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Journal of Alloys and Compounds 262–263 (1997) 163–168

Journal of ALLOYS AND COMPOUNDS

Controlled reduction and oxidation of $La_{0.85}Sr_{0.15}MnO_3$ single crystals

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Abstract

$La_{0.85}Sr_{0.15}MnO_3$ single crystals were grown by the floating zone method. They can be reversibly reduced under controlled oxygen partial pressure. Their defect chemistry is investigated together with the evolution of their cell parameters and that of their electric conductivity which is very sensitive to their oxygen content. On the other hand, stoichiometric crystals can be oxidized with a slow kinetics making possible the preparation of diphasic materials. © 1997 Elsevier Science S.A.

Keywords: Lanthanum manganites; Magnetic materials; Thermogravimetric analysis; Non-stoichiometry; Electrical properties

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1. Introduction

The discovery of giant magnetoresistance [1–3] in the $La_{1-x}A_xMnO_3$ system (A = Ca, Sr) has attracted renewed interest on these mixed-valence perovskites [4–9]. The electric and magnetic properties of these materials are related to the double exchange interaction between Mn^{3+} and Mn^{4+} ions [10–12]. Consequently, the transport properties of these substituted manganites depend on the Mn^{4+}/Mn^{3+} ratio and on structural parameters such as the distance between the Mn–O planes or the Mn–O–Mn bond angles. For a given divalent A ion, both the Mn^{4+}/Mn^{3+} ratio and the crystallographic structure may be modified by changing the substitution degree x or by controlling the oxygen content of the material.

For most polycrystalline samples prepared by solid state reaction or from wet chemical processes, an oxygen excess is found. Conversely, for samples heat treated under reducing conditions an oxygen deficiency can be observed [13–16]. From a structural point of view, an oxygen excess is generally related to cation vacancies, whereas an oxygen deficiency is associated with oxygen vacancies in the perovskite network. To account for these kinds of defect, the chemical formulae may be, respectively written $(La_{1-x}A_x)_{1-y}Mn_{1-y}O_3$ and $La_{1-x}A_xMnO_{3-\delta}$. However, the presence of interstitial oxygen atoms in the structure was pointed out by Alonso et al. [17] for samples prepared under high oxygen pressures.

To obtain reliable data concerning the properties of the non-stoichoimetric materials, a high homogeneity is required. Such an homogeneity can be obtained when all the samples under examination come from the same single crystal. Therefore, in the present article, we report the preparation and the study of reduced single crystals $La_{0.85}Sr_{0.15}MnO_{3-\delta}$ $(0 \leq \delta \leq 0.135)$ equilibrated under low oxygen partial pressures. For this large non-stoichiometry range, three valency states of the manganese ions must be taken into account to discuss the equilibrium conditions of the material at high temperature. A particular attention is paid to the structural evolution of the samples

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0925-8388/97/$17.00
PII S0925-8388(97)00373-3

in relation with their transport properties. Despite the slow kinetics of the reaction, some preliminary results concerning the oxidation of single crystals are also presented.

2. Experimental

The feed rod used for the crystal growth was prepared by solid state reaction of a mixture of La_2O_3 (Prolabo, Rectapur, 99.995%) previously heated at 900°C, $SrCO_3$ (Prolabo, Rectapur, 99%) and MnO_2 (Johnson Matthey, reagent grade) checked by thermogravimetric analysis. The powder mixture was heated in air at 1100°C for 3 days with three intermediate grindings; then, it was isostatically pressed at 1500 bars to obtain a cylindrical rod which was sintered at 1100°C. Using the back-reflection Laue method a [001] oriented seed was cut from a previously grown crystal and used to grow the new single crystal along the same [001] direction. The crystal growth was carried out using the floating zone method in an image furnace [18,19] under a convenient atmosphere. The crystal and the feed rod were rotated in opposite directions at 30 rpm and the translation speed was 7 mm h^{-1}. Under these conditions, a 10-cm long and 4-mm diameter crystal was obtained. All the samples used in the present study were cut in this crystal.

A quantitative analysis of the metallic elements was made by EDAX (JEOL 2000 FX) at the extremities of the single crystal and showed an invariant composition. The homogeneity of a crystal of the same composition and grown in the same conditions was also checked by ICP/AES chemical analyses carried out on crystal fractions cut at 1 cm from one another.

