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State of Atoms and Interatomic Interactions in Perovskite-Type Oxides: XXXIII.[1] Interatomic Interactions in Lanthanum Manganite Doped with Yttrium, Calcium, and Strontium ($La_{0.9}Y_{0.1}Ca_{0.5}Sr_{0.5}MnO_3$)

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Abstract—Analysis of magnetic properties of solid solutions of yttrium-doped lanthanum manganites containing calcium and strontium (1 : 1) has allowed elucidation of the manganese atoms state and the type of exchange interactions between the paramagnetic centers, the latter coinciding with the earlier observed highest magnetic resistivity of the manganites of this composition.

Keywords: lanthanum manganite, perovskite-type oxide, magnetic property, magnetic susceptibility, sol-gel synthesis

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Perovskite-type manganites of rare-earth elements containing various bivalent elements ($A_{1-x}B_xMnO_3$ with A being a rare-earth element and B being an alkaline earth element) have been widely studied [2–4] due to the unique electrophysical properties of the substituted rare-earth elements manganites, including significant decrease in the resistance in the magnetic field whose effect originates from the material composition. Altering the elemental composition of magnetoresistors via introduction of diamagnetic additives at lanthanum site is a promising approach towards development of materials with optimal magnetic resistance. Heterovalent substitution in the heavy elements sublattice leads to the changed ratio of the Mn^{+3}/Mn^{+4} manganese atoms states and, consequently, results in a wide range of structural, magnetic, and transport properties of the oxides.

Magnetoresistivity is known to be a cooperative effect caused by exchange interactions between paramagnetic centers of manganese atoms in different oxidation states. Partial substitution of lanthanum atoms with yttrium in complex lanthanum manganites containing calcium and strontium ($La_{2/3-x}Y_xCa_{1/3-y}Sr_yMnO_3$) revealed that the optimal magnetoresistance could be observed in the cases of materials containing 10 mol % of yttrium and equimolar amounts of the alkaline earth elements: calcium and strontium [5]. Despite numerous studies of the properties of substituted lanthanum manganese, the mechanism of the effect of the substitution of the diamagnetic element on the state of manganese atoms and the magnetoresisting properties has been unclear so far.

Magnetic dilution method based on analysis of properties of isomorphic substitution solid solutions as a function of temperature and the components concentrations allows elucidation of the state of manganese atoms and track the changes in the exchange interactions involving paramagnetic centers.

Earlier the magnetic dilution method was applied to a study of substituted lanthanum manganites of the $(La_{1-z}Y_z)_{0.67}Ca_{0.33}MnO_3$ and $(La_{1-z}Y_z)_{0.67}Sr_{0.33}MnO_3$ compositions at z = 0.1 and 0.2 [6, 7]. It was shown that the introduction of yttrium atoms an the lanthanum sires led to the formation of magnetic aggregates of manganese atoms in different oxidation states, being stable upon infinite dilution. Change of yttrium atoms concentration in the solid solutions from z = 0.1 to

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

z = 0.2 significantly influenced the type of exchange interactions and degree of manganese atoms aggregation in the magnetic-diluted range. The strongest ability of manganese atoms to form clusters showing ferromagnetic exchange interactions was observed in the case of solid solutions doped with alkaline earth elements (calcium or strontium) and containing 10 mol % of yttrium.

Magnetic dilution studies of the effect of the Ca : Sr atoms ratio on the magnetic properties and the manganese atoms state in the yttrium-free lanthanum manganites [$La_{0.67}(Ca_ySr_{1-y})_{0.33}MnO_3$ (y = 0.3, 0.5, 0.7)] [8] revealed that the increase in the calcium atoms concentration from y = 0.3 to y = 0.7 led to non-monotonous change of magnetic properties of the studied solid solutions. In all studied systems a partial disaggregation of manganese atoms was observed, with the competing effects of ferromagnetic and antiferromagnetic interactions.

From analysis of the above-mentioned published data it follows that the introduction of alkaline earth elements and yttrium into a structure of perovskite was accompanied with the formation of aggregates of manganese atoms in different oxidation states; on top of that, the competing opposite (ferromagnetic and antiferromagnetic) interactions appeared. In other words, a relationship was found between the short-range order interactions in the complex oxide systems and the manifestation of the cooperative far-range order properties, like colossal magnetoresistivity.

