

Oxygen-enrichment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ using the fluidization technique

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Abstract. The oxygen-deficient phase of the high T_c superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$, was oxygen-enriched using the fluidization technique to give good superconducting properties. The normal method of oxygen treatment at 900°C for 24 h and at 600°C for 24 h has been reduced to just one treatment at 600°C for 12 h by the fluidization technique to achieve almost the same strength of superconducting signal for the $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder, which establishes the attractiveness of the latter route for the large-scale preparation of superconducting material. The particle sizes were in the range 0–90, 90–180 and 180–420 μm . The fluidized particles were crystalline with orthorhombic distortion. T_c^{onset} , estimated using the a.c. magnetic susceptibility method, was 91.3 K. The volume fraction of superconducting material in the product was 83.7–85.3%, one of the highest values reported so far for $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Keywords. High temperature superconductivity; $\text{YBa}_2\text{Cu}_3\text{O}_7$; fluidization.

1. Introduction

The 90 K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Wu *et al* 1987; Cava *et al* 1987; Rao *et al* 1987c) and the oxide $\text{LnBa}_2\text{Cu}_3\text{O}_7$ (Ln=rare earth) (Dunlap *et al* 1987; Radhakrishnan *et al* 1987; Sampathkumaran 1987; Sreedhar *et al* 1987a; Subba Rao *et al* 1987; Rao 1988; Subba Rao 1988) have been extensively investigated over the past year and a half not only for their interesting physical properties but also with regard to their exploitation for practical applications. Technological exploitation of high temperature superconductor (HTSC) oxides, e.g. wires for superconducting magnets (Jin *et al* 1987; Ohmatsu *et al* 1987; Yamada *et al* 1987; Flukiger *et al* 1988), metal composite monoliths (Yurek *et al* 1988), explosive compaction (shock compression) (Murr *et al* 1987, 1988) etc. requires the processing of large quantities of these materials.

Knowledge of the phase diagram and control of essential primary and secondary properties through manipulation of the microstructure are required to optimise the electronic and mechanical properties. Achievement of this long term aim necessitates an understanding of the process of control of the oxygen stoichiometry, crystal structure, grain size distribution, grain boundary composition, sub-grain domain structure and porosity in the sintered products of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Button *et al* 1987; Murr *et al* 1987, 1988; Yurek *et al* 1988).

2. Dependence of T_c on δ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The oxygen stoichiometry in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, its relationship with the crystal

structure, phase transitions, oxygen ordering in the structure and correlation effects and their role in superconductivity are areas which are being actively investigated at present. For practical applications of $\text{YBa}_2\text{Cu}_3\text{O}_7$, there is great interest in knowing its long-term stability at room and liquid nitrogen temperatures, in vacuum and in various gas environments including air. Often the limitation in the current-carrying capacity of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ is traced to the weak intergranular coupling and depleted surface oxygen profiles which may form poor superconducting regions (Flukiger *et al* 1988; Yurek *et al* 1988). For the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and related high T_c superconductors we should know the precise oxygen treatment conditions which could lead to the production of an oxide material with reproducible physical characteristics. Though some measure of success has been achieved through empirically established procedures, the kinetics of oxygen diffusion and the nature of ordering of the oxide ions in the lattice need to be studied in detail (Dunlap *et al* 1987; Sampathkumaran 1987; Sreedhar *et al* 1987; Murr *et al* 1987, 1988; Bakker *et al* 1988; Flukiger *et al* 1988; Rao *et al* 1988; Ronay and Nordlander 1988; Shafer *et al* 1988; Yurek *et al* 1988).

Since superconducting properties depend on the oxygen stoichiometry, various studies have been carried out in different ambient atmospheres on the preparation, oxygen stoichiometry and dependence of the superconducting transition temperature on the heat treatment/quench temperature of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Benoit *et al* 1987; Bhat *et al* 1987; Dhar *et al* 1987; Engler *et al* 1987; Ganguli *et al* 1987; Harris and Hewston 1987; Harris *et al* 1987; Jorgensen *et al* 1987; Katano *et al* 1987; Keller *et al* 1987; Kini *et al* 1987; Kishio *et al* 1987; Laudise *et al* 1987; Manthiram *et al* 1987; Nagarajan *et al* 1987; Oesterreicher and Smith 1987; Om Prakash *et al* 1987; Ono and Ishizawa 1987; Rao *et al* 1987a, b, 1988; Sawada *et al* 1987; Schneemeyer *et al* 1987; Schuller *et al* 1987; Sreedhar *et al* 1987b; Steinfink *et al* 1987; Takayama *et al* 1987; Tarascon *et al* 1987; Uchida *et al* 1987; van den Berg *et al* 1987; Cava *et al* 1988; Ota *et al* 1988; Rao 1988; Shi *et al* 1988, 1989; Whangbo *et al* 1988). The essential conclusions from these studies are as follows: The phase diagram studies reveal that $\text{YBa}_2\text{Cu}_3\text{O}_7$ is of line-phase composition and has no appreciable homogeneity range with respect to metals (Jorgensen *et al* 1987; Katano *et al* 1987). Structure data shows that $\text{YBa}_2\text{Cu}_3\text{O}_7$ is an oxygen-deficient perovskite mixed oxide (Cava *et al* 1987; Dunlap *et al* 1987; Radhakrishnan *et al* 1987; Rao *et al* 1987; Sampathkumaran 1987; Sreedhar *et al* 1987; Subba Rao *et al* 1987, 1988; Rao 1988; Subba Rao 1988). When $\text{YBa}_2\text{Cu}_3\text{O}_7$ is synthesized in air by the high temperature solid state reaction of the constituent oxides/carbonates, there is further oxygen deficiency, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta \neq 0$). The value of δ can be reduced by an oxygen-annealing treatment at high temperatures followed by slow cooling. Detailed and careful studies have shown that for $\delta = 0.05\text{--}0.20$, the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is orthorhombic and exhibits a high T_c of 91 K, whereas for $\delta = 0.2\text{--}0.4$ the orthorhombic structure is retained but the T_c is reduced to 60 K. Some workers, however, have claimed that the 60 K phase is tetragonal (Kini *et al* 1987). In the range $\delta = 0.4\text{--}0.6$, the structure becomes tetragonal and the T_c falls rapidly to less than 4.2 K for increasing δ . For $\delta = 0.6\text{--}1.0$, no superconductivity is encountered and, in fact, the compound exhibits semiconductor-behaviour. However, the structure remains tetragonal (figure 1). The above changes in structure and superconducting properties are related to the valency of the copper ion and ordering or disordering of the oxide ions in the lattice. It must be pointed out that phases with $\delta > 0.5$ can only be prepared by annealing in vacuum or using gettering techniques.

