A Simple and Reliable Chemical Preparation of YBa$_2$Cu$_3$O$_{7-x}$ Superconductors

An Experiment in High Temperature Superconductivity for an Advanced Undergraduate Laboratory

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The discovery of high temperature copper oxide superconductors (1) (specifically the compound YBa$_2$Cu$_3$O$_7$), often referred to as 1-2-3 superconductors, created an extensive burst in the study of materials science and superconductivity theory that continues unabated even today.

The resulting interest in chemical aspects of superconductivity and ready availability of a refrigerant, liquid N$_2$ (bp = 77 K), necessary to demonstrate superconducting phenomena created a secondary increase in the incorporation of these topics in chemical education (2). Classroom kits are now commercially available that allow one to demonstrate the Meissner effect by levitating a magnet over a superconductor, thereby showing the effects of zero electrical resistance. The synthesis of high $T_c$ superconductors has appeared even in teaching laboratories because their preparation is relatively straightforward (1, 3). However, most of these synthetic procedures consist of the traditional method of ceramic synthesis that involves the grinding of the metal powder oxides in the proper stoichiometry followed by heating in a furnace. These “shake and bake” methods have several disadvantages.

- The repeated mixing and grinding of the oxide powders needs to be conducted in a fume hood to minimize student exposure to dust.
- The grinding itself might be incomplete due to the relatively large grain sizes of commercially available oxides, resulting in failure to achieve the intimate mixing necessary to create a homogeneous composition.
- These “shake and bake” methods do not reflect the various ways ceramic materials synthesis has been transformed through the application of chemical procedures (4).

In fact, much research has been carried out in the past five years to improve the synthesis of these compounds in order to achieve a greater uniformity in their composition. We have adapted one of these methods, homogeneous coprecipitation, for use in the freshman laboratory and have used it successfully in order to introduce the topic of solid-state chemical synthesis to students. The synthetic method produces a reproducibly consistent ceramic precursor powder which can be processed into a reliable superconductor.

Synthesis of YBa$_2$Cu$_3$O$_{7-x}$

YBa$_2$Cu$_3$O$_7$ oxide preceramic powder is prepared by the method of homogeneous coprecipitation (5). An aqueous urea/oxalic acid solution of the metal salts in the proper 1-2-3 stoichiometry is prepared and heated. At a temperature between 80 and 100 °C hydrolysis of urea takes place with the simultaneous evolution of CO$_2$ and NH$_3$ according to the following equation:

$$\text{CO(NH}_2)_2 + \text{H}_2\text{O} \rightarrow 2 \text{NH}_3 + \text{CO}_2$$  

As the urea hydrolyzes, the pH of the solution gradually rises. Increasing the pH causes the metal ions to precipitate out as their hydroxide, oxalate, or carbonate salts. The final stoichiometry of the powder is determined by the final pH of the solution which in turn is determined by the initial molarity of the urea solution. An initially high urea concentration favors the proper 1-2-3 stoichiometry in the preceramic powder. The precipitate is then separated, washed, and dried. It is then heated at 900 °C for at least 16 h in air to burn out all the residual carbon. The powder obtained at this stage is pressed into a pellet and sintered at 900 °C for 4 h, followed by annealing in oxygen at 500 °C for another 16 h. This results in a material with a composition of YBa$_2$Cu$_3$O$_{7-x}$ (0 < x < 0.5). The preceramic powder synthesis part of the experiment can easily be carried out in one 3-4 h laboratory period. The calcining, pellet pressing, and final sintering and annealing necessitate additional work, but the total working time in the laboratory for these steps is short (~1 h).

Experimental

Reagents were purchased from Aldrich and used as received. Sample calcining, sintering, and annealing was done in a Lindberg muffle-type furnace with the temperature monitored with an Omega HH-99A-K digital thermometer and Type K thermocouple. Samarium–cobalt and neodymium–iron–boron magnets were purchased from Edmunds Scientific.

1. In a 250-mL flask, prepare 100 mL of a solution that is 12–14 M in urea and 0.5 M in oxalic acid (C$_2$O$_4$H$_2$2H$_2$O). This typically involves 65 g of urea, 6.4 g of oxalic acid and 35 mL of water.

2. **Warning**—Both the yttrium and copper nitrates are extremely hygroscopic (i.e., they absorb moisture from the air and become nonstoichiometric). In a 50-mL beaker, weigh 2.70 g of Y(NO$_3$)$_3$·6H$_2$O, 5.10 g of Cu(NO$_3$)$_2$·2.5H$_2$O, and 3.80 g of Ba(NO$_3$)$_2$ and stir the mixture with a spatula. Add this mixture to the urea solution and stir to dissolve.

3. Place a 600-mL beaker for boiling water onto a ring stand and clamp the flask inside the beaker. Add enough water to the beaker so as to cover the urea solution. Heat the solution until it is at 90–100 °C and then continue heating for another hour. Evolution of CO$_2$ and NH$_3$ should be observed during heating.

4. After one hour of heating cool a small portion of the solution to room temperature and measure its pH with pH paper. If the pH is 7, allow the solution to cool to room temperature, otherwise, continue heating until the pH reaches a value of 7.

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2The 1990 fall meeting of the Materials Research Society lists 315 abstracts relating to high $T_c$ oxide superconductors while the 1992 spring meeting lists 249 abstracts on the topic.
3Available from Edmunds Scientific Co. 101 E. Gloucester Pike, Barrington, NJ 08007-1380.
wax for five minutes. The pellets are then removed from the wax and air-dried.

Characterization of the YBa$_2$Cu$_3$O$_{7-x}$

The determination as to whether or not the YBa$_2$Cu$_3$O$_{7-x}$ made is a high $T_c$ superconductor is most easily done by observing the Meissner effect (6). Cooling a pellet of the material in liquid nitrogen and levitating a ferromagnet over its surface is a positive test for superconductivity.

Results and Discussion

The procedure produces a fine powder of intimately mixed YBaCu hydroxides, oxalates and carbonates. The method is not inherently sensitive to the initial urea concentration within a range of molarities of urea (10–16 M) (5). The reaction can also tolerate small variations in the initial 1-2-3 starting ratio. Alternately, premade solutions of the metal ions can be used in lieu of having the students weigh out the hygroscopic salts. Also the chloride salts of copper and yttrium can be replaced for the nitrate salts.

The figure shows an X-ray powder diffraction spectrum of a calcined powder prepared by a student compared with that of a powder obtained from a commercial supplier (Aldrich). Comparison of the spectra with those reported in the literature (7) show that both materials contain the Y-Ba-Cu oxide 1-2-3 composition in the orthorhombic (high $T_c$, superconducting) phase. Additional peaks in the student sample at 20 $= 30-32$ $^\circ$ are due to the presence of a non-superconducting Y$_2$BaCuO$_5$ phase. This impurity phase does not interfere with the superconducting properties of the final product as long as it is present in small amounts.

The preparation of the YBaCu precursor powder by heterogeneous coprecipitation represents one of the techniques whereby ceramic synthesis is being transformed through chemical synthesis. It enables students to conduct an experiment that is topical and involves solid state materials chemistry. Student feedback is positive as most seem surprised and pleased that the synthesis actually yields a superconducting material! The experiment provides an interesting and rewarding experience for students and educators alike.

Acknowledgment

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Literature Cited