Changes in oxygen stoichiometry under reducing conditions were determined, at 1000°C, through thermogravimetry by measuring the weight change of a part of the grown crystal (1.3 g) as a function of the oxygen partial pressure $p(O_2)$. Thermogravimetric measurements were made using an Ugine Eyraud thermobalance having a resolution of 10 μg. Various oxygen partial pressures were obtained using H_2/H_2O or N_2/O_2 mixtures, they were measured with a zirconia probe and ranged from 10^{-16} to 10^{-5} atm. Using the results of this preliminary study, several samples with various stoichiometries were obtained by quenching single crystal fragments heated at 1000°C for 16 h under an oxygen partial pressure obtained from CO/CO_2 mixtures. The mass variations of these samples were measured with an accuracy of ± 0.2 mg. The crystallographic characteristics of the reduced samples were obtained by powder X-ray diffraction with a Seeman–Bohlin camera (Co–$K_{\alpha 1}$, $\lambda = 1.7889$ Å) using $Al(PO_3)_3$ as internal standard. Cell parameters were refined by a least square method with the SILEX programme.

The DC electrical conductivity was measured as a function of temperature using a four-probe technique on 8-mm long rectangular-shaped samples. The current flow was parallel to the largest dimension of the sample which contains the [001] cristallographic direction. All the data were collected with a computer driven system, using a Keithley 224 current source and a Keithley 196 digital multimeter for the voltage measurements. Magnetic measurements were carried out with a SQUID magnetometer (Quantum Design MPMS-5).

3. Stoichiometry of the reduced samples

A first aim of this work was to determine the oxygen stoichiometry of the as-grown crystal and the thermodynamic conditions of its reduction. Owing to the lack of a reference state for Sr-doped $LaMnO_3$, a first step consisted in determining the point corresponding to $\delta = 0$. The weakest variation of the sample weight in relation to log $p(O_2)$ was observed for a variation of $p(O_2)$ from 1.4×10^{-10} to 2.5×10^{-6} atm (Fig. 1), it corresponds to a variation $\Delta\delta = -4.5 \times 10^{-3}$. This indicates that between these points $\partial\delta/\partial$ log $p(O_2)$ is close to its minimum value which corresponds to the stoichiometric composition according to a statistical thermodynamic calculation made by Wagner [20]. Moreover, it clearly appeared that no oxygen excess is found in the sample treated at 2.5×10^{-6} atm, since after being reduced under 6.8×10^{-16} atm it could be equilibrated again in less than 16 h under the former pressure. Conversely, in the oxygen excess region the oxidation kinetics of a single-crystalline material is very slow. For example, starting with a sample equilibrated under 2.5×10^{-6} atm, no equilibrium was reached after a 5-day treatment under pure oxygen at 1000°C. Taking into account the weight variations observed upon several attempts at oxidizing single-crystalline samples, the oxygen deficiency, δ, cannot be larger than 5×10^{-3} and is more likely much smaller. Therefore, the sample in equilibrium under $p(O_2) = 2.5 \times 10^{-6}$ atm at 1000°C is considered to have the stoichiometric composition ($\delta = 0$). These equilibrium conditions are in good agreement with those previously reported for polycrystalline samples with close strontium contents [15]. From these conditions, a sample was quenched at room temperature. Its weight after the treatment was the same as the initial one. This clearly indicates that the as-grown crystal has a stoichiometric composition $\delta = 0$.

The second step of this work was to establish the relation between δ and $p(O_2)$. Some points were obtained from the thermogravimetric measurements [$p(O_2) = 2.5 \times 10^{-6}$, 1.4×10^{-10}, 6.8×10^{-14} and 6.8×10^{-16} atm] and complementary data were deduced, with a poorer accuracy, from the weight changes of