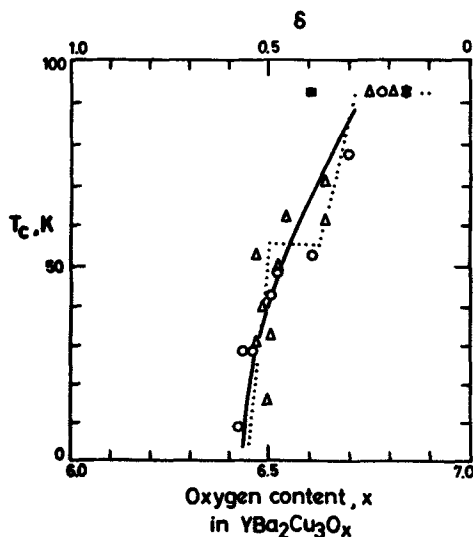


Figure 1. T_c versus overall oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where the empty circles and empty triangles represent the data of van den Berg *et al* (1987) and Jorgensen *et al* (1987) respectively. The filled square and filled hexagon refer to the data of Katano *et al* (1987) and Beno *et al* (1987) respectively (after Whangbo *et al* 1988).

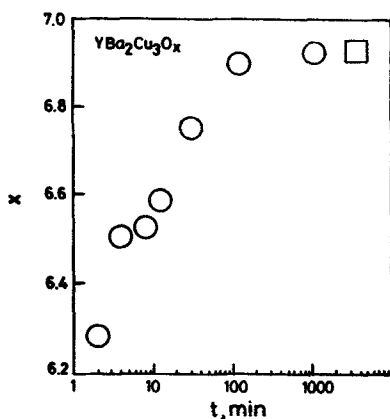


Figure 2. The oxygen content x , in $\text{YBa}_2\text{Cu}_3\text{O}_x$ as a function of annealing time in samples annealed at 400°C . The sample annealed in flowing O_2 is indicated by a square. These data are obtained from an iodine titration technique. The size of the symbol approximates the error in the value of x (after Shi *et al* 1988).

To ensure δ values in the range 0.05–0.20 in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for obtaining optimal superconducting properties, the temperature and times of annealing in the oxygen atmosphere and the rate of cooling to room temperature are important factors. TGA (thermogravimetric analysis) and iodimetric analysis on the small quantities of the mixed oxide produced in experiments have shown that a minimum temperature of 400°C and time of 100 min in oxygen are necessary to obtain $\delta < 0.2$ (figure 2). Slow cooling ($50\text{--}60^\circ\text{C/h}$) ensures oxygen ordering in the crystal lattice and the desired orthorhombic structure. However, when dealing with larger quantities of the materials, it is advisable to carry out the oxygen treatment at higher temperatures (600°C) (Radhakrishnan *et al* 1987; Subba Rao *et al* 1987; Subba Rao 1988).

The stability of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is very important. Freshly synthesized, well-oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$ in fine powder form ($\leq 10\ \mu\text{m}$ size) is very reactive and can

decompose water to hydrogen and oxygen (Yan *et al* 1987). On (unprotected) exposure to air it slowly loses oxygen and shows a deterioration in superconductivity (Barns and Laudise 1987; Frase *et al* 1987; Shelby *et al* 1987; Bansal and Sandkuhl 1988; Barkett *et al* 1987). However, it has been the experience of the present authors that well-sintered and oxygenated polycrystalline pellets (with grain size $> 200 \mu\text{m}$) are stable for months when exposed unprotected to air and moisture.

3. Motivation for the present study

Oxygen-enrichment is an essential step during the final stages of synthesis in the preparation of homogeneous and good quality $\text{YBa}_2\text{Cu}_3\text{O}_7$. It is usually done by heating the samples (which have already been pre-synthesised in air) in a stream of oxygen gas at temperatures of 900 and 600°C for extended periods of time. The above method is cumbersome and time-consuming when large batches of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder are to be oxygen-enriched. For the latter, the treatment may be ineffective due to the inability of oxygen to penetrate or permeate through the bulk of the powder or pellets (owing to kinetic factors such as rates of mass transfer through oxygen gas film and diffusion of oxygen to the interior of the pellet). Further, homogeneity and uniform temperature control becomes a problem when a large quantity of loose powder or pellets of large size (e.g. 4 cm dia, 0.5–1.0 cm thickness) are to be oxygen-treated.

For the first time, the present authors have successfully employed the technique of fluidization for effecting the oxygen-enrichment of large quantities (300 g batches) of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder (Subba Rao *et al* 1988). This technique, due to very effective mixing and heat transfer, is a potentially good method for optimal oxygen enrichment at reduced times and perhaps at reduced temperatures and for the easy preparation of homogeneous, stable and superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder in bulk quantities.

The term fluidization is used to designate the fluid–solid contacting process in which a bed of finely divided solid particles is lifted and agitated by a rising stream of gas (Zenz 1980). At minimum fluidization velocity, the drag force of fluid on the particles becomes equal to their weight and the particles become neutrally buoyant (Porter *et al* 1984; Matsen *et al* 1985). At this point, an infinitesimal increase in the fluid rate lifts or supports the particles. Hence, the particles are envisioned as barely touching or floating on a film of fluid. At low velocities, the amount of lifting is slight and the bed behaves as a boiling liquid, hence the term ‘boiling bed’. There are many types of fluid beds out of which the ‘bubbling bed’ (at high fluid velocities $u > 3 u_{mf}$ most of the gas over and above the minimum fluidization velocity (u_{mf}) escapes in the form of bubbles and this type of bed is called bubbling bed) reactor is the most common and the other types have been designated to overcome the disadvantages of a bubbling fluid bed in specific situations (Porter *et al* 1984; Matsen *et al* 1985; van Swaaij 1985). The basic parameter is the ‘gas superficial velocity’, which must be between the minimum fluidization velocity and the terminal velocity above which a ‘carry-over’ of solids from the bed becomes possible. Temperature is one of the most important reaction variables; the other being the particle size (Kunii and Levenspiel 1969; Ganapathy 1985). Experience with the solid particle catalysts in the fluidized bed reactors in standard chemical

engineering practice has shown that particles with a wide range of sizes perform better than powders having a narrow size range (Geldart 1986).

