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Surface Phenomena in Conducting Materials Based on Lanthanum Chromite

A. P. Shevchik and S. A. Suvorov

St. Petersburg State Institute of Technology (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: saraeva@nm.ru

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Abstract — The composition of the surface of a solid solution based on lanthanum chromite, $La_{0.975}Ca_{0.025} \cdot Cr_{0.9}Al_{0.1}O_3$, and prepared by solid-phase synthesis followed by vacuum sintering and annealing in air was studied by X-ray photoelectron spectroscopy. The spectral line of chromium differs from the lanthanum line in the X-ray photoelectron spectrum in that the left wing of the chromium line is more gently sloping. The gentle slope of the line wing indicates that the given atom occurs in different charge states. For chromium, it appears possible to resolve the Cr^{3+} and Cr^{6+} bands in the X-ray photoelectron spectra, which allows estimation of the Cr^{3+} and Cr^{6+} concentrations.
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Lanthanum chromite $LaCrO_3$ is the highest-melting compound among rare-earth chromites. Its melting point is 2510±20°C [1]. Rare-earth chromites are oxide conductors; this distinguishes them from the majority of other refractory oxides, which are mostly dielectrics. Materials (including resistive) based on rare-earth chromites modified with alkaline-earth oxides and suitable for fabrication of high-temperature heaters operating at temperatures of up to 1800°C in oxidizing gas media have been developed [2, 3].

Resistive materials are multicomponent (multiphase) materials; they contain, along with a conducting component, also a dielectric component in an amount that does not prevent passing of electric current. Resistive materials show particular promise for fabricating oxide electric heaters, because they allow a constant cross section to be provided throughout the heater length [4].

The conducting properties of $LaCrO_3$ are strongly affected by the presence of Cr ions in the oxidation state higher than 3+ in the surface layer of grains of polycrystalline $LaCr^{3+}O_3$ [5]. Doping of the La sublattice in $LaCrO_3$ with an acceptor admixture (most frequently, with alkaline-earth elements) is accompanied by additional transformation of a part of Cr^{3+} ions in oxidizing media into a more oxidized state.

X-ray photoelectron spectroscopy (XPS) is widely used for studying the composition of the grain surface in crystalline materials [6].

The electronic levels of the Cr, La, and O atoms can be readily identified in the spectrum of $LaCrO_3$ [5]. This, in particular, concerns the levels La3*d* (relative binding energy of the doublet 830–835 and 845–850 eV), La4*d* (100–105 eV), La5*s* (35–40 eV), La5*p* (18–20 eV), Cr2*p* (575–585 eV), Cr3*s* (75–80 eV), Cr3*p* (45–50 eV), and O2*s* (20–22 eV). Only the valence levels of chromium (Cr3*d*) and oxygen (O2*p*) are overlapped. The Cr2*p* and Cr2*s* levels form doublets, which may be due to spin–spin coupling of electrons of the Cr3*s* and Cr2*p* levels, on the one hand, with those of the Cr3*d* level, on the other hand. The spin–orbital splitting of the La3*d* level into the $La3d_{3/2}$ and $La3d_{5/2}$ levels is 16.8 eV. Also, the La3*d* levels have satellite lines separated from the main lines by 4 eV; the sattelites are apparently attributable to the electron transfer from the valence band of lanthanum to its *f* band. Similar location of La peaks in the photoelectron spectra of lanthanum oxide compounds of the perovskite structure (lanthanum chromite $LCrO_3$, lanthanum manganite $LaMnO_3$, lanthanum cobaltite $LaCoO_3$, lanthanum ferrite $LaFeO_3$) indirectly indicates that the interaction of La with the *d* element in these compounds is weak.

The photoelectron spectrum of $LaCrO_3$ was calculated theoretically using the MO LCAO model and the Griffith–Rotenberg model of the multiplet structure of free ions. These two models are mutually supplementing.

Using the MO LCAO model, we calculated the electronic configurations and energy levels of molecular orbitals of $(CrO_6)^{9-}$ and $(LaO_{12})^{21-}$. The calculated spectrum is well consistent with the experiment.

