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TITLE: **NEW PREPARATIVE METHODS TO ENHANCE PHASE PURITY AND PHYSICAL PROPERTIES OF CUPRATE SUPERCONDUCTORS**

AUTHOR(S): **R. E. Salomon, R. Schaeffer, J. Macho, Allan Thomas and G. H. Myer. Temple University, and Ben Franklin Superconductivity Center. N. V. Coppa, ERDC**

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NEW PREPARATIVE METHODS TO ENHANCE PHASE PURITY AND PHYSICAL PROPERTIES OF CUPRATE SUPERCONDUCTORS

R.E.Salomon, R.Schaeffer, J.Macho, Allan Thomas and G.H. Myer
Temple University and the Ben Franklin Superconductivity Center,
Philadelphia, Pa. 19122

N.V.Coppa
Los Alamos National Laboratory, Los Alamos, NM. 87545

ABSTRACT

Several methods which avoid the problems inherent in solid state reactions have been developed. These methods include freeze drying, liquid ammonia based processes and a novel xerogel process. They are applicable to both 123, 124 and BISCCO based superconductors and have as their goal the atomic mixing of precursors in order to reduce inhomogeneity in the final product.

The three methods are described and compared to each other and to conventional methods of synthesis. The products prepared by these methods are fully characterized by elemental analysis, XRD, TGA, DSC, resistivity and magnetic susceptibility versus temperature and by SEM.

INTRODUCTION

Several methods which avoid the problems inherent in solid state reactions for the preparation of bulk powders of high T_c superconductors have been developed by us^{1,2,3,4} and others.⁵⁻¹⁰ Solid state reactions start with mechanical mixtures which must react at grain boundaries and these grain boundaries quickly become laden with products thereby slowing the rate of reaction. Accordingly, attempts are made to grind samples to finer particle sizes and these long grinding processes lead to contamination of the final product with material abraded from the grinding apparatus. If the grinding times are reduced, then the particles are not as well mixed and longer times and higher temperatures are required to produce the desired final product. The disadvantages that accrue to these longer processing times and higher processing temperatures are obvious. One well known method of enhancing mixing in a non-mechanical manner is to co-precipitate the precursor metal ions as a salt which can be decomposed to form the oxide. Organic acids and carbonates are the favored precipitating agents although there is concern

about the contamination of product with carbon at the grain boundaries. Furthermore, co-precipitation, doesn't really lead to atomic mixing although if done carefully, it does lead to an intimate mixture of small particles. Finally, it should be mentioned that control of stoichiometry is difficult in coprecipitation because of finite solubilities of the precipitates.

For these reasons, a general study of alternate methods of mixing which would lead to near atomic mixtures was carried out over the past few years. With atomically mixed precursors, one has the opportunity to have diffusionless reactions. With these diffusionless reactions, high processing temperatures are in principal only needed to decompose the anion to the oxide. In general, both the processing time and temperature can be reduced and ideally the phase purity can be enhanced.

In the following, a description of three different methods which have been used to achieve a near atomic mixture of precursor ions will be described. These methods are 1) a freeze drying technique 2) a set of liquid ammonia based methods and 3) a xerogel method.

EXPERIMENTAL

For many of these methods, starting materials in the form of water soluble nitrates and acetates are needed. These materials often contain varying amounts of water of hydration. Determination of this water of hydration by TGA is not always an acceptable method of determining metal to weight ratios since overlap between the loss of water and the decomposition of the anion can occur. Accordingly, analytical methods to determine the exact metal ion content of starting materials are needed. Copper ion can be determined most readily and accurately by electrogravimetry wherein a solution of the copper salt is electrolyzed between platinum electrodes. The copper deposits quantitatively at the cathode in a period of 10 or more hours. The weight gain of the platinum electrode gives the mass of copper in the solution. Yttrium nitrate can be decomposed to the oxide which loses water of hydration at relatively low temperatures. Barium and yttrium can also be determined by atomic absorption spectroscopy. Bismuth, copper and lead solutions can also be prepared by dissolution of the pure metal in nitric acid. Calcium and strontium solutions can be readily analyzed by EDTA titrations. In the following, it will be assumed that 123 material ($YBa_2Cu_3O_{7-x}$) is being produced unless otherwise stated.

