

HIGH-T_c SUPERCONDUCTING MATERIALS. COMPARATIVE STUDY: COPRECIPITATION VS SOLID STATE PHASE PREPARATION

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ABSTRACT: The Bismuth - based compounds (BSCCO type) were prepared by two methods: The conventional method of solid state reaction and a chemical method (oxalate coprecipitation). Superconductor phases obtained by thermal decomposition of the precursors are identified from X-ray diffraction. The electric and magnetic properties of the new compounds are investigated. The results are compared in order to evaluate the potential of preparation methods.

KEYWORDS: BSCCO system, coprecipitation, X-ray diffraction, superconductivity

1 INTRODUCTION

Superconductors are generally obtained by conventional solid state reaction between oxides or carbonates. Wet chemical methods have been extensively used in the last years for preparation of high temperature bismuth based ceramic superconductors, in order to increase the reactivity of precursor powders. The main chemical methods include coprecipitation (oxalates, carbonates, citrates, e.a.), complex formation and sol-gel techniques [1 -11].

In the present paper, the oxalate precursors for the BSCCO system was synthesized in the previously established conditions, at the different pH values. These powder precursors were characterized by DTA and X-ray powder diffraction analysis. The electrical and magnetic measurements were performed for the samples prepared at different pH values and for the samples thermal treated at different temperature, with the aim to establish the instruments of preparing conditions of the samples on the structure, phase formation and electrical and magnetic properties.

2 EXPERIMENTAL

The oxalate precursors were prepared by coprecipitation, using a previously mentioned method, [12, 13], from nitrate solutions of bismuth (III), strontium (II), calcium (II) and copper (II) with an excess of oxalic acid (0.1M) followed by addition of NaOH (0.1M) in order to adjust pH at the desired values. Three samples are prepared at the pH values of 2.5 and 4.

For the comparison, the solid state samples were prepared by wet mixing of the solid state compounds: Bi₂O₃, CuO, CaCO₃ and SrCO₃ (reagent grade) for 1h.

The samples as obtained were characterized by the Differential Thermal Analysis and X-ray powder diffraction. The thermal treatment schedule was established on the basis of the DTA data: The X-ray diffraction patterns were recorded at the different temperature of thermal treatment as follows: 750, 800 and 850 °C, as well as the electrical and magnetic properties. The electrical resistance and the a.c. susceptibility as a function of temperature were carried out.

3 RESULTS AND DISCUSSIONS

The mechanism of thermal decomposition was established by the thermal differential analysis, associate with X-ray diffraction data. The thermal treatment schedule was make as in Table 1:

Table 1. Thermal Treatment Schedule

Temperature °C	Time h			
	Sample C1	Sample C2	Sample S1	Sample S2
600	1	1	-	-
750	4	4	24	24
790	-	-	4	4
800	4	4	-	-
830	-	-	4	4
850(860)	4	4	48	48

Legend:

- C1 - coprecipitate at pH = 4;
- C2 - coprecipitate at pH = 2.5;
- S1 - nominal composition BSCCO 2:2:2:3
- S2 - nominal composition BSCCO 1:1:1:2

The samples obtained at different pH values generally exhibit the same thermal decomposition mechanism. Practically at 500° all four oxalates are decomposed with formation of carbonates. The bismuth carbonate decomposes at 425°. Above 600°, reactions between carbonates and Bi-oxide begin.

