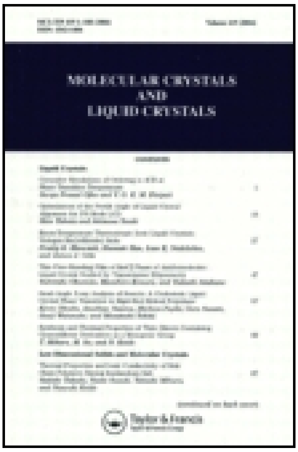

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# Oxalate Route to High Temperature Superconductors

Ronald J. Clark [a], Laura L. Harrison [a], Stephen A. Skirius [a] & William J. Wallace [a]

[a] Department of Chemistry, Florida State University, Tallahassee, Florida, 32306

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# OXALATE ROUTE TO HIGH TEMPERATURE SUPERCONDUCTORS

RONALD J. CLARK, LAURA L. HARRISON, STEPHEN A. SKIRIUS,
WILLIAM J. WALLACE
Department of Chemistry, Florida State University,
Tallahassee, Florida 32306

Abstract Some details of an evaporative approach to the production of ceramic superconductors by the oxalate route are given.

The preparative details of the new generation ceramic superconductors are mentioned far less in the literature than the measurements people make on the samples. Most workers simply mix starting materials such as oxides and carbonates and subject the sample to various high temperature heat treatments, generally in unspecified containers. Many of those in the chemistry community are examining alternate procedures with several motives in mind such as achieving lower processing temperatures and production of purer or more homogeneous material. One of at least a dozen fundamentally different alternate approaches is the oxalate procedure which has a very early history in the field. We are examining the chemical details of the process in order to determine the conditions which allow it to work or those which make it fail.

The approach is conceptually simple. One attempts to precipitate the metals from a homogeneous solution as a very finely divided oxalate solid which can then be decomposed to the oxides, frequently under mild thermal conditions. These oxides react to form the ceramic. If the metals form either a mixed (multiple) oxalate salt which would be homogeneous at the molecular level or form as mixed crystals homogeneous at the submicron level, then one has a far more uniform starting material than produced by standard ceramic procedures. Even the latter material would be far more homogeneous than that available from even the most vigorous mixing of oxides and carbonates.

In the case of the yttrium-barium-copper system, one has immediate problems relative to the various aqueous equilibrium parameters. The Ksp value of barium oxalate is sufficiently large that roughly half is left in solution when oxalic acid is added to a solution of the nitrates. The pH of the solution is between 1.0 and 1.5. When base is added to increase the pH and decrease the barium solubility, a second complication occurs which is the formation of the copper oxalate complex, $Cu(C_2O_4)_2^{2-}$. In addition, unless an organic base is used, contamination with an extraneous metal is almost certain. For any of the metals, there is a third potential complication resulting from the solubility of neutral salts which can be significant. The available equilibrium data seem not good enough to warrant a computational effort to find the best conditions of pH, concentration, and starting metal ratio to obtain a 1:2:3 solid. Even if the better data were obtained, then the experimental conditions would have to be very exactly controlled to obtain good results.

One way to assure that a solid has the same concentration as the solution is the evaporation of the solvent. Since none of the oxalate salts are volatile, they must be left behind. If the evaporation does not create serious inhomogeneities, one has a very powerful preparative technique. Solution techniques using simple pipets and burets or more automated volumetric equipment provide an excellent approach 1) to make subtle compositional variations around a given compound, 2) to replace a cation incrementally, or 3) to dope a cation in trace amounts.

In the following paragraphs, a partial summary of the results found thus far using this technique on the preparation of Y:Ba:Cu samples is given. The results are broken down by anions. The use of acetates which will be discussed last appears to yield a procedure of considerable merit.

## Nitrates

The addition of oxalic acid to a 1:2:3 solution of the nitrate salts produces a very fine blue powder consisting of clumps of submicron "nodules". Even under the highest magnification under SEM, these nodules show no crystallinity. Analysis by SEM-EDS shows that this material contains all three metals with a fairly uniform composition, nodule to nodule. However, the solid is significantly barium deficient as expected from the Ksp values. Solvent removal under vacuum on a rotary evaporator yields a blue solid that upon heat treatment forms an excellent quality superconductor. It was anticipated that in addition to water removal, reactions like the one below would be driven to the right owing to the volatility of the nitric acid.

