

show strong Jahn-Teller (J.T.) effects [13]. While SrFe(VI)O_3 is distorted perovskite insulator, LaNi(III)O_3 is a J.T. undistorted metal in which the transfer energy b_n of the J.T. e_g electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba-La-Cu-O system. This system exhibits a number of oxygen-deficient phases with mixed valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T. Cu^{3+} and the J.T. Cu^{2+} ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

II. Experimental

1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 3 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIEMENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2 θ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the K_2NiF_4 structure ($a=3.79$ Å and $c=13.21$ Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller $x(\text{Ba})$. The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite ($\text{La}_x\text{Ba}_x\text{Cu}_y\text{O}_{1-x}$) as described by Michel and Ravcau [16].

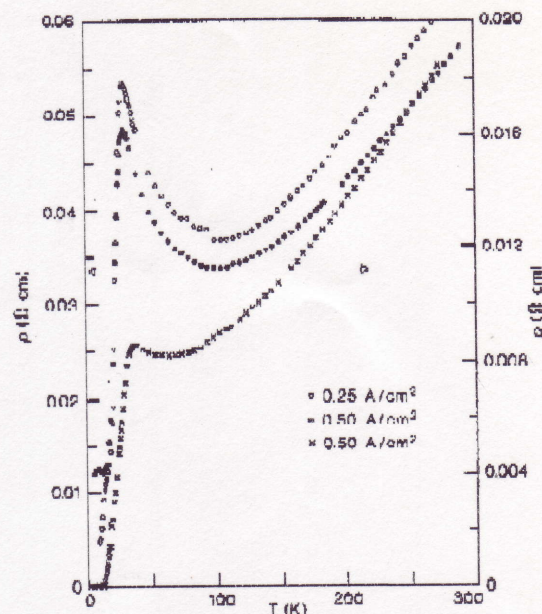


Fig. 1. Temperature dependence of resistivity in $\text{Ba}_x\text{La}_{2-x}\text{Cu}_3\text{O}_{5(1-x)}$ for samples with $x(\text{Ba})=1$ (upper curves, left scale) and $x(\text{Ba})=0.75$ (lower curve, right scale). The first two cases also show the influence of current density

3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by Au wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Heraeus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with $x(\text{Ba}) \leq 1.0$, the conductivity measurements, involving typical current densities of 0.5 A/cm^2 , generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (>90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and O_2 partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted