ISSN 0027-1314, Moscow University Chemistry Bulletin, 2007, Vol. 62, No. 2, pp. 93–95. © Allerton Press, Inc., 2007.
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Surface Composition in Perovskite-Like Cuprates as Probed by X-ray Photoelectron Spectroscopy

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Received December 26, 2005

Abstract—Complex cuprates $La_{0.85}Sr_{0.15}CuO_{2.5-\delta}$ having an anion-deficient perovskite structure and $La_{2-x}Sr_xCuO_{4-\delta}$ ($x = 0.15, 0.6, 1.0$) having a K_2NiF_4 layered structure have been prepared by ceramic technology. X-ray powder diffraction verified that single-phase samples were obtained. X-ray photoelectron spectroscopy (XPS) was used to determine the surface composition of compacted samples. It was found that both the photoionization cross-section and the photoelectron mean free path should be taken into account when calculating the surface composition. The surface was enriched in strontium as a result of segregation, regardless of the bulk composition of the cuprate sample.

DOI: 10.3103/S0027131407020083

Oxide materials with high mixed (electron/ion) conductivity are now in the focus of research on account of their potential for use as materials for cathodes in high-temperature fuel cells, oxygen pumps, various oxygen pickups, and selective oxygen-permeable, electrocatalytically active membranes.

The oxygen ion conductivity in perovskite complex oxides is due to the existence of anion vacancies. Varying the dopant concentration in the cation sublattice, the oxygen partial pressure, or temperature offers a means for intentionally varying the density of anion vacancies. For a sample with a fixed cation composition, the change in the oxygen deficiency is accompanied by a change in the charge of the transition element, which in turn changes the concentration of the majority charge carriers and thus the total conductivity of the material. It was demonstrated [1, 2] that materials based on cuprates with a distorted perovskite structure and the composition $La_{1-x}Sr_xCuO_{2.5-\delta}$ ($0.15 < x < 0.3$) have high electrical conductivities (mostly of the *p* type). As a result of the high density and mobility of anion vacancies, cathodes based on such phases have sufficiently low absolute values of the polarization resistance [3].

Cuprates of composition $La_{2-x}Sr_xCuO_{4-\delta}$ also have an anion-deficient structure; this is a K_2NiF_4-type structure in which perovskite layers alternate with NaCl-type layers. When the strontium concentration in these phases is low, they have metal-type conductivity [4]. At a significant strontium concentration, however, the anion vacancy density increases; in view of the high oxygen mobility in this structure [5], an oxygen electrode based on this phase is expected to have a high reversibility. The catalytic activity of a cathode material in oxygen reduction is also an important criterion. Thus, the investigation of the surface layers of complex cuprates is very topical. X-ray photoelectron spectroscopy (XPS), which enables the profiling of the near-surface layers with 0.5–1.0 nm steps [6, 7], is a useful tool in this context.

The goals of this work were to synthesize complex cuprates $La_{0.85}Sr_{0.15}CuO_{2.5-\delta}$ and $La_{2-x}Sr_xCuO_{4-\delta}$ ($x =$ 0.15, 0.6, or 1.0) and to study the surface cation composition of these samples using XPS.

EXPERIMENTAL

Ceramic technology was used to prepare lanthanum strontium cuprates. The starting chemicals used were commercially available La_2O_3 and $SrCO_3$ (pure for analysis grade) and CuO prepared by the decomposition of malachite at 300°C. Before weighing, La_2O_3 was calcined at 900°C and $SrCO_3$ was at 400°C. The synthesis schedules are displayed in Table 1.

Table 1. Parameters of cuprate synthesis

Sample composition	Annealing schedule
$La_{1.85}Sr_{0.15}CuO_{4-\delta}$ $La_{0.85}Sr_{0.15}CuO_{2.5-\delta}$	1273 K, 20 h, furnace cooling
$La_{1.4}Sr_{0.6}CuO_{4-\delta}$	1393 K, 15 h, quenching to room temperature
$LaSrCuO_{4-\delta}$	1473 K, 7 h, quenching to room temperature

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Table 2. Unit cell parameters for cuprates synthesized

Sample composition	Space group	Unit cell parameters	
		a, b, Å	c, Å
$La_{1.85}Sr_{0.15}CuO_{4-\delta}$	*I*4/*mmm*	3.7801(8)	13.228(4)
$La_{1.4}Sr_{0.6}CuO_{4-\delta}$	*I*4/*mmm*	3.7722(7)	13.189(3)
$LaSrCuO_{4-\delta}$	*I*4/*mmm*	3.7602(2)	13.005(1)
$La_{0.85}Sr_{0.15}CuO_{2.5-\delta}$	*P*4/*mbm*	10.861(3)	3.8584(7)