In the present experiments using a bubbling-bed type reactor, the temperature and time of fluidization as well as the size of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder particles for oxygen-enrichment were optimised. The results are described below.

4. Experimental

To gain experience, the pure phase $\text{YBa}_2\text{Cu}_3\text{O}_7$ was synthesized in 10–15 g batches and characterized. For the fluidization experiments, the preparation was scaled up to 250–300 g batches. For establishing the oxygen stoichiometry, characterization was done by X-ray diffraction and chemical analysis. Superconductivity tests were done by measuring the electrical resistivity as a function of temperature, simple 'coil test' and by the a.c. magnetic susceptibility (range 77–300 K). SEM studies were also undertaken for examining the surface morphology.

4.1 Small-scale preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$

In the literature, various procedures have been described for the laboratory (small-scale) synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Cava *et al* 1987a, 1988; Rao *et al* 1987c; Subba Rao *et al* 1987; Subba Rao 1988; Radhakrishnan *et al* 1987; Rao 1988; Sreedhar *et al* 1987; Sampathkumaran 1987; Dunlap *et al* 1987; Rao *et al* 1987a,b; Rao 1988; Ota *et al* 1988; Uchida *et al* 1987; Dhar *et al* 1987; Kini *et al* 1987; Sawada *et al* 1987; Keller *et al* 1987; Manthiram *et al* 1987; Takayama *et al* 1987; Whangbo *et al* 1988; van den Berg *et al* 1987; Jorgensen *et al* 1987; Katano *et al* 1987; Beno *et al* 1987; Harris and Hewston 1987; Harris *et al* 1987; Shi *et al* 1988; Om Prakash *et al* 1987; Schneemeyer *et al* 1987; Laudise *et al* 1987; Oesterreicher and Smith 1987; Kishio *et al* 1987; Schuller *et al* 1987; Nagarajan *et al* 1987; Tarascon *et al* 1987; Engler *et al* 1987; Ono and Ishizawa 1987; Steinfink *et al* 1987; Bhat *et al* 1987; Ganguli *et al* 1987). Here the standardized procedure of Subba Rao *et al* (1987), Radhakrishnan *et al* (1987) and Subba Rao (1988) was employed, which consisted of thorough mixing, heating and an oxygen-treatment schedule at high temperatures. High purity Y_2O_3 (99.99%; Indian Rare Earths, Kerala), CuO (99.9%; prepared by the thermal decomposition of the nitrate obtained by the dissolution of copper metal (99.9%) in AR nitric acid) and BaCO_3 (99.5%; Glaxo Labs., India) in the appropriate stoichiometric proportions (10–15 g batches) were mixed in powder form using an agate mortar and pestle and heated in a Pt-crucible in air at 950°C for 24 h. Two more repeat grindings and heatings were done in air. The black powder so obtained was then pelletised (WC-lined stainless steel die and plungers, 8 mm dia, 2–3 mm thick, hydraulic press at 4 t/cm² pressure) and again heated in air at 950°C for 24 h and slowly cooled. Since the T_c is critically dependent on the oxygen content, an annealing treatment in oxygen in the final stages of synthesis was one of the essential steps. The pellets were transferred into a tubular furnace with oxygen flow and heat treated at 900°C for 24 h. The temperature was then decreased to 600°C (over a period of 4 h), the annealing was continued for 24 h and then the material was slowly cooled to room temperature (furnace shut-off) in flowing oxygen. Well-sintered and oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples were thus obtained which showed 'HTSC' behaviour.

4.2 Bulk preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$

250–300 g batches of $\text{YBa}_2\text{Cu}_3\text{O}_7$ were prepared by a high-temperature solid-state reaction. The constituent high purity oxides/carbonates were thoroughly mixed employing a planetary ball mill (Fritsch, West Germany) for an hour and then slowly heated in a large alumina crucible in air at 950°C for 24 h. Two repeat grindings and heatings were then resorted to at 950°C . Dry mixing only was carried out and at no stage was wet mixing (with water or alcohol) done. The black powder so obtained had a particle size in the range $5\text{--}90\ \mu\text{m}$. In order to improve the particle size the powder was pressed into lugs (high porosity pellets) of 4 cm diameter and 1.0–1.5 cm thickness—each containing 50–100 g of powder—and sintered at $930\text{--}950^\circ\text{C}$ in air for 12–24 h. The lugs were then broken up, ground and sieved to obtain particles in the size range $180\text{--}420\ \mu\text{m}$ and $90\text{--}180\ \mu\text{m}$. These powders were then used for fluidization experiments. Samples were also prepared in pellet form (8 mm, 12 mm and 40 mm dia and thickness ranging from 2–6 mm) and subsequently oxygen-treated first at 900°C and then at 600°C for 24 h each, as was done in the small-scale preparation. The large pellets were then broken up, ground and sieved to obtain 300 g of powder of particle size in the range $5\text{--}90\ \mu\text{m}$. This powder, including the pellets, was well-oxygenated and exhibited high T_c superconductivity.

4.3 Fluidization experiments

Fluidization of $\text{YBa}_2\text{Cu}_3\text{O}_7$ was carried out in a high temperature fluidization furnace [Fluidtherm Technology (P) Ltd., Madras] which was slightly modified to suit the present requirements. A schematic diagram is shown in figure 3. Essentially it is a vertical furnace with provision for the passage of gas from below and an outlet at the top. The distributor system and work support hold the material to be fluidized in a retort made up of a super alloy. To handle smaller quantities of the

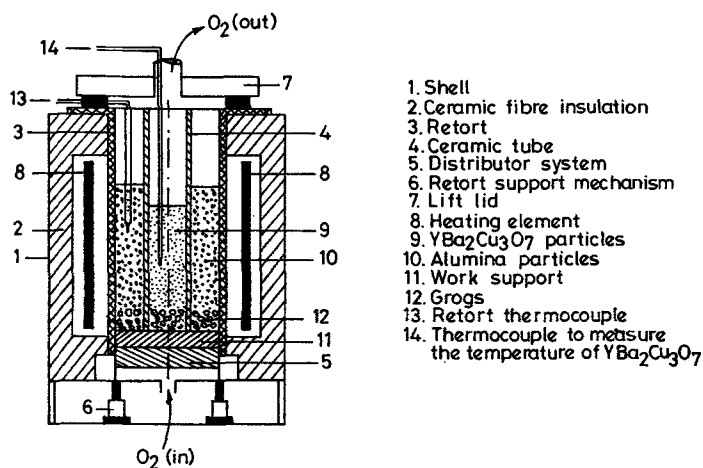


Figure 3. High temperature fluidization furnace used for O_2 -enrichment of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (schematic).