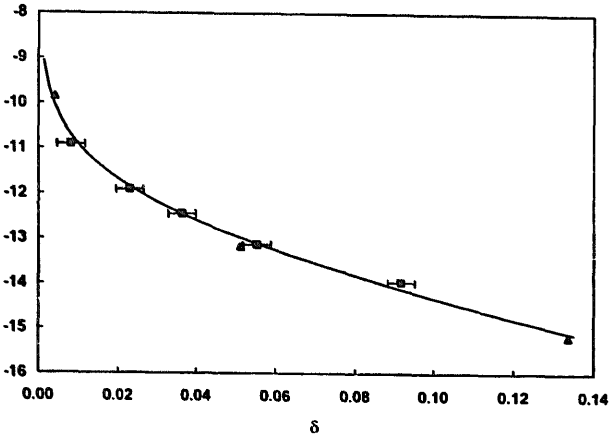

Fig. 1. Experimental dependence of log $p(O_2)$ with the non-stoichiometry δ. The triangles correspond to the initial thermogravimetric study and the squares to the samples equilibrated under CO/CO_2. The curve represents the calculated isotherm.

crystals equilibrated with CO/CO_2 mixtures (Fig. 1). The shape of the log $p(O_2) = f(\delta)$ curve is similar to that obtained for polycrystalline samples containing various strontium amounts [15]. To explain the relation between δ and $p(O_2)$, the evolution of the defect chemistry of the material under study must be examinated. At room temperature, manganese ions are found in two valency states which depend on the oxygen deficiency. For highly reduced samples ($\delta > x/2$) these valency states are 2+ and 3+, whereas for lower non-stoichiometries ($\delta < x/2$) they are 3+ and 4+. At high temperature, it is likely that the three valency states can be found together since no particular feature is observed on the log $p(O_2) = f(\delta)$ curve around $\delta = x/2$. Therefore an attempt was made to reproduce our data by taking into account the two chemical equilibria suggested by Kuo et al. [15]. The first reaction describes the reduction of Mn^{4+} in Mn^{3+} with the formation of oxygen vacancies; using the Kröger–Vink notation, it can be written as:

$$2Mn^{\bullet}_{Mn} + O_O \Leftrightarrow 2Mn^{x}_{Mn} + V^{\bullet\bullet}_{O} + \tfrac{1}{2}O_2 \tag{1}$$

its equilibrium constant is:

$$K_1 = [Mn^{x}_{Mn}]^2[V^{\bullet\bullet}_{O}]P(O_2)^{\frac{1}{2}}/[Mn^{\bullet}_{Mn}]^2[O_O]$$

The concentrations of the manganese ions under their different valency states are related by the disproportionation equilibrium:

$$2Mn^{x}_{Mn} \Leftrightarrow Mn'_{Mn} + Mn^{\bullet}_{Mn} \tag{2}$$

with the following constant:

$$K_2 = [Mn'_{Mn}][Mn^{\bullet}_{Mn}]/[Mn^{x}_{Mn}]^2$$

the equation for electroneutrality is:

$$[Sr'_{La}] + [Mn'_{Mn}] = 2[V^{\bullet\bullet}_{O}] + [Mn^{\bullet}_{Mn}] \tag{3}$$

and that describing the conservation of manganese:

$$[Mn'_{Mn}] + [Mn^{\bullet}_{Mn}] + [Mn^{x}_{Mn}] = 1 \tag{4}$$

These equations can be expressed by taking into account the lanthanum substitution degree $[Sr'_{La}] = x$ and the oxygen deficiency through $[V^{\bullet\bullet}_{O}] = \delta$ and $[O_O] = 3 - \delta$. Then the concentrations of each kind of manganese ions can be calculated as a function of δ, x and K_2. Therefore, for a given strontium content x, the oxygen partial pressure can be expressed as a function of δ, K_1 and K_2. The equilibrium constants were obtained by a least square procedure minimizing the expression $\Sigma[\log\, p(O_2)_{cal} - \log\, p(O_2)_{exp}]^2$. An excellent agreement is obtained between our data and the calculated isotherm (Fig. 1). The values of the calculated constants K_1 and K_2 are reported in Table 1 together with those obtained with the same procedure for the data of Kuo et al. [15]. The satisfying agreement between the experimental and the calculated data suggests that a model taking into account the equilibria (1) and (2) is convenient to describe the behaviour of the three compositions at high temperature. However, a comparison of the values of K_1 and K_2 obtained for the different compositions does not lead to a clear-cut conclusion. It seems a bit surprising to find the lowest value of the disproportionation constant for $x = 0.15$ and the highest value for $x = 0.20$. A possible explanation for these unexpected results may be the use by Kuo et al. of H_2/CO_2 based mixtures which are known to react very slowly below 1500°C; in particular, we believe that the actual oxygen partial pressures are higher than those reported by these authors since an attempt to reduce undoped $LaMnO_3$ at 1000°C under 1×10^{-16} atm led to the decomposition of the sample, which is in contradiction with their data. Some cation non-stoichiometry may also be invoked, for example a small lanthanum deficiency in a sample would increase its Mn^{4+} content.

