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ORIGINAL PAPER

# Structural and Magnetic Properties of $Ln_2CoMnO_6$(Ln = Dy and La) Produced by Combustion Synthesis

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**Abstract** In this article, the structural and magnetic properties of the $Ln_2MnCoO_6$ (Ln = La and Dy) produced by the combustion method are reported. The samples were characterized by X-ray diffraction (XRD) with Rietveld refinement, and their magnetic properties by studying the dependence of the magnetization with the magnetic field and temperature. XRD analysis reveals that the $La_2MnCoO_6$ (LCM) consists of a mixture of crystalline orthorhombic, monoclinic, and rhombohedral phases. This mixture might be originated by the mixing of valence states of the $Co^{+2}/Mn^{+4}$ and $Co^{+3}/Mn^{+3}$. $Dy_2CoMnO_6$ (DCM) presents a mixed composition of hexagonal and orthorhombic structures with the transition metal atoms in mixed valences. Magnetic measurements show that the magnetic transition temperature $T_C$ decreases from 150 K to 85 K when the La ions are replaced by Dy. We also observe that the magnetic order changes from a ferromagnetic to a ferrimagnetic when La is replaced by Dy.

**Keywords** Combustion synthesis · Ferromagnetic materials · X-ray powder diffraction · Perovskite · Manganite

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## 1 Introduction

$LaMnO_3$ compounds have been extensively studied in recent years, due to the wide variety of their physical and chemical properties. The most interesting properties are: colossal magnetoresistance [1–3], metal-insulator transition [4], charge ordering [5], catalytic devices [6], and multiferroic behavior [7]. In general, these properties can be easily adjusted or modified by doping. These compounds are an electrical insulator in a wide range of temperature and present antiferromagnetic order (AFM) below 140 K. The ferromagnetic order can be induced by replacing Lanthanum with a divalent atom [8] (e.g., Sr and Ca) or by doping the Mn site with Ni or Co, and even self-doping in the La site [8, 10, 11]. The conductivity mechanism of these compounds is influenced by the exchange interaction [12] and the Jahn–Teller distortion on the $Mn^{3+}$ ions [13, 14].

Lanthanum manganite half-doped with trivalent Cobalt ($La_2CoMnO_6$) presents multiferroic properties where ferroelectricity coexists with ferromagnetism at relatively high temperatures [7]. The multiferroic and ferromagnetic properties with ordering near room temperature make them interesting for applications in new technologies and developing spintronics.

The structural and magnetic properties of the perovskite $La_2CoMnO_6$ are strongly influenced by the synthesis meth-

od as well as by doping [4, 5, 8, 15]. In this work, the structural and magnetic properties of the complete substitution of La by Dy to form $Dy_2CoMnO_6$ is studied and compared to the $La_2CoMnO_6$. The compounds were prepared following the combustion method. This method is easy to implement, fast, and cheap compared to the traditional solid state reaction, sol-gel, and the Pechini techniques, and it is suitable to use in the industry. This method also allows the preparations of powders at the nanoscale and could favor the emergence of the new properties not yet seen in these materials.

## 2 Experimental Techniques

Samples of the manganites $La_2CoMnO_6$ (LCM) and $Dy_2CoMnO_6$ (DCM) were prepared by combustion synthesis as following described. Nitrates of lanthanides and transition metals and urea were weighed in stoichiometric amounts, diluted in water, and heated at 120 °C until they form a gel. The gel is then brought to 500 °C where a self-propagating reaction (combustion) occurs resulting in a dark powder. The powders were then ground, calcined at 600 °C for 16 h, pelletized and sintered at 1300 °C for 2 h in air; for the characterization X-ray diffractions patterns (XRD) were collected on a Siemens D5000 X-ray diffractometer, with Cu-$K_\alpha$ radiation and ($\lambda = 1.542$ Å) at room temperature. The measurement of the magnetization as a function of temperature ($M \times T$) was performed at the interval 5 to 300 K, and the magnetic field ($M \times H$) measurement was ramped between $-7$ T and 7 T. All these experiments were conducted using a MPMS magnetometer SQUID from Quantum Design. The $M \times T$ curves were obtained on zero field cooling (ZFC) and field cooling (FC) modes, at magnetic field of 100 and 10 kOe and the hysteresis curves were measured under a temperature of 100 K and 300 K.

