

INFLUENCE OF PREPARATION TECHNIQUE ON THE SUPERCONDUCTIVITY OF Bi-Sr-Ca-Cu-O AND Pb-Bi-Sr-Ca-Cu-O SYSTEMS

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KEY-WORDS: Superconductor, superconductivity, high temperature superconductor, BiSrCaCuO, PbBiSrCaCuO, experiments

ABSTRACT: Different preparation procedures of Bi-Sr-Ca-Cu-O and Pb-Bi-Sr-Ca-Cu-O systems were investigated in order to obtain reliable superconducting samples with high T_c . The nominal stoichiometry BiSrCaCu₂O_x has been found as optimal one, in this state of art, for obtaining the material with the largest fraction of the "110 K" phase. We have observed that the doping by Pb can lead to stabilization of this phase and the single-phase material superconducting above 100 K has been prepared.

VPLIV TEHNIKE PRIPRAVE NA SUPERPREVODNOST Bi-Sr-Ca-Cu-O IN Pb-Bi-Sr-Ca-Cu-O SISTEMOV

KLJUČNE BESEDE: Superprevodnik, superprevodnost, visokotemperaturni superprevodnik, Bi-Sr-Ca-Cu-O, Pb-Bi-Sr-Ca-Cu-O, eksperimenti

POVZETEK: Preučevali smo različne metode priprave sistemov Bi-Sr-Ca-Cu-O in Pb-Bi-Sr-Ca-Cu-O z namenom dobiti superprevodne vzorce z visoko vrednostjo T_c . Na tej stopnji se je izkazalo, da je optimalna nominalna stohimetrija BiSrCaCu₂O_x, če smo hoteli izdelati material z največjo vsebnostjo faze "110K". Opazili smo, da dopiranje te faze s Pb vodi k njeni stabilizaciji tako, da smo uspeli pripraviti monofazni material, ki je superprevoden pri temperaturah nad 100K.

1. INTRODUCTION

Since the first discovery of high- T_c ceramic superconductors by Bednorz and Müller⁽¹⁾ intensive studies have been made on copper based oxides in order to seek new types of materials exhibiting superconductivity at even higher temperatures. The Bi-Sr-Ca-Cu-O system has appeared as one of successful results of this effort. The two high- T_c phases have been pointed out by Maeda et al⁽²⁾ with T_c - 80 K and T_c - 110 K, respectively. The recent investigations⁽³⁻⁷⁾ revealed 3 phases, which can be described by the general formula Bi₂Sr₂Ca_{n-1}Cu_nO_x, $n = 1, 2, 3$, where T_c increases when increasing n . Although the structures of the "80K" phase (Bi₂Sr₂CaCu₂O) and the "110K" phase (Bi₂Sr₂Ca₂Cu₃O_x) have been identified, various preparation procedures lead most frequently to multiphase materials. All, up to now known, investigations can be concluded that it is difficult, if not impossible, to obtain a single-phase material with T_c - 110 K.

The only way which, up to now, seems to stabilize the "110 K" phase is the partial substitution of Bi by a suitable element, e.g. by Pb⁽⁸⁾ or the very recently reported doping by combination of Pb and Sb⁽⁹⁾.

We have performed a series of preparation experiments within the Bi-Sr-Ca-Cu-O and Pb-Bi-Sr-Ca-Cu-O systems in order to obtain reliable samples with superconductivity around 110 K (with "110 K" phase as the major phase). Results of this work, including the resistivity and the susceptibility tests of obtained samples are presented.

2. EXPERIMENTAL

Samples used in the reported investigation were prepared by the solid-state reaction using commercial Bi₂O₃, (BiO)₂CO₃, SrCO₃, CaCO₃, CuO and PbCO₃ of the purity better than 99.9%. Appropriate amounts of starting materials were mixed and grounded in a planetary-ball mill with an agate mortar. The resulting fine powder was pressed into pellets (14 mm in diameter and 3 - 5 mm thick) under the pressure of 300 MPa and calcined in air at 800 and 810 - 815 °C in two steps with the intermediate regrinding and pressing into pellets. The calcined pellets were then reground and the powder pressed again (into pellets 1.5-3 mm thick). The following sintering and annealing procedures performed also in air were provided in steps of gradually increased temperature with the intermediate cooling into liquid nitrogen. Details of preparation and nominal compositions are displayed in Tables 1 - 3.