$$Ba(NO_3)_2 + H_2C_2O_4 = BaC_2O_4 + 2HNO_3$$

The critical temperatures of fired samples determined by the AC inductive method are consistently in the range of 92 to 94K and the transitions are sharp being less than 3 K wide even after very simple heat treatment. A number of rare earths can be substituted for the yttrium. In the process of heating, there is an exotherm and a large weight loss at about 300° C which is accompanied by the evolution of brown gas. Clearly the sample does not consist of pure oxalate salts. Careful SEM-EDS examination of the evaporated product shows that small submicron nodules are still present, but they contain primarily copper and little barium or yttrium. The yttrium is found as water insoluble (presumably oxalate) crystals, rectangular in shape often about 10 $\mu$m in size. The barium is found as even larger crystals often as 100 $\mu$m octahedra which are water soluble, presumably as the nitrates. Both types of crystals appear to have grown around the copper nodules.

Our current explanation for this unusual chemistry concerns the evaporation process of the acid. As the nitric acid solution becomes more concentrated approaching the constant boiling composition of about 4M, the yttrium and barium oxalate first dissolve and then reprecipitate as the solution approaches dryness.

The ease with which high quality superconductors are produced is, in retrospect, a surprise. Barium nitrate crystals break readily on grinding. In addition, they melt around 500° C and decompose to the oxide at temperatures well below normal firing temperatures. These factors must allow the sample to become homogeneous.

### Chlorides

Chloride salts give much poorer quality material if it shows any superconductivity at all. This was at first surprising as nitrates and chlorides have much in common as both salts and acids. The barium deficient filtered samples sometimes show a small amount of superconductivity. The evaporated samples generally show none. Barium chloride is presumably formed during evaporation in a manner similar to barium nitrate. However, a lot of chloride is still present in the samples after firing to 950° C. Barium chloride is stable to decomposition to the oxide at temperature up to 1000° C. It also appears that a chloride containing pellet can ruin a normal pellet setting next to it during firing.

### Sulfates

Although we have not actually used sulfate salts, they would seem unlikely to be useful for several reasons. First, barium sulfate is not soluble and cannot be used as a starting material although other sulfates are often soluble. In addition, sulfuric acid will not volatilize under our conditions as nitric and hydrochloric acids can. Finally, compounds like barium sulfate are stable to 1000° C and will not yield the oxide.

### Acetates

Acetate salts present several advantages in the evaporation procedure compared to the other anions. When oxalic acid is added to solutions of the acetates, the pH is higher and the precipitation of the barium is more complete. However, since the copper begins to form the soluble complex at the higher pH, this partially offsets the barium advantage. When the filtered material is fired, fairly deep and sharp superconducting transitions are seen by the AC inductive method.

Owing to the quite different nature of acetic acid and nitric acid vaporizations, the evaporation method seems to work quite well. No material appears to redissolve during evaporation of the water and acetic acid and no large crystals are found. The final blue material consists solely of clumps of the submicron particles containing all three metals at fairly uniform composition. When a series of small particles or clumps are analyzed by

SEM/EDS after evaporation, they are found to have the same mole ratio to within plus or minus a few tenths of a unit to the ideal 1:2:3 ratio. The blue powder after grinding and in pellet form shows even greater homogeneity. The variation for the filtered material seems less than in the evaporated product, but the former is off composition. The blue powder readily fires into black superconductors. After firing, the superconducting pellets can be extremely homogeneous when the composition is correct.

So far, we have not observed a great qualitative difference (by AC induction) between the Tc values and the transition interval of the curves as one varies between evaporated material which is on and somewhat off composition and the filtered material which is significantly off composition. Our goal is now to determine the nature of the materials prepared by evaporation as the composition is systematically varied using several techniques.

One caveat that must be considered while using this approach is that the starting solutions must be carefully analyzed if accurate compositions are to be produced. The starting materials are hydrates and, at best, the nominal molecular weight of hydrates can be considered accurate to no more than plus or minus one water. This means that the masses taken do not necessarily reflect the mole quantities. We did not analyze the solutions during the opening phase of the work when the methodology was being worked out, but we are now using atomic absorption for analysis and are seeking more accurate analytical methods. When materials like CuO, $Y_2O_3$, and $BaCO_3$ are used, the weights represent the number of moles. When barium peroxide or oxide are used, one again has problems with moles being reflected by the mass. Therefore, we are attempting to dissolve pure materials like those above in acetic acid as an approach to the production of solutions of accurately known concentrations.