A comparative study on the structural, dielectric, ferroelectric and magnetic properties of CoFe$_2$O$_4$/PbZr$_{0.52}$Ti$_{0.48}$O$_3$ multiferroic composite with different molar ratios

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Abstract

Magnetoelectric composites have attracted much attention due to their excellent multiferroic properties at room temperature. In this paper, CoFe$_2$O$_4$-PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (CFO-PZT) composite ceramics with different molar ratios (CFO/PZT = 1:4, 1:5, 1:6 and 1:7) were prepared by conventional solid reaction method. Effects of molar ratio on the structure, dielectric, ferroelectric and magnetic properties were comparatively investigated. X-ray diffraction patterns confirmed biphasic structures of the composites, which can be indexed as CFO and PZT, no other obvious phase could be found with the limitation of the XRD resolution. Scanning electron microscopy (SEM) images show that the surface of the prepared samples is not dense enough and many pores are formed, the mean grain size is about 200 nm. The same relaxation behavior was observed in the intermediate temperature range of PZT-CFO composite ceramics. At room temperature, the dielectric constant and dielectric loss of the specimen 1:4 are the highest. The leakage current of the sample 1:4 is the lowest while the sample 1:6 has the largest value. As the CFO content in the composite decreases, both the saturation ($M_s$) and remnant ($M_r$) magnetization decrease. Among them, the sample 1:4 presents better ferroelectric and magnetic properties, the remnant polarization is 1.13 $\mu$C cm$^{-2}$, the saturation magnetization and remnant magnetization are 11.01 and 3.28 emu g$^{-1}$, respectively. The sample 1:6 has the largest coercive field (945.27 Oe) while the sample 1:7 show the smallest value (681.19 Oe). Interface interaction between CFO/PZT may be applied to explain this phenomenon.

1. Introduction

Multiferroic material is a novel multi-functional material which couples electrical, magnetic and structural ordering parameters, and thus produces ferroelectric, ferromagnetic and ferroelastic effects [1–5]. Especially, the magnetoelectric (ME) effect has become a hot topic in recent years due to its intriguing physical properties and practical applications in various of device such as super capacitor, spintronic devices, information storage, sensors, transistors and so on [6–10]. Actually, from a practical application perspective, strong ME effect of multiferroic is the foundation for the application of device. However, the ME effect is usually very weak at room temperature in single phase multiferroic materials mostly because the Curie temperature is below room temperature, therefore they can only show multiferroic properties below room temperature. Although very few single phase multiferroics can present higher Curie temperature than 300 K, the ME effect is still very weak. One typical example is BiFeO$_3$ (BFO), which has high Curie temperature ($T_C \sim$ 1100 K), Neel temperature ($T_N \sim$ 640 K) and high remnant polarization ($P_r \sim$ 100 $\mu$C cm$^{-2}$) [11–15]. However, the magnetization is very weak due to the G-type antiferromagnetic order, inhibiting the observation of strong ME effect. In addition, the
leakage current of BFO is serious because of the existence of defect, impurity, and the volatilization of Bi element at high temperature in the preparing process. The high leakage current density can prevent the observation and acquisition of high polarization because it is impossible to apply strong electric field to this material.