Hence, magnetochemical study of the $x(La_{0.9}Y_{0.1})_{0.67}$·$(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$ isomorphic substitution solid solutions should elucidate the origin of influence of diamagnetic calcium, strontium, and yttrium atoms on the state of manganese atoms in the $(La_{0.9}Y_{0.1})_{0.67}(Ca0_{.5}Sr_{0.5})_{0.33}MnO_3$ magnetoresistive lantha-num manganite, the latter possessing the optimal magnetoresistive properties [5].

In this work we prepared and studied isomorphic substitution solid solutions of lanthanum manganite containing 10 mol % of yttrium and equimolar amounts of calcium and strontium, the general composition being $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$ (x = 0.042, 0.0072, 0.0135, 0.0299, 0.040, 0.0526, 0.0539, and 0.0691).

Paramagnetic component of magnetic susceptibility with respect to 1 mol of manganese atoms (χ_{Mn}) and effective magnetic moment ($\mu_{eff} = 2.84\sqrt{\chi_{Mn}T}$) were calculated from the experimentally determined magnetic susceptibility values, and both temperature and concentration dependences of the derived properties were plotted and analyzed. In particular, the extrapolation of paramagnetic part of magnetic susceptibility to zero concentration of paramagnetic atoms ($x \to 0$) gave the value of effective magnetic moment at infinite dilution ($\mu^{x\to0}$) .

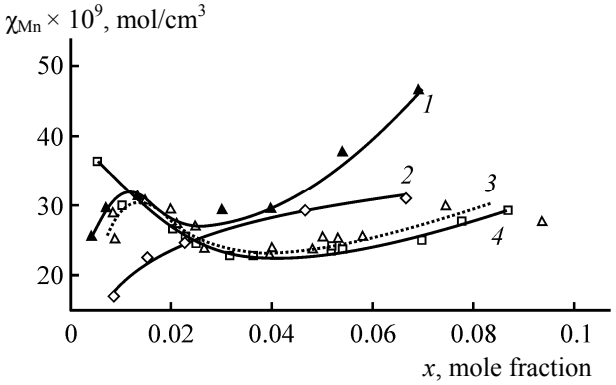


Fig. 1. Paramagnetic part of magnetic susceptibility as a function of manganese atoms concentration (x) for the solid solutions: (*1*) $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$, (*2*) $xLa_{0.33}Ca_{0.67}MnO_3$–$(1 - x)LaAlO_3$, (*3*) $x(La_{0.8}Y_{0.2})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.8}Y_{0.2}AlO_3$, and (*4*) $x(La_{0.9}Y_{0.1})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$.

Isotherms of paramagnetic part of magnetic susceptibility χ_{Mn} (Fig. 1) differed in shape and the χ_{Mn} values for systems of different diamagnetic composition.

In contrast to the $xLa_{0.33}Ca_{0.67}MnO_3$–$(1 - x)LaAlO_3$ solid solutions (Fig. 1, curve *2*), the introduction of yttrium and strontium into the perovskite structure led to more complex shape of the χ_{Mn}–x plots (Fig. 1, curves *1, 3, 4*) and to the change in the type of the exchange interactions as the systems became more concentrated. Interestingly, the isotherms of paramagnetic part of magnetic susceptibility (χ_{Mn}–x) of the $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$ (Fig. 1, curve *1*) and the $x(La_{0.8}Y_{0.2})_{0.67}Ca_{0.33}MnO_3$–$(1 - x)La_{0.8}Y_{0.2}AlO_3$ (Fig. 1, curve *3*) solid solutions were similar in shape but differed in the values of paramagnetic part of magnetic susceptibility. The maximum on the isotherms was assigned to the type of the exchange interactions of paramagnetic centers changing from ferromagnetic to antiferromagnetic at $x \sim 0.02$. The increase in the paramagnetic part of magnetic susceptibility at higher manganese concentration ($x > 0.04$–0.05) was expected and corresponded to growing of the manganese atoms aggregates showing ferromagnetic exchange. The most prominent dif-

Effective magnetic moment at infinite dilution of solid solution at different temperatures $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$

T, K	$\mu^{x\to0}$, μ_B	T, K	$\mu^{x\to0}$, μ_B
90	5.16	220	4.72
100	5.1	240	4.7
120	4.95	260	4.67
140	4.88	273	4.65
160	4.8	293	4.61
180	4.77	320	4.54
200	4.75	350	4.51
		400	4.32

ference in the isotherms of magnetic susceptibility of the systems with different diamagnetic compositions was found in the range of high dilution ($x \le 0.03$): The increasing concentration of manganese atoms led to monotonous increase in the paramagnetic component of magnetic susceptibility. Such behavior of solid solutions with low manganese concentration was due to the influence of the nature of substituting element on the type of exchange interactions in small aggregates of paramagnetic atoms.