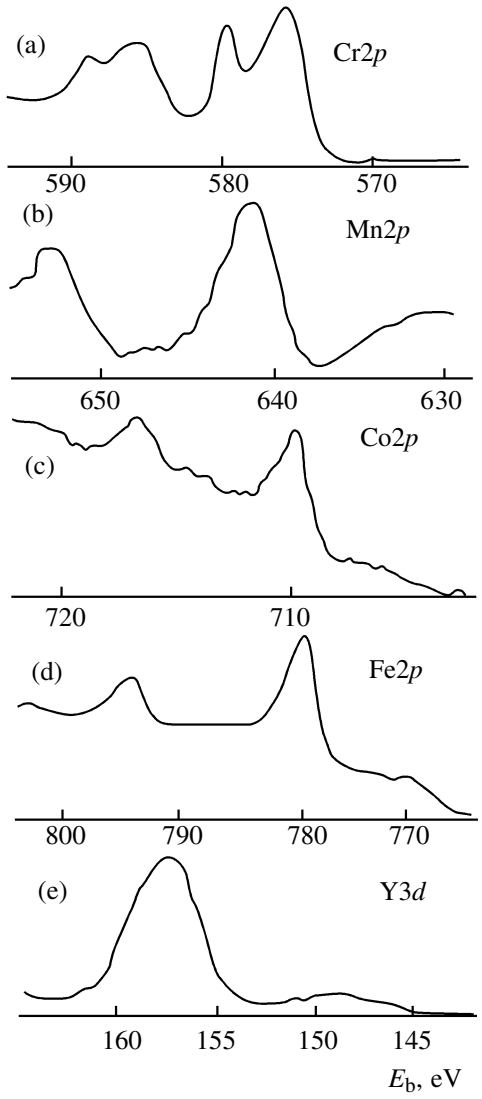

Fig. 1. X-ray photoelectron spectra of the B ion in $La_{0.8}Sr_{0.2}BO_3$: (a) $La_{0.8}Sr_{0.2}CrO_3$, (b) $La_{0.8}Sr_{0.2}MnO_3$, (c) $La_{0.8}Sr_{0.2}CoO_3$, (d) $La_{0.8}Sr_{0.2}FeO_3$, and (e) $La_{0.8}Sr_{0.2}YO_3$.

The system of the molecular orbitals of $(CrO_6)^{9-}$ had the following electronic levels: Cr3d^3 $(2t_{2g})^3$, first occupied level; O2p $(1t_{1g})$, distance from the first level 5.1 eV; O2p $(6t_{1u})$, 5.6 eV; O2p $(1t_{2u})$, 6.0 eV; O2p $(3e_g)$, 7.4 eV; O2p $(1t_{2g})$, 8.8 eV; O2p $(5t_{1u})$, 8.9 eV; O2p $(6a_{1g})$, 9.0 eV; O2s $(2e_g)$, 21.5 eV; O2s $(4t_{1u})$, 22.2 eV; O2s $(5a_{1g})$, 22.9 eV; Cr3p $(3t_{1u})$, 43.5 eV; and Cr3s $(4a_{1g})$, 70.6 eV. For the system of molecular orbitals of $(LaO_{12})^{21-}$, we obtained the following results: first occupied level O2p $(4t_{2g})$; O2p $(9t_{1u})$, distance from the first level 0.6 eV; O2p $(6e_g)$, 0.6 eV; O2p $(4t_{1g})$, 0.7 eV; O2p $(1e_u)$, 0.8 eV; O2p $(1a_{2g})$, 1.2 eV; O2p $(3t_{2u})$, 2.1 eV; O2p $(4t_{2g})$, 2.9 eV; O2p $(8t_{1u})$, 3.2 eV; O2p $(3t_{2g})$, 3.4 eV; O2p $(8a_{1g})$, 3.5 eV; O2p $(3t_{1g})$, 3.7 eV; O2p $(5e_g)$, 4.6 eV; O2p $(1a_{2u})$, 4.6 eV; O2p $(7t_{1u})$, 5.1 eV; La5p $(6t_{1u})$, 12.6 eV; O2s $(2t_{2u})$, 17.6 eV; O2s $(2t_{1g})$, 17.8 eV; O2s $(7a_{1g})$, 19.1 eV; O2s $(5t_{1u})$, 19.2 eV; and La5s $(6a_{1g})$, 25.9 eV.

The multiplet structure of the valence level Cr3d was calculated using the Tanabe and Sugano diagrams. According to the calculations, the photoelectron spectrum should contain a single line corresponding to the Cr3d energy level. This line corresponds to the electron transition from the initial d^3 configuration of chromium (term $^4A_2$) to the d^2 configuration ($^3T_1$).

