ABSTRACT. Among high temperature superconducting oxides, La$_2$CuO$_4$+$\delta$ is still one of the most studied compounds as the appearance of superconductivity is not really understood. La$_2$CuO$_4$ can be oxidized either by a treatment at high temperature and under high oxygen pressure, or by using "soft" chemistry methods at room temperature such as electrochemistry. It seems that two regions of extra oxygen concentration have to be considered: first, one with $\delta \approx 0.05$, which corresponds to a superconducting phase with $T_c \approx 32$K; another one with $\delta \approx 0.08$, which corresponds to a superconducting phase with $T_c \approx 45$K. The former is obtained by treating La$_2$CuO$_4$ under high oxygen pressure. In this case, below $\approx 280$K, the excess oxygen atoms migrate in order to form antiferromagnetic La$_2$CuO$_4$ domains and La$_2$CuO$_4$+$\delta$ ones. The migration of the oxygen atoms is accompanied by anomalies in resistivity and in thermoelectric power. The extra oxygen is found to be in between two LaO layers in a similar position as the oxygen atoms located between two Nd layers in Nd$_2$CuO$_4$ structure. The insertion of extra oxygen causes the displacement of some of the other oxygen atoms. The nature of the bonding between the excess oxygen and the "normal" oxygen atoms of the structure has not yet been completely elucidated. The more oxidized samples ($\delta \approx 0.08$) present a larger orthorhombic distortion than the $\delta \approx 0.05$ samples. It is not clearly established whether or not these $\delta \approx 0.08$ samples present a phase separation at low temperature. The presence of superstructure spots on electron diffraction patterns suggest an ordering of the incorporated oxygen atoms.

1. Preparation, Composition

It is commonly assumed today that a mixed copper oxide becomes superconducting by the introduction of holes in the oxygen sublattice leading to a formal valence state of the Cu cations greater than 2+. For La$_2$CuO$_4$ this can be realized either by doping the La sublattice with a divalent alkali-earth element [1] or by introducing extra oxygen [2] or fluorine [3] or chlorine [3] in the oxygen sublattice. Beille et al. [4] were the first to report that La$_2$CuO$_4$ becomes superconducting by a treatment under oxygen pressure. Although they only reported the existence of traces of superconductivity their experiment was unconfutable. Subsequently, several other groups [5-8] detected the same behavior for samples of undoped La$_2$CuO$_4$ which had been prepared in oxygen-rich atmospheres. The first reproducible samples with an appreciable Meissner effect were synthesized by Demazeau et al. [9] and by Schirber et al. [10]. The
latter authors showed that a heat-treatment at 600° C under an oxygen pressure ranging between 1 and 3 kbar transformed an antiferromagnetic La2CuO4 sample into a superconducting one exhibiting 30% of superconducting volume as determined by Meissner effect measurements. It was then that the sample composition became a problem.

Schirber et al. [10] determined the composition of their samples by x-ray microanalysis, iodometric titration, and thermogravimetry. They found that the La/Cu ratio was equal to 2; the iodometric titration led to a δ=0.032 oxygen excess, while the thermogravimetry indicated that weight loss corresponded to δ=0.13. This large difference would be explained, according to these authors, if the extra oxygen atoms were incorporated as superoxide O2-. This interpretation was corroborated by XPS results obtained by Rogers et al. [11]. On the other hand, Zhou et al. [12] showed that a sample of formula La2CuO4.05 (determined by iodometric titration), heated at 250° C under nitrogen, exhibited a phase transition to an antiferromagnetic state accompanied by an oxygen loss from the entire volume. Moreover, they observed a continuing superficial loss of oxygen around the temperature of the phase transition. This allowed them to conclude that the superoxide identified by XPS was associated with the superficial oxygen, but not to the extra oxygen responsible for the superconductivity.

More recently, Wattiaux et al. [13] showed that it is possible to obtain the superconducting La2CuO4+δ by electrochemical oxidation of La2CuO4 in an alkaline solution (1 N KOH) at room temperature. This method of preparing the superconducting phase has been used by several other groups who utilized either NaOH or KOH [14-16]. By controlling the charge passing through the electrochemical cell it is possible to vary the amount of extra oxygen incorporated into the structure. It seems that the electrochemical method leads to larger amounts of extra oxygen incorporated than that utilizing heat-treatments under high oxygen pressure. Values of δ=0.09 and δ=0.18 have been reported by Grenier et al. [17] and Chou et al. [16], respectively. On the other hand, Rudolf et al. [18] contest that oxygen be incorporated in the structure by electrochemical process. These authors believe that the starting product is actually an oxyhydroxide containing lanthanum vacancies La2-xCuO4-3x(OH)3x and that the electrochemical oxidation reaction implies a proton loss. The superconducting compound would then contain lanthanum vacancies, La2-xCuO4. Recently Takayama et al. [19] have shown that it is possible to realize the oxygen insertion into La2CuO4 by treating the samples in a solution of KMnO4. In this case too, values of δ=0.09 can be obtained. These authors believe that the amount of inserted oxygen can be varied by changing the concentration of the KMnO4 solution.

2. Structure

2.1. La2CuO4

The structure of La2CuO4, of K2NiO4 type, belongs to space group Cmca (Fig. 1) with lattice parameters a = 5.360 Å, b = 13.181 Å, and c = 5.393 Å. The atoms are located in the following positions: La in (8f) (0yz), Cu in (4a) (000), O1 in (8f) (0yz), and O2 in (8e) (1/4,y,1/4). The Cu atoms are surrounded by an oxygen octahedron.