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Preparation of the High-Tc Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
Using Organometallic Precursors

by

Leonard V. Interrante, Zhiping Jiang, and David Larkin

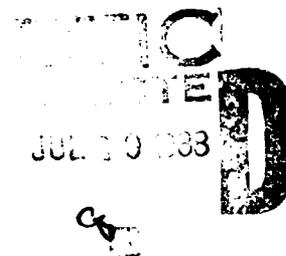
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Preparation of the High-Tc Superconductor $YBa_2Cu_3O_{7-x}$ Using Organometallic Precursors

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Organic-soluble precursors to the high-Tc "1-2-3" superconductor, $YBa_2Cu_3O_{7-x}$, have been prepared using polyesters derived from the interaction of citric acid (CA) or ethylenediaminetetraacetic acid (EDTA) with ethylene glycol. Mixtures of the nitrate, carbonate and/or acetate salts of the three metal ions with CA or EDTA and ethylene glycol were heated to obtain homogeneous green solids containing the desired 1:2:3 ratios of Y^{3+} , Ba^{2+} , and Cu^{2+} ions. Pyrolysis at 850 °C - 960 °C in oxygen gave the superconducting, orthorhombic, $YBa_2Cu_3O_{7-x}$ phase. Films of the superconductor were prepared by dropping ethylene glycol solutions of these precursors onto zirconia and alumina substrates, followed by pyrolysis to 950 °C in O_2 . The results of TGA/DSC and FTIR studies of these precursors, as well as XRD, FTIR, pyrolysis/GC, electrical and magnetic property measurements on the pyrolysis products are presented and discussed in the context of the probable precursor structures and pyrolysis chemistry. Preliminary studies were also carried out on the chemical vapor deposition (CVD) of Y_2O_3 using the tris-(2,2,6,6-tetramethyl-3,5-heptanedionato)- yttrium complex. The pyrolysis products are identified by g.c./FTIR and Auger studies of the Y_2O_3 films are described.

The recent discovery(1,2) of the high-Tc superconductor, $YBa_2Cu_3O_{7-x}$, has stimulated intensive investigation into its synthesis, structure and potential applications. A key requirement for the practical application of this and related high-Tc oxide superconductors is a better method for the fabrication of these materials in useful final forms (e.g., fibers and thin films)

The methods currently in use for the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ typically involve either repeated grinding and sintering of the parent oxides(3) or co-precipitation(4-6) from aqueous solutions with carbonate, oxalate or organic carboxylates followed by calcination. These methods generally require the use of high calcining temperatures ($>900^\circ\text{C}$) and further annealing in oxygen up to 950°C to produce the desired orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. Moreover the powders so obtained are typically inhomogeneous and contain other oxide phases. Use of this powder in the fabrication of pressed pellets has resulted in unacceptably low critical currents, owing, in part, to the presence of impurity phases, voids and grain boundary defects.(7) Moreover it is extremely difficult to prepare thin films or continuous fibers by means of the above approaches.

A number of groups have successfully prepared $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films by means of vacuum deposition techniques.(8-10) However, these depositions are expensive to perform and are not easily adaptable to large scale production or to fiber preparation. A potential solution to this problem is to employ metal-organic polymers which could be used to make thin films by spin- or dip-coating followed by pyrolysis. Furthermore, such precursors or their appropriately modified relatives could also be useful in the fabrication of continuous fibers by dry or melt spinning methods. Recently $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films have been made using acetate/acetic acid(11) and higher carboxylate salt(12) systems.

Another potential source of processible precursors is the citric acid/ethylene glycol system which has been employed previously in the preparation of highly dispersed perovskite, spinel and related complex oxides. This method provides soluble, metal-organic, polymer precursors which have been used for the fabrication of oxide thin films as well as for the production of oxide powders with excellent homogeneity, good stoichiometry control and uniform sizes at relatively low temperatures(13,14).

Recently, the preparation of thin films of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor has been reported using this system(15); however, the structure and pyrolysis reactions for these precursors have apparently not been investigated. In this paper we report the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting powders and thin films using both citric acid/ethylene glycol- and ethylenediaminetetraacetic acid [EDTA]/ethylene glycol-derived polyesters as well as the results of studies of the structure and pyrolysis chemistry of the precursors.

