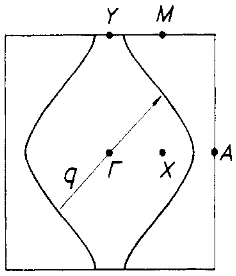

Figure 8. Fermi surface associated with the half-filled band of Figure 7. The wave vectors of the region including Γ surrounded by the two curves lead to filled band levels, while those of the other region lead to empty band levels. Here $A = (a^*, 0, 0)$.

hancement has been attributed to strong electron-electron interaction and treated by using a modified Hubbard model,[19] which corrects for the on-site repulsion of two electrons. However, recent work suggests that the enhancement of χ_ρ is most strongly dependent on the degree of charge transfer, ρ.[24] The enhancement observed for $(ET)_2C(CN)_3$, $\chi_\rho/\chi_{exptl} = 3.2$ for $\rho = 0.5$, agrees well with the latter explanation.

Band Electronic Structure

To understand the origin of the metal-insulator transition of $(ET)_2C(CN)_3$ at ~175 K, we performed tight-binding band calculations[1,25] based upon the extended Hückel method.[26] Figure 7 shows the dispersion relations of the top two occupied bands of $(ET)_2C(CN)_3$, where the dashed line indicates the Fermi level. These bands are mainly derived from the HOMO's of four ET molecules in every unit cell. With the formal oxidation of two $(ET)_2{}^+$ per unit cell, the upper band is half-filled. The Fermi surface associated with this band is shown in Figure 8, where an extended Brillouin zone scheme is used due to the folded nature of each band in Figure 7. The Fermi surface of Figure 8 shows a good nesting with the vector $\mathbf{q} \simeq a^* + b^*/2$. The presence of the $b^*/2$ component in the nesting vector suggests that $(ET)_2C(CN)_3$ would undergo a Peierls distortion that doubles the *b* axis, which would be the origin of the metal-insulator phase transition at ~175 K. These predictions were verified by very long X-ray axial photographs of $(ET)_2C(CN)_3$ at 125 K, which revealed the presence of a *b*-axis doubling as anticipated.

Concluding Remarks

$(ET)_2C(CN)_3$, synthesized and characterized in the present work, is the first 2:1 salt of ET with a planar-triangular anion. The electrical properties of this salt measured as a function of temperature show that it undergoes a metal-insulator phase transition at ~180 K. The magnetic susceptibility measured as a function of temperature and the tight-binding band electronic structure calculated for $(ET)_2C(CN)_3$ lead to the conclusion, as confirmed by X-ray diffraction observations, that the metal-insulator phase transition is caused by a Peierls transition which results from the doubling of the *b* axis.

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Supplementary Material Available: Tables of complete crystallographic data and anisotropic thermal parameters at 125 and 298 K (3 pages); tables of observed and calculated structure factors at 125 and 298 K (24 pages). Ordering information is given on any current masthead page.

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Homogeneous Coprecipitation as a Means toward High-T_c and Sharp-Transition $YBa_2Cu_3O_{7-x}$ Superconducting Oxides[1]

R. S. Liu,[2] C. T. Chang,* and P. T. Wu†

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$YBa_2Cu_3O_{7-x}$ superconducting powders have been prepared from an aqueous solution that contains Y, Ba, and Cu salts and oxalic acid via homogeneous coprecipitation using urea. The dried precipitate was found to have a stoichiometry as desired and a particle size of 0.3 ± 0.08 μm that has a specific surface area of 5.3 m^2/g. Subsequent calcination at 900 °C for 16 h and sintering at 950 °C for 16 h yielded a good superconductor with high reproducibility. The resulting powder has a T_c at 93 K with a sharp-transition width of $\Delta T = 1$ K. This process can be employed in a large-scale preparation of the $YBa_2Cu_3O_{7-x}$ powder.