Fortunately, this limitation of ME effect in single phase multiferroics is absent in composite multiferroics. By combining a ferroelectric phase with ferromagnetic, composite multiferroic material has strong magnetoelectric coupling effect at room temperature [16–21]. The magnetoelectric coupling effect of composite is considered to be the piezoelectric effect of the ferroelectric phase and the magnetostRICTive effect of the ferromagnetic phase. In order to achieve strong magnetoelectric coupling effect, it is necessary to improve the magnetic properties under the action of an electric/magnetic field. It has been found that by adjusting the composition of the composite material, the magnetic/ferroelectric properties can be effectively adjusted to improve the magnetoelectric coupling coefficient [22–28]. Till now, several composite materials have been studied, including Co0.5Ni0.5Fe2O4/Ba0.8Sr0.2TiO3 [29], (Ni, Zn)Fe2O4–BaTiO3 [30], Co0.8Cu0.2Fe2O4–xBa0.6Sr0.4TiO3 [31], NiO.3CuO.7Fe2O4/BaTiO3 [32], PZT/CFO [33], and NiFe2O4–BaTiO3 [34]. Among them, CoFe2O4(CFO) is the most studied magnetic material in the magnetoelectric composites due to its good magnetization, large magnetostriiction coefficient and chemical stability. In addition, PbZr0.52Ti0.48O3 (PZT) was usually selected as the ferroelectric phase in composite multiferroics materials because it is presents high piezoelectric coefficients and low dielectric loss. In addition to the intrinsic properties of the magnetic and ferroelectric phase in the composite, the relative content of the two phases plays key role in determining the coupling effect. Although some previous works have been carried out to investigate the multiferroic properties of CFO-PZT films and ceramics, there are few works aim to study effect of low concentration of CFO on the structure and properties especially prepared by conventional solid reaction method. In the current work, CoFe2O4–PbZr0.52Ti0.48O3 (CFO-PZT) composite ceramics were prepared by traditional solid reaction method, and the effects of molar ratio between CoFe2O4–PbZr0.52Ti0.48O3 on the microstructure, dielectric properties and multiferroic properties were investigated.

2. Experimental procedures

2.1. Samples preparation

All chemical reagents used in this study were purchased from Sinopharm Chemical Regent Beijing Co., Ltd, including ZrO2 (≥99.8%), TiO2 (≥98.5%), PbO (≥99.8%), Co2O3 (≥99.9%), and Fe2O3 (≥98.5%). All of these reagents are used without further purification.

CFO magnetic particles were prepared by solid state reaction method. The starting materials were weighted according to stoichiometry and then mixed and ball milled for 8 h. After obtained slurry drying, the mixtures were calcined at 500 °C for 4 h, and then the calcined powders were mixed again for 12 h and then dried at 120 °C.

Similarly, PZT particles were prepared by solid state reaction method. PbO, ZrO2 and TiO2 powders with the molar ratio of 1: 0.52: 0.48 were weighted and mixed with distilled water and then ball milled for 8 h by the planetary ball mill (XQM-4, Tencan powder Co., Ltd, China). After the obtained slurries dried at 120 °C for 24 h, the mixture was fired at 500 °C for 8 h in a chamber furnace (KBF1700, Nanjing Nanda instrument plant, China), and then the calcined powders were milled again for 12 h and then dried at 120 °C.

To prepare CFO-PZT composite ceramics, CFO and PZT particles with the molar ratios of 1:4, 1:5, 1:6 and 1:7 were mixed and then milled for 8 h, subsequently the mixtures were dried at 120 °C. After that, the powder mixtures were pressed at 12 MPa into pellets with the size of 10 mm diameter and 1 mm thickness using liquid paraffin as a binder. After liquid paraffin was burnt off at 500 °C, the samples were sintered at 900 °C for 4 h. For the measurement of electric properties, two sides of the sintered samples were polished and pasted with conductive silver paste, then burnt at 500 °C for 30 min and cooled naturally to room temperature to form effective electrical contact.

2.2. Samples characterization

The crystal structure of the CFO-PZT composite ceramics was determined by x-ray diffraction (XRD, Rigaku D/max2400) using Cu (Kα) radiation source (λ = 1.5406 Å) in the 2θ range of 20°–80° with the sweeping speed of 0.05°/s. The morphology of the prepared samples was determined by the field emission scanning electron microscopy (SEM) (S-3700N, Hitachi, Japan). Room temperature magnetic properties were carried out on a MPMS SQUID VSM dc Magnetometer (Quantum Design). FE hysteresis loops were characterized by using a FE test unit (TF2000, aix-ACCT Inc., Germany). The frequency and temperature dependence of dielectric constant and loss were investigated in the frequency range of 20Hz–2 MHz by using impedance analyzer (E4980A, Agilent, USA). The relative dielectric constant (εr) was calculated from the capacitance by using the following equation:

\[
\text{εr} = \frac{C}{\varepsilon_0 \frac{A}{d}}
\]
where \( C \) is the capacitance (F), \( d \) is the thickness (m) of the samples, \( \varepsilon_0 \) is the vacuum dielectric constant \((8.85 \times 10^{-12} \text{ F m}^{-1})\) and \( S \) is the effective electrode area on the samples.

