

# Effect of $\text{CoFe}_2\text{O}_4$ content on the dielectric and magnetoelectric properties in $\text{Pb}(\text{ZrTi})\text{O}_3/\text{CoFe}_2\text{O}_4$ composite

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**Abstract** Ferroelectric  $\text{Pb}(\text{Zr}_{0.53}\text{Zr}_{0.47})\text{O}_3$  (PZT) and ferromagnetic  $\text{CoFe}_2\text{O}_4$  (CFO) composite ceramics,  $[(1-x)\text{PZT}-x\text{CFO}]$  for  $x=10, 20, 30, 40$  and  $50$  wt.%, were prepared by a conventional solid-state reaction method. X-ray diffraction studies revealed that only PZT and CFO phases were present in the composite samples and no other phase was detected. The 0.9PZT-0.1CFO composite ceramic displayed better piezoelectric properties. The piezoelectric resonance frequency increased with the CFO content, but the resonance peak attenuated rapidly and disappeared when the CFO content equaled to 0.5. The permittivity peak temperature was the same as that of pure PZT ceramics. 0.9PZT-0.1CFO composite also had the highest magnetoelectric (ME) coupling coefficient among the studied PZT-CFO composite ceramics. The ME coefficient linearly increased with ac frequency up to 100 kHz.

**Keywords** Composite · Dielectric · Piezoelectric · Magnetoelectric properties

## 1 Introduction

The detailed illustrations on the coupling effect between two physical parameters in materials may be dated back to

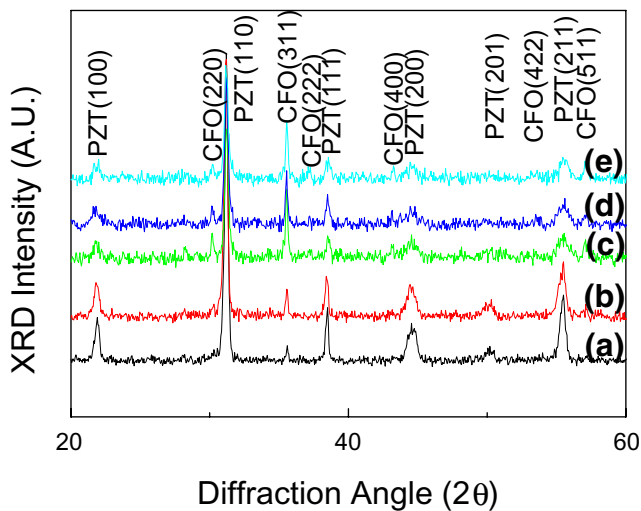
the 1980s when Newnham proposed ten connectivity patterns in the composites [1]. Magnetoelectric (ME) effect is one of them referring to the appearance of an electric polarization upon applying a magnetic field and/or the appearance of magnetization upon applying an electric field. Recently, the discoveries on the high piezoelectric constant in PMN-PT single crystals and nanostructured materials that enhance the ME effect significantly make the ME effect very promising for applications in current and magnetic sensors, magnetic-electric transformers [2–6]. Basically most of the investigations concentrate on the bulk materials where long-range interaction plays an important role in generating high ME effect, such as the 1–3 and 2–2 laminates [3]. The 0–3 composite for such objective is still a challenge. The main reason is the multiphase structure of the composite which results in the cancellation of magnetostriction in magnetic phase and the block of piezoelectric response in piezoelectric phase. In this work,  $\text{Pb}(\text{Zr}_{0.53}\text{Zr}_{0.47})\text{O}_3$  (PZT)/ $\text{CoFe}_2\text{O}_4$  (CFO) composites containing 10–50% CFO were prepared using conventional solid state reaction process, and structural, dielectric, piezoelectric and magneto-electric properties were investigated in order to obtain high ME coefficient in the composites.

## 2 Experimental procedure

The CFO crystalline powders were firstly prepared using  $\text{Co}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  as raw materials. After weighing, the batch materials were wet ball milled for 12 h. Then the powders were calcined at 900 °C for 1 h. PZT powders were commercial PKI552 (Piezo Kinetics Inc. USA). The crystalline powders were weighed according to the formula of  $(1-x)\text{PZT}-x\text{CFO}$  ( $x=10, 20, 30, 40$  and  $50$  wt.%), and

