

Features of Interfaces in Layered $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ Oxides: Products of Solid-State Synthesis

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Abstract—The interfaces in complex $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ oxides ($0.1 < x < 1.5$) obtained by the ceramic method were studied in detail. To determine the chemical composition of the interfaces and their effect on the properties of ceramics, the magnetic and electric properties were investigated and X-ray phase and micro X-ray analyses were performed. It was found that the mechanical stability of the samples is determined by the presence of lanthanum in the surface layer.

DOI: 10.3103/S1062873811050431

INTRODUCTION

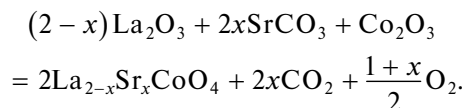
Layered oxides, particularly $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ oxides, have a number of interesting features. First, many authors note that admixture phases are present in addition to the main quasi-two-dimensional perovskite-like phase during their preparation [1–3]. Their final composition is not yet fully established: it is either a three-dimensional perovskite structure or lanthanum oxide. In this respect, a question arises as to the composition of the interfaces and their effect on the process of synthesis and the properties of obtained oxides. Second, the compensated antiferromagnetic order is rapidly broken upon substituting a strontium atom for the lanthanum atom in antiferromagnetic La_2CoO_4 and at $x = 0.6$, the oxides become ferromagnetic. The character of the magnetic ordering is far from understood. It is assumed that at $x \geq 0.3$, spin correlations appear that gradually create regions of non-compensated magnetic ordering with an increase in x , or that in increasing x from 0 to 0.6, T_N falls rapidly and the antiferromagnetic state quickly becomes ferromagnetic [2, 4].

EXPERIMENTAL

Lanthanum oxide of extra pure grade, strontium carbonate of extra pure grade, and cobalt(III)oxide of analytical grade were used to obtain complex $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ oxides. Magnetic susceptibility data indicate the absence of ferromagnetic admixtures that could distort the measurement results in the initial compounds. The source lanthanum oxide and strontium carbonate were preliminarily annealed at $T = 1073$ K to remove adsorbed water and carbon dioxide.

A series of complex oxides was synthesized by the ceramic method. The stoichiometric mixture of the

corresponding oxides and carbonates was calculated according to the equation for the reaction



The interval x in the formula was $0.0 \leq x \leq 1.5$. This interval was chosen so as to study all possible degrees of the oxidation of cobalt and to follow the change in the oxide structure in dependence on x (the strontium portion): a gradual increase in the distortions of the oxygen octahedron containing cobalt atoms or a sharp stratification into two phases (orthorhombic and tetragonal) after a certain x value.

Since there are data in the literature as to the presence of admixture phases under different conditions of synthesis, the samples were studied by X-ray phase analysis (XPA) and scanning electron microscopy, with a microanalysis of the sample composition and possible coexisting phases. Such studies were not performed earlier.

The results from our analysis of the samples obtained at temperatures of 1200–1350 K confirmed the XPA data that the main phase is the required perovskite-like structure and that the admixture phase La_2O_3 was present as well. The samples were quite homogeneous and had the same composition at different surface points, with the exception of white regions that contained only La_2O_3 . Electron photomicrographs of the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CoO}_4$ sample obtained by slow cooling in a furnace and fast quenching from the temperature of synthesis are shown in Fig. 1

The obtained ratio of elements indicates their subsequent locations on the La : Co : Sr surface of the cooled samples, the strontium content being less than that corresponding to the formula. In hardened sam-

ples, the strontium content rises sharply, probably because (according to the XPA data) an additional phase of La_2SrO_x is formed upon the quenching of the samples, and regions enriched with cobalt appear. Quenching of the samples thus introduces a new intergrain boundary and leads to a worsening of the microstructure of oxides. A change in the conditions of synthesis changes the chemical composition of the intergrain boundaries. The reduced strontium content in the sample as a result of its transition to the La_2SrO_x phase leads to the change of the portion of cobalt in the degree of oxidation of three.

Let us note one other feature of cobaltates: their high ability for intercalation. Their application naturally requires resistance to reactions with external reagents (carbon dioxide and water) and internal degradation processes. However, samples rapidly lose their form in air and become powders. Similar behavior has been observed in cuprates of the same composition. Although this process takes place much more slowly, admixtures of alkaline-earth carbonates have been found in samples after two–three weeks of storage. The mechanism of this process for cobaltates is not yet understood. The possibility of the cobaltate surface reacting with an external medium is not even mentioned in the literature, though this certainly would lead to a change of the properties of the material in due time. Since increased lanthanum content has been recorded in the surface layer of crystallites, $\text{La}(\text{OH})_3$ is the main product at the reaction with the external medium, as is confirmed by X-ray photoelectron spectroscopy data. Interaction with water vapor in the atmosphere thus occurs upon the sample's contact with the surrounding medium.

Cobaltates' mechanochemical properties are interesting as well. Cracks $\sim 0.1 \mu\text{m}$ wide are seen in the photomicrographs of a series of samples. The coefficients of the thermal expansion (CTEs) for complex cobalt oxides are approximately $(10\text{--}12) \times 10^{-6} \text{ K}^{-1}$ (700–1200 K). When CTEs are taken into account, fast cooling by 1000 K can lead to the appearance of breakups in the sample of exactly such values.

