Suspicious electron-doped CMR in sintered La$_{1-x}$Ce$_x$MnO$_3$

Hsiung Chou*, C. B. Wu and S. G. Hsu

Department of Physics and Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

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Abstract

La$_{0.7}$Ce$_{0.3}$MnO$_3$ (LCeMO) is known usually called an electron doped colossal magnetotresistance material, which contains multiphase of n-type LCeMO, CeO$_2$ and Mn-O. However, the present energy dispersion spectroscopy measurement shows that the La$_{0.85}$Ce$_{0.017}$MnO$_{3+\delta}$ is the main phase in the bulk solid of material, which doesn’t have the LCeMO phase. This finding is consistent with the XRD data analysis which indicates that the composition is La$_{0.87}$Ce$_{0.014}$MnO$_{2.93}$. Since the highly localized $f$ electrons of Ce ions may not be transferred to Mn ions significant oxygen deficiency is needed to drive La$_{0.87}$Ce$_{0.014}$MnO$_{2.93}$ into n-type state that, which conflicts with the observation of a low $T_c$ fact of the vacuum annealed sample and to the natural tendency for the absorption of excess oxygen that yields a positive $\delta$. Similar properties are also found in La$_{1-x}$Te$_x$MnO$_{3+\delta}$, La$_{1-x}$Sn$_x$MnO$_{3+\delta}$ and La$_{1-x}$Zr$_x$MnO$_{3+\delta}$ systems. The present study casts doubt on the interpretation of n-type electronic property in bulk solid of LCeMO and proposed that the n-type CMR may be formed in metastable state.
Colossal magnetoresistance (CMR) materials have many interesting fundamental properties [1,2] and potential applications in information industry. By substituting x fraction of divalent alkaline-earth ions at the trivalent La sites of LaMnO$_3$ (LMO), i.e. (La$_{1-x}$B$_x$)MnO$_3$, an x portion of Mn$^{3+}$ ions was usually assumed to be converted into Mn$^{4+}$ ions, which renders insulated parent compound into ferromagnetic conductors [3-6]. The substitution of tetravalent Ce [7-21], Te [22-26], Sn [27-29] or Zr [30] ions at the La sites was assumed to yield a Mn$^{2+}$ and Mn$^{3+}$ mixed state. It was argued that the strong electron-phonon coupling [31] might cause electron doped LaMnO$_3$ to behave as hole doped. Based on these assumptions, p-n oxide junction or spintronic device might be realized in the future [32-35]. However, the single phase tetravalent doped CMR, such as La$_{0.7}$Ce$_{0.3}$MnO$_3$ (LCeMO), has not been realized in the bulk form [13]. LCeMO was reported to contain substantial CeO$_2$ [13] and Mn-O [8] impurites by powder x-ray diffraction (XRD) patterns and magnetization measurements. Ganguly, Gopalakrishnan and Yakhmi suspected that LCeMO has a lanthanum deficient La$_{0.7}$MnO$_3$ phase with Pbnm symmetry [10]. However, most follow up papers [8,12,13,19,25-28,30] still regarded these compounds as n-type LCeMO samples simply followed earlier reports [9,10,16,22-24,29]. The electronic states of the La$_{0.7}$T$_{0.3}$MnO$_3$ (T=tetravalence ions) have been studied by x-ray absorption spectroscopy (XAS) [14,15,17,24], Photoemission spectroscopy [11,20,24,25,29] and Iodometric titration method [9]. X-ray absorption spectroscopy (XAS) found that the Ce ion is in the 4+ state and the Mn ion has a valence between 2+ and 3+, and concluded that La$_{0.7}$Ce$_{0.3}$MnO$_3$ was
possibly in the n-type state. \( \text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3 \) was identified earlier by XRD measurement to a single phase by Mandel and Das [7] and Philip et.al. [9]. However, the same compound was found to contain CeO\textsubscript{2} impurities by Mitra et.al. later [13]. The Mn-O impurity was found by the low temperature antiferromagnetic magnetization measurements [8]. The ignorance of the presence of impurities might be the cause of misinterpretations of XAS data to conclude that the compound is n-type.

Hall measurements can identify the type of carrier. However, the Hall measurements of the \textit{in situ} epitaxial film grown by Raychaudhuri et al [17] showed the compound to be n-type, while the post-annealed epitaxial films grown by Yanagida et al [19] found it to be p-type. Yanagida et al also observed segregation of the Ce-rich and Mn-deficient nanoclusters from a lanthanum deficient manganite, which was argued to be responsible for the ferromagnetic-metal to paramagnetic-insulator transition. Since Raychaudhuri et.al. did not specify the microstructure or composition of their samples, phase segregation could also present in their samples.