## 3 Results and Discussion

Figure 1a and 1b shows the X-ray diffraction patterns of the manganites $La_2CoMnO_6$ (LCM) and $Dy_2CoMnO_6$ (DCM). The Rietveld analysis of both diffractograms was conducted by using the GSAS software considering the mixed valence of the transition metals. The cells parameters obtained by Rietveld refinement are listed in Table 1.

The transition metals nitrates used as precursors brings a mixture of $Mn^{+2}$ and $Mn^{+3}$ in its composition [9] and depending on the temperature of the reaction and the composition of the others cations, they could turn to $Mn^{+3}$ or $Mn^{+4}$ after combustion. On the other hand, the lanthanides are considered to have +3 valence in its nitrate and compound oxide [9]. Considering other reports [10, 16–20], the mixed valence states of the transition metals $Co^{+2}/Mn^{+4}$ and $Co^{+3}/Mn^{+3}$ in the LCM compound could be distributed in three different symmetries: orthorhombic (ICSD-

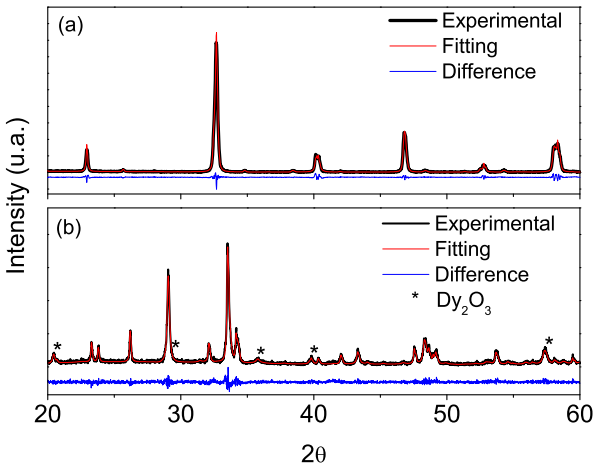


**Fig. 1** X-ray powder diffracts raw of the LCM (**a**) and DCM compounds (**b**)

**Table 1** Structural parameters of the LCM and DCM samples obtained by Rietveld refinement of the samples prepared by the combustion method. The angle is the same and equal to 90.0 for all phases

| Space-group | LCM | | | DCM | | |
|---|---|---|---|---|---|---|
| | #167 | #14 | #62 | #62 | #185 | #206 $Dy_2O_3$ |
| Symmetry | R-3H | P21n | Pbnm | Pnma | $P6_3$ cm | Ia-3 |
| ICSD | 151839 | 98240 | 151836 | 91711 | 99785 | 66736 |
| Fraction (%) | 55 | 15 | 30 | 46 | 41 | 3 |
| $a$ (Å) | 5.4961 | 5.5067 | 5.5158 | 5.5813 | 6.1566 | 10.6628 |
| $b$ (Å) | 5.4961 | 5.4781 | 5.4702 | 7.4905 | 6.1566 | 10.6628 |
| $c$ (Å) | 13.4325 | 7.7605 | 7.7631 | 5.2553 | 11.0822 | 10.6628 |
| $\beta$ | 90 | 89.9 | 90.0 | 90.0 | 90.0 | 90.0 |
| $\gamma$ | 120.0 | 90.0 | 90.0 | 90.0 | 120.0 | 90.0 |
| Vol. (Å$^3$) | 351.2 | 234.1 | 234.2 | 219.7 | 363.8 | 1212.3 |
| $\chi^2$ | 2.46 | | | 1.26 | | |
| $RF^2$ (%) | 0.56 | | | 6.35 | | |

