

Microstructures, ferromagnetic, and ferroelectric properties in polyvinylpyrrolidone-assisted $\text{CoFe}_2\text{O}_4/\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ multiferroic composite thick films

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Received: 16 March 2009 / Accepted: 15 July 2009 / Published online: 29 July 2009
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Abstract $\text{CoFe}_2\text{O}_4/\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (CFO/PZT) multiferroic composite thick films with different CFO mass fractions have been prepared onto Pt/Ti/SiO₂/Si substrate by a hybrid sol–gel process and spin coating technique. Polyvinylpyrrolidone (PVP) was employed to be an assistance to the sol–gel solution for enhancing the film thickness and promising a crack-free film surface. After annealing at 650 °C in air for 1 h, phase structure, microstructure, magnetic and ferroelectric properties as well as leakage current of multiferroic thick films were investigated. X-ray diffraction indicated a deeply buried distribution of CFO particles in the PZT matrix. Scanning electronic microscopes showed crack-free surfaces and a decreasing film thickness from 7.2 μm to 6.2 μm with increasing CFO content. Furthermore, the saturated magnetization and remanent magnetization were also hence increased. In addition, mass fraction of CFO in PZT matrix was also estimated from 0.36% to 4.58% according to the relationship between M_s and magnetic content. Ferroelectric hysteresis loops revealed saturated polarization (P_s) and remanent polarization (P_r) were diluted by CFO till its mass fraction rising to 1.8%. After that, polarization was increased with further increasing CFO content. Enhanced leakage was demonstrated to be partially contributed to them. A critical content of 1.8% was hence confirmed, where ferroelectric and magnetic properties can be

balanced, indicating a possible stress-transferred magnetoelectric coupling effect in this composite.

Introduction

In the recent years, complicated multiferroic materials have drawn many interests due to its potential multifunctional applications on transducers, sensors, and actuators [1]. The most important is the coexistence of several primary ferroics in these materials, including ferroelectric, ferromagnetic, and ferroelastic. Furthermore, interplay among them is also thought to be the main source of magnetoelectric coupling effect [2]. Bulk ceramics and diversified films were hence studied with the different interposition, including 0-3 type, 2-2 type, and 1-3 type, which driven the complicated multiferroic materials forward continually [3–12]. In particular on $\text{CoFe}_2\text{O}_4/\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ due to the large magnetostrictive coefficient of CoFe_2O_4 and a good piezoelectric candidate of $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ [13–17], both of them can produce a large strain under their magnetic/electric field, finally leading to a magnetic-mechanic-electric coupling effect by means of their crossed interfaces [2]. In the literatures, alternated CFO/PZT layered thin films were studied by Nan [14] and sequence of depositing PZT and CFO was believed to have a noticeable effect on ferroelectric and ferromagnetic properties. Liu [15] improved a modified nanocomposite film which took the mixed PZT and CFO solution together as the precursor solution for spin-coating. Multiferroic CFO/PZT nanofibers were also fabricated using electrospinning [16]. However, most efforts have been spent on the nano-metric thickness, and at most, a CFO-PZT composite thick film with 1 μm was reported by Wan [17] using sol–gel technique assisted by PVP.

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In the present work, $\text{CoFe}_2\text{O}_4/\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (abbreviated as CFO/PZT) multiferroic composite thick films with different CFO content were prepared by a hybrid sol–gel processing and spin coating technique. Polyvinylpyrrolidone was introduced into the precursor solution due to its ability to enhance the film thickness as well as avoiding the crack on the surface. Phase structure suggests a deeply buried distribution of CFO in the PZT matrix, which is corresponding to our deposition purpose. Scanning Electronic Microscope (SEM) reveals a series of multiferroic films above $5\ \mu\text{m}$ with a crack-free surface. Magnetic properties indicated a CFO content dependent magnetization and CFO content independent coercive magnetic field. Ferroelectric behavior was diluted by CFO ferrite. Acceptable leakage current was also observed, which promised a true ferroelectric property. Finally, a critical CFO content of 1.8% was estimated, where a magnetoelectric effect could be predicted based on its dense microstructure and balanced ferroelectric and magnetic properties [14].

