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The synthesis of cuprate superconductors via a dual-precipitation route

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A precipitation technique is described which is used to produce high-quality samples of superconducting $YBa_2Cu_3O_7$ ($T_c = 91$ K). The method makes use of two precipitation stages using hydroxide and oxalate as the precipitants. The precipitate is in the form of a fine particulate powder, which is an intimate mixture of the three cations in their precipitant form, enabling efficient formation of the superconducting phase; this is, we believe, a viable approach for circumventing the inherent drawbacks of the well-established oxalate route.

1. Introduction

The most widely employed preparative technique for the new high-T_c copper-oxide-based superconducting materials such as $YBa_2Cu_3O_7$ ($T_c = 91$ K) has been the classical solid-state reaction of the relevant oxides, hydroxides or carbonates [1]. Even with repeated grinding and firing the final compound is often inhomogeneous and multi-phased, with a large distribution of grain sizes. The reasons for this lie in the relatively poor initial mixing of the starting materials. In response to these drawbacks, wet-chemical routes have been employed to synthesize these materials largely with a view toward industrial-scale preparation. One of the most common routes is the development of an oxalate precipitate in conjunction with a mixture of metal cations, in the correct stoichiometric ratio [2]. As a result of such uniform mixing, it is more likely that the desired product will be formed, eliminating the formation of unwanted phases.

Although the above precipitation can yield ultrafine and homogeneous powders, many problems result from the considerable pH dependence of the precipitation conditions [3]. It is found that at low pH (0–2.0), barium is not fully precipitated from the aqueous solution, due to the small stability constant of the barium oxalate (log $\beta = 2.3$). As the pH is increased above 2.0–3.0, the formation of a stable copper bisoxalato complex ($(Cu(C_2O_4)_2^{2-}$; log $\beta = 10.2$), which is soluble in aqueous solution, presents a definite obstacle to ensuring the required copper content of the precipitate. Therefore, by using oxalic acid alone, it is not possible to create a precipitate of the desired stoichiometry. It is of course possible to compensate for the loss in copper content in the final precipitate by using an increased initial copper ratio and operating at an elevated pH [4]; however, this would introduce problems of filtrate recycling if the method were to be employed on an industrial scale. Addition of non-aqueous solvents to the existing solution has been shown to be useful in facilitating complete precipitation of the metal cations [5], but this too would clearly be undesirable if a scaled-up bulk-manufacturing process was being considered, because of safety problems and expense. This paper introduces a method which uses only an aqueous solvent and largely avoids the problems of pH dependence.

2. Experimental procedure

All the chemicals used were of high-purity grade purchased from the Aldrich Chemical Company without further purification. The water used throughout the experimental work was previously doubly distilled and deionised. An aqueous mixture of yttrium, barium and copper nitrates with a molar ratio of 1:2:3 (using 0.005 mol yttrium) was made and its elemental content was analysed by inductively coupled plasma–atomic emission spectrophotometry (ICP–AES, Phillips PU7450) in order to verify the correct cationic ratio. Sodium hydroxide (0.1 mol) in solution was then slowly added to this mixture, until the pH of the initial solution was around 12.5. This was then followed by addition of an oxalic-acid solution (using 0.02 mol acid), both steps being performed under constant vigorous stirring. The resulting pale-blue precipitate was then cooled, filtered and washed with ice-cold, doubly distilled water. After filtration the elemental composition of the filtrate was analysed once more by ICP–AES. The precipitate was then subsequently dried in air at 423 K for 6–8 h. A sample of the dried precipitate was then taken and subjected to a thermogravimetric analysis (TGA/DTG, performed on a Mettler M3 balance/TC10 TA processor), at a heating rate of 7 K min^{-1} to a temperature of 1153 K.

The remaining precipitate was calcined in air at 823 K for 12–14 h in order to decompose both the organic components and metal hydroxides within the mixture. The resulting fine powder was then pressed into a pellet and sintered at 1173 K for 18 h, and then re-pelletized prior to further firing at 873 K in flowing oxygen for 18 h. Microwave measurements were carried out on the final material using a conventional X-band electron paramagnetic resonance (EPR) spectrometer (Bruker ESP 300E) employing 100 kHz field modulation and a standard rectangular TE_{102} mode cavity. X-ray diffraction (XRD) measurements were performed on a Phillips PW3020 X-ray powder diffractometer employing CuK_α radiation.

3. Results and discussion

The presence of the $YBa_2Cu_3O_7$ phase was verified by powder XRD (Fig. 1). This was shown to be superconducting using the EPR technique. A strong signal was observed in a zero magnetic field as the sample was cooled below T_c, ca. 90 K (Fig. 2). The origin of this response and its utility as a characterisation technique are discussed elsewhere [6]. The high purity of the material produced here was reflected in the virtual absence of a $g = 2$ EPR signal. It is now generally accepted that, although based on paramagnetic Cu^{2+} ($3d^9$), cuprate superconductors do not possess intrinsic EPR signals above T_c [6]. However, related phases in the $YO_{1.5}$–BaO–CuO ternary phase diagram, which often appear as impurities in samples of $YBa_2Cu_3O_7$ (e.g. Y_2BaCuO_5, $Y_2Cu_2O_5$ and $BaCuO_2$) possess characteristic EPR "fingerprints". This has rendered EPR a highly sensitive test of phase purity, with detection limits at levels far below those for XRD [7]. It is interesting to note that these results do indicate that the dual, as opposed to co-precipitation, technique does not appear to markedly effect the purity of the final phase. The fact that yttrium and copper ions are precipitated prior to those of barium does not necessarily yield localized yttrium/copper and barium rich environments, which would be expected to lead to the formation of impurities of a similar nature, i.e. $Y_2Cu_2O_5$ and $BaCO_3$.