Introduction

Solid-state reactions are the most commonly adopted processes for the preparation of high-T_c superconducting ceramics such as $YBa_2Cu_3O_{7-x}$.[3] These methods, usually, involve a series of laborious cycles of heating and grinding with an unavoidable compositional inhomogeneity. In order to attain higher homogeneity and also better control of stoichiometry, coprecipitation has been employed by various workers.[4-7] Kini et al.[5] used K_2CO_3 as the

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precipitant in the presence of KOH to prepare a superconducting powder, with a possible contamination of potassium ion. Another effort using oxalate ion as precipitant has been hindered by undesirable stoichiometry.[6,7]

We report in this paper the preparation of $YBa_2Cu_3O_{7-x}$ superconducting powders of high homogeneity. Homogeneous precipitation has been known to produce highly uniform particles and is widely employed in the manufacturing of high-quality ceramics.[8] In conventional coprecipitation, the addition of a base such as ammonia and/or KOH to a solution may induce a locally uneven pH distribution in the solution. In the case of homogeneous coprecipitation, urea is dissolved together with other reactants. Upon heating, urea decomposes into CO_2 and NH_3, thus gradually elevating the pH throughout the solution. The simultaneous evolution of CO_2 has the advantage of preventing undesirable bumping during digestion. The preparation of a tertiary system of Y, Ba, and Cu via a hitherto unnoticed homogeneous coprecipitation using urea has worked successfully in the present investigation.

Experimental Procedures

All chemicals were of high-purity grade purchased from Merck AG without further treatment. Deionized water was used throughout all chemical procedures. An aqueous mixture containing Y, Ba, and Cu salts with a molar ratio of 1:2:3 ([Y] = 0.068 M), 0.5 M oxalic acid, and 2–15 M urea was used. The mixture was heated in an oil bath at 90–100 °C for 1 h. Slow evolution of CO_2 and NH_3 could be observed during heating. After cooling, the pH of the solution was measured, and a pale blue precipitate was filtered out, washed with water and acetone, and finally dried at 140 °C for 6 h. The dried powder was subjected to calcination at 900 °C in air for 16 h. It was then pressed into a pellet with ϕ = 10 mm × 2 mm under a pressure of 2 ton cm^{-2} and sintered in air at 950 °C for 16 h.

Particle size was measured by means of laser scattering with a Coulter model N4 particle analyzer, and surface area, by the BET method at liquid-nitrogen temperature with a Quantasorb SD. The chemical composition analysis of the calcined pellet was determined by EDX on an EDAX SW9100. The structure was determined on a Philips powder X-ray diffractometer using Cu Kα radiation. The ac electric resistivity measurements were made by using a standard four-probe technique. Fine copper wire, which served as the voltage and current leads, was attached to samples by using air-drying silver paste. A Linear Research Inc. LR-400 personal computer interface, which is capable of fully automated data acquisition, was employed in the resistivity measurement. An ac mutual-inductance bridge was used for the magnetic susceptibility measurements. The temperature (T > 40 K) was determined with a calibrated platinum resistor close to the specimen.

Results and Discussion

1. Urea Hydrolysis. The homogeneous coprecipitation is based on urea hydrolysis upon heating:

$$CO(NH_2)_2 + H_2O \xrightarrow{\Delta} 2NH_3 + CO_2$$

Hydrolysis takes place at a temperature between 80 and 100 °C with a simultaneous evolution of CO_2 and NH_3, and thus effects a gradual elevation of the pH. The hydrolysis can be effectively supressed at a desired pH by cooling the solution to room temperature. As shown in Figure 1, the reaction mixture containing nitrate salts of Y, Ba, and Cu together with 0.5 M oxalic acid was heated to 90–100 °C within 1 h. The final pH was dependent on the concentration of urea. The slow evolution of CO_2 constantly stirred the solution and thus effectively prevented it from bumping. The uniform elevation of pH throughout the solution was effected by the gradual release of NH_3, and consequently a fine precipitate formed. A similar precipitate was obtained from chloride salts.

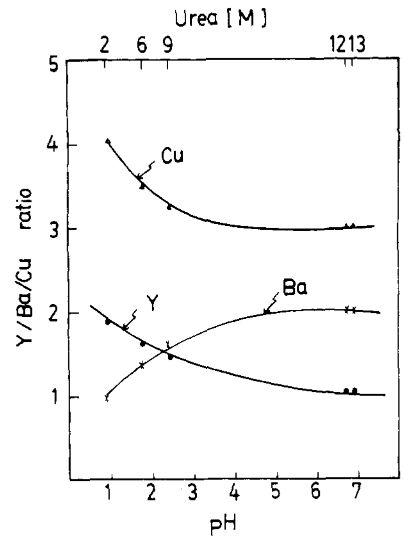

Figure 1. Dependence of the urea concentration on the final pH of the solution, and the chemical composition of the calcined specimens at various pHs as analyzed by EDX (calcination at 900 °C for 16 h).