The first method of preparation to be described is the freeze drying method. The goal of this method of preparation is a precursor material

that is a random solid solution of Y, Ba and Cu nitrates in the appropriate stoichiometry. To achieve this end, an aqueous nitrate solution is ultrasonically aerosolyzed and allowed to impinge on the surface of liquid nitrogen at near zero velocity head. The micron sized droplets freeze throughout, thereby trapping the metal ions. The "snow" containing precursor ions is rapidly transported to a freeze dryer with a shelf temperature maintained at ca. -25 C and a condenser temperature at -55 C. The salt containing ice sublimates in a period of days. During this period of sublimation, adjustment of the shelf temperature is carried out to facilitate this rate process without allowing melting to occur. The samples are eventually transferred to a vacuum drying oven where the last traces of water are removed without allowing melting in water of hydration with subsequent phase separation.

Materials prepared in this manner have some unusual properties the most interesting of which is the large heat of solution which conforms to the interpretation of a random solid solution which has a higher enthalpy than the corresponding enthalpy of the phase separated system. X-ray diffraction studies also do not reveal the presence of any crystalline phases. Of course, both results could also be explained by the presence of amorphous pure solid phases.

Even though we have succeeded in our initial goal of preparing atomically mixed precursors, it turns out that during the subsequent thermal processing some unmixing occurs. Samples have been taken from partially thermally processed materials and examined by XRD and the results show that some phase separation occurs. Nevertheless, this unmixing occurs at the sub-micron level and after a final high temperature anneal, phase and chemically pure product is obtained. More detailed reports on the kinetics and mechanism of the thermal decomposition of this random solid solution will be provided in a forthcoming publication¹¹. Recently, this technique has been applied to the preparation of pure and doped 124 high T_c superconductors.¹² It appears that this freeze dry method of preparing precursors is particular useful for synthesizing materials that are thermally sensitive or which do not readily lead to the desired product for thermodynamic or kinetic reasons. The one negative aspect of this technology, especially when applied to the preparation of BISSCO materials, is that some freeze drying equipment may not be compatible with the type of strongly acidic solutions needed to dissolve bismuth. The use of acid traps in the freeze dryer can overcome some of these problems. Recently Song et al.¹³ have prepared some bismuth based superconductors by a freeze drying methodology.

Liquid ammonia is a medium dielectric solvent which can dissolve a variety of inorganic salts. The heat of vaporization of liquid ammonia is about half of that of water. It also seems that the energy required to remove ammonia from inorganic solids is smaller than that required to remove water of hydration. This smaller energy facilitates a more rapid removal of the solvent which aids in avoiding phase separation. Whether or not this rationale is correct, we have found that the spray pyrolysis of these liquid ammonia solutions readily yields intimate mixtures of the precursor salts which can be formed into final product with lower temperatures and processing times. We are aware of the fact that spray pyrolysis of aqueous solutions has recently made its way into the commercial market but it is not clear whether this will be competitive. In the method described here, the ammonia is used only as a solvent and transport agent and it can be recycled. Attempts to utilize the flammability of ammonia to develop a flame spray method to produce thin films of superconductor are underway.

In the liquid ammonia method described here, gaseous ammonia is condensed on a cold finger cooled with dry ice-acetone in a suitable three-necked flask which contains a total of approximately 6 g of the starting reagents. The flask contains a stirring bar and is itself surrounded by a dry-ice acetone cold bath. Typically, 400 ml of liquid ammonia are collected in this fashion and the resulting solution is stirred for an hour to ensure dissolution. In one case, the solution is sprayed onto a heated plate (ca.

600 C) where ammonia is lost and some decomposition/reaction occurs. In the second case, gaseous carbon dioxide is bubbled into the liquid ammonia solution resulting in the solidification of the solvent and precipitation of the metal ions. Solidification is a result of the formation of carbamates (mostly ammonium carbamate). Any water present could lead to the formation of the less desirable carbonates. Further details are provided elsewhere.⁴

The carbamates are especially easy to process since ammonium carbamate can be readily sublimed. Both nitrate and acetate anions can be used in this ammonia based methodology. One special advantage which accrues to the use of liquid ammonia is the ease of dissolving bismuth salts, which are so difficult to dissolve in aqueous solutions. The liquid ammonia method also lends itself to the preparation of films of superconductors. If the ammonia solution is sprayed through an artists air brush (maintained at dry ice temperatures) onto the surface of a MgO substrate heated to 600 C, reasonably thick films of superconductor are obtained.