3. Results and discussion

3.1. Crystal structure

Figure 1 shows the XRD patterns of CFO, PZT and CFO-PZT composite ceramics with different molar ratios at room temperature. The diffraction peaks can be indexed as CoFe\(_2\)O\(_4\) (JPCDS No-01-079-1744) and PbZr\(_{0.52}\)Ti\(_{0.48}\)O\(_3\) (No. 07-070-4058). In the XRD patterns, it is found that in addition to the above crystal structure, no peak of other crystal symmetry is traced. This indicates that there is no reaction between the ferroelectric phase and the ferromagnetic phase, no any atom of the two phase diffuses into another, and the two phases are independent.

Figure 2 shows the enlarged part of the main peaks of PZT and CFO shown in figure 1. It is observed that the angle of (110) diffraction peaks of PZT maintain the same value, indicating that the lattice strain is near the same of all the specimens. Although a deviation of 0.02° of the angle of (113) diffraction peaks of CFO is observed in the sample with the molar ratio of 1:5, the slight difference may be caused by error, which was induced by measuring instrument. Moreover, the diffraction peak intensity of CFO is reduced with the decrease of molar ratio, which can be ascribed to the decreased relative content of CFO in the composites.
3.2. Surface morphology

In order to investigate the structure, the pellets of CFO-PZT were recorded, as shown in figure 3. It can be seen from figure 3 that the grains are sphere-like, the average grain size is about 200 nm, but there are some pores on the surface. There are several reasons for forming these pores. For one hand, the pressure is not high enough, resulting the loose crumb structure. For another hand, the liquid paraffin is insufficiently burnt at the high temperature of 500 °C if the heating rate is too fast, thus some paraffin may be burnt at higher sintering temperature 900 °C. At this time, many gas can be formed and thus pores are formed in the preparing process. Another factor that can affect the pore formation is the grain boundaries between the two phases. As it mentioned above that there is not any obvious chemical reaction between the two phases, thus there should be many grain boundaries existed in the composites, and these grain boundaries can inhibit the grain growth of the two materials. As it can be seen that the grain size is small. As a result, more boundaries and pores are increased. This result indicates that the addition of PZT in to CFO or to say the addition of CFO in to PZT can refine the crystalline structure.

Furthermore, it was found that when the molar ratio is 1:4, the particles are uniform, while the other samples show some cracks on the surface. Figure 3(a) shows that the ferromagnetic phase is almost completely surrounded by the ferroelectric phase in the red circle. It is noticed that the ferromagnetic phase exhibits a distinct spinel structure without surrounded by PZT absolutely in figure 3(d). Moreover, it is found that when the molar ratio is larger than 1:4, the grains appear to be adsorbed on the entire surface. It can be seen that the cracks on the surface are obvious, and the ferromagnetic phase is also the most exposed. This may be that the content of CFO in the sample 1:7 is smaller than other specimens.

In order to characterize the distribution of the two phases in the composites, EDS spectrums of the sample 1:5 was applied, as shown in figure 4. Table 1 is the mass percentage and atomic percentage of the surface energy spectrum. Although the molar ratio of the elements is not consistent with the chemical equivalent, but it can be concluded that the ceramic consists of CFO and PZT, indicating a magnetoelectric composite structure. The deviation of content from the theoretical value may be ascribed to the small sweeping area. Figure 5 shows the mean grain size of PZT as a function of mola ratio in the composites, it found that the mean grain size decreases with increasing the concentration of PZT in the composites, i.e., with decreasing the mola ratio. These results

![Figure 3. SEM images of CFO–PZT ceramics with different ratios: (a) 1:4, (b) 1:5, (c) 1:6, (d) 1:7.](image-url)
indicate that content of CFO in the composites plays important role in determining the grain size of PZT in CFO-PZT magnetoielectric composites.