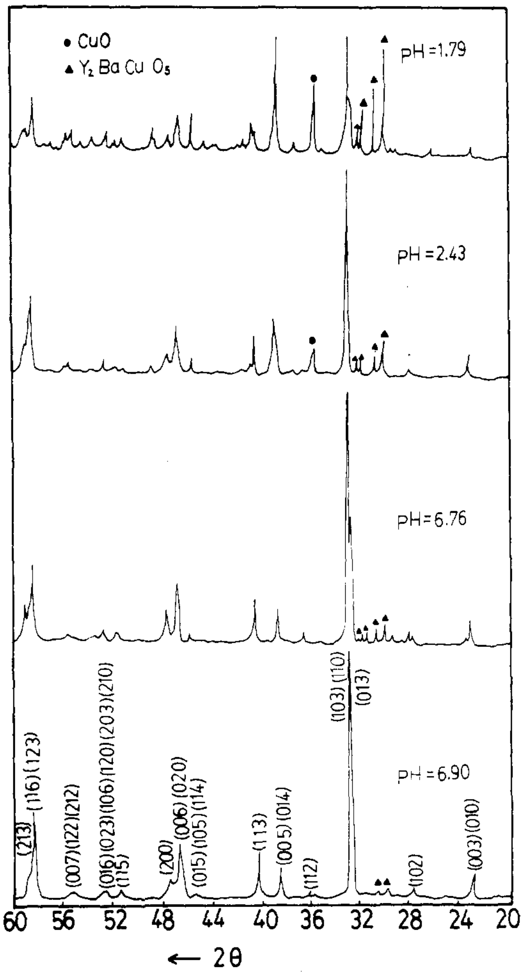

Figure 2. XRD patterns of the calcined powders obtained from nitrate salts at different pHs (calcination at 900 °C for 16 h).

2. Composition of the Coprecipitate and Calcined Powders. The precipitate from the reaction mixture was filtered out, washed, and dried at 140 °C for 6 h. A pale blue powder with a specific surface area of 5.3 m^2/g and a particle size of 0.3 ± 0.08 μm was obtained. The thermograms (Figure S1 (supplementary material)) show gradual weight loss from 100 to 260 °C. Abrupt weight loss accompanied by exothermic peaks at 260 °C (Cl^-) and 300

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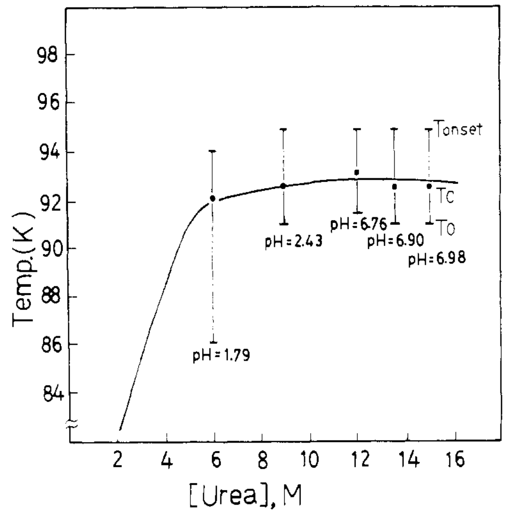

Figure 3. Dependence of superconducting temperature on the urea concentration and final pH values for the specimens resulting from nitrate precursors.

°C (NO_3^-) was observed, which is indicative of the loss of organic moieties. Subsequent heating up to 800 °C effected the decomposition of $BaCO_3$ into BaO. The IR and XRD spectra, shown in Figures S2 and S3 (supplementary material), agree with the thermograms. The IR spectra of the precursor at 140 °C are complicated and show absorptions (cm^{-1}) at 1635 (C═O in metal oxalate), 1300 (doublet, C–C), 800 (C–O–M) and 500–370 (M–O, O–M–O). The calcined product at 550 °C shows typical $BaCO_3$ (1420, 850, 680 cm^{-1}) absorptions together with a broad absorption at 500 cm^{-1}, corresponding to copper and yttrium oxides. All absorptions disappear upon heating to 900 °C, indicating complete decomposition of carbonates. The corresponding XRD spectra show the existence of metal oxalates in the precursor and their decomposition into carbonate and finally into oxides at higher temperatures. The chemical composition as determined by EDX, of the precursor precipitated from the reaction mixture varies greatly at lower pH and attains 1:2:3 (Y:Ba:Cu) composition as the pH approaches 7 (Figure 1). The corresponding XRD spectra in Figure 2 show that at lower pH the precursor is a multiphase powder containing $YBa_2Cu_3O_{7-x}$, CuO, Y_2BaCuO_5, and some other unidentified impurities. As the pH is raised, the pure orthorhombic superconducting phase of $YBa_2Cu_3O_{7-x}$ increases at the expense of other phases.