Experimental

Tetraisopropyl titanate ($(\text{C}(\text{H}_3)_2\text{CHO})_4\text{Ti}$), acetylacetonate ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), lead acetate ($(\text{CH}_3\text{COO})_2\text{Pb}\cdot 3\text{H}_2\text{O}$), zirconium acetylacetonate ($(\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3)_4\text{Zr}$), polyvinylpyrrolidone, and 2-methoxyethanol ($\text{CH}_3\text{OC}_2\text{H}_4\text{OH}$) were used to prepare PZT sol–gel solution [18]. Co_3O_4 and Fe_2O_3 were used to prepare CFO powder by a conventional solid state reaction method and finally sintered at $1100\ \text{°C}$. The obtained CFO powder and commercial PZT powder (APC-850) were modified by a high energy ball milling process with proper commercial ESL400 as dispersant. Modified CFO and PZT nanoparticles were finally collected. Subsequently, CFO nanoparticles were dispersed into the collected PZT sol–gel solution with mass ratio ranged from 1/25 to 1/5 to form different CFO/PZT composite slurries. In addition, PZT nanoparticles were also dispersed into PZT sol–gel solution as a mass ratio of 2:3 to get the PZT slurry. Both kinds of slurries and PZT sol were deposited on the Pt/Ti/SiO₂/Si substrate by spin coating technique according to the diagram shown in Fig. 1. PZT sol–gel solution was used as a buffer layer closing to substrate and a cap layer ending the coating process. CFO/PZT slurry layer was deposited in the central part to avoid a possible surface leakage caused by low resistivity of CFO particles [19]. The coating speed and time is 3000 rpm and 30 s, respectively. The resultant films were then annealed at $650\ \text{°C}$ for 1 h in the air atmosphere. According to the different CFO content in PZT matrix, the films were marked as pure PZT, 1/25, 1/20, 1/15, 1/10, and 1/5, numerator and denominator dedicate the mass ratio between CFO modified

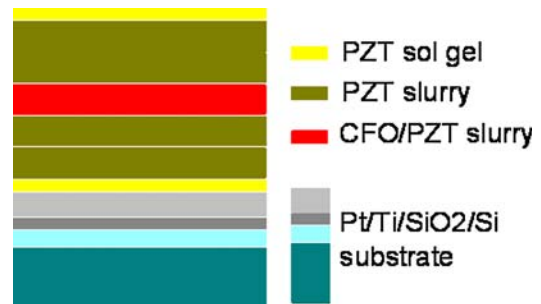


Fig. 1 Diagram of CFO/PZT thick films deposition sequence

particles and PZT sol–gel in the middle layer of Fig. 1. Furthermore, the thicknesses were measured via a surface profiler as 7.2, 6.9, 6.8, 6.8, 6.6, and $6.2\ \mu\text{m}$.

Phase structures were evaluated using an X-ray diffractometer (2400, Rigaku, CuK_α radiation). Cross-sections and surface morphologies of the thick films were observed with an FE-SEM (6340F). Magnetic behavior was detected by a Lakeshore Vibration Sample Magnetometer (7404). After deposition of gold top electrodes with the size of $0.5 \times 0.5\ \text{mm}^2$ on the surface of thick films using E-beam, ferroelectric hysteresis loops and leakage current were measured using a Precision Pro ferroelectric analyzer (Radiant Technologies Inc., USA) with high voltage interfaces. The applied voltage is triangle waveform and the frequency is 100 Hz for P–E hysteresis measurement. The measuring time, soak time, and step delay were all selected as 500 ms during I–V test.