Experimental Section

Syntheses of Precursors

Citric acid/ethylene Glycol Precursor to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, BaCO_3 and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (molar ratio 1:2:3) were mixed with excess citric acid and 40 mL ethylene glycol in a small beaker. The mixture was heated and stirred at about 90°C until all the solids had dissolved. The resultant solution was maintained at

120 °C with stirring for ca. 2 h until ca. 10 mL of green viscous solution remained; the evolution of NO_x along with the excess ethylene glycol was noted during this period. This solution was heated in vacuo at 140 °C for several hours, leaving a green glassy solid. This solid could be redissolved in ethylene glycol and was also readily soluble in 2-methoxyethanol and tetrahydrofuran.

EDTA/ethylene Glycol Precursor to YBa₂Cu₃O_{7-x}. The same procedure was followed as above, only using EDTA in place of the citric acid. The precursor after heating and evaporation of excess ethylene glycol was also a green glassy solid.

Citric acid/ethylene Glycol/Cu²⁺ System. CuSO₄·5H₂O (1g) and citric acid (0.77g) (molar ratio 1:1) were mixed with 25 mL ethylene glycol, heated at 100 °C for 5h, then the resulting solution was heated in vacuo at 150 °C, leaving a green glassy solid.

Citric acid/ethylene Glycol/Ba²⁺ System. BaCO₃ (1g) and citric acid (4.87g) (molar ratio 1:5) were mixed in 40 mL ethylene glycol and heated at 140 °C. The BaCO₃ gradually dissolved forming a brown solution. After all the solid had dissolved, the solution was heated in vacuo at 150 °C, yielding a brown glassy solid.

Polyester from Citric acid and Ethylene Glycol. Citric acid was mixed with excess ethylene glycol in a small beaker. The clear, colorless solution was maintained at 100 °C for 8h, acquiring a pale yellow color. After heating in vacuo at 140 °C, a yellow glassy solid was obtained.

Tris-(2,2,6,6-tetramethyl-3,5-heptanedionato)-yttrium This complex was obtained as a white solid by the method described by Sievers, et. al.(16) It was recrystallized from hexane and sublimed in vacuo before use (m.p. = 170-2 °C).

Chemical Vapor Deposition Procedure. A horizontal hot-wall quartz-tube reactor was employed. The precursor was heated using an oil bath at 120-140 °C using air or nitrogen as a carrier gas. The pressure in the reactor was maintained at ca. 0.5-2.0 torr by continuous pumping. The substrates were Si wafer pieces or SiC fibers which were maintained at ca. 600 °C using an external tube furnace. Deposition rates varied from ca. 0.1 - 1 μm/hr depending on the precursor temperature and the flow rate into the reactor.

Pyrolyses of Polymeric Precursors. Pyrolyses were carried out in a quartz tube under a flow of oxygen with the precursor contained in an alumina boat. The temperature was increased using a programmable controller from room temperature to 960 °C over 8 h, held at this temperature for several hours and then slowly cooled to room temperature, all under flowing oxygen. The resultant black product gave an XRD powder diffraction spectrum consistent with expectations for the superconducting orthorhombic phase of YBa₂Cu₃O_{7-x}; no other crystalline phases were evidenced.

Fabrication of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Films Using the Polyester Complexes.

Solutions of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ precursors (10% by weight) in ethylene glycol were dropped onto zirconia and alumina plates and dried slowly on a hot plate at 200°C . The resultant samples were placed in a furnace and heated at 500°C in air for 1h. This coating, drying and heating process was repeated 5 times; after which the coated samples were heated at 950°C for 1h in O_2 . Scanning electron micrographs of a fracture cross-section of this film indicated a relatively fine grained, dense microstructure and a film thickness of ca. $70\mu\text{m}$.

