

Metal–semiconductor transition in the defective perovskite $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$

G. V. Bazuev, V. N. Krasil'nikov, N. A. Kirsanov, and N. V. Lukin
*Institute of Solid State Chemistry, Urals Branch of the Russian Academy of Sciences,
620219 Ekaterinburg, Russia*

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Abrupt and reversible changes in the oxygen content and the electrical conductivity have been detected at $\sim 500^\circ\text{C}$ in the anion-deficient perovskite $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$, which was synthesized as part of this study. These changes accompany a transition from a metallic to a semiconducting behavior. The changes were found by x-ray diffraction, differential thermal analysis, thermogravimetry, and measurements of the electrical conductivity. The anomalies observed here are shown to be accompanied by a structural phase transition and are linked with a sharp change in the $\text{Cu}^{3+}/\text{Cu}^{2+}$ cation ratio in the low- and high-temperature phases.

The copper–oxide-based perovskite-like compounds have attracted much interest because numerous high- T_c superconductors have been found in this group. As part of the search for new complex oxides of Cu holding promise for high- T_c superconductivity, we have synthesized, under ordinary conditions, the lanthanum cuprate $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$, $0.15 \leq x \leq 0.40$, with the structure of a defective perovskite. This is the first such synthesis. This compound is like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in having a wide range of homogeneity in terms of O_2 . In this range, two structurally distinct phases have been found. Study has shown that $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ does not exhibit a superconductivity. Still, the anomalous thermal and electrical transitions which are observed in this material, and which stem from a change in the valence of the Cu, make this compound a suitable model for the copper–oxide-based superconductors.

The lanthanum cuprate $\text{LaCuO}_{2.5}$ with the perovskite structure does not form under ordinary synthesis conditions. The compound $\text{La}_2\text{Cu}_2\text{O}_5$ which was produced in Ref. 1 is not a perovskite-like compound. It belongs to the homologous series $\text{La}_{4+4n}\text{Cu}_{8+2n}\text{O}_{14+8n}$ and has a high electrical resistance. Bringley *et al.*² have produced perovskites $\text{LaCuO}_{3-\delta}$ ($0 \leq \delta \leq 0.5$) with tetragonal ($0 \leq \delta \leq 0.18$), monoclinic ($0.21 \leq \delta \leq 0.38$), and orthorhombic ($0.41 \leq \delta \leq 0.5$) unit cells at a high O_2 pressure (0.2–1.0 kbar). It was found that one of these phases does not exhibit a superconductivity. The first two of these phases are metallic conductors, and the last is a semiconductor.

By replacing some of the Cu in $\text{LaCuO}_{2.5}$ by Ni, we have succeeded in stabilizing the anion-deficient perovskite-like modification of this compound in air. The $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ was synthesized at 950–1000 $^\circ\text{C}$ from the starting oxides La_2O_3 (99.99%), CuO (highly pure), and NiO (highly pure) by a ceramic procedure. It was found that this compound exists in the interval $0.15 \leq x \leq 0.40$. At smaller values of x , the synthesis product consists primarily of $\text{La}_2\text{Cu}_2\text{O}_5$. At $x > 0.40$, the samples contain

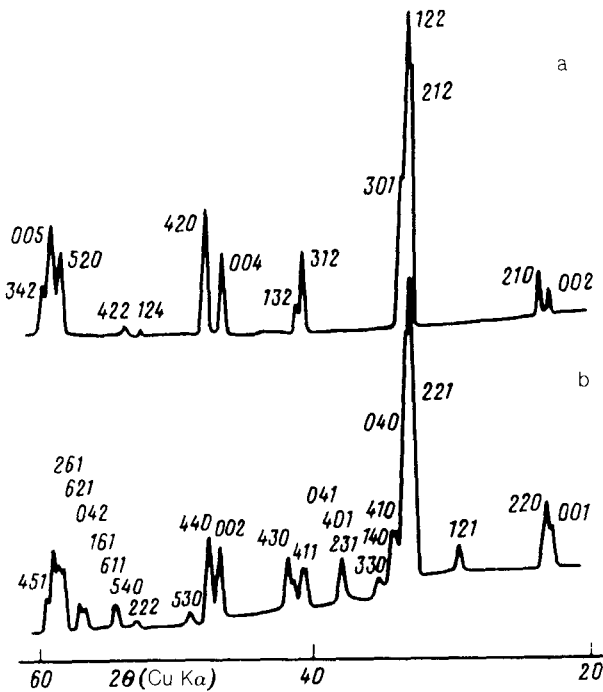


FIG. 1. Some x-ray diffraction patterns. a— $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.75}$; b— $\text{LaCu}_{2.75}\text{Ni}_{0.25}\text{O}_{2.53}$.

several phases. Reducing the amount of La tends to accelerate the formation of a single-phase product. Samples with the composition $\text{La}_{1-z}\text{Cu}_{0.83}\text{Ni}_{0.17}\text{O}_{2.5+\delta}$ contained no impurities over the interval $0 \leq z \leq 0.25$.