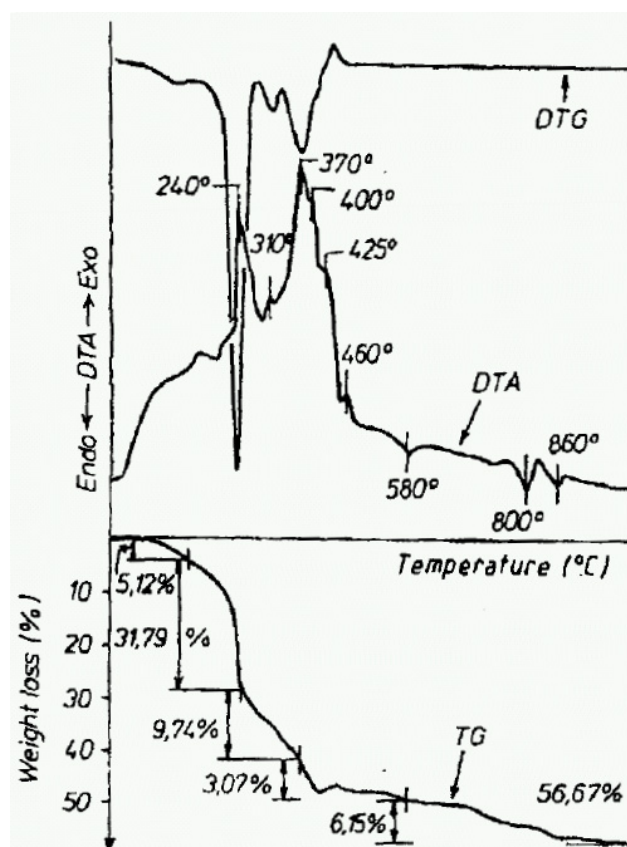


Figure 1. ATD-TG curves for oxalate coprecipitate

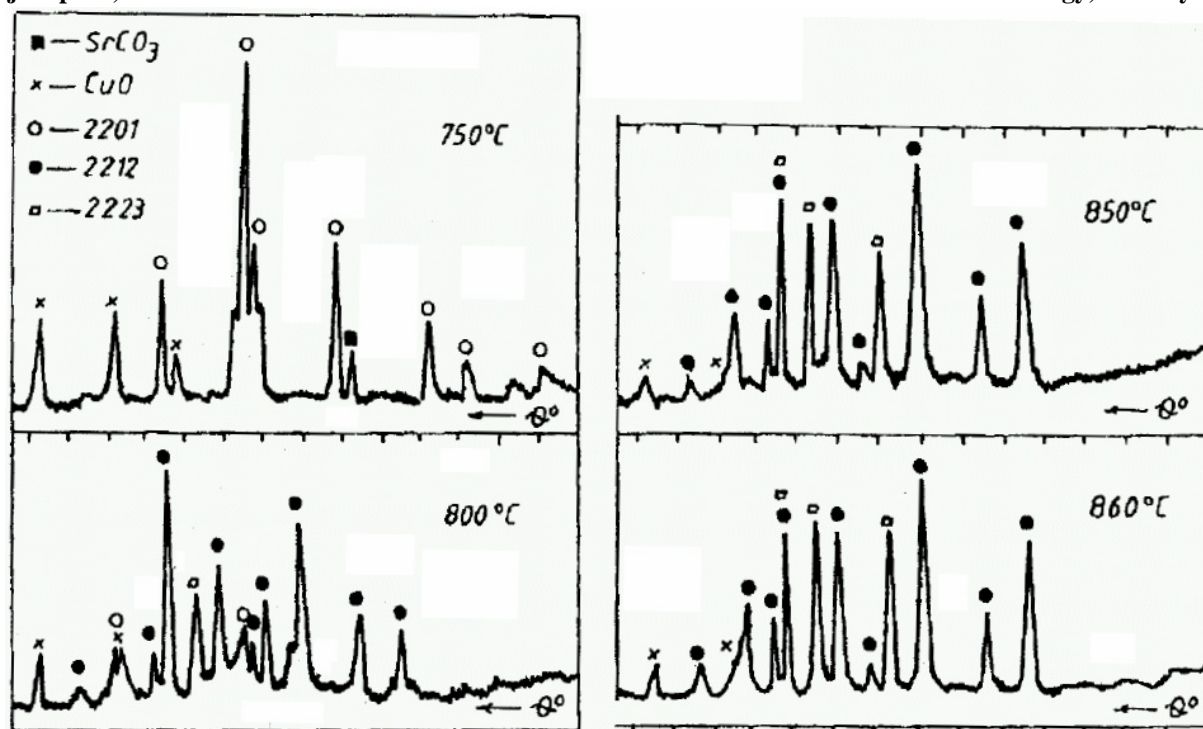


Figure 2. The X-ray diffraction diagrams for the coprecipitate thermal treated above 600°C

In table 2 is presented the mechanism of thermal decomposition of oxalate coprecipitate (nominal composition 2223). It can be seen that the decomposition of oxalate coprecipitate begins at 300-450°C with formation of Strontium and calcium carbonate and bismuth and copper oxides.

