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(21) International Application Number: PCT/AU93/00300 (22) International Filing Date: 22 June 1993 (22.06.93) (30) Priority data: PL 3080 23 June 1992 (23.06.92) AU (71) Applicant (for all designated States except US): THE UNIVERSITY OF QUEENSLAND [AU/AU]; St Lucia, QLD 4072 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only) : BHARGAVA, Atit [IN/AU]; PAGE, David [AU/AU]; YAMASHITA, Toru [JP/AU]; MACKINNON, Ian, Donald, Richard [AU/AU]; Centre for Microscopy and Microanalysis, The University of Queensland, St Lucia, QLD 4072 (AU).	(74) Agent: CULLEN & CO.; Level 12, 240 Queen Street, Brisbane, QLD 4000 (AU). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims.</i>	
(54) Title: SUPERCONDUCTING OXIDES BY COPRECIPITATION AT CONSTANT pH (57) Abstract <p>High temperature superconductors (e.g. Y-Ba-Cu-O) can be formed at commercial quantities with high phase purities by conducting the coprecipitation process at a constant pH. By selecting a precipitate (e.g. oxalates) which confers plastic properties to the precipitated product, a variety of shaped HTSC compounds can be made.</p>		

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TITLE

SUPERCONDUCTING OXIDES BY COPRECIPITATION AT CONSTANT PH.

FIELD OF THE INVENTION

5 THIS INVENTION relates to superconductors and particularly high temperature superconductors and to an improved preparation of high temperature superconductors and fabrication of articles containing high temperature superconductors.

10 BACKGROUND ART

High temperature superconductors were first disclosed in 1987 and are characterised by having superconductor transition temperatures (T_c) above the temperature of liquid helium and many with a T_c above the temperature of liquid nitrogen (77.3K). The three broad families of high temperature superconductors (HTSC) are as follows -

- 15 (i) the Y-Ba-Cu-O system
(ii) the Bi-Pb-Sr-Ca-Cu-O system; and
20 (iii) the Tl-Ba-Ca-Cu-O system.

The system (i) which is reported in Phys. Rev. Lett. 58 405 (1987) is easy to synthesise and has a wide composition range over which superconductivity may appear. It has a relatively low T_c which is approximately 90°K.

25 System (ii) does not contain rare earth elements and has a high T_c which is approximately 108K. However it has a narrow composition range which permits superconductivity. System (ii) is reported in Japan J. Appl. Phys 27 L 1041 (1988).

30 System (iii) which is reported in Nature 332 138 (1988) has a high T_c which is approximately 120K but the toxicity of thallium is of concern.

Other high temperature conducting systems include -

- 35 (a) The 214 system. ie. $(La, Ba)_2CuO_4$
(b) 124($YBa_2Cu_4O_8$) and 247 ($Y_2Ba_4Cu_7O_{15}$)

- (c) The $\text{Bi}_2\text{Sr}_2\text{CuO}_6 (\text{CaCuO}_2)_n$ ($n=0,1,2$) system and its variants with Pb stabilisation
- (d) The $\text{Tl}_2\text{Ba}_2\text{CuO}_6 (\text{CaCuO}_2)_n$ ($n=0,1,2,3$) system
- (e) The $(\text{Nd,Ce})_2\text{CuO}_4$ system and its variants.

5 The two main techniques to form HTSC are grinding the respective HTSC precursors together or solution co-precipitation of the respective HTSC precursors.

10 Grinding HTSC precursors is a lengthy process and requires several grinding and sorting stages to obtain a particle size distribution and mix which will be suitable for formation of the HTSC. However, it is difficult to obtain phase purity and repeatable results. Phase purity is critical in the efficiency of the HTSCs
15 and with many HTSC families, even slight variations from the correct ratio of the various components will result in loss or degradation of HTSC properties.

20 Solution co-precipitation is a technique to prepare precursor (for example of HTSC compounds) compounds so that they are mixed in a very intimate manner, perhaps as closely as on a molecular level. In solution co-precipitation, the various precursor components are initially dissolved in an aqueous solution (usually containing an acidifying agent such as nitric
25 acid). The dissolved precursors are precipitated from solution by addition of a precipitating agent. These agents have included carbonates, acetates, formates, hydroxides and oxalates. The resultant co-precipitate is filtered usually by a centrifuge and subjected to a low
30 temperature calcination process to remove or decompose the anion to provide a mixture of the respective cation oxides. Further heating at elevated temperatures of about 900C results in transformation of the cation oxides to the high temperature superconducting material.

35 To obtain HTSC compounds having high efficiency and a high transition temperature, it is critical to ensure that the respective precursors are present in the

correct ratio. The ratio must be extremely carefully controlled to obtain the high phase purity required.

Grinding has not generally been successful in being able to obtain commercial amounts of consistently pure products.

To date, solution co-precipitation of HTSC precursors has also not been able to provide consistent phase purities on anything more than extremely small amounts and therefore this technique has been unsuitable in commercial applications which includes continuous or large scale processing.

STATEMENT OF INVENTION

We have now developed a technique which allows co-precipitation to occur and wherein the co-precipitated precursors may have a consistent phase purity to allow production of HTSC compounds having high efficiency. The technique can be used to generate HTSC compounds on a commercial scale.

The technique may be used to co-precipitate precursors to all copper oxide based ceramics, such as semiconductor, insulator and superconductor phases in YBCO, BSSCO and thallium based systems.

The technique involves the surprising and unexpected discovery that minimising the variation in the pH of the solution during the co-precipitation process can result in the co-precipitate precursors having a high and consistent phase purity. The co-precipitates may also exhibit a narrow variation in particle size ranges.

Therefore, in one form, the invention resides in a method for co-precipitating superconducting precursor components, the method comprising the steps of -

dissolving the superconducting precursor components into solution,
adding a precipitating agent to the aqueous solution, and
maintaining the pH of solution substantially

constant during the co-precipitation process.

The precursor components may be those which form copper, bismuth and thallium based HTSC compounds.

Suitably aqueous solutions are used. It is
5 found that the pH of the aqueous solution does not significantly vary (ie. variations of greater than 0.1) upon initial dilution of the solution. Therefore, while not wishing to be bound by theory, there appears to be a buffer effect present.

10 The co-precipitation process suitably is caused to occur within the buffer range or just outside of the buffer range. That is, it is preferred that the initial aqueous solution is diluted until just before the pH begins to significantly vary and that the co-
15 precipitation process is carried out at this dilution value. We believe that this maximises the buffer effect during the precipitation process and therefore minimises the pH variation during co-precipitation.

Suitably, the superconductor precursor
20 components are those which form high temperature superconductors. The superconductor precursor components are preferably dissolved in an acidic aqueous solution. The solution may be acidified by an organic or inorganic acid and nitric acid is a typical acidifying agent. The
25 initial pH may vary depending on the type of superconducting components dissolved therein and various other variants such as volume of water and acidifying agent used but typically, the initial pH range is between 0.1 to 3 and suitably about 0.7 (for the yttrium based
30 family) and about 0.45 (for the bismuth based family).

Suitably, the precipitating agent is a
dicarboxylic acid or derivatives thereof. The
derivatives may include salts, esters anhydrides, amides
and the like. Ammonium oxalate is one suitable
35 derivative. A suitable dicarboxylic acid is oxalic acid.

We also note that the co-precipitated precursor oxalates used by our technique can be calcined to the

precursor oxides at a fraction of the time currently used to form precursor oxides by other processes. While again not wishing to be bound by theory, we believe that the improved times results from the high phase purity we achieve by our technique, the intimate mixing, and possibly the constant particle size obtained.

The advantage of being able to calcine the coprecipitate precursors at a much quicker rate than hitherto achieved, is that conventional high through volume driers such as drop tube furnaces, fluidized bed furnaces and inclined furnaces can be used to form the precursor oxides in commercial quantities.

In another form, the invention resides in a method for forming shaped articles or products which contain HTSC material.

Since the discovery of high temperature superconductors (HTSC) in 1987, there have been various techniques developed to fabricate shaped articles containing HTSC. These shaped articles can include wires, tapes, coils, thick and thin films, coatings, tubes, rods and other bodies. These shaped articles find applications in power transmission, levitation trains, magnetic shielding, microwave cavities, magnets and energy storage devices. With a large number of existing and potential uses of HTSC containing articles, there is a need to develop a process which allows manufacture of a variety of shaped articles easily and which can be readily adapted to any type of shape.

There are various known techniques which have been used to provide shaped articles containing HTSC. In one known technique, Calcined 123 powder is placed into suspension by using toluene as a solvent and other organics as dispersants. It is necessary to add dispersants so as to deflocculate or disperse the slurry because agglomeration of the slurry results in the poor quality of formed products. This slurry can be cut into shapes. However, the additives such as dispersants need

to be burned out in a very controlled manner from the "green" product. This results in increased porosity and lack of product density and can also result in the formation of cracks, faults and defects. It is also
5 known to use thickening agents such as cellulose to aqueous solutions in order to form a slurry.

Another known technique is disclosed in U.S. Patent 5,026,683 and uses a powder in tube method. This process consists of filling a hollow metal tube with an
10 HTSC powder and then rolling the tube to reduce the overall wire diameter. This process is expensive and requires the use of very sophisticated machinery to give multi-filament, circular cross-section wires. This process is also not suitable for YBCO superconductors as
15 these compounds require heat treatment in oxygen which does not readily flow through the metal walls. Therefore, it is not possible to obtain high J_c with YBCO powders by this process. There may also be physical limitations on the length and the diameter of wires made
20 by this process.

Another technique is disclosed in U.S. Patent 4,975,416 which consists of heating an oxide composition to above the melting temperature and then cooling the melt through an orifice to form a wire. This wire is
25 then suitably heat treated to make it superconducting. Although some success is obtained by this process for the oxide materials, it is not possible to form wires in the YBCO system by this process because of its incongruent melting behaviour. (A compound which melts incongruently
30 results in more than one compound upon melting, none of which is the original composition). Wires made by this process are also very brittle and cannot be formed into coils with any ease.

A further known technique of forming wire/coils
35 is by extrusion which forces a ceramic paste through an orifice. This process can be adapted for HTSC compounds. In the process a powder of Calcined 123 compound is mixed

with a binder, dispersant, plasticizer and a solvent. The formed slurry is extruded through a die forming flexible green wires. At this green or unfired state the wires can be coiled or wrapped around a former. The wires are then heat treated to burn out the additives and to sinter the HTSC form.

Again, this technique suffers from the disadvantage of forming a non-homogenous mixture due to the separate addition of binder, dispersant, plasticizer and solvent.

Australian Patent 603001 discloses a method of forming super conductive products using casting or screen printing HTSC powders to form bulk shapes or coatings. However, in this method a calcined HTSC powder is used which is already inherently brittle. Therefore, in order to form a stable suspension, additives are necessary such as deflocculants and plasticizers and these must be in relatively large amounts - up to 40% in order to provide a sufficiently plastic/flowing mass.

We have now developed a technique which can be adapted to allow manufacture of a large number of different shaped products and articles containing HTSC materials and wherein the resultant formed article or product can be substantially more dense than conventional techniques. By optimizing parameters of slip casting process we may remove substantially voids, cracks or faults which can adversely affect the superconducting nature of the article or product.

Our co-precipitation approach allows similar downstream processing for all copper oxide based ceramics. This downstream processing includes all shapes such as those prepared by slip casting, extrusion, thick film and doctor blading.

Ceramic materials including HTSC compounds are known to be inherently non-plastic. Therefore in order to form shapes such as wires and crucibles, plasticity providing agents such as binders, dispersants, lubricants

and plasticizers must be added. The present invention can produce a precursor mix with no additives, and which is plastic. This plastic mix may be added to HTSC compounds or their precursors, metals and other ceramics thereby providing a mix which may be shaped by conventional techniques.

We can achieve this by using a co-precipitation technique to form the precursor HTSC precipitates and by selecting a precipitating agent which confers plastic properties to the precipitated product, and which can also be easily removed, such as by heating, to provide the resultant product.

In this manner, there is no requirement to include separate additives to the precipitated product such as dispersants, plasticizers and the like. This, in turn, allows our precipitated product to be substantially homogeneous while still having plastic properties sufficient to allow the precipitated product to be shaped by extrusion, moulding, casting and the like. The finally formed HTSC compound can also be more dense.

In another form, therefore, the invention resides in a method for shaping HTSC containing materials comprising the steps of -
dissolving HTSC precursor components into solution, adding a precipitant which will cause the precursor components to precipitate, the precipitant being selected to provide plastic properties to the co-precipitated product, subjecting the resultant co-precipitated product to a shaping step, and, removing the precipitant from the shaped product.

Suitably, the precipitant is an organic dicarboxylic acid or derivative thereof. A suitable organic dicarboxylic acid is oxalic acid and the derivatives may include salts, esters, anhydrides, and amides.

The resultant co-precipitated product may be treated to increase or decrease its viscosity depending

on the particular type of shaping step required. Water can be added or removed to adjust the viscosity and therefore the plasticity of the precipitate.