The melting point was investigated by the DTA method after each individual step of the heat treatment in order to optimize the next step.

Superconducting properties of obtained samples were tested by means of the electrical resistance and the magnetic susceptibility (magnetization) measurements. The electrical resistance was measured using a standard ac four-probe method (current = 100 μ A, f = 78 Hz) and the ac magnetic susceptibility measurements were done with 1 kHz alternating magnetic field of 0.8 μ T.

Different phases were identified by means of the X-ray diffraction analysis using Ni filtered Cu K α radiation.

3. RESULTS AND DISCUSSION

a) Bi-Sr-Ca-Cu-O

The main goal of the investigation was to achieve a procedure which provides the material with the maximal content of the so called "110K" phase. In Fig. 1. we can see the influence of the nominal composition of Bi-Sr-Ca-Cu-O on the development of superconductivity in studied samples. One can see that the stoichiometry 1112 brings the most promising result with the substantial amount of the phase which becomes superconducting around 110 K (the mid-point of the transition 107 K). The substitution of Bi₂O₃ for (BiO)₂CO₃ in starting material was found to have a minor influence on the behaviour of samples.

In order to optimize this phase the several-steps the thermal treatment with the intermediate grinding and pressing into pellets was varied. The best sample coming out of these experiments displayed behaviour which is shown in Fig.2. in comparison with that of the original sample commented above. This sample with the zero resistivity almost at 100 K exhibit no low temperature transition "tail" in the temperature dependence of the resistance. The change of the stoichiometry from 2223 to 1112 by the addition of CuO powder and the following thermal treatment in order to increase the volume fraction of the "110 K" phase was also performed. This attempt, however, produced only a slightly better result (besides a higher content of the residual CuO in the sample detected by the X-ray analysis) than the additional annealing of the 2223 sample itself as seen in Fig.3.

b) Pb-Bi-Sr-Ca-Cu-O

The Pb doped samples were ground only after calcination and no more in the course of following heat treatment. The prolonged sintering lead to the increased diameter of pellets from 14 to ~ 16-17 mm.

The presence of Pb in the material evidently stabilizes one of the superconducting phases, either the "80 K" or the "110 K" phase, dependent on the nominal composition. Fig.4. displays results obtained on the three representative samples. The material Pb_{0.3}Bi_{0.7}Sr₁Ca_{1.5}Cu₂O_x contains almost 100% content of the phase which has the superconducting transition with the mid- point at 108 K. This result was obtained consistently by the resistivity and the susceptibility measurements and proved by the X-ray analysis.

4. CONCLUSIONS

We have found that the 1112 nominal composition together with the optimal heat treatment (see Table 1) can lead to a satisfactory result when seeking to obtain superconductivity at 110 K in the Bi-Sr-Ca-Cu-O system. When inspecting the large number of our experiments with this systems we find possibilities for further optimization of the

technology, in particular by slight varying the stoichiometry around 1112 composition and a short time final exposure of the sample at higher temperatures followed by slow cooling. Nevertheless, it seems that there is no way to obtain a single-phase sample with superconductivity above 100 K unless the system is doped by additional element. We have managed to stabilize the "110 K" phase by the partial substitution of Bi by Pb. This is in agreement with results reported in literature(8).

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Table 1

Molar ratio of Bi:Sr:Ca:Cu (nominal composition)	Calcinating	annealing, cooling	marking of samples
	temperature (°C) / time (hours)		
1:1:1:2	800/20 + G 810/18 + G	850/22 + (*) + G 865/22 + (*) + G 880/95 + (*) + G 890/0.3 + 880/72 + (**)	a
1:1:1:2	800/10 + G 810/24 + G	845/22 + 850/26 + (*) 865/18 + 880/90 + (**)	b
2:2:3:4	800/12 + G 810/18 + G	850/22 + (*) 867/24 + 872/22 + + 878/20 + (*) 880/64 + (*) 890/0.3 + 880/160 + (**)	c
2:2:2:3	810/22 + G 815/30 + G	850/44 + (*) + G 855/60 + (**)	d ₁
2:2:2:3	810/22 + G 815/30 + G	850/42 + (*) + G 870/12 + 880/44 + (*) + + G 890/0.3 + 880/20 + (**)	e