The model describing our data is that of a random distribution of the oxygen vacancies on the perovskite

Table 1
Equilibrium constants determined at 1000°C for various strontium contents x

x	0.10 [15]	0.15	0.20 [15]
$K_1/\mathrm{atm}^{1/2}$	0.11×10^{-7}	0.17×10^{-6}	0.10×10^{-7}
K_2	0.094	0.021	0.38

lattice taking place together with a disproportionation of Mn^{3+} ions. No extended defects are to be considered in such a model in contrast to the results reported for undoped $LaMnO_{3-\delta}$ [21]. Disproportionation at high temperature was taken into account by Mizusaki et al. [22] to interpret the reduction of $La_{1-x}Sr_xFeO_{3-\delta}$ and by Kuo et al. for the above-mentioned data. It was also taken into account in the oxygen excess region to explain the electrical conductivity and the defect chemistry of $La_{1-x}Sr_xMnO_{3+\delta}$ [23,24]. Therefore this model seems suitable to interpret a large number of data in addition to those reported here.

4. Properties of the reduced samples

Powder X-ray diffraction patterns were recorded for all the samples except for the most reduced one ($\delta = 0.135$) which was reoxidized during the initial thermogravimetric study. For $\delta \leq 0.055$, X-ray diffraction indicates that the samples are single phase (Fig. 2) since all the reflections can be indexed in the orthorhombic system with the Pbnm space group (no. 62). For $\delta = 0.092$, no indexation was possible hitherto but no indication of a decomposition was found either. Moreover, at the reduction temperature (1000°C) the most reduced sample ($\delta = 0.135$) seems to be made of a single phase since after its reoxidation it was still in single crystalline form. However, at room temperature a decomposition cannot be completely discarded; such a decomposition was reported for oxygen deficient $LaMnO_{3-\delta}$ below 600°C [25] with the formation of a compound containing ordered anion vacancies.

In stoichiometric $La_{0.85}Sr_{0.15}MnO_3$, the *b* parameter is found smaller than the a parameter, unlike what is found in undoped $LaMnO_3$ [25] or in samples with low strontium content [5,7]. This result is in agreement with that obtained by Kawano et al. by neutron diffraction [7] but not with the extrapolation presented in [5]. In the interpretation of the diffraction pattern, an inversion between the *a* and *b* parameters can easily be done since the indexation of most lines does not make it possible to choose between the settings corresponding to Pbnm and Pnam. For the sample under study, the reported parameters are based on the observation of the 021 reflection which is allowed for Pbnm but not for Pnam. Moreover, our data showed that the a parameter presents a weak variation with the oxygen deficiency, a behaviour which is similar to that observed in function of the lanthanum substitution degree *x*.

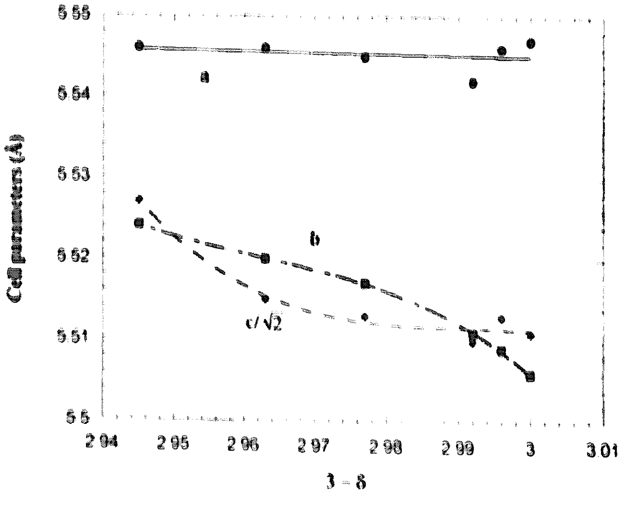

Fig. 2. Cell parameters as a function of the non-stoichiometry δ in the Pbnm S.G.

