Thermodynamic properties and spin dynamics of some micro and nanostructured magnetoresistive lanthanum manganites

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Abstract

The spin dynamics and thermodynamic properties of micro- and nanostructured lanthanum manganites $La_{0.67}Ca_{0.33}Mn_{1-x}Me_xO_3$ (Me = Al; $x = 0$–0.05) have been studied in order to evidence new features related to the effect of different compositional variables on the thermodynamic and magnetic behaviour. By electron paramagnetic resonance (EPR) spectroscopy, the influence of the grain size and the Mn substitution effects on the spin dynamics were investigated. A solid state electrochemical method was used to obtain the relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen. The influence of the oxygen stoichiometry change on the thermodynamic properties has been investigated. The results were correlated with the average Mn valence values as determined by redox titration. In this paper an alternative method is proposed to estimate the contribution made by oxygen vacancies in balancing the local charge in CMR manganites.
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1. Introduction

The perovskite-type compounds based on substituted lanthanum manganites are receiving considerable attention due to their wide-ranging electrical, magnetic and catalytic properties. To investigate and to improve these properties, a great amount of work was performed involving the preparation, structural studies, and physical properties and their relationships. However, there has been only limited information on the thermodynamic behaviour of the colossal magnetoresistive (CMR) manganites, as well as on the correlation existing between the magnetic and thermodynamic characteristics. The properties of the rare-earth manganites are strongly affected by the A- and B-site substitution and by the oxygen nonstoichiometry. Despite the exhaustive study of the effects of the rare-earth replacement in these manganites, the influence of the substitution at Mn sites with closed-shell ions, as well as the dependence of the magnetotransport properties on the oxygen stoichiometry change are much less

investigated.[1–4] At the same time, the properties of CMR materials depend on the size scale and the modifications of these properties connected with the nanocrystalline state could have important consequences for applications. Due to the progress in methods for experimental analysis of the distribution of elements at interfaces, some information has been accumulated on the chemical stabilities and properties of micro and nanostructured magnetoresistive compounds. However, the fundamental understanding was limited to rather simple cases. Such analyses need the thermodynamic data, because the driving forces for chemical reactions and diffusion can be given properly in terms of thermodynamic properties. This constitutes a considerable field of investigation, which is starting to be explored for both basic and applicative purposes.[5–9]

In this study, the spin dynamics and thermodynamic properties of the micro and nanostructured $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ ($x = 0$–0.05) lanthanum manganites were investigated. By means of electron paramagnetic resonance (EPR) spectroscopy, the effects of Mn substitution with diamagnetic ions (Al) on the spin dynamics were studied over a wide temperature range (-123 to $285\,°C$). Particular attention is devoted to the discussion concerning the influence of the grain size reduction on the exchange

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coupling integral between Mn spins and the polaron activation energy.

The solid-oxide electrolyte galvanic cells method has been employed in order to obtain the thermodynamic properties represented by the partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the partial pressures of oxygen. The variation of the thermodynamic data with the oxygen stoichiometry change was examined by use of a coulometric titration technique coupled with EMF measurements. The results are correlated with the average Mn valence values as determined by redox titration. In this paper an alternative method is proposed to estimate the contribution made by oxygen vacancies in balancing the local charge in the magnetoresistive samples. The method consists of correlating the results obtained from EMF and solid-state coulometric titration experiments with the ratio of manganese ions calculated from redox titration measurements. The effect of different compositional variables (grain size, dopants, oxygen stoichiometry change) is discussed in relation to the variation of the predominant defects in the perovskite-structure.

2. Experimental

2.1. Synthesis

The substituted lanthanum manganites of general formula $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ ($x = 0$–0.05) were prepared by two methods:

(a) Sol–gel route with diethylene-triaminepentaacetic acid (H5DTPA) as gelling agent. The powders were sintered at $650\,°C$ for $48\,h$. The mean grain sizes estimated from SEM images were found to be of $90\,nm$. A number of 34-35 nano-crystallites/grain was determined, the dimensions of the nano-crystallites being in the $10\,nm$–$45\,nm$ range.
(b) Conventional solid-state reactions and sintering at $1200\,°C$ for $10\,h$.