Table I shows the details of the ICP–AES measurements made on the original nitrate mixture and filtrate. Table I indicates highly efficient removal of all metal cations from solution, with in excess of 99% precipitation occuring in each case. By first adding the hydroxide solution one is able to afford complete precipitation of all the copper and yttrium ions as their hydroxides, with the excess hydroxide forcing the pH up to around 12.5. The alkaline environment that exists prior to the addition of the oxalate solution is, therefore, most conducive to the formation of the barium-oxalate complex, and as the pH remains above 9.0 even after addition of the oxalic acid the hydroxides do not redissolve. Also, the solution is not sufficiently alkaline to yield further soluble hydroxylated complexes of copper.

The TGA analysis of the dehydrated precipitate is shown in Fig. 3. The decomposition appears to take place in three stages. There is a steady weight loss from

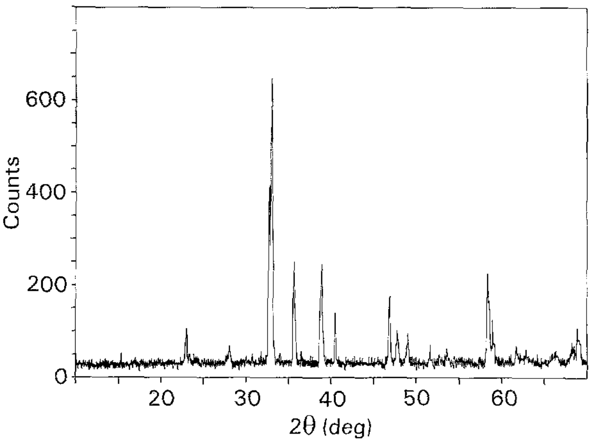

Figure 1 CuK_α X-ray powder diffraction pattern for a bulk sample of $YBa_2Cu_3O_7$.

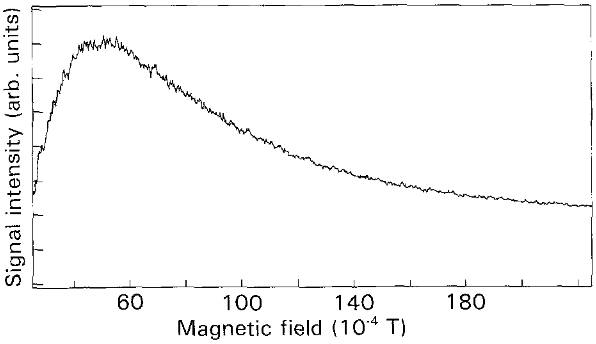

Figure 2 Low-field microwave absorption for $YBa_2Cu_3O_7$ prepared by the dual-precipitation route, measured at 77 K, for a frequency of 9.47 Hz.

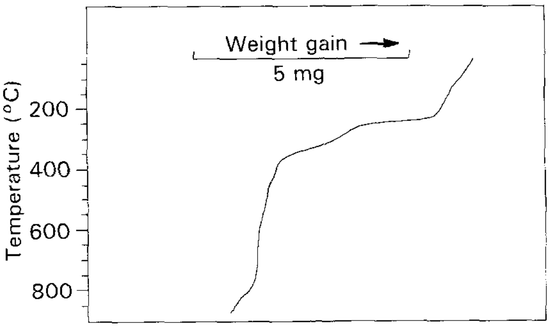

Figure 3 TGA/DTG trace of the dehydrated oxalate / hydroxide precipitate.

TABLE I ICP–AES data for successive stages of the dual-precipitation route

Metal/cation	[M] in original nitrate solution ($\times 10^{-2}$ mol dm^{-3})	Relative ratio in nitrate solution	[M] in filtrate, corrected for dilution ($\times 10^{-5}$ mol dm^{-3})	Metal ions precipitated from solution (%)
Y/Y^{3+}	2.9	1.00	3.2	99.89
Ba/Ba^{2+}	5.9	2.03	2.48	99.99
Cu/Cu^{2+}	9.2	3.17	1.1	99.99

323–673 K corresponding to the decomposition of the copper hydroxide. At 673 K and 748 K two much sharper weight losses are noted, due to the breakdown of the barium oxalate and yttrium hydroxide, respectively. After these initial decompositions, no further weight losses are observed until 1023 K. During this period the oxides of yttrium and copper are thermally stable, as is barium carbonate, these being the initial decompositional products. At around 1073 K the first phase changes are observed with the likely reaction of barium carbonate and copper oxide, and carbon dioxide is evolved [8].

4. Conclusion

The dual-precipitation technique provides a highly efficient and relatively simple route to producing high-quality samples of $YBa_2Cu_3O_7$. By employing the precipitation conditions outlined it is possible to achieve excellent stoichiometry and mixing within the precipitate prior to firing. This eventually leads to a final material of high purity and homogeneity.

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