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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[†] and G. Amoretti[‡]

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

[†]Istituto di Strutturistica Chimica dell'Università, 43100 PARMA, Italy

[‡]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 $T_c \sim 110\text{K}$ and $T_c \sim 80\text{K}$ respectively. The lower- T_c phase was identified as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ (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 $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$ (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) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$; | (d,e) $\text{Bi}_2\text{Pb}_{0.4}\text{Sr}_{2.2}\text{Ca}_{2.2}\text{Cu}_{3.3}\text{O}_z$; |
| (b) $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$; | (f) $\text{Bi}_2\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_z$; |
| (c) $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_z$; | (g) $\text{Bi}_2\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_z$. |

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 $75 - 110\text{K}$ 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 $T \sim 105K$ (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 $110K$ 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.

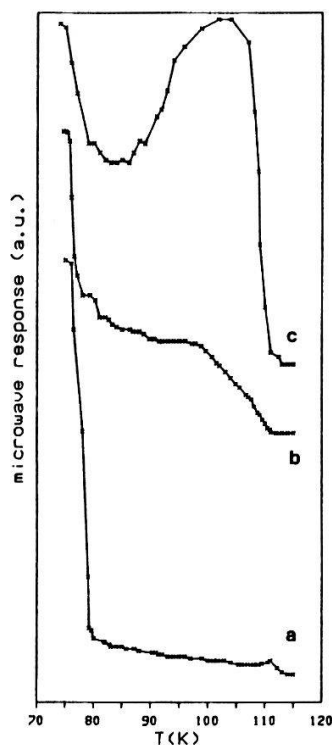


Fig. 1

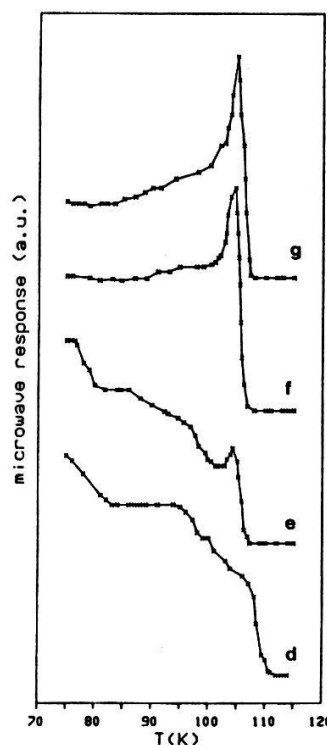


Fig. 2

3. References

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