3.3. Dielectric properties

Figure 6 illustrates frequency dependent dielectric constant and loss of CFO-PZT composites with the frequency ranges from 20 Hz to 2 MHz. There are several points should be addressed. First of all, the dielectric constant decreases monotonically with decreasing the molar ratio, i.e., the decrease of CFO content. The reason is that the conductivity of CFO is better than that of PZT, thus the carriers in CFO far larger than that in PZT. These carriers can generate polarization under the action of applied electric field. Secondly, the dielectric constant of all the specimens decreases with increasing the frequency, this behavior can be attributed to the polarization mechanisms. It is well known that the polarization mechanism includes displacement polarization, space charge polarization, turning-direction polarization, interface polarization and so forth. Among them, the polarization time of displacement polarization is so short (usually less than 1 ns) that it can be completely generated in all the frequency range (the maximal frequency is only 2 MHz in this experiment). As a consequence, the polarization can contribute to the dielectric constant in the range of whole frequency. In contrast, the relaxation time (including space charge polarization, turning-direction polarization, etc) is relatively longer, which usually ranges from microsecond to several seconds. Therefore, all the polarization can be formed in the low frequency range and larger dielectric constant can be observed because all the polarization contributes to it. However, with the increase of frequency, more and more polarization has been unable to keep pace with the frequency, and thus the polarization is increased, which in turn result in reducing the dielectric constant. Finally, it can be found
from figure 6(a) that although the dielectric constant of all the samples decreases with the frequency, the sample for the molar ratio 1:7 shows the best frequency stability of dielectric constant. As it was discussed above that the decrease of dielectric constant with frequency is ascribed to the relaxation polarization, therefore, less relaxation polarization should be in the sample (1:7) than other samples. So, the relaxation polarization should be induced by the CFO phase, of which there are many carriers, such as electrons. The electrons can accumulate at the grain boundaries if the resistance of the grain boundaries is high enough. Under the action of electric field with low frequency, the electrons can move back and forth with the electric field, which is equivalent to polarization. When the frequency of the applied field is high, the movement of electrons can’t keep pace with the field and thus weak polarization is reduced.

It is found from figure 6(b) that the dielectric loss (tan δ) presents similar behavior to that of dielectric constant. It decreases abruptly in the low frequency while it tends to be stable under high frequency. Moreover, the loss decreases with decreasing the molar ratio, the maximum value (∼14.5 at 20 Hz) is obtained in the sample when the molar ratio is 1:4, while the specimen (1:7) has the minimal loss (less than 1 at 20 Hz). When the frequency is larger than 0.1 MHz, the loss of all the samples is reduced to less than 1. By comparing figure 6(a) with figure 6(b), it can be concluded that for one hand, the decrease of loss with frequency may be induced by the conduction loss, the loss (Joule heat) should decrease with increasing the test frequency. When the frequency is high enough, other loss, such as relaxation loss, plays a major role in the loss. Furthermore, the decrease of loss with reducing the molar ratio can also attributed to the conductive loss, which was mainly due to by the addition of conductive component (CFO) of the conductivity increase of the current system, which led to increase the conductivity.

In addition to the frequency, temperature is another factor that can affect the polarization process as well as the dielectric properties. Temperature dependence of dielectric constant of the samples measured with different frequency is shown in figure 7. It is found that the dielectric constant increase with the rise of temperature on the whole, but all the composites show a relaxation peak in the $\varepsilon_r \sim T$ curves. This peak is related with the phase transition temperature of PZT [33], which has been tuned by the addition of CFO due to the interface interation. The increase of dielectric constant with temperature is the result of increased conduction electrons, which increases with the temperature increasing because more electrons can transfer form valance band to conductive band due to thermal activation. These conduction electrons can accumulate at the grain boundary if the resistance of the grain boundary is high enough. At low frequency, these electrons can move back and forth under the action of applied field, forming polarization and thus increasing the dielectric constant. With the increase of temperature, more and more electrons can be motivated and then jump from valance band to conductive band, therefore larger dielectric constant can be found. As a consequence, the dielectric constant increases with temperature in the aggregate. However, with the increase of the test frequency, the electrons can’t keep up with changes in the electric field, polarization is reduced and hence the dielectric constant decrease with the frequency.