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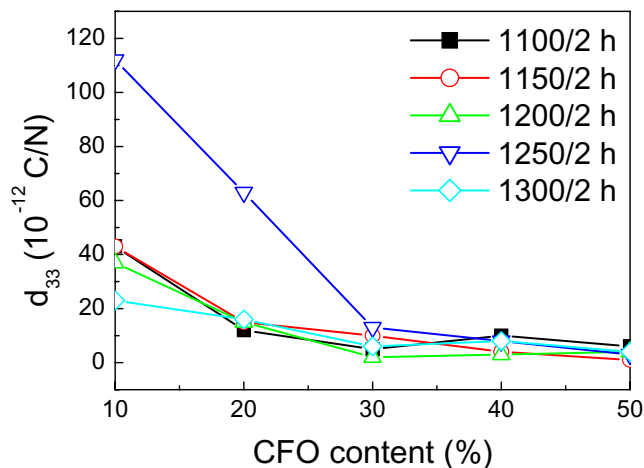
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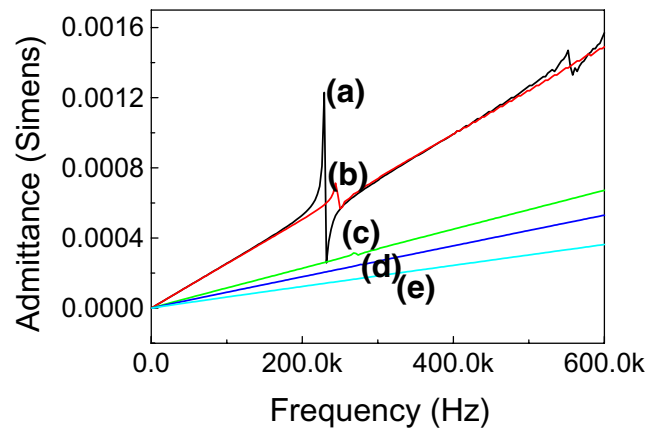
**Fig. 1** XRD patterns of CFO/PZT composites sintered at 1250°C for 2 h; a–e, CFO=10–50 wt.%

wet ball milled, dried, and pressed into discs under a pressure of 1,000 kg/cm<sup>2</sup>. The different sintering temperatures ranged from 1100, 1150, 1200, 1250 to 1300 °C were used to study the effect of sintering temperature on the properties of the composites. The final discs had a black color. The samples were electrically poled in a silicon oil bath at an electric field of 30 kV/cm during cooling from 100 °C to room temperature.

The crystallographic phases of the composites were determined by x-ray diffraction (XRD). The dielectric and piezoelectric properties were measured using a HP4284A Precision LCR Meter with a Delta 9023 chamber, Agilent 4294A Precision Impedance Analyzer and  $d_{33}$  meter (Radiant Technologies), respectively. For the ME measurement, an electromagnet, equipped with water-cooled solenoids, was used and it can generate a direct current (dc) magnetic bias  $H_{\text{bias}}$  up to 3 kOe. A pair of Helmholtz coils were used to produce an alternative current (ac) magnetic field  $H_{\text{ac}}$  of 6 Oe, which was superimposed on  $H_{\text{bias}}$ . The



**Fig. 2**  $d_{33}$  as a function of CFO content



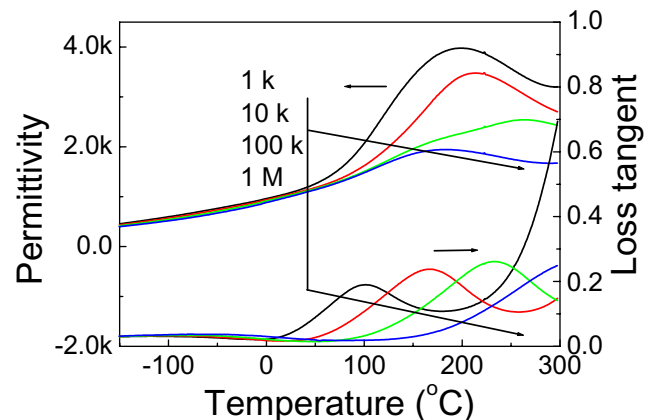
**Fig. 3** Admittance as a function of frequency. a–e, CFO=10–50 wt.%

sample was placed at the center of small Helmholtz coils. The Helmholtz coils were driven by a signal generator (HP 33120A) via a power amplifier (Sorensen DHP Series), monitored by an oscilloscope (HP 54522A). The magnetic field was measured using a Hall-effect probe situated adjacent to the sample and connected to a Gaussmeter (Model 7030, Gausee/Teslameter, SYPRIS). The ME coefficient was determined under an open-circuit condition, using a network analyzer (Multi-Purpose FFT Analyzer, CF-5220, ONOSOKKI).