The most detailed information on the state of paramagnetic atom in the solid solutions could be extracted from the values of effective magnetic moment at infinite dilution ($\mu^{x\to0}$). The tabulated values of $\mu^{x\to0}$ were found via extrapolation of the experimental data on the magnetic susceptibility and the effective magnetic moment.

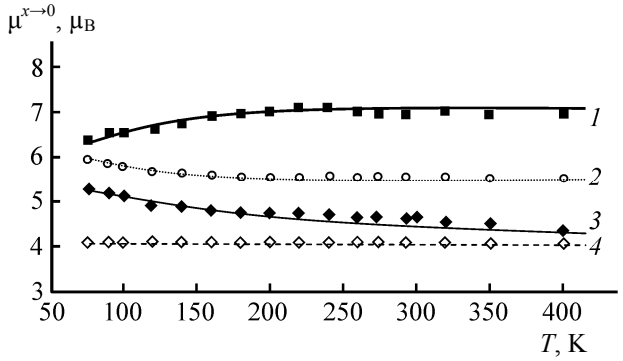


Fig. 2. Effective magnetic moment of the solid solutions at infinite dilution as function of temperature: (*1*) $x(La_{0.9}Y_{0.1})_{0.67}Ca_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$, (*2*) $x(La_{0.9}Y_{0.1})_{0.67}Sr_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$, (*3*) $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$, and (*4*) $xLa_{0.33}Ca_{0.67}MnO_3$–$(1-x)LaAlO_3$.

The effective magnetic moment at infinite dilution of the studied $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$ solid solutions decreased on cooling from ~5.16 μ_B at 90 K to ~4.3 μ_B at 400 K. The determined $\mu^{x\to0}$ could not be explained by the presence of single atoms of Mn(III) [^5E_g] and Mn(IV) [$^4A_{2g}$], their effective magnetic moments being 4.92 and 3.88 μ_B, respectively, independently of temperature [9].

Figure 2 displays the effective magnetic moment at infinite dilution of solid solutions of the manganites with different diamagnetic composition as functions of temperature.

Of the discussed systems, complete disaggregation of paramagnetic atoms was only observed for the $xLa_{0.33}Ca_{0.67}MnO_3$–$(1-x)LaAlO_3$ solid solutions, their effective magnetic moment at infinite dilution reaching 4.1±0.1 μ_B independently of temperature. In the case of the $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1-x)La_{0.9}Y_{0.1}AlO_3$ solid solutions, the determined $\mu^{x\to0}$ values evidenced the formation of the magnetically bonded aggregates of manganese atoms.

Interestingly, the introduction of only strontium or only calcium atoms into the perovskite structure led to complete disaggregation of manganese atoms at infinite dilution of the solid solution [6, 7]; similar effect was observed upon variation of the Ca–Sr ratio in solid solutions of lanthanum manganites [8]. Introduction of yttrium atoms at lanthanum atom sites as a doping additive at constant content of strontium or calcium resulted in a pronounced enhancement of magnesium atoms aggregation [10].

The changes of effective magnetic moment at infinite dilution with temperature variation suggested the presence of dimeric clusters containing manganese atoms in different oxidation states, the interaction between them being ferromagnetic. We calculated the cluster magnetic susceptibility in the frame of Heisenberg–Dirac–van Vleck model of isotropic exchange [8].

$$\chi_{dim} = \frac{Ng^2}{6kT}\,\frac{\sum\limits_{S=0}^{2S} S'(S'+1)(2S'+1)\exp\left(-\dfrac{E(S')}{kT}\right)}{\sum\limits_{S=0}^{2S}(2S'+1)\exp\left(-\dfrac{E(S')}{kT}\right)}.$$

Here $E(S') = -J[(S'+1) - S(S+1) - S_2(S_2+1)]$; $S' = (S_1 + S_2), S_1 + S_2 - 1, \ldots, S_1 - S_2$; $S_1 = 3/2$[Mn(IV)];

S_2 = 2[Mn(III)]; k is the Boltzmann's constant; T is absolute temperature; and J is exchange parameter.