The X-ray diffraction patterns of the doped lanthanum manganites were all identified as belonging to the orthorhombic perovskite-type structure.

2.2. Measurements

The transition temperature T_C was obtained from a.c. magnetic susceptibility curves.[3,10] X-band EPR investigations were carried out in the temperature range -125 to $285\,°C$. In order to evaluate the EPR parameters, the derivative spectra were fitted with a Lorenzian lineshape, the fit parameters being the half-width at half-height, $\delta H_{1/2}$, of the corresponding absorption line and the resonance field, H_0. Since the sample size effects due to magnetic losses affect the spectrum, we have used a small amount of powdered material $m = 0.5\,mg$ for each sample.

The solid-oxide electrolyte galvanic cell method was employed to obtain the thermodynamic properties of the samples. The design of the apparatus, as well as the theoretical and experimental considerations related to the applied method, are described elsewhere.[11] As we showed in previous papers,[11,12] the thermodynamic stability limits of the lanthanum manganites are conveniently situated within the range of oxygen chemical potentials that can be measured using galvanic cells of the type:

$$(-)Fe,\text{wüstite}/ZrO_2(Y_2O_3)/ABO_3(+) \tag{1}$$

where for simplicity, we denote ABO_3 as a lanthanum perovskite-type oxide.

The measurements were performed in vacuum at a residual gas pressure of $10^{-5}\,Pa$. The electromotive force was measured with a Keithley 197 microvoltmeter at $50\,°C$ intervals between 600 and $1000\,°C$, each time waiting until equilibrium values are recorded. By solid-state coulometric titration[11] the precise change of the oxygen stoichiometry was obtained. The titration was performed at $850\,°C$ using a Bi-PAD type Tacussel Potentiostat. After the titration and equilibration, by changing the temperature under the open-circuit condition, the variation of EMF with temperature was again recorded.

For determining the manganese concentration and the average oxidation state in mixed-valence La-Mn perovskites, a redox titration method previously proposed by Licci et al.[13] was used. The method is based on two independent iodometric titrations, carried out under controlled conditions, which make it possible to separately determine both, the total amount of Mn and the equivalent Mn charge in the same fraction of material.

3. Results and discussion

3.1. Influence of doping on the EPR data

The behaviour of two EPR parameters, integral intensity (I_{EPR}) and linewidth ($\delta H_{1/2}$), was investigated in order to evidence the doping influence on both the exchange coupling integral (J) between Mn spins and the polaron activation energy (E_a). In the paramagnetic regime the EPR spectra for all investigated samples consists of a single line with $g \approx 1.99$. At high temperatures, the EPR integral intensity follows a ferromagnetic Curie–Weiss (CW) temperature dependence $I_{EPR}(T) = C/(T - \theta)$, arising from the ferromagnetic coupling of the Mn^{4+} and Mn^{3+} subsystems. From the linear behaviour of $1/I_{EPR}$ as function of temperature, the CW temperatures θ given in Table 1 were obtained.[3] The T_C and θ values are reduced when x increases, showing a general weakening of double exchange (DE) mechanism upon doping. According to the results obtained in previous studies,[3,14,15] the characteristic features of the EPR integral intensity and the linewidth in

Table 1
Critical temperature T_C, Curie–Weiss temperature θ, exchange coupling integral J between Mn spins and the polaron activation energy E_a in the paramagnetic regime of microstructured $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$

Sample	x	T_C (K)	θ (K)	J (K)	E_a (meV)	δH_0 (G)
$La_{0.67}Ca_{0.33}MnO_3$	0	263	339	116	120	24
$La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$	0.01	217	318	93	109	111
	0.05	189	249	73	98	133