By plasticity is meant that the precipitate or slurry is of sufficient viscosity to allow it to be moulded, extruded, cast, coated and the like. Various additives may be added to the precipitated product. These may include HTSC compounds/precursors, inert fillers and the like. Various additives may also be added to the solution prior to precipitation to allow intimate mixing to occur.

The precipitant can be removed by a heating step, sufficient to burn off or decompose the precipitant. If the precipitant is an oxalate, the heating step should be sufficient to reduce the oxalate to form the various cation oxides.

If desired, the heating step may be continued or adjusted to result in the shaped product having HTSC properties. Suitably, the initial precipitation technique is similar or identical to that disclosed above with buffering of the pH of the medium during the co-precipitation process.

BRIEF DESCRIPTION OF THE DRAWINGS

- Figure 1 is a schematic view of process scheme.
- Figure 2 is a schematic flow sheet of Example 1.
- Figure 3 are pH values of Example 1.
- Figure 4 is an XRD plot of Y-123 powder.
- Figure 5 shows XRD plots of HTSC materials formed at different times from oxides.
- Figure 6 is an XRD plot of HTSC formed directly from oxalates.
- Figure 7 is a susceptibility v temperature for wire prepared by Example 4.
- Figure 8 is an XRD plot of wire prepared by Example 4.
- Figure 9 is a susceptibility v temperature for Y-123 wire prepared by example 5.
- Figure 10 is a J_c v sintering temperature of Y-123 wire

prepared by Example 5.

Figure 11 is a plot of resistivity v temperature of a Y-123 wire prepared by Example 3.

5 Figure 12 is a susceptibility v temperature for the samples prepared by Example 7.

Figure 13a is a transmission electron micrograph of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ powder YBCO calcined powder (500C).

Figure 13b is a transmission electron micrograph image formed from calcined precursors.

10 Figure 14 is an XRD plot of BSSCO powder of Example 11.

Figures 15a and 15b are scanning electron micrographs of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ powders.

Figure 16 is a susceptibility v temperature for wire made by Example 8.

15 Figure 17 is an XRD of Pb doped BSSCO powder of process 2 in Example 10.

Figure 18a is an XRD plot of Bi-2223 precursor powder of process 1 of Example 10.

20 Figure 18b is an SEM micrograph of the powder of process 1 of Example 10.

Figure 18c is an SEM micrograph of the powder of Example 10.

Figure 19 is an XRD plot of Y-211 powder made by Example 9.

25 Figures 20a and 20b are SEM photos of sample of process 2, Example 10.

Figure 20c is a magnetic susceptibility v temperature of sample of process 2, Example 10.

DETAILED DESCRIPTION

30 EXAMPLE 1:

This example illustrates the co-precipitation process to manufacture pre-cursors and HTSC powders of the compound $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-d}$ (123). An overall schematic process is illustrated in figure 1.

35 78.0g of reagent grade yttrium oxide, Y_2O_3 , and 500g of reagent grade copper nitrate trihydrate $\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$, and 360.6g of barium nitrate, BaN_2O_6 , are

charged into a 20 litre measuring plastic container. To the above mixture is added 10 litre of de-ionised water and 240ml of concentrated nitric acid. The above mixture is mechanically mixed until it turns into a clear blue solution. This mixing is accomplished in about 6 hours. At the end of mixing, a pH meter is used to continuously monitor the pH of this solution. Initially, a pH of about 0.7 is reached for this solution. It is seen that with addition of water the pH initially does not rise. It is to be noted that the pH of water is about 7.0 and such a water addition is expected in other systems to increase the pH of a solution. However, only after about 4 litre of water addition, the pH shows a perceptible increase. At about 6 litre of water addition, the pH of the solution is about 0.9. (The volume of the solution is now about 17 litres). Such behavior indicates that there is a buffer zone present in the nitrate solution. This zone is controlled by addition or subtraction of water. We observe that if sufficient water is added to surpass this buffer zone then we obtain consistency in co-precipitation. The aqueous solution may be buffered and then surpassed by substituting water addition with addition of other solvents in the final stage. These solvents may be those that do not cause immediate precipitation such as acetic acid. However, this addition shows no observable improvement in precipitate properties.

To another plastic container are weighed out 1008g of oxalic acid. 16 litre of de-ionised water are added to the oxalic acid and mechanically stirred. In about 4 hours, the solution is clear. A pH meter is now used continually to monitor the pH. At this stage the pH is about 0.8. To this mixture of oxalic acid and water is added 850 ml of ammonium hydroxide and allowed to mix for about 15 minutes. The pH of the mixture is now about 3.45. It is also feasible to achieve a pH of 3.45 by taking a mixture of oxalic acid and ammonium oxalate.

The two solutions (i.e. nitrates and oxalic acid) have the same volume; for example, in this case, 17 litre. The two containers with their respective solutions are connected to peristaltic pumps which drive the two solutions at identical speeds into a reaction tank. This reaction tank also acts as a convenient medium for quality control measurements. Within the reaction tank, and included with the pumping lines, the mixed solutions rapidly form a blue precipitate which consists of the respective cation-oxalate co-precipitates. In this example, these co-precipitates are yttrium-oxalate, barium-oxalate and copper oxalate as well as mixed oxalates such as barium and copper and oxalate. From the reaction tank, the mixture may then be transferred to a centrifuge for filtration. Alternately, the precipitated oxalate mix in the reaction tank may be sufficiently dried and used directly for forming. A schematic flow sheet of this arrangement is shown in Figure 2.

The reaction tank is placed on a magnetic stirrer and constantly stirred. About 2000ml of the reacted mix is maintained in the reaction tank by controlling the flow rate out of the second peristaltic pump. Such a volume in the reaction tank increases the homogeneity of the final co-precipitate and also serves as another location for quality control measurements. A pH meter is used to constantly read the pH of the reacted mix as well as that of the filtrate. It is observed that both pH values are constant during the course of the reaction. pH of the reaction mix gives an indication of the consistency of the co-precipitation process and values are shown in Figure 3 for a number of runs. The pH of the slurry is generally observed to be about 1.3, with an average variation of ± 0.1 .

The slurry at this stage can be used for at least three different applications and may require at least three different viscosity treatments. These are

respectively:

- (i) calcination to form HTSC powders,
- (ii) extrusion to form wires/coils and
- (iii) slip casting to form bulk bodies and/or to coat
5 thick films.

There are several synthesis procedures for obtaining HTSC compound powders. The most commonly practiced technique is by calcination of a stoichiometric mix of oxides, carbonates and similar chemicals. Such a
10 calcination process can give phase pure $Y_1Ba_2Cu_3O_{7-d}$ (123) in a reproducible manner. However, achieving homogeneity and adequate oxygenation may be a problem for large amounts of powders. In all cases, the time required for complete conversion of raw materials (e.g. oxides,
15 carbonates etc.) to the HTSC compound is several hours. In addition, intermittent grinding of the partially calcined powders are often required during this lengthy process.

The advantage of proceeding from a solution is realised by several authors and there are various reports
20 of such processing. A spray drying process has been used to dry a slurry of carbonate co-precipitated powders which then required long calcination times with intermittent slurring to obtain $Y_1Ba_2Cu_3O_{7-d}$ (123) powder.
25 A spray dried nitrate solution of $Y_1Ba_2Cu_3O_{7-d}$ (123) cations to obtain powders which were then calcined for long hours to obtain $Y_1Ba_2Cu_3O_{7-d}$ (123) powder has also been used.

Our co-precipitated powders can react to form the 123 powder in a matter of a few minutes. This
30 process is valid for other co-precipitated HTSC powders such as the bismuth-based HTSC compounds. Figure 4 is an XRD plot of the Y-123 powder.

Example 2:

The coprecipitated oxalate as obtained from the
35 centrifuge of Example 1 is dried in a vacuum oven at 100°C. After about 12 hours, the precipitate is a dry mass which can be easily ground in a mortar and pestle or

in a food processor to give a loose fluffy powder. This powder may then be heat treated by two different methods. The end products of both methods are pure $Y_1Ba_2Cu_3O_{7-d}$ (123) powders with identical physical and chemical properties.

5 Method 1

(1) The powder is transferred to a refractory beaker (eg alumina) and heat treated in a muffle furnace to decompose the oxalates to the oxides of the respective cations. A temperature may be selected that is below the
10 first binary eutectic but above the decomposition temperature of each oxalate. Thus, for example for the batch prepared above, a temperature of 500C is selected. The powder in the alumina beaker is transferred to the muffle furnace and heat treated at a rate of 5C/min to
15 500C at which it is held for 15 hours. The powder is then cooled down to room temperature at 5C/min. Further experiments have shown that if the depth of the powder in the refractory container is small, (eg 5mm), the time at 500C can be reduced to 5-10 minutes. Oxalate powders
20 thus calcined at 500C for various times were analysed by x-ray diffraction. It is observed that in about 10 minutes, an oxalate co-precipitated powder as prepared by our process can decompose to form oxides thereby giving the same result as those obtained by other methods after
25 several hours of heat treatment. The rapid calcination of oxalate powders may not be possible with precursors formed by (i) improper co-precipitation methods or (ii) other methods.

Figure 13a shows transmission electron
30 micrograph of the calcined powder and it is clearly seen from the extent of lattice fringe images with individual crystals that the particle size is less than 20 nm and the various particles are intimately mixed. Figure 4 shows an XRD of Y-123 powder made from these calcined
35 powders and Figure 13b shows a transmission electron micrograph of the $YBa_2Cu_3O_{7-d}$ (123) powder. The unit cell dimensions of this micrograph indicate the HTSC

superconducting phase is present.

Once the oxalates are decomposed to form the oxides, they are heat treated at higher temperatures to form the HTSC material. Figure 5 shows XRD patterns of oxide powders as obtained above after heat treatment for various times at 950C. It is observed that the oxides have reacted to form the HTSC material in about 5 minutes. This time is considerably reduced when compared with conventional firing periods of several hours.

The advantage with the above two step firing is that we may conveniently store powders which have been heat treated at 500C. In comparison, the dried oxalate powders tend to absorb water while the 123 HTSC compound slowly degrades under humid conditions.

Method 2:

The dried oxalate powder as obtained after drying in a vacuum oven may be directly calcined to produce the HTSC powder. In this example 80gm of oxalate powder was placed in a shallow (~1cm height) alumina boat and fired at 950C for various times in a muffle furnace. Results obtained from this procedure are shown in Figure 6.

Thus, either Method 1 or Method 2 may be used to convert the oxalates into the oxides; the high reactivity of the precursor powders to firing and subsequent transformation to HTSC material is due to (i) the proper co-precipitation of oxalate precursors and (ii) the fine, intimately-mixed nature of the co-precipitated powders.

Since the reaction time for these co-precipitated oxalate powders is in the order of a few minutes, we are able to use a variety of industrial equipment for calcinations. This equipment includes a tunnel kiln, drop tube furnace, a fluidised bed furnace and a horizontal zone furnace.

Further, due to the high reactivity of our oxide mixture (or the powder as obtained after 500C

calcination) we are able to produce pure $Y_1Ba_2Cu_3O_{7-d}$ (123) powders but with a range of particle size distributions. The mixture of oxides as obtained after 500C calcination is transferred to a refractory container and charged into a furnace. The sample may then be heat treated in different ways to yield a variety of particle sizes in a controlled manner. In each case, the material is HTSC $Y_1Ba_2Cu_3O_{7-d}$. Electron micrographs of the various powders thus obtained are shown in Figures 15a and 15b and illustrate a variety of particle sizes which can be obtained in a reproducible manner. Thus, for example, we may use the following three firing schemes :

(a) Heat the furnace at 5C/minute to 800C and hold for 20h. The furnace is then cooled at 5C/min to 475C where it is held for 5h. The furnace is then cooled to room temperature at 5C/minute. The heat treatment of this sample is carried out in an atmosphere of flowing oxygen. The particle size obtained by such a process is less than a micron as shown in Figure 15a.

(b) Heat the furnace at 5C/minute to 900C and hold for 1h. The furnace is then cooled at 5C/minute to 475C and held for 5h, after which it is cooled to room temperature at 5C/minute. The heat treatment of this sample is carried out in flowing oxygen. A typical particle size of HTSC powder thus obtained is 1micron, as shown in Figure 15b.

(c) The furnace is heated to 950C at 5C/minute and held for 30 minutes. The sample is then cooled at 5C/minute to 475C and held for 5h, after which it is cooled at 5C/minute to room temperature. The heat treatment of this sample is carried out in flowing oxygen. A typical grain size of HTSC powder obtained by this method is about 2.5micron.

