

Influence of powder processing procedure on the superconducting behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics

DHANANJAI PANDEY, V S TIWARI, A K SINGH and
SANGEETA CHAUDHRY

School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

MS received 7 October 1987; revised 19 January 1988

Abstract. In order to synthesize $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powder, we first coprecipitate yttrium and barium by adding ammonium carbonate to a solution of barium and yttrium chlorides mixed in the 2:1 ratio at the molar level. Ceramics, prepared from powders obtained by calcining the coprecipitated powder with copper oxide, exhibits a very sharp drop in resistivity near 110 K with T_c^{midpoint} of 107 K and a resistivity anomaly at 260 K.

Keywords. Co-precipitation; superconductivity; yttrium; barium; powder processing.

PACS Nos 74·10; 74·70

The recent discovery of superconductivity in rare-earth cuprate perovskites has led to an unprecedented spurt in the field of oxide superconductors. Soon after the first report of superconductivity in multiphase $(\text{Y}_{0.6}\text{Ba}_{0.4})_2\text{CuO}_4$ near 90 K by Wu *et al* (1987), several groups independently identified the superconducting phase (Cava *et al* 1987; Grant *et al* 1987; Rao *et al* 1987; Siegrist *et al* 1987). Since then several possible models for the crystal structure of this phase have also been proposed (Beno *et al* 1987; David *et al* 1987; Gallagher *et al* 1987; Hazen *et al* 1987). In all the structural models proposed, there is near unanimity on the role played by one-dimensional Cu-O chains along the *b* axis of the orthorhombic cell. It is now generally believed that the removal of oxygen atoms from these chains either leads to a lowering of T_c or to the destruction of superconducting behaviour (Tarascon *et al* 1987). In view of this, most of the efforts to improve the onset temperature T_c^{onset} , the 10–90% transition width and the temperature at which the specimens become resistanceless, have been directed towards the optimization of oxygen content in the structure through a control of processing variables (see for example Gopalkrishnan *et al* 1987).

The specimens in these investigations have generally been prepared by the conventional ceramic method involving calcination of a mixture of Y_2O_3 , BaCO_3 and CuO followed by sintering of these powders at suitable temperatures around 900°C for an optimum duration. In view of the severe limitations of the solid state diffusion during calcination of Y_2O_3 , BaCO_3 and CuO powders mixed at a particulate level, uniform distribution of Y^{+3} and Ba^{+2} ions in the 1:2 ratio at the submicroscopic level cannot be achieved in the conventional method of preparation. In order to see the effect of uniform distribution of Ba^{+2} and Y^{+3} ions on the superconducting behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, we have prepared these materials by a

novel route developed in connection with (Ba, Ca) TiO₃ ferroelectric ceramics (Pandey *et al* 1987; Tiwari *et al* 1988). In this communication, we report resistivity anomaly near 260 K in a YBa₂Cu₃O_{7-y} specimen prepared by this route. This anomaly is followed by an abrupt drop in resistivity near 110 K which continues upto 100 K where the resistivity value has fallen to 5% of the room temperature value. The zero resistivity state is achieved at 94 K and the 10–90% width is found to be about 4 K. The T_c^{midpoint} in these ceramics is nearly 107 K which is about 15 K greater than those prepared by the conventional route under identical conditions.

In the method employed by us for the synthesis of YBa₂Cu₃O_{7-y} powders, we have first coprecipitated yttrium and barium ions by adding ammonium carbonate solution to molar solutions of barium and yttrium chlorides, premixed in the desired proportion, under controlled pH value. The filtrate was checked for the absence of Y⁺³ and Ba⁺² ions which ensured complete coprecipitation. X-ray diffractometer record taken from the precipitate suggests the formation of a solid solution YBa₂(CO₃)_{3.5} in favour of the orthorhombic BaCO₃ structure. However, the possibility of some of the yttrium remaining as amorphous Y₂(CO₃)₃ cannot be ruled out by X-ray diffraction. In fact, we find that the precipitates obtained by adding ammonium carbonate to yttrium chloride solution are amorphous only. Thus the result of coprecipitation can be either a precursor carbonate solid solution of yttrium and barium or an intimate mixture of the individual carbonates only. The change in the cell parameter of the coprecipitated powder as compared to the standard value given for orthorhombic BaCO₃ suggests that either all of yttrium or some part of it has definitely gone into the formation of a solid solution of yttrium and barium carbonate. The precursor coprecipitated powder was thoroughly mixed with CuO and then calcined in air at 900°C initially for 12 h. The powder so obtained was reground and recalcined at the same temperature for another 12 h. Since the mixing of Y⁺³ and Ba⁺² ions in the precursor was achieved at a finer level (atomic level if the solid solution is formed) using a wet technique, more uniform supply of Y⁺³ and Ba⁺² ions during calcination with CuO is expected. The YBa₂Cu₃O_{7-y} powder so obtained was pelletized at a pressure of 4.4×10^5 KNm⁻² and sintered in flowing oxygen at 900°C for 6 h followed by slow cooling to 200°C in another 6 h.

