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Effect of solution pH on the synthesis of the $YBa_2Cu_4O_8$ superconductor via an EDTA solution process

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High critical temperature, T_c, $YBa_2Cu_4O_8$ superconducting oxides have been prepared by a solution technique using ethylenediaminetetraacetic acid (EDTA) as complexing agent. The use of an appropriate complexing agent leads to complete mixing of the Y^{3+}, Ba^{2+} and Cu^{2+} cations, and thus facilitates formation of $YBa_2Cu_4O_8$ at a lower temperature. The effect of pH on the homogeneity of samples is discussed. The superconducting $YBa_2Cu_4O_8$ sample with $T_c = 80$ K was obtained after heat treatment at 820 °C. Characterization of the sample by X-ray diffraction (XRD), thermal analysis, scanning electron microscopy (SEM), electron-probe microanalysis (EPM), electrical resistivity, magnetic susceptibility and other spectroscopic analyses are reported.

1. Introduction

During the past few years, since the first discovery of high critical temperature, T_c, superconducting oxides by Bednorz and Müller [1], there has been much activity aimed at finding new types of superconducting materials and exploring improved synthetic routes which might bring forth better physical properties. Generally, the widely used solid-state reaction method permits oxide chemicals to be directly calcined into superconductors. However, a series of grinding and prolonged heatings have inherent disadvantages such as inhomogeneity, high porosity and lack of reproducibility. On the other hand, various "solution methods" have been developed to produce excellent materials for superconductive properties studies. Coprecipitation reactions with oxalates [2], hydroxides [3] or carbonates [4] and complexation with citrates [5] and/or EDTA [6] have been reported for preparing superconducting materials. The main advantage of these solution techniques is that the final product is more homogeneous. Solution methods have previously been used to prepare superconducting powders [7], but few have considered the effect of pH on compositional fluctuations. The compositional fluctuation in several of the solution methods would cause the formation of other second phases. The purpose of this report is to present the details of the experimental procedures and theoretical considerations for a simple solution technique which has been successfully used to fabricate highly pure $YBa_2Cu_4O_8$ superconductor. The method is based on the formation of metal complexes which are homogeneously dispersed in a solvent and where compositional uniformity is maintained during evaporation of the excess solvent (congruent evaporation). The procedures of this technique and the quality of the resulting superconductor were characterized with a pH meter, thermal analysis, inductively coupled plasma (ICP), X-ray powder diffraction (XRD), resistivity, magnetic susceptibility measurements and iodometric titration.

2. Experimental procedure

The following procedure was used to investigate the title system. The samples, with the nominal composition of $YBa_2Cu_4O_8$, were prepared by the so-called "solution technique" with high purity $Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$. A solution of Y^{3+}, Ba^{2+} and Cu^{2+} with a cationic ratio of 1.0:2.0:4.0 was mixed with $EDTA/NH_4OH$. The molar ratio of EDTA to the total metal cation concentration was chosen at unity. The pH of the solution was adjusted to the desired value. The liquid precursors were then heated at 120 °C to evaporate excess solvent. Samples were heated at 500 °C in order to remove the organics. The products, containing metal oxides and carbonate, were shown to be amorphous by XRD. The above powder was further calcined at 700 °C for 6 h and subsequently ground and pressed into pellets and sintered in flowing O_2 for several days.

XRD patterns of the sintered samples were obtained using monochromatic CuK_α radiation. T_c was determined by electrical resistivity measurements using an ordinary four-probe method for rectangular samples cut from the pellets. A SQUID magnetometer (Quantum Design Co.) was employed to measure the temperature dependence of the magnetic susceptibility in

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a field of 20 Oe. The oxygen contents were determined by an iodometric method [8].

3. Results and discussion

In an earlier paper [7], an EDTA solution process was proposed in which three basic reactions were involved during formation of the gel precursor; i.e. metal chelate formation, evaporation of solvent and gel formation. Before discussing the theoretical solubility of individual metal ions, all possible reactions in the solution system are:

1. Precipitation

$$M^{n+} + nOH^- \rightarrow M(OH)_n$$
$$(\text{for } M^{n+} = Y^{3+} \text{ and } Cu^{2+})$$

2. Complex formation

$$M^{n+} + EDTA^{4-} \rightarrow M(EDTA)^{n-4}$$
$$(\text{for } M^{n+} = Y^{3+}, Ba^{2+} \text{ and } Cu^{2+})$$
$$M^{n+} + NR_3 \rightarrow M(NR_3)^{n+}$$
$$(\text{for } M^{n+} = Cu^{2+})$$
$$M^{n+} + mOH^- \rightarrow M(OH)_m^{n-m}$$
$$(\text{for } M^{n+} = Y^{3+}, Ba^{2+} \text{ and } Cu^{2+})$$

In the title system, there are two competitive reactions; namely precipitation and complexation. It is extremely important to determine which one is dominant during the evaporation of the solvent.