EXAMPLE 3:

This example illustrates that it is possible to extrude wires from a plastic body/mass entirely consisting of co-precipitated oxalates. About 10g of wet

oxalate slurry was transferred to a mortar and pestle. The viscosity of the slurry was about that of bread dough. It was further ground in the mortar and pestle to break any possible agglomeration and to increase homogeneity. The mass was then extruded through a 0.6mm die using about 400kPa applied pressure. Binders, lubricants, or solvents were not used. Wires thus obtained were dried for 2 days at room temperature. After the wires were dry, they were placed in an alumina boat and then transferred into a tube furnace. The tube furnace was then heated from room temperature to 250C where it was held for 3 hours, at the end of which it was heated at 5C/minute to 960C. When the furnace reached 960C it was held for about 10 minutes and then shut down and allowed to cool. The entire heat treatment was performed in a flowing oxygen atmosphere. It is observed that the wire held shape, although there was a significant amount of porosity. However, the wire sample showed a superconducting transition at 91K as observed by a magnetic susceptibility measurement. If the wire is heated directly to 960C without the 250C hold, it breaks into pieces due to a fast release of water. Figure 11 shows a plot of resistivity v temperature of such a wire.

EXAMPLE 4:

This example shows that oxalates and 123 and/or other HTSC compounds can be mixed to still form a plastic mass which can then be formed into a shaped ceramic.

About 10g of calcined $Y_1Ba_2Cu_3O_{7-d}$ (123) powder is mixed with about 5g of co-precipitated oxalate paste. The oxalate paste had a viscosity about that of toothpaste. The mix was ground in a mortar and pestle by hand to increase homogeneity and break any possible agglomeration. It was then extruded through a 0.6 mm die using about 400kPa applied pressure. The wires thus formed were dried at room temperature for about 2 days. After adequately drying, the wires were placed on an alumina boat and transferred into a tube furnace. The

furnace was then heat treated at 5C/minute to 250C where it was held for 3 hours, after which it was heated at 5C/minute to 970C. At 970C the furnace was held for 10 hours, after which it was cooled at 5C/minute to 450C where it was held for 5 hours. The entire firing process was carried out under flowing oxygen. Figure 7 shows a superconducting transition in a sample of wire made by this process, as evidenced by a sharp drop to zero resistance when cooled to below 91K. Figure 8 shows an XRD plot of a sample of wire made by this process. XRD on the surface shows a high degree of orientation which is illustrated by increased intensity of the 001 reflections. A typical critical current density, J_c , of a sample made by this process is about 10^2A/cm^2 .

15 EXAMPLE 5:

This example illustrates that a more conventional process of adding binder to the HTSC compound may be used to fabricate shapes such as wires. However, due to the inherent fine particle size and homogeneity of our powders, we may reduce the amount of such binders to about 2 weight percent. In conventional processes which require additions of binder, this fraction is greater than 10 weight percent. As a consequence of such reduction in organic binder, less material which is non-superconducting need be removed from the sintered body and thus, we are able to obtain dense wires with high current carrying capacity.

Wires have been extruded using the more conventional route in which a binder is added. 10g of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-d}$ (123) powder as made by calcination of the co-precipitated YBCO oxalate precursor was mixed with 0.2g of commercial HPMC (binder) and 50ml of water by means of a magnetic stirrer in a glass beaker. In about 40 minutes, sufficient water had evaporated to leave a residue that had viscosity similar to toothpaste. This viscous mass was then extruded and processed as in Example 2 listed above. Magnetic susceptibility and

phase purity results obtained from this sintered wire are similar to those for Example 2. The magnetic susceptibility plot for this wire sample after sintering is shown in Figure 9. However, the current carrying capacity J_c , as measured on a 0.6mm diameter wire over lengths of several millimetres, is $\sim 10^3 \text{A.cm}^{-2}$. The variation of critical current density, J_c , measured by transport, for wires prepared by this method and sintered for various temperatures is shown in Figure 10. Repeat measurements of J_c for different samples processed by the same methods are also shown in this figure.

EXAMPLE 6:

The co-precipitation process gives an oxalate mixture that is inherently plastic and can stay in suspension without the use of defloculants. In fact, the oxalate powder used in this process, once dried, can be re-suspended in water without the addition of any organic agent. Therefore, it becomes possible to use, for forming, an aqueous mix of oxalates either by themselves or with varying amounts of calcined HTSC powder and other additives such as silver and/or superconducting compounds. It further becomes possible to mix these additives in solution, thereby obtaining intimate mixing at an extremely fine-scale (e.g. sub-micrometer).

A slurry is prepared by addition of water to oxalate co-precipitate powder in a glass beaker. The slurry is continuously mixed by a magnetic stirrer and water is added till the slurry pours evenly. A mold was prepared from plaster of paris using a preformed crucible or some other suitable shape. The slurry is poured into the mold, and after about 5 seconds, drained out. In this manner, a coating of the slurry mixture (e.g. YBCO precursor oxalates) remained on the mold. After about 2 hours, the coating releases itself from the mould and can be easily extracted and left to dry in open air. Such a process of slip casting a ceramic slurry is known.

In order to increase resistance to cracking

during drying of the cast form, oxide powder or HTSC compounds may be added to the slurry. The oxide powder is obtained by calcining oxalates at 500C. Both calcined oxide powders and HTSC compounds behave similarly in this type of oxalate slurry, and therefore, provide similar products upon suitable firing.

EXAMPLE 7:

The example illustrates the use of a co-precipitated oxalate slurry, made by dissolution of a dried oxalate powder, with an addition of HTSC oxides for the slip-casting of shapes which show superconducting properties and a critical current density $>10^2 \text{ A.cm}^{-2}$.

The following describes one specific example to make a crucible of approximate dimensions 1.0cm diameter, 1.0cm height with 1.0mm thick walls.

6.0 g of oxalate powder is added to 60ml of water in a glass beaker and mechanically stirred by magnetic stirrer for 3 days. After this time, it is observed that the mixture had become quite viscous and poured like honey. To this viscous mixture was added 12.0g of oxide powder. This oxide powder had been prepared by calcining dry oxalate powder to 500C for 10h in a muffle furnace. A homogenous mix is obtained in about 5 minutes, and then the slurry is poured into a pre-formed plaster of paris mould. After about 30 seconds, the slurry is poured out, thereby leaving a coating about 1.5mm thick on the inside of the mould. After about 2hours, the cast mixture of oxalate and oxide releases from the mould and retains the shape of the mould. The "green-body" in the shape of a crucible is dried in air for 3 days. Once dried, it is then fired to sinter the body, thereby forming the superconducting compound (e.g. $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-d}$ (123)) in the shape of the crucible. This sintered body also maintains sufficient mechanical strength to withstand handling and to contain liquids, such as liquid nitrogen.

A suitable firing scheme for these slip-cast bodies may involve firing the "green-body" crucible at

0.5C/minute to 500C, where it is held for 2h. This first firing allows the water to escape very slowly, thereby limiting the formation and propagation of cracks. After the hold at 500C, the furnace is heated at 5C/minute to
5 960C and held for 2h, after which the furnace is cooled to 475 C and held for 5h. The hold at 475C is essential for converting a maximum proportion of the tetragonal phase (YBCO) to the superconducting orthorhombic phase. The complete firing scheme may be undertaken in a flowing
10 oxygen atmosphere, or, as also demonstrated, in air.

An electron micrograph illustrates the fine grained morphology of the surface of slip cast bodies and the high bulk density (>90%). An optimum selection of the firing scheme may be used to texture (*i.e.* grain
15 orientation) or to improve individual grain morphology. Figure 12 shows magnetic susceptibility measurements on pieces of slip cast crucible fired at 960C (curve "a"), 930C (curve "b") and 910C (curve "c") for 10 hours in flowing O₂. It is observed that there is a superconducting
20 transition at 91K as is expected for Y₁Ba₂Cu₃O_{7-d} (123) material. Critical current density measurements on a piece of the crucible using a four-point probe yielded a J_c value of ~200A.cm⁻² at 77K and 0T field for transport of electrons over millimetre lengths.

25 EXAMPLE 8:

This example shows the use of a slurry to add Y₂BaCuO₅ (211), which is non-superconducting, in a defined fashion - in terms of size, amount and shape - to use as
30 part of flux pinning experiments in which the objective is to surround small grains of 211 phase with 123 material.

About 10g of calcined Y₁Ba₂Cu₃O_{7-d} (123) powder is mixed with about 5g of co-precipitated Y₂BaCuO₅ (211), oxalate paste. The oxalate paste has a viscosity about
35 that of toothpaste. The mix was ground in a mortar and pestle, or by a mechanised mixer under mild vacuum. These latter mixing methods allow controlled mixing conditions

as well as de-airing of the oxalate+HTSC mixture. This mixture was then extruded through a 1.0 mm die using about 400kPa applied pressure. The wires thus formed were dried at room temperature for about 2 days. After
5 adequate drying, the wires were placed on an alumina boat and transferred into a tube furnace. The furnace was then heat treated at 5C/minute to 260C where it was held for 3 hours, after which it was heated at 5C/minute to 990C. At 990C the furnace was held for 10 hours, after
10 which it was cooled at 5C/minute to 450C where it was held for 5 hours. The entire firing process was carried out under flowing oxygen. Figure 16 shows the results from magnetic susceptibility measurements for this wire. The result shows that the sample becomes superconducting
15 at the transition temperature of $\sim 91\text{K}$. The current carrying capacity, J_c , of this wire is $\sim 300\text{A.cm}^{-2}$. A method to obtain higher performance of superconductivity, particularly under an applied magnetic field, involves dispersion of 211 phase into a 123 matrix. This potential
20 use of 211 phase to provide pinning centres has been described in *Supercond. Sci. Technol.*, 4, S49, 1991. This example demonstrates that an intimate mixture of 211 and 123 phases may be made at a sub-micron scale through the use of an oxalate slurry formed by the
25 co-precipitation process.

EXAMPLE 9:

This example illustrates the application of the process of co-precipitation to the manufacture of the compound $\text{Y}_2\text{Ba}_1\text{Cu}_1\text{O}_5$. It further illustrates that our
30 process may be used to successfully manufacture copper oxide-based compounds other than the 123 stoichiometry. Whilst the compound $\text{Y}_2\text{Ba}_1\text{Cu}_1\text{O}_5$ is not known to be superconducting, it is used for a variety of HTSC-related applications, including those for doping and as a
35 substrate. The chemicals are taken in the molar stoichiometry Y:Ba:Cu :: 2:1:1

45.16g yttrium oxide is added to a 1 litre

capacity flask. To the flask are also added 100ml concentrated nitric acid and the volume is made to 1 litre by addition of de-ionized water. The mixture is mechanically stirred till it becomes clear. A typical pH value of the clear solution thus obtained is 0.15.

52.47g of barium nitrate is added to a 1 litre flask. To the flask are also added 49.29g of copper nitrate and the volume is made to 1 litre by addition of de-ionized water. The mixture is mechanically stirred till it becomes clear. A typical pH value of the clear solution is 4.1.

The two solutions above are now mixed together to obtain a clear solution. A typical pH value of this clear solution is 1.0. (Alternatively, we may add only 500 ml to the mixture of barium and copper nitrate. The two nitrate solutions when mixed will have a typical pH value of 0.7. If further water is added to a maximum of 500ml, the buffering effect may be seen).

To a 2 litre container is added 126.07g of oxalic acid and the volume is made to 2 litre by addition of de-ionized water. The mixture is mechanically mixed till it becomes clear. A typical pH of this solution is 3.5. To the oxalic acid solution is added 150ml of ammonium hydroxide. The pH is now typically at 3.9. Alternatively a mixture of ammonium oxalate and oxalic acid may be used to achieve the same pH.

Using the on-line mixing and centrifuge assembly as described in example 1, the nitrate solution is mixed with the oxalic acid solution, thereby obtaining co-precipitation of yttrium, barium, copper oxalates and mixed cation oxalates. A typical pH of the reacted mix is 1.3.

The slurry thus obtained is dried in a vacuum oven at the boiling point of water. The dry mass is extracted in about 12 h and ground by a food processor. The loose powder may then be further ground by a mortar and pestle.

The ground oxalate powder is transferred to a refractory container and charged into a muffle furnace. The furnace is heated at 5C/minute to 500C and held for 10h. The furnace is then cooled to room temperature. The powder, now black is hand ground in mortar and pestle, and charged into the furnace as before. The furnace is heated to 980C and held for 12 h. It is then cooled at 5C/minute to room temperature. The green powder obtained is characterized by x-ray diffraction and electron microscopy to be pure $Y_2Ba_1Cu_1O_5$, as shown in Figure 19.

Similar to Example 1, we may heat treat the 500C calcined powder at different temperatures and times to obtain a variety of particle size distributions.

EXAMPLE 10:

This example illustrates the process of co-precipitation as applied to the manufacture of bismuth- and lead-based HTSC precursor and compounds of the formula $(BiPb)_2Ca_2Sr_2Cu_3O_{10}$. The chemicals are weighed in the molar stoichiometry (Bi:Pb):Sr:Ca:Cu :: (1.65:0.35):2:2:3.

100.05g of reagent grade bismuth nitrate $Bi(NO_3)_2 \cdot 5H_2O$ is charged into a 1 litre flask. To this are added 25ml concentrated nitric acid and the volume is made up to 300ml by adding de-ionized water. The mixture is mechanically stirred till it becomes clear. The pH of the clear solution is typically 0.1.