Table 2 Thermal decomposition of oxalate coprecipitate (nominal composition 2223)

Temperature range (°C)	Mass loss (%)	Species lost	Thermal effects (°C)		X-ray phase composition
			endo	exo	
					BiOHC ₂ O ₄ + SrC ₂ O ₄ ·H ₂ O + CaC ₂ O ₄ ·H ₂ O + CuC ₂ O ₄
20-250	4.78	H ₂ O	240		BiOHC ₂ O ₄ + SrC ₂ O ₄ + CaC ₂ O ₄ + CuC ₂ O ₄
250-300	29.25			290	
300-450	3.19	CO, CO ₂		415	Bi ₂ O ₃ , + SrCO ₃ + CaCO ₃ + CuO
450-800	8.51	CO ₂	775		"2201" + Bi ₄ Sr ₇ O ₁₃ + CuO + SrCO ₃
800-1000	1.59	CO ₂	845		"2201" + "2212"
			890		
			940		melting

The mechanism of thermal decomposition of the oxalate precursor above 600°C is similar to that established by the solid state reaction.

At 750° the superconductor 2201 phase is formed in all cases, as it can be seen from X-ray diffraction pattern. With the increase of temperature of thermal treatment, the superconductor 2201 phase is converted to 2212 phase. The conversion is partial at 800° and complete at 850°. In the sample initially prepared at pH = 4, and thermally treated at 800° and 850°, crystalline nuclei of

high T_c superconductor phase are formed, identified by X-ray powder diffraction. It seems that the other samples, coprecipitated at lower or higher pH values, contain lower quantities of 2223 phase.