Table 3. Binding energies for XPE peaks and relevant lines

Cu						
E_b, eV	1070	954	934	124	78	
Line	$2s$	$2p_{1/2}$	$2p_{3/2}$	$3s$	$3p$	
Sr						
E_b, eV	358	280	260	134	37	
Line	$3s$	$3p_{1/2}$	$3p_{3/2}$	$3d$	$4s$	
La						
E_b, eV	851	834	274	210	195	102
Line	$3d_{3/2}$	$3d_{5/2}$	$4s$	$4p_{1/2}$	$4p_{3/2}$	$4d$

The phase composition was monitored by X-ray powder diffraction (Guinier-deWolf camera, CuK_α radiation, germanium internal standard). Powders were compacted into disks (two disks for each cuprate) under a load of ~4 t/cm^2. After heat treatment at 600°C for 20 h, the disks were subjected to XPS surface analysis.

The surface analysis was carried out on a Leybold LHS-10 electron spectrometer. X-ray photoelectron spectra were measured at 10^{-7} Pa pressure in the analyzer chamber. The exciting radiation used was MgK_α with a photon energy of 1253.6 eV and a line width of ~0.7 eV. A hemispherical energy analyzer was used for the electron energy expansion. The energy analyzer was calibrated against the Au $4f_{1/2}$ line with E_b = 83.9 eV; the instrumental resolution for this line was 0.9 eV. The E_b measurement accuracy was ~0.1 eV. The signal detector/amplifier used was an EMI electron multiplier, which ensured an amplified signal intensity of 10^4 to 10^5 pulse/s. From the measured spectra, the copper, strontium, and lanthanum line intensities were determined and the surface cation composition was calculated. The interpretation of the XPS spectra was based on the peak intensities, peak shapes, and binding energies.

RESULTS AND DISCUSSION

X-ray powder diffraction verified the absence of impurities in the samples: all X-ray diffraction lines from $La_{2-x}Sr_xCuO_{4-\delta}$ (x = 0.15, 0.6, 1.0) and $La_{0.85}Sr_{0.15}CuO_{2.5-\delta}$ samples were indexed in a tetragonal unit cell. The unit cell parameters calculated from the results of indexing are listed in Table 2.

From the XPS analysis of the surface, the kinetic energies of photoelectrons were derived. The binding energies corresponding to copper, strontium, and lanthanum lines were calculated from the photo effect law:

$$E_{\mathrm{kin}} = h\nu - E_{\mathrm{b}} + \varphi, \qquad (1)$$

Here, E_{kin} is the kinetic energy of a photoelectron, E_{b} is the binding energy of an electron, $h\nu$ is the MgK_a photon energy, φ is the photoelectron work function (equated to zero in the experiment). The peaks associated with the La $3d_{5/2}$, Sr $3d$, Cu $2p_{3/2}$, and O $1s$ levels have close spectral parameters; above all, they differ in their intensities (Table 3).

Thus, in all samples the surface contains copper, lanthanum, and strontium cations; this means that qualitatively the surface composition does not differ from the bulk composition. For quantifying the surface cation composition, we used the intensities of the lines associated with the La $3d_{5/2}$, Sr $3d$, and Cu $2p_{3/2}$ core levels. The energy difference between XPS lines is sufficiently great, and the calculations from

$$n_i/\sum_{i=1}^{m} n_i = \left(\frac{I_i}{\sigma_i}/\sum_{i=1}^{m}\frac{I_i}{\sigma_i}\right)\times 100\% \qquad (2)$$

are not quite adequate (this simplified relationship only accounts for the photoionization cross-section σ). Therefore, calculating the concentration of each cation, we took into account not only the photoionization cross-section, but also the electron mean free path Λ, using the relationship

$$n_i/\sum_{i=1}^{m} n_i = \left(\frac{I_i^*\sqrt{E_i}}{\sigma_i}/\sum_{i=1}^{m}\frac{I_i^*\sqrt{E_i}}{\sigma_i}\right)\times 100\%. \qquad (3)$$

Here, $n_i/\sum_{i=1}^{n} n_i$ is the element concentration for each cation, E_i is the kinetic energy of ith cation ($\Lambda \sim \sqrt{E_i}$), I_i is the peak intensity for the ith cation, and m is the number of cations (in the case at hand, m = 3) [6]. The photoionization cross-sections were 26.5 (La $2d_{5/2}$), 5.29 (Sr $3d$), and 15.9 (Cu $2p_{3/2}$). The results of the calculations are displayed in Table 4.