Figure 1 depicts the temperature dependence of resistivity (normalized with respect to the resistivity at 300 K) in one such specimen. The measurements were performed using standard four-probe arrangement and a current of 10 mA. There are three discernible kinks marked as P, Q and R occurring nearly at temperatures 260 K, 110 K and 100 K respectively. The abrupt fall in resistivity at Q (~110 K) is very striking. The foot structure beyond R is probably due to slight oxygen deficiency along the Cu-O chains as indicated by the poor resolution of the XRD peaks near 32.5°. The sharp drop from U to V, where the resistivity has decreased by 30% within a temperature interval of 1 K, makes us believe that by optimizing annealing conditions, zero resistivity state can be achieved near 107 K.

One of the characteristic features of the conventionally prepared specimens, which show metallic behaviour below room temperature, is the linear temperature dependence of resistivity from room temperature down to T_c^{onset} (Murphy *et al* 1987). In our case, there is a kink at P near 260 K which is not followed at lower temperatures by an exactly linear resistance drop upto Q. Indeed there are oscillatory trends in the region PQ and the slopes at P and Q (shown by dotted lines in the figure) do not match. In view of the foregoing, one may be tempted to propose that isolated

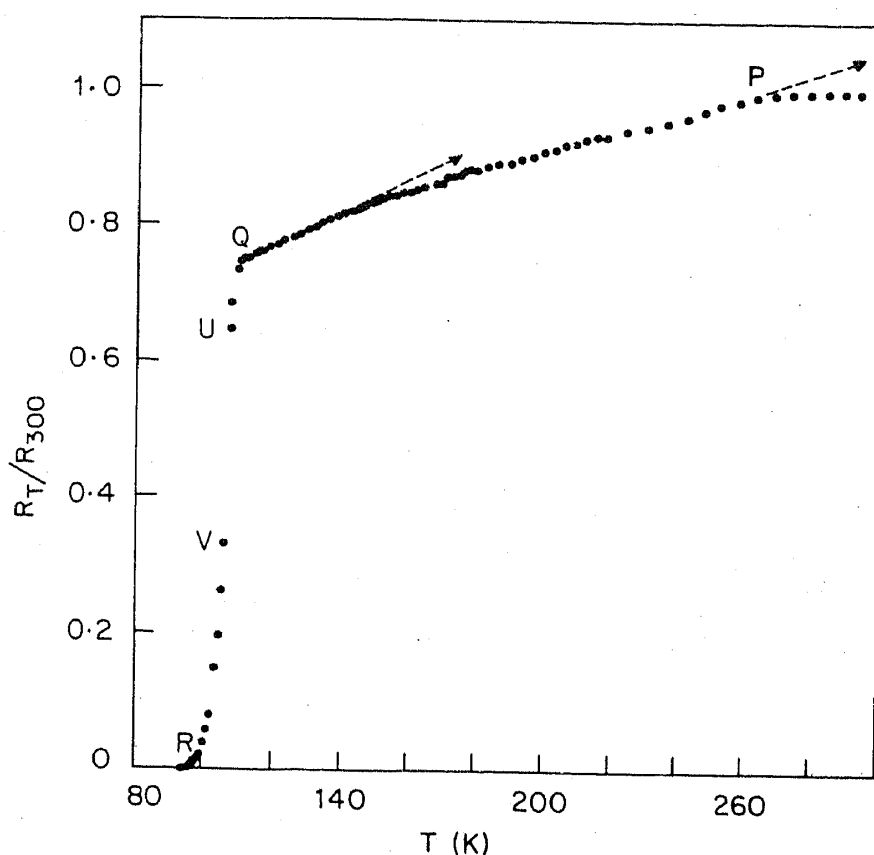


Figure 1. Normalized electrical resistance plotted against temperature for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. Note the resistance anomaly at 260 K and the gradual change in slope from P to Q until a sharp drop in resistivity at 110 K.