powder ($\sim 250\text{--}300$ g), a sillimanite tube (4 cm dia; 25 cm length) is introduced concentrically in the retort in which $\text{YBa}_2\text{Cu}_3\text{O}_7$ is introduced. The space between retort and the sillimanite tube is filled with alumina powder (~ 90 μm size). Alumina powder 'grog' (~ 1 mm) is also used as a protective layer to trap falling $\text{YBa}_2\text{Cu}_3\text{O}_7$ particles and to avoid direct contact of the fluidizing material with the work support and distributor system (metal parts) at the high operating temperatures ($\sim 900^\circ\text{C}$).

The $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder to be fluidized was loaded into the sillimanite ceramic tube. When pure oxygen gas was passed from bottom at the desired rate, the alumina powder in the annular space (between the retort and the sillimanite tube) and the $\text{YBa}_2\text{Cu}_3\text{O}_7$ particles inside the sillimanite tube fluidized simultaneously. When the furnace was switched on, the fluidization reached equilibrium conditions at the set temperature in a short time (1–2 h). The flow rate at higher temperatures was altered to maintain stable fluidization. After fluidization (O_2 -enrichment) for a specified period of time at a prescribed temperature, the furnace was switched off and allowed to cool. After cooling, the fluidized particles were scooped out and packed for further characterization.

The following flow rates of oxygen were used for the fluidization of $\text{YBa}_2\text{Cu}_3\text{O}_7$: (i) Room temperature, 25 l/min; (ii) 600°C , 15 l/min; (iii) 900°C , 11 l/min. Three batches were fluidized: Batch 1: 250 g with $180\text{--}420$ μm particle size range was fluidized in O_2 at 900°C for 6 h and subsequently at 600°C for 12 h and cooled by switching off the furnace. Batch II: 150 g with $90\text{--}180$ μm particle size range was fluidized in O_2 at 600°C only for 12 h (skipping the 900°C step) and cooled in furnace as before. Batch III: 300 g with a particle size range $5\text{--}90$ μm (which had already been oxygen-treated at 900°C and 600°C for 24 h each) was further oxygen-treated by fluidization at 600°C for 6 h and then furnace-cooled. This was done to see whether there is further enrichment of oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and whether any further improvement occurred in the superconducting properties (signal strength). Also, a part of the sample, while fluidizing, was intermittently quenched (in an O_2 atmosphere) from 600°C to room temperature after varying times of fluidization (1–6 h) and tested for HTSC behaviour.

4.4 Characterization of $\text{YBa}_2\text{Cu}_3\text{O}_7$

4.4a Characterization by powder X-ray diffraction and chemical analysis: The $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples (oxygen-treated, before and after fluidization) were characterized by powder X-ray diffraction (XRD) (Philips-PW-1140; Cu K_α radiation; 35 kV and 15–20 mA). The patterns were indexed and the LSQ-fit lattice parameters were obtained from high angle lines using a computer programme.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ acts as a powerful oxidizing agent due to the fact that either Cu^{3+} or the peroxide ion O_1^{2-} is present in the crystal lattice ($\text{Y}^{3+}\text{Ba}_2^{2+}\text{Cu}_2^{2+}\text{Cu}_1^{3+}\text{O}_{7.0}$ or $\text{Y}^{3+}\text{Ba}_2^{2+}\text{Cu}_3^{2+}\text{O}_6^{2-}\text{O}_1^{1-}$). This property can be used for the chemical estimation of the amount of Cu^{3+} -ion in the substance by the usual iodimetric or ferrous/ferric methods. Presently the iodimetric method was used, in which the total Cu^{2+} concentration (A) was estimated by the dissolution of a known quantity of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in dilute HCl and subsequently the liberation of I_2 by a treatment with KI and estimation of the I_2 by a standard thiosulphate solution (Harris and Hewston 1987; Harris *et al* 1987; Kishio *et al* 1987; Takayama *et al* 1987).

Subsequently, the total ($\text{Cu}^{3+} + \text{Cu}^{2+}$) content (B) was determined by the treatment of known $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with a solution of HCl and KI. The quantity $(B - A)$ is equal to Cu^{3+} and accordingly the δ value in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was calculated. δ will be zero if Cu^{3+} content is one per formula unit. Duplicate runs were made in many cases. The accuracy in the determination of the δ value was ± 0.05 and it is comparable to that obtained by the TGA technique.

4.4b Characterization by physical techniques. Coil (quick) test for superconductivity with $T_c > 77\text{ K}$: A quick test set-up for checking the superconductivity of compounds, when their T_c is equal to or above liquid N_2 temperature, has been designed and fabricated. The test can be done in a few minutes and it establishes very reliably, the superconductivity of the sample. The only disadvantage is that the temperature is not varied.

The set-up is based on the inductance principles, where the coil inductance is affected by the susceptibility of the sample inside the sample coil (i.e. an increase for magnetic specimens and a decrease for superconducting diamagnetic samples); the inductance of a coil changes very appreciably when its core is a substance that exhibits magnetic phase transition (para \rightarrow ferro or para \rightarrow diamagnetism). The set-up, schematically shown in figure 4, consists of two coils each containing 400 turns of 30 swg diameter copper wire mounted suitably on a perspex base. The coils form the two arms of the bridge circuit connected to a carrier frequency amplifier which applies 1 V at a frequency of 5 kHz and 1 V bridge excitation. The coils, which have an air-core, are dipped in liquid N_2 and balanced with the bridge circuit to obtain a