It was stated that the temperature dependence of effective magnetic moment at infinite dilution of the studied solid solutions was well fitted with the Heisenberg–Dirac–van Vleck model, the exchange parameter being J 7±1 cm^{-1}.

Interestingly, the temperature dependence of experimentally determined effective magnetic moment was different depending on the sample composition. In the case of x = 0.0042 the μ_{eff} was independent of temperature, at x = 0.007–0.04 the μ_{eff} was increasing with temperature, and at x > 0.05 the dependence was more and more steeply decreasing (Fig. 3).

The changes of the μ_{eff} values for solid solutions containing different concentration of the paramagnetic element correlated with the paramagnetic component of magnetic susceptibility. At low concentration of manganese atoms the magnetic aggregates of manganese atoms grew with increasing fraction of Mn(III) atoms, and the competition between ferromagnetic and antiferromagnetic interactions came into play. Further increase in the manganese atoms concentration (x > 0.04) led to the formation of large paramagnetic aggregates with the variable exchange parameter. Similar behavior was observed in the case of solid solutions of lanthanum manganites containing 10% yttrium atoms, and the change of temperature dependence of the effective magnetic moment took place at the same range of manganese atoms concentration (x) [10]. In the cases of solid solutions of lanthanum manganites containing calcium or strontium atoms as well as their mixture the decrease in effective magnetic moment was observed in the range of magnetically diluted solid solutions [8, 11].

In other words, incorporation of calcium and strontium atoms into the perovskite structure did not result in sufficiently strong short-range order interactions, and manganese clusters stable upon infinite dilution were not formed. Introduction of yttrium atoms into the crystal lattice enhanced clustering of the paramagnetic atoms so that fairly stable and large manganese atom clusters were found in the solid solution at $x \to 0$. Variation of the ratio of the alkaline earth atoms Ca–Sr could evidently optimize the short-range interactions, leading to the formation of dimeric clusters with ferromagnetic exchange operative, the interatomic interaction energy being sufficiently large (>100 kJ/mol [12]). Predominantly ferromagnetic

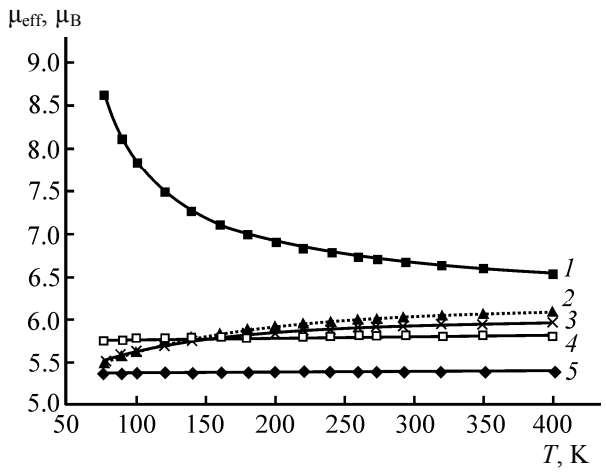


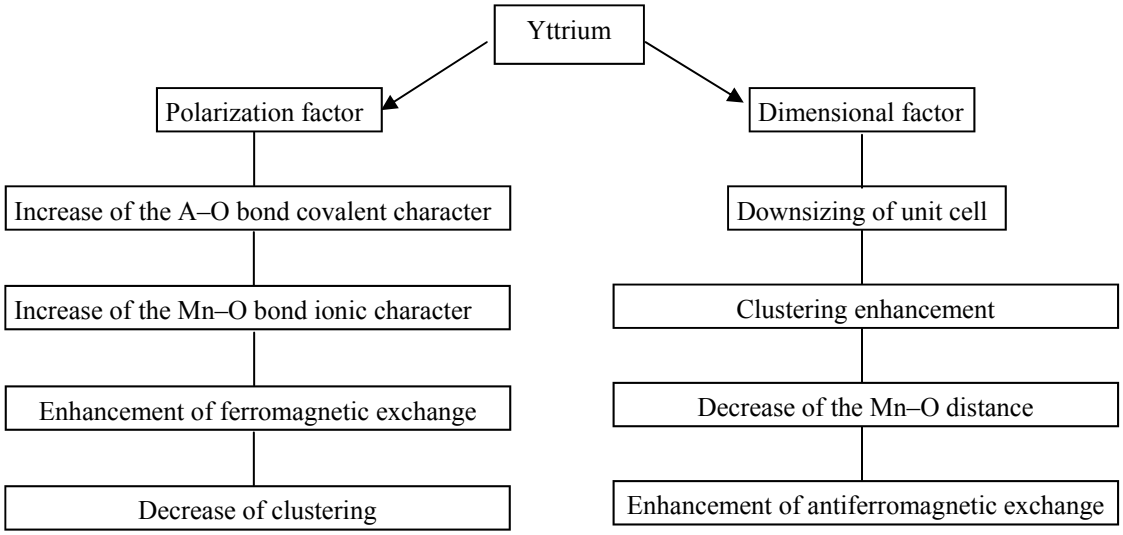
Fig. 3. Effective magnetic moment as function of temperature for the $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)\cdot La_{0.9}Y_{0.1}AlO_3$ solid solutions at x: (*1*) 0.0691, (*2*) 0.04, (*3*) 0.0299, (*4*) 0.0072, and (*5*) 0.0042.