The temperature dependence of resistance is given in Fig. 2 for $\text{La}_{1.7}\text{Sr}_{0.3}\text{CoO}_4$. The dependence has a nonmetallic character, and resistance increases with decrease in the temperature. Curves *a* and *b* refer to different parts of the sample. It is seen that at low temperatures the dependence for them is the same but the resistance values differ and are rather high; at low temperatures it is in fact possible that microcracks appear or widen and the percolation conditions for the charge carrier worsen. There is probably tunnel conductivity between the grains (granules). At high temperatures, the two curves almost coincide. With a drop in temperature, the electron activation energies needed to overcome the intergranule tunnel barriers for different parts of the sample differ strongly in different regions of the sample and the $R(T)$ no longer coincide.

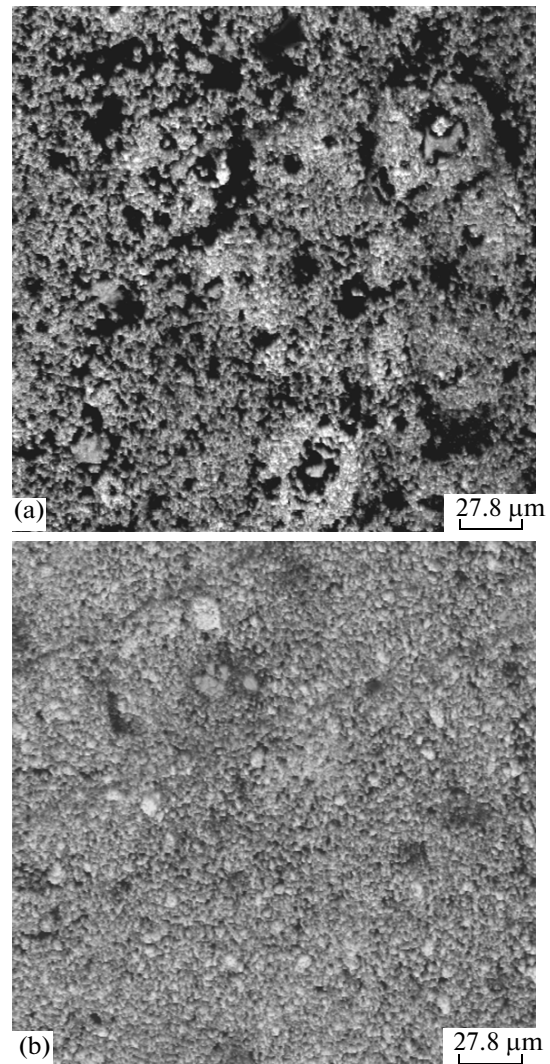


Fig. 1. Photomicrographs of the LaSrCoO_4 sample: (a) quenching in air from the temperature of synthesis; (b) cooling in the furnace.

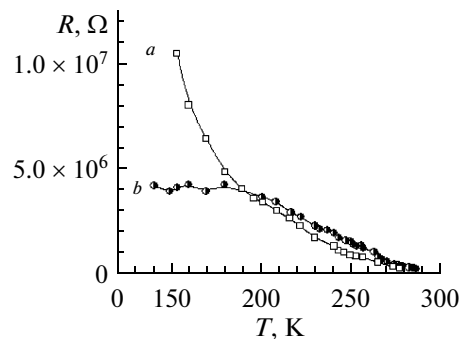


Fig. 2. Temperature dependence of resistance for $\text{La}_{1.7}\text{Sr}_{0.3}\text{CoO}_4$.

Since the component ratio changes when the conditions of the synthesis change, it may be assumed that “low” temperatures cannot be considered to be suffi-

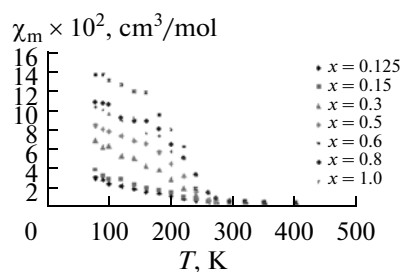


Fig. 3. Temperature dependence of molar magnetic susceptibility for $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ (measured in a field of 5000 Oe).

cient for complete attainment of the solid-state reaction. The samples were therefore synthesized at higher temperatures and the temperature was increased gradually. The mode of preliminary annealing was maintained, and the temperature was increased from 1500 to 1700 K. According to the XPA data, the samples had a perovskite-type structure, and according to the data of scanning electron microscopy and microanalysis of the sample composition, the average sample composition corresponded to the chemical formula. Analysis of the microstructure, however, showed that the element ratio was 2 : 1 or 1 : 1 at different points. Such ratios correspond to the perovskite-like tetragonal $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ and perovskite LaSrO_x structures, respectively. In addition, we recorded points corresponding to the lanthanum oxide La_2O_3 . It is known that the conventional stage of a solid-state reaction is nucleation, and it occurs faster when the reaction product is structurally close to at least one of the

reagents. The initial reagents for the synthesis were lanthanum oxide, strontium carbonate and cobalt oxide. CoO is the closest in structure to $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$. The nucleation centers of the perovskite-like phase can be formed on surface of the cobalt oxide, and phases containing lanthanum and strontium are probably formed as admixtures.

CONCLUSIONS

The magnetic susceptibility of samples with any strontium content declines upon an increase in temperature, becoming almost zero after $T = 250$ K (Fig. 3). The transition from the ferromagnetic to the paramagnetic state at the temperature of 250 K thus occurs in all $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ samples. Interestingly, the susceptibility of samples increases upon quenching. This is logical, since part of the Sr moves to the admixture phase upon quenching, the proportion of diamagnetic Co(III) in the main structure is reduced, and susceptibility is determined only by the behavior of paramagnetic Co(II) .

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