Synthesis, at Ambient Pressure, of the 80 K Superconductor $YBa_2Cu_4O_8$ by Triethylammonium Oxalate Co-precipitation

J. S. Ho,[a] **R. S. Liu,**[b] **C. T. Chang**[a] **and P. P. Edwards**[b]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China and Institute of Atomic and Molecular Science, Academia Sinica, Taipei, PO Box 23–166, Taiwan, Republic of China*
[b] *IRC in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK*

Co-precipitation has been used to prepare a precursor material which, upon calcination and sintering, forms monophasic, homogeneous and fine $YBa_2Cu_4O_8$ powders.

The variability and instability of oxygen content $(7 - \delta)$ in the high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ is one of the major factors limiting its potential application. In contrast, the 80 K superconductor $YBa_2Cu_4O_8$ is characterised by a fixed oxygen stoichiometry and an excellent thermal stability up to 850 °C.[1] Bulk samples of $YBa_2Cu_4O_8$ have previously been synthesised under high (oxygen) pressure.[1–5] The phase has also been prepared at ambient pressure by reaction-rate enhancing compounds (*e.g.* $NaCO_3$ or K_2CO_3),[6,7] precursors,[8,9] anionic oxidation–reduction[10] and a modified citrate gel process.[11] The oxalate co-precipitation method has been frequently adopted for the preparation of various cuprate oxide superconductors, such as $YBa_2Cu_3O_7$[12] and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$.[13] Compared with the conventional solid-state reactions, the chemical co-precipitation approach has the advantage of high product purity and homogeneity, low synthesis temperatures and reduced reaction times. Here, we demonstrate the synthesis—under ambient pressure—of $YBa_2Cu_4O_8$ using co-precipitation involving oxalic acid as a precipitant with triethylamine for pH adjustment. Experiments carried out at different pH values allows the metal stoichiometry of the co-precipitate to be controlled.

High purity $Y(NO_3)_3{\cdot}nH_2O$ (n = 4–6), $Ba(NO_3)_2$ and $Cu(NO_3)_2{\cdot}6H_2O$ powders (Merck AG) with a cationic molar ratio of Y : Ba : Cu = 1 : 2 : 4 (using 0.005 mol of Y^{3+}) were dissolved in distilled/deionized water. An aqueous solution of oxalic acid (as a precipitant) and triethylamine (as a base) was prepared by mixing 0.025 mol of oxalic acid and 25 ml of triethylamine in 10 ml of water. We then examined the co-precipitate at various pH values. A constant concentration of oxalic acid is maintained and the amount of triethylamine varied in order to control the solution pH. The solution of the metal nitrate salts was then added dropwise into the oxalic acid–triethylamine solution with vigorous stirring. During the mixing, a pale-blue co-precipitate rapidly formed. The solution was then cooled, with stirring, in an ice-water bath. After separation of the co-precipitate and filtrate, the chemical composition of the former was analysed using a Plasmakon S35 inductively coupled plasma atomic emission spectrometer (ICP–AES). The co-precipitate was subsequently dried at 120 °C in air for 10 h and then calcined at 700 °C in air for 10 h to eliminate any organic components. The resulting fine black powder was pressed into a pellet and sintered at 805 °C in flowing oxygen for 2–4 days and subsequently quenched in air.

Thermogravimetric analysis (TGA) of the dried co-precipitate was performed using an STA-780 instrument (Stanton Redcroft) at a heating rate of 5 °C min^{-1} in air from room temp. at 850 °C. X-Ray diffraction (XRD) pattern of the sintered powders was obtained using a Spectrolab CPS-120 diffractometer employing Cu-Kα radiation. The average grain size was examined by scanning electron microscopy (SEM, Cambridge Instruments S-250). The details of electrical