CMR manganites could be caused by spin-lattice relaxation of the entire exchange-coupled Mn^{3+}–Mn^{4+} spin system under the condition of a strong relaxation bottleneck. In this scenario, I_{EPR} is proportional to the total susceptibility χ_{total} of Mn^{3+} and Mn^{4+} spins

$$I_{EPR} \propto \chi_{total} = \chi_S + \chi_\sigma \tag{2}$$

where χ_S and χ_σ are the renormalized static susceptibilities of the Mn^{4+} and Mn^{3+} spin systems, respectively. By fitting Eq. (2) to the $I_{EPR} * T$ data we can get an estimate of J (Table 1). For the $La_{2/3}Ca_{1/3}MnO_3$ sample, the value of J is of the same order of magnitude as the values obtained for $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$,[15] $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$,[15] and $Pr_{0.6}Ca_{0.4}MnO_3$[16] from EPR measurements by using the bottleneck scenario. As one can see, the effect of Al doping is to perturb DE coupling between Mn^{4+} and Mn^{3+} ions, causing a severe decrease in J.[3]

The temperature dependent part of the linewidth could arise from a thermally activated process involving the adiabatic hopping of small polarons.[3,15] In this case, $\delta H_{1/2}$ can be expressed by [15]

$$\delta H_{1/2}(T) = \delta H_0 + BT^{-1} \exp\left(\frac{-E_a}{k_B T}\right) \tag{3}$$

where E_a and δH_0 are the polaron activation energy and the residual linewidth, respectively.

The resulting values of the polaron activation energy, E_a, for the investigated samples are summarized in Table 1. One can see that E_a decreases with increasing doping level x. The substitution of Mn with diamagnetic ions produces changes in Mn–O distance.[1] Due to the linear relationship between the Mn–O distortion and the Mn^{3+} content, one could expect to find in our samples a strong dependence of the E_a values on the Mn^{3+}/Mn^{4+} ratio.[17] The Mn valence is in turn a function not only of the composition but equally importantly the thermal history of the phase. Consequently, an understanding of the high temperature defect chemistry of the phases is vital, if an understanding of the low temperature electronic and magnetic properties is to be achieved.

3.2. The effect of oxygen stoichiometry

In order to obtain further insight into physical mechanisms controlling the magnetoresistive properties of the lanthanum manganites, investigations from a thermodynamic point of view are very important. Moreover, few experimental data are available in the literature.

Emphasizing the role of charge ordering in explaining the magnetotransport properties of the manganites, Jonker and van Santen[18] considered that the local charge in the doped manganites is balanced by the conversion of Mn valence between Mn^{3+} and Mn^{4+} and the creation of oxygen vacancies, as well. Consequently, the proposed ionic structure of $La_{1-x}A_xMnO_{3-\delta}$ is $La_{1-x}^{3+}A_x^{2+}Mn_{1-x+2\delta}^{3+}Mn_{x-2\delta}^{4+}O_{3-\delta}^{2-}V_\delta^0$, where V_δ^0 stands for the fraction of oxygen vacancies.

As discussed previously,[18] the CMR properties may entirely be determined by the valence conversion between Mn^{3+} and

Mn^{4+}. Thus, the creation of oxygen vacancies could reduce the double exchange effect, resulting in a decrease in the CMR effect. In practice, however, quantifying of oxygen vacancies is a challenge to existing microscopy and spectroscopy techniques.[19]

In this paper an alternative method is proposed to estimate the contribution made by oxygen vacancies in balancing the local charge in the microstructured $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_{3-\delta}$ ($x = 0$; 0.05) samples. The method consists of correlating the results obtained from EMF and solid-state coulometric titration experiments with the ratio of manganese ions calculated from redox titration measurements.