Table 1: Preparation procedures of the investigated samples of the Bi-Sr-Ca-Cu-O system, (*) - rapid cooling into liquid nitrogen, (**) - slow cooling ($\Delta T/\Delta t < 40^\circ \text{C/hour}$), G - grinding, fine milling and next pressing into pellets

Table 2

Molar ratio of Bi:Sr:Ca:Cu (nominal composition)	Calcinating	annealing, cooling	marking of samples
	temperature (°C) / time (hours)		
2:2:2:3	810/22 + G 815/30 + G	850/44 + (*) + G 855/60 + (**)	d ₁
2:2:2:3	810/22 + G 815/30 + G	850/44 + (*) + G 855/60 + (**) 880/160 + (**)	d ₂
2:2:2:3 + CuO = 1:1:1:2	(G)	910/0.08 + (*) + G 910/0.08 + 880/160 + (**)	f

Table 2: Preparation procedures of the investigated samples of the Bi-Sr-Ca-Cu-O system, (*) - rapid cooling into liquid nitrogen, (**) - slow cooling ($\Delta T/\Delta t < 40^\circ \text{C/hour}$), G - grinding, fine milling and next pressing into pellets

Table 3

Molar ratio of Pb:Bi:Sr:Ca:Cu (nominal composition)	Calcinating	annealing, cooling	marking of samples
	temperature (°C) / time (hours)		
0.3:0.7:1.5:1:2	800/10 + G 810/24 + G	845/22 + (*) 850/26 + (*) 855/110 + (**)	g
0.3:0.7:1:1:1.8	800/10 + G 810/24 + G	845/22 + (*) 850/26 + (*) 855/110 + (**)	h
0.3:1:1:1:1.5	800/10 + G 810/24 + G	845/22 + (*) 850/26 + (*) 855/110 + (**)	i

Table 3: Preparation procedures of the investigated samples of the Pb-Bi-Sr-Ca-Cu-O system, (*) - rapid cooling into liquid nitrogen, (**) - slow cooling ($\Delta T/\Delta t < 40^\circ \text{C/hour}$), G - grinding, fine milling and next pressing into pellets

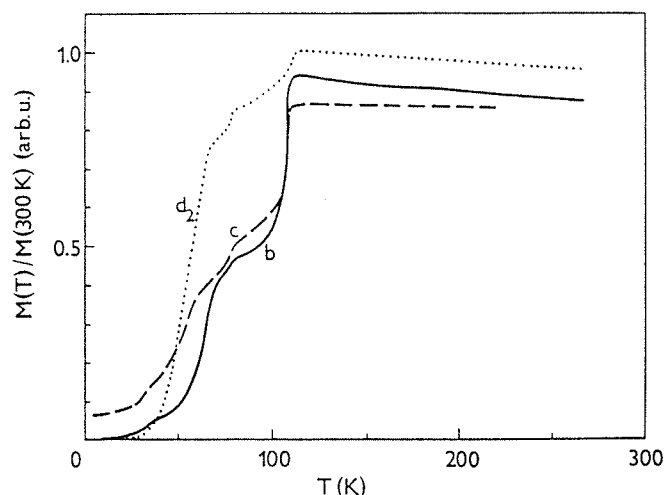
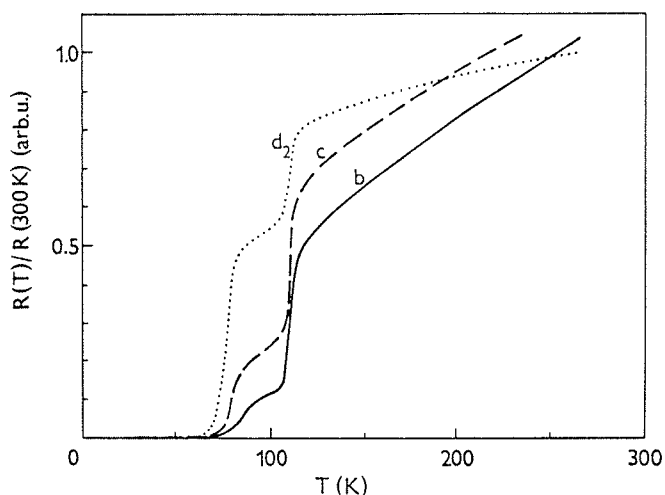