The X-ray photoelectron spectrum of a $LaCrO_3$-based solid solution of the composition $La_{0.8}Sr_{0.2}CrO_3$ was examined in [7]. The samples were prepared by a solid-phase procedure. The starting compounds were mixed in a required ratio, pelletized, and fired in the temperature range from 1000 to 1100°C for 12 h. The resulting pellets were ground, after which pelletizing and firing for 12 h were repeated. This procedure yielded a single-phase product, as confirmed by X-ray phase analysis.

The X-ray photoelectron spectrum was recorded on a Kratos XSAM 800 Auger/ESCA system. The spectra were excited with MgK_α radiation and were calibratred against the carbon C1s line (binding energy 284.5 eV).

The binding energies of the inner levels of the elements (La3d, Cr2p, O1s, Sr3d) were determined. The binding energy of the La3$d_{5/2}$ line was 833.2 eV. The spectrum contained a satellite peak shifted by ~4 eV relative to the main line. The binding energy of the Sr3$d_{5/2}$ line was 133.7 eV. The spin–orbital splitting of the Sr3$d_{5/2,3/2}$ lines was 1.7 eV. The spectrum of lanthanum chromite of the composition $La_{0.8}Sr_{0.2}CrO_3$ contains two resolved Cr2$p_{3/2}$ peaks with energies of 575.6 and 579.2 eV (Fig. 1). The spectrum of the oxygen O1s state is a well-resolved doublet with binding energies of the peaks of 528 and 531 eV (Fig. 2).

To analyze the composition of the surface, we used the XPS data. The content of the La, Sr, and Cr atoms on the surface was calculated from the areas of the corresponding peaks in the photoelectron spectrum. The relative peak areas (%) were as follows: La3$d_{5/2}$ 31.9, Sr3$d_{5/2}$ 26.8, and Cr2$p_{3/2}$ 41.3. Thus, the ratio of the Cr cations to the sum of La and Sr cations on the surface appeared to be 0.7.

Alkaline-earth metal cations M^{2+} (M = Ca, Sr, and/or Ba), when present in a solid solution based on lanthanum chromite, give rise to vacancies in the oxy-

gen sublattice. These vacancies can be partially filled by Cr ions in an oxidation state higher than 3+, or by additional O atoms. Measurements of the electrical conductivity of $La_{1-x}Sr_xCrO_3$ show that partial (up to 30%) replacement of La^{3+} by Sr^{2+} leads to predominant formation of Cr^{4+}.

It was found that Cr in $La_{0.8}Sr_{0.2}CrO_3$ is present in two different oxidation states, namely, 3+ and 4+ or 6+. Sr is present in the form of the Sr^{2+} ion and is distributed in the $LaCrO_3$ lattice nonuniformly. Oxygen mainly participates in metal–oxygen bonds, although hydroxy groups can be formed on the surface in a minor amount.

The X-ray photoelectron spectrum of a $LaCrO_3$-based solid solution of the composition $La_{0.7}Ca_{0.3}\cdot Cr_{0.9}M_{0.1}O_3$, where M = Mn, Fe, Ni, Cu, was examined in [8].

Measurements of E_b of the La4*d* line show that La in all the complex oxides occurs as the La^{3+} cation. The binding energies of the Ca2$p_{3/2}$ lines are shifted relative to pure elemental Ca and correspond to those of Ca^{2+}.

All the spectra contain the Cr2$p_{3/2}$ lines with the energies characteristic of Cr_2O_3 and CrO_2 and thus corresponding to Cr^{3+} and Cr^{4+}. The intensity ratio $I(Cr^{4+})/I(Cr^{3+})$ in all the examined samples is close (0.96–0.97). This fact suggests that the Cr^{4+}/Cr^{3+} ratio is approximately constant and hence only slightly dependent on modification of the Cr sublattice with other *d* elements.

Peaks corresponding to the state of the O lattice were identified in the experimental spectrum of the O1*s* state. The spectrum mainly reflects the bonds of O with Cr and La, because it exhibits features characteristic of such compounds as La_2O_3, Cr_2O_3, CrO_2, CrOOH, and LaOOH.

The binding energies obtained are somewhat higher than those characteristic of La_2O_3 and closer to the value for CaO. Presumably, partial replacement of La by Cr causes weakening of the La–O bonds in the lattice. The existing M–O bond (where M = La, Ca) is intermediate in strength between the La–O and Ca–O bonds. Broadening of the O1*s* line from the high-energy side is most probably caused by the presence of an additional line from hydroxide impurities and by adsorption of oxygen on the sample surface.

The binding energies (E_b) of the inner levels of the elements (La4*d*, Cr2*p*, O1*s*, and also Ca2*p*) were determined (Table 1). Changes in the shape of the La4*d* and O1*s* lines with variation of the metal M were considered.

