ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 5, pp. 807–811. © Pleiades Publishing, Ltd., 2007.
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# States of Atoms and Interatomic Interactions in Perovskite-like Oxides: XXI.[1] Effect of Dopant Nature on the Magnetic Properties of Lanthanum Manganites $x(La_{1-y}Y_y)_{0.67}Ca_{0.33}MnO_3–(1-x)La_{1-y}Y_yAlO_3$

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Received October 26, 2006

**Abstract** — A procedure of sol–gel synthesis was developed and solid solutions of lanthanum manganites doped with calcium and yttrium, containing 10 and 20% of yttrium, were obtained. The temperature and concentration dependences of the magnetic characteristics of the solid solutions were examined to reveal exchange interactions in the doped manganites and reasons for their different magnetic behavior. The properties of yttrium-substituted manganites vary nonmonotonically with increasing concentration of yttrium.
**DOI:** 10.1134/S1070363207050015

Magnetoresistive manganites with the perovskite structure are the subject of intensive studies in recent years. This is associated with the giant magnetoresistance (GMR) effect found in these compounds. The essence of the GMR consists in an abrupt decrease of the resistance in a magnetic field, which makes manganites promising materials in modern engineering. The giant magnetoresistance is a cooperative phenomenon associated with exchange interactions between different-valence paramagnetic atoms and depends on their ratio which, in its turn, depends on the nature of the doping cation.

At present a wide range of various $R_{1-x}A_xMnO_3$ manganites (R is a rare-earth element and A is a doping bivalent cation) has been obtained and studied. However, the problem of the mechanism of the dopant effect on the GMR is still unsolved.

The effect of the nature of the doping cation on the physicochemical properties of a material can be traced by the magnetic dilution method which allows to study magnetic characteristics of dilute solid solutions of isomorphous substitution. Magnetic dilution studies in the $La_{0.67}(Ca, Sr, Ba)_{0.33}MnO_3$–$LaAlO_3$ systems [2, 3, 4] showed that the state of manganese atoms and the character of exchange interactions substantially depend on the nature of the doping element. Published data on the magnetoresistance of the $La_{2/3-x}Y_x \cdot Ca_{1/3-y}Sr_yMnO_3$ compounds [5] point to the fact that the magnetic properties are affected not only by the nature of the doping bivalent element, but also by substitution of lanthanum by other trivalent elements (yttrium). Introduction of one or another substituent cation into the structure affects the geometry of the latter, which is most pronounced in magnetic characteristics. Replacement of a part of lanthanum atoms by yttrium having a smaller radius results in stronger electron polarization of oxygen atoms and in a certain distortion of the coordination polyhedra.

In this work an attempt was made to trace how magnetic characteristics of solid solutions of lanthanum manganite doped with calcium change as various quantities of yttrium are introduced into the lanthanum sublattice. The results were compared with those found earlier [2] for the $La_{1-0.33x}Ca_{0.33x}Mn_xAl_{1-x}O_3$ solid solutions. As $La_{1-y}Y_yAlO_3$ were impossible to obtain by the ceramic procedure, we developed a procedure for sol–gel synthesis by reactions (1) and (2).

We prepared $La_{1-y}Y_yAlO_3$ diamagnetic matrices ($y$ 0.1, 0.2) and $x(La_{1-1}Y_y)_{0.67}Ca_{0.33}MnO_3–(1-x) \cdot La_{1-y}Y_yAlO_3$ ($0.01 \le x \le 0.1$; $y$ 0.1, 0.2) solid solutions, and measured their magnetic susceptibility in the temperature range 77–400 K.