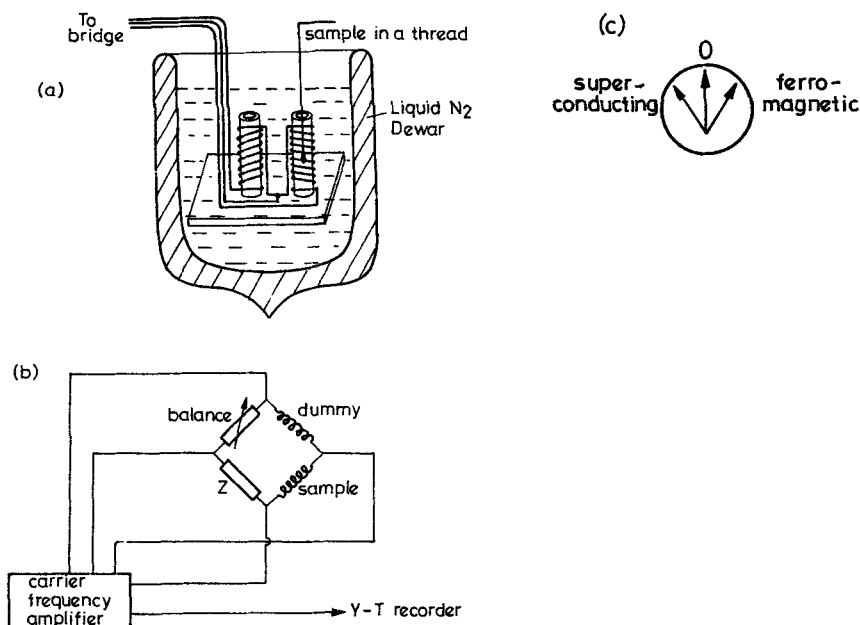


Figure 4. Coil test set-up for establishing superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$ at liquid N_2 temperature, (a) coils, (b) bridge circuit, and (c) response meter.

'null' indication. The test sample for superconductivity (0.1–0.2 g piece tied to a cotton thread) is pre-cooled and introduced into one coil. The imbalance produced due to a change in the inductance of the coil and the associated change from para→diamagnetism due to the superconductivity transition, is indicated by a movement of the needle to one side of the null point. This can be recorded on a Y–T recorder. Alternatively when a sample (e.g. gadolinium metal) which changes from para→ferromagnetism on cooling is introduced, the needle will move to the opposite side of the null position. The strength of the signal (extent of departure from the null position) is an indication of the content in a given sample of the superconducting phase. On the other hand, in the case of a sample, e.g. strontium titanate (SrTiO_3), which is diamagnetic and remains so till liquid N_2 temperature is introduced, the movement of the needle from the 'null' position is nil. Of course, there will be a slight change in the resistance of the coils when they are cooled to liquid N_2 temperature (and actually have liquid N_2 as the core), but this can be offset by balancing the 'null' point under those conditions before introducing the test sample.

The above coil test was done on all the samples synthesized earlier and it indicated whether they are superconducting at 77 K or not. For testing, the powder samples obtained after fluidization are either packed in small paper packets or loosely pressed into discs at room temperature.

(i) *a.c. susceptibility measurement*: The a.c. magnetic susceptibility measurements (at 77 Hz) were carried out in the range 77–300 K using a calibrated mutual inductance bridge and cryostat. Details of the apparatus, circuitry and calibration procedures have been discussed elsewhere (Ranganathan and Rangarajan 1982; Ranganathan 1983). A clear indication of the onset of superconductivity is obtained when the susceptibility changes abruptly from paramagnetic to diamagnetic behaviour on cooling. The temperature measurement was accurate to ± 0.1 K.

(ii) *Electrical resistivity measurement*: The four-probe electrical resistivity measurements on pellets of $\text{YBa}_2\text{Cu}_3\text{O}_7$ were carried out in the range 77–300 K using the van der Pauw–Montgomery method that employs an indigenously fabricated set-up (van der Pauw 1961; Montgomery 1971; Umarji 1980; Janaki 1985). Ultrasonically diffused indium metal contacts were made on the pellets using the apparatus supplied by Fibra-Sonics Inc., USA (model G 35A). Fine gauge copper wires were soldered to the samples and the ohmic contacts were secured. The temperature measurement was accurate to ± 1 K. A Keithley nanovoltmeter (model 181, USA) was used to measure the voltage drop across the sample for currents passed in the range 5–20 mA. The compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ was estimated to undergo the superconducting transition completely (zero resistance) when no voltage drop was noted (± 10 nV; thermal noise; also, when the polarity of the current input to the sample is changed there will be no corresponding reversal of sign in the voltage in the nanovoltmeter reading) for varying currents passed through the sample from a d.c. constant current supply unit.

(iii) *Surface morphology*: The surface morphology of the standard, fluidized and unfluidized samples were examined by scanning electron microscopy (Cambridge Stereoscan, UK; Model 180).

5. Results and discussion

5.1 Standard samples obtained by the small-scale preparation technique

Results showed that the $\text{YBa}_2\text{Cu}_3\text{O}_7$ prepared on a small-scale yielded well-defined single phase material that exhibited excellent superconducting characteristics. The XRD pattern showed a well-defined orthorhombic perovskite structure with no detectable second-phase impurities. The LSQ-fit lattice parameters obtained, $a = 3.815$, $b = 3.886$, $c = 11.66$ Å, are in excellent agreement with the data reported in literature (Cava *et al* 1987; Rao *et al* 1987a; Steinfink *et al* 1987; Uchida *et al* 1987). Iodimetric analysis gave δ values in the range 0.05–0.15 (± 0.05) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, well within the range required for the high T_c material.

The coil test for superconductivity above 77 K showed a strong 'positive' signal, whereas the a.c. magnetic susceptibility (77 Hz) data showed a diamagnetic transition to the superconducting state starting at 90.2 K (figure 5). The volume of the sample that is superconducting was estimated using lead as the standard. It was found that more than 63% of the sample volume was superconducting in $\text{YBa}_2\text{Cu}_3\text{O}_7$. The four probe electrical resistivity data on sintered pellets showed typical metallic behaviour at room temperature ($\rho_{300\text{ K}} \simeq 4 \text{ m}\Omega \text{ cm}$) and a sharp transition to the superconducting state starting around 93–94 K. Zero resistance was noted at $T_c^0 = 91.5 \pm 1 \text{ K}$ (figure 6). The width of the transition (ΔT_c , corresponding to the

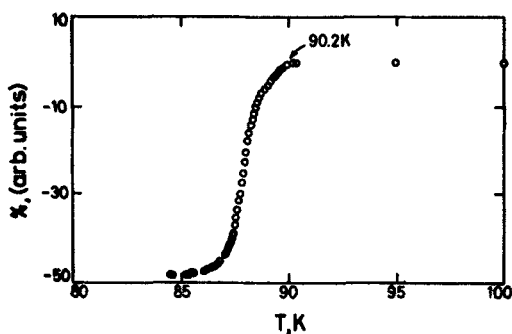


Figure 5. a.c. susceptibility versus temperature plot for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (small-scale preparation) showing the transition to superconductivity.