Characterization of Precursor and Pyrolysis Products. X-ray powder diffraction patterns were measured using a Philips diffractometer employing $\text{Cu K}\alpha$ radiation and a Ni filter. DSC and TGA measurements of the precursors were carried out using a Perkin-Elmer DSC7/TGA7 Thermal Analysis System with heating rates of $10^\circ\text{C}/\text{min}$. Infrared spectra were determined using a Perkin-Elmer FT-1800 Infrared Spectrophotometer in KBr-pellet samples. Pyrolysis/GC experiments were performed using a SHIMADZU GC-9A Gas Chromatograph with a silicone-packed column by heating the precursor in an atmosphere of oxygen and collecting the volatile liquid fraction in a dry-ice cooled trap. The gaseous fraction was separately analyzed using a molecular sieve column. G.C./FTIR measurements were carried out on the products of the $\text{Y}(\text{THD})_3$ pyrolysis using the Perkin-Elmer FT-1800 Infrared Spectrophotometer. In this case the compound was sublimed under N_2 at ca. 0.6 torr through a quartz tube held at 600°C and the volatile pyrolysis products collected in a cold trap.

Electrical Conductivity and Magnetic Susceptibility Measurements.

The electrical conductivity of a pressed pellet sample was measured as a function of temperature using a four-probe ac technique. A ca. $2 \times 3 \times 1 \text{ mm}$ sample was cut from a cold-pressed pellet of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powder obtained from the citric acid/ethylene glycol precursor. After annealing in oxygen at 950°C for 5 h the sample was wired with Au leads using Ag paint contacts. Measurements were carried out in a specially designed cryostat from room temperature down to 77°K using a $0.1 \mu\text{A}$ ac current. The magnetic susceptibility measurements were carried out with an ac inductance bridge from room temperature to 80°K .

Results and Discussion

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ precursors derived from the citric acid/ethylene glycol and EDTA/ethylene glycol mixtures were green, homogeneous, clear, glassy solids. These solids were soluble in ethylene glycol and other organic solvents. On heating to $350 - 400^\circ\text{C}$ for a half hour on the hot plate both precursors darkened and shrank in volume without melting or foaming; the products were black, apparently still homogeneous, glassy solids.

Figure 1 shows the results of TGA studies of these two precursors. The precursors derived from citric acid and EDTA display a similar curve shape, suggesting that a similar pyrolysis process occurs for these solids in the presence of air. Both precursors show weight losses in three distinct regions. A gradual weight loss is first observed above ca. 150 °C. This is followed by a sharp weight loss at 360 - 450 °C. The third weight loss occurs in the range 750 - 810 °C.

The volatile by-products of the pyrolysis of the citric acid/ethylene glycol system in air were identified using gas chromatography. In addition to a liquid, identified as mainly ethylene glycol, CO₂ and CO were observed as gaseous products between 200 and 350 °C. Above 350 °C, CH₄ and C₂H₆ were found in addition to CO₂ and CO. The proportion of CO₂ to CO in each case was at least 5:1 and the relative amounts of the two hydrocarbons was substantially less.

Differential scanning calorimetry measurements are also consistent with the loss of ethylene glycol in the early stages of the conversion of this precursor to the 1-2-3 superconductor. As is shown in Figure 2, a small endotherm is observed at around 200 °C which is attributed to the evaporation of ethylene glycol. This is followed in the DSC by a broad exotherm from 220 to 400 °C, which associated with the thermal decomposition reaction.

Comparing the TGA curves for the citric acid/ethylene glycol precursor in air and nitrogen, almost identical behaviour is observed up to ca. 350 °C, whereupon the curves deviate sharply, with appreciably less weight loss occurring under N₂, presumably due to conversion of some of the organic components of the precursor to carbon. The close similarity in these curves up to 350 °C and the observation of CO₂ and CO as gaseous products, suggest that the thermolysis of citric acid along with the loss of ethylene glycol is responsible for the weight loss in this region. The rapid drop in weight beyond about 350 °C in air suggests that oxidation of the organic components is occurring in this region, leading to CO₂ and CO and presumably H₂O. The CH₄ and C₂H₆ which are observed in this region presumably arise from thermolysis of the ethylene groups.

Figure 3 shows the XRD patterns of the solid pyrolysis products of the citric acid/ethylene glycol precursor after extended heating in oxygen at different temperatures from 500 - 960 °C. From these results, it is apparent that a mixture of CuO, Y₂O₃ and BaCO₃ is present by at least 500 °C and the orthorhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ starts to appear at 800 °C. This phase was fully developed after heating at 960 °C for 5h in oxygen. It was also found that the EDTA/ethylene glycol precursor forms the same intermediates and the orthorhombic 1-2-3 phase at similar temperatures. The formation of BaCO₃ as an intermediate in both systems and its subsequent thermal decomposition to BaO (or to the 1-2-3 phase directly) also explains the third weight-loss at 750 - 810 °C observed by TGA.

