# Coexistence of magnetic and ferroelectric properties in $Y_{0.1}Co_{1.9}MnO_4$*

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The magnetic, conductivity, and dielectric properties have been investigated in single-phase polycrystalline $Y_{0.1}Co_{1.9}MnO_4$. The temperature-dependent magnetisation reveals the ferromagnetic transition in sample at a low temperature (∼186 K). Magnetisation as a function of field $H$ ($M$–$H$ loop) indicated the weak ferromagnetism of the sample at room temperature. The constant $\varepsilon$ and dielectric loss tg$\delta$ measurements represent a ferroelectric phase transition at a higher temperature (∼650 K), while the conductivity shows an insulator–metallic transition. The ferroelectric hysterisis loops and capacitance–voltage measurements confirm the ferroelectric nature of the sample at room temperature. The observed ferromagnetism and ferroelectric nature in this material suggests a potential multiferroic application.

**Keywords:** spinel oxide, dielectric, conductivity, magnetic
**PACC:** 7240, 7280G, 7280T, 7740

## 1. Introduction

Multiferroic materials have attracted considerable attention in recent years due to the simultaneous occurrence of ferromagnetic and ferroelectric polarisations and a coupling between them.[1−6] As a consequence, they have a spontaneous magnetisation that can be switched by an applied electric field and a spontaneous electrical polarisation that can be switched by an applied magnetic field. Due to the coupling between ferroelectric and magnetic fields, multiferroics offer the new applications and phenomena. First, the ability to couple the ferromagnetic and polarisations allows an additional degree of freedom in device designing. Secondly, this multiferroic property could lead to the emergence of new storage media, such as multiple-state memory elements. Aside from the potential applications, the fundamental physics of multiferroic materials is rich and fascinating.

Multiferroicity in conventional spinel oxides has been predicted and studied.[7,8] However, the strength of magnetoelectric coupling was found to be weak. The doping of rare metal ions is supposed to introduce noncentrosymmetric charge ordering and consequently polarisation in the spinel structure.[8,9] Bi-substitution in $Co_2MnO_4$ was found to stabilise the ferroelectric transition and enhance the dielectric constant due to the polarisation of Bi $6s^2$ lone pair of electrons accommodated at octahedral sites.[9,10]

Although the properties of many spinels are known, there appears to have been very little exploration on dielectric and magnetic properties of doped cobalt manganite spinels, in which the doped ions have no lone pair of electrons such as Y ion. In this work, the electrical, dielectric and magnetic properties of Y-doped $Co_2MnO_4$ have been studied. It was found that Y-substitution in $Co_2MnO_4$ stabilises the ferroelectric transition and the ferromagnetic nature can be preserved. The results indicate the multiferroic behaviour of $Y_{0.1}Co_{1.9}MnO_4$.

## 2. Experimental

Powder samples of $Y_{0.1}Co_{1.9}MnO_4$ were synthesised by the conventional solid-state reaction method. Mixtures of $Y_2O_3$, $MnO_2$ and $Co_2O_3$ were calcined at 800 °C and 900 °C in air with intermediate grinding respectively. Finally the product was pressed into pellets, sintered at 1150 °C for 15 hours in air and then cooled to room temperature.

Powder x-ray diffraction (XRD) was conducted by using x-ray diffractonmeter (MXP18AHF) with Cu K$\alpha$ radiation to investigate the crystal structures. Microstructure of the sintered sample was investigated by high-resolution scanning electron mi-

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croscope (KYKY2800B). The two faces of the pellet were polished and coated with Ag paste as electrodes. The dc conductivity measurements were performed by standard four-probe technique in the temperature range 413–1013 K. The dielectric and ac conductivity measurements were carried out using a ZL5-LCR impedance meter operated over the frequency range from 12 to 100 kHz. Magnetisation measurements were performed in bulk samples using a superconducting quantum interference device (SQUID) magnetometer (MPM-7) and VSM magnetometer (Lake Shore 7410). Room temperature ferroelectric measurements were performed using Premier II test system (Radiant Technologies) at 10 Hz.

## 3. Results and discussion

Figure 1 shows the XRD pattern for the sample $Y_{0.1}Co_{1.9}MnO_4$ at room temperature. The XRD peaks of the sample could be indexed as the single phase with a cubic spinel structure (space group $Fd3m$).

