

Structural and magnetic study of self-doped

$\text{La}_{1-x-y}\text{Ca}_x\text{O}_y\text{MnO}_3$

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Abstract

A detailed study of the combined effect of divalent ion and A-site vacancy self-doping in ferromagnetic $\text{La}_{1-x-y}\text{Ca}_x\text{O}_y\text{MnO}_3$ manganite system is presented. It is found that the system can accommodate high vacancy content, with a strong lattice distortion for $y > 0.12$. Near the stoichiometric maximum T_c ($x = 0.33$, $y = 0$), vacancies do not degrade T_c , and the magnetoresistance can even be enhanced.

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Previous studies on non-stoichiometric manganites have raised the relevance of self-doping with A-site vacancies. In particular, thin films of $\text{La}_{1-x}\text{MnO}_3$ [1] and $(\text{La}-\text{Ca})_{1-x}\text{MnO}_3$ [2] prepared by MOCVD have shown Curie temperatures near 290–300 K with high magnetoresistance. In addition, X-ray diffraction on these films did not show any residual phase, like Mn_3O_4 . To address this problem and understand the role of A-site cationic vacancies (\emptyset) beyond the $\text{La}_{1-x}\text{MnO}_3$ system, polycrystalline $\text{La}_{1-x-y}\text{Ca}_x\text{O}_y\text{MnO}_3$ samples with excess Mn were prepared in the range $x < 0.33$ and $y < 0.45$ (see Ref. [3] for details). Samples were prepared by standard solid-state reactions by repeated calcining and milling. The final conditions were used: (a) Cold pressed reacted powders were sintered in air at 1300°C for 10 h; Further annealings of the samples were done at: (b) 1000°C under flowing oxygen for 24 h or (c) 1350°C in air for 60 h. Chemical compositions were determined by AAS, EDS in SEM and RBS techniques.

The structure and phase analysis of the samples was done by X-ray diffraction with Rietveld refinement. Electrical resistivity, magnetoresistance, AC magnetic susceptibility and SQUID magnetization measurements were used to study the effect of combined Ca and self-doping on the electrical and magnetic properties. The manganite structure in the composition ranges studied includes rhombohedral and orthorhombic phases, eventually coexisting in mixed form. XRD analysis shows that most samples contain haussmanite (Mn_3O_4) phase coexisting with perovskite manganite phase. No other crystalline phases could be detected by XRD. The relative content of Mn_3O_4 for each sample was determined by the area ratio of the two main diffraction peaks of each phase. This method was calibrated using powder samples with known phase mixture. The result was applied to determine the vacancy content y' in the manganite phase. Fig. 1 shows that the manganite phase accommodates a large fraction of vacancies, that goes beyond $y' = \frac{1}{8}$, the reported limit for $\text{La}_{1-x}\text{MnO}_3$ [4,5], confirmed in our $x = 0$ sample. One can see that O_2 annealing (b), that is known to promote vacancies in both cation lattices, favors the reaction of Mn_3O_4 with

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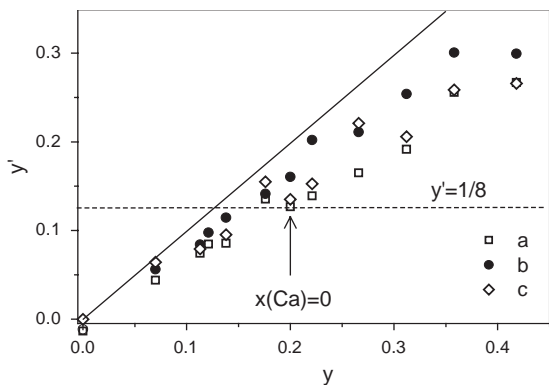


Fig. 1. Vacancy content of manganite phase (y') versus nominal vacancy (y). Solid line represents $y' = y$ (if no Mn_3O_4 was present).