The magnetic susceptibility measurements of the 1-2-3 powder obtained from the pyrolysis of the polymer precursor at 960 °C for

5h indicated a T_{onset} of 90K whereas electrical conductivity measurements of a pressed pellet of this powder after annealing in O_2 at 950 °C for 5h indicated a T_{onset} of 97K (Figure 4). These results are consistent with those of previous studies of 1-2-3 superconductor samples derived from solid-state reaction (17).

Figure 5 compares the XRD patterns of an intimate mixture of CuO , Y_2O_3 and $BaCO_3$ prepared by grinding the component compounds together in a mortar and the powder obtained from the polymeric precursor after heating both samples in oxygen at 850 °C for 15h. The superconducting phase was found to be only a minor product of the inorganic mixture whereas the polymer precursor formed pure $YBa_2Cu_3O_{7-x}$ under the same conditions. This observation is consistent with previously reported work(6) which showed that 900 °C was needed for the complete formation of the superconductor phase when this same inorganic mixture was employed. Therefore it appears that the citric acid/ethylene glycol precursor forms the 1-2-3 superconducting phase at a temperature at least 50 °C lower than that needed for the inorganic mixture precursor, presumably due to the fine grained, intimately mixed microstructure of the latter material.

Thin films of the 1-2-3 superconductor were prepared on zirconia and alumina substrates by adding ca. 10% solutions of the citric acid/ethylene glycol precursor to the surface of the substrate followed by drying and pyrolysis in oxygen to 950 °C. XRD patterns indicate that the 1-2-3 orthorhombic phase is the only crystalline phase formed under these conditions. Detailed microstructural and physical property studies of these films are in progress.

Further insight into the pyrolysis chemistry involved in the conversion of this precursor to the 1-2-3 superconductor was obtained from infrared measurements. FTIR spectra were obtained on this precursor, the polyester derived from citric acid and ethylene glycol alone, and on the separate CuO and BaO precursor systems after heating in air for an extended period at various temperatures (Figure 6). The spectrum of the polyester (Fig. 6a) shows a strong, broad peak near 1200 cm^{-1} and a weaker peak at 1050 cm^{-1} which can be assigned to the asymmetric stretching vibrations of the ester C-O(OR) group (18). In the range of the C=O stretching vibration, only one peak was observed at 1740 cm^{-1} , suggesting that all of the citric acid COOH groups had reacted with the ethylene glycol to form esters.

In the spectrum of the 1-2-3 precursor (Fig. 6b), a new peak appears at 1610 cm^{-1} in addition to the ester C=O and C-O peaks at 1740 cm^{-1} and 1200 cm^{-1} . This peak is consistent with the presence of COO⁻ groups coordinated in a monodentate fashion to a metal ion (19). In addition, two sharp peaks are observed at 1075 and 1080 cm^{-1} , which appear in the spectrum of ethylene glycol and are attributed to the presence of excess ethylene glycol in the precursor. In the spectrum of the precursor after heating to 250 °C (Fig. 6c) these peaks are lost, as is expected from the pyrolysis g.c. results. At this point the ester peaks are largely unperturbed but the peak at 1610 cm^{-1} in the original precursor has shifted to 1580 cm^{-1} and changed in appearance suggesting that a change in the coordination of some of the metal ions has occurred.

Upon heating to 350 °C (Fig. 6d), the ester C=O and C-O peaks have decreased substantially in relative intensity and a set of new

bands at 1560 and 1405 cm^{-1} have grown in. These bands are typical of a COO^- group acting as a bidentate ligand toward a metal ion, and are assigned to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretches, respectively (18,20). By 450 $^{\circ}\text{C}$ (Fig. 6e) the ester peaks have completely disappeared and the large split peak at ca. 1460 cm^{-1} is suggestive of bidentate COO^- groups along with possibly the coordinated CO_3 ion. The latter is suggested in particular by the comparison with the spectrum of BaCO_3 (Fig. 6f) which has a single strong peak in this region plus a sharp peak at around 950 cm^{-1} similar to that in spectrum 6e. In contrast to this precursor spectrum, both the BaCO_3 and the BaO precursor (Fig. 6g) spectra after heating to 400 $^{\circ}\text{C}$ show little or no sign of an OH stretch, suggesting that this feature in spectrum 6e is associated with one or both of the other two metal ions in the precursor. These results, along with the XRD spectra, are consistent with the formation of BaCO_3 beyond about 450 $^{\circ}\text{C}$.

