other. Very recently, Zhao et al. demonstrated that BTF thin films with nearly (00l)-orientation by pulsed laser deposition exhibit a robust magneto–electric coupling, due to a short-range magnetic ordering arising from the existence of Fe-rich nanodomains [16]. Such thin films, however, suffer from substrate-based constraints and confined overall connectivities [23].

Recently, remarkable progress in MF field has been achieved from bulk to the lower-dimensional and nanoscale structures for novel multifunctional devices [24–28]. It is noteworthy that ideal

* Corresponding author.
E-mail address: hqfan@nwpu.edu.cn (H. Fan).

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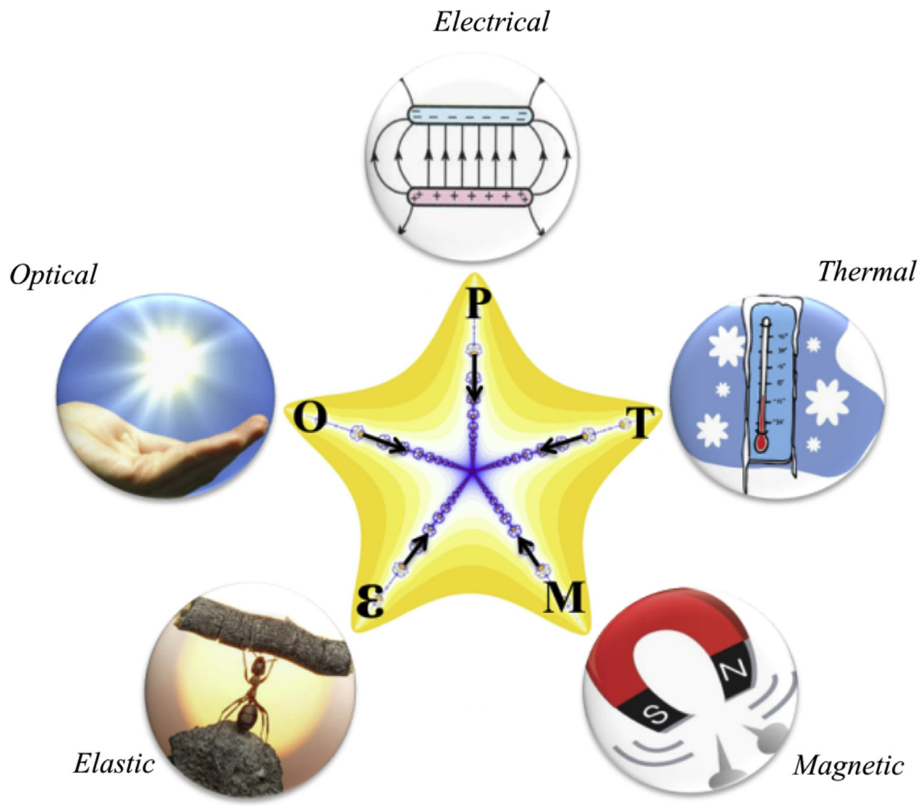

Fig. 1. Schematic representation of phase controls in BTF. Reversible electric–magnetic–thermal–optic-elastic interactions are presented. The magnetic field, temperature, electric field, light and stress control the magnetization M, entropy (denoted as T), electric polarization P, optical properties O and strain ε, respectively. In essence, they tune and interact with each other.

one-dimensional (1D) nanofibers (NFs) as an alternative to magnetoelectric thin films, free of substrate based constraints, have displayed MF coupling that is orders of magnitude greater than what have been found in ideal thin films [23]. Furthermore, MF NFs have been employed as exceptional fillers in polymer composites to couple a variety of functions together within a single system, due to ease of fabrication, enabling additional connectivities and causing slightly larger degree of crystallinity and Young's modulus of the polymer than other geometries of nanofillers [29–31]. As a result, many researchers have focused on synthesizing NFs via the anodized aluminum oxide (AAO) template-electrodeposition [32], wet etching [33], sol–gel processing [34], and electrospinning [26], among which electrospinning is particularly convenient, universal and effective.

Motivated by the above efforts, Aurivillius BTF MF NFs were prepared by electrospinning and calcination in this work. Macro- and microscopic FE properties were investigated, and weak ferromagnetism at RT was also realized. Magnetoelectric (ME) coupling was also investigated in detail.

2. Experimental

2.1. Preparations of BTF nanofibers

For BTF NFs, 1.875 g $Bi(NO_3)_3 \cdot 5H_2O$, 0.787 g TBT and 0.312 g $Fe(NO_3)_3 \cdot 9H_2O$ are dissolved in DMF (45 mL). Then, 5.5 g PVP ($M_w = 1{,}300{,}000$, Sigma–Aldrich) was slowly added in the solution with magnetic stirring for 36 h to form the clear yellow precursor solution for electrospinning. Next, the precursor solution was loaded into a 20 mL plastic syringe with a copper pin. The applied electrospinning parameters were distance of 20 cm between collector covering aluminum foil and pin-tip, an optimized voltage of 19.5 kV and feed rate of 0.3 mL/h. Finally, the NFs were dried in vacuum overnight at 90 °C and then calcined at 300 °C for 2 h in oxygen atmosphere to make PVP fully burning and 600 °C for 2 h in the protection of nitrogen atmosphere at a rate of 30 °C/h to protect the morphologies of NFs.

2.2. Characterization and measurements

Crystal structures of the ceramics were detected by using X-ray diffraction (XRD; X'Pert PRO MPD, Philips, Eindhoven, The Netherlands) with a nickel filter (Cu*Kα* radiation) in the 2θ range of 15–75° at RT. Raman spectra were obtained by an instrument (LabRAM HR800, Horiba Jobin Yvon, Lyon, France) with the exciting source of 514.5 nm line from an argon ion laser in a backward scattering geometry. The surface morphologies and structures of the specimens were characterized with a field emission scanning electron microscope (FESEM; JSM-5610, JEOL, Tokyo, Japan) operated at 15 kV. Transmission electron microscopy (TEM; JEM-3010, Questar, New Hope, USA) and high-resolution transmission electron microscopy (HRTEM) were acquired by a FEI TecnaiF30G2 field emission microscope operated at 300 kV. The thermo-gravimetric (TG) and differential scanning calorimetry (DSC) curves of the BTF NFs were simultaneously performed with TG/DSC (STA 409PC, Netzsch, SELB, Germany) apparatus at a heating rate of 10 °C/min in flowing argon. Piezoelectric force microscopy (PFM) images were measured using an atomic force microscopy (AFM; SPI3800N&-SPA400, Seiko, Tokyo, Japan) via the Dual AC Resonance Tacking mode (DFRT) under an AC modulation voltage of 10 V (the silicon