In this study, \( \text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3 \) compound was formed by standard solid state reaction by mixing 99.995\% pure \( \text{La}_2\text{O}_3 \), CeO\textsubscript{2} and MnO\textsubscript{2} powders. The initial mixture was calcined at 900\(^\circ\)C and 1050\(^\circ\)C in air for 24 hours. The powder was then pressed into pellets and sintered at 1280\(^\circ\)C in air for 72 hours with several intermediate grinding processes. The magnetization and transport properties and the XRD pattern were measured and compared with previous reports to ensure the formation of the similar compound. The magnetization
and electric transport measurements were carried out by the superconducting interference device (SQUID) and a standard four points probe capable of applying magnetic field up to 1 Tesla. The compositional distribution was taken quantitatively by energy dispersion spectrum (EDS) in a field emission scanning electron microscopy (SEM).

The sample was then investigated by EDS and SEM to find the presence of CeO$_2$ and Mn-O impurities. EDS excluded the presence of the n-type La$_{0.7}$Ce$_{0.3}$MnO$_3$ phase. EDS found only the La-deficient La$_{0.9}$MnO$_{3+\delta}$ (LMO) phase [36,37] with the low Ce-content La$_{0.85}$Ce$_{0.02}$MnO$_{3+\delta}$ as the primary phase. The XRD measurements had the same observation as those of EDS. The diffraction pattern, which was fitted to the n-type La$_{0.7}$Ce$_{0.3}$MnO$_3$ with an orthorhombic structure with the Pnma space group [8] is now found to be better fitted the Lanthanum- and oxygen-deficient La$_{0.87}$Ce$_{0.02}$MnO$_{2.93}$ with a rhombohedral structure with $R\bar{3}C$ space group. This finding suggests that the previous assignment of electronic valence of Ce and Mn ions might be due to a misinterpretation of contributions from impurities, which prompts a need to clarify whether the Ce doped LaMnO$_3$ compound is a n-type materials.

The magnetization and resistivity as functions of the temperature are plotted in Fig. 1. The R-T curve (solid curve) exhibits two metallic-like-insulating-like transition peaks at 266K and 240K. The zero-field-cooling (ZFC) remnant magnetization measurement indicates that a very sharp paramagnetic-ferromagnetic transition at ~266K, which essentially coincides with the R-T insulator-like to metallic-like transition at 266K. The antiferromagnetic transition at ~50K observed by Gebhardt, Roy and Ali, which was attributed to the MnO$_2$
compounds [8], is hard to be identified in the present study. The XRD characteristic peaks of the Mn-O compound are not observed in the current XRD data, as shown in the Fig. 2. Fig. 2 shows the characteristic XRD peaks of CeO$_2$ consistent with the observation of Mitra et.al., though Mitra et.al. attributed them as evidence of n-type La$_{0.7}$Ce$_{0.3}$MnO$_3$. The CeO$_2$ implies the presence of Ce$^{4+}$, which may lead to misinterpretation as electron doped LCeMO.

In complementary to XRD measurements the energy dispersion spectroscopy (EDS) and a scanning electron microscopy (SEM) may provide better understanding of LCeMO. To calibrate the cation reading, large area images over mm scale were taken for La$_{0.7}$Ca$_{0.3}$MnO$_3$ and LaMnO$_{3+\delta}$ synthesized by the solid state reaction method. The samples have been characterized to have a single phase by XRD measurements. Figure 3 shows the back scattering electron image (BEI) of the bulk La$_{0.7}$Ce$_{0.3}$MnO$_3$. In BEI, heavier atoms (or ions) yield larger back scattering cross section and exhibit as white image, whereas the light atoms (ions) exhibit in dark image. The scattered white droplets are Ce-rich compounds for Ce ions are the heaviest ions in the samples. La and Mn ions can hardly be found even though the electron beam has a long penetration depth that can penetrate through the thin part of the irregular droplet. The black blocks are a few micrometers in size and contain light ions. EDS reading confirms that these black blocks are Mn-O compounds. However, the amount of the oxygen content is uncertain in the present EDS measurements. Nevertheless, the large grain size of the Mn-O compound contributes insignificant XRD features that can only be traced by the Rietveld simulation [35]. The major morphology of the sample is the huge
gray grains with grain sizes ranged from a few micrometers to nearly 10 micrometers, which
distribute over the most part of the figure. The EDS scanning indicates that the gray grains
are basically $\text{La}_{0.9}\text{MnO}_{3+\delta}$ with very limited solubility of Ce to form $\text{La}_{0.85}\text{Ce}_{0.017}\text{MnO}_{3+\delta}$.

