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Superconductivity of the $Y_{1-x}La_xBa_2Cu_3O_y$ system prepared in air

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Résumé.— Les oxydes $Y_{1-x}La_xBa_2Cu_3O_y$ 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). $YBa_2Cu_3O_y$ et $LaBa_2Cu_3O_y$ ont respectivement une symétrie orthorhombique et quadratique. Une transformation orthorhombique $\rightarrow$ 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 $0 \leq x \leq 0,75$. Ceux de symétrie quadratique ne présentent pas de transition supraconductrice comme par exemple $LaBa_2Cu_3O_y$. Cependant ce dernier composé est supraconducteur à 70 K lorsqu'il est préparé sous oxygène ($y=6,7$).

Abstract.— The $Y_{1-x}La_xBa_2Cu_3O_y$ 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. $YBa_2Cu_3O_y$ and $LaBa_2Cu_3O_y$ 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 $0 \leq x \leq 0.75$. Those with the tetragonal symmetry do not exhibit a superconducting transition as for example $LaBa_2Cu_3O_y$. However this last compound prepared under pure oxygen atmosphere has been found to be superconducting ($T_{cr} = 70K$).

Recently several series of high T_{cr} superconducting oxides have been discovered. For example La_2CuO_4 [1] $La_{2-x}Ba_xCuO_4$ [2, 3] and $YBa_2Cu_3O_7$ [4-8] have been found to be superconductors at 40 K, 30 K and 92 K respectively.

The crystal structure of $YBa_2Cu_3O_7$ 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_5 pyramids [9]. For this oxide, the square planar CuO_4 groups are parallel to the (100) plane. $LaBa_2Cu_3O_y$ ($y = 6.7$) 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_5 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 $YBa_2Cu_3O_7$ and $LaBa_2Cu_3O_y$ 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 $Y_{1-x}La_xBa_2Cu_3O_y$ 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_2O_3 , La_2O_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 ($\text{CuK}\alpha$). 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 $\text{LaBa}_2\text{Cu}_3\text{O}_y$ 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 $\text{YBa}_2\text{Cu}_3\text{O}_7$ type structure. In contrast, $\text{LaBa}_2\text{Cu}_3\text{O}_y$ 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 x .

The lattice parameters of these compounds are given in table I. When x increases, the b parameter remains practically constant, a and c increase and the orthorhombic deformation decreases. We note that the c parameter ($11.80\text{\AA}$) of $\text{LaBa}_2\text{Cu}_3\text{O}_y$ obtained in air is greater than that prepared in pure oxygen ($11.73\text{\AA}$) [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 $H = 100\text{ Oe}$. $\text{YBa}_2\text{Cu}_3\text{O}_y$ 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 $T_{\text{cr}} = 93\text{ K}$ [4, 5, 7]. No superconducting transition has been detected on our $\text{LaBa}_2\text{Cu}_3\text{O}_y$ 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 $\text{Y}_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ 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

Fig.1.-Part of the X-ray powder spectra of $\text{Y}_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ prepared in air.

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 $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ 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 $LaBa_2Cu_3O_y$ 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 $500^\circ C$.

x	a (Å)	b (Å)	c (Å)	T_{cr} (K)	% Vol.
0	3.824	3.890	11.72	88	54
0.25	3.833	3.899	11.76	61	18
0.50	3.848	3.899	11.77	49	13
0.75	3.881	3.898	11.78	46	7
1.0	3.901	3.901	11.80	—	—

order to clarify these explanations, a detailed X-ray powder diffraction analysis and a study by electron

microscopy are now in progress.

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