

## Surface segregation and charge state of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

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Nuclear magnetic resonance and secondary ion mass-spectroscopy have been used to study the surface charge and surface chemical compositions of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  nanoparticles of 12 and 50–100 nm size. It is found that the surface of particles is characterized by an increased content of Sr and Mn ions than the bulk, while the difference depends on particle size. The surface segregation process is considered to be a possible mechanism for cation rearrangement. Thus, the observed magnetically dead layer on a particle surface may be formed due to increase in the Sr and Mn ions concentrations up to values corresponding to an antiferromagnetic state.

Методами ядерного магнитного резонанса и вторичной ионной масс-спектропии проведены исследования зарядового состояния и химического состава поверхности наночастиц  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  с размерами 12 и 50–100 нм. Обнаружено, что для поверхности частиц характерно повышенное содержание ионов Sr и Mn по сравнению с объемом, причем это различие зависит от размера частиц. В качестве возможного механизма перераспределения катионов рассматривается процесс поверхностной сегрегации. Таким образом, наблюдаемый немагнитный слой на поверхности частиц может быть сформирован в результате увеличения концентрации ионов Sr и Mn в поверхностном слое до величин, соответствующих антиферромагнитному состоянию.

The doped lanthanum manganites  $\text{La}_{1-x}(\text{Ca},\text{Sr},\text{Ba})_x\text{MnO}_3$  (LDMO) are under a keen scientific interest for more than 50 years because of a surprising correlation between electrical conductivity and magnetism observed therein [1]. A partial substitution of the trivalent rare-earth ion for a bivalent alkaline-earth ion results in the appearance of Mn ions of various valences in equivalent crystallographic positions, and in the emergence of a ferromagnetic ordering [2, 3] in these compounds. Ferromagnetic exchange efficiency between the adjacent spins depends on the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  chain state, since any disturbance of the crystal-line structure causes a spin disorder and hinders the double exchange [4].

A natural area of the structural and spin disorder is the crystal surface of some elementary cells in thickness which acts as a

buffer between the regular structure of the internal volume and the environment. A contribution of the surface into the material physical properties has been clearly demonstrated in the course of LDMO research. When the surface layer fraction in the total volume is small, single crystals and films of these compounds exhibit the colossal negative magnetoresistance effect. Intergranular boundaries in ceramic materials make the magneto-resistant characteristics worse. In the case of nanoparticles of less than 200 nm size, the transport properties are mainly influenced by the intergranular magnetoresistance (low field magnetoresistance). In very thin nanoparticles, the surface role becomes predominant. Magnetic studies of the ultrafine powders show a super-paramagnetic (SPM) behavior, while no low field magnetoresistance is observed above the SPM temperature. The

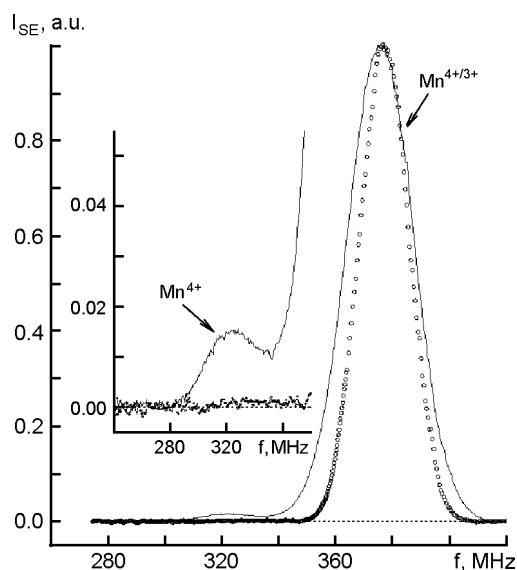


Fig. 1.  $^{55}\text{Mn}$  NMR spectra recorded for S2 (solid line) and S3 ( $^{\circ}$ ) LSMO samples at 77 K. Inset: the same spectra in an expanded scale, showing the details of NMR spectra at about 320 MHz.

purpose of this work is to study the relationship between the magnetic properties of the  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) nano-powders and the structure peculiarities of the granule external layer.