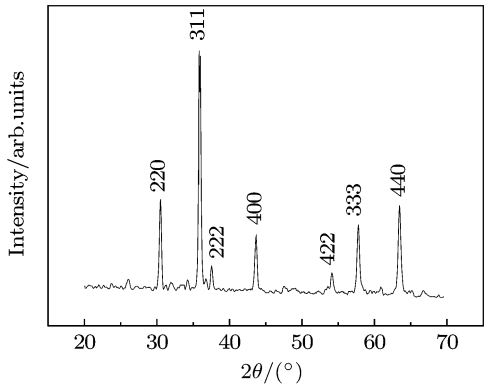



**Fig. 1.** XRD pattern for $Y_{0.1}Co_{1.9}MnO_4$.

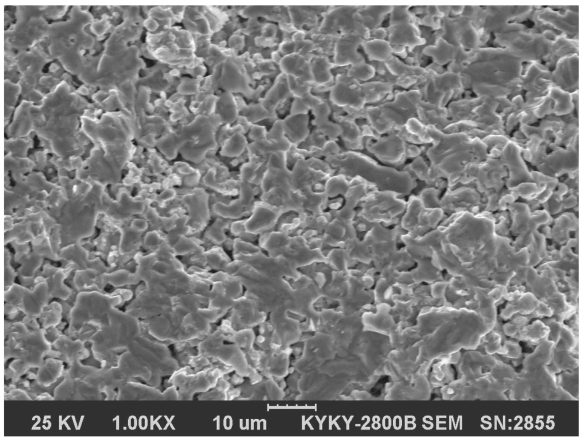



**Fig. 2.** Scanning electron microscope (SEM) photograph for $Y_{0.1}Co_{1.9}MnO_4$.

Figure 2 shows the SEM photographs of the fracture surface of the samples. It can be seen that the $Y_{0.1}Co_{1.9}MnO_4$ sample is relatively dense with some scattered pores.

Figure 3 shows the temperature dependent magnetisation for $Y_{0.1}Co_{1.9}MnO_4$ measured after zero field cooling (ZFC) in the presence of a 0.1 T magnetic field. The ferromagnetic transition occurs at a temperature ∼186 K. There is a super-exchange interaction between the ions at $A$ and $B$ sites through the intermediate oxygen ions in spinel oxides. As in $Co_2MnO_4$ spinel, $Co^{2+}$–$O^{2-}$–$Co^{3+}$ is found to maintain the antiferromagnetism due to the super-exchange interaction between the cobalt ions.[9] The magnetic exchange interaction is influenced by doping ions and causes $A$-site frustration. The appearance of ferromagnetism in $Y_{0.1}Co_{1.9}MnO_4$ may be attributed to the canting antiferromagnetically due to $Co^{3+}$ replaced by $Mn^{3+}$ and $Y^{3+}$ ions.[8,9] Inset of Fig. 3 shows the magnetisation as a function of field $H$ for $Y_{0.1}Co_{1.9}MnO_4$ at 300 K. It is clear that nonzero remanent magnetisation ($M_r$) and coercive field ($H_c$) are observed indicating a weak ferromagnetism at room temperature in this compound.

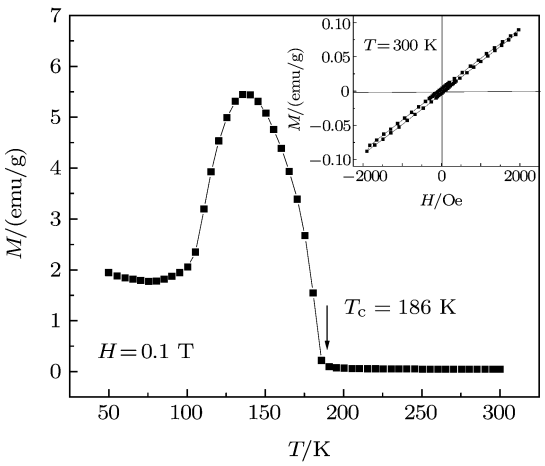



**Fig. 3.** Temperature dependence of magnetisation for $Y_{0.1}Co_{1.9}MnO_4$. The inset is magnetisation as a function of field $H$ at 300 K (1 Oe=79.5775 A/m).

The dc conductivity measured in the temperature range 413–1013 K is shown in Fig. 4, which exhibits an insulator behaviour in the temperature range 413–613 K, with resistivity reducing from 10 Ω·cm to 3.8 Ω·cm. The dc conductivity behaviour in this temperature range can be described as a small polaron hopping process:[11]

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{kT}\right),$$

where $\sigma_0$ is a temperature-dependent term, $k$ denotes Boltzmann constant, and $E_a$ is the activation energy for conductivity. Based on the above relation, the $\ln(\sigma T)$ versus $1000/T$ plot exhibits a straight line with a slope of $E_a/k$, as shown in the inset of Fig. 4. The dc conductivity activation energy calculated from the plot is about 0.19 eV. For the temperature range above 613 K, the dc conductivity shows metallic behaviour, with resistivity increasing to 5.1 Ω·cm at 1013 K.