[1] For communication XX, see [1].

$$(0.8 - 0.264_x)LaO_{1.5} + (0.2 - 0.066_x)YO_{1.5} + 0.33xCaCO_3 + xMnO_{1.5} + (1 - x)AlO_{1.5} \longrightarrow La_{0.8-0.264x}Y_{0.2-0.066x}Ca_{0.33x}Mn_xAl_{1-x}O_3 + 0.33CO_2, \quad (1)$$
$$x\ 0.005–0.1,\ y\ 0.2,$$

$$(0.9 - 0.297_x)LaO_{1.5} + (0.1 - 0.033_x)YO_{1.5} + 0.33xCaCO_3 + xMnO_{1.5} + (1 - x)AlO_{1.5} \longrightarrow La_{0.9-0.297x}Y_{0.2-0.033x}Ca_{0.33x}Mn_xAl_{1-x}O_3 + 0.33CO_2, \quad (2)$$
$$x\ 0.005–0.1,\ y\ 0.1.$$

The paramagnetic component of magnetic susceptibility per 1 mol of manganese atoms and the effective magnetic moment were calculated, and their temperature and concentration dependences were plotted. The effective magnetic moments at infinite dilution were determined by extrapolation of magnetic susceptibility to $x \to 0$.

The isotherms of the paramagnetic component of magnetic susceptibility per 1 mol of manganese atoms for systems with various yttrium contents substantially differ from the isotherms for solid solutions containing no yttrium (Fig. 1). The isotherms for solid solutions with 10% of yttrium lie higher than the isotherms for manganites with $y$ 0.2; these latter are between the isotherms for lanthanum manganite without yttrium. In the case of $La_{0.67}Ca_{0.33}MnO_3$–$LaAlO_3$, the magnetic susceptibility monotonically increases over the whole concentration range. Introduction of 10 and 20% of yttrium drastically changes the character of the isotherms of magnetic susceptibility. In the solid solutions containing 10% of yttrium, $\chi_{Mn}$ decreases as the concentration increases, and starting from $x \approx 0.04$, its monotonic increase is observed. The isotherms of magnetic susceptibility in the case of manganites containing 20% of yttrium show a maximum at $x \approx 0.02$. The fact that the concentration dependences of $\chi_{Mn}$ for solid solutions containing no yttrium and doped with yttrium have different shapes suggests formation of clusters differing in their composition and to different exchange interactions within the clusters. Increase in $\chi_{Mn}$ points to ferromagnetic exchange within small aggregates, and, on the contrary, decrease in $\chi_{Mn}$ points to the antiferromagnetic character of exchange interactions.

Examination of the magnetic susceptibility isotherms allows the following conclusions. Introduction of 10% of yttrium into lanthanum sites results in formation of clusters with antiferromagnetic exchange, and further increase in the fraction of the paramagnetic favors prevalence of ferromagnetic exchange.

The maximum in the isotherm of magnetic susceptibility of lanthanum manganites with 20% of yttrium points to formation of clusters with ferromagnetic exchange. As $x$ increases, larger aggregates are formed in solid solutions, and the exchange in them appears to be antiferromagnetic.

The temperature dependences of the effective magnetic moments $\mu_{eff}$ (Fig. 2) for these systems, too, vary in shape, providing evidence for different characters of exchange within paramagnetic clusters. The fact that the temperature dependence of $\mu_{eff}$ in the case of yttrium-substituted manganites is less pronounced

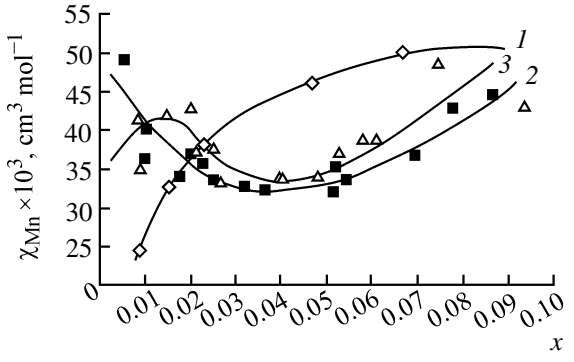


**Fig. 1.** Plots of magnetic susceptibility vs. composition at $T$ 100 K for (*1*) $x La_{0.67}Ca_{0.33}MnO_3$–$(1 - x)LaAlO_3$; (*2*) $x(La_{0.9}Y_{0.1})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$; and (*3*) $x(La_{0.8}Y_{0.2})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.8}Y_{0.2}AlO_3$.