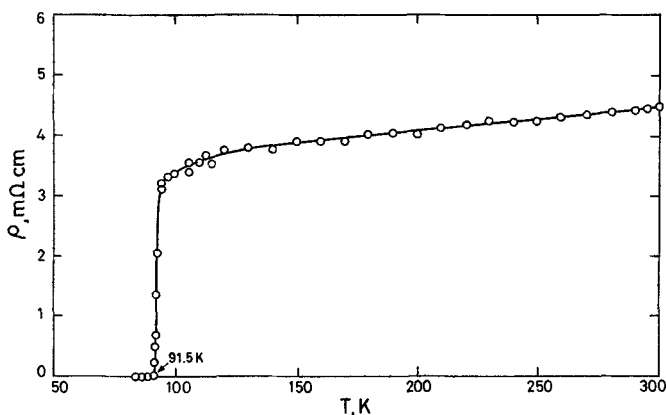


Figure 6. Resistivity vs. temperature plot of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (small-scale preparation) showing the superconducting transition ($T_c^0 = 91.5 \text{ K}$).

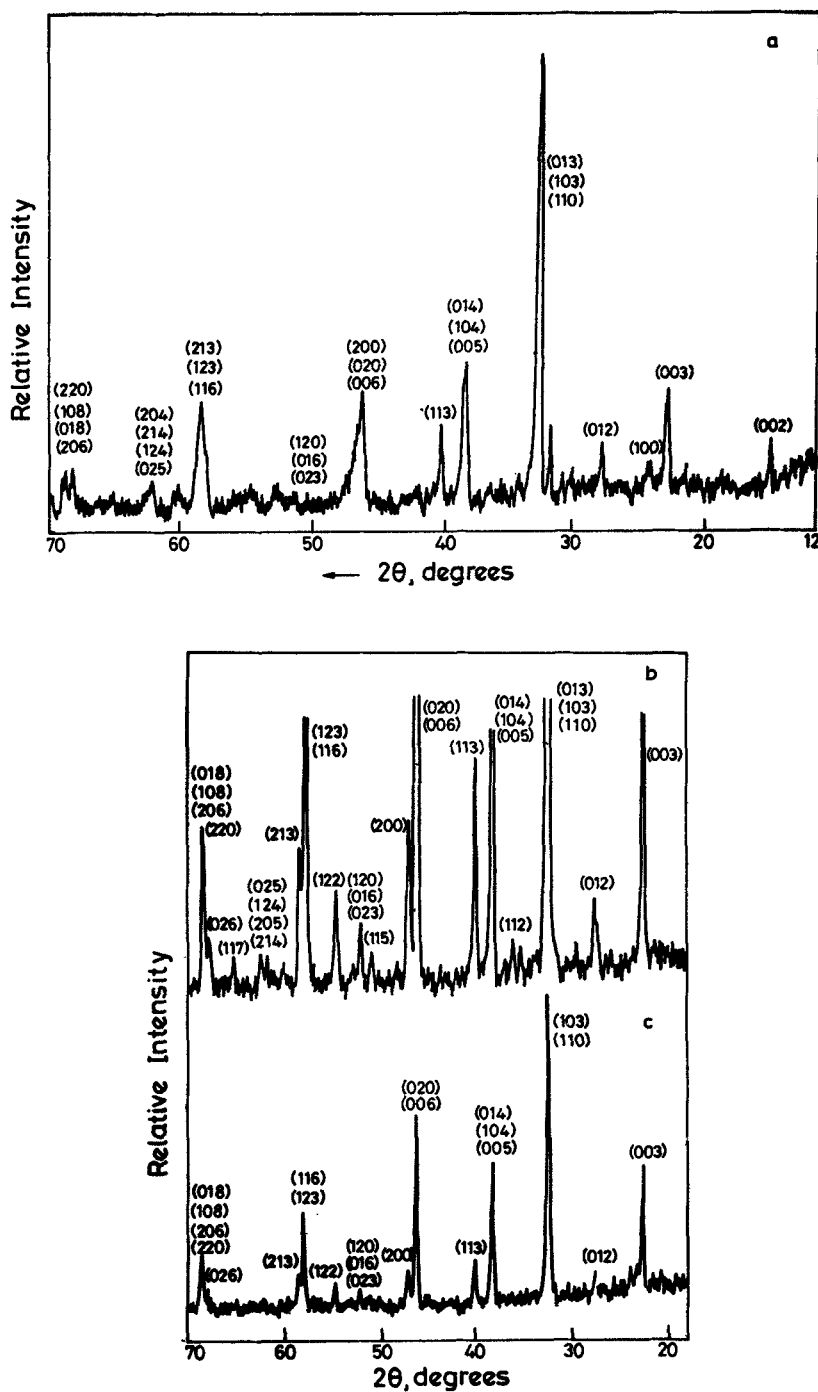


Figure 7. (a) XRD pattern of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the unfluidized condition showing a tetragonal structure (particle size 90–180 μm ; Cu K_α radiation). XRD patterns of fluidized $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Cu K_α radiation): (b) 900°C for 6 h and 600°C for 12 h; particle size 180–420 μm showing an orthorhombic structure, and (c) 600°C for 12 h; particle size 90–180 μm showing an orthorhombic structure.

difference in temperature for 90% drop and 10% drop in resistivity) ranged from 1.5–2.5 K for different sets of measurements on identical samples.

Powder samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with a particle size range 5–90 μm (prepared in bulk), which have been oxygen-treated similar to the standard samples obtained in the small-scale preparation, also exhibited 'positive' coil test for superconductivity and orthorhombically distorted perovskite structure in XRD studies.

5.2 Unfluidized and fluidized $\text{YBa}_2\text{Cu}_3\text{O}_7$

The XRD patterns showed that the as-synthesized $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder (without the oxygen treatment) of particle size range 90–180 μm and 180–420 μm has a tetragonal structure (without the orthorhombic distortion) as indicated by the merging of the (103, 013), (020, 200) and (123, 213) peaks (figure 7a). The δ values estimated by iodimetry ranged from 0.33–0.50 indicating fairly high oxygen deficiency in the samples of both the particle size ranges. The coil test for superconductivity above 77 K showed a negligibly small 'positive' signal for powder with the particle size range 90–180 μm , whereas no positive signal was shown by the powder with the size range 180–420 μm .