According to Ringbom's definition [9], the general form of the overall conditional stability constant for a mononuclear complex is

$$\beta'_n = [MY_n]/[M'][Y'] \tag{1}$$

where [M′] is the apparent free metal ion concentration that has not reacted with complexant Y. Similarly, [Y′] is the apparent ligand concentration not bound to the central metal ion M. Y is either protonated or non-protonated, or in the form of complexes with other metal ions.

To find the relationship between the apparent and real free metal ion concentration, let L be the interfering complexant which reduces the free metal ion concentration. Therefore

$$[M']/[M] = ([M] + [ML] + [ML_2] + \cdots)/[M] \tag{2}$$

By use of the overall stability constants, γ_n, of the complexes formed in the side-reaction, the above equation can be rewritten as

$$[M']/[M] = 1 + [L]\gamma_1 + [L]^2\gamma_2 + \cdots = \alpha M(L) \tag{3}$$

and

$$[M'] = \alpha M(L)[M] \tag{4}$$

Taking the negative logarithm each side gives

$$pM' = -\log\alpha M(L) + pM \tag{5}$$

Solution properties, such as concentration, the occurrence of precipitation, viscosity and pH, all affect the above solution process. The concentration of metal ions and complexant, and the viscosity of the solution after water evaporation, were beyond the scope of present report. The major problem associated with the above solution technique is the occurrence of precipitation during solvent evaporation. It should be emphasized that the optimal pH value of the initial solution is important to the chemical homogeneity. The idea behind the present study is to lower the concentration of free metal ions in solution by the formation of soluble complexes. When water evaporates from the solution, the point in the pM′–pH diagram shifts along a line towards lower pH and higher pM′ values if the initial pH value of the solution is higher than the maximum in the pM′–pH diagram. From Equation 5, the pH dependence of the solubility of metal ions can be derived if all the constants and the solubility of metal salts used for the system are known. It is noted that pM should be derived from $K_{sp}(M - OH)/[OH^-]^n$ at a higher pH range. At a lower pH range, the metal ions are not readily precipitated by the hydroxide ion, and also the complexability of EDTA is lowered; therefore, the solubility of metal salts should be system dependent [10]. To simplify the consideration, only the conditional stability constant of the title system was considered.

As shown in Fig. 1, in the higher pH range the yttrium ion will precipitate as $Y(OH)_3$ and in the lower pH range all the metal ions will be present as free ions. Clearly, the ideal pH for this Y–Ba–Cu–O system is in the 10.8–4.0 range. To confirm the theoretical optimal condition, a series of reaction conditions for this Y–Ba–Cu–O system were carried out with different initial solution pH values.

The precursor for the $YBa_2Cu_4O_8$ compound was prepared and the pH of the solution adjusted to the fixed value using ammonia. The liquid precursors were then heated in order to evaporate water and the pH of the solution measured at room temperature during the evaporation. The EDTA complexes, with

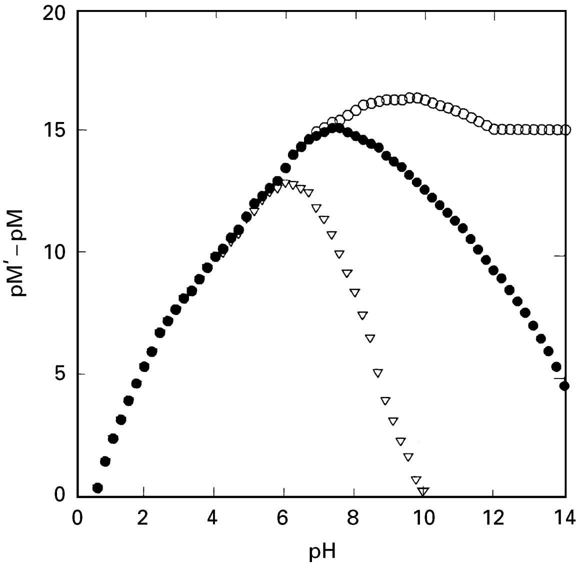

Figure 1 Conditional stability constants calculated for the EDTA complexes of yttrium (▽), barium (○) and copper (●) ion as function of pH.