In a 1 litre beaker are charged reagent grades of 14.5g lead nitrate $Pb(NO_3)_2$, 52.91g strontium nitrate $Sr(NO_3)_2 \cdot 4H_2O$, 59.04g calcium nitrate $Ca(NO_3)_2$ and 90.6g copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$. To these powders are added 300ml of de-ionized water and mechanically stirred till the solution is clear. The pH of the clear solution is typically about 2.4.

The two solutions noted above are mixed together and mechanically stirred for 10 minutes. The pH is now continuously monitored. At this stage the mixed solutions have a pH of 0.15. As the volume of the

solution is made to 1 litre, the pH of the mix rises to 0.45. Just as in Example 1, addition of water initially does not change the pH perceptibly. However, with further addition, a buffer effect is observed at a pH of about
5 0.4.

To a 6 litre flask are charged 190.0g reagent grade ammonium oxalate $(\text{NH}_4\text{COO})_2\text{H}_2\text{O}$ and 4 litres of de-ionized water. The mixture is mechanically stirred till it becomes clear. A typical pH value of this clear
10 solution is 6.6.

The solution of ammonium oxalate and the solution of nitrates are then mixed together using the peristaltic pumps and filtered using the centrifuge as described in Example 1. A typical pH of the precipitated
15 mixture is 1.6, with an average variation of less than +0.2.

The precipitate is dried in a vacuum drying oven at the boiling point of water and in about 12 hours the precipitate is dry. It is then ground by a food
20 processor followed by mortar and pestle to obtain a fine light blue coloured powder.

The powder is then calcined to convert the oxalates to a fine mixture of oxides. This may be done in a muffle furnace where the powder, in a refractory
25 container, is heated at 5C/minute to 500C for 10h, and cooled to room temperature at 5C/minute. High resolution transmission electron micrographs of this calcined powder show that the powder consists of intimately mixed oxide grains of size less than 20nm. X-ray microanalysis shows
30 that these grains are typically oxides of copper, bismuth, calcium, strontium or lead, depending on the copper-oxide family under consideration.

The powder obtained above is then converted to HTSC precursors or HTSC materials as described in Process
35 1 and Process 2.

Process 1 : This process of heat treatment gives a precursor which is ready to be converted into the

three layer HTSC superconductor $(\text{Bi,Pb})_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$. The powder obtained after calcining at 500C is transferred into a muffle furnace. The furnace is then heat treated at 5C/minute to 800C and held at this temperature for 2h. It is then cooled to room temperature at 5C/minute. The powder is ground up by hand and then placed into the muffle furnace. The muffle furnace is heat treated at 5C/minute to 840C and held for 10h. The furnace is then allowed to cool down to room temperature and the powder taken out. The powder is re-ground and then charged into the furnace and heated again at 5C/minute to 840C where it is held for 10h. The muffle is then cooled to room temperature at 5C/minute. The powder thus obtained is a suitable precursor for making the compound $(\text{Bi,Pb})_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$. Figure 18 illustrates, by XRD (Figure 18a) and SEM micrographs (Figures 18b and 18c), the development of various phases during the conversion of the initial oxalate to the final precursor. Our process allows the synthesis of this precursor in various particle sizes. These various particle sizes achievable, gives greater flexibility in processing of the powders, particularly in wire manufacture by the process known as "powder-in-tube".

Process 2 : This process converts the precursor obtained in Process 1 to the superconductor phase $(\text{BiPb})_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$. The precursor powder obtained in Process 1 is pressed into a disk, for example, less than 2cm diameter and about 0.5cm thick. The disk is placed on a refractory setter such as MgO and transferred into the muffle furnace. The muffle is heated at 5C/minute to 860C and held for 15h. The sample is then cooled to room temperature at 5C/minute. Figures 17, 20A-C illustrates, by XRD, SEM and magnetic susceptibility data, the development of the three layer HTSC compound $(\text{Bi,Pb})_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$ via this process. Note that a high phase purity (about 99.9%) is obtained by this process and the superconducting transition has an onset

temperature of 108K.

EXAMPLE 11:

This example illustrates the process of co-precipitation as applied to the manufacture of bismuth- and lead-based HTSC precursor and compounds of the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ (or 2212). Reagent grade chemicals are weighed according to the molar stoichiometry : Bi:Sr:Ca:Cu :: 2:2:1:2.

100g bismuth nitrate is added to a 1 litre flask. To this flask is added 50ml nitric acid and the mixture shaken to dissolve most of the bismuth nitrate. De-ionized water is added to make the volume to 1 litre and the mixture is mechanically stirred till it becomes clear. A typical pH value of the clear solution is about 0.15.

43.64g strontium nitrate, 24.33g calcium nitrate, 49.83g copper nitrate are added to a 1 litre flask. De-ionized water is added to make the solution to 1 litre and mechanically stirred till the solution becomes clear. A typical pH value of the clear solution is 3.4.

The two nitrate solutions are mixed and mechanically stirred for 10 minutes. A typical pH of the clear solution is 0.4.

142.11g ammonium oxalate is added to a 4 litre container and the volume made up to 4 litres by adding de-ionized water. The mixture is mechanically stirred till it becomes clear. A typical pH of the clear solution is 6.7.

Using the on-line mixing system and the centrifuge, the nitrate solution and the oxalate solutions are mixed to form the co-precipitate and the slurry collected in the centrifuge. A typical pH of the reactant mix is 1.2, with an average variation of ± 0.1 .

The precipitated oxalates thus obtained are dried for 12h in a vacuum oven at the boiling point of water. The dried mass is ground in a food processor

followed by fine grinding by hand in a mortar and pestle. The blue ground powder is then transferred to a refractory container and charged into a muffle furnace for heat treatment. The furnace is heated to 500C at 5C/minute and held for 10h. It is then cooled to room temperature at 5C/minute to room temperature. The powder, now black, is ground by mortar and pestle and re-charged as before into the furnace. The furnace is heated to 800C at 5C/minute and held for 2h. It is then cooled to room temperature at 5C/minute. The powder is removed, re-ground and then re-charged into the furnace. The furnace is heated to 840C at 5C/minute and held for 10h. The sample is then cooled to room temperature at 5C/minute. The powder is removed, re-ground, and recharged into the furnace as before. The furnace is heated at 5C/minute to 840C and held as before for 10h. It is then cooled to room temperature at 5C/minute. X-ray diffraction data in Figure 14 illustrate that the powder consists of the HTSC phase $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$.

At such stage of the production of the 2212 phase, various modifications to the average particle size distribution can be made by appropriate modifications to the heat treatment.

EXAMPLE 12:

Due to the inherent plasticity present in our co-precipitated powder it becomes possible to add cationic mixtures (or compounds) containing barium, yttrium, copper, or silver (as may be required for the YBCO system) or strontium, bismuth, calcium, lead or silver (as may be required for the BSSCO system). The addition may be made to dried co-precipitated powder which may contain one, few or all of the cations required in the desired final compound. The process may be facilitated through water medium to permit a simple drying operation.

The already dried co-precipitates are ground up and transferred to water where they are stirred by a

mixer. This mixing makes a finely dispersed suspension. In a separate container is prepared a solution of the new or additional cation. This solution is then mixed to the co-precipitate solution, which is then stirred and
5 evaporated to dryness. Because the co-precipitated powders have the ability to form a fine suspension with water, it allows remixing of dried powders with fresh powders/precipitates/solution.

Example: To add barium cation to a co-precipitated mixture which has the molar ratio Y:Ba:Cu::
10 1:1.5:3.0 such that the final stoichiometry is 1:2:3.

The starting co-precipitate is made by the process described earlier in the text and consists of yttrium, barium, and copper oxalates. It is determined
15 by I.C.P. (Inductively coupled plasma atomic emission spectroscopy) results that the cationic ratio of Y:Ba:Cu is 1:1.5:3.0. (Such a composition finds application in bulk HTSC shapes as it yields a fraction of the insulating compound Y-211 which is expected to act as
20 flux pinning centres). To 800 g of the dried co-precipitate powder is added 500 ml of water and the mixture is stirred vigorously. In another container 79.2g of barium nitrate is weighed out and dissolved in 1 litre of water. The barium nitrate solution is added to
25 the co-precipitate mix and stirred vigorously for 30 minutes in a blender. The blended mix is transferred to a hot plate where it is continuously stirred till almost dry. At this stage it is transferred to a vacuum oven where the mixture is allowed to dry at the boiling point
30 of water. Transmission electron microscopy on the dried powder indicated that the powder consists of well mixed cations on a nanometer level similar to powders obtained earlier. Similarly TEM on this powder after calcinating at 500C (to eliminate oxalate anion) shows that the
35 cations are well mixed on a nanometer level.

The new mix prepared may be treated in a manner similar to that described earlier in the text for co-

precipitated powders. Thus for example, we may fire it in the same manner to form superconducting Y-123. XRD and I.C.P. results confirm that the cation stoichiometry of the resulting powder is 1:2:3.

5 EXAMPLE 13:

Using the calcined co-precipitated oxalate powders, sputtering targets were fabricated. Calcined powders were ground and pressed into discs and then sintered at between 920C and 980C where the superconducting phase is stable. Since dense targets are required for thin film fabrication via a well-known sputtering process, the density of those targets were measured. It was found that a 500C calcined powder (mixture of oxides, no $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ phase) gave 40-60% higher density than high temperature (>800°C, mainly $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$) calcined powders after sintering the final products. This difference in density can be attributed to the intermediate phase/s which assist the densification during transformation from 500C calcined oxide phases to a superconducting phase.

Various other changes and modifications can be made to the embodiments without departing from the spirit and scope of the invention as claimed.

CLAIMS:

1. A method for co-precipitating superconducting precursor components, the method comprising the steps of dissolving the superconducting precursor components into solution, adding a precipitating agent to the aqueous solution, and maintaining the pH of solution substantially constant during the co-precipitation process.
2. The method as claimed in claim 1, wherein the precipitating agent confers plastic properties to the co-precipitated product.
3. The method as claimed in claim 2, wherein the precursor components are those which form high temperature superconductors.
4. The method as claimed in claim 3, wherein the precipitating agent is selected from a dicarboxylic acid, or an ester, amide, anhydride or salt thereof.
5. The method as claimed in claim 4, wherein the precipitating agent is selected from oxalic acid or ammonium oxalate.
6. The method as claimed in claim 5, wherein the pH of the solution is maintained within a range of ± 0.1 units during the co-precipitation process.
7. The method as claimed in claim 6, wherein the precursor components are yttrium components, barium components and copper components.
8. A co-precipitate obtained by the method of claim 1.
9. The co-precipitate as claimed in claim 8, which comprises co-precipitated oxalates.
10. Precursor oxides obtained by heating the co-precipitated oxalates of claim 9 to a temperature sufficient to decompose the oxalates to oxides but insufficient to convert the oxides to a superconducting composition.
11. A high temperature superconductor composition (HTSC) obtained by heating the co-precipitate oxalates of

claim 9 or the precursor oxides of claim 10 or a mixture
of co-precipitated oxalates and precursor oxides or a
mixture of oxalates and HTSC to a temperature sufficient
to convert to oxalates or oxides or the mixture to the
5 HTSC.

12. A HTSC shaped article formed by subjecting the
co-precipitate oxalates of claim 9, to a shaping step,
and heating the shaped oxalates sufficiently to convert
the oxalates to a HTSC material.

10 13. The article of claim 12 formed as a wire by
passing the oxalates through a die.

14. The article of claim 12 formed as a sheet by
applying the oxalates as a layer to a surface.

15 15. The article of claim 12 formed as a pressed
article by subjecting the oxalates to a pressing step.

AMENDED CLAIMS

[received by the International Bureau on 30 November 1993 (30.11.93); original claims 1-15 replaced by amended claims 1-24 (3 pages)]

1. A method for coprecipitating superconducting precursor components comprising:

forming a first solution containing superconducting precursor components;

forming a second solution containing a precipitating agent;

mixing the first and second solutions together while maintaining the pH of the mixed solution substantially constant during the coprecipitation process.

2. The method of claim 1, wherein the mixed solution is buffered to maintain the pH substantially constant.

3. The method of claim 2, wherein the first solution is buffered prior to admixture with the second solution to maintain the pH of the mixed solution substantially constant.

4. The method of claim 1, wherein the pH of the mixed solution is within a range of ± 0.1 pH units during the coprecipitation process.

5. The method of claim 3, wherein the first and second solutions are essentially aqueous.

6. The method of claim 5, wherein the precipitating agent confers plastic properties to the coprecipitated product.

7. The method of claim 6, wherein the precipitating agent is selected from the group consisting of dicarboxylic acid or an ester, amide, salt or anhydride thereof.

8. The method of claim 7 wherein the precipitating agent is selected from the group consisting of oxalic acid or ammonium oxalate.

9. The method of claim 7 wherein the first solution contains compounds of yttrium, barium and copper in a 1:2:3 molar stoichiometry and the pH of the mixed solution is at 1.3 ± 0.1 during the coprecipitation process.

