

Mössbauer study of tin-doped 1-2-3 and 2-1-4 high T_c superconductors

G. Quintana

*Departamento de Física, Facultad de Ingeniería, Universidad de Buenos Aires,
Paseo Colón 850, 1063 Buenos Aires, Argentina*

and

R.C. Mercader

*Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata,
C.C. 67, 1900 La Plata, Argentina*

Samples of $\text{YBa}_2(\text{Cu}_{0.85}\text{Sn}_{0.15})_3\text{O}_{7-y}$ (1-2-3), $\text{La}_2(\text{Cu}_{0.95}\text{Sn}_{0.05})\text{O}_{4-x}$, and $\text{La}_{1.85}\text{Ba}_{0.15}(\text{Cu}_{0.95}\text{Sn}_{0.05})\text{O}_{4-x}$ (2-1-4), with different oxygen stoichiometry, have been studied by Mössbauer spectroscopy. These measurements reveal the existence of two inequivalent sites for Sn in the (1-2-3) compounds. The (1-2-3) spectra display two quadrupole doublets which we associate with Sn in Cu(1) and Cu(2) sites, respectively. La compounds show a single quadrupole doublet.

1. Introduction

The superconducting properties of copper oxide-based high T_c superconductors are very sensitive to the oxygen content and arrangement which, in turn, are controlled by the annealing time and temperature, the oxygen partial pressure, and the quenching rate used in preparing the material.

Although Mössbauer spectroscopy allows determining specific structural elements, the analysis of substitutions for copper in the (1-2-3) system is complicated because of the two distinct copper sites in the structure. Conflicting conclusions have been reached in many doping cases, especially for Sn [1–12].

Most authors, based on ion sizes, consider that Sn substitutes Cu ions in both sites in the (1-2-3) compounds. However, other authors think that Sn may substitute Y and Ba [3], or only Cu(1) [4]; or that at higher concentrations, Sn occupies more likely Ba, Y, and Cu(2) sites than Cu(1) sites [7]. Besides, when authors agree on Sn substitution for Cu at both sites, they still disagree about the Mössbauer spectral analysis.

Changing the oxygen stoichiometry by means of different preparation methods can help to ascertain the location of Sn probes. In this work, we perform annealing

treatments with the purpose of changing the oxygen stoichiometry and determine its influence on the Sn environments for the (1-2-3) system and also for the (2-1-4) system that has only one Cu site.

2. Experimental

Samples of $\text{YBa}_2(\text{Cu}_{0.85}\text{Sn}_{0.15})_3\text{O}_{7-y}$, $\text{La}_2(\text{CuO}_{0.95}\text{Sn}_{0.05})\text{O}_{4-x}$, and $\text{La}_{1.85}\text{Ba}_{0.15}(\text{Cu}_{0.95}\text{Sn}_{0.05})\text{O}_{4-x}$ were prepared by conventional solid-state reactions of appropriate amounts of Y_2O_3 , BaCO_3 , CuO and SnO_2 for the (1-2-3) compound and La_2O_3 , BaCO_3 , CuO and SnO_2 for the La compounds.

The transmission Mössbauer spectra were recorded with a constant acceleration spectrometer using a 50 μm Pd filter. The absorber and the BaSnO_3 source were kept at room temperature. The spectra were fitted to lines of Lorentzian shape by means of a nonlinear least squares program with constraints, using a fixed ratio 1:1 for the area of the two components of the doublets. The isomer shifts are measured with respect to BaSnO_3 at room temperature.

For $\text{YBa}_2(\text{Cu}_{0.85}\text{Sn}_{0.15})_3\text{O}_7$, the resistance–temperature relationship was measured by means of the standard ac four-probe method. The incorporation of tin depresses slightly the T_c with respect to the undoped samples. The resistance goes to zero at 91 K, with a temperature transition width (10%–90%) of 5 K.

The oxygen-deficient samples were produced by annealing portions of the master batch at different temperatures in air (600 °C, 750 °C and 850 °C) or in argon followed by rapid quenching. The annealing time varied from 24 to 147 hours.

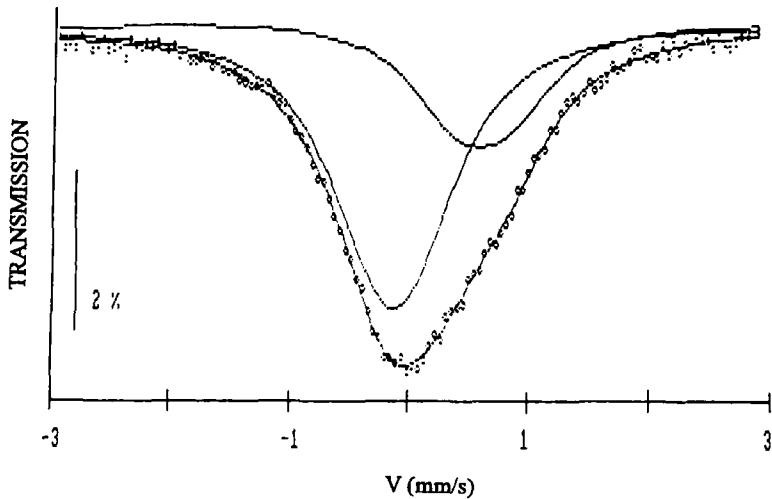
X-Ray diffraction patterns show that the oxygenated samples have an orthorhombic structure, while the oxygen-deficient samples are tetragonal. A small proportion of other phases is also present.