Results and discussion

X-ray diffraction results can be seen in Fig. 2. PZT perovskite phase was obviously observed, but there is no

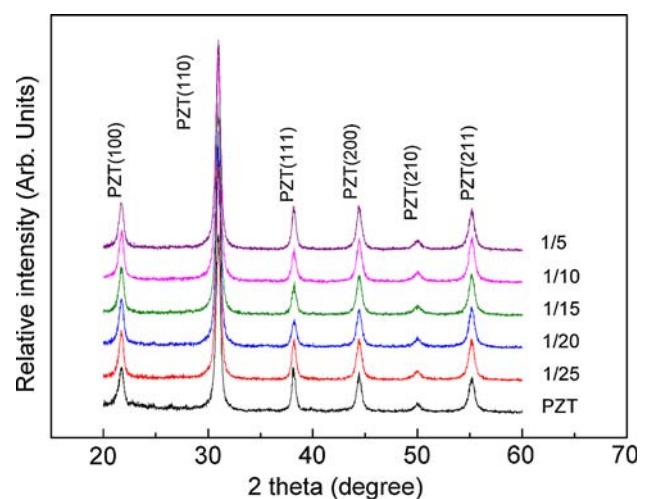
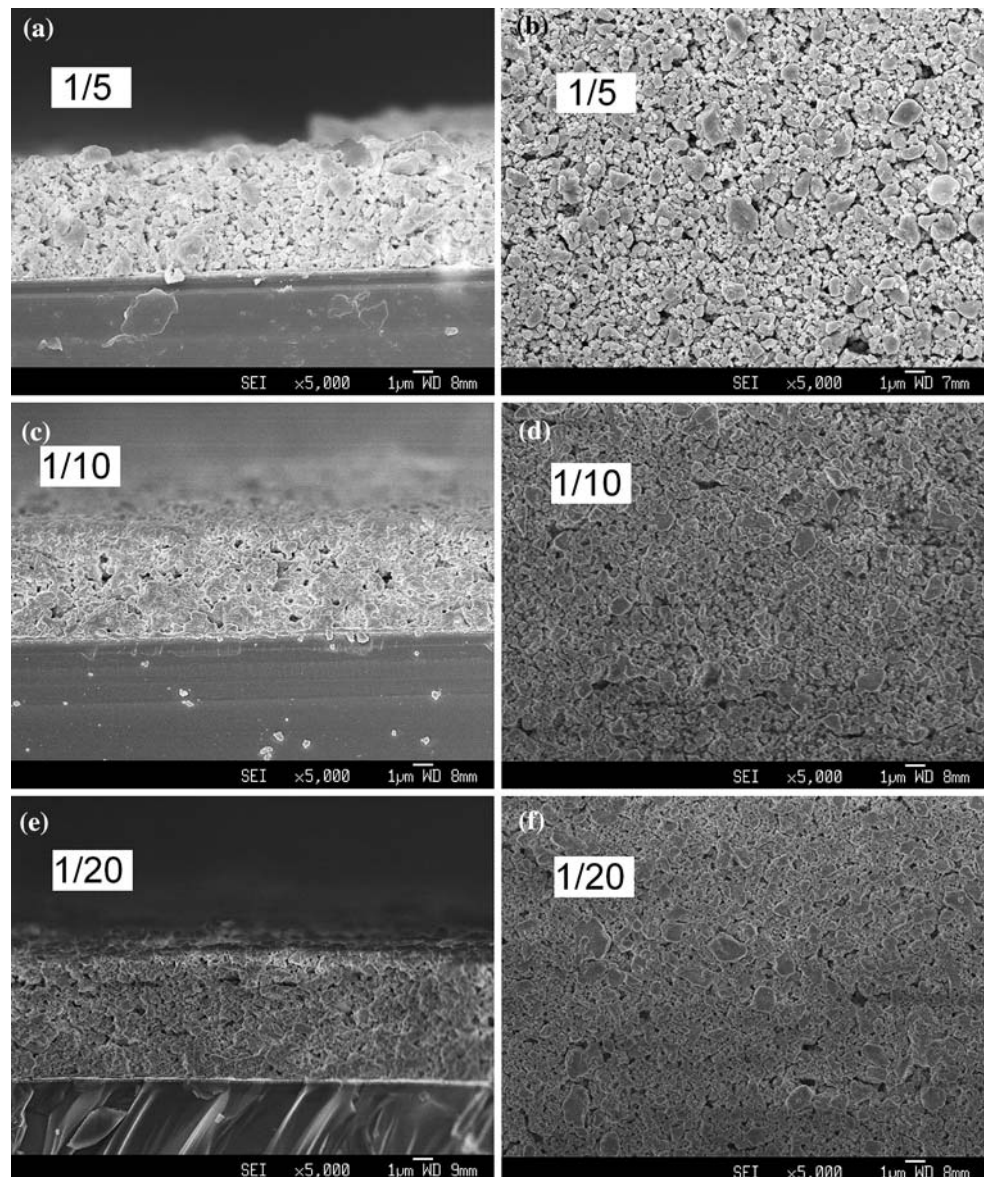