In order to monitor the coordination of the Cu^{2+} ions during the pyrolysis of the precursor, the IR spectra of the CuO precursor was also determined as a function of temperature. Comparison of spectrum 6h with that of the original 1-2-3 precursor (Fig. 6b) reveals many common features with the exception of the strong bands at 1200 and 950 cm^{-1} which arise from the SO_4^{2-} ion used as the counterion in the CuO precursor preparation and the C=O band at 1610 cm^{-1} which is split in the CuO precursor spectrum. This may indicate more than one (COO^-) coordination environment involving the Cu^{2+} ions or H-bonding to some of the COO^- groups (21).

The splitting of the 1610 cm^{-1} band is apparently lost on heating the CuO precursor to 250 $^{\circ}\text{C}$ (Fig. 6i) and a shoulder has appeared on the C=O peak at 1775 cm^{-1} , as might arise from a free COOH group. After heating to 450 $^{\circ}\text{C}$ (Fig. 6j) the ester C=O peaks have disappeared but the band attributed to the monodentate coordinated COO^- group at 1650 cm^{-1} is still apparent, as was observed for the 1-2-3 precursor after heating to this temperature; however, there are also major differences in the C=O stretching region of these spectra which can be resolved by the addition of the CuO and BaO precursor spectra (Fig. 6j and Fig. 6g) suggesting that the mode of coordination to the COO^- groups is substantially different for the Cu^{2+} and Ba^{2+} ions in these samples. In particular these results suggest that the COO^- groups coordinate in a bidentate fashion to the Ba^{2+} ion and end up as CO_3^{2-} groups after heating in air to 450 $^{\circ}\text{C}$. On the other hand the Cu^{2+} ions appear to remain associated in a monodentate fashion with the COO^- groups which, along with the presence of the OH groups, may contribute to the ready formation of CuO on heating to >450 $^{\circ}\text{C}$.

In the case of the Y_2O_3 CVD precursor, g.c./FTIR studies carried out on the gaseous products of pyrolysis in nitrogen or vacuum indicate that isobutylene is the major hydrocarbon produced with propylene as the second highest component. Lesser amounts of various C_1 , C_2 , C_3 , and C_4 saturated and unsaturated hydrocarbons were also observed suggesting radical cleavage of the tertiary butyl groups. The mass spectrum of this compound also shows a major peak at $m/e = 57$ which corresponds to $M + 1$ for butylene.

Preliminary efforts to use this compound as precursor for the CVD of Y_2O_3 have centered on the production of dense, polycrystalline films on SiC fibers and Si wafers and have led to uniform, high quality films both with and without added oxygen. Auger spectra obtained for such films deposited on single crystal silicon show the presence of Y and O with varying amounts of carbon depending on the carrier gas used and the deposition rate. It was found that even in the absence of added oxygen the carbon incorporation in these films could be reduced to on the order of 1% or less by slowing down the deposition rate to ca. 0.1 $\mu\text{m}/\text{h}$.

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Figure 1. TGA data for polymeric precursors to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.
a : Precursor from citric acid/ethylene glycol in N_2 .
b : Precursor from EDTA/ethylene glycol in air.
c : Precursor from citric acid/ethylene glycol in air

Figure 2. DSC curve for the citric acid/ethylene glycol 1-2-3 precursor system.

Figure 3. XRD patterns of the citric acid/ethylene glycol precursor system after heating in O_2 at different temperature.

(\square Y_2O_3 , \circ BaCO_3 , \triangle CuO , \ddagger $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$)

Figure 4. Results of conductivity and magnetic susceptibility measurements on the precursor-derived 1-2-3 superconductor.