The free energy change of the cell (1) is given by the expression:

$$\Delta G_{cell} = \mu_{O_2} - \mu_{O_{2(ref)}} = 4FE \tag{4}$$

where E is the steady state EMF of the cell in volts; μ_{O_2}, $\mu_{O_{2(ref)}}$ are, respectively, the oxygen chemical potentials of the sample and the reference electrode and F is the Faraday constant ($F = 96.508$ kJ/V equiv.). By using the experimental values of the electromotive force of the cell and knowing the free energy change of the reference electrode,[20–22] the values of the relative partial molar free energy of the solution of oxygen in the perovskite phase, the relative partial molar enthalpies and entropies, and the partial pressures of oxygen were calculated according to the known relationships.[11] The variation of the thermodynamic data was analysed at the same stoichiometry change $\Delta\delta = 0.02$. Thus, the effect of the oxygen stoichiometry can be correlated with the influence of the B-site dopant. In Fig. 1, two sets of data obtained before and after the isothermal titration experiments are plotted. The $\Delta\bar{G}_{O_2}$ values are decreasing after titration for both the samples. It is interesting to note that the $\Delta\bar{G}_{O_2}$ values are higher for the lanthanum manganite with Al at the B-site dopant compared with the values obtained for the Ca-doped compound, suggesting a higher concentration of oxygen vacancies in the Al-doped compound. At the same devi-
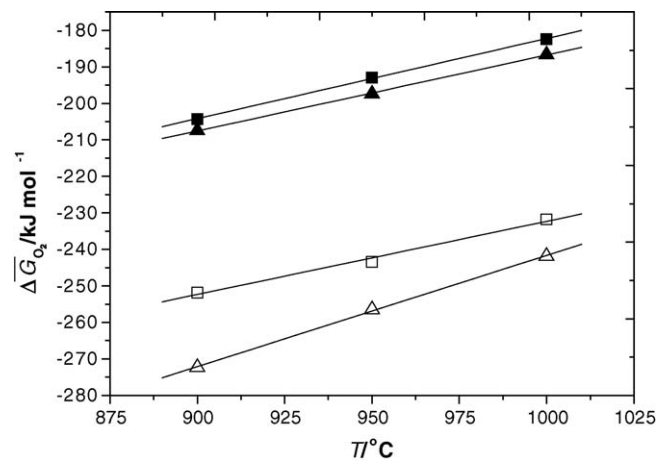

Fig. 1. The variations of $\Delta\bar{G}_{O_2}$ with temperature before and after titration ($\Delta\delta = 0.02$) for microstructured $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ ($x = 0$; 0.05). (▲) $La_{0.67}Ca_{0.33}MnO_3$ (■) $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_3$ (△) $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (□) $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_{3-\delta}$.
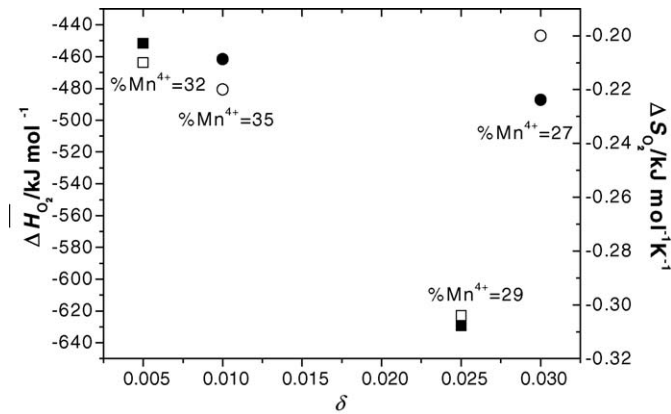
Fig. 2. $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ as a function of oxygen nonstoichiometry and the Mn^{4+} content for microstructured $La_{0.67}Ca_{0.33}Mn_{1-y}Al_yO_3$ ($y = 0$; 0.05). (■) $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (□) $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (●) $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_{3-\delta}$ (○) $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_{3-\delta}$.