The main peaks in the XRD pattern that was proposed to be the LCeMO phase was very
similar to those of $\text{La}_{0.894}\text{MnO}_3$ (LMO) [37,38] shown in Fig. 2. Both LCeMO and LMO
phases can used to fit the x-ray data using the same X-ray analysis technique of Rietveld [36].
By fitting the XRD pattern with Mitra et.al’s parameters for the Pnma space group and the
orthorhombic structure with $a=5.508(7)\text{Å}, b=5.543(2)\text{Å}$ and $c=7.833(5)\text{Å}$ and with the
presence of CeO$_2$, the result shows a large residual (error) at the locations of all peaks with
$\chi^2=10.75$. The peaks at around $31.5^\circ, 37^\circ, 40.5^\circ, 58.5^\circ, 68.5^\circ$ and $78.5^\circ$ in the current XRD
in Fig. 3(a) disagree with fitted ones. The peak at around $26^\circ$ predicted by the fit did not
exist in XRD data. In Fig. 3(b), the structure parameters of Dezanneau’s [37] (with the
space group= $R\overline{3}C$, rhombohedral structure, and $a= b=5.5097(1)\text{Å}, c=13.3395(3) \text{Å}$ and
$\alpha=\beta=90^\circ, \gamma=120^\circ$) and of CeO$_2$ and Mn$_3$O$_4$ compounds are used to fit the XRD data. The
presently fitted structured parameters have higher accuracy of $\chi^2=4.059$ as shown in the Fig.
3(b). The two peaks, namely the tiny peaks at $31.5^\circ$ right on the left prominent with
maximum intensity and the small independent peak at $37^\circ$ can not be fitted by this
combination. Based on this result, one may assume that a limited amount of Ce may
dissolve into the structure as $\text{La}_{0.9}\text{Ce}_\varepsilon\text{MnO}_{3+\delta}$, where $\varepsilon$ is the solubility of Ce. By using the
composition $\text{La}_{0.85}\text{Ce}_{0.017}\text{MnO}_3$ based on the EDS observation in combination with CeO$_2$ and
Mn$_3$O$_4$ the fitted XRD pattern, Fig. 3(c), which has a higher accuracy ($\chi^2=2.909$) with main phase to be La$_{0.87}$Ce$_{0.014}$MnO$_{2.934}$ ($a=b=5.531(8)\text{Å}, c=13.370(6)\text{ Å and } \alpha=\beta=90^\circ, \gamma=120^\circ$).

The combined content of La and Ce is about 0.88, which is similar to Dezanneau et al.’s finding of La$_{1-x}$MnO$_{3+\delta}$ with $x>0.1$ that is always decomposed into La$_{0.9}$MnO$_{3+\delta}$. The very small solubility of Ce does not contribute sufficient electron, so that a large oxygen deficiency, $\delta \leq -0.1$, is needed to drive La$_{0.87}$Ce$_{0.014}$MnO$_{2.934}$ into n-type region, which conflicts with the fact of low $T_C$ of the air annealed samples [7] and to the natural tendency that prefers a positive $\delta$ [22].

The most direct way to investigate the type of carriers in thin films is the Hall measurement. Raychaudhuri [17] and Yanagida et al. [19] have carried out the Hall measurements for epitaxial LCeMO films and Gao et al. [29] for LSnMO films. The carriers in the in-situ epitaxial films grown by Raychaudhuri were concluded to be conduction electrons only for $T<T_C$ by assuming a simple spherical Fermi surface. When the epitaxial films were fabricated at high temperature with post annealing [19], Ce-rich nanoclusters were formed to precipitate from the matrix leaving a lanthanum deficient manganite which is responsible for the magnetic and electric transition with p-type carriers. The growth of thin films is usually a non thermal equilibrium process. The in-situ epitaxial film can form a metastable phase. In contrast, the fabrication process used in this study is driven by thermal energy under thermal equilibrium, which yielded a p-type La$_{0.87}$Ce$_{0.017}$MnO$_{2.93}$.