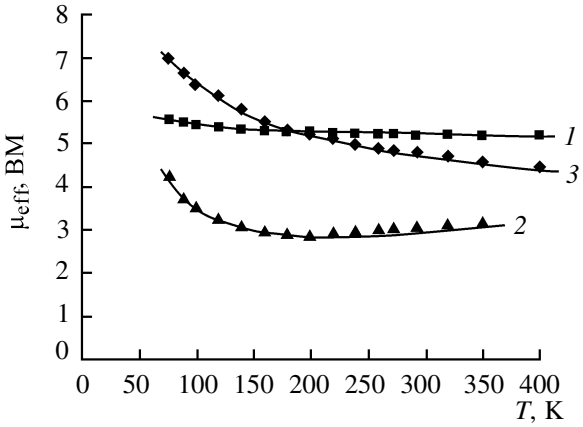


**Fig. 2.** Plots of effective magnetic moment vs. temperature for (*1*) $x(La_{0.9}Y_{0.1})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$ ($x$ 0.0696); (*2*) $x(La_{0.8}Y_{0.2})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.8}Y_{0.2}AlO_3$ ($x$ 0.0610); and (*3*) $xLa_{0.67}Ca_{0.33}MnO_3$–$(1 - x)LaAlO_3$ ($x$ 0.0668).

compared to the $La_{0.67}Ca_{0.33}MnO_3$–$LaAlO_3$ systems points to a rather rigid geometry of the existing aggregates.

The effective magnetic moment at infinite dilution ($\mu_{x\to 0}$) is the most informative characteristic for describing exchange interactions in paramagnetic clusters. The temperature dependences of $\mu_{x\to 0}$ for systems with various yttrium contents differ in their character and values. As was found earlier, in the $La_{0.67}Ca_{0.33}$·$MnO_3$–$LaAlO_3$ solid solutions at infinite dilution only single manganese atoms, Mn(III) and Mn(IV), exist.

In the case of solutions doped with yttrium, the terms effective magnetic moment cannot be described in of single atoms. In solid solutions with 10% of yttrium $\mu_{x\to 0}$ 6.9 BM is almost independent of temperature. Such a high value suggests absence of single Mn(III) ($\mu_{eff}$ 4.92 BM) or Mn(IV) atoms ($\mu_{eff}$ 3.88 BM). The Mn(II) state ($\mu_{eff}$ 5.9 BM) cannot be realized in our case, since the samples are calcined in air. It is quite evident that no deaggregation of manganese atoms occurs at infinite dilution, i.e. clusters of these atoms with prevailing ferromagnetic exchange are preserved. If we assume formation of Mn(III)–Mn(III), Mn(III)–Mn(IV), and Mn(IV)–Mn(IV) dimers with a sufficiently large exchange parameter ($J > 90$ cm$_{-1}$), then the magnetic moment at $x\to 0$ should be 6.3, 5.6, and 4.9, respectively. This does not agree with the obtained value. Probably, the aggregates are larger.

The compositions of the trimers and the corresponding $\mu_{x\to 0}$ values (BM) can be as follows [6].

| | |
|---|---|
| Mn(III)–Mn(III)–Mn(III) | $\mu_{x\to 0}$ 7.5 |
| Mn(III)–Mn(IV)–Mn(III) | $\mu_{x\to 0}$ 6.9 |
| Mn(III)–Mn(IV)–Mn(IV) | $\mu_{x\to 0}$ 6.3 |
| Mn(IV)–Mn(IV)–Mn(IV) | $\mu_{x\to 0}$ 5.74 |

Therefore, the magnetic moments of 6.9 MB in solid solutions with 10% of yttrium can be attained due to formation of, for example, trimeric clusters of manganese atoms in various valence states.

The magnetic moment at $x = 0$ of Mn(III) tetramets is 8.5 BM, and that of Mn(IV) tetramers, 6.48 BM. These situations are not realized in our case. Tetramers containing equal numbers of Mn(III) and Mn(IV) will have $\mu_{x\to 0}$ 7.48 BM, which, too, does not agree with the obtained value of the magnetic moment. However, if among the tetramers there are clusters with Mn(III) dominating, for example, aggregates of three Mn(III) atoms and one Mn(IV), the antiferromagnetic exchange within trivalent manganese atoms will decrease the sufficiently high $\mu_{x\to 0}$ of about ~7.98 BM. Moreover, the antiferromagnetic exchange should affect the pattern of the temperature dependence of $\mu_{x\to 0}$; as a result, we observe that $\mu_{x\to 0}$ increases with temperature (Fig. 3).