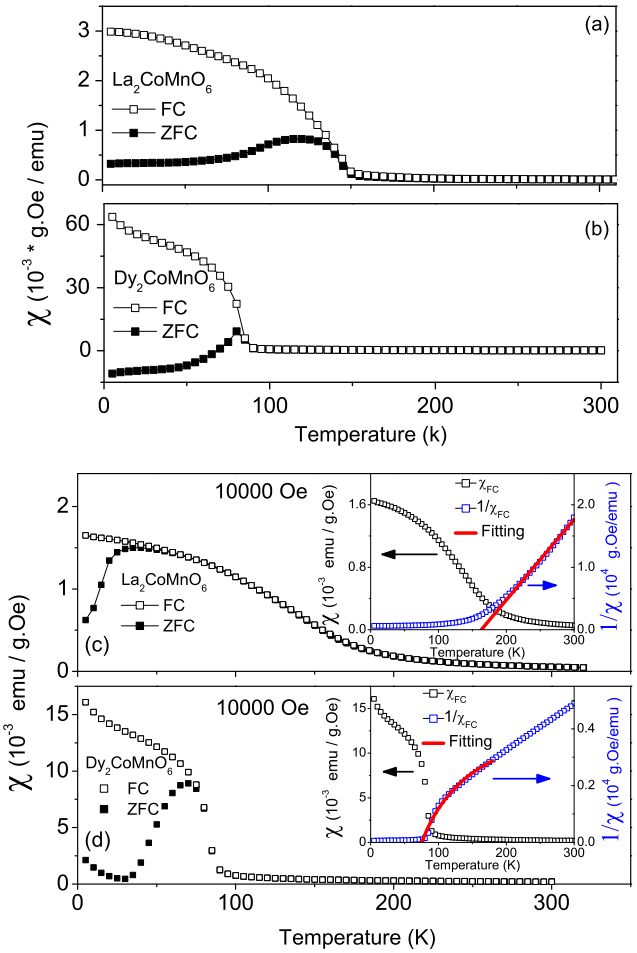


**Fig. 2** Magnetic measurements results for LCM and DCM for magnetic fields of 100 Oe (**a** and **b**) and 10 kOe (**c** and **d**) as a function of temperature. The *open* and *solid square symbols* represent the FC and ZFC measurements, respectively. The *insert* in the (**c**) and (**d**) panels shows the Curie–Weiss fit in FC measurement at 10 kOe for LCM and DCM samples. We use $\chi = M/H$ in graph

151836), monoclinic (ICSD-98240), and rhombohedral (ICSD 151839). In the case of the DCM compound, the mixed valence state of the transition metal enabled the XRD diffractograms to be indexed using the orthorhombic (ICSD 91711) and the hexagonal (ICSD 99785) symmetries. A small amount of unreacted dysprosium oxide (ICSD 66736) was also detected and it is marked with (*) in Fig. 1b. The symmetries and the lattice parameters of the samples are listed in Table 1.

Figures 2a and 2b show the results of the magnetic susceptibility versus temperature measurements of LCM and DCM samples. The open (solid) square symbols are for the FC (ZFC) curves. The susceptibility responding under a low applied magnetic field (100 Oe) are shown in panels (a) and (b) while those obtained from the application of a high magnetic fields (10 kOe) are shown in panels (c) and (d). The insets in Figs. 2c and 2d show the Curie–Weiss (CW) fitting of the susceptibility in the high field zone. As it is shown, the substitution of the La ion by Dy decreases the magnetic transition temperature from 150 K to 85 K. The magnetic behavior of DCM changes from ferromagnetic to ferrimagnetic as shown by the change of the concavity of the inverse of susceptibility $(1/\chi)$ versus temperature curve near the transition temperature [14]. The LCM sample shows small anomalies in the magnetization curve, at low magnetic fields in the temperature range between 210 K and 280 K. The anomalies for this compound are observed better on the $(1/\chi)$ curves (data not shown) and probably can be attributed to the presence of different symmetries in this compound. They are imperceptible in measurements taken in high magnetic fields (10 kOe). This behavior which can be attributed to the high intensity of the paramagnetic phase above the critical temperature (150 K) will be discussed in more detail in another paper.

The measurement data of $(1/\chi)$ as a function of temperature under a high magnetic field such as 10 kOe and above the transition temperature $(T_C)$ for the LCM sample fit the Curie–Weiss law $1/\chi = (T - T_C)/C)$. Thus, the fitted parameters are $C = 6.83 \times 10^{-3}$ K g Oe/emu and $\theta = 176$ K. On the other hand, for the case of the DCM sample, the curve can only be adjusted with the modified CW equation $(1/\chi = ((T - (C/\chi_0))/C) - (b/(T - \theta_p)))$, which describes the behavior of the ferrimagnetic materials above $T_C$. The parameters obtained after fitting are $C = 5.68 \times 10^{-2}$ K g Oe/emu, $C/\chi_o = 46.23$, $b = 54951.86$ and $\theta_p = 47.8$ K. The intersection of the linear extrapolation of the curve $(1/\chi)$ with the $x$-axis give the $\theta_f = 10.5$ K. In Fig. 2, a decrease in the irreversibility temperature is seen for the both samples, when the applied magnetic field applied is increased to 10 kOe. This behavior reveals the characteristic of the frustrated ferromagnetic systems which exhibit a cluster-glass interaction [21–23]. In addition, a low temperature and in a low magnetic field, the DCM sample (Fig. 2b) shows a negative value of magnetization for the ZFC mode, in contrast to the LCM sample (Fig. 2a). This result can be understood by considering the AFM interaction between (Co, Mn) and Dy ions placed at two different sites on the $A_2BB'O_6$ perovskite structure [24].

