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Oxalate materials prepared by evaporation as precursors to superconducting ceramics

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Some unexpected chemistry will be discussed which occurs during the production of high T_c superconductors by an oxalate route. Evaporation (rather than filtration) of a 1:2:3 Y:Ba:Cu nitrate solution containing excess oxalic acid was done, in order to make sure that the solid had the same composition as the solution. It was assumed that the removal of water and nitric acid by vacuum would quantitatively yield the salts as oxalates. Surprisingly, the evaporation changed what was initially a homogeneous, but off-composition, material into a rather inhomogeneous material. During the evaporation, the yttrium and barium were apparently redissolved from their initial form as submicrometre particles containing all three metals. They were redeposited as 10–100 μm rectangular and octahedral crystals. However, this material yields very good superconductors upon simple grinding and heat treatment as measured by conductivity and a.c. induction.

1. Introduction

Numerous alternative synthetic routes for the preparation of high temperature ceramic superconductors are being explored, particularly by the chemistry and ceramics communities [1–3]. In previous papers [4 and 5] we showed that good quality superconductors could be produced using oxalate precursors prepared under special evaporation conditions starting with nitrate salts.

The preparation of standard 1:2:3 material is difficult to control by simple precipitation and filtration using nitrate salts and oxalic acid. The K_{sp} of barium oxalate is not sufficiently small for quantitative precipitation. Increasing the pH reduces the solubility of barium oxalate as expected but complexation, particularly of copper, produces new problems. Solubility of the neutral salts may also produce problems. These same problems would be encountered with the salts of other strong acids such as halides and sulphate.

The approach used to solve these problems which produced the materials referred to earlier [4 and 5] was to evaporate the water, and the nitric acid produced by the reaction, under vacuum on a rotary evaporator. This assures that a 1:2:3 solid must be produced from a 1:2:3 solution. Standard procedures were used in the subsequent thermal treatment. Material with high T_c values and quite narrow transitions were produced.

However, several aspects of the procedure compelled us to look at this process further in spite of the good T_c values.

2. Experimental procedure

Evaporation on a rotary evaporator was generally done under conditions such that the distillate could be quantitatively trapped. The bulk of the condensation was done with ice water and the remainder was done with a final trap (or two) cooled by liquid nitrogen to prevent loss. In the experiments, either mechanical or aspirator vacuums were used and various times (10–60 min) were allowed to elapse after evaporation seemed complete. The time required for evaporation was not particularly dependent upon which vacuum was used so long as the other conditions were the same. Generally, the higher vacuums were used when the distillate was of concern and the simpler aspirator vacuum was used when the focus was on the solid. Control experiments were run using known amounts of nitric acid to test that the evaporation and trapping was quantitative. Titrations were done using standard base with phenophthalin indicator.

When filtered samples were used, either medium porosity glass frits or 0.45 μm cellulose filters were used. Copper oxalate alone could not be retained by the glass frits but when the other elements were present, filtration was rapid and complete.

The products were examined by optical microscopy and scanning electron microscopy (SEM) often with energy dispersive spectroscopy (EDS) analysis. Either a Jeol JSM 840 or 8400 instrument with Kevex EDAX attachments was used. Elemental maps were obtained on a Jeol 8600A electron microprobe. Thermogravimetric analysis (TGA) and differential

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thermal analysis (DTA) experiments were run on DuPont 951 and 1600 modules, respectively. The oxalate samples had to be handled carefully during TGA experiments to avoid physical loss from the pan during times of rapid gas evolution particularly around 300 °C.

All high temperature firing was done either in platinum or in alumina containers.

3. Results

Several surprises were found when the products of the evaporation process were examined in detail. When a 1:2:3 solution of the nitrate salts was treated with oxalic acid in quantities ranging from 30% deficient to 80% excess, a blue powder of uniform appearance resulted. The solution from this operation had a pH of 1.0–1.4 and was colourless indicating essentially no copper content.

The filtered powder from the process above, consisted of clumps of small spherical nodules averaging about 0.5 μm in size. This material showed no obvious crystal facets. Some typical analytical data of these particles by EDS are shown in Table 1. These analyses were done several ways. In one approach, the beam was focused on an individual nodule within a clump. The beam would presumably penetrate deep enough so that the results were influenced by several nodules. Attempts were also made to analyse individual nodules that were isolated from the clusters. In addition, the analysis of the powder, as a whole, at lower magnification was done. There was some variation in the analyses as must be expected owing to the various sample presentations, but the results show remarkable uniformity. No individual particle found among these submicrometre particles had significantly different physical appearance from the others, nor were particles found by analysis to be noticeably enriched or deficient in any metal relative to the general average. The Y:Ba:Cu ratio was about 1:0.5:2 which is clearly barium deficient relative to the starting solution. This would be expected from the K_{sp} data. The addition of sulphuric acid to the filtrate yielded barium sulphate. The anion content of the solid which could contain oxygen, carbon, and nitrogen from the oxalate or nitrate could not be analytically determined under our conditions but was almost certainly oxalate based upon solubility.