Similar dependence on the fabrication technique has been observed in La$_{1-x}$Te$_x$MnO$_{3+\delta}$.
(LTeMO) [22-26], La$_{1-x}$Sn$_x$MnO$_{3+δ}$ (LSnMO) [27-29] and La$_{1-x}$Zr$_x$MnO$_{3+δ}$ (LZrMO) [30] systems. In LSnMO and LZrMO systems, the coexistence of Mn$_2$O$_3$, Mn$_3$O$_4$, LaMnO$_{3+δ}$ or La$_2$Sn$_2$O$_7$ impurities had been confirmed by XRD [28]. Even in the LTeMO system, which exhibited the best resolved XRD pattern, the EDS investigation indicates that the final compound by pre-treated in a oxygen free atmosphere, the Ar atmosphere, contains very limited amount of Te can hardly been detected by EDS. The Te might be evaporated during Ar annealing processes and forming very few TeO$_2$. The phases in the LTeMO system are found to be La$_{0.9}$MnO$_{3-δ}$, Mn-O and Te-O. These impurity phases provide signals in XAS and photoemission spectroscopy measurements that were misinterpreted as the evidence of n-type CMR. The $T_C$ of LTeMO system increases with the doping of Te and with the amount of oxygen content for $x\leq0.15$, which implies the increasing of $T_C$ might be attributed to the hole doping due to the excess oxygen content [22]. Therefore, the investigation of microstructure by SEM and EDS in these systems is essential.

To conclude, we have examined the microscopic morphology and composition distribution of La$_{0.7}$Ce$_{0.3}$MnO$_3$ bulk by a SEM and EDS techniques. EDS excludes the presence of the La$_{0.7}$Ce$_{0.3}$MnO$_3$ phase, instead, a La deficient La$_{0.87}$Ce$_{0.014}$MnO$_{2.934}$ is observed. This finding gets mutual support by reanalyzing the XRD pattern which has been misinterpreted by other groups. Similar situations might have happened in LTeMO, LSnMO and LZrMO systems which prompts a need to clarify whether the Ce doped LaMnO$_3$ compound is a n-type materials. From the LCeMO films grown in-situ and by post annealed
reveal that the n-type CMR may be formed in a metastable state but not in the thermal equilibrium state.

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Captions:

FIG. 1: The resistivity and the zero field remnant magnetization of La$_{0.7}$Ce$_{0.3}$MnO$_3$ as a function of temperature.

FIG. 2: The comparison of x-ray diffraction patterns of Mitra’s result, (a), of the present data, (b); and of La$_{0.9}$MnO$_{3+\delta}$, (c).

FIG. 3: The Rietved refinement results for using (a) Mitra’s result, the orthorhombic structure with Pnma space group and $a=5.5087\text{Å}$, $b=5.5431\text{Å}$ and $c=7.8335\text{Å}$; (b) Dezanneau’s result, the rhombohedral structure with $R\bar{3}C$ space group, and the CeO$_2$ impurity; (c) EDS result of La$_{0.85}$Ce$_{0.02}$MnO$_{3+\delta}$ and CeO$_2$ and MnO$_2$ impurities.

FIG. 4: The back scattering image of La$_{0.7}$Ce$_{0.3}$MnO$_{3+\delta}$ bulk. The scattered white droplet and the black blocks with micrometers size are identified to be CeO$_2$ and Mn-O impurities. The main phase, the gray grains, is La$_{0.85}$Ce$_{0.02}$MnO$_{3+\delta}$. 

La$_{0.7}$Ce$_{0.3}$MnO$_3$

$T_c=272K$
$T_p=266K$
La$_{0.7}$Ce$_{0.3}$MnO$_3$ (from Mitra et al.)

La$_{0.7}$Ce$_{0.3}$MnO$_3$ (current study)

La$_{0.894}$MnO$_3$ (from Dezanneau et al.)
CeO

La$_{0.85}$Ce$_{0.017}$MnO$_{3+\delta}$

Mn-O

10µm Electron Image 1
Pmna $\text{La}_{0.3}\text{Ce}_{0.1}\text{MnO}_3 + \text{CeO}_2$

R3cH $\text{La}_{0.84}\text{MnO}_3 + \text{CeO}_2 + \text{Mn}_3\text{O}_4$

R3cH $\text{La}_{0.88}\text{Ce}_{0.0144}\text{MnO}_3 + \text{CeO}_2 + \text{Mn}_3\text{O}_4$