It seemed pertinent to compare the surface and bulk compositions of the samples. Containing alkaline-earth and rare-earth elements, the complex oxides in question are chemically reactive to water and carbon(IV) oxide. As a consequence, the surface of the samples under ambient conditions can contain either adsorbed or chemisorbed water and carbon dioxide molecules, as well as chemical compounds such as carbonates or hydroxocarbonates [8]. Table 5 displays the cation composition in the cuprates synthesized as determined

Table 4. Cation surface composition

Sample composition	Cation composition (including σ)			Cation surface composition (including σ and λ)		
	n (La) %	*n* (Sr) %	*n* (Cu) %	*n* (La) %	*n* (Sr) %	*n* (Cu) %
$La_{0.85}Sr_{0.15}CuO_{2.5-\delta}$	21.9	51.3	26.8	17.0	64.9	18.1
$LaSrCuO_{4-\delta}$	12.1	60.9	27.0	9.0	73.5	17.5
$La_{1.4}Sr_{0.6}CuO_{4-\delta}$	32.4	48.7	18.9	25.2	61.9	12.9
$La_{1.85}Sr_{0.15}CuO_{4-\delta}$	23.1	49.5	27.4	18.0	63.2	18.8

Table 5. Average oxidation number of copper (Z_{Cu}) and cation composition of the samples synthesized

As-batch sample composition	Z_{Cu}	Element concentration*, at. %		
		La	Sr	Cu
$La_{0.85}Sr_{0.15}CuO_{2.49}$	2.13 ± 0.02	18.7 ± 0.3 (18.9)	3.5 ± 0.6 (3.4)	22.1 ± 0.4 (22.3)
$La_{1.85}Sr_{0.15}CuO_{3.99}$	2.13 ± 0.03	26.6 ± 0.4 (26.5)	2.2 ± 0.5 (2.2)	14.5 ± 0.4 (14.3)
$La_{1.4}Sr_{0.6}CuO_{3.81}$	2.22 ± 0.02	20.5 ± 0.6 (20.6)	8.6 ± 0.3 (8.8)	14.8 ± 0.4 (14.7)
$LaSrCuO_{3.61}$	2.22 ± 0.02	15.1 ± 0.8 (15.1)	14.9 ± 0.4 (15.1)	14.8 ± 0.5 (15.1)

* In parentheses, the theoretical concentration of the element to be determined in a sample of the given composition is indicated.

by XPS and iodometry. The cation concentration in all samples corresponds to their bulk composition to the experimental error.

Analyzing the results compiled in Tables 4 and 5, we infer that the surface segregation of strontium occurs regardless of the as-batch (bulk) composition of the sample. Cuprates surfaces have highly reactive surfaces. For this reason, selective strontium segregation to the surface occurs and, thus, the surface free energy decreases. Surface enrichment with strontium was also observed in previous XPS investigations of complex oxides of 3d elements and alkaline-earth elements [9–11].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-03-32715a).

REFERENCES

1. Yu, H.-C. and Fung, K.-Z., *Mater. Res. Bull.*, 2003, vol. 38, p. 231.
2. Mazo, G.N., Savvin, S.N., Mychka, E.V., Dobrovol'skii, Yu.A., and Leonova, L.S., *Elektrokhimiya*, 2005, vol. 41, p. 516.
3. Yu, H.-C. and Fung, K.-Z., *J. Power Sources*, 2004, vol. 133, p. 162.
4. Hong, D.J.L. and Smyth, D.M., *J. Solid State Chem.*, 1993, vol. 102, p. 250.
5. Opila, E.J. and Tuller, H., L., Wuensch B.J., Maier J, *J. Am. Ceram. Soc.*, 1993, vol. 76, p. 2363.
6. *Metody analiza poverkhnosti* (Methods of Surface Analysis), Zanderna, A.M., Ed., Moscow, 1979.
7. Alov, N.V., *Zh. Anal. Khim.*, 2005, vol. 60, p. 331.
8. Kudryashov, I.A., *Cand. Sci. (Chem.) Dissertation*, Moscow, 2000.
9. Mazo, G.N., Alov, N.V., and Kudryashov, I.A., *Perspektivnye Mater.*, 2001, no. 5, p. 16.
10. Liu, H-X., Cocke, D.L., Naugle, D.G., and Pandey, R.K., *Solid State Ionics*, 1989, vols. 32-33, p. 1125.
11. Gunasekaran, N., Saddawi, S., and Carberry, J.J., *J. Catal.*, 1996, vol. 159, p. 107.