Fig. 2 XRD patterns of CFO/PZT composite thick films

Fig. 3 SEM morphologies and cross-sectional micrographs of typical CFO/PZT composite thick films



CFO spinel phase (magnetic behavior discussed below demonstrated the existence of CFO phase), indicating a deeply buried distribution of CFO in the PZT matrix.

The typical cross-sectional pictures and topographies of multiferroic films are shown in Fig. 3. Because the CFO content in the composites was not large and the top coated layers were constituted by PZT slurry and its sol, so it was reasonable to observe that all the films showed a similar surface morphology. Furthermore, the crack-free surface was attributed to the effect of PVP on the composite thick films due to its increasing structural relaxation of thick films through the retardation of the condensation reaction. On the other hand, the film thickness exhibited a slight decrease with increasing the mass fraction of CFO for

multiferroic composites, indicating the effect of CFO composition on the multiferroic film thickness.

Magnetic hysteresis loops were measured along in-plane direction at room temperature. It can be seen in Fig. 4a, the maximum external magnetic field is 11 kOe. It is clearly seen that saturated magnetization (M_s) is proportional with the magnetic content. As we know, the magnetic behavior in the multiferroic thick films is totally coming from the contribution of CFO particles. When CFO particles are increased from film 1/25 to the film 1/5, the M_s of multiferroic thick films is naturally increasing monotonously. It is known that pure CFO thin film has a M_s value of 320 emu/cc at room temperature [20]. Whereas the M_s value is mainly determined by the CFO content, therefore,

