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Structural characterization of $La_{2-x}Sr_xCu_{1-y}Zn_yO_{4-\delta}$ ($y = 0, 0.02$) samples prepared by the wet-chemical method

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ABSTRACT

In this work we report on the preparation and structural characteristics of good quality superconducting samples of $La_{2-x}Sr_xCu_{1-y}Zn_yO_{4-\delta}$ ($x = 0.05, 0.08, 0.10, 0.115, 0.15, 0.18, 0.21, 0.25$ and $y = 0, 0.02$) using a wet-chemical method. Previous studies in optimally doped samples prepared with this method demonstrated that the cation distribution inside these samples is improved compared to similar samples obtained by the traditional solid-state method. Since this fact is very important for the study of the superconducting cuprates because their physical properties are strongly correlated with the microstructure and chemical homogeneity, we have extended this wet-chemical method to produce polycrystalline samples with strontium concentrations of interest to superconductivity. In particular, compounds with strontium doping as low as $x = 0.05$ and 0.08, located at the onset of superconductivity (underdoped region), up to dopant concentrations situated in the highly overdoped region ($x = 0.25$) were prepared and characterized. X-ray diffraction measurements and subsequent Rietveld analysis were used to identify the principal lattice parameters of the samples and their doping dependence. Zero field cooling magnetization and resistivity measurements allowed following the critical temperature as a function of the charge carrier concentration. Our experimental results obtained here are compared to others reported on similar $La_{2-x}Sr_xCuO_{4-\delta}$ samples showing that good quality single-phase polycrystalline samples, with several carrier concentrations, can be obtained using the wet-chemical method explored here.

1. Introduction

Recent experiments involving high-T_c cuprate superconductors have shown an ubiquitous phase separation phenomenon at nanometer scale [1–3]. The interplay between these different phases (antiferromagnetic insulator, superconducting, and so on) seems to be essential to understand many of the physical properties [4,5] of these materials. The cause of this phenomenon remains to be explained. There exist experimental studies pointing out to the importance of the *dopant atoms* at the atomic scale as the principal source for this intrinsic disorder inside the CuO_2 planes [6]. In addition, the conditions in which the superconducting compounds are prepared can lead to samples with the same nominal composition but different physical properties, in particular different critical temperatures (see for example [7] and references therein). It should be pointed out that the mobility of ions (in particular the oxygen ions) seems to be crucial for T_c and also for theories which try to explain the superconductivity and other physical properties of the cuprates [5,6]. These facts demonstrate the relevance of homogeneity and structural parameters of the superconducting samples to the study of the physical properties in the high-T_c cuprate superconductors [8–10].

Whatever the method used to obtain superconducting cuprate samples, their homogeneity is intrinsically related to the distribution of cations and oxygen atoms. In this sense, equally distributed cations are essential to obtain good homogeneity of the samples. Usually the cuprates are obtained via the *solid-state reaction method* (SSRM) [11]. In this method the homogeneity of the samples is achieved after several long grinding and pre-sintering steps which produce a uniform distribution of the sample's components. Nevertheless, the limited mobility of the components can lead to non-uniform phases, producing atomic disorder at different scales. Other techniques like, for example, the wet-chemical method (WCM), have been shown to be more efficient in improving the cation and oxygen distribution in ceramic superconducting samples. In $La_{2-x}Sr_xCuO_{4-\delta}$ (LSCO), which is a cuprate superconductor

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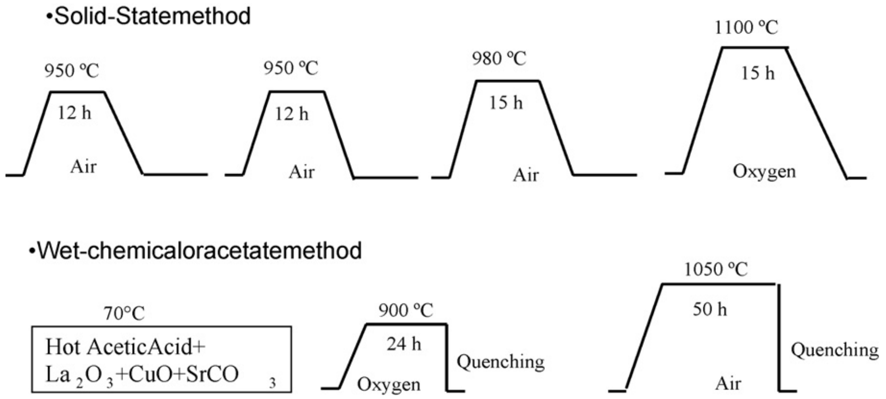

Fig. 1. Wet-chemical and solid-state methods used for the preparation of the samples.

with a maximum T_c of about 39 K and in which some studies have shown phase separation at different levels [5], samples with better strontium concentrations were obtained by using a spray-drying method [12]. In line with that, a refined wet-chemical method was also used in Ref. [13] to produce optimally doped $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ samples which showed a better homogeneity of the strontium distribution as revealed by EDX-measurements.