When a base like triethylamine was added to the solution in quantities adequate to yield a pH 5 solution, the filtered solid had the same superficial appearance as that above—the salt [$NHEt_3NO_3$] is colourless and soluble in water. Clumps of submicrometre nodules were again seen. There was, again, no appearance of crystallinity in the nodules nor were any particles of unusual shape seen. A typical EDS analysis taken under comparable analytical conditions to those used above is shown in Table I. It is clear that base treatment has increased the barium content but the material is now copper deficient. Since these ratios are relative to yttrium, its loss would not be readily revealed. However, our calculations indicate low solubility under most conditions. Interestingly, the loss of copper and the addition of barium to the solid makes little change in the general appearance of the nodules. The filtrate has a blue copper colour at pH 5 relative to previous pH ~ 1 solutions which were essentially colourless. The bis-oxalato complex of copper $[Cu(C_2O_4)_2]^{2-}$ has about the same appearance as the aqueous copper ion [6].

TABLE I Typical SEM–EDS Analysis[a] of oxalate precipitates from nitrate solutions

Sample	Yttrium[a]	Barium[a]	Copper[a]
Filtered powder	1.00	0.53	2.36
Filtered powder PHS	1.00	1.71	2.07
Evaporated solution ground-low magn	1.00	2.09	3.31
Copper nodules only	0.05	–	1.00
Yttrium rectangular	1.00	–	0.79
Barium octahedral	–	1.00	0.56

[a] mole ratios

An elemental map is shown in Fig. 1. The dot density is proportional to the relative concentrations of the three elements yttrium, barium, and copper. A small, representative 2 μm piece of the filtered material shows that the chemical homogeneity is more than superficial. There are no regions in which any of the metals are either concentrated or deficient.

The evaporation of the pH 1 solution produced from the metal nitrate salts and oxalic acid gave a solid which upon a quick superficial SEM examination appeared similar to the earlier materials. The intent of the evaporation was to bring the soluble metals out of solution by removal of solvent and was expected to drive the equilibria

$$M(NO_3)_2 + H_2C_2O_4 \rightarrow MC_2O_4 + 2HNO_3$$

$$M(NO_3)_3 + 3/2H_2C_2O_4 \rightarrow 1/2M_2(C_2O_4)_3 + 3HNO_3$$

to the right by the removal of nitric acid which is the only volatile component other than water under our conditions. Again, clumps of submicrometre nodules are seen as the predominant material. However, EDS analysis given in Table I shows the resemblance is only superficial as the nodules are quite rich in copper while containing only traces of the other two metals. A more careful SEM analysis of the material, to be discussed later, reveals other features.

It was clear even before the electron microscopy work was done that the chemistry is more complicated than expected based upon the equations above. When the blue oxalate powder produced by evaporation was fired, an exothermic reaction was seen when the temperature approaches 300 °C which heated the product to a temperature represented by a dull red glow. Brown fumes were seen in the muffle furnace. When the firing was done in an alumina boat within a quartz tube in a tube furnace using a slow air purge, the brown fumes of nitrogen oxides were clearly produced over the temperature interval of 300–600 °C. Even when the tube was purged free of brown fumes by a fast flow of oxygen at 400 °C, after the initial reaction

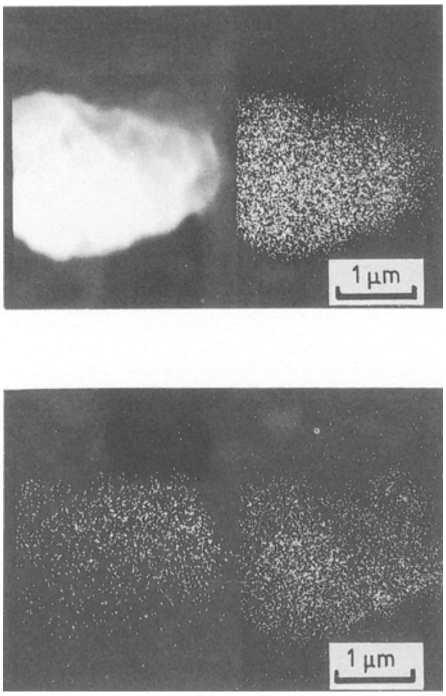

Figure 1 Elemental map of a representative 2 µm filtered oxalate particle showing compositional uniformity of the three elements before evaporation. Upper left, particle; upper right, barium; lower left, yttrium; lower right, copper.

has subsided, the brown fumes reappeared on slower air flow and continued to occur over the 400–600 °C temperature range.