10. The method of claim 7 wherein the first solution contains compounds of yttrium, barium and copper in a 2:1:1 molar stoichiometry and the pH of the mixed solution is at 1.3 ± 0.1 during the coprecipitation process.
11. The method of claim 7 wherein the first solution contains compounds of bismuth, lead, calcium, strontium and copper in a 1.65:0.35:2:2:3 molar stoichiometry and the pH of the mixed solution is 1.6 ± 0.2 .
12. The method of claim 7 wherein the first solution contains compounds of bismuth, strontium, calcium and copper in a 2:2:1:2 molar stoichiometry and the pH of the mixed solution is 1.2 ± 0.1 .
13. Coprecipitated oxalates formed by the method of any one of the preceding claims.
14. Oxides obtained by heating the coprecipitated oxalates of claim 13 to a temperature sufficient to decompose the oxalates to oxides but insufficient to completely convert the oxides to superconducting material.
15. A shaped article formed by subjecting the coprecipitated oxalates of claim 13 to a shaping step.
16. A shaped superconducting article formed by subjecting the article of claim 15 to a heating step sufficient to convert the oxalates to a superconducting material.
17. A superconducting composition formed by heating the oxalates of claim 13 to a heating step sufficient to convert the oxalates to a superconducting material.
18. A superconducting composition formed by heating the oxides of claim 14 to a heating step sufficient to convert the oxides to a superconducting material.
19. The shaped superconducting article of claim 16 in the form of a wire.
20. The shaped superconducting article of claim 16 in the form of a sheet.
21. A dried co-precipitated oxalate formed by

subjecting the oxalate of claim 21 to a drying step.

22. A shaped article formed by contacting the dried oxalate of claim 22 with a liquid to form a plastic mass, and subjecting the plastic mass to a shaping step.

5 23. A superconducting article formed by subjecting the article of claim 22 to a heating step sufficient to convert the oxalates to a superconducting material.

10 24. A mixture comprising the oxalates of claim 13 admixed with other superconducting precursor components, or non-superconducting components.

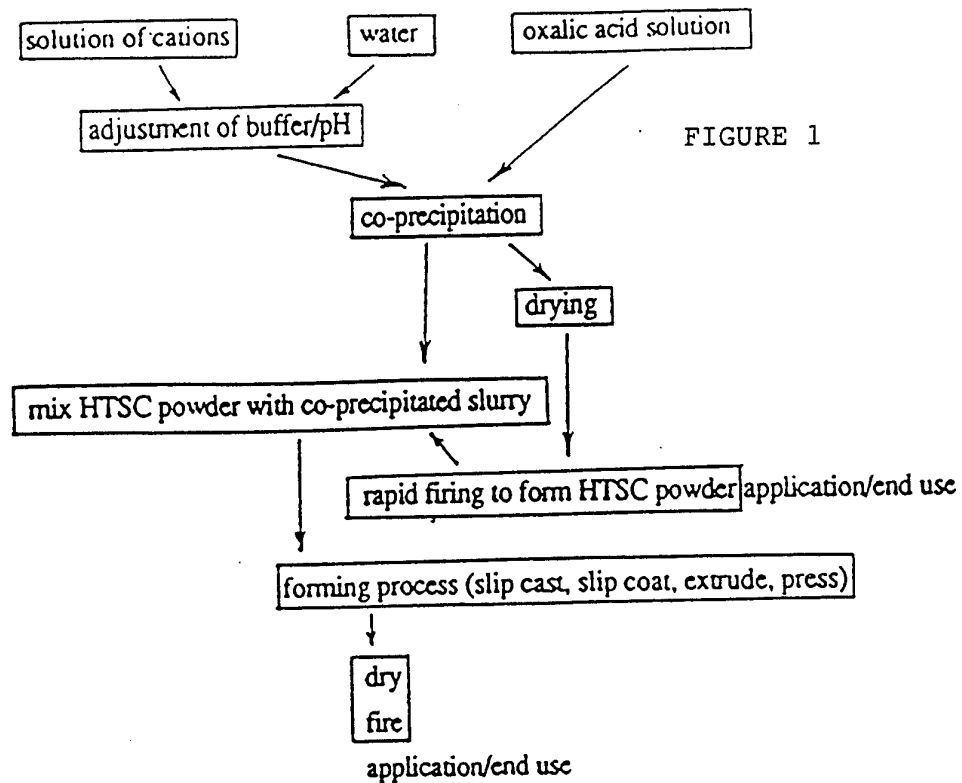
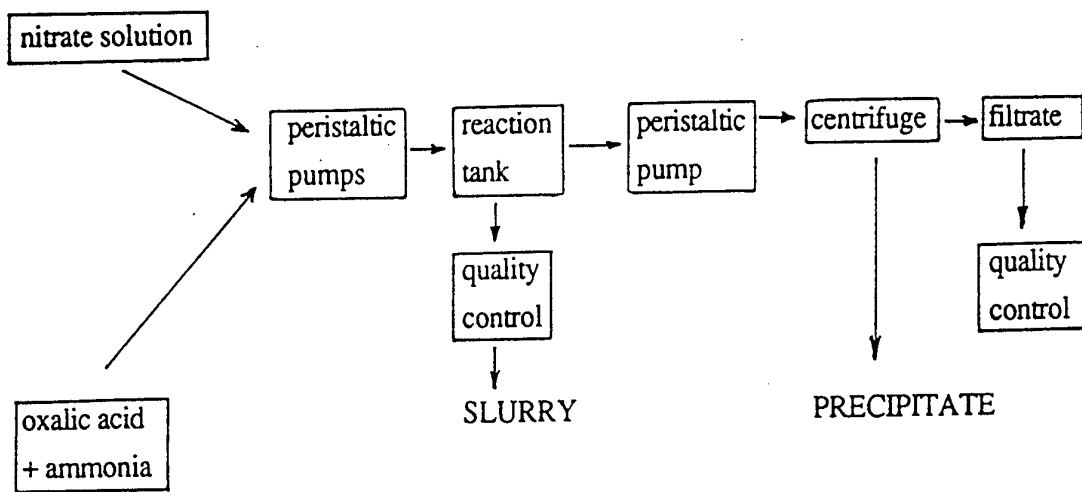


FIGURE 2



SUBSTITUTE SHEET

■ pH nitrate
▨ pH mix
□ pH oxalate

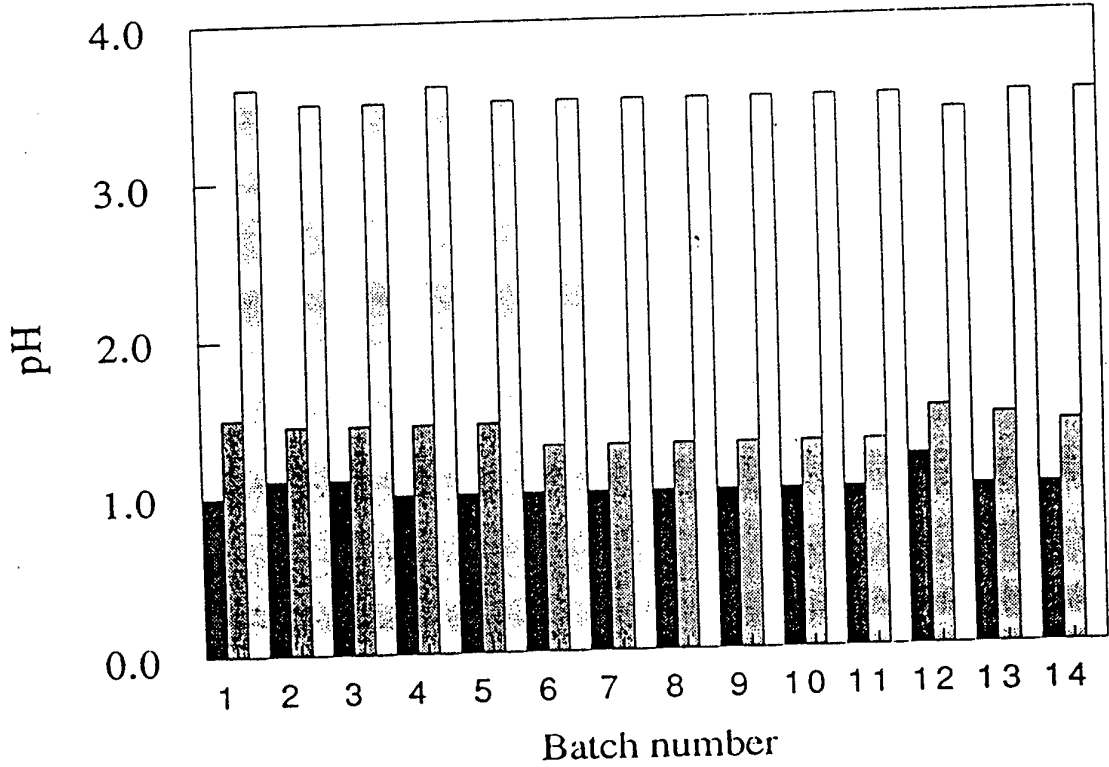
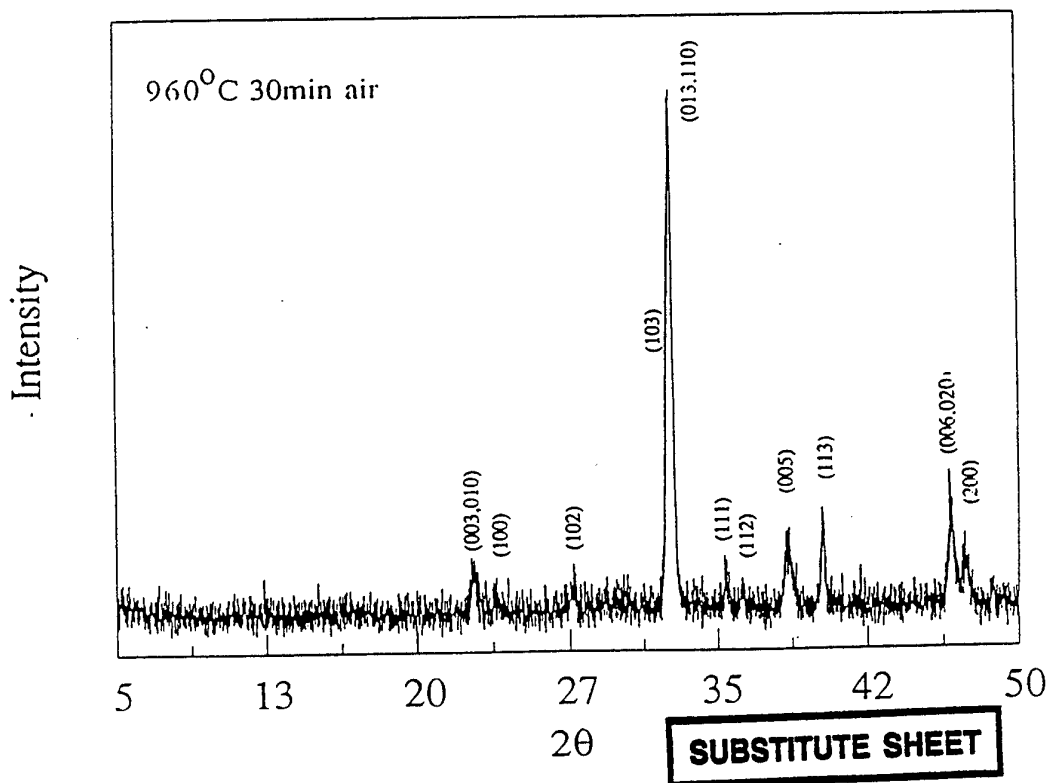


