Synthesis and magnetoelectric properties of multiferroic composites of lead lanthanum zirconate titanate and mesoporous cobalt ferrite

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ABSTRACT

We describe herein a facile synthetic approach to $CoFe_2O_4$ (CFO)/lead lanthanum zirconate titanate (PLZT) multiferroic composites. The composites were prepared by synthesizing mesoporous CFO through a novel temple-free strategy and subsequent generating PLZT inside mesoporous CFO. The coexistence of both CFO and PLZT phases in the composites was confirmed by XRD. The porosity and pore structures were determined from N_2 physisorption analysis and TEM. The composites were found to possess multiferroicity at room temperature and a maximum magnetoelectric voltage coefficient of 36.7 mV/cm Oe. This work is anticipated to pave the way for enhancing the magnetoelectric coupling of multiferroic composite materials.

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Multiferroic magnetoelectric materials with coexistence of ferroelectric and ferromagnetic orders have attracted tremendous attention due to their potential applications in multifunctional devices, including microwave devices, sensors and digital memory [1–5].The prominent feature of such materials is the magnetoelectric (ME) effect [1,6] which is defined by the cross-coupling between the ferroelectric and ferromagnetic orders [7–10]. Although the ME effect has been observed as an intrinsic effect in single-phase materials [6,11–13], such as the most studied bismuth ferrite ($BiFeO_3$) [14–16], these materials are rare in nature and this phenomenon often occurs at low temperature and is too weak to be practically used.

The development of magnetoelectric materials, therefore, has focused on the composite materials composed of piezoelectric and magnetostrictive components, which have potential to produce a large ME response at room temperature because of the coupling interaction between piezoelectric and magnetic phases [2,4,17]. It should be noted that, in such a composite, the ME effect is witnessed as an extrinsic product property [2,17], resulting from the elastic coupling interaction across magnetostrictive-piezoelectric interfaces. When applying a magnetic field to a composite, the strain derived from the magnetostrictive phase is transferred to the piezoelectric phase to induce an electric field across the piezoelectric phase via the piezoelectric effect, and vice versa [18–21]. Since the ME coupling depends on the stress-mediated transfer at the interface between the ferroelectric and ferromagnetic components, the dimension of the interface has a great impact on the ME effect [2,22,23]. To enhance the coupling interaction, a large interface area is

thus desirable. A variety of the multiferroic composite systems with different interfaces, including multilayer and laminate configurations [7, 17,24–26], columnar structures [27,28] and nanopillars within a matrix [29,30], have been examined.

As cobalt ferrite ($CoFe_2O_4$, CFO) is a typically magnetic material with large magnetostriction [31,32], mesoporous CFO has been envisioned as an appealing ferromagnetic constituent with large coupling interface for high-performance multiferroic composites. Haffer et al. [22] synthesized a multiferroic composite consisting of $BaTiO_3$ and mesoporous CFO using mesoporous KIT-6 silica as a template. Chien et al. [23] employed the polymer template to fabricate mesoporous CFO and then deposited PZT into CFO framework. Although these methods are indeed promising, the currently available approaches to mesoporous CFO typically involve templates and multi-step syntheses, which are laborious, costly, and time consuming.

Herein, we present a novel template-free method for the preparation of the CFO/PLZT composites. The controlled thermal decomposition of Fe-Co binary oxalate yields the mesoporous CFO, which was subsequently mixed with PLZT to undergo the hydrothermal process. The prepared nanostructured composites have been characterized in terms of their structure and dielectric properties. Room-temperature multiferroicity has been successfully demonstrated in the composites.