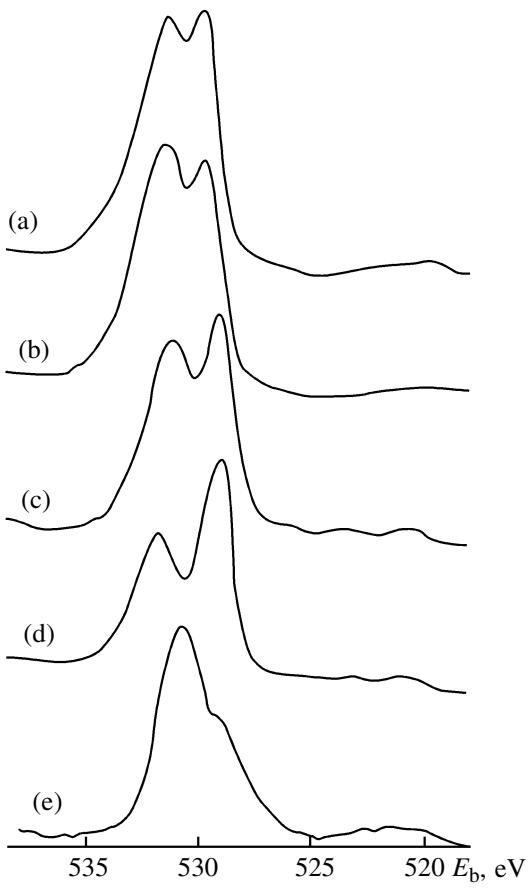

Fig. 2. X-ray photoelectron spectra of the oxygen O1*s* lines: (a) $La_{0.8}Sr_{0.2}CrO_3$, (b) $La_{0.8}Sr_{0.2}MnO_3$, (c) $La_{0.8}Sr_{0.2}CoO_3$, (d) $La_{0.8}Sr_{0.2}FeO_3$, and (e) $La_{0.8}\cdot Sr_{0.2}YO_3$.

The electron binding energies were measured for the "sharpest" lines: La4$d_{3/2}$, Fe2$p_{3/2}$, Ca2$p_{3/2}$, Cr2$p_{3/2}$, Cr2$p_{1/2}$, Mn2$p_{3/2}$, Ni2$p_{3/2}$, Cu2$p_{3/2}$, and O1*s*. The spectra were taken from polycrystalline samples; therefore, the lines are somewhat broader and weaker compared to the spectrum from single crystals.

The spectrum of the La4*d* line is a $4d_{5/2}$–$4d_{3/2}$ doublet (Fig. 3). The distance between its components in the spectra of $La_{0.7}Ca_{0.3}Cr_{0.9}Mn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}\cdot Cr_{0.9}Cu_{0.1}O_3$ is the same, 2.7 eV. In $La_{0.7}Ca_{0.3}Cr_{0.9}\cdot Fe_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Cr_{0.9}Ni_{0.1}O_3$, the splitting increases to 2.8 and 3.0 eV, respectively. An increase in the splitting is usually associated with an increase in the localization of electrons on the anion, namely, with a shift of the electron density toward O anions. The intensity ratio $I(d_{5/2})/I(d_{3/2})$ remains constant in all the spectra. The binding energy of the La4$d_{3/2}$ line

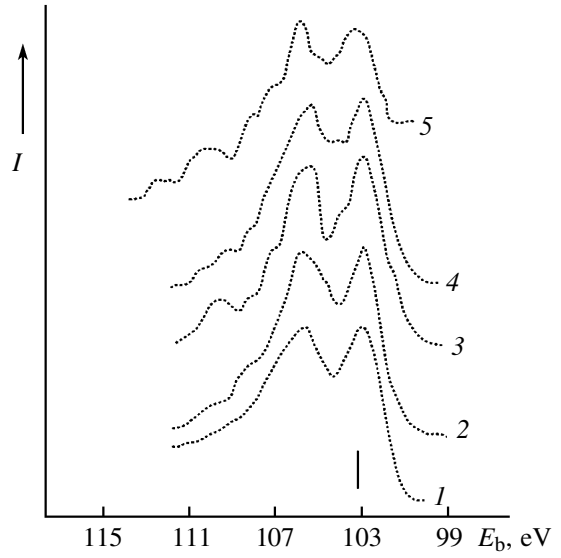

Fig. 3. X-ray photoelectron spectra of La4$d_{5/2;3/2}$ lines: (*1*) La_2O_3, (*2*) $La_{0.7}Ca_{0.3}Cr_{0.9}Ni_{0.1}O_3$, (*3*) $La_{0.7}Ca_{0.3}Cr_{0.9}Mn_{0.1}O_3$, (*4*) $La_{0.7}Ca_{0.3}Cr_{0.9}Fe_{0.1}O_3$, and (*5*) $La_{0.7}Ca_{0.3}Cr_{0.9}Cu_{0.1}O_3$.