The region of homogeneity of $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ in air was found by iodometric titration to be extremely wide ($0 \leq \delta \leq 0.25$). In this interval of δ , we detected two phases, differing in crystal structure (Fig. 1). The first forms during slow furnace cooling or when rapidly cooled samples are annealed in air at 400°C . This phase has a high oxygen content ($\delta_{\text{max}} \approx 0.25$) and a distorted-perovskite structure. The x-ray diffraction pattern of this phase differs from those of the tetragonal $\text{LaCuO}_{3-\delta}$ compound² ($0 \leq \delta \leq 0.2$) in that several reflections have an additional splitting. The x-ray diffraction made it possible to classify $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.75}$ as being orthorhombic with lattice constants which are related to the lattice constant a_p of the cubic perovskite cell by $a \approx \sqrt{5}a_p$, $b \approx \sqrt{5}a_p$, $c \approx 2a_p$. For $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.75}$ at 295 K , we found $a = 8.608 \pm 0.004\text{ \AA}$, $b = 8.442 \pm 0.005\text{ \AA}$, $c = 7.866 \pm 0.003\text{ \AA}$, $V = 571.7\text{ \AA}^3$, $d_{\text{meas}} = 7.0\text{ g/cm}^3$, $d_{\text{x-ray}} = 7.12\text{ g/cm}^3$, and $z = 10$. The formula for this phase can thus be written $\text{La}_{10}(\text{Cu}_{1-x}\text{Ni}_x)_{10}\text{O}_{25+\delta}$.

The second phase ($\delta_{\text{min}} = 0$) can be produced by quenching samples from 600°C or above on a cooled metal plate. The x-ray diffraction pattern of $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.53}$ (Fig. 1b) was indexed in orthorhombic symmetry with the lattice constants $a = 10.8736 \pm 0.0025\text{ \AA}$, $b = 10.7894 \pm 0.0020\text{ \AA}$, $c = 3.8941 \pm 0.0009\text{ \AA}$, $z = 8$.

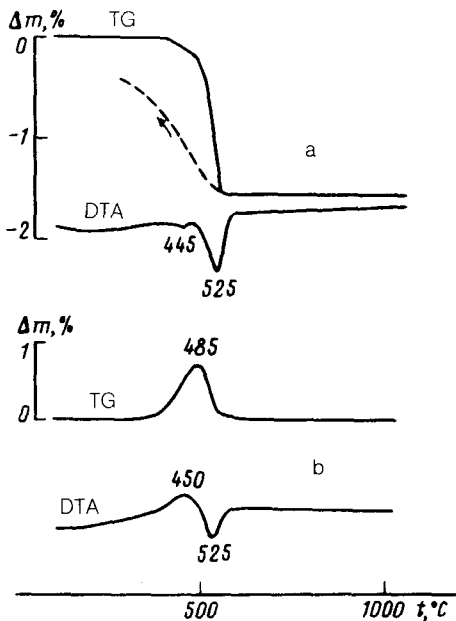


FIG. 2. DTA and TG curves of (a) $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.75}$ during heating and cooling (dashed line) and (b) $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.53}$ during heating. The heating rate was 10 deg/min.

The lattice constants of this phase are related to that of the cubic perovskite by $a \approx 2\sqrt{2}a_p$, $b \approx 2\sqrt{2}a_p$, $c = a_p$. The chemical formula for this phase can be written $\text{La}_8(\text{Cu}_{1-x}\text{Ni}_x)_8\text{O}_{20}$. The presence of reflections on the x-ray diffraction pattern of the high-temperature phase which are not part of the set characterizing the basic perovskite cell is evidence of an ordered arrangement of oxygen vacancies.

The transition from the low-temperature modification to the high-temperature one occurs at about 500°C. According to differential thermal analysis (DTA) and thermogravimetry (TG) of $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.75}$ (a Q-1500D "derivatograph" was used for these measurements), this transition is accompanied by a sharp decrease in the mass of the sample (Fig. 2). From the change in mass it was found that the composition of the sample above 535°C is $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.50}$. The oxygen content remains the same up to 1000°C.

The curve of the mass change upon cooling (the dashed curve in Fig. 2) is evidence that the process is reversible and that the sample absorbs oxygen from the air. During natural cooling to 300°C, the increase in mass was about 70% of the loss of mass detected during heating. An additional hold at 400°C in air completely restored the original oxygen content of the sample.