All the chemicals used were of analytical grade and used without further purification. $FeSO_4 \cdot 7H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were mixed in a molar ratio of 2:1 by magnetic stirring in air. Meanwhile, a proper amount of $C_2H_2O_4 \cdot 2H_2O$ was dissolved in deionized water at 60 °C. Then, the latter was added dropwise into the former under vigorous magnetic stirring, during which a yellow precipitate formed. The resulting precipitate was filtered, washed with deionized water and

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ethanol, and dried at 60 °C for 12 h. The as-obtained yellow powder precursor was calcined in air at 300 °C for 1 h with a heating rate of 1 °C/min. Finally, a dark CFO powder was obtained.

According to the formula $Pb_{0.93}La_{0.07}(Zr_{0.60}Ti_{0.40})_{0.9825}O_3$, the stoichiometric amount of $Pb(NO_3)_2$, $La(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$ was mixed at 60 °C under magnetic stirring, and then tetrabutyl titanate dissolved in ethanol and KOH dissolved in deionized water were added to form a precursor solution. At the same time, the as-prepared mesoporous CFO was mixed with as-obtained precursor solution with the molar ratio of 1:1, followed by stirring at 60 °C for 3 h. The suspension was then transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for 8 h. The CFO/PLZT composite powders were obtained after filtration and drying. For electrical measurements, the composite powder was pretreated with a small amount of polyvinyl (PVA) and finally pressed into pellets. The pellets were sintered at 1100 °C for 3 h to form the composite ceramics. Electrical contacts were soldered after depositing a thin layer of silver paste on each side of the pellet.

X-ray powder diffraction (XRD) was carried out on a Bruker AXS D8-Focus diffractometer using CuKα radiation. N_2 physisorption analysis at 77 K was conducted by using Micromeritics ASAP 2020 HD88 system. Prior to measurement, the samples were degassed at 150 °C for 5 h. The specific surface areas were calculated with the Brunauer-Emmett-Teller (BET) methods. Pore size evaluation was based on Barrett-Joyner-Halenda (BJH) method. The microstructure was confirmed by transmission electron microscopy (TEM) with a Philips CM12 microscope operated at 120 kV. Dielectric measurements were accomplished using an Agilent 4294A precision LCR meter as a function of frequency (100 Hz to 100 kHz) at room temperature. Polarization versus electric field (P-E) loops were attained using Radiant Precision LC at an electric field frequency of 100 Hz. The magnetization measurements were performed using a LakeShore7400 vibrating sample magnetometer (VSM). Magnetoelectric (ME) voltage coefficient was measured as a function of DC magnetic field by an ME measurement system [33], wherein H_{ac} was generated through along straight solenoid with 200-turncoils driven by a single generator, H_{dc} was supplied by a pair of NbFeB permanent magnets, the output voltage signal was provided to Charge Amplifier and then detected using Spectrum Analyzer (Agilent, 35670A).

The room temperature X-ray diffraction pattern for CFO/PLZT composite sample is presented in Fig. 1. The observed diffraction peaks can be indexed as the perovskite tetragonal crystalline structure (JCPDS card No. 53-0698) with space group P4mm for PLZT (peaks marked with an asterisk), which is confirmed by the splitting of (001)/(100), (101)/(110) and (002)/(200) peaks [34] with the peak intensity ratio of nearly 2:1, and as the cubic spinel structure (JCPDS card No. 22-1086) with space group $Fd\overline{3}m$ for CFO (peaks marked with a dot). The
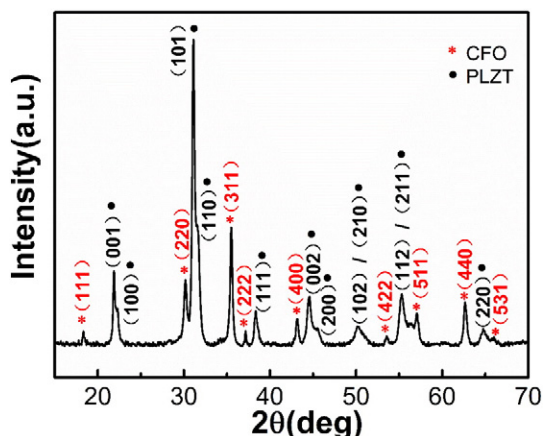
absence of any impurity peak indicates that there are no side chemical reactions taking place between the two constituent phases.