The *c* parameter increases with the oxygen deficiency whereas it decreases with decreasing strontium content [5]. This means that for a similar Mn^{4+}/Mn^{3+} ratio, the *a*,*b* planes are more distant from one another in the oxygen deficient material than in the corresponding strontium-substituted material ($x = 0.15 - 2\delta$), thus the antiferromagnetic coupling along the *c* axis [26] should be weaker in the former material.

The conductivity of the samples (Fig. 3) is very sensitive to their oxygen content, when δ increases from 0 to 0.092 it is divided by approx. 50 at room temperature and by more than 10^4 at 100 K. The metallic behaviour which is observed between 210 and 240 K for the stoichiometric sample disappears completely for $\delta \geq 0.04$. The decrease of the conductivity is due to the decrease of the hole (Mn^{4+}) concentration and also to the oxygen vacancies which break the path of the electron hoppings. However, the modification of the crystalline structure should also be taken into account. For $\delta \leq 0.04$, a more detailed study of the conductivity is presented elsewhere together with that of the magnetoresistance [27]. The most reduced sample ($\delta = 0.092$) exhibits the highest resistivity, but it is worth noting that with such an oxygen deficiency it should contain only Mn^{2+} and Mn^{3+} ions at low temperature. Therefore, for this composition there is no more hole doping but rather electron doping. It is likely that for a non-stoichiometry close to $x/2$ the resistivity would be higher than that reported here for the two closest compositions since the carrier concentration should be very weak.

5. Oxidized samples

Partial oxidations of crystal fractions were carried out between 750°C and 900°C for times ranging from 12 h to 4 days (Table 2). Whereas no weight increase could be detected after this treatment (partly because of the small size of the samples), the resistivity of the annealed samples is always lower than that of the

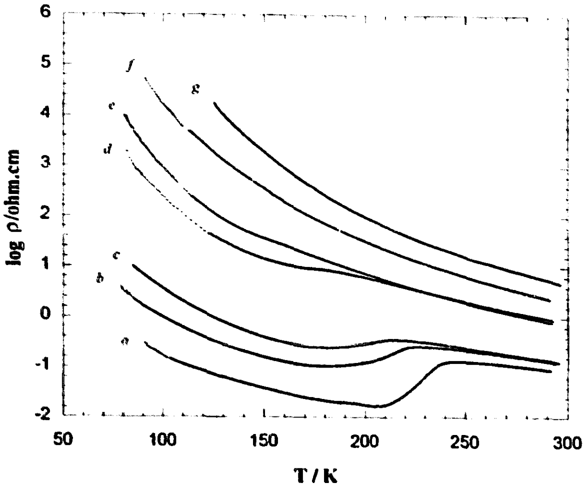

Fig. 3. Resistivity of the reduced samples as a function of the temperature for $\delta = 0$ (a), 0.004 (b), 0.008 (c), 0.023 (d), 0.037 (e), 0.055 (f) and 0.092 (g).

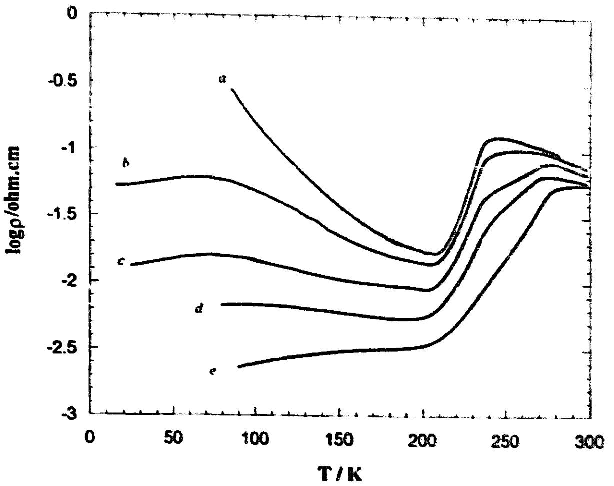

Fig. 4. Resistivity of the oxidized samples as a function of the temperature for the as-grown crystal (a) and for samples treated as indicated in Table 1 (b, c, d and e).