interactions arising at growing of the clusters were likely responsible for enormous magnetoresistance of those systems. Hence, we concluded that the ferromagnetic dimers were the basic structural units determining the optimal magnetoresistance properties of the manganites containing yttrium, calcium, and strontium as diamagnetic dopants. The dimers formation occurred in the systems containing 10 mol % of Y and equimolar amounts of Ca and Sr, the general formula being $(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$.

The attempts to rationalize the effect of substitution in the lanthanum sublattice reported so far [5] were reduced to the analysis of the dimensional factor. Clearly, the non-monotonous change of magnetic properties with increasing concentration of yttrium atoms, with change of the Ca–Sr ratio, and with simultaneous introduction of Y, Ca, and Sr evidenced the insufficiency of taking into account only the dimensional factor. At least two factors were operative simultaneously, one of them being the degree of ionic character of the Mn–O bond. That was to a large extent determined by the nature of the nearest neighbors in the lanthanum sublattice, i.e., the nature of the diamagnetic substituents.

Doping of lanthanum manganite with small yttrium atoms leads to decrease in the unit cell parameter, simultaneously the Mn–O average distance decreases, the orbitals overlapping is enhanced, and hence the absolute value of the antiferromagnetic exchange parameter is increased and manganese atoms clustering

Scheme 1.



is enhanced. On the other hand, polarization of oxygen atom orbitals by yttrium atom is stronger than by lanthanum atom; hence, the ionic character of the Mn–O bond is enhanced, and the contribution of ferromagnetic exchange grows. Thus, two opposite effects emerge at the incorporation of yttrium atoms in the lanthanum positions. At a given concentration of yttrium this or that effect prevails. In the case of 10 mol % of yttrium, the clustering trend was the strongest (being dependent on the dimensional factor), and the ferromagnetic exchange was the highest (being governed by the polarization factor) (Scheme 1).

The difference in behavior of oxide systems containing calcium and strontium is evidently due to the fact that the effect of Sr atom, being larger and forming the stronger bond with oxygen, is opposite to that of Y from both above-discussed points of view. With increasing Sr–Ca ratio the unit cell grows larger, the orbitals overlapping decreases, and the ferromagnetic contribution to the exchange is enhanced. However, simultaneously the ionic character of the A–O bond grows, the covalent character of Mn–O bond is increased, and hence the antiferromagnetic exchange is enhanced. As a result, at the alkaline earth elements ratio of 1 : 1 both factors were balanced (Scheme 2).

Simultaneous introduction of 10 mol % of yttrium and equimolar amounts of calcium and strontium resulted in significant changes of the short-range interactions. In the case of the systems containing only the alkaline earth dopants a complete disaggregation of manganese atoms was observed at infinite dilution, whereas in the case of the systems containing only yttrium as dopant relatively large manganese atoms aggregates ($n > 3$) were preserved at infinite dilution of the solid solutions [6–8]. In the solid solutions of the $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)La_{0.9}Y_{0.1}AlO_3$ composition, only the dimers composed of Mn(III) and Mn(IV) atoms were found at infinite dilution, the interaction between the atoms being of ferromagnetic type. This confirmed that the cooperative effects like enormous magnetoresistance were determined by the short-range interactions. On top of that, we confirmed that the magnetic dilution method was an appropriate instrument to discover the character of such interactions.