The N_2 adsorption-desorption isotherms and corresponding pore size distribution plots are shown in Fig. 2, suggesting the mesoporosity nature of the pristine CFO and the CFO/PLZT composites. A typical Langmuir tape-IV isotherm and a distinctive hysteresis loop at relatively higher pressure are observed from the mesoporous CFO sample. The total pore volume is 0.28 cm^3 g^{-1} and the BET surface area is 203 m^2 g^{-1}. A narrow distribution of pore size (mainly 2–5 nm) with a pronounced peak at 3.2 nm is found in the porous CFO. With regard to the composites, a clearly less apparent type-IV behavior than pure CFO and dramatic reduction in the intensity of the peak at 3.2 nm in the pore size distribution plot imply disappearance of pore structures with filling of the PLZT particles in the accessible pores in the CFO framework. Accordingly, the total pore volume and the BET surface area have been decreased to 0.13 cm^3 g^{-1} and 67 m^2 g^{-1} respectively in the composites.

Fig. 3 shows the TEM images of the mesoporous CFO and CFO/PLZT composites. It can be clearly seen that homogeneous worm-like mesopores are randomly distributed within the CFO sample (Fig. 3a). On the other hand, as shown in Fig. 3b, large regions of pores are no longer observed in the composites, indicative of successful pore filling. These findings are consistent with the N_2 physisorption results.

Fig. 4(a) displays the frequency dependent dielectric constant (ε) and loss (tan δ) of the composite ceramic in the frequency range of 100 Hz to 100 kHz measured at room temperature. A salient feature revealed by the dielectric spectra is the rapid decrease of the dielectric constant with frequency. This trend can be explained by the Maxwell-Wagner interfacial polarization mechanism, which is usually related to the interfaces between materials having different permittivity and conductivity and often occurs inside inhomogeneous ceramics [35,36]. The large interfaces between the more conductive CFO phase and the more insulating PLZT phase trap the mobile charge carriers, resulting in space charge polarization dominant at lower frequencies [32]. The accumulation of uncompensated charges generated by strongly inhomogeneous polarization leads to the formation of inner local fields and results in large dielectric losses, especially at low frequencies.

The field dependence of the magnetization (M-H loops) for pristine mesoporous CFO and the CFO/PLZT composite was measured at room temperature, as shown in Fig. 4(b). Obviously, both samples exhibit typical hysteresis loops, confirming their ferromagnetic state. The M-H hysteresis of CFO results from ordered magnetic structure derived from
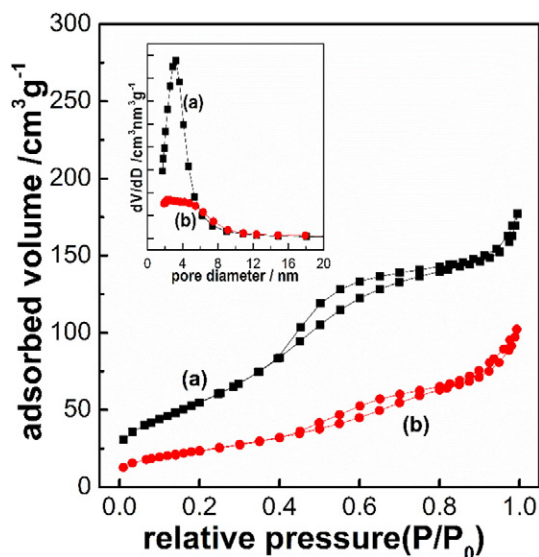

Fig. 1. XRD pattern of the CFO/PLZT composites.

Fig. 2. N_2 adsorption–desorption isotherms and corresponding pore size distribution plots (inset) of (a) mesoporous CFO and (b) CFO/PLZT composites.