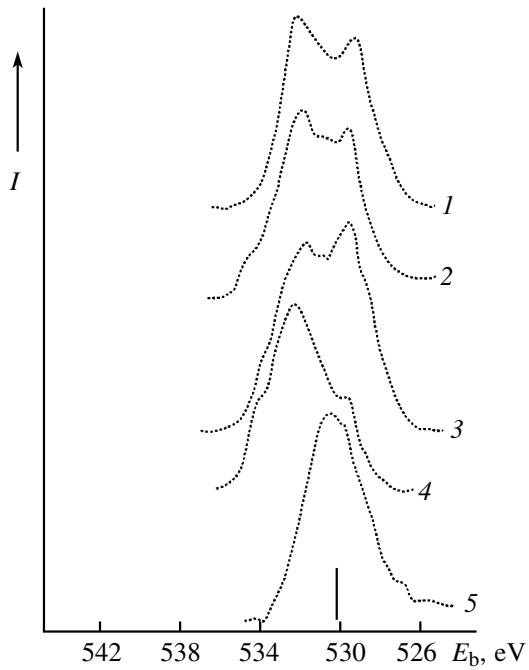

Fig. 4. X-ray photoelectron spectra of oxygen O1*s* lines: (*1*) La_2O_3, (*2*) $La_{0.7}Ca_{0.3}Cr_{0.9}Ni_{0.1}O_3$, (*3*) $La_{0.7}Ca_{0.3}Cr_{0.9}Mn_{0.1}O_3$, (*4*) $La_{0.7}Ca_{0.3}Cr_{0.9}Fe_{0.1}O_3$, and (*5*) $La_{0.7}Ca_{0.3}Cr_{0.9}Cu_{0.1}O_3$.

is 101.7 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Ni_{0.1}O_3$, 101.6 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Cu_{0.1}O_3$, and 101.5 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Mn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Cr_{0.9}Fe_{0.1}O_3$. A satellite structure (shoulders) is present on the high-energy side of the La4$d_{5/2}$ line. Resolution of the spectrum into components gives the separation of the sattelite line of 1.6, 1.3, 1.8, and 1.8 eV from the main peak in $La_{0.7}Ca_{0.3}Cr_{0.9}M_{0.1}O_3$ with M = Mn, Fe, Ni, and Cu, respectively. Also, all the spectra contain a satellite separated from the main line by 4.3 eV.

Table 1. Binding energies of inner electrons of elements entering into the composition of lanthanum chromites $La_{0.7}Ca_{0.3}Cr_{0.9}M_{0.1}O_3$

M	E_b, eV				
	La4$d_{3/2}$	Ca2$p_{3/2}$	Cr2$p_{1/2}$	Cr2$p_{3/2}$	O1*s*
Mn	101.5	346.8	585.8, 587.6	576.3, 576.8	529.6, 530.6, 531.4, 534.2
Fe	101.5	347.1		576.7, 576.8	529.8, 530.7, 531.5, 532.2
Ni	101.7	347.4	586.2, 586.9	576.6, 576.0, 577.2	528.8, 529.4, 530.4, 530.8
Cu	101.6	347.1	586.2, 586.9		529.8, 530.4, 530.8, 532.2

The Cr spectrum shows a complex pattern. In the spectra of $LaCrO_3$-based solid solutions, there are Cr2$p_{1/2}$ lines with the energies of 586.2 and 586.9 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Ni_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Cr_{0.9}Cu_{0.1}O_3$, and 585.8 and 587.6 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Mn_{0.1}O_3$. The Cr2$p_{3/2}$ lines have the binding energies of 576.3 and 576.8 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Mn_{0.1}O_3$, 576.7 and 576.8 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Fe_{0.1}O_3$, and 576.6, 576.0, and 577.2 eV in $La_{0.7}Ca_{0.3}Cr_{0.9}Ni_{0.1}O_3$.