Table 2
Comparison of the transition temperature T_C, Curie–Weiss temperature θ, exchange coupling integral J between Mn spins, polaron activation energy E_a and residual line width δH_0 in the paramagnetic regime of micro- and nanosized $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ manganites

Sample	T_C (K)	θ (K)	J (K)	E_a (meV)	δH_0 (G)
$La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (microstructure)	245	306	87	104	42
$La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (nanostructure)	201	271	39	83	70

ation of the oxygen stoichiometry ($\Delta\delta = 0.02$), the energy values increase with temperature. Regarding the changes of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ (Fig. 2), one can observe that for $La_{0.67}Ca_{0.33}MnO_3$ compound, both the variations of enthalpy and entropy decrease with the stoichiometry change. Instead, for the Al-doped manganite, higher values of $\Delta\bar{S}_{O_2}$ are obtained after titration. This finding can be explained by the relative redox stability of the B^{3+} ions which seems to modify (at the same A-site composition) both the mobility and the concentration of the oxygen vacancies. The data are tentatively interpreted as indicating an increase of order in the oxygen sublattice with the change in the stoichiometry.

The mean valence states of Mn were determined using redox titration. From the Mn^{4+} content of the samples (Fig. 2), one can see that the starting microstructured compounds are nearly stoichiometric. The values of Mn^{4+} obtained after the variation of oxygen stoichiometry with $\Delta\delta = 0.02$, attest the decrease of the Mn^{4+} concentration and the increase of the charge due to the oxygen vacancies. Thus, in the case of $La_{0.67}Ca_{0.33}MnO_{3-\delta}$, the charge introduced by Mn valence conversion is $(x - 2\delta) = 0.29^+$ and the charge due to the oxygen vacancy is $2\delta = 0.04^-$, which means that 88% of the residual charge introduced by Ca doping is balanced by the conversion of Mn^{3+} to Mn^{4+} and 12% by oxygen vacancies. However, the substitution of Al for Mn leads to oxidation, from Mn^{3+} to Mn^{4+}, resulting in a higher concentration of Mn^{4+} (Fig. 2). This result together with the EPR data suggests that the mixed-valence perovskites exhibit a critical dependence of properties on the oxygen stoichiometry. It can be concluded that the remarkable behaviour of the Al substituted samples could be explained not only qualitatively by the structural changes upon doping, but also by the fact that the double exchange energy is extremely sensitive to the chemical defects in oxygen sites. This is also confirmed by the observations of Abdelmoula and coworkers,[23] who reported a decrease of the transition temperature T_C and of the exchange energy as δ increases in the nonstoichiometric substituted lanthanum manganites.

3.3. The effects of the grain size on the spin dynamics and thermodynamic data

The effects of the grain size reduction on the spin dynamics in the paramagnetic regime of nanostructured $La_{0.67}Ca_{0.33}MnO_3$ could be also discussed in terms of the bottlenecked spin-relaxation scenario.[10] The results obtained for the nanostructured sample are presented in Table 2, together with the data obtained for $La_{0.67}Ca_{0.33}MnO_3$ samples with micrometer-scale-size grains. As one can see, the effect of decreasing grain size is to perturb the DE coupling between Mn^{4+} and Mn^{3+} ions, causing a reduction in J.

The dilution of J could be expected to result from the structural changes and the contribution of the inner core and outer surface layers.[10] Thus, one can imagine that the observed decrease of J could be partially attributed to both the increase of the Mn–O bond and the decrease of the Mn–O–Mn bond angles due to the change in the annealing temperature. More likely, the increased influence of the outer layer as the grain size decreases is mainly responsible for the degradation of the DE interaction. Due to the presence of a large strain and a great number of oxygen vacancies, dangling bonds, etc. in the surfaces, the spins are heavily disordered resulting in a magnetically disordered state. It could mean that the exchange coupling between Mn spins in the surfaces is much weaker than that in the inner core.[24] Since the surface of the smaller grains occupies a greater volume fraction, the magnetic interaction between Mn^{3+} and Mn^{4+} ions in the smaller grains is influenced more by the surface layer, explaining the decreasing of the DE effect in the surfaces at reduced grain sizes.