While the relaxation peak is the product of the relaxation polarization such as turning-direction polarization. As it can be seen that the peak position shifts to high temperature range with increasing the test frequency. The peak position increases from 300 °C (at 100 Hz) to 400 °C (at 1 MHz), this peak is unlikely the Curie temperature of CFO because of the relaxation characteristics [21, 22].
Temperature dependence of the dielectric loss is shown in figure 8. The dielectric loss decreases as frequency raises while it increases with the rise of temperature. In addition, the abrupt point of dielectric loss moves towards high temperature with the increase of frequency. This is because the polarization relaxation loss is predominant in the low temperature region, while the conductive loss increases exponentially in the high temperature region because the density of carriers increases exponentially with temperature and therefore the conductive loss increases abruptly. When the frequency is very low, the dielectric loss is mainly caused by leakage current, and the polarization relaxation loss is almost negligible. For instance, when the temperature is 400 °C, the dielectric loss of all the specimens at 1000 kHz is less than 1, but this value increased suddenly with the decrease of frequency, the value is larger than 5 at 10 kHz, 50 at 1 kHz and 500 at 100 Hz. With the increase of frequency, the polarization relaxation loss increases and the leakage loss decreases [22–25].

In order to comparatively investigate effect of molar ratio on the dielectric properties, temperature dependents dielectric constant and loss at the same test frequency (10 kHz) are presented in figure 9. Clearly, the positions of the relaxation peak for different samples are near 400 °C, only the sample (1:6) shows slight lower temperature. As the peak is related to relaxation polarization (turning direction polarization) and the phase transition of PZT, the temperature corresponds to the peak is connected with the active energy of the switching process. The peak intensity is affected by the content of relaxation polarization in all the polarization mechanism. As the sample (1:4) has the highest peak, thus the dipoles may be the largest, while the sample (1:5) is the weakest. The relaxation polarization is determined by the microstructure, thus pores, defects, impurities, grain boundaries can affect this relaxation phenomenon. It can be seen from figure 9(b) that at the same temperature (400 °C), the sample with the molar ratio 1:6 has the largest dielectric loss (~6) while the specimen (1:5) presents the smallest one (0.25). As we have discussed above that the serious loss at high temperature is attributed to the conductive loss, therefore the sample (1:4) should shows the largest loss at the same temperature and test frequency because the concentration of CFO in the highest among all the samples. The inconsistent results between the experiment and hypothesis may be that the sample with molar ratio 1:6 may has the most carriers. Impurities and defects can affect the energy band structure, which in turn determine the carrier density at the same temperature. But this can’t be verified from the SEM results and XRD results, maybe further study is needed.
3.4. Ferroelectric properties

Room temperature $P-E$ curves of CFO–PZT ceramics with different molar ratios were measured under different maximum electric fields, as shown in figure 10. Obviously, all samples showed typical hysteresis loops, confirming the ferroelectric properties of the composites. The $P-E$ curves are similar to the reported literature [25, 27]. It can be found that both remnant polarization ($P_r$) and coercive field ($E_c$) for all the specimens increase as the maximum applied electric field increases, which is a normal behavior in almost all ferroelectric materials, and typically manifests as a region switching process. It may be that more domains can be switched when
applying larger field. In general, when the maximal applied field is 55 kV cm$^{-1}$, the value of $P_r$ is about 1 $\mu$C cm$^{-2}$, and $E_c$ is $\sim$20 kV cm$^{-1}$. The sample with the molar ratio of 1:6 shows the largest remnant polarization while the sample (1:7) has the smallest value. Actually, the ferroelectric properties of the CFO-PZT composites are theoretically contributed by the ferroelectric phase PZT because CFO isn’t ferroelectric material, therefore, the polarization should increase with increasing the concentration of PZT, i.e., with the increase of the molar ratio. As a consequence, the sample with the molar ratio of 1:7 should have the largest polarization. The abnormal experimental results may be that these $P$-$E$ curves are affected by the leakage current because the measurement data typically includes the contribution from the conduction current. Larger leakage current can expand the $P$-$E$ curves and thus the polarization and coercive field may be overestimated than the intrinsic values. It is necessary to deduce the contribution of leakage current to the ferroelectric properties.