Fig. 1: Temperature dependence of /A/ the normalized electrical resistance $R(T)/R(300 \text{ K})$ and /B/ the normalized magnetization $M(T)/M(300 \text{ K})$ measured on samples with the nominal stoichiometry $\text{BiSrCaCu}_2\text{O}_x$ (b), $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (d₂) and $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ (c)

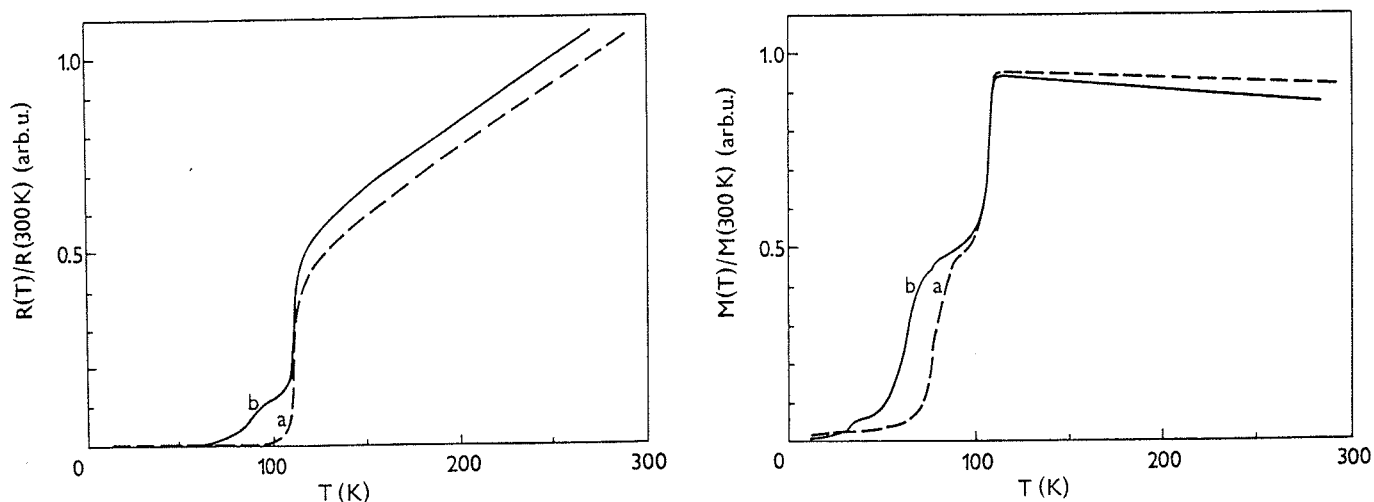


Fig. 2: Temperature dependence of the /A/ the normalized electrical resistance $R(T)/R(300\text{ K})$ and /B/ the normalized magnetization $M(T)/M(300\text{ K})$ measured on two samples with the nominal stoichiometry $\text{BiSrCaCu}_2\text{O}_x$ after different thermal treatment (see Table 1)