The magnetism of nano-sized LSMO was studied by the nuclear magnetic resonance (NMR), because it probes locally spin and charge states and the dynamics thereof. Changes of the surface layer state in the manganite nano-particles at the particle sizes changing were studied by the secondary ion mass-spectroscopy (SIMS).

The S1 (the particle size 12 nm) and S2 (bimodal distribution of particles of 50 and 100–120 nm size) samples were obtained chemically by co-precipitation using the SHF heating and ultrasound treatment [5]. When making powders, chemically pure  $\text{La}_2\text{O}_3$ ,  $\text{Mn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$  were taken as initial reagents in accordance with the final product stoichiometry.  $\text{NH}_4\text{OH}$  and  $\text{Na}_2\text{CO}_3$  were used as precipitators of the metal salt solution. Lanthanum oxide was preliminary dissolved in nitric acid. The precipitation was carried out under stirring for 1 hour at room temperature. The watered precipitate obtained was washed in distilled water to remove the reaction by-products. After filtration, the hydrogel was treated by ultrasound and dried in the microwave kiln (2.45 GHz, 600 W) till a constant sample mass. A monophase LSMO

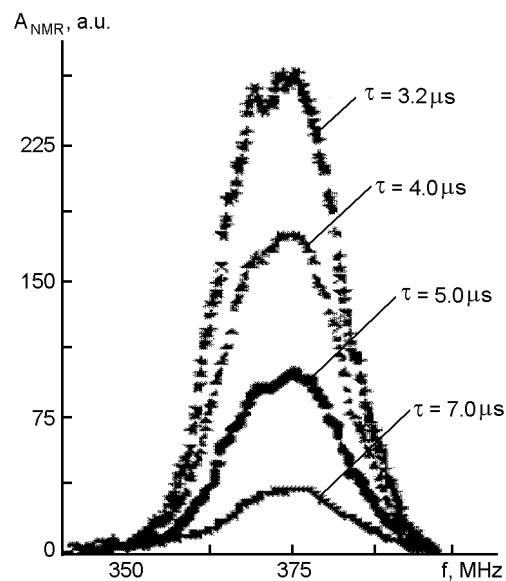


Fig. 2.  $^{55}\text{Mn}$  NMR spectra of S1 LSMO powders at 77 K.

nano-powder was synthesized at  $600^{\circ}\text{C}$ . The phase composition was studied by the X-ray analysis. Using transmission electron microscopy (TEM), the morphological structure peculiarities of the phases involved in the synthesis were studied. For comparison, a ceramic sample (S3) with predominant volume properties was used obtained by solid phase synthesis followed by agglomeration.

The NMR studies of the  $^{55}\text{Mn}$  nuclei in the nano-powder LSMO samples have shown that nano-sized crystals were characterized by the existence of two areas differing in magnetic properties — the grain surface and its internal volume [6, 7]. It followed from the experiment that the about 2 nm thick surface layer of the S1 and S2 sample particles is neither magnetic nor conductive. Besides, in the sample S2, along with the state of the  $\text{Mn}^{3+/4+}$  ion typical of a ferromagnetic lanthanum manganite, an additional line was observed in the spectra that corresponds to the localized state of the  $\text{Mn}^{4+}$  ions in the surface layer of nano-granules (Fig. 1). This line was absent in the S3 ceramics and nano-sized S1 sample (Fig. 2). The preparation technology being the same for all the samples, the difference in magnetic properties could be caused only by the different particle size, that is, it is due mainly to the surface layer contribution. To determine the surface composition of the LSMO particles of different sizes, the method SIMS was used that is sensitive to the surface composition (Fig. 3). The analysis has shown (Table) that in all the samples