Another way to achieve the goals of atomic mixing, without the need for much elaborate equipment, is to immobilize the ions of the solution in a gel

and to remove the water from this gel to produce a dry gel or "xerogel." This gel can be dehydrated at room temperature or at slightly elevated temperatures to speed up the process.

A variety of gelling agents, in pure form and as mixtures, have been tested and it was found that for the preparation of 123 and 124, ordinary gelatin, 2-3 % by weight of the solution, serves admirably. In practice, a stoichiometric acetate solution (caution: nitrates form explosive gels) is prepared and then 2-3 % by weight of the gelling agent is added and the solution is allowed to gel. Once the gel is formed, it is dried under vacuum or in a circulating dry air chamber. The xerogel so formed, is then thermally decomposed to yield the desired product. The only disadvantage of this method is the need to introduce the organic gelling agent which ultimately could lead to contamination of the sample with carbon.

This xerogel method is quite distinct from the now classic "sol-gel" method. In the sol-gel, method one must first prepare a colloidal precursor solution which is followed by dispersion of the colloidal particles to form the sol. This is followed by gelation of the colloidal dispersion which is achieved by hydrolysis or polycondensation of the colloidal precursors. This last step involves aging and drying under ambient conditions. One of the major advantages of the xerogel method over the sol-gel method is that colloidal particles are not needed and soluble precursors (acetates, formates, nitrates, etc.) can be used. Additionally, the rigid control of conditions (concentration, temperature and pH) required in the sol-gel process are not required in the xerogel method.

RESULTS

The XRD results on 123 and 124 materials indicates that very high phase purity material can be obtained. The elemental composition of both precursors and final products demonstrates the close control of stoichiometry that is possible with these methods. For example, average metal ratios for 123 from liquid ammonia methods (carbamate process and spray pyrolysis), as determined by atomic absorption, are within the error range of the instrument. Phase purity was established with XRD (Rigaku) using standard conditions. Samples of 123 were consistently produced with phase purities in excess of 98 %. One such pattern, prepared using the ammonia process (carbamate) is given in Fig. 1. Figure 2 shows results of resistivity and magnetization on the same sample of 123. The transition temperature at midpoint is about 93 K.

Both the carbamate and xerogel methods produce precursors which are

very stable even under high atmospheric humidity. This could prove quite useful in the preparation of bulk superconducting devices and wires. These precursors are much less frangible than ceramic superconductors and accordingly, the firing step could be saved as the final step. In the case of 123 produced by the xerogel method, an additional indication of the high phase purity is the extrapolated value of the the pre-transition resistivity versus temperature to absolute zero.

The 124 powders made by the xerogel process show the same high phase purity as the 123 according to XRD results. This is confirmed by TGA

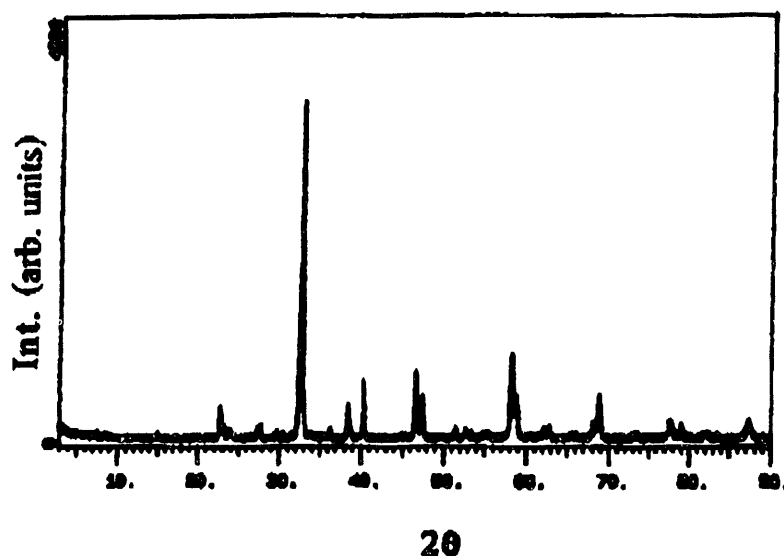


Fig.1 XRD Pattern of 123 Produced By Carbamate Method in Liquid Ammonia

studies in which no weight loss occurs from 0 to 800 C during increasing and decreasing temperature regimes. One of the main advantages of the xerogel process to the preparation of 124 material is that all the processing can be carried out under 1 atm of oxygen rather than the 200 atm traditionally needed.