Dramatic changes in the behaviour of the fluidized $\text{YBa}_2\text{Cu}_3\text{O}_7$ were noted: A batch I sample, with the particle size range 180–420 μm , which was fluidized in oxygen gas (11 l/min flow rate) at 900°C for 6 h and then at 600°C for 12 h (15 l/min O_2 flow rate) and subsequently cooled slowly to room temperature, showed an XRD pattern with well-defined orthorhombically distorted structure (figures 7b and c).

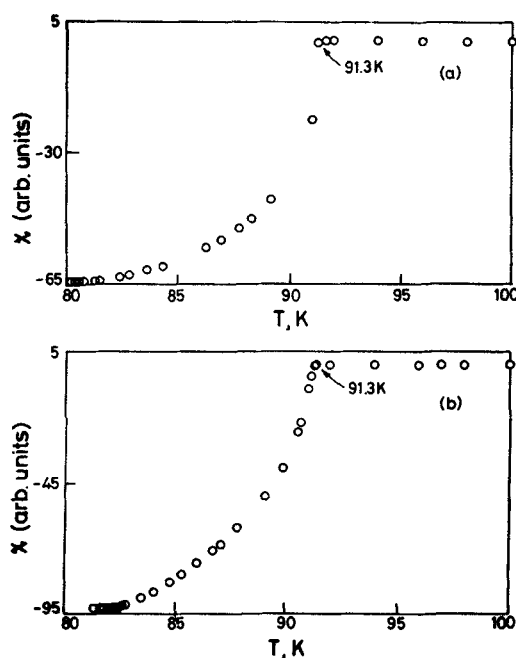


Figure 8. a.c. susceptibility vs. temperature plots for fluidized $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder. (a) 900°C for 6 h; 600°C for 12 h and slow cooled; particle size range 180–420 μm , (b) 600°C for 12 h and slow cooled; particle size range 90–180 μm .

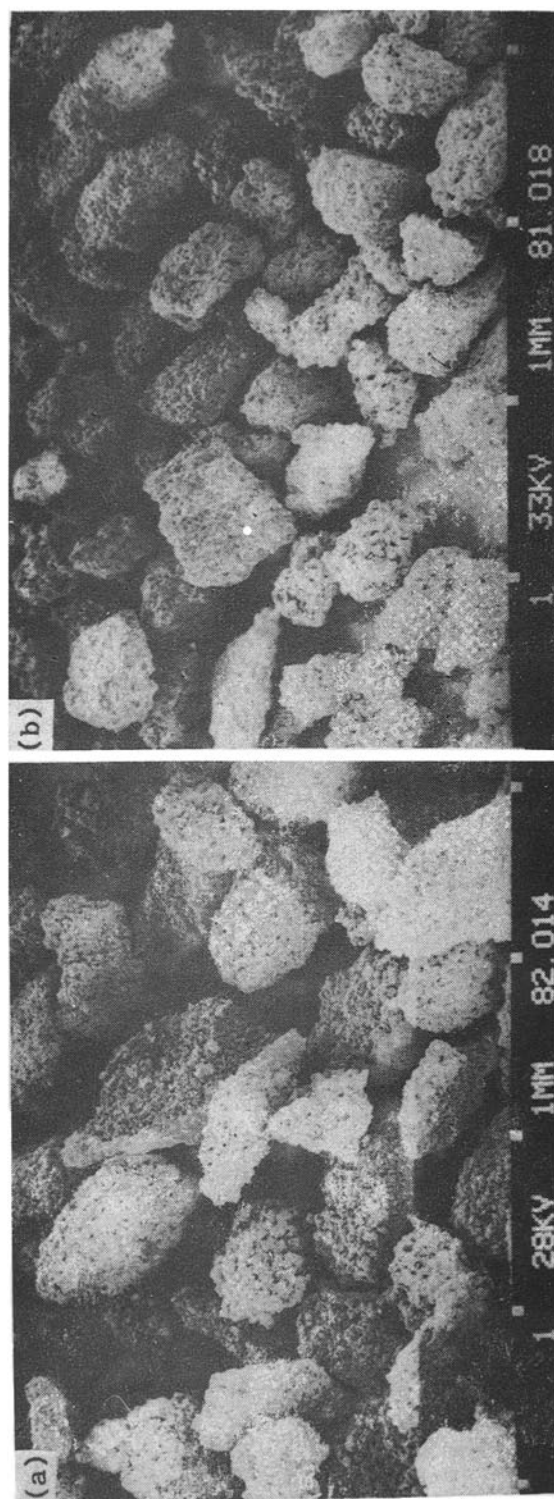


Figure 9. a-b. For caption, see p. 76.