The O1*s* spectra were also measured for all the samples (Fig. 4). The spectrum shape depends on the modifying element M. According to the data obtained, the spectrum of the oxygen O1*s* state covers the range from 527.8 to 532.4 eV. In this range, a number of peaks overlap, giving resolved maxima or shoulders. The peaks at 529.4 and 529.8 eV have the most stable positions. Heating to 250°C does not alter the peak positions and intensities; therefore, these peaks were assigned to states of oxygen in the lattice.

EXPERIMENTAL

We examined a multicomponent resistive material containing Ca- and Al-doped lanthanum chromite $La_{0.975}Ca_{0.025}Cr_{0.9}Al_{0.1}O_3$ and yttrium oxide Y_2O_3 [TU (Technical Specifications) 48-4-524–90].

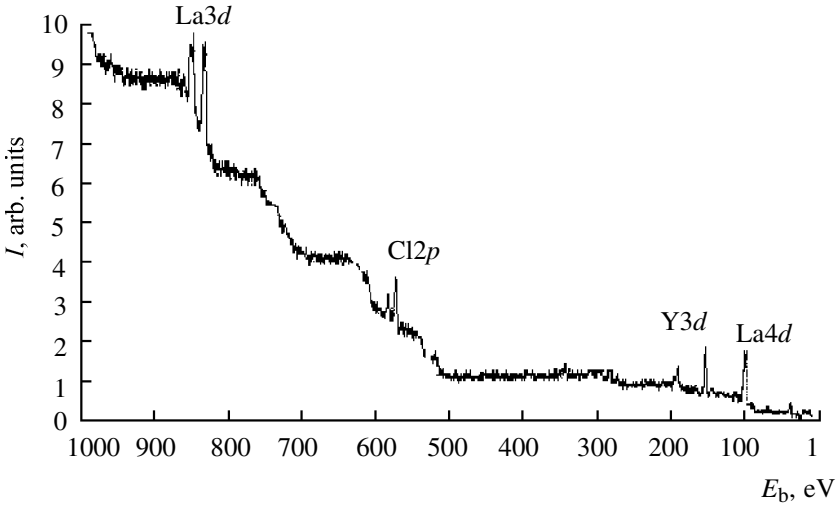

Fig. 5. Total X-ray photoelectron spectrum of the resistive composite.

Weighed portions of $La_{0.975}Ca_{0.025}Cr_{0.9}Al_{0.1}O_3$ prepared in advance and Y_2O_3 were mixed in a required ratio in a vibrating mill for 2 h; the weight ratio of the material to milling bodies was 1 : 9.

The resulting mixture was moistened with a 5% aqueous solution of polyvinyl alcohol to a moisture content of 5%. The charge was pelletized with a hydraulic press at a pressure of 50 MPa. The pellets were placed in corundum crucibles, covered with a grainy powder of Y_2O_3, and fired in air at 1300°C for 3 h. The furnace temperature was raised at a rate of up to 300 deg h^{-1}. Firing was followed by natural cooling. The pellets fired in air were placed in a molybdenum container, covered with a grainy powder of Y_2O_3, and heat-treated in a vacuum at 1800°C for 2 h (heating rate up to 15 deg min^{-1}). The treatment was followed by natural cooling. After the repeated heat treatment, the pellets were crushed to a particle size less than 1 mm. The crushed material was subjected to magnetic separation and grinding in a vibrating mill for 8 h at 1 : 12 ratio of the material to the milling bodies.

According to X-ray phase analysis, the material prepared contained lanthanum chromite and Y_2O_3. The BET specific surface area of the powders was 0.65–0.80 $m^2 g^{-1}$.

In the course of examining the resistive composite $La_{0.975}Ca_{0.025}Cr_{0.9}Al_{0.1}O_3$–$Y_2O_3$ intended for resistive heating elements, we measured the X-ray photoelectron spectrum of the material (Figs. 5–7). We recorded the bands of the main components: La, Y, and Cr (Table 2).

The Cr bands (Fig. 8) differ from the Y and La bands in the X-ray photoelectron spectrum in that the left wings of the Cr bands are gently sloping, whereas the right wings and the wings of the Y and La bands are steep.

The gentle sope of the Cr band suggests the presence of Cr atoms in different oxidation states. The Cr^{3+} and Cr^{6+} bands in the X-ray photoelectron spectrum can be resolved [9]. After the band resolution (Fig. 8), it is possible to estimate the Cr^{3+} and Cr^{6+} concentrations. The results of quantitative determination of the Cr^{3+} and Cr^{6+} content in the resistive composite are given in Table 3.