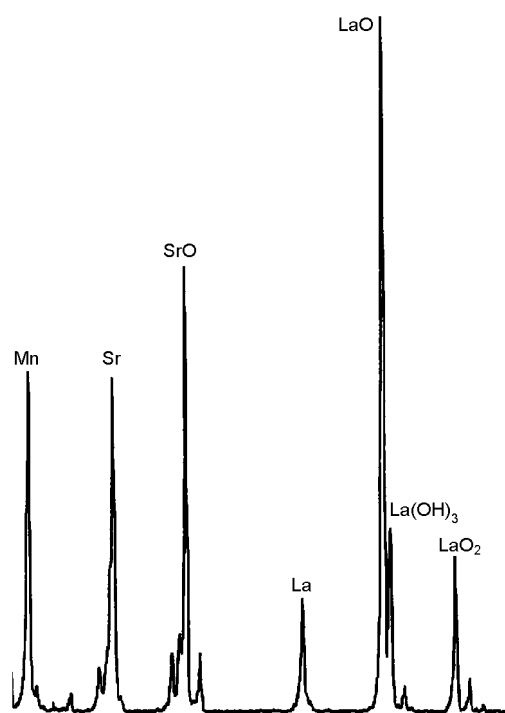


Fig. 3. SIMS spectra of S1 sample.

under study, there is an increased content of Sr ions in the 2 nm thick surface layer (the stoichiometric composition value is 0.43). It is of importance that a correlation between the particle size and the surface composition has been experimentally observed: the smaller the particle size is, the larger is the Sr and Mn ion amount in the surface layer. The values of the  $Mn/(La + Sr)$  ratio presented in the Table are not absolute (due to a weak sensitivity of the method to Mn, its quantity is underrated) but they represent clearly a trend to the surface composition change as a function of the particle size.

Three possible phenomena are known which can contribute to the composition inhomogeneity in ceramics: phase separation, absorption, and surface segregation (internal adsorption). Phase separation belongs to the space effects and is described by a corresponding phase diagram. Absorption and

segregation appear as a result of maintaining equilibrium at the solid surface/environment boundary or at the grain surface and are mainly defined by the nature of the atom or ion bonds in the interface area. In the case of absorption, equilibrium is attained due to contact between the vapor phase and the surface, while equilibrium at the internal adsorption is attained by a diffusion contact between a solid volume and an interface area. The surface segregation of alkaline-earth atoms in the ceramic samples of perovskites  $BaTiO_3$  and  $SrTiO_3$  was found in experiment and described in [8]. The authors have suggested a theoretical model where a stress state of the crystal lattice at the boundary with the environment is considered as a motive force of the cation rearrangement between the particle bulk and surface. As the lattice has lost its three-dimensional translation symmetry in these ionic crystalline compounds, a negative space charge occurs side by side with the interface which must be compensated by a layer of positively charged ions at the surface. The authors have shown an influence of the alloying atoms on the segregation characteristics — when alloying by atoms of another valence and other ionic radii, a prevailing rearrangement of dopants into the surface area was observed. In this case, the motion is done not only due to the electrostatic forces but also to the influence of elastic forces of the crystal lattice which occur because of the difference of the ionic radii.

From the data of our experiments, the arrangement of cations between the surface layer and the internal volume of 50 and 12 nm size particles was estimated. The particle was assumed to be spherical and atoms in the surface layer to be arranged homogeneously, i.e. without any radial concentration gradient. The cation ratio in this case was determined by the average concentration value in the layer.

As the unit volume, a cube volume of the reduced perovskite cell  $ABO_3$  ( $a \approx 0.39$  nm) per one formal unit was taken. Basing on the particle size and the surface layer thick-

Table. The composition of the surface layer  $La_{0.7}Sr_{0.3}MnO_3$  as determined by SIMS

Sample	Particle size, nm	Sr/La	Mn/(La + Sr)	$La_{1-x}Sr_xMnO_3$
S1	12	0.96	0.77	$La_{0.51}Sr_{0.49}MnO_3$
S2	50, 200	0.90	0.61	$La_{0.53}Sr_{0.47}MnO_3$
S3	ceramics	0.72	0.51	$La_{0.59}Sr_{0.41}MnO_3$

ness, the number of the formula units belonging to each area can be calculated. Knowing the cation concentrations, it is possible to determine and compare the number of cells occupied by the La and Sr ions both at the surface and in the bulk.