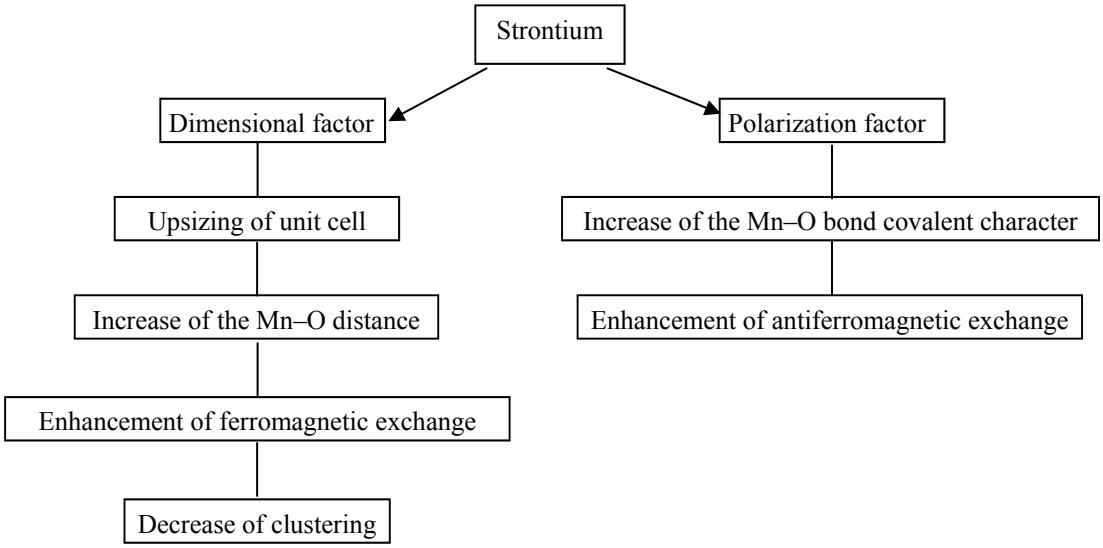
EXPERIMENTAL

X-ray diffraction analysis was performed utilizing a DRON-3 diffractometer using FeK_α radiation. Manganese content was quantified via atom absorption spectroscopy; the accuracy of determination of the x index in the general formula of the solid solution was ±3%.

Magnetic susceptibility was measured with the Faraday method at 16 fixed temperatures in the 77–400 K range, the measurement error was below 1%. Calculation of the paramagnetic part of magnetic susceptibility accounted for diamagnetism using the susceptibility of the $La_{0.9}Y_{0.1}AlO_3$ diamagnetic matrix measured over the same temperature range.

The $x(La_{0.9}Y_{0.1})_{0.67}(Ca_{0.5}Sr_{0.5})_{0.33}MnO_3$–$(1 - x)\cdot La_{0.9}Y_{0.1}AlO_3$ solid solutions were prepared via a sol-gel procedure. The starting compounds (lanthanum,

Scheme 2.



yttrium, and manganese(III) oxides, all of "special pure" grade; calcium and strontium carbonates, both of the "analytically pure" grade; and γ-Al_2O_3 prepared via thermal decomposition of "analytically pure" grade alumina) were mixed in a ratio corresponding to the solid-phase reaction equation

$$(0.9 - 0.297x)LaO_{1.5} + (0.1 - 0.033x)YO_{1.5} + 0.50xCaCO_3 + 0.50xSrCO_3xMnO_{1.5} + (1 - x)AlO_{1.5} \rightarrow La_{0.9-0.297x}Y_{0.1-0.033x}Ca_{0.50x}Sr_{0.50x}Mn_xAl_{1-x}O_3 + 0.33CO_2,$$

$$x = 0.005–0.07.$$

Stoichiometric amounts of the starting compounds were dissolved in nitric acid (1 : 1) upon continuous heating. The formed solution was twice evaporated in order to decrease the acidity (monitored with an indicator paper). After evaporation, citric acid and ethylene glycol were added, their amounts being calculated as $v = \Sigma n_i v_i$ with n_i, charge of the ith cation stable in the aqueous solution; v_i, number of moles of the ith metal calculated from the taken starting reagents.

The solution was heated at a sand bath till transformation into a citrate gel; the gel was cooled down and placed to a muffle furnace to be thermally decomposed at 100 to 800°C (the heating rate of 4 deg/min). The so prepared fine disperse system was triturated into a homogeneous powder. The pellets were prepared from the product powder and annealed at 1450°C during 50 h. The prepared samples were single-phase and did not contain any admixtures.

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