FIGURE 3

FIGURE 4



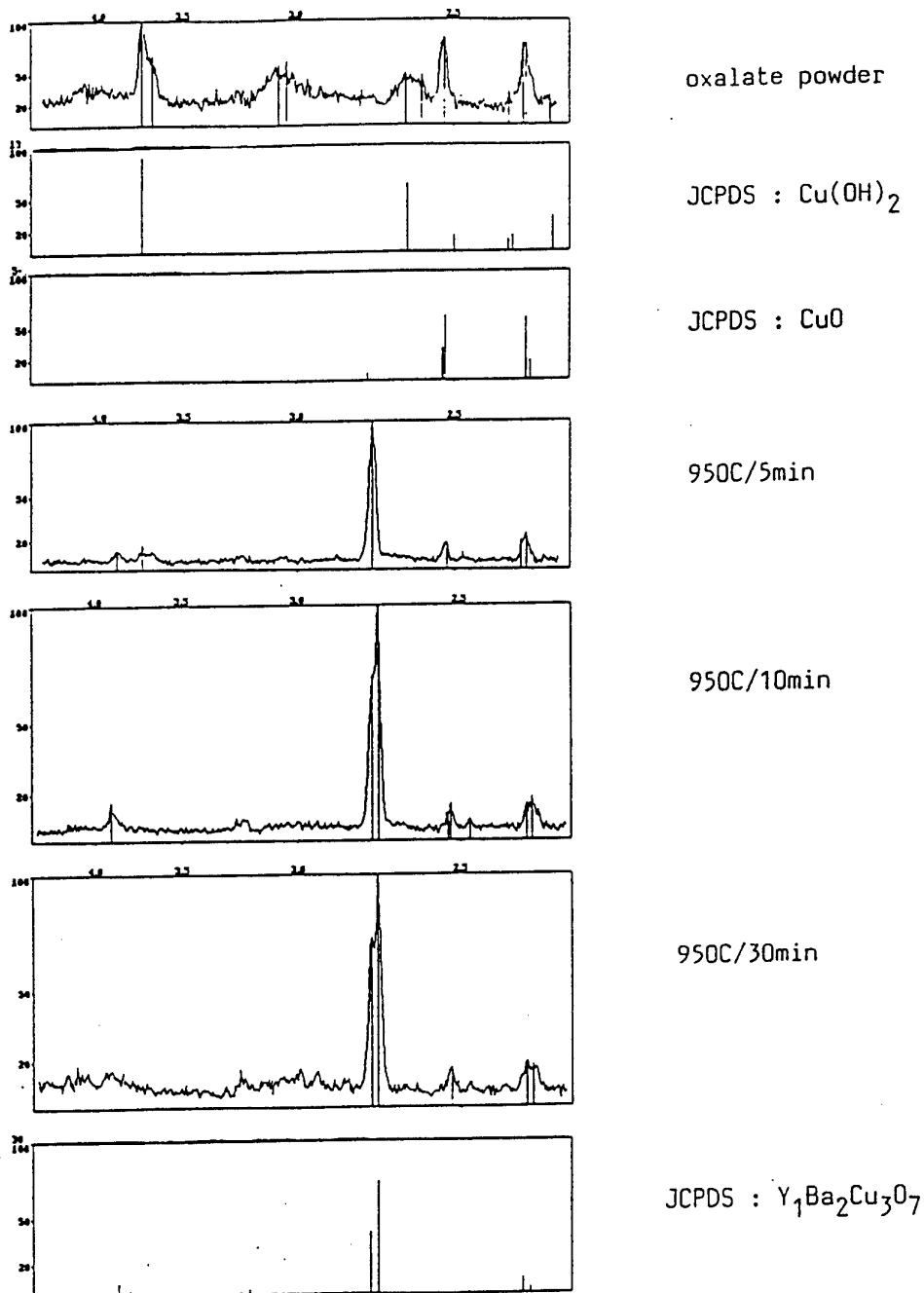


FIGURE 5

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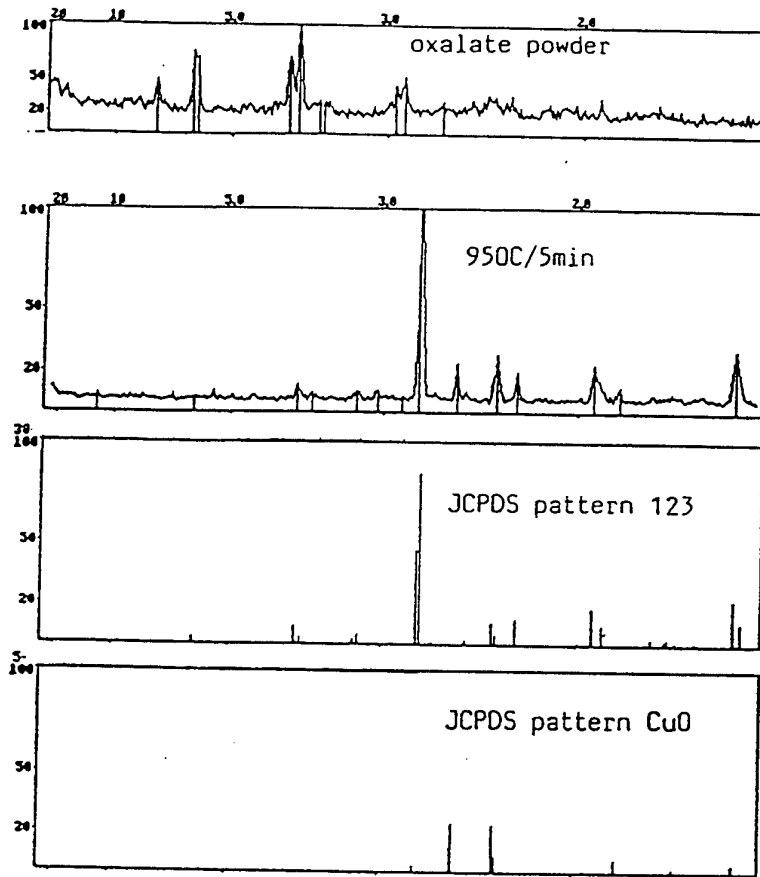


FIGURE 6

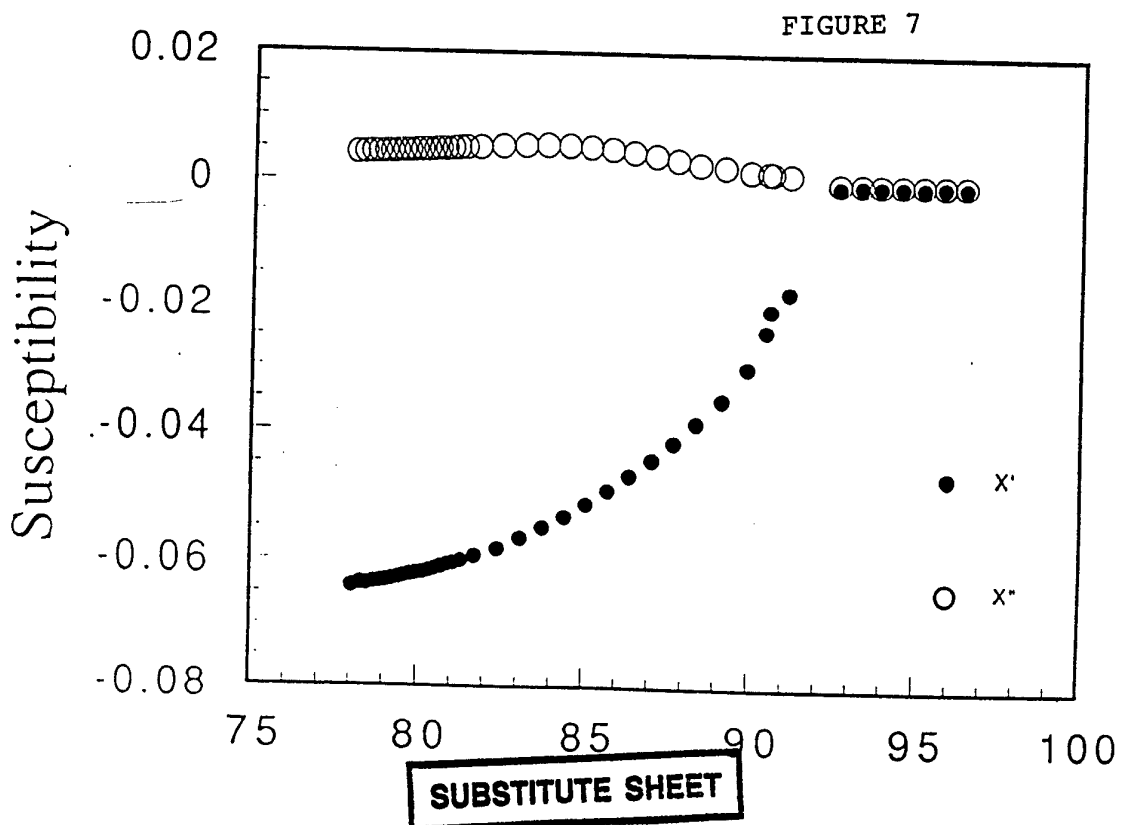


FIGURE 7

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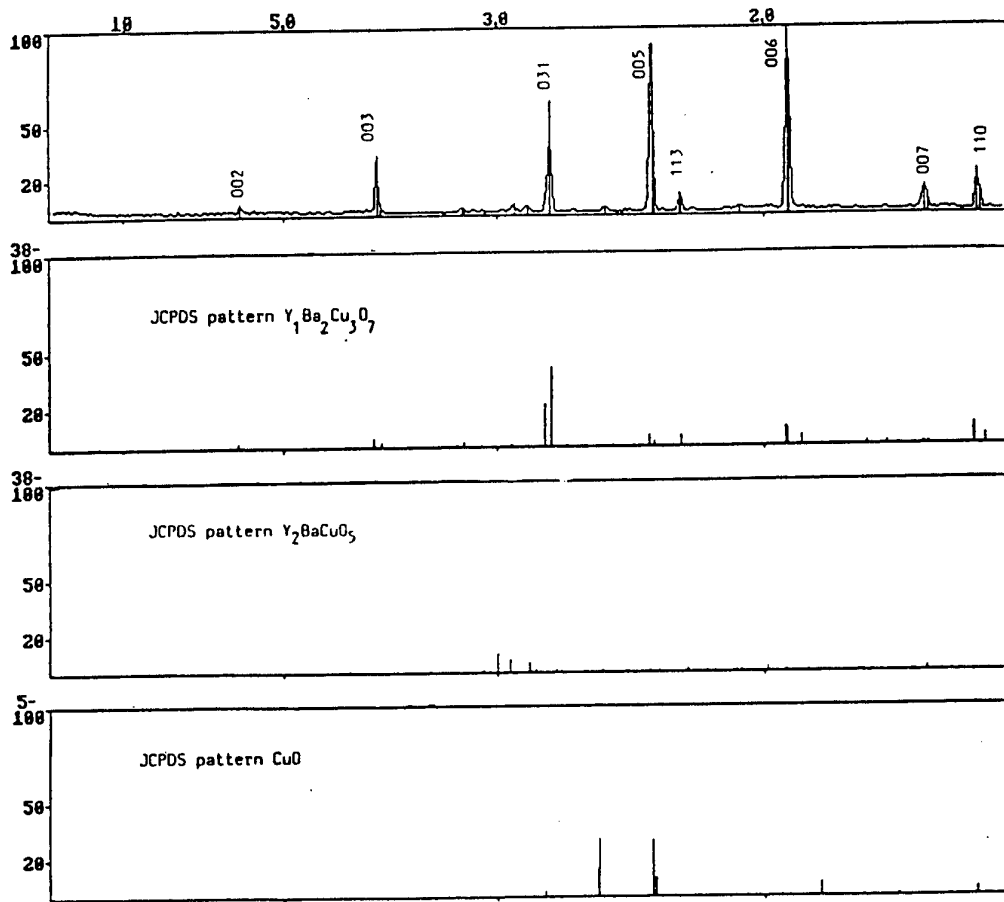