Assuming that the ratio of the components for each particle laid at synthesis should be retained on average, the surface enrichment in this or that element should proceed at the expense of its content decrease in the bulk. As the calculations show, to attain an experimental concentration in the surface layer of the samples with 50 nm particles, Sr ions should be withdrawn out of the internal volume in the amount corresponding to 7 % of the number of lanthanum sublattice crystallographic positions belonging to that volume. Such a defectness in the cation sublattice is quite possible, so that at particle size  $\geq 50$  nm, we have in the volume a charge balance  $\text{La}^{3+}_{0.7}\text{V}_{0.07}\text{Sr}^{2+}_{0.23}\text{Mn}^{3+}_{0.7}\text{Mn}^{4+}_{0.3}\text{O}_3$  (V – Sr vacancy) corresponding to a metallic state.

A different situation is observed for particles of 12 nm size. In this case, only one fourth of the whole particle volume accounts for the internal volume. The amount of strontium in the internal volume is insufficient to fill the external layer up to the concentration observed in the experiment. Perhaps these missing 16 % might be compensated by exit of manganese ions onto the surface. The experimental data (Table) confirm this assumption. The maximum manganese quantity in the surface layer is seen to be observed just for nanoparticle of 12 nm size.

The results obtained allow to explain the reason for the non-magnetic layer appearance at the surface of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  nanoparticles. The exit of strontium ions into subsurface layer changes the ratio of the solid solution components and takes it out of the limits of the ferromagnetic state region. When estimating, we proceeded from the average value of Sr concentration over the surface layer thickness. In fact, as shown in [8], there is a concentration gradient towards the particle surface. Knowing the average strontium concentration at the surface and its value in the internal volume and assuming as the first approximation

that the dependence inside the surface layer is linear, the Sr/La ratio at the interface can be determined. As the estimates show, these values for particles of 50 and 12 nm size are 0.7 and 0.8, respectively. In the phase diagram  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  such concentrations correspond to anti-ferromagnetic state [9].

As is shown in [7], the nano-particle magnetic domain structures of the S1 and S2 samples differ essentially from one another. The S1 samples are single magnetic domain particles, while the S2 ones are characterized by a multi-domain structure. The presence of localized  $\text{Mn}^{4+}$  states in the S2 samples can be explained by the effects of partitioning into domains and by the surface separation of Sr ions. In this case, an area containing only  $\text{Mn}^{4+}$  ions may well appear on a granule surface. So, the appearance of the localized  $\text{Mn}^{4+}$  states in the S2 samples can be explained by the nano-particle surface enrichment in strontium.

The results obtained in this work give information on the magnetic and crystal structures of the of the nano-powder surface. The complex studies of the samples by the  $^{55}\text{Mn}$  NMR and SIMS methods have shown that the formation of a 2 nm thick magnetically dead layer at the particle surface is a result of its enrichment in Sr and Mn ions up to concentrations corresponding to the anti-ferromagnetic state.

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## **Поверхнева сегрегація та зарядовий стан $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$**

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Методами ядерного магнітного резонансу і вторинної іонної мас-спектроскопії проведено дослідження зарядового стану та хімічного складу поверхні наночастинок  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  з розмірами 12 і 50–100 нм. Виявлено, що для поверхні частинок характерний підвищений склад іонів Sr і Mn, а їхня концентрація залежить від розміру частинок. Як можливий механізм перерозподілу катіонів розглядається процес поверхневої сегрегації. Таким чином, немагнітний шар, що спостерігається на поверхні частинок, може бути сформований в результаті збільшення концентрації іонів Sr і Mn у поверхневому шарі до величин, що відповідають антиферомагнітному стану.