The most obvious explanation is that nitrate ion was present in the evaporated material. When the filtered precipitation product was fired under the same conditions, the brown fumes were not seen.

Titration of the condensate trapped during the evaporation process revealed that the nitrate ion contained in the solution of the combined metal salts does not vaporize quantitatively as nitric acid, as expected from the equations above. In the case of the 1:2:3 solutions only about 70–80% of the nitric acid was found by NaOH titration. Work with the individual metal nitrate solutions revealed that well over 90% of the expected nitric acid was removed by evaporation with copper and yttrium, but no more than 20% with barium. Evaporation of test aliquots of 0.10 M nitric acid yielded a condensate in which the acid is essentially quantitatively recovered.

We could find no evidence that the nitric acid was trapped in the oxalate powder as solvates of nitric acid of the type $BaC_2O_4 \cdot xHNO_3$. Although oxalate salts are often extensively hydrated, the fact that our powders were not acidic, plus the temperature range over which the fumes were evolved, strongly implies that the nitrate was present in a different form other than acid solvates or adsorbed acid.

More careful SEM examination of blue oxalate powder produced by evaporation reveals phases in addition to the submicrometre nodules of copper oxalate mentioned earlier (Fig. 2a) which contain little barium or yttrium. In a representative sample, one finds approximately 10 µm rectangular crystals shown in Fig. 2b. The EDS analysis of these crystals, shown in Table I, reveals them to be quite rich in yttrium with small concentrations of copper but essentially no barium. The cubes are generally coated with the copper nodules and even when a clean surface is found, small concentrations of copper are present. It appears that the yttrium cubes grow around the copper oxalate nodules. These yttrium rich crystals do not dissolve in water when examined under an optical microscope so it appears that they must be oxalates rather than nitrates.

The barium, in a typical sample is found as 100 µm octahedral crystals generally coated with submicrometre copper oxalate nodules as shown in Fig. 2c. Those copper nodules also appear to be embedded within the crystals. These octahedral crystals have exactly the habit found for barium nitrate. The crystals dissolve in water while being observed by a microscope. The size of the yttrium and barium crystals demand that they should be widely dispersed in the copper nodules and therefore less frequently seen. In addition, the large crystals are sometimes almost totally buried in clumps of nodules.

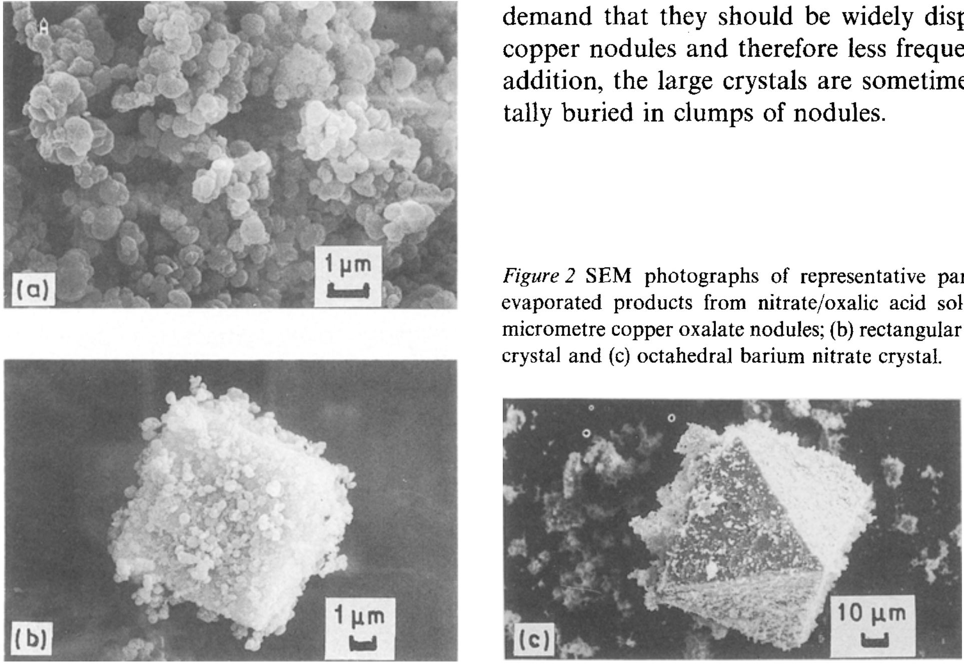

Figure 2 SEM photographs of representative particles found in evaporated products from nitrate/oxalic acid solutions: (a) submicrometre copper oxalate nodules; (b) rectangular yttrium oxalate crystal and (c) octahedral barium nitrate crystal.