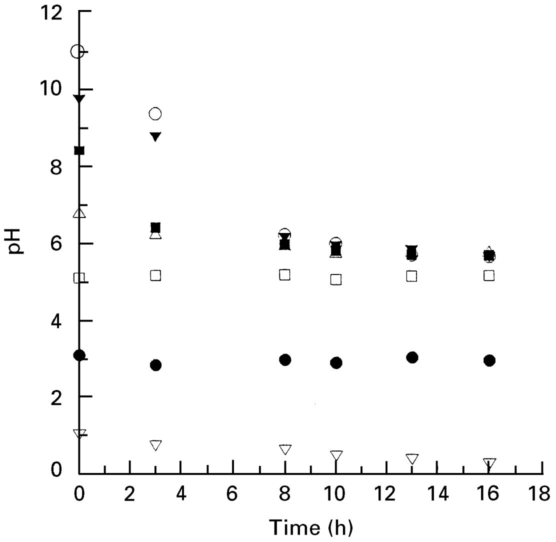

Figure 2 Variation of the pH of the liquid precursors versus evaporation time.

the metal ions in solution, were buffered at pH values in the 6.0–8.0 range. At lower pH values, decomplexation occurs because of protonation of the carboxylate ligands, and at higher pH values the sol could be precipitated by the hydroxide ion. Water was evaporated at 120 °C from the resulting blue solution. During evaporation of water, the liquid became dark blue and the pH of the solution monitored. Fig. 2 shows the pH variation during the evaporation of the excess solvent, the pH was observed to decrease in the process. As shown in Fig. 1, the point in the diagram shifts along the line towards lower pH and log(solubility) values. There are two types of behaviour: (1) the initial solution of lower pH with saturated EDTA salts virtually maintained constant pH during evaporation of water, whereas (2) the initial solution of higher pH decreased in the evaporation process and finally stayed at pH 5.8. The blue liquid precursors yield a viscous solution and finally become a gel.

Thermogravimetric experiments confirmed a continuous weight loss up to 500 °C. The gel was first fired at 500 °C for 10 h in order to remove all volatile moieties. After pyrolysis at 500 °C, on examining the thermogram as shown in Fig. 3, it can be concluded that pyrolysis is essentially complete for the sample prepared at pH = 6.80. After calcination at 700 °C, a grey powder was obtained that exhibits the XRD pattern of a mixture of Y_2O_3, CuO and $BaCO_3$.

For the precursors which were prepared at lower pH, the elemental distribution was quite scattered. Fig. 4 shows the ICP analysis results of the powders which were calcined at 700 °C for 10 h. The composition of the Y–Ba–Cu–O system was analysed by ICP/AES and, assuming that there was no deviation for the yttrium ion, the stoichiometry of the yttrium ion was 1.00. The standard deviations was averaged over 25 individual experimental points. From these results, it is evident that the precursor YBCO prepared from EDTA chelation at a higher pH range is much more appropriate for obtaining an homogeneous sample than that prepared at a lower pH range.

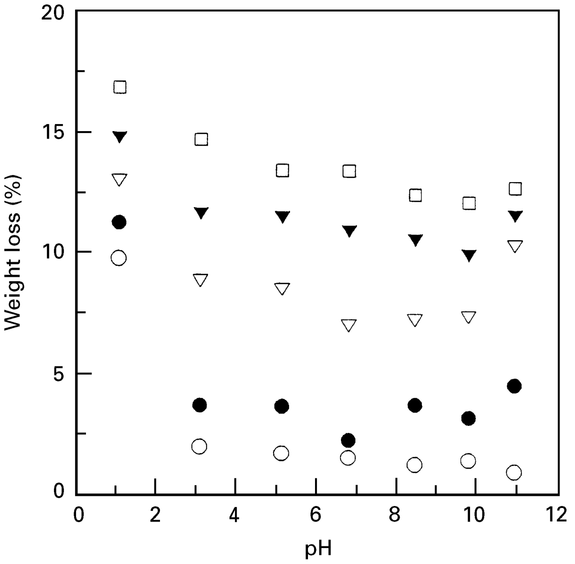

Figure 3 Relations between weight loss and initial pH of the EDTA–metal complex solutions. Temp. (°C): ○, 700; ●, 750; ▽, 800; ▼, 850; □, 900.

