Magnetodielectric effect in CoCr$_{2-x}$Fe$_x$O$_4$

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Abstract. Conventional multiferroics show the multiferroic behaviors below two successive transitions (a ferroelectric transition and a ferromagnetic transition). In the present study, we report the magneto-dielectric (MD) effect (both in-plane and out-of-plane) in CoCr$_{2-x}$Fe$_x$O$_4$ which undergoes only a ferromagnetic transition. We found the MD effect in the pure ferromagnetic phase (T$_S$<T<T$_C$) of CoCr$_2$O$_4$. And such MD effect is temperature dependent. The magnitude of the MD effect gradually decreases with approaching Curie temperature (T$_C$) and finally becomes zero at T$_C$. With doping Fe into CoCr$_2$O$_4$, we found the magnitude of MD effect increases and the MD effect exists in a wider temperature region because T$_C$ increases and T$_S$ decrease with doping Fe. Our results show the coupling between the ferromagnetic and ferroelectric orders. It suggests that both the ferromagnetic and ferroelectric properties originate from the same transition.

1. Introduction

Multiferroics are materials in which ferromagnetism, ferroelectricity and ferroelasticity coexist in the same phase [1-3]. This implies that they possess spontaneous magnetization which can be reoriented by external magnetic field, spontaneous polarization which can be reoriented by an applied electric field and spontaneous deformation which can be reoriented by an applied stress. However, it is customary to exclude ferroelasticity and only consider ferromagnetic and ferroelectric characteristics (magnetoelectrics) [4]. Multiferroics have attracted great interest in the past few years since their application potential on the dual read-write memory devices and spintronic devices [1, 2]. Besides the applications, the science of these materials is truly fascinating because the coupling between ferromagnetism and ferroelectricity challenges the conventional mechanism which shows ferroelectric ordering is incompatible with the ferromagnetic ordering [5].

Due to the incompatibility of ferromagnetism and ferroelectricity, there are rare single phase multiferroics [5]. Most of the single phase multiferroic materials (such as BiFeO$_3$, YMnO$_3$ and BiMnO$_3$) have a ferroelectric transition at high temperature and a ferromagnetic (or ferrimagnetic/antiferromagnetic) transition at low temperature [6]. Very recently, based on the spiral spin model [7, 8], a number of new multiferroic systems (TbMnO$_3$, DyMnO$_3$ and MCr$_2$O$_4$ with M=Mn, Fe and Co) were discovered [6, 9, 10]. With decreasing temperature, they undergo a magnetic transition to the ferromagnetic (or ferrimagnetic/antiferromagnetic) state firstly. Then, spiral spin transition occurs at lower temperature, the materials get to multiferroic state with the emerging of ferroelectricity induced by the spiral spins. All the above multiferroics show the magnetoelectric
coupling below two successive transitions. Here we report a magnetoelectric coupling phenomenon which undergoes only one transition: the ferromagnetic transition, which may imply the ferromagnetic and ferroelectric properties have the same origin.

In the present work, we studied magneto-dielectric effect [11-14] (MD effect: the external magnetic field dependence of dielectric permittivity ($\varepsilon$)) in the pure ferrimagnetic phase of CoCr$_2$XFe$_x$O$_4$. When the magnetic field is parallel with the AC electric field (in-plane), we found that $\varepsilon$ gradually decreases and finally saturates with increasing the magnetic field. Such a MD effect exist in the pure ferrimagnetic phase ($T_S<T<T_C$) of CoCr$_2$O$_4$, which was known the multiferroic properties only exist below the spiral transition ($T<T_S$) [9]. The magnitude of the MD effect gradually decreases with approaching Curie temperature ($T_C$) and finally becomes to zero at $T_C$, which is quite similar with the change of magnetization with temperature (M-T curve). With doping Fe into CoCr$_2$O$_4$, we found the magnitude of MD effect increases and the MD effect exists in a wider temperature region because $T_C$ increases and $T_S$ decrease with doping Fe. When the magnetic field is perpendicular with the AC electric field (out-of-plane), it show similar results, the only difference is that $\varepsilon$ increases with increasing the magnetic field and the magnitude of the MD effect under the same field is smaller than the parallel case. Our results suggest the coupling between the ferromagnetism (or ferrimagnetism /antiferromagnetism) and ferroelectricity exist in ferromagnetic insulators.