Since the shape of $P$-$E$ curves are determined by the test frequency, in order to investigate the ferroelectric properties of the prepared ceramics, frequency dependence of $P$-$E$ curves was measured, as shown in figure 11. It is obvious that the loops of all the samples become more and more slim with the increase of test frequency, indicating that the leakage current has distinct effect on the ferroelectric hysteresis loop. It can be known from the measuring principle of the device that the polarization is obtained by the integral over time of the current in the loop, while the current includes three parts: polarizing current, charging and discharging current, and leakage current. Among them, the polarization current is generated by domain switching, and it determines the intrinsic polarization. The charging and discharging current are the result of linear polarization, and leakage current is caused by the conductivity of sample because it is not perfect insulators. Therefore, the charging and discharging current as well as leakage current can enlarge the measured remnant polarization, only the value measured at high frequency is close to the intrinsic value of polarization. It can be seen from figure 11 that when the frequency increases from 0.2 to 2 kHz, the remnant polarization of the sample (1:4) decreases from 2.29 to 1.13 $\mu$C cm$^{-2}$, which has been reduced by 50.65%. When the molar ratio is 1:5, the value of $P_r$ decreases from 1.71 to 0.56 $\mu$C cm$^{-2}$, which is decreased by 67.25%. It decreases from 3.29 to 0.74 $\mu$C cm$^{-2}$, reduced by 77.51% when the molar ratio is 1:6. Corresponding, for the sample with the molar ratio of 1:7, the remnant

![Figure 10. Room temperature $P$-$E$ curves under different maximum fields of CFO–PZT composites with different molar ratios, (a) 1:4, (b) 1:5, (c) 1:6, (d) 1:7.](image)
polarization decreases from 0.83 to 0.45 $\mu$C cm$^{-2}$, reduced by 45.73%. These results indicate that the leakage current of the sample (1:6) plays more important effect on the loops, while the leakage current of the sample (1:7) is the smallest. As a result, the polarization obtained from figure 11 measured at low frequency cannot represent the true ferroelectric properties of the prepared composite ceramics.

Because only the Pr measured at high frequency can express the intrinsic ferroelectric properties of ferroelectric materials, to investigate the effect of molar ratio on the ferroelectric properties of the sample, $P-E$ curves measured at high frequency (2 kHz) are comparatively presented in figure 12(a) and the ferroelectric parameters (Pr and Ec) are listed in table 2. It is observed that the sample (1:4) has the best Pr, while the specimen with the molar ratio 1:7 shows the smallest value. Since the leakage current can affect the measured value, and considering the fact that the polarization should increase with increasing PZT content, the abnormal phenomenon, but in all probability, is resulted by the leakage current. For this, the leakage current density as a function electric field ($J-E$ curves) of the samples were measured, as depicted in figure 12(b). It is noted that the sample with the molar ratio 1:6 shows the largest leakage current, while the sample 1:4 present the smallest value in the positive field range. Therefore, it can be calculated that sample 1:4 shows better ferroelectric properties. This indicates that there is a critical point of the CFO-PZT molar ratio around the ratio of 1:4. Once the CFO-PZT molar ratio exceeds this value, the polarization of the PZT phase is destroyed [25].