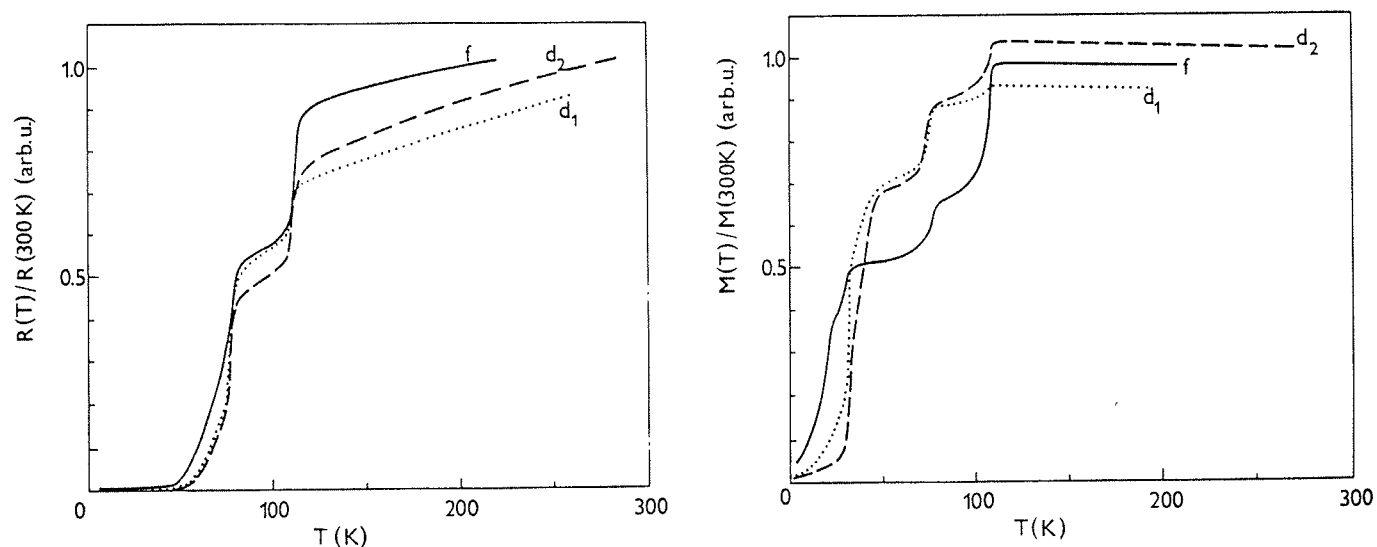


Fig. 3: Temperature dependence of the /A/ the normalized electrical resistance $R(T)/R(300\text{ K})$ and /B/ the normalized magnetization $M(T)/M(300\text{ K})$ measured on samples with the nominal stoichiometry $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (d_1 - original procedure, d_2 - after additional thermal treatment at 880°C , f - with modified composition by addition of CuO see text and Table 2)

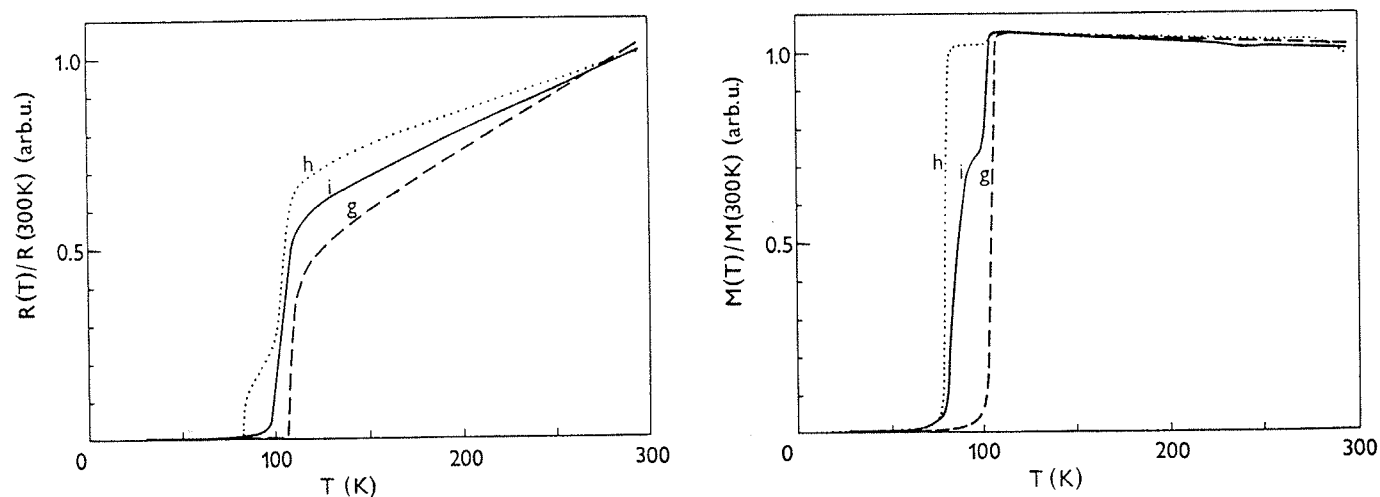


Fig. 4: Temperature dependence of the /A/ the normalized electrical resistance $R(T)/R(300\text{ K})$ and /B/ the normalized magnetization $M(T)/M(300\text{ K})$ measured on Pb-doped samples the nominal stoichiometry $\text{Pb}_{0.3}\text{Bi}_{0.7}\text{SrCa}_{1.5}\text{Cu}_2\text{O}_x$ (g), $\text{Pb}_{0.3}\text{Bi}_{0.7}\text{SrCaCu}_{1.8}\text{O}_x$ (h) and $\text{Pb}_{0.3}\text{BiSrCaCu}_{1.5}\text{O}_x$ (i)