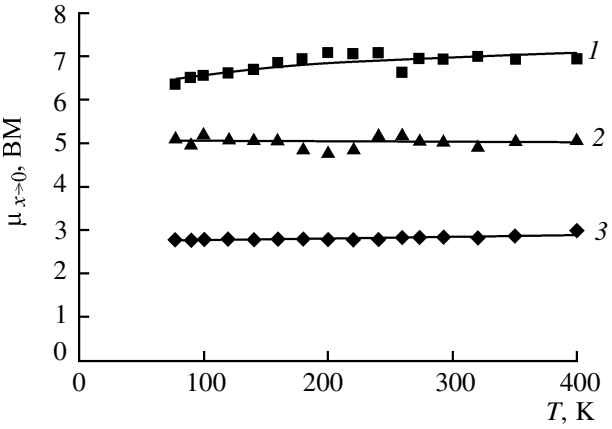


**Fig. 3.** Plot of effective magnetic moments at infinite dilution vs. temperature for the systems: (*1*) $x(La_{0.9}\cdot Y_{0.1})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$; (*2*) $x(La_{0.8}Y_{0.2})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.8}Y_{0.2}\cdot AlO_3$; and (*3*) $xLa_{0.67}Ca_{0.33}MnO_3$–$(1 - x)LaAlO_3$.

Therefore, we can assert that in the solid solutions containing 10% of yttrium trimers either interact with one another or, which is more probable, get enlarged to tetramers consisting of three Mn(III) and one Mn(IV) atoms. Further enlargement of paramagnetic clusters including tetravalent manganese atoms enhances ferromagnetic exchange.

In lanthanum manganites with 20% of yttrium, the magnetic moment decreases at $x\to 0$ to 5.0 BM, implying strong ferromagnetic exchange. Deaggregation seems to occur more intensively than with a 10% doping, but existence of single atoms at infinite dilution is still impossible.

As mentioned above, the magnetic moment of 5 BM corresponds to Mn(IV) dimers with ferromagnetic exchange, containing an admixture of monomers. Further increase of $x$ leads to enlargement of clusters with ferromagnetic exchange. Therewith, the effective magnetic moment increases to 5.9 BM, and larger aggregates with antiferromagnetic exchange begin to form only at $x \sim 0.02$, as is the case with y 0.1. At a certain concentration of the paramagnetic, the magnetic susceptibility begins to decrease. Extrapolation of magnetic susceptibility to infinite dilution at $x >$ 0.02 (the portion of the curve after the susceptibility maximum, corresponding to antiferromagnetic exchange) gives the magnetic moment ~6.51 BM, which corresponds to formation of clusters with the same

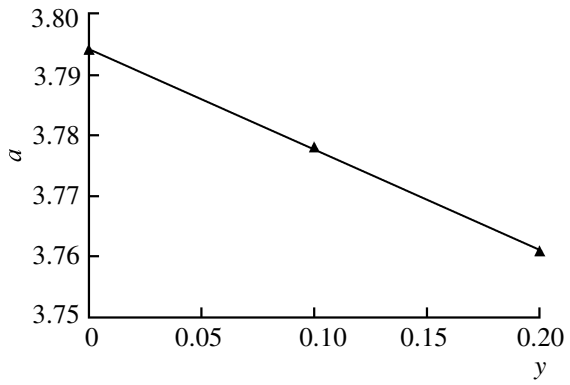


**Fig. 4.** Plot of unit cell parameter ($a$) vs. yttrium content ($y$) in the solid solutions.

composition as in the case of the solid solutions with 10% of yttrium.

Thus, the $\chi_{Mn}$ isotherms for lanthanum–yttrium manganites fundamentally differ in their shape and value both from those of the $La_{0.67}Ca_{0.33}MnO_3$–$LaAlO_3$ solid solutions and from each other. Moreover, an increase in the amount of the doping element does not cause a monotonous change in the magnetic characteristics.