Fig. 3 presents comparative results for the $\Delta\bar{G}_{O_2}$ variations with the temperature for the Al-doped lanthanum manganites prepared by solid state reactions and sol–gel method. Between 600 and 850 °C, enhanced values of $\Delta\bar{G}_{O_2}$ were systematically found for the nanocrystalline specimen. Instead, at 950 and 1000 °C, the energy values of the nano- and microcrystalline samples are closest, suggesting an increase in the nano-grains size with temperature. This trend infers that for compounds with the same composition, but obtained by different methods (sol–gel method and solid state reactions, respectively) the variations of the thermodynamic data can be explained as a consequence of the grain-size dependent properties.

Considering the partial pressure of oxygen as a key parameter for the thermodynamic characterisation of the materials, we investigated the variation of the $\log p_{O_2}$ data with the stoi-
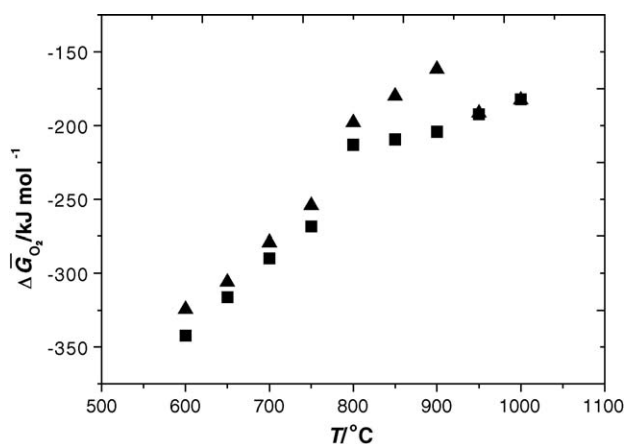
Fig. 3. The temperature dependence of $\Delta \bar{G}_{O_2}$ values for micro and nanostructured $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_3$ samples. (■) Microstructure; (▲) nanostructure.

chiometry change ($\Delta \delta = 0.02$) of the nano and microstructured $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_3$ samples (Fig. 4). While, before titration, at 950 and 1000 °C, the log p_{O_2} values of the nano- and microcrystalline samples are closest, after titration they are found to have distinctly different values; the corresponding log p_{O_2} values obtained for the stoichiometry change $\Delta \delta = 0.02$, being markedly enhanced in nanocrystalline solids.

Regarding the partial molar heats and the partial molar entropies of solution obtained after titration for the microstructured $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_{3-\delta}$ sample ($\Delta \bar{H}_{O_2} = -487.2 \pm 2.8\,kJ\,mol^{-1}$; $\Delta \bar{S}_{O_2} = -0.200 \pm 0.017\,kJ\,mol^{-1}\,K^{-1}$), they are comparatively higher than those of the nanostructured lanthanum manganite with the same composition ($\Delta \bar{H}_{O_2} = -595.7 \pm 8.2\,kJ\,mol^{-1}$; $\Delta \bar{S}_{O_2} = -0.304 \pm 0.006\,kJ\,mol^{-1}$ K^{-1}). The decrease of $\Delta \bar{H}_{O_2}$ and $\Delta \bar{S}_{O_2}$ values in the nanostructured samples suggest the increase of the binding energy of oxygen and an increase of order in the oxygen sublattice
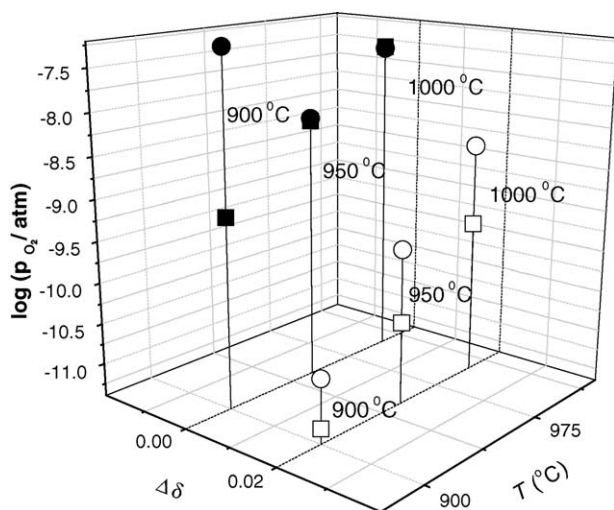
of the perovskite-type structure. The data obtained for the nanocrystalline ceramics can be discussed only in relation to the significant changes in the overall defect concentration, suggesting a reduced energy of oxygen vacancy formation. At the same time, the results show that the deviations from oxygen stoichiometry could significantly improve the oxygen storage capacity of nanocrystalline oxides.