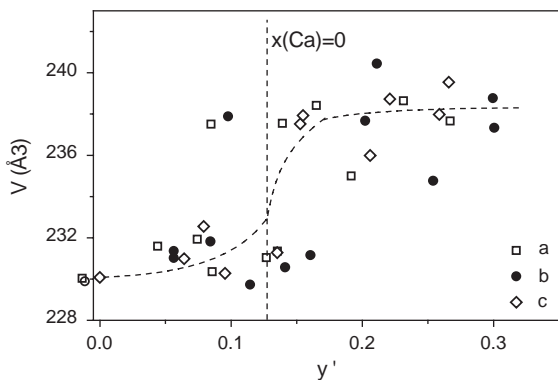


Fig. 2. Cell volume as a function of vacancy content. Strong lattice distortion occurs for $y' = \frac{1}{8}$.

the perovskite phase. It is expected that in the present study there should be no Mn vacancies. An important result is that the accommodation of such large amount of A-site vacancies (>0.12) leads to a strong distortion of the manganite phase, represented in Fig 2. This orthorhombic cell distortion is characterized by an increase of the cell volume, keeping the shorter a lattice parameter constant, and increasing b and c . One possible explanation may be the formation of a vacancy structure ordering with Mn displacement to the A-sites, leading to the perovskite related $\text{LnMn}_7\text{O}_{12}$ structure as intergrowth or interleaved planes in the main phase. This possibility was revealed by TEM and electron diffraction in $\text{Nd}_{0.50}\text{MnO}_{3+d}$ thin films [6]. We notice that while the $\text{LaMn}_7\text{O}_{12}$ phase is stable only at high pressures, $\text{CaMn}_7\text{O}_{12}$ phase is stable [7].

For the compositions studied, a ferromagnetic metallic behavior below T_c is found, confirming the stability of the Mn sublattice. T_c ranges from 220 K up to about 270 K, observed for the $x' = 0.33$ stoichiometric sample. In the following we concentrate on the properties of this

Table 1

Properties of samples 1, 2 and 3 for the 3 conditions

	T_c (K)	MR (%)	x' (Ca)	y' (\emptyset)	a (Å)	b (Å)	c (Å)	Vol. (Å^3)
1a	263.5	26	0.336	0.013	5.460	5.474	7.697	230.0
1b	268.5	33	0.336	0.011	5.460	5.470	7.697	229.9
1c	262	30	0.332	0	5.457	5.472	7.705	230.1
2a	262	31	0.246	0.192	5.456	5.571	7.731	235.0
2b	265	33	0.227	0.254	5.465	5.556	7.732	234.8
2c	262	34	0.241	0.206	5.473	5.564	7.751	236.0
3a	266.5	32	0.334	0.086	5.446	5.495	7.697	230.4
3b	267	32	0.324	0.110	5.460	5.470	7.693	229.7
3c	266	44	0.331	0.095	5.467	5.475	7.694	230.3

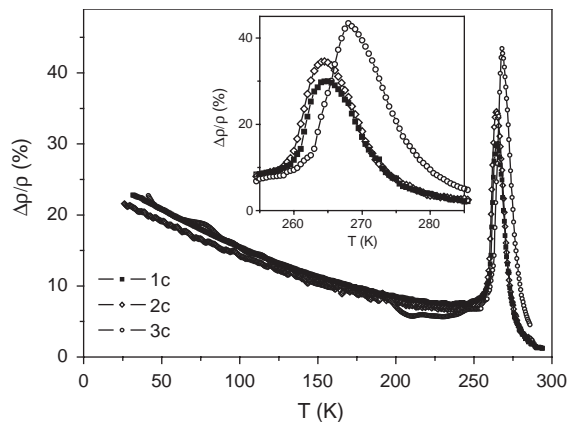


Fig. 3. temperature dependence of the magnetoresistance at $H = 7.5$ kOe for samples in Table 1 with treatment (c).

and two other samples which present a close T_c value with vacancy contents $y' \sim 0.1$ and ~ 0.2 . Some representative structural and magnetic parameters are presented in Table 1. MR is the maximum magnetoresistance for a field $H = 7.5$ kOe. Fig. 3 shows the temperature dependence of the magnetoresistance measured at $H = 7.5$ kOe, under treatment condition (c). One can see that such strong vacancy content does not degrade the magnetic and electric properties.

In particular, for the treatment (c) shown, the incorporation of $y' \sim 0.10$ vacancies (mainly La) leads to an increase of both T_c (by 4 K) and the MR peak (by 14%). Further $y' \sim 0.20$ (with Ca removal) gives properties close to the stoichiometric sample, with however a cell volume 5% higher.

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