FIGURE 8

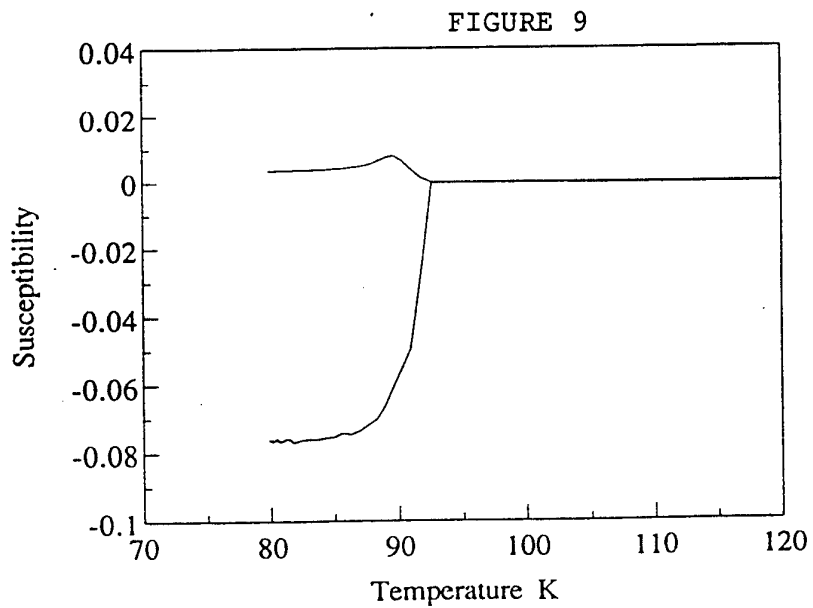


FIGURE 9

SUBSTITUTE SHEET

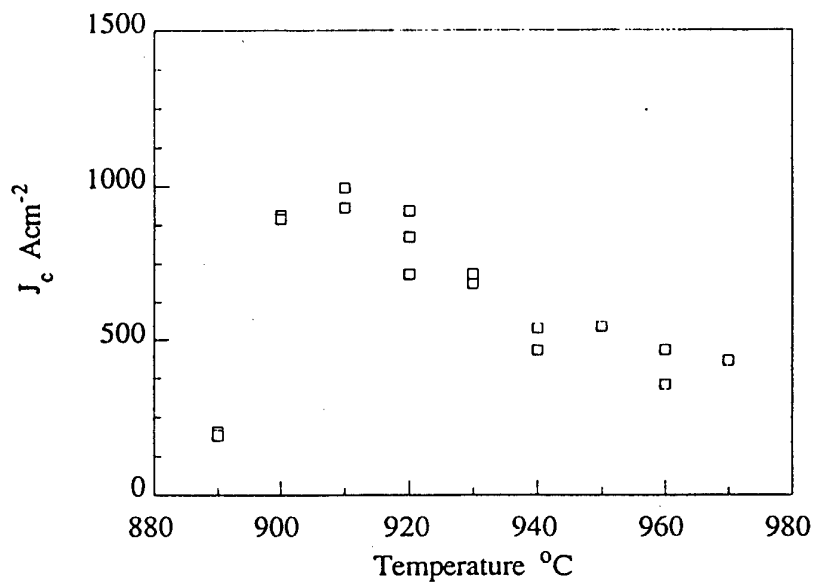
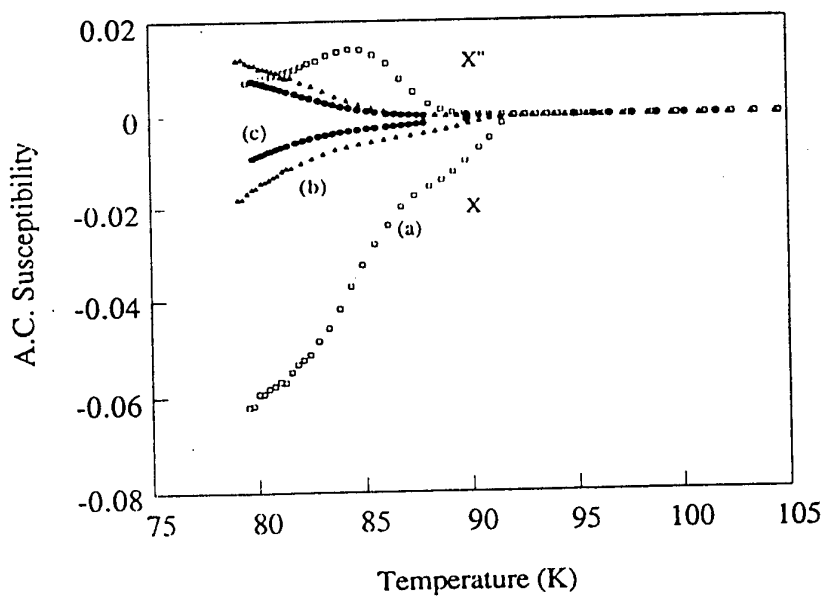


FIGURE 10

FIGURE 12



SUBSTITUTE SHEET

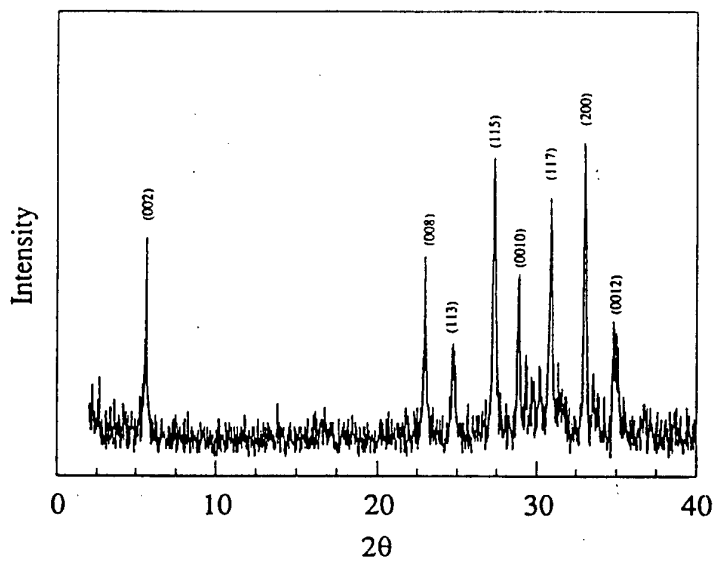
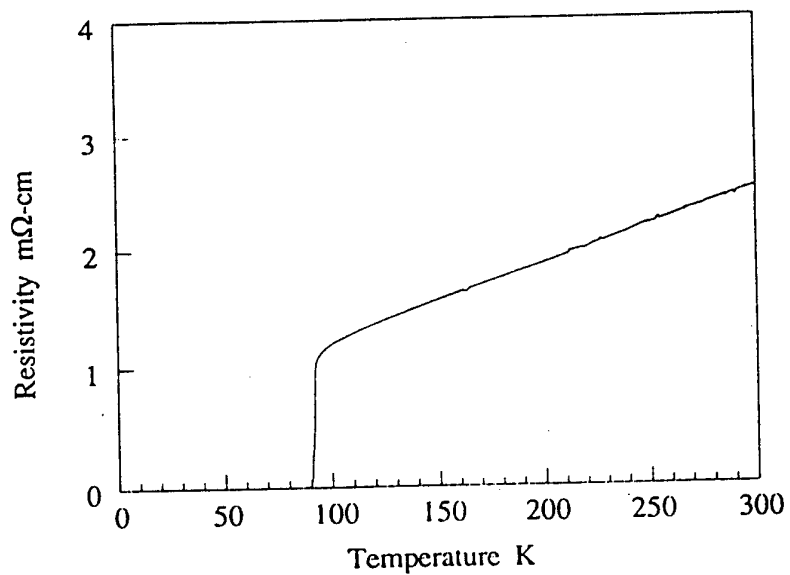


FIGURE 14

FIGURE 11



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FIGURE 13a

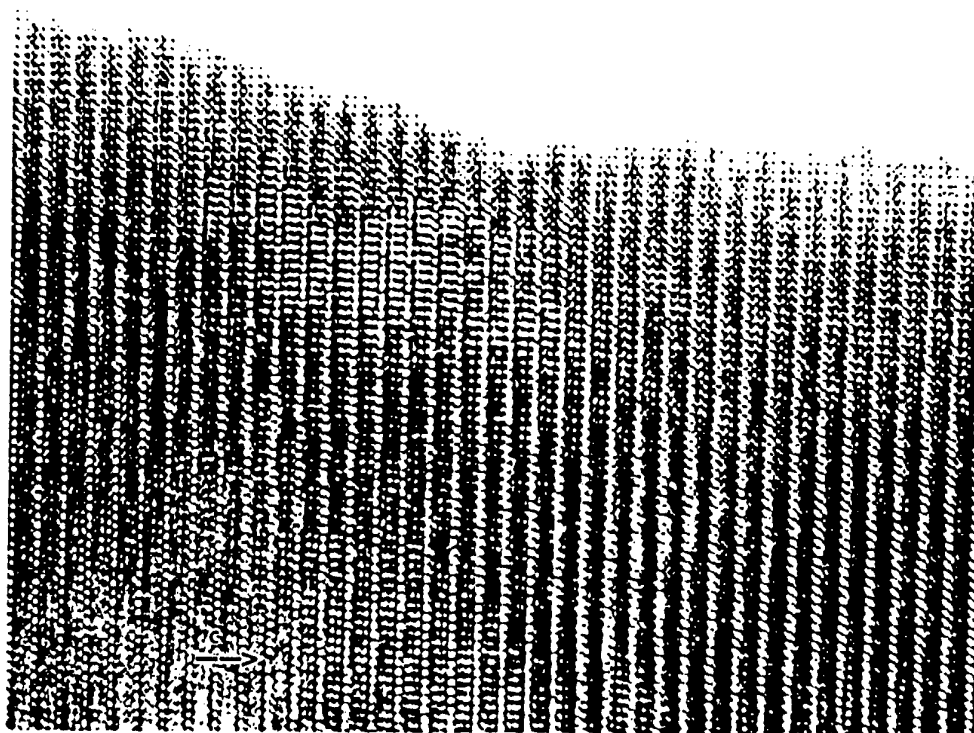


FIGURE 13b

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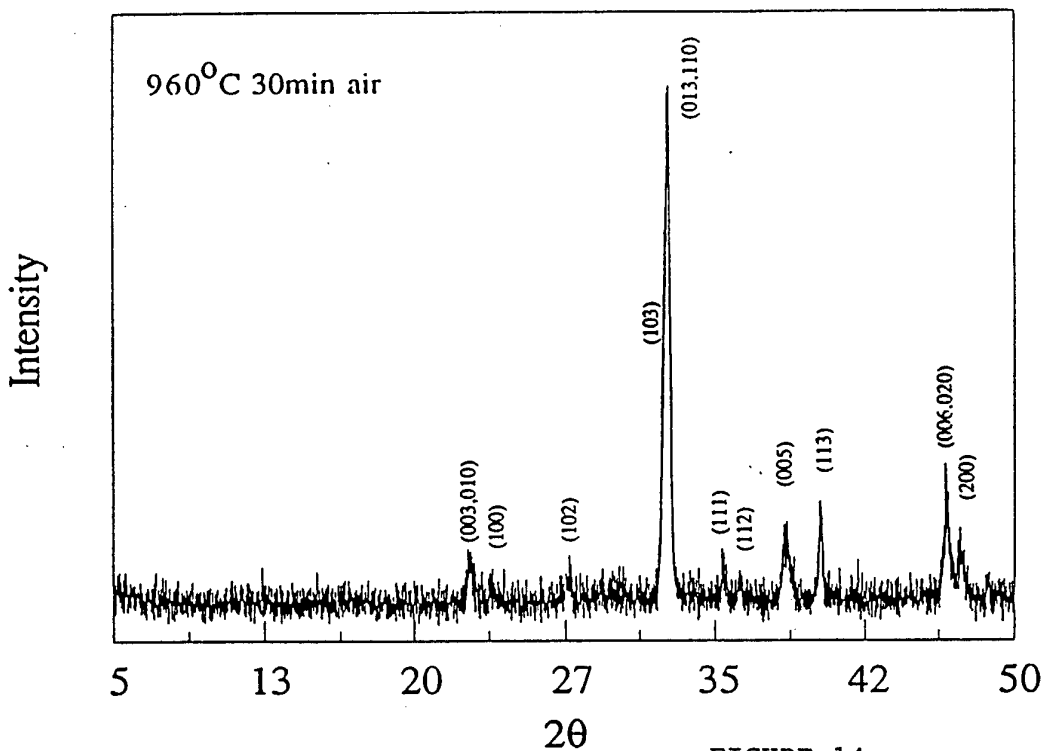


