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Superconductivity of the Y$_{1-x}$La$_x$Ba$_2$Cu$_3$O$_y$ system prepared in air

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Résumé.- Les oxydes Y$_{1-x}$La$_x$Ba$_2$Cu$_3$O$_y$ ont été étudiés pour montrer l’influence de la substitution Y-La et celle de la stoechiométrie en oxygène sur leur structure cristalline et leurs propriétés supraconductrices. Les échantillons ont été préparés à l’air de manière à fixer la pression partielle d’oxygène (880°C pendant 24 h et recuit à 500°C pendant 48 h). YBa$_2$Cu$_3$O$_y$ et LaBa$_2$Cu$_3$O$_y$ ont respectivement une symétrie orthorhombique et quadratique. Une transformation orthorhombique → quadratique apparaît pour $x > 0.75$. Dans les conditions de préparation utilisées tous les composés de symétrie orthorhombique sont supraconducteurs et la température critique décroît lorsque $x$ augmente dans l’intervalle $0 <= x <= 0.75$. Ceux de symétrie quadratique ne présentent pas de transition supraconductrice comme par exemple LaBa$_2$Cu$_3$O$_y$. Cependant ce dernier composé est supraconducteur à 70 K lorsqu’il est préparé sous oxigène ($y = 6.7$).

Abstract.- The Y$_{1-x}$La$_x$Ba$_2$Cu$_3$O$_y$ oxides have been investigated in order to know the influence of Y-La substitution and oxygen stoichiometry on both crystal structure and superconducting properties. The samples have been prepared in air (heating at 880°C for 24 h and annealing at 500°C for 48 h) in order to fix the oxygen partial pressure. YBa$_2$Cu$_3$O$_y$ and LaBa$_2$Cu$_3$O$_y$ have an orthorhombic and a tetragonal symmetry respectively. An orthorhombic to tetragonal transformation has been found for $x > 0.75$. All the compounds having the orthorhombic symmetry are superconductors with critical temperature decreasing from 88 K to 46 K as $x$ increases in the composition range $0 <= x <= 0.75$. Those with the tetragonal symmetry do not exhibit a superconducting transition as for example LaBa$_2$Cu$_3$O$_y$. However this last compound prepared under pure oxygen atmosphere has been found to be superconducting ($T_{cr} = 70$ K).

The crystal structure of YBa$_2$Cu$_3$O$_7$ is of orthorhombic symmetry. It can be described as a stacking along the $c$ axis of three layers: one layer of square planar CuO$_4$ blocks inserted between two layers of corner-sharing CuO$_6$ pyramids [9]. For this oxide, the square planar CuO$_4$ groups are parallel to the (001) plane. LaBa$_2$Cu$_3$O$_y$ ($y = 6.7$) obtained in oxygen has a tetragonal cell and shows a superconducting transition at 70 K [10]. The structure of this last oxide is also built with two layers of corner-sharing CuO$_6$ pyramids and one layer of CuO$_4$ square planes, but in this case the orientation of the CuO$_4$ square planes is parallel to (001) plane (10). In fact, the structure of YBa$_2$Cu$_3$O$_7$ and LaBa$_2$Cu$_3$O$_y$ are different.

The main purpose of the present work is to show the influence of the Y-La substitution and oxygen stoichiometry on both crystal structure and superconducting properties of the Y$_{1-x}$La$_x$Ba$_2$Cu$_3$O$_y$ oxides prepared in air i.e. under a fixed oxygen partial pressure. X-ray powder diffraction data and magnetic measurements are reported.

We have investigated this system for $x = 0, 0.25, 0.50, 0.75$ and 1. The samples were prepared by thoroughly mixing appropriate amounts of BaCO$_3$, Y$_2$O$_3$, La$_2$O$_3$ and CuO powder, each 99.9 percent pure.
The mixed powders were pressed in pellet form and heated in gold crucibles at 880°C for 24 hours in air. After this first treatment, the product was crushed, pressed and annealed in air at 500°C for two days and then cooled in three hours.

After preparation, the specimens were examined by conventional X-ray diffractometry (CuKα). This examination shows that each compound of nominal composition \(x = 0, 0.25, 0.50,\) and 0.75 is a single phase. In our experimental conditions, it is not possible to obtain LaBa\(_2\)Cu\(_3\)O\(_y\) as a pure phase, BaCuO\(_2\) appearing always as an impurity phase. For \(x = 0, 0.25, 0.50,\) and 0.75, the compounds crystallize in the orthorhombic YBa\(_2\)Cu\(_3\)O\(_y\) type structure. In contrast, LaBa\(_2\)Cu\(_3\)O\(_y\) has a tetragonal symmetry. As shown in figure 1, the convergence of the (006-020) and (200) reflections confirms the orthorhombic to tetragonal transformation with increasing \(z\).