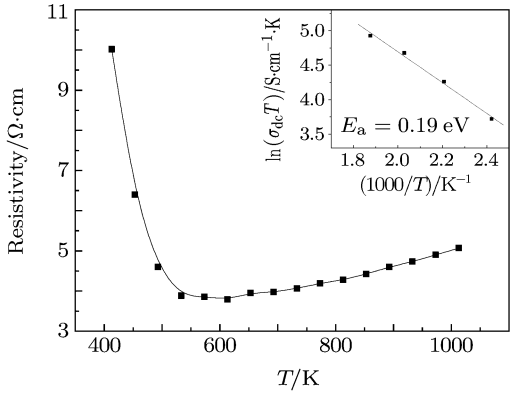



**Fig. 4.** Temperature dependence of dc resistivity for $Y_{0.1}Co_{1.9}MnO_4$. The inset shows $\ln(\sigma_{dc}T)$ vs $1000/T$ plot.

The ac conductivity ($\sigma_{ac}$) for $Y_{0.1}Co_{1.9}MnO_4$ was measured at frequency 10 kHz as shown in Fig. 5. The frequency dependence of ac conductivity was calculated using the dielectric data in the relation: $\sigma_{ac} = \omega\varepsilon_0\varepsilon \mathrm{tg}\,\delta$, where $\omega$ is angular frequency and $\varepsilon_0$ is vacuum dielectric constant. An insulator–metallic transition is also observed at about 613K. The ac conductivity activation energy that calculated from the $\ln(\sigma T) - 1000/T$ plot, as showing in inset of Fig. 5, is about 0.16 eV.

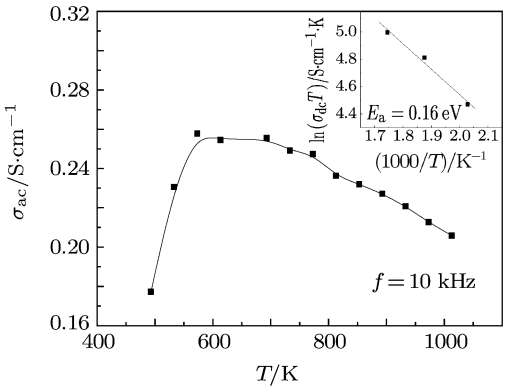



**Fig. 5.** Temperature dependence of ac conductivity for $Y_{0.1}Co_{1.9}MnO_4$. The inset shows $\ln(\sigma_{ac}T)$ vs $1000/T$ plot.

Figure 6 shows the dielectric constant $\varepsilon$ and dielectric loss $\mathrm{tg}\,\delta$ as a function of temperature for $Y_{0.1}Co_{1.9}MnO_4$. The dielectric constant $\varepsilon$ is found to increase with increasing temperature and there is a significant change at about 650 K. An obvious change in dielectric loss $\mathrm{tg}\,\delta$ is also observed at this temperature. The substantial variation in dielectric constant and dielectric loss means that there is a clear ferroelectric transition in the high temperature range. In this material, the hopping of charges between cations with different valence states is considered to be the origin of electrical conductivity.[10] The polarisation has a strong effect on the hopping of charge carriers and leads to the conductivity anomaly at high temperatures.

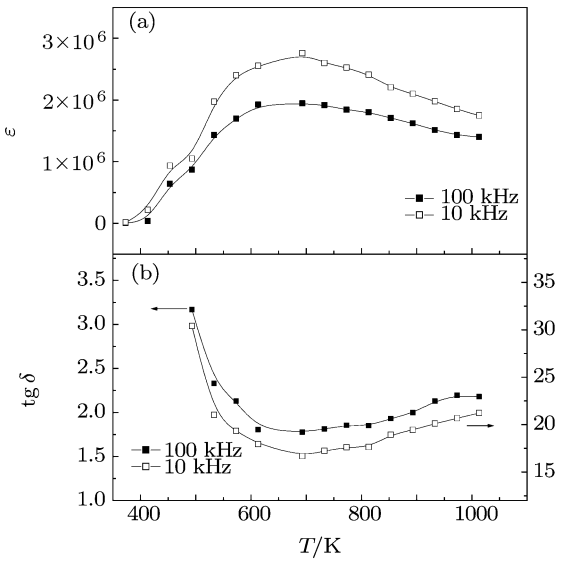



**Fig. 6.** Temperature dependence of the dielectric constant $\varepsilon$ and dielectric loss $\mathrm{tg}\,\delta$ for $Y_{0.1}Co_{1.9}MnO_4$.