2. Experimental
The polycrystalline samples CoCr$_2$XFe$_x$O$_4$ (X=0 and 0.5) were prepared from CoO, Cr$_2$O$_3$, and Fe$_2$O$_3$ by the conventional solid state reaction method. The diameter and thickness of the cylinder is 8mm and 1mm respectively. The samples with good spinel structure were initially characterized by X-ray diffraction. The temperature dependence of the DC magnetization of CoCr$_2$XFe$_x$O$_4$ was measured by a Quantum Design SQUID. Silver paste was painted as electrodes. The temperature dependence of dielectric permittivity was measured with 3 kHZ by a dielectric measurement system (including a LCR 3532 meter and a cryostat for temperature changing). The change of dielectric permittivity with magnetic field up to 5T both in-plane and out-of-plane (in-plane: the direction of the magnetic field is parallel with the AC electric field; out-of-plane: the direction of the magnetic field is perpendicular with the AC electric field) was measured with 3 kHZ by the combination of the dielectric measurement system and a super-conducting magnet.

3. Results
Fig. 1 (a) and (b) show the temperature dependence of magnetization (M) and dielectric permittivity ($\varepsilon$) for a pure polycrystalline CoCr$_2$O$_4$. The onset of the magnetization (Fig 1(a)) at $T_C=96K$ is due to the ferrimagnetic transition. The tiny anomalies in both M-T (Fig 1(a)) and $\varepsilon$-T (Fig 1(b)) which are discerned at 28 K, correspond to the spiral transition ($T_S$). These results keep good consistence with the reported results of CoCr$_2$O$_4$ single crystal [9] and polycrystal [15]. It was reported [9] that the multiferroic properties only exist in the multiferroic phase (Fig 1(a) region B) which is below the spiral transition temperature $T_S$. In the following, we shall show the multiferroic properties in the pure ferromagnetic phase (Fig 1(b) region A: $T_S<T<T_C$).

Here it should be mentioned that direct measurement of ferroelectricity (or polarization P) caused by magnetic field becomes difficult when ferroelectricity is weak. In such a situation, measuring the change of dielectric permittivity ($\varepsilon = dP/dE$) by magnetic field (i.e., magnetodielectric effect) becomes a much more sensitive tool to detect the existence of coupling between P and M. [11, 12] Magnetodielectric effect can be described by, $MD = \varepsilon(H) / \varepsilon(0) - 1$ where $\varepsilon(H)$ is the dielectric permittivity under field H and $\varepsilon(0)$ is the dielectric permittivity without field” line 41 of page 2 of our paper.

Fig.2 shows the magnetodielectric effect (in-plane) at various temperatures in pure ferromagnetic phase of CoCr$_2$O$_4$ polycrystal. The magnetodielectric effect is defined as $MD = \varepsilon(H) / \varepsilon(0) - 1$, where $\varepsilon(H)$ is the dielectric permittivity under magnetic field and $\varepsilon(0)$ is the dielectric permittivity
without field. As shown in Fig 2a at 30K, MD gradually decreases with the increase of the external magnetic field along the positive direction. After removing the magnetic field, MD can go back to the original value. MD has the same variance while applied a magnetic field with opposite direction. At a relative higher temperature 84K, Fig 2b shows similar results as Fig 2a, but the magnitude of MD effect under the same magnetic field is smaller than that of 30K. MD finally becomes zero at 114K above Tc (Fig 2c). Fig 2d shows the change of the magnitude of magnetodielectric effect (MD) with temperature. It obviously shows the MD effect only exist below Tc become to zero at Tc, which is much similar with the change of the magnetism with temperature (M-T curve) of the common ferromagnetic materials, indicating that the ferromagnetic properties (M) must couple with the dielectric properties (ε). The switching of M under magnetic field makes the change of ε. It may suggest a small ferroelectric polarization (P) changes with the switching of the ferromagnetic domains.

Figure 1. The temperature dependence of magnetization (M) and dielectric permittivity (ε) for a polycrystalline CoCr2O4.

Figure 2. The temperature dependence of parallel (in-plane) MD effect for CoCr2O4. (a), (b) and (c) show perpendicular MD results at 30K, 84K, and 114K respectively.

Fig.3 (a) and (b) show the temperature dependence of M and ε of CoCr1.5Fe0.5O4 polycrystalline. Comparing with the pure CoCr2O4, the Tc of CoCr1.5Fe0.5O4 increases to 175K, while the spiral transition temperature (T_s) decreases to lower temperature (<4K, beyond the temperature range of the Squid). Therefore the pure ferrimagnetic phase of CoCr1.5Fe0.5O4 is wider than that of pure CoCr2O4. We can study the MD effect in a wider temperature and closer to the room temperature.

Figure 3. The temperature dependence of magnetization of CoCr1.5Fe0.5O4.

Figure 4. The temperature dependence of parallel (in-plane) MD effect for CoCr1.5Fe0.5O4. (a), (b) and (c)
(M) and dielectric permittivity \( (\varepsilon) \) for a polycrystalline Co\(_{1.5}\)Fe\(_{0.5}\)O\(_4\). show perpendicular MD results at 19K, 145K, and 181K respectively.