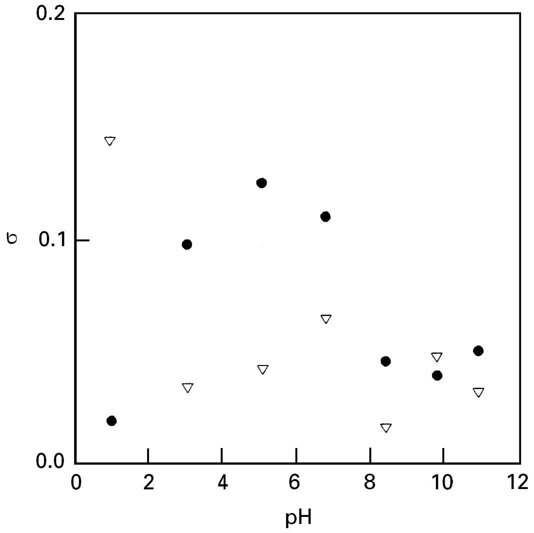

Figure 4 The effect of the pH on the homogeneity of barium (▽) and copper (●) ions (25 specimens prepared at a certain pH value were randomly taken for analysis by means of ICP/AES for the elements Y, Ba and Cu). The degree of homogeneity for specific element is defined as $\sigma^2 = \sum(X - X_i)^2/(n - 1)$ and $X = \sum X_i/(n - 1)$, where X_i is stoichiometric factor of the ith specimen prepared at a certain pH value. X_i for both Ba and Cu are adjusted to Y, taking Y = 1.0).

Compositional mapping of the sintered samples shows the chemical homogeneity of the samples prepared at different pHs. The EPM line scan maps shown in Fig. 5a and b indicate that the sample prepared at higher pH (pH = 6.80; see Fig. 5a) is of better homogeneity, whereas the sample synthesized from powders at lower pH (pH = 1.05; see Fig. 5b) is heterogeneous.

Fig. 6 shows the XRD patterns for samples prepared at different pH values and sintered at 820 °C for 40 h. The samples prepared at lower pHs (pH < 3.10) were composed mainly of $BaCO_3$, Y_2O_3 and CuO. At higher pHs, almost single phases $YBa_2Cu_4O_8$ was obtained. Small amounts of non-superconducting

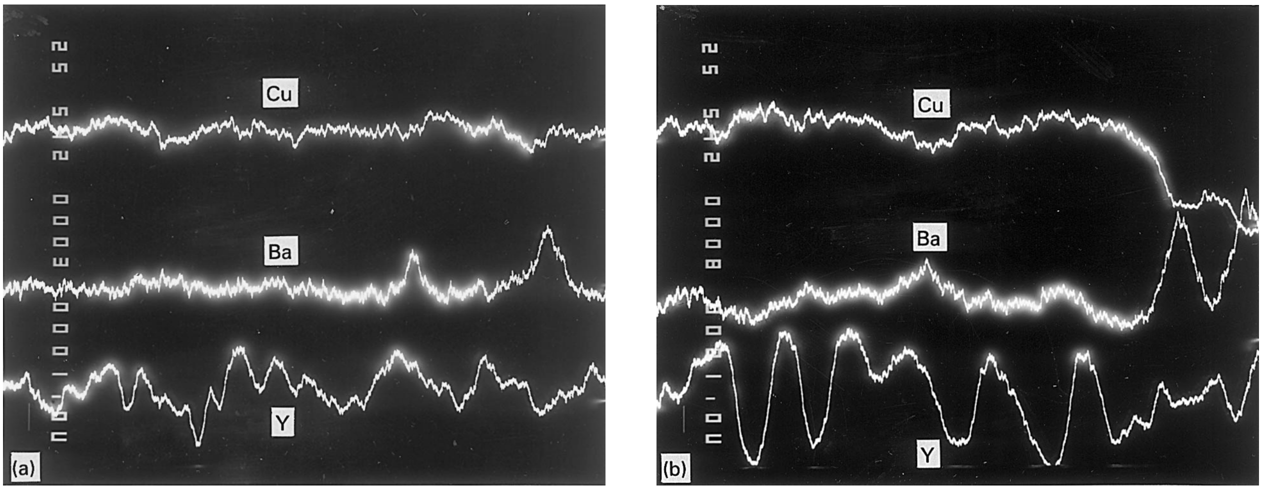

Figure 5 Compositional maps of sintered $YBa_2Cu_4O_8$. (a) The line scans for the sample prepared at pH = 6.80; (b) the line scans for the sample prepared at pH = 1.05.