Figure 7 shows the ferroelectric hysterisis loop of $Y_{0.1}Co_{1.9}MnO_4$ at room temperature and the residual polarisation intensity of 0.99 $\mu$C/cm$^2$ is observed. Obvious leakage current is also observed in $P$–$E$ loop, which may be due to the increase in oxygen vacancy because of Y ions doping at Co sites. The inset in Fig.7 shows the capacitance versus voltage of $Y_{0.1}Co_{1.9}MnO_4$, using an applied voltage of 10 V. An obvious loop, as seen in $C$–$V$ curve, indicates a signature of ferroelectric behaviour in the sample.[9] The results above indicate the coexistence of ferroelectric and magnetic properties in this material.

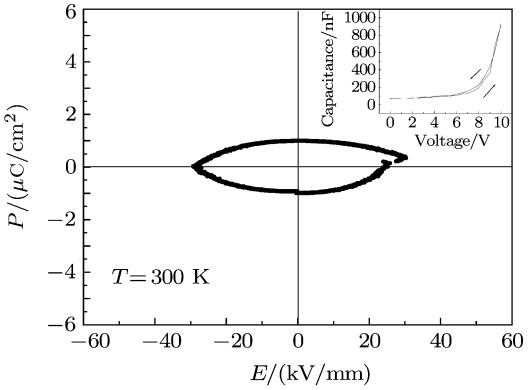



**Fig. 7.** The ferroelectric hysterisis loops for $Y_{0.1}Co_{1.9}MnO_4$. The inset shows capacitance versus voltage plot.

From the studies we found that the ferroelectric transition in Bi-doped spinel oxide can be attributed to the polarisation of Bi $6s^2$ lone pair of electrons accommodated at octahedral sites.[9,12] The polarisation in Y based compounds may have another mechanism due to the fact that Y has no lone pair of electrons. The x-ray absorption spectroscopy (XAS) study reveals a strong anisotropic $Y_{4d}$–$O_{2p}$ hybridisation in hexagonal $YMnO_3$.[13] The strong $Y_{4d}$–$O_{2p}$ hybridisation contributes large anomalies in Born effective charges on the off-centring Y–$O_p$ sites, which is commonly responsible for the ferroelectricity. The local structures in ferroelectric phase shows that the Y–O bond lengths change by huge amounts.[13,14] The results manifest that the Y $d^0$-ness with rehybridisation is the driving force for the ferroelectricity in hexagonal $YMnO_3$ and this scenario is applicable to ferroelectricity of other hexagonal manganites.[13]

In this study, Y-doped $Co_2MnO_4$ spinel exhibits multiferroicity with high ferroelectric and low magnetic transition temperature, which is analogous to hexagonal manganites. Neither the lone pair nor the spin frustration is responsible for the ferroelectricity of this material. In $Co_2MnO_4$ spinel, cations ($Co^{2+}$, $Co^{3+}$ and $Mn^{3+}$) occupy two non-equivalent sites: tetrahedral (A) and octahedral (B) sites. Y ions are likely to occupy octahedra positions and create a non-centrosymmetric arrangement, leading to a strong hybridisation between Y and O ions. In this case, we tentatively attribute the appearance of this higher-temperature dielectric and resistivity anomaly to the strong Y–Op hybridisation. The origin of polarisation and thus the driving force of ferroelectricity in Y-doped manganite spinel may be a structure distortion due to off-centre movements of Y–Op sites that originate from the strong $Y_{4d}$–$O_{2p}$ hybridisation.

## 4. Conclusions

The magnetisation, dc and ac conductivity, as well as dielectric constant $\varepsilon$ and dielectric loss $\mathrm{tg}\,\delta$ have been measured in Y-doped $Co_2MnO_4$ spinel. The ferromagnetic transition was observed at temperature ∼186 K and the dielectric measurement showed the ferroelectric transition at high temperatures. An insulator–metallic transition was observed at about 613 K by the dc and ac conductivity measurement. The capacitance–voltage curve and ferroelectric hysterisis exhibits a ferroelectric characteristics loop. The results indicate the multiferroic behaviour of $Y_{0.1}Co_{1.9}MnO_4$.

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