The second special feature of the magnetic behavior of the solid solutions under study consists in that the temperature dependence of the effective magnetic moment for yttrium-substituted lanthanum manganites is less pronounced than for $La_{0.67}Ca_{0.33}$·$MnO_3$–$LaAlO_3$. Such regularity points to a more rigid geometry of manganese clusters in lanthanum manganites doped with yttrium.

Infinite dilution of yttrium-containing solid solutions does not produce complete deaggregation of manganese atoms. To the contrary, introduction of 10% of yttrium into lanthanum sites enhances tendency of this manganite for clusterization, and at infinite dilution ferromagnetic clusters of four manganese atoms are present. Such ratio between doping elements is optimal for aggregation of paramagnetic atoms, which is responsible for the unusual physicochemical properties of these compounds, including giant magnetoresistivity. According to [5], lanthanum manganites doped with yttrium show a maximum magnetoresistance at the yttrium content of ~10%.

Introduction of yttrium atoms into lanthanum sites should result in structure compression, i.e. decrease in the unit cell parameter. By X-ray diffraction analysis we obtained the dependence of the unit cell parameter of the solvent $La_{1-y}Y_yAlO_3$ on the yttrium content in the samples (Fig. 4). The unit cell parameter linearly decreases with increasing fraction of yttrium. The fact that the unit cell parameter varies in this way is quite expectable, since lanthanum atoms ($r$ 0.132 nm) are replaced by the smaller yttrium atoms ($r$ 0.097 nm) [7] which, in addition, can produce stronger electron polarization of oxygen atoms. It appears in this case that introduction of 10% of yttrium gives rise to vigorous clusterization of manganese atoms, but further increase in the yttrium content, on the contrary, destabilizes the aggregates.

We suggest that cluster formation at initial yttrium concentrations is mostly affected by the polarizing effect of "small" yttrium. This favors aggregation of different-valence manganese atoms around calcium, thus providing the paramagnetic atoms with a certain free space and stabilizing distortions of angles between oxygen polyhedra. As the concentration of yttrium increases, another factor comes into play, viz. structure compression. The essentially decreased unit cell parameter prevents manganese(III) atomswhich are substantially larger than their replaced aluminum atoms [$r$ 0.0615 nm for Mn(III) and 0.053 nm for Al(III)] from forming sufficiently large groups.

It is obvious that the competition between the two factors is responsible for the appearance of maxima both in cluster formation according to our data and in magnetoresistance characteristics.

## EXPERIMENTAL

The synthesis of the $x(La_{1-1}Y_y)_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{1-y}Y_yAlO_3$ solid solutions was carried out by the sol–gel procedure. The starting materials (special purity grade lanthanum, yttrium, manganese(III) oxides, analytical grade calcium carbonate, and $\gamma$-$Al_2O_3$ obtained by thermodecomposition of analytical grade aluminum nitrate) were mixed in ratios meeting the equations of solid state reactions (1) and (2).

The mixtures were dissolved in $HNO_3$ (1 : 1) under continuous heating. The resulting solution was twice evaporated to reduce its acidity (control with litmus paper). After evaporation, citric acid and ethylene glycol were added to the solution in quantities calculated by the formula $\nu = \Sigma n_i \nu_i$, where $n_i$ is the charge of the $i$th metal cation stable in aqueous solution and $\nu_i$, number of moles of the $i$th metal, calculated with regard to the quantities of the starting reagents.

The solution was heated on a sand bath until its conversion to a citrate gel. After cooling, the gel was placed into a muffle furnace and decomposed by

heating from 100 to 800°C at a rate of 4 deg $min^{-1}$. The resulting finely dispersed system was ground to a homogeneous powder, pressed into pellets, and sintered at 1500°C for 50 h. The synthesized samples are single-phase and contain no admixtures.

X-ray diffraction analysis was carried out on a DRON-3 diffractometer using Cu$K_\alpha$ radiation. The content of manganese was determined by atomic absorption spectroscopy. The error of the analysis was 3% of the $x$ index in the solid solution formula.

The magnetic susceptibility was measured by the Faraday method in the temperature range 77–400 K. The error of the measurements did not exceed 1%.

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