X-ray analysis of the blue oxalate powder obtained by evaporation shows a clear pattern for barium nitrate. A few other peaks are seen in the X-ray pattern, but thus far we have not been able to assign them to a specific phase, particularly to confirm the nature of the yttrium crystals. On the other hand, the X-ray pattern of the filtered powder yields only a few peaks, generally rather broad. Thus the filtered submicrometre nodules which contain all three metals have had little time to grow crystals and are basically amorphous to X-rays. However, they are birefringent under cross polarized light and appear crystalline at 1000 × when examined under the optical microscope.

The size of yttrium and barium crystals can be controlled by the evaporation conditions. "Flash" vaporization was carried out by allowing the oxalate/nitrate solution/slurry to flow drop wise into a heated rotary evaporator. Each drop took only seconds rather than tens of minutes to evaporate. This operation yielded very fine crystals which still showed some separation and segregation but on a much smaller scale than was found by normal evaporation. Similarly, rapid evaporation without heating which can result in the freezing of the oxalate/nitrate solution/slurry also resulted in very fine crystals. By controlling the conditions of the rotary evaporation (time, vacuum, bath temperature) the growth of the yttrium oxalate and barium nitrate crystals can be controlled to some degree. As one would expect, as the evaporation is carried out more slowly, the crystals become larger. The latter part of the evaporation seems most important. Growth of the barium nitrate crystals will not begin until the volume of water/nitric acid has been reduced below the barium nitrate solubility and then the growth would be expected to have a dependency on time and temperature.

Thermal measurements on the material were made. Differential thermal analysis in air confirmed an exothermic reaction at approximately 300 °C and a number of smaller endotherms at both higher and lower temperatures. The exotherm at 300 °C was also seen in a nitrogen atmosphere. The exotherm can be attributed among other things to either air oxidation of the oxalate, nitrate reaction with the oxalate, or possibly both. Thermogravimetic measurements show a number of weight loss regions, the largest occurring at about 300 °C for the main oxalate decomposition. A representative example is shown in Fig. 3. The lowest temperature weight loss presumably represents removal of hydrate water and the sublimation of any excess oxalic acid. The highest temperature weight loss represents carbonate decomposition to oxide. Oxalate decomposition to form carbonates is fairly common in certain metals [7]. Thermograms are difficult to obtain quantitatively as the rapid gas evolution at 300 °C caused solid material to be lost from the TGA pan. Owing to the complexity of the system, the thermal data is inadequate to help determine whether one has a series of isolated compounds or a rather homogeneous mixture containing mixed salts.

The 100 µm barium nitrate crystals contained in the evaporated material were reduced rapidly in size by simple grinding. This is readily determined by monitoring the dispersion by PLM-dispersion staining using a refractive index 1.521 HD liquid (25 °C).

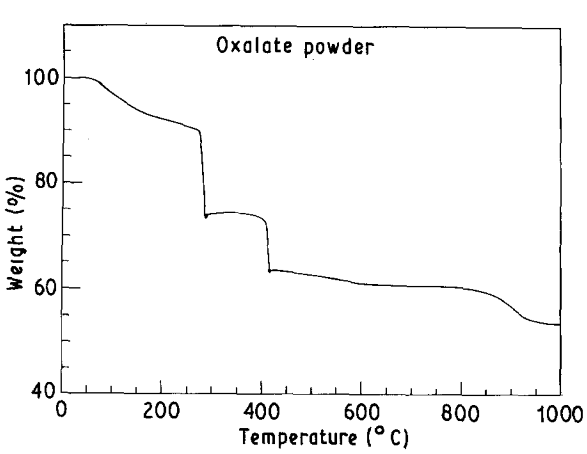

Figure 3 Thermogravimetric analysis of oxalate/evaporation powder—heated 10° C min^{-1} in air.