3. **Superconducting Characteristics.** The superconducting powders obtained from various media were subjected to physical measurements including conductivity and magnetic susceptibility and the results are shown in Figure 3 and 4, respectively. Superconducting powders with higher T_c and smaller ΔT are obtained from a mixture of higher pH, i.e. higher concentration of urea.

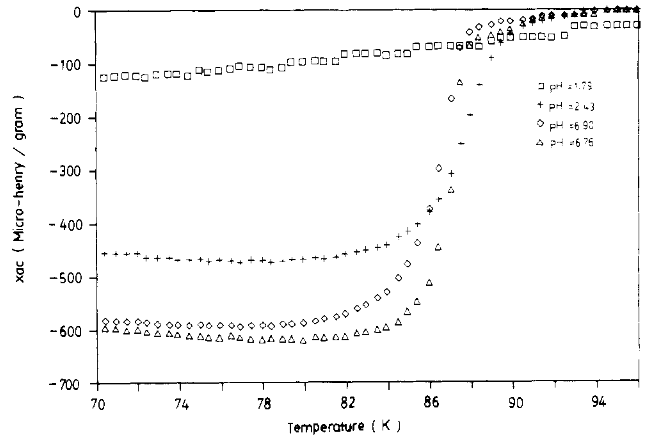

Figure 4. χ_{ac} measurement of the specimens resulting from nitrate salts at different pHs.

Corresponding measurements of magnetic susceptibility also demonstrate this same trend of pronounced diamagnetic character in specimens from solutions of pH near 7. Properties of superconducting powders obtained at optimum conditions: T_{onset} = 95 K, T_c = 93 K, T_0 = 91 K, and ΔT = 1 K (from nitrate precursor); T_{onset} = 95 K, T_c = 93 K, T_0 = 88 K, and ΔT = 2 K (from chloride precursor). Both powders show a very similar resistance drop near the transition temperature; however, it is unclear whether the powder from chloride precursors exhibits poorer metallic properties at higher temperatures.

Conclusion

A high-T_c superconducting oxide powder, $YBa_2Cu_3O_{7-x}$, has been synthesized by means of homogeneous coprecipitation using Y, Ba, and Cu nitrate or chloride salts as starting materials and oxalic acid/urea as precipitants. A precipitate of high stoichiometry and homogeneity was obtained by heating the aqueous solution at 90–100 °C for 1 h with the resulting pH near 7. Subsequent calcination of the pale blue precipitate at 900 °C for 16 h and sintering at 950 °C for 16 h is recommended to obtain a better superconducting powder. The experimental conditions are easily controlled, and a finer and more uniform powder is obtainable in a reproducible way. A high T_c, 93 K, accompanied by a very sharp-transition width, ΔT = 1–2 K, can be easily attained.

Registry No. $YBa_2Cu_3O_{7-x}$, 109064-29-1; YCl_3, 10361-92-9; $BaCl_2$, 10361-37-2; $CuCl_2$, 7447-39-4; $Y(NO_3)_2$, 10361-93-0; $Ba(NO_3)_2$, 10022-31-8; $Cu(NO_3)_2$, 3251-23-8; oxalic acid, 144-62-7; urea, 57-13-6.

Supplementary Material Available: TGA–DTA thermograms of the coprecipitates from nitrate (a) and chloride (b) salts with a heating rate of 10 °C/min (Figure S1) and infrared spectra and XRD patterns of a nitrate precursor for the superconducting powder $YBa_2Cu_3O_{7-x}$ and its calcined products (Figures S2 and S3) (3 pages). Ordering information is given on any current masthead page.