Taking into account that this last method proved to improve the sample's homogeneity in optimally doped compound ($x = 0.15$), we decided to use this method to obtain a complete set of samples with several strontium concentrations. Thus, in this article we present a study of $La_{2-x}Sr_xCu_{1-y}Zn_yO_{4-\delta}$ ($y = 0, 0.02$) samples prepared by the wet-chemical method cited in Ref. [13]. The chosen Sr concentrations were in the range from $x = 0.05$ to 0.25, which is relevant to superconductivity. The prepared samples had a strontium doping level including both *underdoped* samples and highly *overdoped* ones. Additional samples with 2% of zinc have been prepared for each strontium concentration (x). The main goal is to verify the possible influence of this preparation technique on the structure of $La_{2-x}Sr_xCu_{1-y}Zn_yO_{4-\delta}$ samples, in particular on the lattice parameters, and also to verify how their critical temperatures are modified. This article is divided into three sections. After this introduction, in Section 2 the details of the sample preparation and measurement techniques used in this work are discussed. Section 3 reports the results of X-ray diffraction (XRD) measurements. The principal structure parameters obtained by Rietveld analysis of the X-rays spectra and the critical temperatures of the samples according to magnetic and electric transport measurements are discussed, and compared to the results of previous studies performed for samples obtained by other preparation methods.

2. Experimental part

Several samples belonging to the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ ($y = 0, 0.02$) system were prepared by the wet-chemical method following Ref. [13]. Initially pure (99.99%) oxide and carbonate compounds, La_2O_3, CuO, ZnO and $SrCO_3$, were dried at 150 °C. After eliminating the moisture, the powders were weighed in adequate stoichiometrical proportions. The starting mixture was then dissolved into 50 ml of ultra-pure acetic acid (CH_3COOH). We mixed the components under constant stirring heated to around 70 °C. As pointed out in Ref. [13] the first stage is crucial, since by the dissociation of the oxides and carbonate during the dissolution, the metal ions are mixed at the atomic level with a better distribution than the one obtained by using mechanical grinding.

After a few minutes of stirring, the milky grey solution turned transparent with a dark blue tone and black fallout on the bottom of the ceramic crucible (or glass vessel). The rest of the acid was then evaporated in an oven. The reaction products were scraped from the ceramic (glass) and ground for 5 min to obtain a homogeneous powder. Annealing under flowing oxygen followed. The furnace was heated at a rate of around 300 °C/h to 900 °C and kept at this temperature for 24 h, followed by a quenching to room temperature. The formerly azure powder had turned dark grey and was ground in an agate mortar for 1 h. After the grinding, pellets were pressed with 2.5 tons/cm^2 of pressure. The final sintering consisted of heating the furnace to 1050 °C at 300 °C/h, keeping the furnace at 1050 °C for 50 h, followed by a rapid quenching to room temperature. The quenching was chosen to prevent the formation of a secondary phase at around 900°. The total time needed to synthesize the samples is roughly four days.

In order to compare the samples obtained, another set of samples (only selected Sr concentrations) for the same system, $La_{2-x}Sr_xCu_{1-y}Zn_yO_{4-\delta}$ ($y = 0, 0.02$), were prepared by the solid-state reaction method [11,14]. The highly pure (at least 99.99%) powders were stoichiometrically weighted and ground for 1 h. After the grinding, the samples were put inside the furnace and heated to 950 °C. The increase (decrease) rates of the furnace temperature were 300 °C/h (45 °C/h), and the sintering time was 12 h. The samples were then reground for 1 h, pressed into pellets and the last sintering treatment was repeated. Two additional treatments with the final sintering temperatures of 980 and 1100 °C, respectively and a sintering time of 15 h each one were performed subsequently. The last sintering was performed in flowing oxygen to prevent the formation of oxygen vacancies. Details about this process can be found in Ref. [11], and a comparison of both methods is shown in Fig. 1.

X-ray diffraction patterns were obtained in a (X'Pert PRO PANalytical) powder diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Data was collected in step-scanning mode ($20° \leq 2\Theta \leq 80°$) with 2 s counting time at each step at room temperature. Orthorhombic *Bmab* and tetragonal *F*4/*mmm* space groups of the unit cell were assumed for the XRD data and fitted with the FULLPROF program (Thierry Roisnel and Rodriguez-Carvajal, 2006). The resistivity curves were measured within the linear-response regime with a low applied current density. The resistivity was determined by using an AC-Linear Research Inc. bridge, model LR-700A, and the temperature was controlled through a Lake-Shore temperature controller, model 340. The magnetic measurements were performed in a SQUID magnetometer in the zero field cooling conditions.

3. Results and discussion

X-ray spectra were measured at room temperature for all the samples (with and without zinc) prepared according to the wet-chemical method as described above. A selection of spectra for several compounds is shown in Fig. 2. In all the XRD measurements, taken for the samples prepared according to the WCM, the Rietveld refinement [15] confirmed that the Bragg peaks belong to the crystalline structure of the LaSrCuO system according to the reference data in the International Centre for Diffraction Data (ICDD) database [16]. The differences between the experimental and theoretical positions, respectively were always very small. No significant impurity peaks (relative intensity above 5%) were detected in the spectra.

We also note that the X-ray spectra for the 2% zinc-doped samples were equivalent to the spectra of zinc-undoped samples from a qualitative point of view, showing Bragg peaks at the same position. Besides the strong reduction of T_c in the Zn-doped samples which is discussed later on, this is indicating that the zinc was introduced into the LSCO unit cell without a significant modification of the lattice parameters. An example of a Rietveld analysis for the spec-