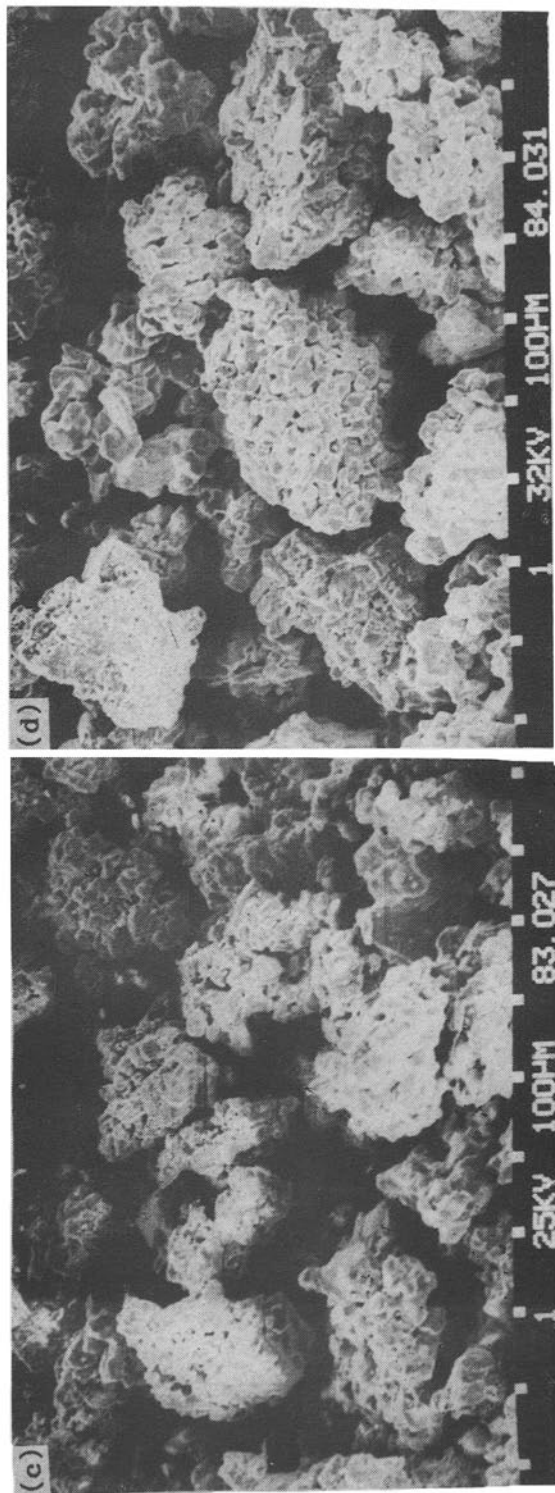


Figure 9. Surface morphology of unfluidized and fluidized powders of YBa₂Cu₃O₇, as seen by SEM. (a) unfluidized and (b) fluidized corresponding to a particle size range 180–420 μ m (magnification: 50 \times); (c) unfluidized and (d) fluidized corresponding to a particle size range 90–180 μ m (magnification: 100 \times).

The relative (hkl) peak intensities were much larger than those encountered in the standard samples (small-scale preparation). This indicated excellent crystallinity and oxygen ordering in the fluidized powder. Iodimetric estimation gave a δ value in the range 0.08–0.17 (± 0.05), which revealed that oxygen pick up had been optimal. The coil test showed a very strong 'positive' signal for superconductivity above 77 K. Ac susceptibility study showed a well-defined superconducting transition with a T_c^{onset} at 91.3 K (figure 8a). The volume fraction of the superconducting phase is 85.3%, one of the highest values reported for $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the literature so far.

The batch II sample (particle size range 90–180 μm), which had been fluidized only at 600°C for 12 h and slow cooled (without the 900°C treatment) also showed orthorhombic splitting, though not as well-defined as that of batch I. The estimated δ values were in the range 0.18–0.20, slightly larger than for batch I, but significantly narrow in the range of values encountered. The high T_c superconductivity was established by the coil test (strongly positive), and a.c. susceptibility techniques (figure 8b). The superconducting volume fraction was estimated to be 83.7% for batch II, which is only slightly less than that encountered in batch I. The above observations indicate that while 91 K superconductivity can be induced in $\text{YBa}_2\text{Cu}_3\text{O}_7$ by fluidization at 600°C for 12 h, achievement of a high degree of crystallinity and optimal δ values need longer times and/or higher temperatures of fluidization.

SEM photographs of samples of batches I and II before and after fluidization, did not indicate significant changes in morphology (figure 9), although the XRD patterns showed a change from the tetragonal to the orthorhombic structure. On a microscopic level, it is well-known that the oxygenated orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ shows an extensively twinned structure (Sampathkumaran 1987; Rao *et al* 1988; Sreedhar *et al* 1987).

Fluidization experiments were done on batch III (5–90 μm) samples at 600°C for 6 h. This batch of samples had already been oxygen-treated earlier (similar to the small-scale preparation method; oxygen flow at 900°C for 24 h; 600°C for 24 h and slow cool) and the purpose was to find out whether further oxygen enrichment occurs and the superconductivity signal strength (coil test) increases. Some samples were also quenched from 600°C to room temperature after a given period (1 to 6 h) of fluidization. Results showed that there were no improvements in the crystallinity and the oxygen content of the samples of batch III after fluidization at 600°C for 6 h followed by slow cooling. The superconductivity signal strength (positive signal by the coil test) was only marginally improved (~ 5 –10%) over that of the starting material. On the other hand, quenching of the samples from 600°C (from the fluidized condition) decreased the superconducting signal strength consistently and the samples quenched after 6 h equilibration (at 600°C) did not show superconductivity by the coil test above 77 K. The above result shows that slow cooling from 600°C to room temperature (over a period of 4–6 h) which ensures annealing and 'ordering' of the oxygen ions in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ lattice, is an essential step in the synthesis of the high T_c material.

It was also noted that the 5–90 μm size range powder of batch III showed a tendency to 'agglomerate' to larger particle sizes during fluidization, whereas such behaviour was not encountered in the samples of batches I and II which had a larger particle size range, 180–420 μm and 90–180 μm respectively. Possibly, the 'agglomeration' may act against efficient oxygenation in the fluidization technique but more studies are needed for unequivocal inference.

6. Summary and conclusions

Small-scale preparation (~ 10 – 15 g/batch) of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with optimal oxygen content has been successfully carried out and the material has been characterised to establish its high temperature superconducting property ($T_c = 90.2$ K). Oxygen-enrichment of large quantities of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (which would be needed for practical applications) by the currently available laboratory method is cumbersome and time-consuming.

An alternative technique of fluidization, therefore, was employed for the first time for the oxygen-enrichment of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The fluidization technique is one of the established methods of Chemical Engineering practice for efficiently carrying out heterogeneous gas-solid reactions. The present results have shown that 250–300 g batches of 'as-synthesized' powder of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (particle size ranging from 90–420 μm) can be successfully oxygenated by fluidization at 900°C for 6 h, followed by 600°C , 12 h and slow cooling to give optimal δ values (in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\delta = 0.05$ – 0.20) and high T_c superconductivity with a T_c of 91 K. A lower temperature (600°C vs. 900°C) of fluidization seems to be equally effective, but fluidization times greater than 12 h are needed. Slow cooling from 600°C is an essential step and quenching should be avoided. Scope exists for the optimisation of the fluidization conditions to suit the desired quantities and particle size range of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Scaling-up from 250 g batches to 1–2 kg quantities is feasible if suitable design changes are incorporated in the fluidization reactor. The method should, in principle, be extendable for the direct synthesis of the HTSC powder from the constituent oxides/carbonates where both the synthesis and oxygen-enrichment can be carried out in a sequential manner by adjusting the gas flow and temperature in the reactor.

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