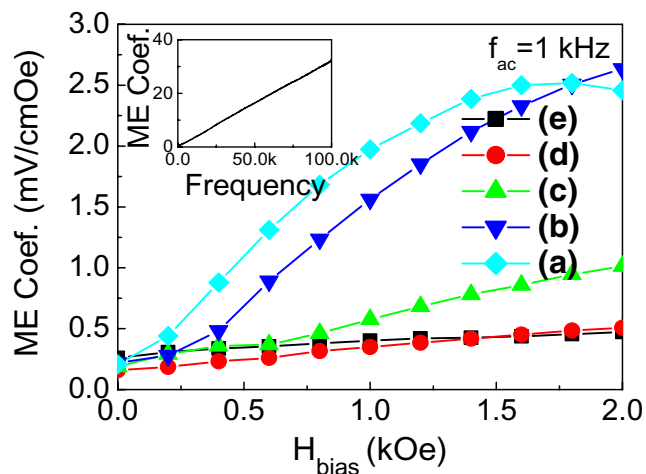
### 3 Results and discussion

Figure 1 shows the XRD patterns of CFO/PZT composites. It can be seen that only two phases, spinel CFO and perovskite PZT, exist in the composite. No chemical reaction products between the CFO and PZT were detected by XRD. The intensity of diffraction peaks of CFO increases with increasing CFO content.

Figure 2 shows  $d_{33}$  as a function of CFO content for composites sintered at temperatures ranging from 1100 to 1300 °C. For all samples, the composites sintered at 1250 °C



**Fig. 4** Relative permittivity and loss tangent as a function of temperature and frequency for sample 1250-1



**Fig. 5** ME coefficient at 1 kHz as a function of dc bias. *Inset* is the ME coefficient as a function of ac frequency. *a–e*, CFO=10–50 wt.%

show the highest  $d_{33}$  values. While for different compositions sintered at the same temperature, the composite with 10 wt.% CFO reveals the highest  $d_{33}$  value. Because of the semiconducting property of ferrite CFO, the samples with a high CFO content could not be effectively poled and thus  $d_{33}$  was found to be quite small. The results indicate that the piezoelectric constant of the composites dramatically reduces with increasing CFO content.

Figure 3 shows the admittance as a function of frequency for the composites sintered at 1250 °C for 2 h. One can see that the resonance frequency  $f_s$  increases with increasing CFO content since the capacitance of the composite decreases with increasing CFO content. Sample (d) has a recognizable resonance peak, but sample (e) does not show any resonance peak at all.

The relative permittivity and loss tangent as a function of temperature and frequency for sample 1250-1 (sintered at 1250 °C, containing 10 wt.% CFO) are shown in Fig. 4. The Curie temperature for PZT and CFO are 200 and 520 °C [7], respectively. The Curie temperature of the sample 1250-1 is the same as that of PK1552 ceramic, viz. 200 °C at 1 kHz, and the relative permittivity value at 25 °C greatly reduces from 3,400 for pure PZT ceramic to 470 for the composite containing 10 wt.% CFO. The peak width of the composite 1250-1 increases considerably. The peak temperature increases with increasing frequency, exhibiting some relaxor-like ferroelectric properties [8]. An additional peak is clearly observed at 182 °C at 1 MHz. This peak is similar to the kink occurred in the permittivity—temperature characteristics of pure PZT ceramics [7].

Figure 5 shows the ME coefficient at 1 kHz as a function of dc magnetic bias. *Inset* is the ME coefficient as a function of ac frequency. For all samples, the ME coefficients increase with increasing dc bias. This means that the dc bias induced alignment of magnetic domains may increase the coupling between the magnetostriction in CFO and the piezoelectric response in PZT. On the other hand, the  $d_{33}$  value has an important effect on the ME coefficient. The higher the  $d_{33}$ , the larger the ME coefficient. Moreover, the ac frequency also has a crucial impact on the ME coefficient. Especially, the ME coefficient will reach its maximum value at its piezoelectric resonance frequency. Here, the piezoelectric resonance frequency is about 230 kHz, the ME coefficient was found linearly increasing with the frequency up to 100 kHz. At 100 kHz, the maximum value of ME coefficient is 32 mV/cm-Oe, ten times larger than that obtained at 1 kHz for a dc bias of 2 kOe. It is expected that the ME coefficient value will be larger at its piezoelectric resonance frequency.

#### 4 Conclusions

Ferroelectric PZT and ferromagnetic CFO composite ceramics were prepared via a conventional solid-state reaction method. The 0.9PZT-0.1CFO composite ceramic exhibited better piezoelectric and ME properties than other samples. The maximum non-resonant ME coefficient is 32 mV/cm-Oe at 100 kHz, ten times larger than that obtained at 1 kHz for a dc bias of 2 kOe.

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