Compared with other samples, the sample (1:6) has smaller remnant polarization and larger leakage current. This may be that the surface morphology of the ratio of 1:6 is worse and the density is lower than other samples. And the polarization is higher than the polarization reported in the CFO-PZT core–shell structure [26]. This is because the enhanced polarization in the core–shell composite can be attributed to the large leakage current density caused by the space charge effect [28, 29]. In addition to the sample (1:6), the coercive field of other proportions of ceramics decreases as the FE phase increases. The result may be due to the preparation process or the non-uniform distribution of the FE and FM phases.
3.5. Magnetic properties

The magnetic hysteresis loops ($M-H$) of the samples with different ratios are shown in figure 13. The magnetic parameters of the hysteresis loops of different samples are also listed in table 3. As it can be seen that both the remnant magnetization ($M_r$) and the saturation magnetization ($M_s$) are reduced as the ferromagnetic phase in the composite ceramic is reduced. This is due to the fact that the magnetic phase CFO in the composites plays a major magnetic role in the composites because PZT is a nonmagnetic material, and the magnetic properties of the composites should decrease as the PZT concentration increases. The difference is that the coercive force ($H_c$) of the molar ratio of 1:6 is the largest, one reason is the interface interaction between the two phases [28–30], while this statement can’t be verified from the XRD and SEM results. Another factor that can influence the coercive field is the grain size and shape. In addition, the defect such as oxygen vacancies may affect the coercive field. As it is observed from the $J-V$ curves that the leakage current density of the sample 1:6 is the largest, thus more defects may be existed in it. These defects can’t only determine the conductive properties, but also affect the domain switching process and thus affect the coercive field. Since the measured magnetization is a macroscopic property rather than a nanoparticle, the anomalous results cannot be attributed to the uneven

### Table 2. Ferroelectric parameters of CFO–PZT composite ceramics.

| Molar ratio | $P_r$ ($\mu$C cm$^{-2}$) | $P_s$ ($\mu$C cm$^{-2}$) | $E_c$ (kV cm$^{-1}$) |
|-------------|--------------------------|--------------------------|----------------------|
| 1:4         | 1.13                     | 1.92                     | 15.98                |
| 1:5         | 0.56                     | 2.65                     | 16.69                |
| 1:6         | 0.74                     | 2.82                     | 22.54                |
| 1:7         | 0.45                     | 2.23                     | 10.13                |

Figure 12. Room temperature $P-E$ curves (a) and leakage current density (b) of CFO–PZT ceramics with different molar ratios.

Figure 13. $M-H$ curves of CFO–PZT composites with different molar ratios. Inset shows the enlarged part near the origin point.
distribution of magnetic and ferroelectric phases. The possible cause may be an interfacial effect between the two phases, which affects the coercivity \cite{32-34}.

### 4. Conclusions

CoFe$_2$O$_4$/PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (CFO-PZT) composite ceramics with different sample/composite (1:4, 1:5, 1:6 and 1:7) have been successfully prepared by conventional solid reaction method. XRD results show bi-phase structure of the composites. All ceramics exhibit relatively nonuniform performance, with some pores existed on the surface. The grain is sphere like and the size is about 200 nm for all the samples. The sample 1:4 shows larger dielectric constant and loss due to the higher concentration of CFO phase with larger carrier density. All sample present relaxation peak in the temperature dependence of dielectric constant because the phase transition temperature of PZT has been affected by the interface interaction, showing typical relaxation phenomenon. The sample 1:4 presents better ferroelectric and magnetic properties. The saturation magnetization, remnant magnetization of the sample 1:4 is the largest, they are 11.01 emu g$^{-1}$ and 3.28 emu g$^{-1}$, respectively. The sample 1:6 has the largest coercive field mostly due to the stronger interface interaction between the two phases. In all, the sample 1:4 has larger dielectric constant, polarization as well as magnetization.

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### References

[1] Gao R L, Bai L, Xu Z Y, Zhang Q M, Wang Z H, Cai W, Chen G, Deng X L and Fu C L 2018 *Advanced Electronic Materials* **4** 1800030
[2] Zhao T et al 2006 *Nat. Mater.* **5** 823
[3] Gao R L, Chen Y S, Sun J R, Zhao Y G, Li J B and Shen B G 2012 *Appl. Phys. Lett.* **101** 152901
[4] Fukunaga M et al *Phys. Rev. Lett.* **103** 2009077204
[5] Gao R L, Fu C L, Cai W, Chen G, Deng X L and Cao X L 2016 *Mater. Chem. Phys.* **181** 277–83
[6] Feyerherm R et al *Phys. Rev. B* **79** 2009134426