starting crystal (Fig. 4), this clearly indicates an oxidation. The shape of all the curves is characteristic of a more complex behaviour than that of the stoichiometric crystal and it is worth noting that at low temperature all the samples exhibit a metallic behaviour. It seems that the electrical conductivity of the samples under study is the sum of two contributions, one more or less similar to that of the stoichiometric material and the other related to an oxidized phase. As abovementioned, the oxidation of strontium-substituted lanthanum manganites under ordinary pressures is generally interpreted by the formation of cation vacancies. The kinetics of this reaction is slow for single crystals since it requires cation diffusion. In the material under study, a thin surface layer of an oxidized phase is formed upon annealing, whereas the core keeps its original stoichiometry. Therefore, the sample is equivalent to two resistances in a parallel configuration. A relevant parameter to take into account the relative contributions of the two phases is their thickness. This is obvious in comparing the resistivities of samples (d) and (e) oxidized in the same conditions. For sample (d), the presence of two phases is indicated by the bump observed near 240 K and by the transition from a semi-conducting to a metallic behaviour near 100 K. The thickness of the oxidized layer should be the same for both samples, but the lower thickness of sample (e) makes it difficult to detect the presence of its unoxidized fraction; the resistivity curve has a shape similar to that observed for a single crystal with a strontium content $x = 0.175$ [28]. This does not mean that this sample is completely oxidized but that its mean conductivity is dominated by that of the oxidized layer. The comparison of the resistivity curves of samples (c) and (d), which have the same thickness, indicates that the oxidized layer of sample (d) is thicker than that of sample (c). As the latter was treated for the same period of time but at lower temperature, this results from a slower cation diffusion.

Table 2
Characteristics of the oxidized samples

Sample	Thickness (mm)	Oxidation conditions
b	2.0	12 h/760°C/O_2
c	0.50	99 h/750°C/air
d	0.50	95 h/900°C/air
e	0.29	95 h/900°C/air

The presence of two phases in the oxidized samples is also confirmed by their magnetization curves which are all similar to that of sample (c) presented in Fig. 5. The oxidized layer of this sample has a Curie temperature T_C close to 280 K, whereas T_C is close to 240 K for the stoichiometric core. From the intensity of the magnetization in the shoulder region around 270 K, it appears that the oxidized fraction of the material is clearly smaller than the unoxidized fraction. A more detailed study of this region under different magnetic fields would be useful to estimate the relative fraction of both phases. All the features observed on the magnetization curve have their counterparts on the resistivity curve, which illustrates the close relationship between the electrical and magnetic properties of these materials.

6. Conclusion

It has been shown that single crystals of $La_{0.85}Sr_{0.15}MnO_3$ grown by the floating zone method are stoichiometric. They can easily and reversibly be reduced under low oxygen partial pressures. The re-

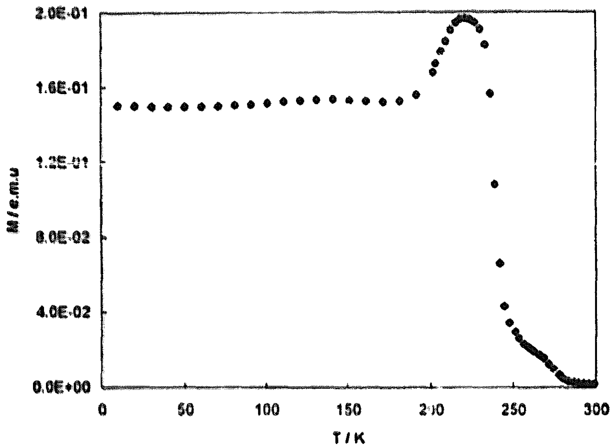

Fig. 5. Magnetization curve (B = 0.05 T) as a function of the temperature for oxidized sample (c).

duction isotherms can be interpreted by taking into account a disproportionation of the Mn^{3+} ions at high temperature. The low temperature conductivity of the samples is highly sensitive to oxygen deficiency but its evolution depends also on that of the cell parameters. The oxidation of single-crystalline material has a slow kinetics since it requires cation diffusion. Therefore diphasic samples can be obtained by controlling the oxidation time as revealed by the resistivity and magnetization measurements.

