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## Classification

Physics Abstracts

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

B. Chevalier, B. Buffat, G. Demazeau, B. Lloret, J. Etourneau, M. Hervieu<sup>+</sup>, C. Michel<sup>+</sup>, B. Raveau<sup>+</sup> and R. Tournier<sup>++</sup>

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence Cedex, France

<sup>+</sup>Laboratoire de Cristallographie et Sciences des Matériaux, ISMRA, Boulevard du Maréchal Juin, 14032 Caen Cedex, France

<sup>++</sup>CRTBT-CNRS, 25 avenue des Martyrs, 38042 Grenoble Cedex, France

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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,  $\text{BaCuO}_2$  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  $H = 100$  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  $T_{\text{cr}} = 93$  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

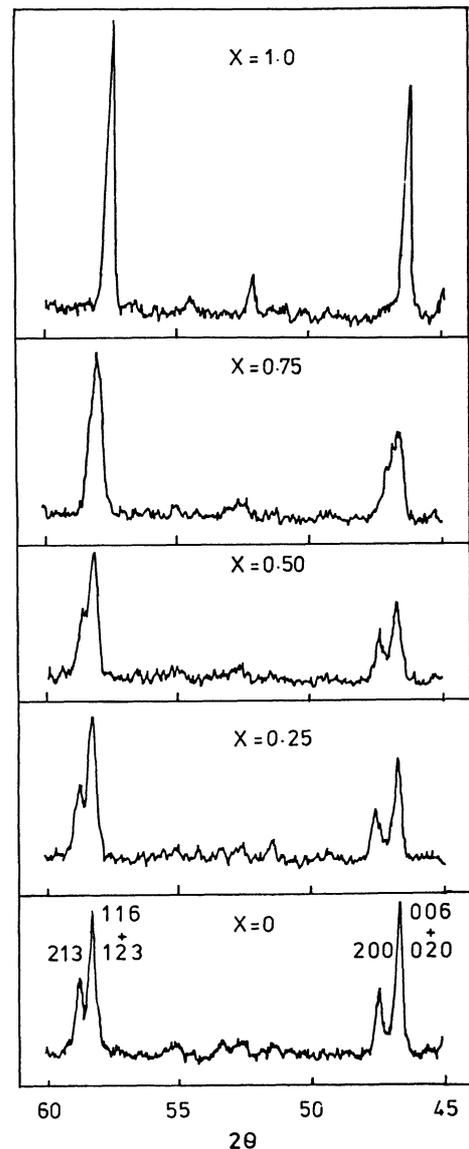


Fig.1.-Part of the X-ray powder spectra of  $\text{Y}_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  prepared in air.

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  $\text{CuO}_4$  square planar groups (parallel either to the (001) plane or to the (100) plane). In

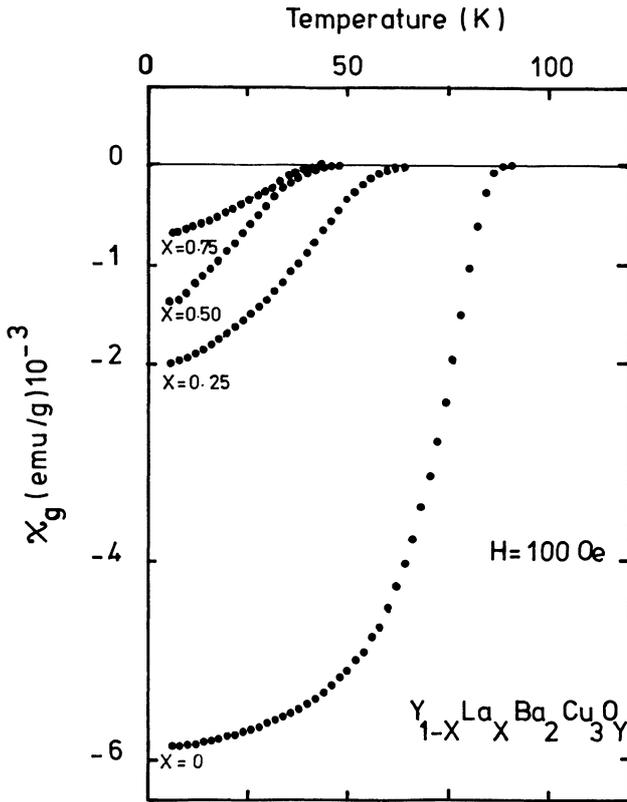


Fig.2.-Magnetic susceptibility per gram versus temperature for  $Y_{1-x}La_xBa_2Cu_3O_y$  with  $x = 0, 0.25, 0.50$  and  $0.75$  (samples cooled in zero magnetic field).

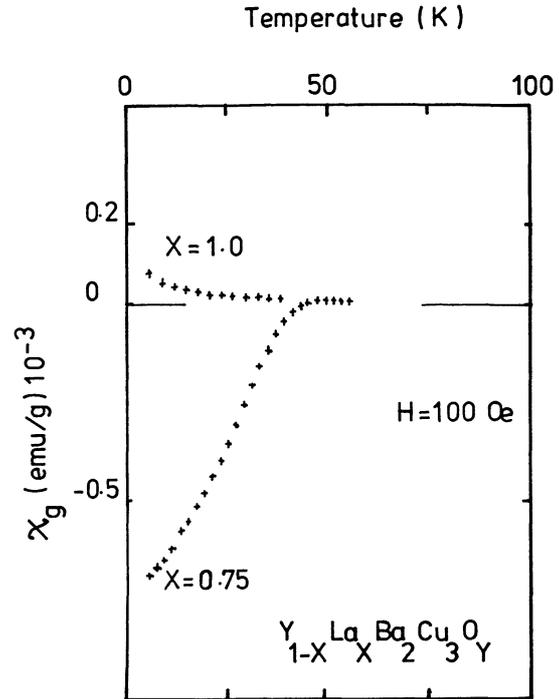


Fig.3.-Magnetic susceptibility per gram versus temperature for  $LaBa_2Cu_3O_y$  and  $Y_{0.25}La_{0.75}Ba_2Cu_3O_y$  (samples cooled in zero magnetic field).

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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