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**Autor:** Buluggiu, E. / Giori, D.C. / Valenti, A.

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ESR AND X-RAY ANALYSIS OF SUPERCONDUCTING TRANSITIONS  
IN  $c \approx 31$  AND  $c \approx 37\text{\AA}$  BSCCO SYSTEMS

E. Buluggiu\*, D.C. Giori\*, A. Valenti\* and A. Vera\*, G. Calestani<sup>†</sup> and G. Amoretti<sup>‡</sup>

\*Istituto di Scienze Fisiche dell'Università, 43100, PARMA, Italy

<sup>†</sup>Istituto di Strutturistica Chimica dell'Università, 43100 PARMA, Italy

<sup>‡</sup>Dipartimento di Fisica dell'Università, 43100 PARMA, Italy

**Abstract:** The effect of starting composition on the formation and superconductivity of the two crystallographic phases characterized by  $c \approx 31\text{\AA}$  and  $c \approx 37\text{\AA}$  in pure and  $Pb$ -doped  $Bi - Sr - Ca - Cu - O$  systems has been examined by x-ray diffraction and field-modulated microwave absorption techniques.

### 1. Introduction

The complex behaviour of the superconducting transition in the  $Bi - Sr - Ca - Cu - O$  system has been attributed to the existence of two phases with  $T_c \sim 110K$  and  $T_c \sim 80K$  respectively. The lower- $T_c$  phase was identified as  $Bi_2Sr_2CaCu_2O_z$  (2212) and shows a layered structure with  $c \approx 31\text{\AA}$ . In analogy with the  $Tl$ -based compounds, the higher- $T_c$  phase has been assumed to have a composition  $Bi_2Sr_2Ca_2Cu_3O_z$  (2223), with  $c \approx 37\text{\AA}$ . We have studied the superconducting properties of several pure and  $Pb$ -doped compounds, which are representative of the two crystallographic phases, by x-ray diffraction and field-modulated microwave absorption.

### 2. Results and Discussion

The examined samples are:

- |                             |   |
|-----------------------------|---|
| (a) $Bi_2Sr_2CaCu_2O_z$ ;   | (d,e) $Bi_2Pb_{0.4}Sr_{2.2}Ca_{2.2}Cu_{3.3}O_z$ ; |
| (b) $Bi_2Sr_2Ca_2Cu_3O_z$ ; | (f) $Bi_2Pb_{0.4}Sr_2Ca_3Cu_4O_z$ ;               |
| (c) $Bi_2Sr_2Ca_3Cu_4O_z$ ; | (g) $Bi_2Pb_{0.4}Sr_2Ca_4Cu_5O_z$ .               |

Samples d and e have the same nominal composition but were subjected to different thermal treatment. The x-ray powder diffraction pattern show that samples a-d have the  $c \approx 31\text{\AA}$  structure and f-g the  $c \approx 37\text{\AA}$  one. Sample e shows predominantly the  $c$ -longer phase peaks, but appreciable  $c \approx 31\text{\AA}$  contribution is still present. We have recorded the low-field non-resonant microwave absorption, which characterizes the new high- $T_c$  materials in the superconducting phase [1]. The details of X-band ESR measurements are reported in [2]. In Figs. 1 and 2 the absorption profiles vs temperature are shown for a-c and d-g respectively. In a temperature-sweep mode a peak in the derivative absorption is expected at  $T_c$  [3]. It appears (Fig. 1) that samples with  $c \approx 31\text{\AA}$  are characterized by a complex superconductive transition in the  $75 - 110K$  temperature range. By increasing the  $Ca$  and  $Cu$  content, the relative importance of the  $110K$  absorption region increases

correspondingly. However, the absence of a sharp peak indicates a possible wide distribution of transition temperatures. It must be noticed that, in spite of the significant increase of the higher- $T_c$  absorption in Fig. 1, the x-ray diffraction patterns don't show any appreciable trace of the  $c \approx 37\text{\AA}$  phase.

As regards the *Pb* containing samples, those showing the  $c \approx 37\text{\AA}$  structure are characterized by a single transition at  $T \sim 105\text{K}$  (Fig. 2) more pronounced for higher nominal *Cu* content. The case of sample *e* is indicative of superposition of spectra in line with the mixed structure shown by the x-ray data. The influence of the thermal treatment is illustrated by the behaviour of sample *d* that, by annealing, is progressively transformed into the *c*-longer compound *e*, as evidenced by the appearance of the characteristic peak.

In the  $c \approx 31\text{\AA}$  samples, the  $110\text{K}$  transition was frequently attributed to intergrowths of the  $c \approx 37\text{\AA}$  phase. This explanation seems us somewhat doubtful. In fact, apart from the lack of a specific x-ray indication in this sense, the ESR spectra show systematic differences between the two *c* possibilities in the superconductive onset and in the absorption profile. Moreover, in sample *c* (Fig. 1) an important contribution of higher- $T_c$  transition is found, without any x-ray evidence of the  $c \approx 37\text{\AA}$  phase. A different explanation may be related to electronic structure modification induced by *Ca*, *Sr* or *Cu* substitution for *Bi*, which could influence the transition temperature.

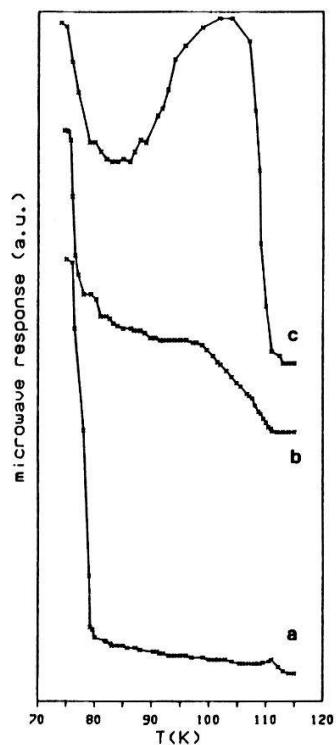


Fig. 1

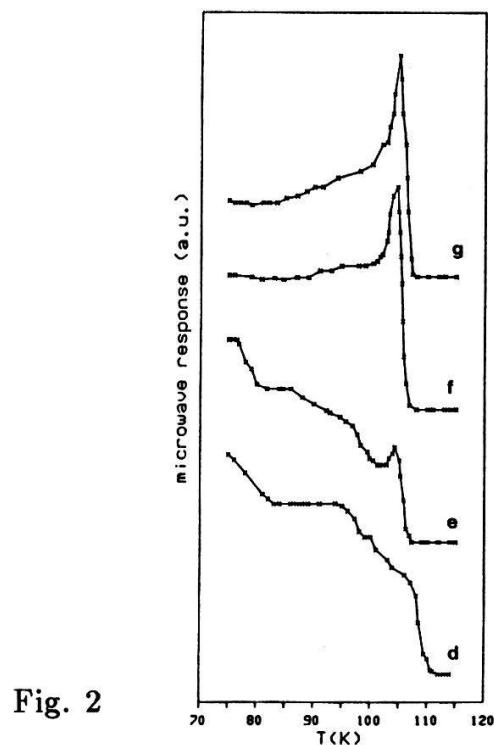


Fig. 2

### 3. References

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