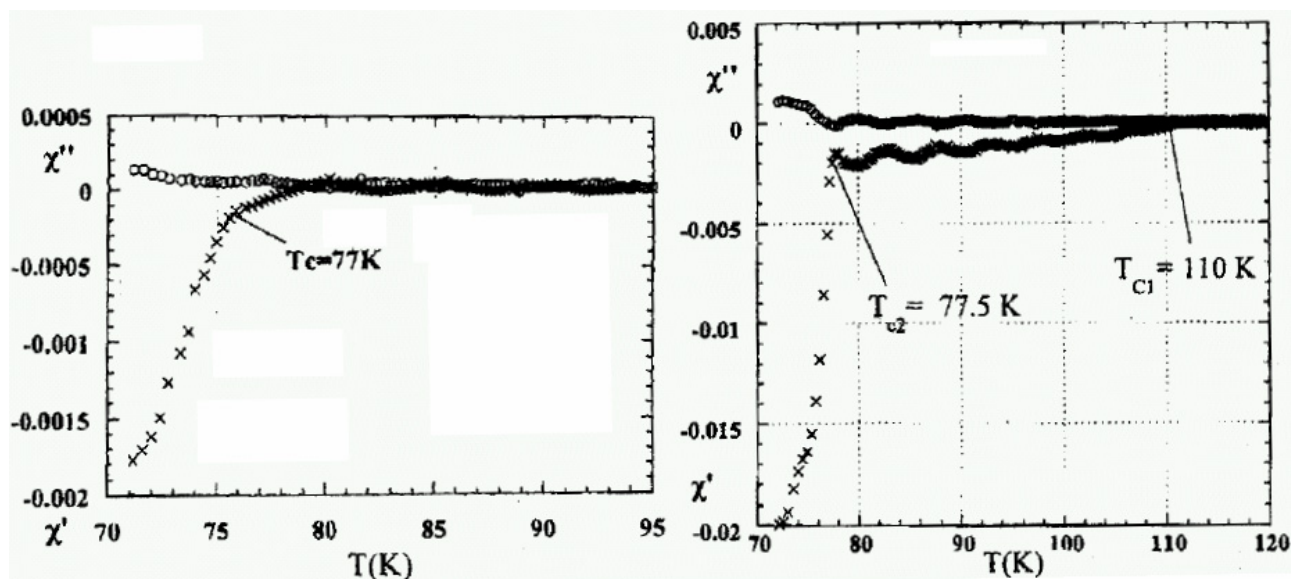


Figure 3. Sample C1 (pH = 4) thermal treated at 750°C respectively 850°C

The magnetic properties of BSCCO samples are investigated by using ac susceptibility measurements over the temperature range from 77 to 300 K. From the magnetic measurements, the superconductor transition temperatures were determined.

The ac magnetic susceptibility as a function of temperature for the coprecipitated precursors (c1 and c2) and for solid phase samples (S1 and S2), thermal treated at 750°C and 850°C are represented in the figures 3, 4 and 5, respectively. It can be seen that the coprecipitated samples thermal treated at 750°C exhibit only one superconducting transition at 77 and 79 K respectively. For the samples heated at 850°C, two-phase transition are present; the transition at ~110 K indicates the formation of 2223 superconducting phase in low quantity. X-ray diffraction diagrams have proved this fact also.