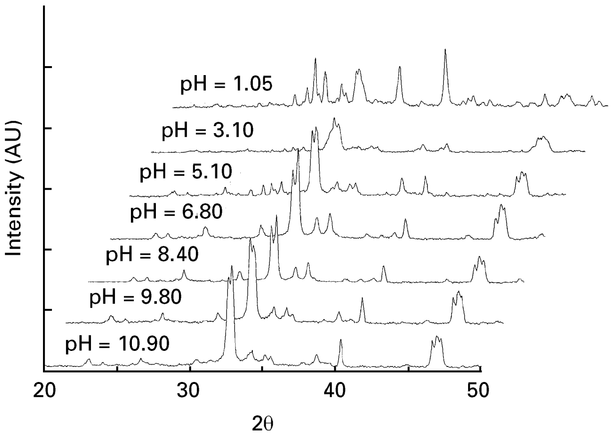

Figure 6 Stacked plot of the XRD profiles for the $YBa_2Cu_4O_8$ samples.

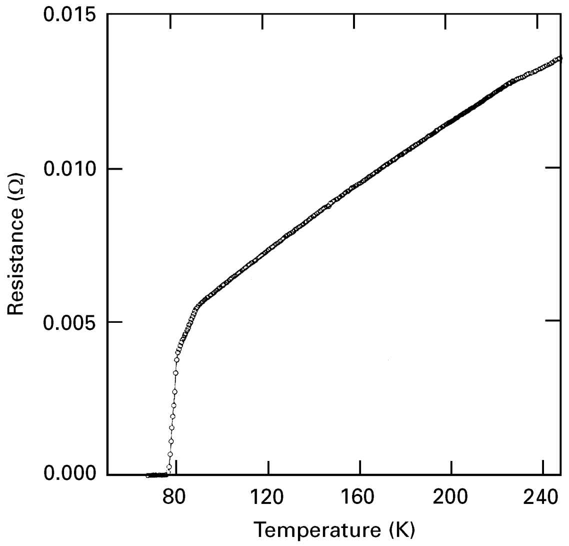

Figure 7 Temperature dependence of the resistance of the $YBa_2Cu_4O_8$ sample sintered at 810 °C for three days.

phases, such as CuO, were present when the samples were prepared at higher pHs (pH > 8.40).

An example of a resistivity–temperature curve for a sample sintered at 820 °C for 72 h and annealed at 400 °C for 24 h is shown in Fig. 7, while an example of a magnetic susceptibility curve is shown in Fig. 8. The resistivity drop-off in the sample made from the above solution powders is sharp, and within a range of 4–5 K, and transition temperatures are in the 86–84 K range. These samples show a two-step drop in the Meissner effect; the superconducting behaviour of these materials has been discussed in more detail by Graebner *et al.* [11] and Maartense *et al.* [12].

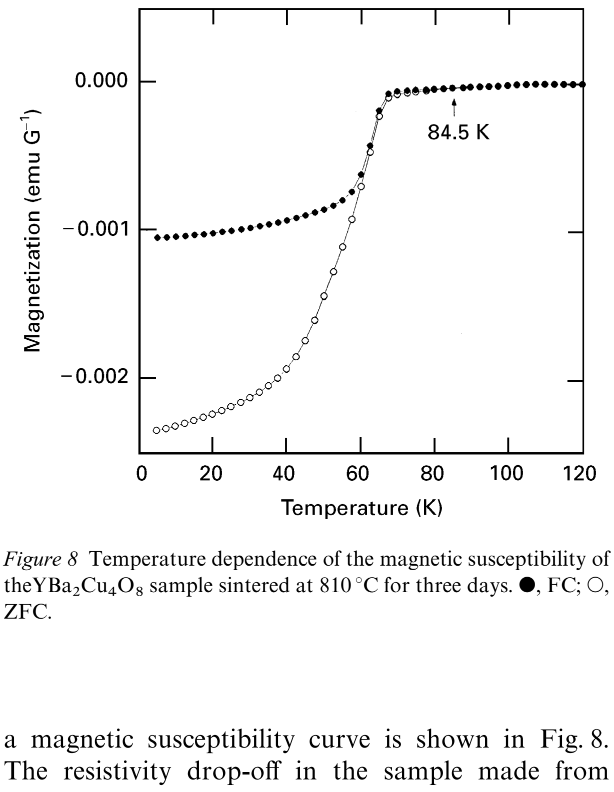

Figure 8 Temperature dependence of the magnetic susceptibility of the$YBa_2Cu_4O_8$ sample sintered at 810 °C for three days. ●, FC; ○, ZFC.

4. Conclusion

Using the EDTA solution mix techniques, we obtained polycrystalline $YBa_2Cu_4O_8$ materials with T_c (onset) of ca. 80 K. The optimal pH of the initial solution was investigated both experimentally and theoretically. By means of this method it was easy to produce $YBa_2Cu_4O_8$ under ambient oxygen pressure which was suitable for doping with other metal ions such as Ca, Fe, Co and Ni.

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