superconducting regions started appearing below 260 K but the percolative superconducting path involving a reasonable fraction of the entire specimen is established only below 110 K. The small increase in slope in going from P to Q can then be taken to represent a gradual increase in the fraction of superconducting regions. While it is premature to conclude that T_c^{onset} in our specimens is definitely 260 K, we wish to emphasize that the observation is first of its kind in the single phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. This, however, does not rule out the possibility of some other phase present below the detection limit of routine X-ray diffraction. It should be noted that Jayaram *et al* (1987) also reported resistivity anomalies above 230 K but in multiphase specimens where the phase responsible for the anomaly is yet to be identified. Chen *et al* (1987) reported weak superconducting signals through inverse AC Josephson effect upto 240 K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. In the light of our synthesis procedure, we feel that the state of ordering of Ba^{+2} and Y^{+3} ions, which will depend on (i) the constituents used during calcination, (ii) the reaction mechanism, (iii) the kinetics of reaction and (iv) the rate of cooling after the sintering of the specimens, is mainly responsible for the appearance of the 260 K anomaly. To settle this point, X-ray diffraction work is in progress and the details will be reported in due course.

One of us (DP) is thankful to Dr H R Krishnamurthy for motivating him to start work on high T_c superconductors. The encouragement and generous help received from Dr R Krishnan, Dr A P B Sinha, Professors T V Ramakrishnan, V V Chalam,

P Ramachandra Rao, S Lele, G Singh and Drs Om Parkash and L Pandey are gratefully acknowledged.

References

- Beno M A, Soderholm L, Capone D W, Hinks D G, Jorgensen J D, Schuller I K, Segre C U, Zhang K and Grace J D 1987 Preprint March 1987
- Cava R J, Batlogg B, van Dover R B, Murphy D W, Sunshine S, Siegrist T, Remeika J P, Rietman E A, Zahurak S and Espinosa G P 1987 *Phys. Rev. Lett.* **58** 1676
- Chen J T, Wenger L E, Mc Ewan I J and Logothetis E M 1987 *Phys. Rev. Lett.* **58** 1972
- David W I F, Harrison W T A, Gunn J M F, Moze O, Soper A K, Day P, Jorgensen J D, Hinks D G, Beno M A, Soderholm L, Capone D W, Schuller I K, Segre C U, Zhang K and Grace J D 1987 *Nature (London)* **327** 310
- Gallagher P K, O'Bryan H M, Sunshine S A, Murphy D W 1987 *Mater. Res. Bull.* **22** 1007
- Gopalakrishnan I K, Yakhmi J V and Iyer R M 1987 *Nature (London)* **327** 604.
- Grant P M, Beyers E M, Engler E M, Lim G, Parkin S S P, Ramirez M L, Lee V Y, Nazzari A, Vazquez J E and Savoy R 1987 *Phys. Rev.* **B35** 7242
- Hazen R M, Finger L W, Angel R J, Prewitt C T, Ross N L, Mao H K, Hadjilacos C G, Hor P H, Meng R L and Chu C W 1987 *Phys. Rev.* **B35** 7238
- Jayaram B, Agrawal S K, Gupta A and Narlikar A V 1987 *Curr. Sci.* **56** 572
- Murphy D W, Sunshine S, van Dover R B, Cava R J, Batlogg B, Zahurak S M and Schneemeyer L F 1987 *Phys. Rev. Lett.* **58** 1888
- Pandey D, Tiwari V S, Singh T B, Pandey L, Parkash O and Ramachandrarao P 1987 *Phase transitions* **9** 11
- Rao C N R, Ganguly P, Raychaudhuri A K, Mohan Ram R A and Sreedhar K 1987 *Nature (London)* **326** 856
- Siegrist T, Sunshine S, Murphy D W, Cava R J and Zahurak S M 1987 *Phys. Rev.* **B35** 7137
- Tarascon J M, Greene L H, Bagley B G, Mckinnon W R, Barboux P and Hull G 1987 *Proc. Int. Workshop on Novel Mechanisms of Superconductivity*, Berkeley, June 1987 (in press)
- Tiwari V S, Pandey D and Groves P 1988 (To be published)
- Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908