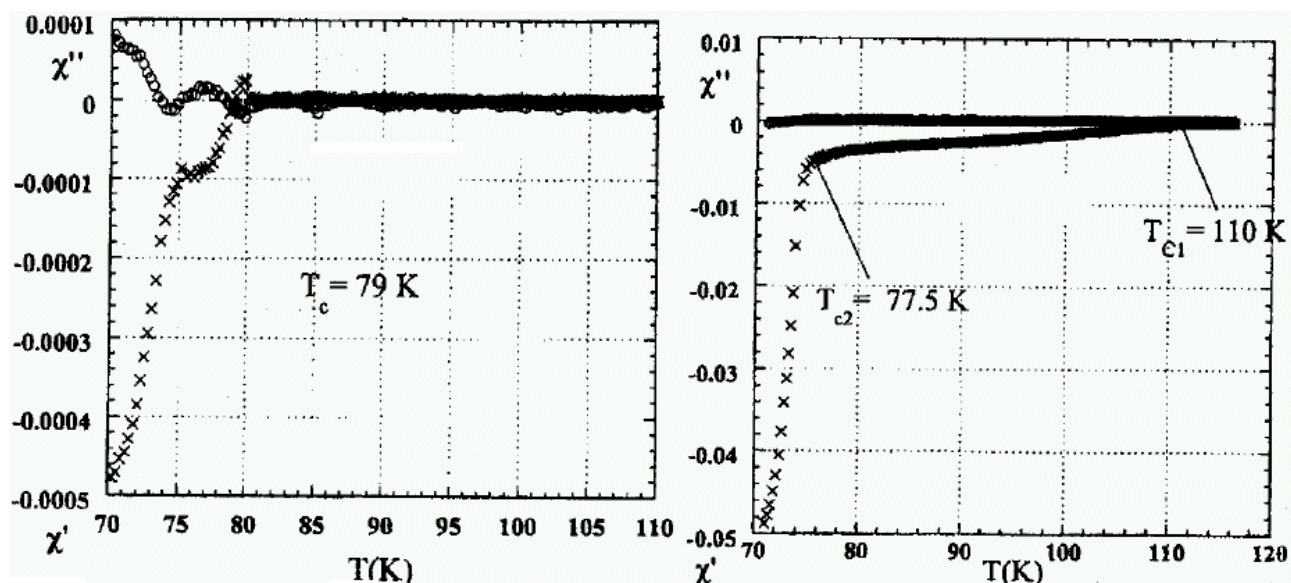


Figure 4. Sample C2 (pH = 2.5) thermal treated at 750°C respectively 850°C

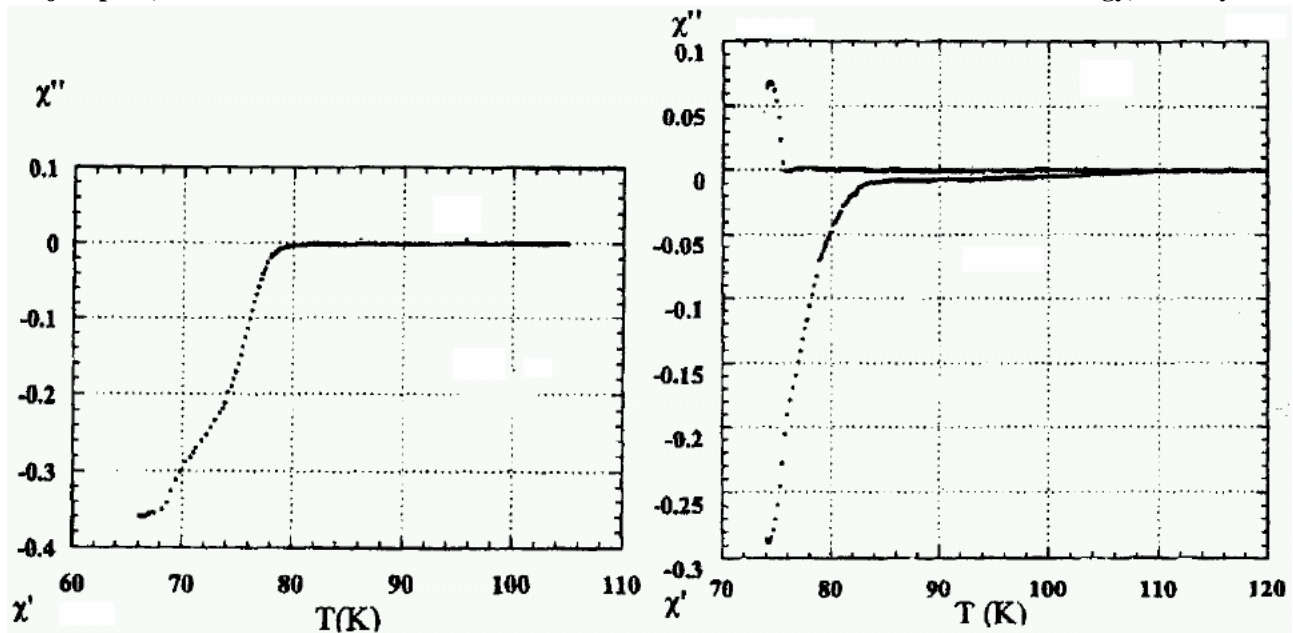


Figure 5. Sample S1 and S2 thermal treated at 850°C

There is no significant change in T_c and magnetic characteristics between the coprecipitated samples prepared at pH = 2.5 and pH = 4. From the magnetic susceptibility curves of the solid state samples thermal treated at 860°C (48 hours), it can be seen: the sample S1 (nominal composition 1112) exhibits only one phase transition at $T_c \sim 79\text{K}$; the sample S2 (nominal composition 2223) exhibits two phase transitions, with T_c 84K and T_c 106K (a very weak one). That proves the formation of a very low quantity of 2223 superconducting phase.

4 CONCLUSION

The oxalate coprecipitation is a suitable method for the synthesis of the precursor for the superconducting materials.

The DTA-TG and X-ray diffraction data indicate that the mechanism of the thermal decomposition for the oxalate precursors is practically identical with that of solid state reaction.

The difference mainly consists in a higher reactivity of the oxalate precursor's powder, and much shorter time for the thermal treatment comparatively with solid state reactions.

There is no significant difference in the behavior of the oxalate precursors prepared at different pH values.

The ac susceptibility measurements show that for an almost similar thermal treatment schedule but a shorter time, the oxalate coprecipitated samples contain a higher quantity of high T_c superconductor phase 2223.

From the magnetic measurements and T_c determination for the both coprecipitates and solid state samples, it is observed that the T_c values are quite low and probably request a longer thermal treatment.

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