FIGURE 14

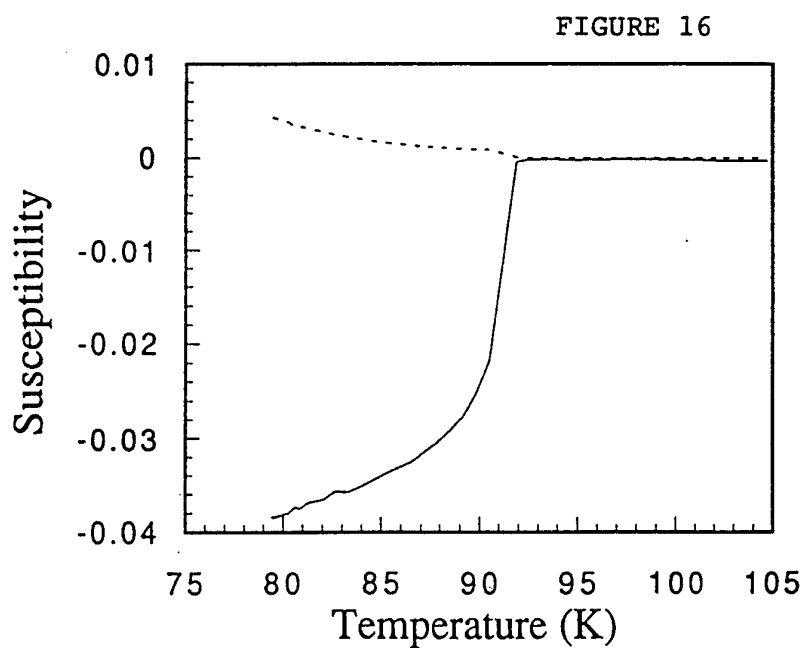


FIGURE 16

SUBSTITUTE SHEET

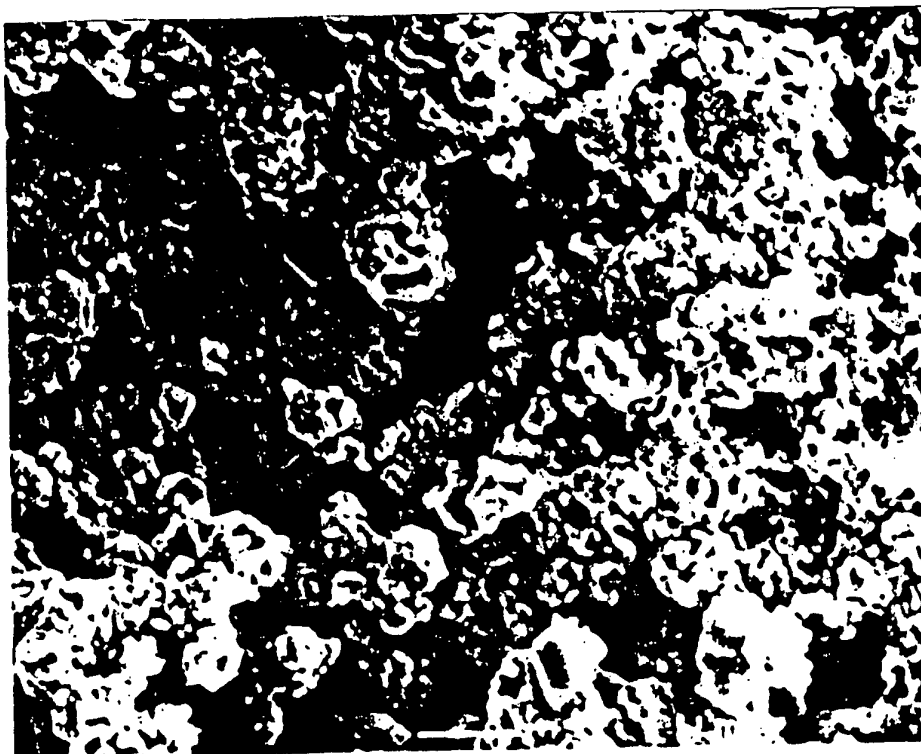
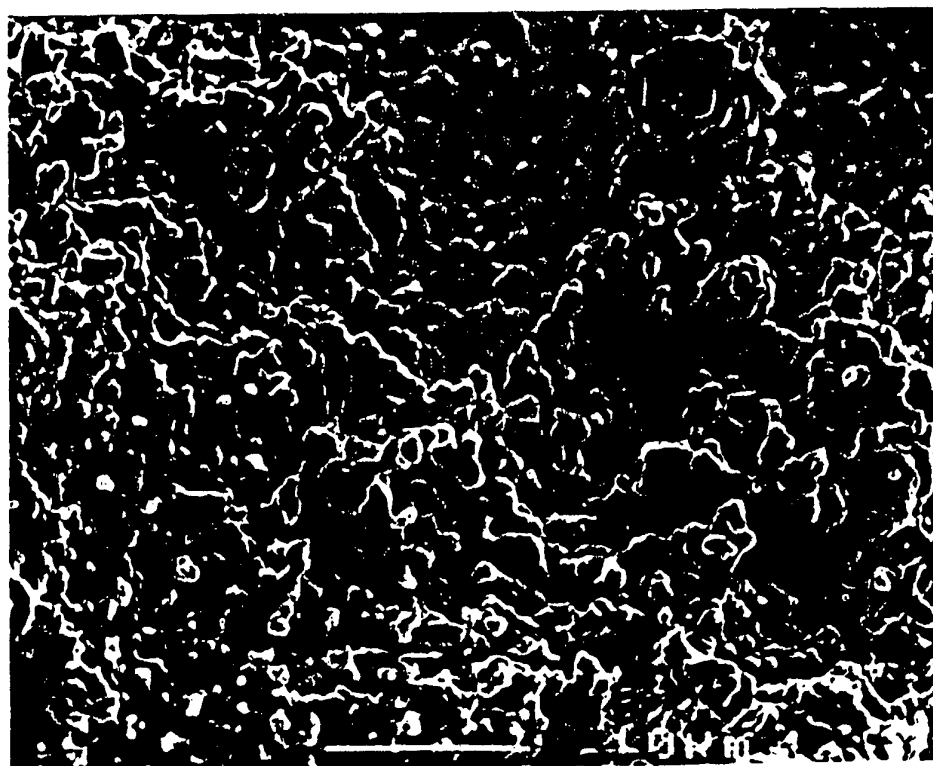


FIGURE 15a

FIGURE 15b



SUBSTITUTE SHEET

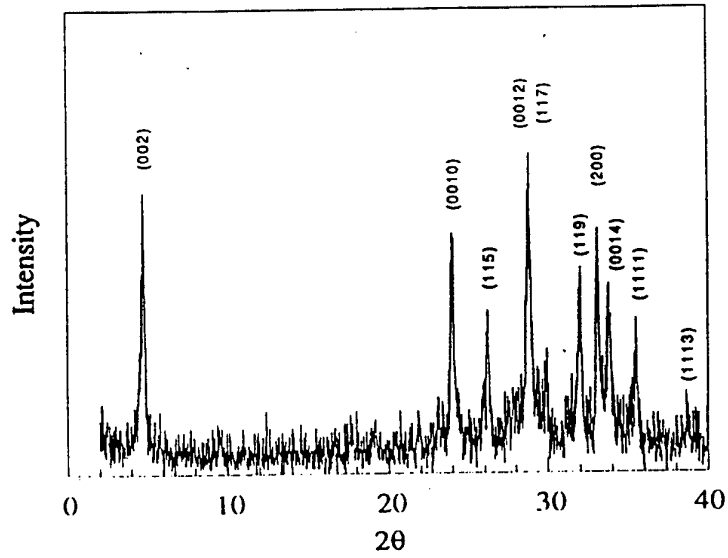
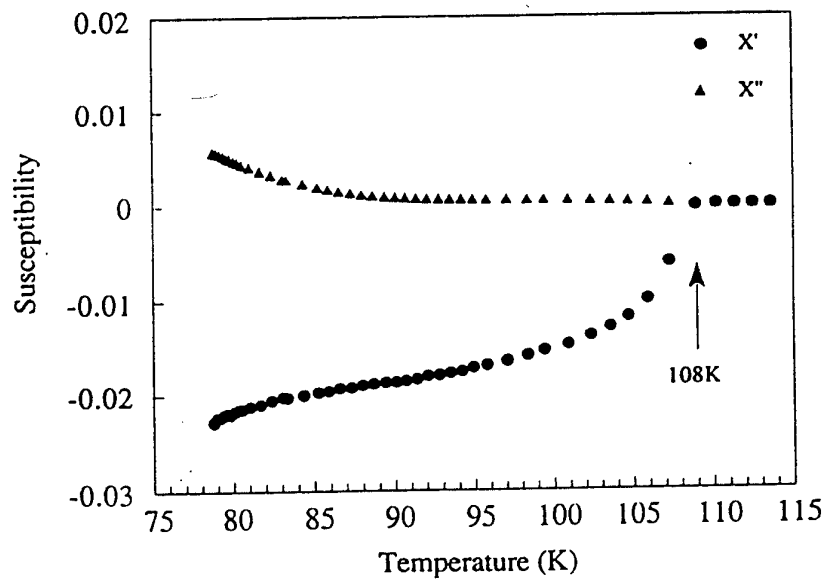


FIGURE 17

FIGURE 20c



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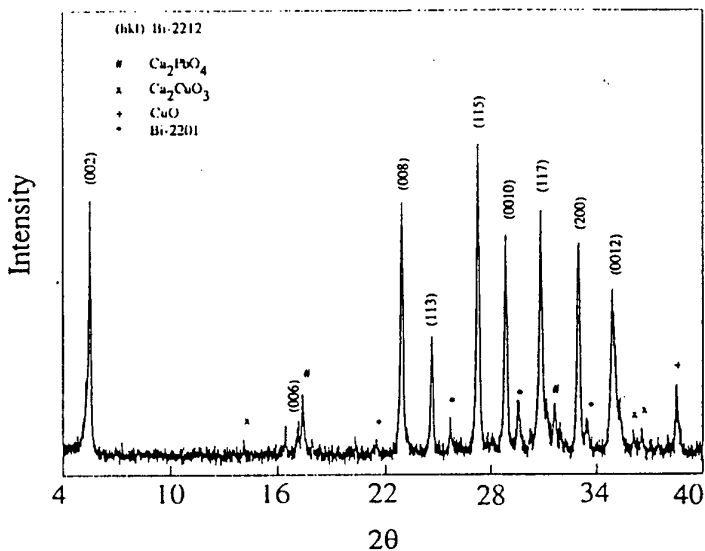
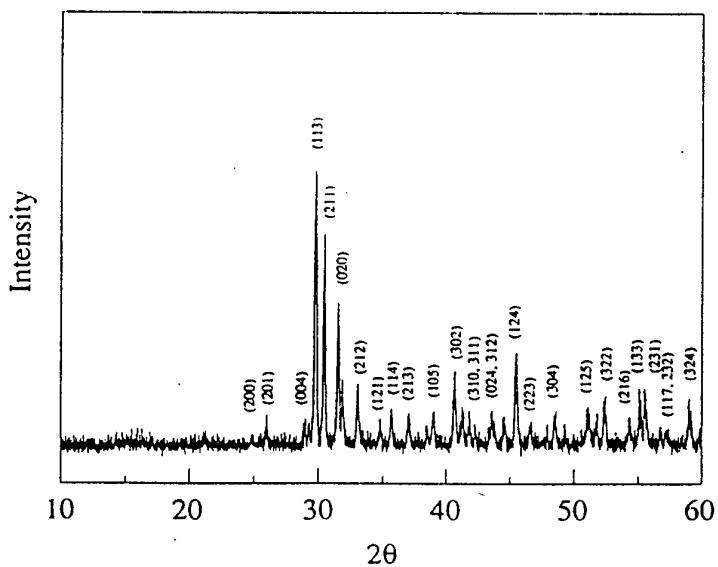


FIGURE 18a

FIGURE 19



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FIGURE 18b



FIGURE 18c

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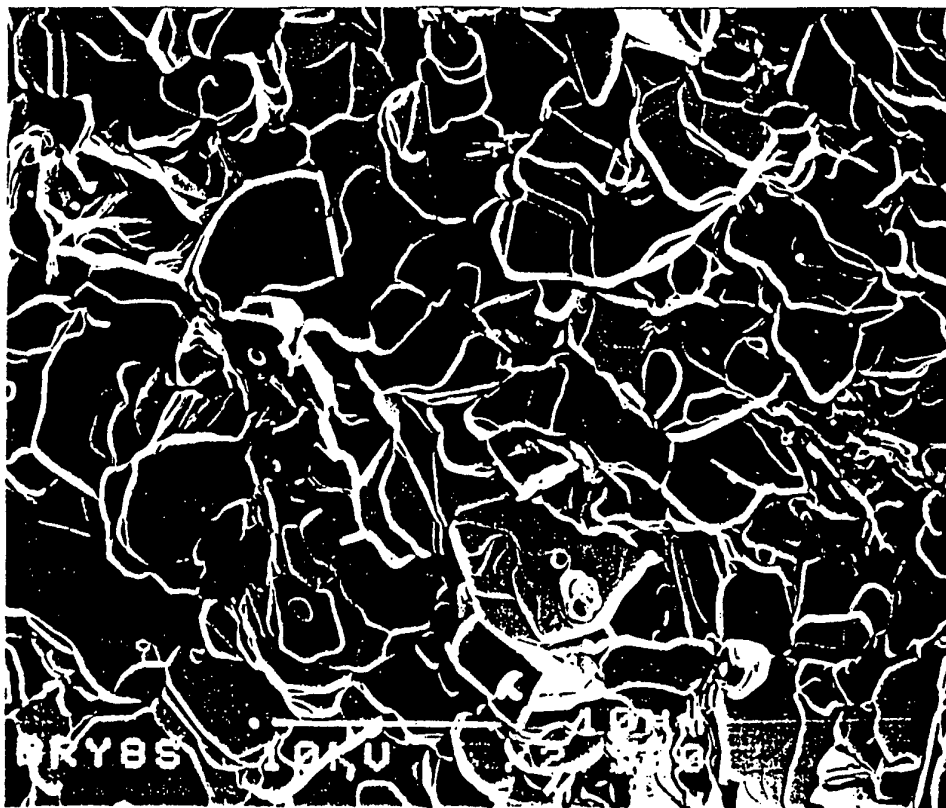


FIGURE 20a

FIGURE 20b



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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	Patent Abstracts of Japan, C-630, page 154, JP,A, 1-138120 (MEIDENSHA CORP.) 31 May 1989 (31.05.89)	1-5, 8-15
X	Patent Abstracts of Japan, C-706, page 72, JP,A, 2-22164 (MATJUSHITA ELECTRIC CO. LTD.) 25 January 1990 (25.01.90) MATSUSHITA ELECTRIC <u>IND</u> CO LTD	1-5, 8, 11-15
X	Derwent Abstracts Accession No. 89-051893/07, class U14, JP,A,64-003010 (NIPPON MINING K K) 6 January 1989 (06.01.89)	1-5, 8-15
X	Derwent Abstracts Accession No. 89-004954/01, Class U14, JP,A, 63-285116 (KOJUNDO KAGAKU KENK.) 22 November 1988 (22.11.88)	1-5, 8-15
X	Derwent Abstracts Accession No. 91-159235/22, class L03, JP,A, 3-093609 (HOKKAIDO GLUTSU IT) 18 April 1991 (18.04.91)	1-5, 8-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 93/00300

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	302418	JP	1037419	US	4956340		
US	4804649	EP	313148	JP	1141820	US	4923849
END OF ANNEX							