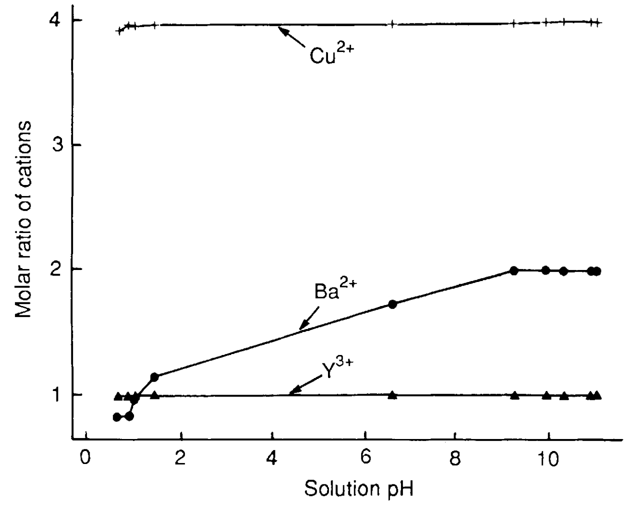

Fig. 1 Elemental analyses of co-precipitates obtained at different pH values

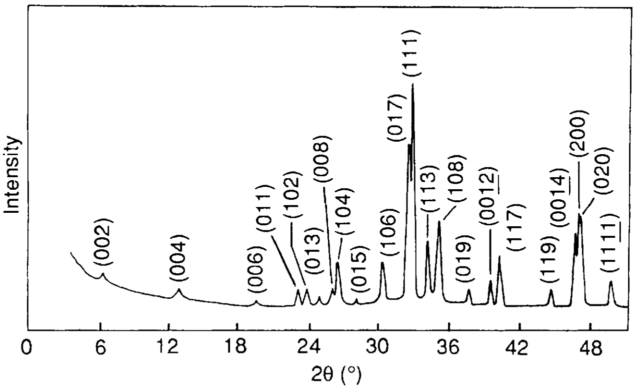

Fig. 2 An XRD pattern of $YBa_2Cu_4O_8$

resistivity and magnetisation measurements are outlined elsewhere.[11]

In any co-precipitation synthesis, there are problems associated with the content of stoichiometry; the variability in the final metal composition generally arises from differences in the relative solubility of the constituent cations. Here, adjustment of the solution pH is very important, although alkali bases (*e.g.* KOH *etc.*) may introduce detrimental contamination *via* alkali cations. We have found that triethylamine is an excellent choice for pH control in the co-precipitation of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$.[13]

In Fig. 1 we show the elemental analyses of the co-precipitates at pH values varying from 0.7 to 11. For pH values between 0.7 and 9.3, we observe an increase in the Ba and Cu contents of the co-precipitates. When the solution pH values are in the approximate range 9.3–11.3, all cations are completely precipitated with a desired stoichiometry of Y : Ba : Cu = 1 : 2 : 4.

A TGA analysis was carried out on a dried co-preicpitate obtained at optimum pH. A two-step weight loss was observed. The first weight loss (at *ca.* 250 °C) corresponds to the decomposition of copper oxalate while the second (*ca.* 400 °C) is related to the decomposition of Ba and Y oxalates.[14] At 580–850 °C, no distinct weight loss was observed. This indicates that all the organic constituents can be completely eliminated when the co-precipitates are subsequently calcined at 700 °C.

In Fig. 2 we show an XRD pattern of a sintered $YBa_2Cu_2O_8$ sample. The pattern can be indexed on the basis of an orthorhombic unit cell with lattice constants $a \simeq 3.84$, $b \simeq 3.87$ and $c \simeq 27.2$ Å.[6] Importantly, there is no evidence for the presence of $YBa_2Cu_3O_7$ in the material. The average diameter of the sintered particles is about 5 μm. Such fine particles are generally difficult to obtain *via* conventional reactions.

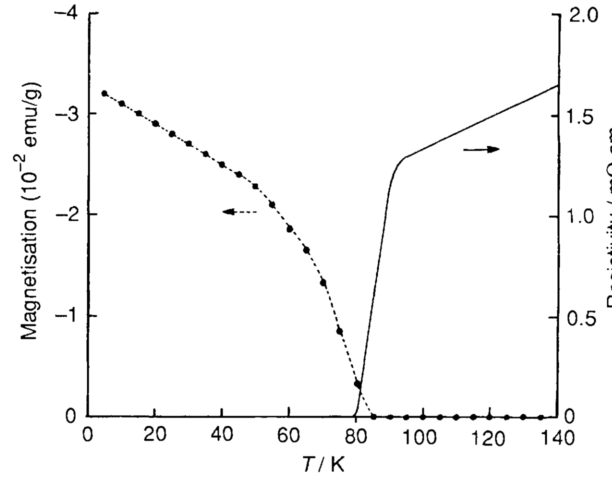

Fig. 3 The temperature dependence of the electrical resistivity and magnetisation (field-cooled; 25 G) of $YBa_2Cu_4O_8$

In Fig. 3 we show the temperature dependence of the electrical resistivity and magnetisation of $YBa_2Cu_4O_8$. The sample has metallic behaviour in its normal state ($T > T_c$) and exhibits superconductivity with $T_{c(onset)}$ 88, $T_{c(mid)}$ 85 and $T_{c(zero)}$ 79 K. We also show the corresponding Meissner signals. The sample has an onset (diagmagnetic) signal beginning around 85 K, which is consistent with the superconducting transition temperature as measured by electrical resistivity.

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