The relationship between the ionic radius, the tolerance factor, and the magnetic structure is still unclear in order to understand the influences of the $Dy^{3+}$ on the magnetic structure. The ionic radius of the Dysprosium (0.912 Å) is smaller than the Lanthanum radius (1.16 Å), and the Goldschmidt tolerance factor $t = (R_A + R_O)/(\sqrt{2} \times (((R_B + R'_B)/2) + R_O))$ decreases from 0.844 to 0.802, when the LCM change to DCM, thus increasing distortions which could destroy the long-range FM ordering [25, 26]. Although the Dy have a high magnetic moment $\mu_{\text{eff}} = 10.83\ \mu_B$, all that was observed was an increase of the magnetization in the FC curve (Fig. 2b). The increase in the FC susceptibility and the reduction of $T_C$ from 150 K to 85 K can also be understood as

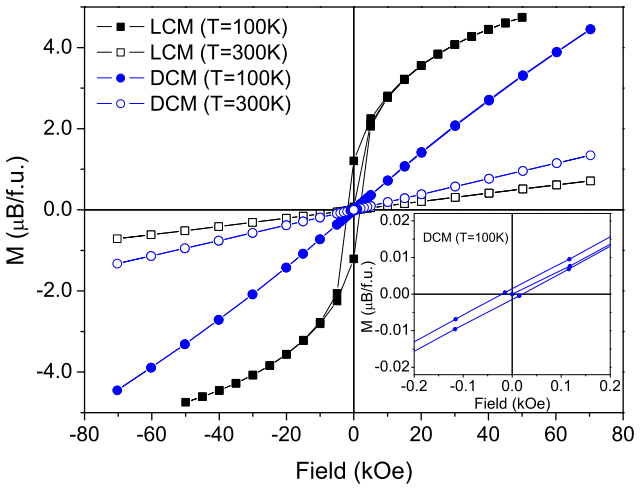


**Fig. 3** Measurements of the hysteresis loop in the LCM and DCM samples at different temperatures 100 K and 300 K

a way to destroy the long-range FM order [27] similar to the behavior of spin-glasses [28].

The magnetization as a function of the applied magnetic field at different temperatures for both, the LCM and the DCM samples is shown in Fig. 3. The LCM sample is paramagnetic at 300 K but at a lower temperature (100 K); a strong FM behavior is observed with coercive field 1.8 kOe, remanent magnetization of the 1.41 $\mu_B$, and magnetic saturation close to 5.0 $\mu_B$, which matches the theoretical value. The DCM sample shows little hysteresis in both temperatures (100 K and 300 K); this can be attributed to presence of AFM order with a high transition temperature [27]. The hysteresis parameters of the DCM sample, at 100 K, are $M_r$ (0.17 $\mu_B/f.u.$) and $H_c$ (21 Oe), which are better distinguished in the zoomed inset in Fig. 3. For the Curie–Weiss adjustment, the $\mu_{\text{eff}}$ for LCM and DCM was calculated as 1.7 $\mu_B$ and 5.2 $\mu_B$.

## 4 Conclusions

The structural and magnetic properties of the manganites ($La_2CoMnO_6$ and $Dy_2CoMnO_6$) system were investigated by XRD and magnetization measurements. Crystallographic studies indicate that the LCM and DCM samples have different coexisting crystal structures which could be attributed to the mixed valence ions present in these samples. Moreover, replacing the La by Dy increases the ferromagnetic behavior on the low field and changes the magnetic order from ferromagnetic to ferrimagnetic on the high field. Reduction of $T_C$ and $T_{\text{irr}}$ are indicative of the spin or cluster-glass order.

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