Fig 4 shows magneto-dielectric effect (in-plane) of Co\(_{1.5}\)Fe\(_{0.5}\)O\(_4\) at various temperatures. It is similar with that (Fig 2) of pure CoCr\(_2\)O\(_4\). The magnitude of MD effect under the same magnetic field gradually decreases with the increase of temperature and becomes to zero at \( T_C \) (175K). The only difference is that the magnitude of MD of Co\(_{1.5}\)Fe\(_{0.5}\)O\(_4\) is larger than that of pure CoCr\(_2\)O\(_4\) at the same temperature, which is due to the increase of coupling between M and \( \varepsilon \) by doping some Fe (increasing of \( T_C \)). It indicates that doping Fe can enhance the coupling between ferromagnetic and ferroelectric properties, and widen the multiferroic region.

Fig 5 shows the magneto-dielectric effect (out-of-plane) of CoCr\(_{1.5}\)Fe\(_{0.5}\)O\(_4\) at various temperatures. Interestingly, the dielectric permittivity increases with the increase of magnetic field, which is opposite with the in-plane case. However, with the increase on temperature, the magneto-dielectric effect also becomes smaller and finally disappears at \( T_C \). Comparing Fig 5 with Fig 4, we found that the magnitude of MD effect out-of plane is smaller than that of MD effect in-plane. It indicates the anisotropy of the coupling between M and \( \varepsilon \).

4. Discussion

The above magneto-dielectric results (Fig 2, Fig 4 and Fig 5) in CoCr\(_{2-x}\)Fe\(_x\)O\(_4\) show there must be coupling between the magnetization (M) and the dielectric permittivity (\( \varepsilon \)). As we know the definition of the dielectric permittivity is that \( \varepsilon = dP / dE \). When we measure the MD effect with an external magnetic field, the small AC electric field is a constant field, so \( dE \) is unchangeable during the measurement. Therefore the change of the dielectric permittivity must be ascribed that \( dP \) is changed by the external magnetic field H. This may poses a potential challenge to the convention view [9] that the ferrimagnetic state hosts a cubic structure with central symmetry.

Fig 6 shows the analysis of the MD effect with different structure view. Fig 6a shows the MD effect in-plane and out-of-plane of CoCr\(_{1.5}\)Fe\(_{0.5}\)O\(_4\) at 19K. Obviously, it is easy to get \( \varepsilon(H) \perp \varepsilon(0) > \varepsilon(H)\parallel \). In the following, we will analyze the MD results (Fig 6a) with a cubic ferrimagnetic state with central symmetry and a tetragonal ferromagnetic state with off-center symmetry respectively.

Generally, the ferrimagnetic state is considered as a cubic state with central symmetry. \( \varepsilon(0) \) is measured in such a multi-domain state (as shown in Fig 6b) with an AC electric field. After applied a magnetic field which is perpendicular with the electric field, M switches to the direction of the
magnetic field (Fig 6b1). Similarly, Fig 6b3 show the state while applied a magnetic field parallel with the AC electric field. ε(H) and ε(H) of the single domain state are got. Comparing the Fig 6b1, b2 and b3, all the three states have a cubic structure with central symmetry, only the directions of M are different, which has no influence on the dP. So, the dielectric permittivity of the three states should be the same ε(H) = ε(0) = ε(H). It is different from the experimental results as shown in Fig 6a. Therefore, it is difficult to understand the MD results with a cubic structure with central symmetry.

Recent results [16, 17] with a high-resolution synchrotron XRD clearly show that the ferromagnetic transition is a structural phase transition. The structure of the ferromagnetic state is non-cubic. The lattice distortion and the spontaneous magnetization (M) couples each other. Therefore, we assume the ferrimagnetic CoCr2₋xFeₓO4 state host a tetragonal structure with off centre symmetry and the direction of P is conforming to the M (as shown in Fig 6c2) because the M of the ferrimagnetic CoCr2₋xFeₓO4 is along <001> direction [9]. ε(0) is measured in such a multi-domain state with an AC electric field. After applied a magnetic field which is perpendicular with the electric field, both M and P switches to the direction of the magnetic field (Fig 6c1). Similarly, Fig 6c3 show the state while applied a magnetic field parallel with the AC electric field. ε(H) and ε(H) of the single domain state are got respectively. In this case, it is can be considered as ferroelectrics (such as BaTiO3)[18, 19]. Since the dielectric permittivity of BaTiO3 along a axis (ε ) is larger than dielectric permittivity along c axis (ε ) [20]. Then, it is easy to understand why ε(H) > ε(0) > ε(H).

5. Conclusion
Our magneto-dielectric results show the coupling between the ferromagnetic and ferroelectric orders. The disappearance of the MD effect at TC implies that both the ferromagnetic and ferroelectric properties originate from the same transition and the ferromagnetic state may posses a non-central symmetry. The ferromagnetic insulators are a kind of weak ferroelectrics. Doping Fe instead of Cr can enhance the coupling between M and P and make the MD effect exist in a wider temperature range.

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