Acknowledgements

This work was supported by the European Union program 'Training and Mobility of Researchers', in the frame of the 'Oxide Spin Electronics Network' (OXSEN). One of us (A.M.D.) is grateful to Universidad Nacional Autónoma de México (UNAM) for financial support.

References

[1] R. von Helmolt, B. Holzapfel, L. Schultz, K. Samwer, Phys. Rev. Lett. 71 (1993) 2331.
[2] K. Chahara, T. Ohno, M. Kasai, Y. Kozono, Appl. Phys. Lett. 63 (1993) 1990.
[3] S. Jin, T.H. Tiefel, M. Mc Cormack, R.A. Fastnachat, R. Ramesh, L.H. Chen, Science 264 (1994) 413.
[4] Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, N. Furukawa, J. Phys. Soc. Jpn 63 (1994) 3931.
[5] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, Y. Tokura, Phys. Rev. B 51 (1995) 14103.
[6] H. Kamata, Y. Yonemura, J. Mizusaki, H. Tagawa, K. Naraya, T. Sasamoto, J. Phys. Chem. Solids 56 (1995) 943.
[7] H. Kawano, R. Kajimoto, M. Kubota, H. Yoshizawa, Phys. Rev. B 53 (1996) 2202.
[8] J.F. Mitchell, D.N. Argyriou, C.D. Potter, D.G. Hinks, J.D. Jorgensen, S.D. Bader, Phys. Rev. B 54 (1996) 6172.
[9] C.N.R. Rao, A.K. Cheetham, R. Mahesh, Chem. Mater. 8 (1996) 2421.
[10] C. Zener, Phys. Rev. 82 (1951) 403.
[11] P.W. Anderson, H. Hasegawa, Phys. Rev. 100 (1955) 675.
[12] P.G. de Gennes, Phys. Rev. 118 (1960) 141.
[13] K. Kamata, T. Nakajima, T. Hayashi, T. Nakamura, Mat. Res. Bull. 13 (1978) 49.
[14] S. Tamura, A. Yamato, J. Mater. Sci. 15 (1980) 2120.
[15] J.H. Kuo, H.U. Anderson, D.M. Sparlin, J. Solid State Chem. 83 (1989) 52.
[16] J. Mizusaki, H. Tagawa, K. Naraya, T. Sasamoto, Solid State Ionics 49 (1991) 111.
[17] J.A. Alonso, M.J. Martínez-Lope, M.T. Casais, Eur. J. Solid State Inorg. Chem. 33 (1996) 331.
[18] A. Revcolevschi, R. Collongues, CR Acad. Sci., Paris 266 (1969) 1767.
[19] A. Revcolevschi, Rev. Int. Hautes Temp. 7 (1970) 73.
[20] C. Wagner, Prog. Solid State Chem. 6 (1971) 1.
[21] J.A.M. van Roosmalen, E.H.P. Cordfunke, J. Solid State Chem. 93 (1991) 212.
[22] J. Mizusaki, M. Yoshihiro, S. Yamauchi, K. Fueki, J. Solid State Chem. 58 (1985) 257.
[23] J.A.M. van Roosmalen, J.P.P. Huijsmans, L. Plomp, Solid State Ionics 66 (1993) 279.
[24] J.A.M. van Roosmalen, E.H.P. Cordfunke, J. Solid State Chem. 110 (1994) 109.
[25] F. Abbattista, M. Lucco Borlera, Ceramics Int. 7 (1981) 137.
[26] J.B. Goodenough, A. Wold, A.J. Arnott, N. Menyuk, Phys. Rev. 124 (1961) 373.
[27] A.M. De León-Guevara, P. Berthet, J. Berthon, F. Millot, A. Revcolevschi, A. Anane, C. Dupas, K. Le Dang, J.P. Renard, P. Veillet, Phys. Rev. B (in press).
[28] A. Anane, C. Dupas, K. Le Dang, J.P. Renard, P. Veillet, A.M. Deleón-Guevara, F. Millot, L. Pinsard, A. Revcolevschi, J. Phys. Condens. Matter 7 (1995) 7015.