4. Conclusions

In this study new features related to the effect of different compositional variables (the dopants, grain size, oxygen stoichiometry change) on the thermodynamic and magnetic properties of some CMR manganites are evidenced. Bearing in mind the role of charge ordering and of the defects chemistry in explaining their magnetic and thermodynamic behaviour, it should be possible to enhance the CMR properties of these materials by using a corresponding chemical route. The doping of Mn sites with various foreign cations and the decrease of the grain sizes proved to be efficient methods in obtaining variation of the CMR effects. However, further systematic investigations are necessary, as the preparation method should be carefully controlled in order to obtain samples with the desired magneto-transport properties.

References

1. Blasco, J., Garcia, J., de Teresa, M., Ibarra, M. R., Perez, J., Algarabel, P. A. *et al.*, Structural, magnetic and transport properties of the giant magnetorezistive perovskites $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_{3-\delta}$. *Phys. Rev. B*, 1997, **55**, 8905–8910.
2. Sun, J. R., Rao, G. H., Gao, X. R., Liang, J. K., Wang, H. K. and Shen, B. G., Structural and magnetoresistive properties of $La_{0.7}Ca_{0.3}Mn_{0.96}(Al_{1-x}In_x)_{0.04}O_3$. *J. Appl. Phys.*, 1999, **85**, 3619–3622.
3. Giurgiu, L. V., Grecu, M. N., Filip, X., Raita, O., Darabont, Al., Gavre, D. *et al.*, Spin dynamics investigated by EPR in the paramagnetic regime of $La_{2/3}Ca_{1/3}Mn_{1-x}Me_xO_3$ (Me = Al In). *Appl. Mag. Reson.*, 2003, **24**, 351–360.
4. Sawaki, Y., Takenaka, K., Osuka, A., Shiozaki, R. and Sugai, S., Al-substitution effect on charge transport in $La_{1-x}Sr_xMnO_3$: incoherent metallic state in a double-exchange ferromagnet. *Phys. Rev. B*, 2000, **61**, 11588–11593.
5. Schoonman, J., Nanostructured materials in solid state ionics. *Solid State Ionics*, 2000, **135**, 5–19.
6. Ten Wolde, A. and Schoonman, J., Towards a molecular construction kit. In *Nanotechnology*, ed. Arthur ten Wolde. Hague, 1998, pp. 147–214.
7. Maier, J., Thermodynamic aspects and morphology of nano-structured ion conductors. Aspects of nano-ionics. Part I. *Solid State Ionics*, 2002, **291**, 154–155.
8. Navrotsky, A., *Thermochemistry of Nanomaterials Communication and Integration in Nanomaterials*, NSF Sponsored Workshop, Brasov, Romania, September 30–October 2, 2002.
9. Tanasescu, S., Marinescu, C. and Maxim, F., Thermodynamic properties of nano- and micro- structured perovskite-type compounds. *Solid State Phenomena*, 2004, **99–100**, 117–122.
10. Raita, O., Grecu, M. N., Filip, X., Darabont, Al., Gavre, D., Blasco, J. *et al.*, Effects of In doping investigated by ESR in colossal magnetoresistive manganite $La_{2/3}Ca_{1/3}MnO_3$. *J. Optoelectron. Adv. Mater.*, 2003, **5**, 279–287.
11. Tanasescu, S., Totir, N. D. and Marchidan, D. I., Thermodynamic data of the perovskite-type $LaMnO_{3\pm x}$ and $La_{0.7}Sr_{0.3}MnO_{3\pm x}$ by a solid state electrochemical technique. *Electrochim. Acta*, 1998, **43**, 1675–1681.