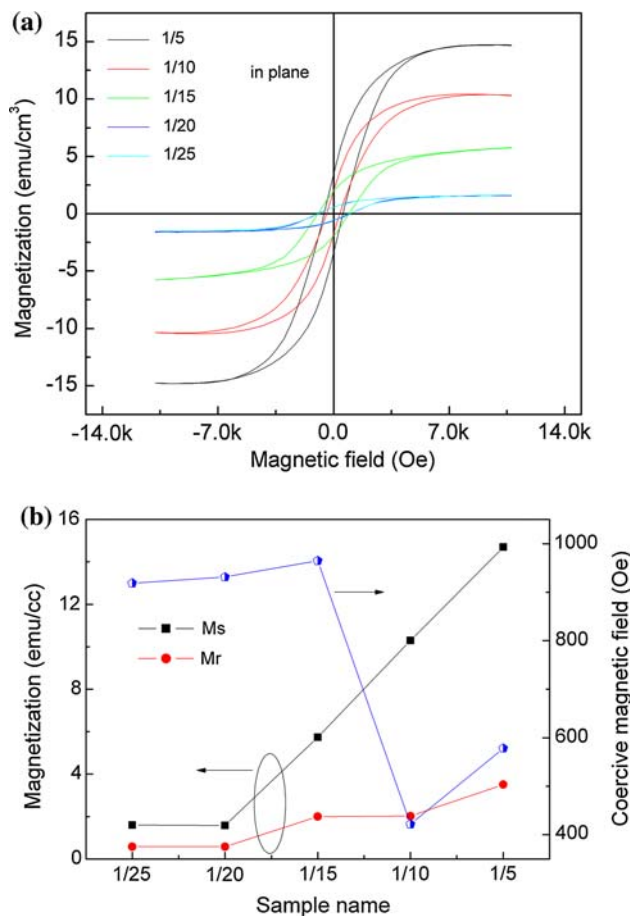


Fig. 4 Room temperature magnetic hysteresis loops of CFO/PZT composite thick films (a), and their magnetic parameters (b)

the mass fraction of CFO in PZT matrix could be roughly estimated as 4.58, 3.23, 1.8, 0.49, and 0.36% for the thick films from 1/5 to 1/25 by dividing the M_s of pure CFO film using measured M_s value in multiferroic films. In addition, remanent magnetization (M_r) value also shows an increase trend with increasing CFO ratio. However, their increased step is more moderate due to the small M_r values in the composite thick films, as can be seen in Fig. 4b. In addition, the coercive magnetic field (H_c) values below 1.8% of CFO content remain similar, which may be attributed to their extremely low mass fractions in the PZT matrix. With the low CFO content, the H_c values would be easier to be affected by the sample holder or other measured environments, causing the possible error in obtaining real H_c values. That is also why these H_c values are even larger than those of 1/10 and 1/5. It is known that H_c value expresses the magnetic domain wall and domain rotation. Larger domains in the composites will bring with a larger H_c value due to its more difficulty to be activated. It is also why the value of 1/5 is larger than that of 1/10 due to its large CFO content.

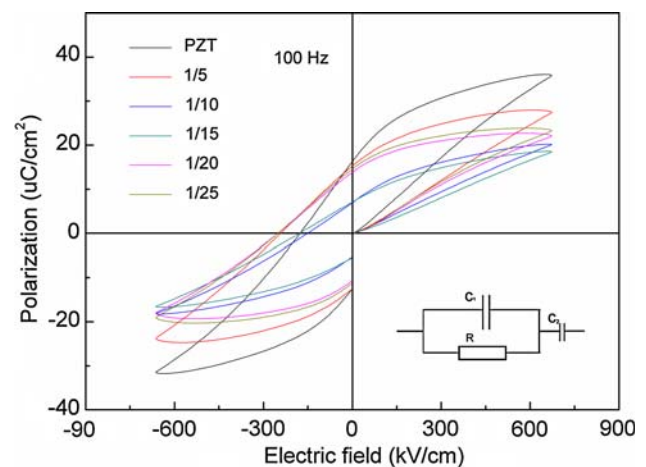


Fig. 5 Room temperature ferroelectric hysteresis loops of CFO/PZT under 100 Hz, equivalent circuit is shown in inset

Figure 5 shows the ferroelectric P–E curves of all multiferroic thick films and pure PZT thick film at room temperature and under 100 Hz. All the thick films show a normal hysteresis behavior. Saturated polarization (P_s) and remanent polarization (P_r) were decreased with increasing CFO content to 1.8%, and then increased as the CFO content further increased to 4.58%. The initial decrease of P_s and P_r was attributed to the dilute influence of CFO on PZT thick films, as reported in CFO/PZT thin films [15]. On the other hand, it is known that CFO ferrite particle has a low resistivity [19], more CFO particles bring with a large conductivity to the multiferroic thick films. In the circuit way, just like the capacitance (PZT) is parallel connected an electric resistivity (CFO), and then series connected a capacitance again, as seen in the inset of Fig. 5. When an alternate voltage was applied, not only switched charge caused polarization in the capacitance part, but also the charges passing through the electric conductivity partially contributed to the overall polarization as a leaky one. As shown in Fig. 5, with the further increase of CFO content, both of polarization values show some larger values.