Thus, in the examined lanthanum chromite $La_{0.975} \cdot Ca_{0.025}Cr_{0.9}Al_{0.1}O_3$ the mean content of Cr(III) and Cr(VI) is 69 and 31 at. %, respectively (Table 3).

Let us assume that Cr(VI) is formed in the resistive composite by partial oxidation of Cr(III) and complete oxidation of Cr(IV).

Table 2. Identification of bands in the X-ray photoelectron spectrum of the resistive composite

Element	Electronic level	Binding energy, eV	
		test substance	reference
La	3*d*	836.4, 840.3	833.7, 835.1
		853.2, 857.0	~845–850
	4*d*	~103	101.1, 101.7
Y	3*d*	159.7, 161.5	156.8 (main line)
Cr	2*p*	578.6, 588.3	~575–585

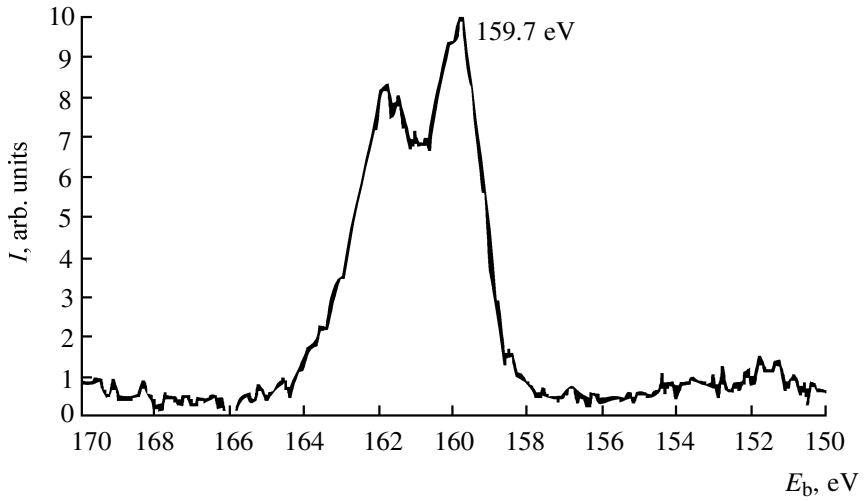

Fig. 6. Y3*d* band in the X-ray photoelectron spectrum of the resistive composite.

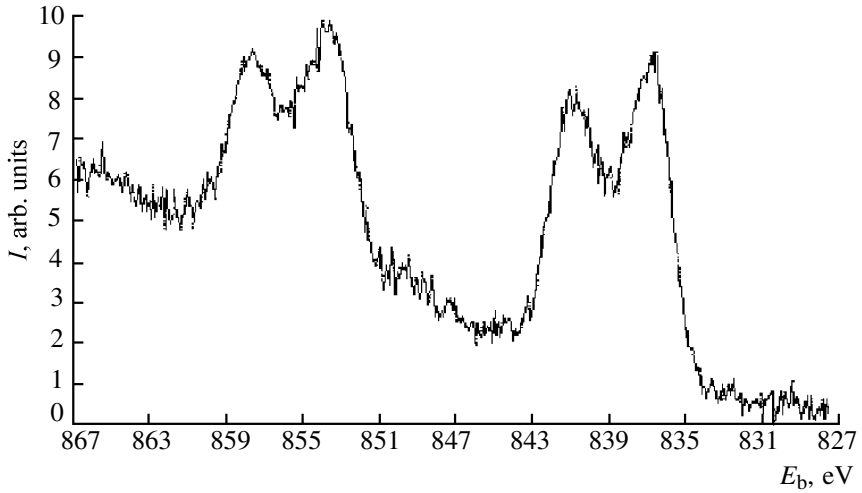

Fig. 7. La3*d* bands in the X-ray photoelectron spectrum of the resistive composite.

Since the Cr(VI)/Cr(III) atomic ratio in the composite is 31 : 69, the amount of oxidized Cr(III) is 0.254.

Table 3. Content of Cr^{3+} and Cr^{6+} in the resistive composite

Band no.	Cr charge state	Binding energy, eV	Atomic concentration, %
1	+3	578.6	74.85
	+6	581.0	25.15
2	+3	588.3	63.06
	+6	591.0	36.94

Thus, the composition of the $LaCrO_3$-based solid solution in which Cr occurs in the tri- and hexavalent states can be presented as $La_{0.975}Ca_{0.025}Cr(III)_{0.621} \cdot Cr(VI)_{0.279}Al_{0.1}O_{3.406}$. In this notation of the formula of the $LaCrO_3$-based solid solution, excess O is required to provide electroneutrality of the crystal lattice. However, the oxygen stoichiometry of $LaCrO_3$ in an oxidizing medium is stable [10]. Therefore, it can be suggested that the superstoichiometric amount of O will bind Cr(VI) and pass into the gas phase.