Fig. 4. The variation of log Δp_{O_2} with temperature and oxygen stoichiometry change for micro- and nanostructured $La_{0.67}Ca_{0.33}Mn_{0.95}Al_{0.05}O_3$ samples. (■) Microstructure, before titration (●) nanostructure, before titration (□) microstructure, after titration (○) nanostructure, after titration.

12. Tanasescu, S., Totir, N. D. and Marchidan, D. I., Thermodynamic properties of some perovskite type oxides used as SOFC cathode materials. *Solid State Ionics*, 1999, **119**, 311–315.

13. Licci, F., Turilli, G. and Ferro, P., Determination of manganese valence in complex La-Mn perovskites. *J. Magn. Magn. Mater.*, 1996, **164**, 268–272.

14. Shengelaya, A., Zhao, G. M., Keller, H. and Muller, K. A., EPR evidence of Jahn-Teller polaron formation in $La_{1-x}Ca_xMnO_{3+y}$. *Phys. Rev. Lett.*, 1996, **77**, 5296–5299.

15. Shengelaya, A., Zhao, G. M., Keller, H., Muller, K. A. and Kochelaev, B. I., EPR in $La_{1-x}Ca_xMnO_3$: relaxation and bottleneck. *Phys. Rev. B*, 2000, **61**, 5888–5890.

16. Gupta, R., Joshi, J. P., Bhat, S. V., Sood, A. K. and Rao, C. N. R., An electron paramagnetic resonance study of $Pr_{0.6}Ca_{0.4}MnO_3$ across the charge-ordering transition. *J. Phys. Condens. Mater.*, 2000, **12**, 6919–6926.

17. De Teresa, J. M., Dorr, K., Muller, K. H. and Shultz, L., Strong influence of the Mn^{3+} content on the binding energy of the lattice polarons in manganese perovskites. *Phys. Rev. B*, 1998, **58**, 5928–5931.

18. Jonker, G. H. and van Santen, J. H., Magnetic compounds with perovskite structure. *Physica*, 1953, **19**, 120–130.

19. Wang, Z. L., Yin, J. S., Jiang, Y. D. and Zhang, J., Studies of Mn valence conversion and oxygen vacancies in $La_{1-x}Ca_xMnO_{3-y}$ using electron energy-loss spectroscopy. *Appl. Phys. Lett.*, 1997, **70**, 3362–3364.

20. Charette, G. G. and Flengas, S. N., Thermodynamic properties of the oxides of Fe, Ni, Pb, Cu, and Mn, by EMF measurements. *J. Electrochem. Soc.*, 1968, **8**, 796–804.

21. Kelley, K. K., *U.S. Bur. Mines Bull.*, 1960, no. 584.

22. Kelley, K. K. and King, E. G., *U.S. Bur. Mines Bull.*, 1961, no. 592.

23. Abdelmoula, N., Guidara, K., Cheikh-Rouhou, A., Dhahri, E. and Joubert, J. C., Effects of the oxygen nonstoichiometry on the physical properties of $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ manganites $(0 \le \delta \le 0.15)$. *J. Solid State Chem.*, 2000, **151**, 139–144.

24. Zhang, N., Ding, W., Zhong, W., Xing, D. and Du, Y., Tunnel-type giant magnetoresistive in the granular perovskite $La_{0.85}Sr_{0.15}MnO_3$. *Phys. Rev. B*, 1997, **56**, 8138–8142.