The lattice parameters of these compounds are given in table I. When \(z\) increases, the \(b\) parameter remains practically constant, \(a\) and \(c\) increase and the orthorhombic deformation decreases. We note that the \(c\) parameter (11.80Å) of LaBa\(_2\)Cu\(_3\)O\(_y\) obtained in air is greater than that prepared in pure oxygen (11.73 Å) [10]. This fact could result from a different oxygen stoichiometry between those two samples. In these oxides, the treatment under oxygen atmosphere creates new Cu-O bonds and increases the average valence of copper, thus leading to a decrease of the lattice parameters [6].

For these compounds the magnetic susceptibility has been measured with a SQUID magnetometer on a sample cooled in zero field. Figures 2 and 3 show the thermal dependence of the susceptibility obtained on these materials for \(H = 100\) Oe. YBa\(_2\)Cu\(_3\)O\(_y\) prepared in air is superconducting with a critical temperature equal to 88 K (Tab. I). This value is very close to that obtained on this oxide prepared in oxygen \(T_{cr} = 93\) K [4, 5, 7]. No superconducting transition has been detected on our LaBa\(_2\)Cu\(_3\)O\(_y\) sample prepared in air (Fig. 3.). At the conclusion of this work, we received a preprint from Nakay et al. which confirmed our result [11]. The behaviour of this last oxide shows clearly the influence of the oxygen stoichiometry on its superconducting properties since a transition occurs only after treatment under oxygen atmosphere.

In the Y\(_{1-x}\)La\(_x\)Ba\(_2\)Cu\(_3\)O\(_y\) system, the compounds annealed in air with \(x = 0.25, 0.50\) and 0.75 are superconducting (Figs. 2 and 3). For \(0 \leq x < 0.25,\) the critical temperature decreases rapidly, then remains constant around 50-45 K as \(x\) increases (Tab. I). We note that the percentage of superconducting volume estimated by the diamagnetic signal decreases as \(x\) increases. This observation could be explained by a decrease of the oxygen content with rising \(x\).

The conclusion of this study is that only the orthorhombic phases of this system prepared in air become superconducting. Three ranges of behaviour for the critical temperature have been determined: (i) a fast decrease for \(0 < x < 0.25,\) (ii) a constant region near 50-45 K for \(0.25 < x < 0.75,\) (iii) no observable superconductivity above 4.2 K for \(x = 1.\) The critical temperature changes observed here could be explained by two parameters which depend on the lanthanum content: (i) the oxygen stoichiometry since the oxygen contents of YBa\(_2\)Cu\(_3\)O\(_y\) and LaBa\(_2\)Cu\(_3\)O\(_y\) have been shown to be different [10], (ii) the orientation of the CuO\(_4\) square planar groups (parallel either to the (001) plane or to the (100) plane). In
Fig. 2. - Magnetic susceptibility per gram versus temperature for $Y_{1-x}La_xBa_2Cu_3O_y$ with $x = 0, 0.25, 0.50$ and $0.75$ (samples cooled in zero magnetic field).

Fig. 3. - Magnetic susceptibility per gram versus temperature for $LaBa_2Cu_3O_7$ and $Y_{0.25}La_{0.75}Ba_2Cu_3O_y$ (samples cooled in zero magnetic field).

Table I. - Crystallographic and superconducting data of the $Y_{1-x}La_xBa_2Cu_3O_y$ oxides after annealing in air at $500\,^\circ C$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$T_c$ (K)</th>
<th>% Vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.824</td>
<td>3.890</td>
<td>11.72</td>
<td>88</td>
<td>54</td>
</tr>
<tr>
<td>0.25</td>
<td>3.833</td>
<td>3.899</td>
<td>11.76</td>
<td>61</td>
<td>18</td>
</tr>
<tr>
<td>0.50</td>
<td>3.848</td>
<td>3.899</td>
<td>11.77</td>
<td>49</td>
<td>13</td>
</tr>
<tr>
<td>0.75</td>
<td>3.881</td>
<td>3.898</td>
<td>11.78</td>
<td>46</td>
<td>7</td>
</tr>
<tr>
<td>1.0</td>
<td>3.901</td>
<td>3.901</td>
<td>11.80</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In order to clarify these explanations, a detailed X-ray powder diffraction analysis and a study by electron microscopy are now in progress.

References