Solid state carbon-13 nuclear magnetic resonance (NMR) with magic angle spinning was used in an attempt to determine whether the oxalate precipitate consisted of individual metal oxalates or some chemically more uniform multiple metal salt comparable to the alums. Several individual samples of pure metal oxalates were examined. Resonance occurred at about 163, 170, and 170 p.p.m. for the copper, barium, and yttrium oxalates relative to TMS using an exterior *p*-di-*t*-butylbenzene standard. Natural abudance C-13 was measured. The resonances were generally about 2–3 p.p.m. wide using a 200 MHz spectrometer. Not every preparation yielded exactly the same spectrum. For instance, one preparation of barium oxalate consisted of three resonances. In addition, there was a time dependence of the resonance intensity when proton cross polarization was used. Presumably the hydrogens of the hydrate water are responsible for the cross polarization [8] results and the degree of hydration is responsible for the differing spectra. Oxalates are known to form a number of hydrates [9].

When a mixed oxalate sample was examined, a single resonance at about 170 p.p.m. was found. These results do not really allow us any conclusion relative to the question of how many oxalate phases are present in the precipitates. Carbon-13 enrichment and a careful control of hydration will be required to get more refined data.

Efforts to make superconductors by this evaporation route using chloride salts basically failed [9] and it is now becoming clear why this occurred. On distillation, hydrochloric acid and nitric acid form azeotropes at a concentrations of about 4 M for HCl and 15 M for HNO_3 (at 101.3 MPa). This would cause some amounts of the oxalate salt to be redissolved during the evaporation and would probably result in the formation of barium chloride in the product. Unlike barium nitrate, barium chloride is stable at firing temperatures and is not expected to yield barium oxide as barium nitrate does [9]. The only superconductors that were obtained with chloride salts was through filtration as the chloride would stay in solution as either soluble salts or hydrochloric acid.

Starting from a 1:2:3 solution, the fired product had a low content of superconducting phase as the filtered solid would be seriously deficient in barium. When the solution is barium rich, then the quality of the final material would be better but that is not the way we wished to attempt the preparation.

Use of sulphate salts as the starting materials would be expected to fail totally by the evaporation procedure owing to the insolubility in water and the high temperature stability of barium sulphate and the fact that sulphuric acid is not nearly as volatile as nitric or hydrochloric acid.

4. Discussion

It is clear from the previous discussion that the goal of obtaining a highly homogeneous precursor is not actually met by this particular evaporative version of the oxalate procedure although high-quality, high T_c material results. The addition of oxalic acid to a 1:2:3 solution of yttrium, barium, and copper nitrates yields a precipitate that consists of clumps of submicrometre nodules which contain all three metals in a mixture which is homogeneous at that size range. This solid is barium deficient. Evaporation of water and nitric acid from the slurry to bring down the remaining barium causes a major redistribution of material. If the process were only simple evaporation, there are several types of inhomogeneity that might result. In one, the soluble portion of the barium oxalate would come out of solution and cover the surface of the yttrium–barium–copper oxalate particles formed during initial precipitation. In what would seem to be the worst case, the barium oxalate would be found as separate particles. Instead, after a typical 60 min evaporation process, the barium is not even found to be present as an oxalate salt. In addition, the yttrium and barium have been predominately redissolved from their initial form and redeposited (separately) as relatively large, well formed crystals. The yttrium is present as 10 μm oxalate rectangular crystals and the barium as 100 μm nitrate octahedra.

The reason for this behaviour is not altogether clear. There is no sign of redox chemistry during the evaporation process. The explanation may lie in the way nitric acid evaporates. The concentration of nitric acid in the 1:2:3 solution after the addition of oxalic acid on completion of the reaction should be 0.1–0.2 M. In general agreement, the solution has a pH of slightly greater than one. During evaporation, the nitric acid is expected to concentrate through loss of water until it ultimately becomes a constant boiling solution of about 15 M HNO_3 and then both nitric acid and water should co-distill as an azeotrope [10 and 11]. The increasing concentration of acid decreases the pH, and thereby increases the solubility of oxalate salts.

The final question to ask is how such a non-uniform precursor can yield such good superconductors. On this, we can only speculate. First, the material has the proper overall composition. In addition, the blue powder is ground before being calcined. It appears from optical observations that the larger crystalline particles break up readily during the grinding. The melting of the barium nitrate at about 500 °C may help in its distribution. After calcining, the black powder is again thoroughly ground before it is pressed into pellets. Still, these observations point out, once again, how mobile the ions must be in a fine powder at high temperatures, as our material is probably no more homogeneous than that used in the standard procedures.

We are in the process of modifying the procedure to obtain better homogeneity and smaller particle size. We think we have a good procedure using acetates rather than nitrates of the metals.

Another caveat relative to the procedure is the fact that the nitrates are generally variably hydrated and if accurate overall composition is required, they must be analysed. The hydrate number given on a reagent bottle is only a nominal value.

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