All three methods lead to very small particle size (as revealed by SEM) and the freeze drying method leads to an exceptionally narrow distribution of particle sizes.

As previously mentioned, it seems to be the case with all three methods, that some unmixing occurs as the temperature is raised during the thermal processing step. Of course, once the oxide is formed, no additional unmixing

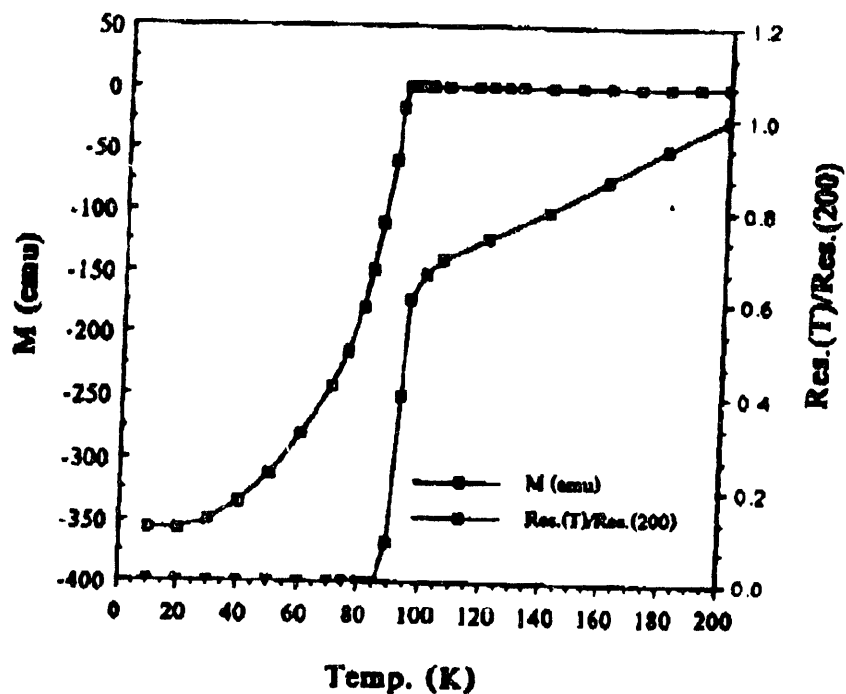


Fig.2 Resistivity and Magnetization as a Function of Temperature for 123 Produced by the Carbamate Method in Liquid Ammonia

occurs. As a general rule, rapid thermal processing minimizes subsequent phase separation.

CONCLUSION

The goal of achieving diffusionless reactions in the preparation of high T_c superconductors has been only partially realized. The tendency for phase separation is so strong that materials which are initially randomly mixed tend to unmix as the processing temperature is raised. It is for this reason that attempts are being made to choose alternate anions (e.g. formates) which decompose to the oxide at lower temperatures. Alternatively, it is found that a rapid thermal ramp to the decomposition temperature results in the least amount of phase separation.

Of the three methods described in the above, the freeze drying method should lead to the least amount of contamination. It also is especially useful for preparing thermally sensitive compounds such as the 124 material. It does require the most elaborate equipment and careful handling of precursors. The liquid ammonia based methods, offer a great deal of promise for scale-up and

for the preparation of thin films. It also is particularly useful for the preparation of bismuth based superconductors. The carbamate route, may be especially useful for the preparation of wires if a method of allowing for the escape of ammonia and carbon dioxide can be found. Needless to say, great care is needed in the handling of liquid ammonia. The xerogel method is in principle the easiest to utilize. As mentioned previously, the effective phase purity of 123 made by this technique is outstanding (based on resistivity vs temperature studies). One possible drawback is the presence of undesirable impurities such as sulfur or phosphorous in some of the gelling agents. The formation of stable sulfates and phosphates must be avoided. Both the xerogel method and the freeze drying method require a time consuming dehydration step. In this regard the xerogel method has a major advantage in that the rate of dehydration is proportional to the vapor pressure of the solid and since the xerogel can be dehydrated at or slightly above room temperature, the vapor pressure of the xerogel will be at least 1000 times greater than that of ice at ca. -20 C.

It seems likely that commercialization of high temperature superconductors will rely on several different synthetic paths dependent upon the nature of the desired product and other factors such as cost and safety considerations. It has been shown that the three methods described in the above can be used to produce good quality high T_c superconducting powder and in the case of the liquid ammonia method, to produce superconducting thick films. It is too early to tell if the latter will be competitive with other methods of producing thick films.

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