3. Results and discussion

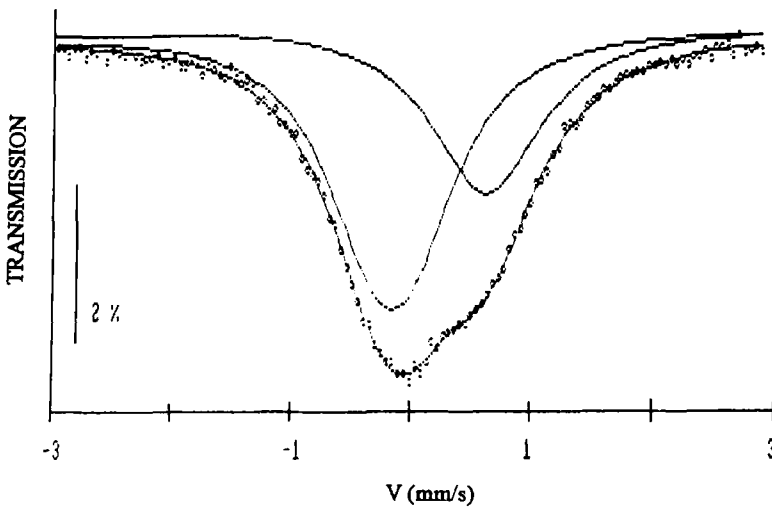
The Mössbauer spectra of the oxygenated samples differ from those of the oxygen deficient ones, fig 1. Both could be fitted with two quadrupole doublets of parameters displayed in table 1. This is coherent with Sn atoms placed at two different positions in the structure. Several fits were attempted with different linewidths, but in all cases χ^2 increased for values other than those shown in table 1.

The isomer shifts suggest a +4 valence state for Sn. In the oxygenated samples, the presence of Sn increases the sample oxygen content [12]. This is a natural consequence of tetravalent Sn which requires a higher oxygen coordination. In our 15% Sn-doped samples, the oxygen stoichiometry is about 7.30 [12]. We assume that these extra oxygen atoms are incorporated only at O(5) positions, which are vacant in the fully ordered orthorhombic compound.

When the samples are deoxygenated, it is known that only the oxygen atoms in the O(5) and O(1) positions leave the sample, while around the Sn in the Cu(2) position, the oxygen configuration does not change. As mentioned before, we noticed



(a)



(b)

Fig. 1. Mössbauer spectra of tin-doped 1-2-3.
(a) Oxygenated, (b) deoxygenated sample.

that in the deoxygenated sample the Mössbauer parameters of subspectrum I do not differ from the ones obtained for the oxygenated sample, but in the case of subspectrum II, there is a reduction in the quadrupole splitting.

In a former paper on $Y_2BaCu_{09}Sn_{0.1}O_s$ (green phase) [13], the Mössbauer spectra displayed one unresolved quadrupole doublet, with parameters $QS = 0.16 \pm 0.06$,

Table 1

Mössbauer parameters of the subspectra in mm/s with respect to BaSnO₃. (A is the relative percentual area.)

	Doublet I				Doublet II			
	<i>QS</i>	<i>IS</i>	Γ	A	<i>QS</i>	<i>IS</i>	Γ	A
Oxygenated sample	0.29 ±0.05	-0.11 ±0.05	1.09 ±0.05	68 ±5	0.47 ±0.05	0.60 ±0.05	0.95 ±0.05	32 ±5
Deoxygenated sample	0.33 ±0.05	-0.15 ±0.05	1.01 ±0.05	62 ±5	0.22 ±0.05	0.64 ±0.05	1.01 ±0.05	38 ±5

$IS = 0.01 \pm 0.02$, and $\Gamma = 0.91 \pm 0.05$ mm/s. In the green phase, there is only one Cu site, and its coordination is similar to the Cu(2) coordination in the (1-2-3) compound. The hyperfine parameters are slightly different from those of Sn in the Cu(2) site in the (1-2-3) compound, reflecting the different transport properties of the green phase.

Based upon size considerations (ionic radii for Sn⁴⁺, Cu²⁺, Ba²⁺ and Y³⁺: 0.71, 0.72, 1.34 and 0.89 Å, respectively) it is likely that at dilute Sn concentration the impurity substitutes Cu at the two inequivalent sites. In consequence, subspectrum I is associated with Sn⁴⁺ occupying Cu(2) sites in the planes, with a coordination similar to that of the single Cu site in the green phase, and subspectrum II with Sn⁴⁺ at Cu(1) sites in the linear chains.

In addition, our Mössbauer spectra of La₂(Cu_{0.95}Sn_{0.05})O₄ and La_{1.85}Ba_{0.15}(Cu_{0.95}Sn_{0.05})O₄ are in agreement with results reported in the literature [14] and [15], and display one quadrupole doublet, $QS = 0.47 \pm 0.05$, $IS = 0.04 \pm 0.05$, $\Gamma = 0.84 \pm 0.05$ and $QS = 0.29 \pm 0.05$, $IS = 0.014 \pm 0.05$ and $\Gamma = 0.86 \pm 0.05$ mm/s, respectively. This agrees with the single Cu site picture for these compounds. When the samples were heated, we observed no change in the Mössbauer parameters. This implies that no oxygen atoms were liberated by heating, leaving the Sn environment unperturbed, indicating also that oxygen in the (2-1-4) system is more strongly bound to Cu in the elongated Cu octahedron than O(1) and O(5) in the (1-2-3) compound.

In conclusion, the present results strongly indicate that Sn goes to both Cu sites in the (1-2-3) structure because, under different oxygen stoichiometries, changes are observed by Mössbauer spectroscopy. For similarly treated samples of (2-1-4) compounds, no difference is observed, in agreement with the single site for Cu and its strongly bound oxygen in these structures.

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