Let us determined the amount of Cr that passed into the gas phase in the form of CrO_3 and the amounts of Cr^{3+} and Cr^{6+} remaining in the crystal

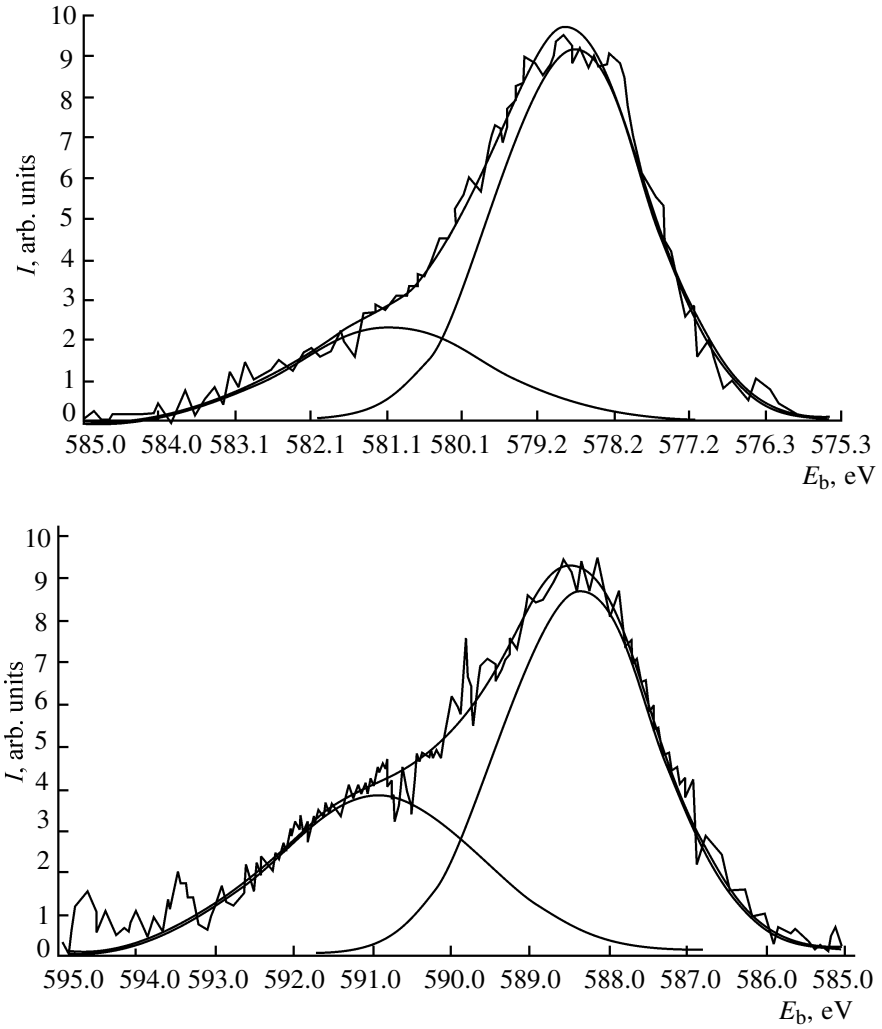

Fig. 8. Resolution of Cr bands in the X-ray photoelectron spectrum of the resistive composite.

lattice, assuming that the Cr(VI) : Cr(III) atomic ratio in the lattice (39 : 61) is preserved.

For the dissociation products of the $LaCrO_3$-based solid solution, $La_{0.975}Ca_{0.025}Cr(III)_{x_1}Cr(VI)_{x_2}Al_{0.1}O_3$ and x_3CrO_3, taking into account the conditions of material balance with respect to Cr, electroneutrality of the crystal lattice, and Cr(VI) : Cr(III) atomic ratio, we obtain $x_1 = 0.478$, $x_2 = 0.215$, and $x_3 = 0.207$.

Thus, dissociation of a $LaCrO_3$-based solid solution yields a $La_{0.975}Ca_{0.025}Cr(III)_{0.478}Cr(VI)_{0.215} \cdot Al_{0.1}O_3$ solid solution, and 0.207 mol of CrO is released per mole of this product.

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