In order to demonstrate it, leakage current density of CFO/PZT composite thick films is shown in Fig. 6. Compared with pure PZT thick films, the leakage current in multiferroic thick films is becoming large gradually with increasing CFO content and they are also ascending rapidly with increasing electric field. It is corresponding to the leakage-capacitance structure mentioned above. However, the average leakage values are below 10^{-5} A/cm² before the applied electric field of 500 kV/cm. Normally, the larger leakage currents in CFO/PZT thick films often mainly results from two aspects: one is the mixed valence for the magnetic ions (e.g., Fe²⁺ and Fe³⁺), from oxygen vacancies, or from both. Hence it is reasonable to see the

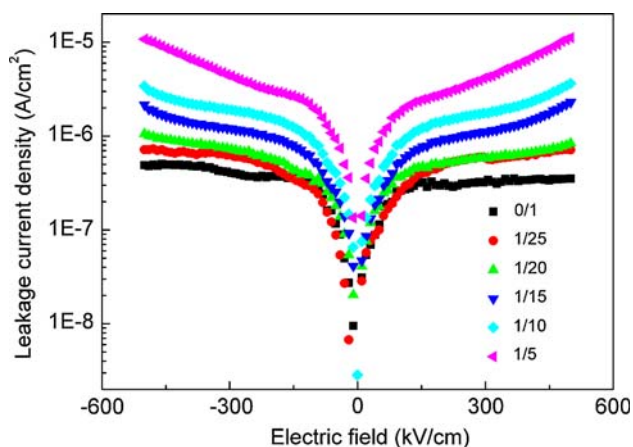


Fig. 6 Leakage current densities of CFO/PZT composite thick films at room temperature

more CFO content brings with larger leakage in multiferroic films. The other is due to the air porosity existed in the thick films, which is also the main source for leakage in PZT thick films compared with denser PZT single crystal [21]. Large leakage current usually leads to a pseudo-hysteresis loop, such as the one observed in BiFeO₃ [22], and even the low electric field endurance [23]. Hence, controlling the leakage in an acceptable value is also promising the real ferroelectric hysteresis loop other than the conductivity of loss.

From the results above, we can see that ferromagnetic and ferroelectric properties have been observed simultaneously in all multiferroic thick films. The influence of CFO content on ferromagnetic and ferroelectric properties could be separated into two parts: below 1.8% of CFO content, M_s and M_r values are not large, which are hence bringing with less leaky contribution to the ferroelectric behavior, the decreased polarization should be attributed to the dilution of CFO content. On the other hand, when the CFO content is reaching 3.23% or more, the M_s and M_r are further increased. Meanwhile, large CFO content also enhances the leaky contribution to the ferroelectric behavior, causing a larger P_s and P_r value. Gradually increasing leakage current densities demonstrate this point. Finally, a critical CFO content of 1.8% is observed where the ferroelectric behavior bears less disturbance of leakage, along with its ferromagnetic behavior and dense microstructure, a magnetoelectric coupling effect should be predicted, which could be a candidate in the multifunctional devices design.

Conclusion

Crack-free CFO/PZT multiferroic composite thick films (above 5 μm) with CFO content ranging from 0.36% to

4.58% have been successfully deposited onto Pt/Ti/SiO₂/Si substrate by a sol-gel processing assisted by PVP. Single PZT perovskite phase was observed from X-ray diffraction, and the lack of spinel CFO phase was attributed to its deeply buried in the central part of PZT matrix. Ferromagnetic and ferroelectric properties were obtained simultaneously at room temperature which strongly dependent on the CFO content. With proper CFO content of 1.8%, a magnetoelectric coupling effect in this thick film could be predicted based on its dense microstructure, which would be a potential candidate in multifunctional devices.

Acknowledgments This work was supported by the tier-2 research grant of ARC 04/06 funded by Ministry of Education, Singapore.

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