The range of reversible variations in the oxygen content in $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ is thus $0 \leq \delta \leq 0.25$. In this regard, this new compound is similar to the cuprate $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, in which δ varies from ~ 0.1 to 1 with the temperature in air. In contrast with the latter case, however, in which there is a continuous decrease in the oxygen index over the temperature range³ 450–950°C, the corresponding process in $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ occurs essentially discontinuously.

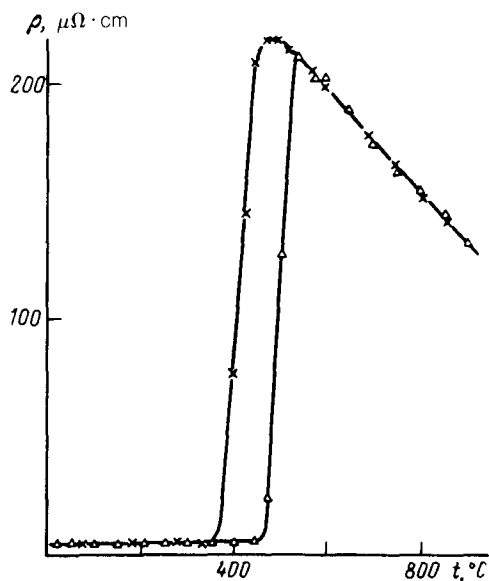


FIG. 3. $\rho(T)$ plot for a sintered $\text{LaCu}_{0.81}\text{Ni}_{0.19}\text{O}_{2.74}$ sample during heating (triangles) and cooling (crosses) in air.

The reversible phase transition observed in $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ near 500°C is unique in nature and scale. According to our information, it has no analog among oxide compounds. The observed effect stems from an abrupt change in the valence state of the copper upon the restructuring of the crystal lattice. The presence of nickel complicates efforts to determine the $\text{Cu}^{3+}/\text{Cu}^{2+}$ ratio very accurately in the oxidized phases ($\delta > 0$). If we assume that the nickel is present as Ni^{2+} , we conclude that the average valence state of the copper in $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.75}$ is $+2.67$. This result means that the stabilized compound may contain more Cu^{3+} cations than any other oxide compound of copper which has been synthesized in air. In reduced phases ($\delta = 0$), the copper is divalent according to the TG measurements.

It was found that $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ ($\delta \approx 0.25$) is a metallic conductor over the range $4.2\text{--}770\text{ K}$. We did not detect a transition of this phase to a superconducting state. Samples with $\delta \approx 0$ produced by quenching at a temperature above the phase-transition point exhibit semiconducting properties.

Measurements of the electrical resistivity ρ over the range $20\text{--}900^\circ\text{C}$ in air revealed a sharp anomaly in the oxygen-rich samples near the phase transition. As can be seen from Fig. 3, the resistivity of a sintered $\text{LaCu}_{0.81}\text{Ni}_{0.19}\text{O}_{2.74}$ sample increases abruptly at 475°C . In the interval $450\text{--}540^\circ\text{C}$, ρ increases from 5 to $220\ \mu\Omega \cdot \text{cm}$, i.e., by a factor of 44. For the $\text{LaCu}_{0.75}\text{Ni}_{0.25}\text{O}_{2.75}$ sample we see a jump in ρ from 2 to $78\ \mu\Omega \cdot \text{cm}$. Above 550°C the samples acquire a semiconducting temperature dependence $\rho(T)$. These results show that there is an abrupt transition from a metallic state to a semiconducting state in $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ ($0.15 \leq x \leq 0.40$, $\delta < 0.25$) at $\sim 500^\circ\text{C}$. This transition is reversible, and there is a sharp decrease in the resistivity at 450°C in an atmosphere containing oxygen (Fig. 3). The hysteresis seen on the $\rho(T)$ plot evidently means that the reversible structural transition occurs at a lower temperature.

Since diffusion of oxygen in the interior of the densely sintered ceramic is hindered, the temperature interval of the transition depends on the rate at which the sample is heated or cooled. The plot of $\rho(T)$ in Fig. 3 corresponds to the equilibrium state of the test sample in an air atmosphere. To reach equilibrium, we held the sample at a fixed temperature for 4–5 min during the heating. Because of the hysteresis, a longer time is required to reach equilibrium during cooling. Complete restoration of the original value of ρ requires about half an hour at 400 °C.

In summary, this study has shown that a sharp and reversible change in the valence state of copper in the course of a structural phase transition at ~ 500 °C in the oxygen-deficient perovskite $\text{LaCu}_{1-x}\text{Ni}_x\text{O}_{2.5+\delta}$ ($0.15 \leq x \leq 0.40$) in air results in an abrupt change in the oxygen content and a transition from a metallic state to a semiconducting state. Because of the variable valence of the copper, this system is of interest as a model of the high- T_c superconductors based on the cuprates of various metals.

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