(\circ R, \triangle X)

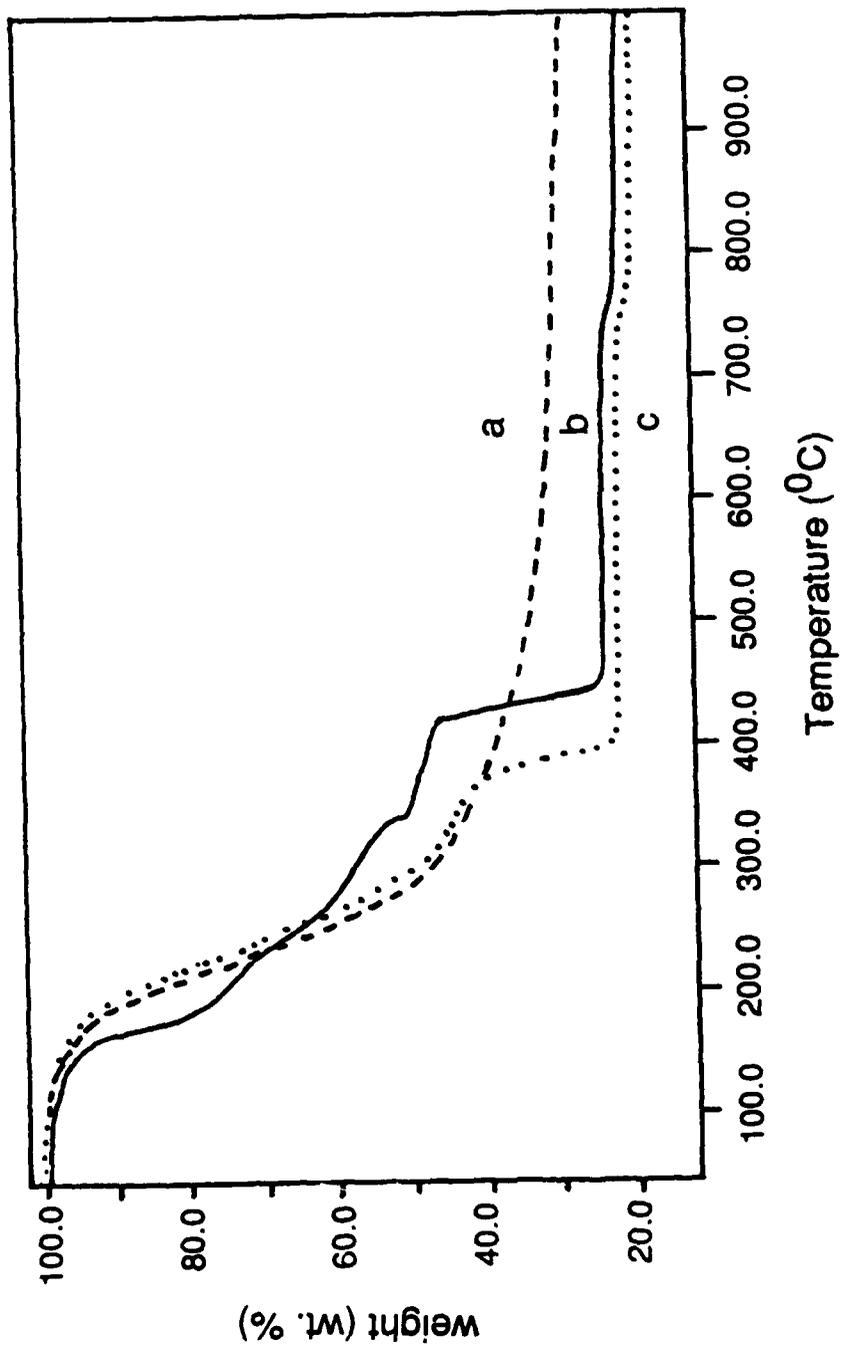
Figure 5. XRD patterns of both the inorganic mixture and polymeric precursor after heating in O_2 at 850°C for 15h.

(\square Y_2O_3 , \circ BaCO_3 , \triangle CuO , \ddagger $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$)

Figure 6. FTIR spectra of precursors and solid pyrolysis products after heating in air at various temperatures.

(a) polyester from citric acid and ethylene glycol.
(b) 1-2-3 precursor. (c) 1-2-3 precursor, 250°C , 2h.
(d) 1-2-3 precursor, 350°C , 1h. (e) 1-2-3 precursor, 450°C , 1h.
(f) BaCO_3 (g) BaO precursor, 400°C , 1h. (h) CuO precursor.
(i) CuO precursor, 250°C , 2h. (j) CuO precursor, 450°C , 1h.

15



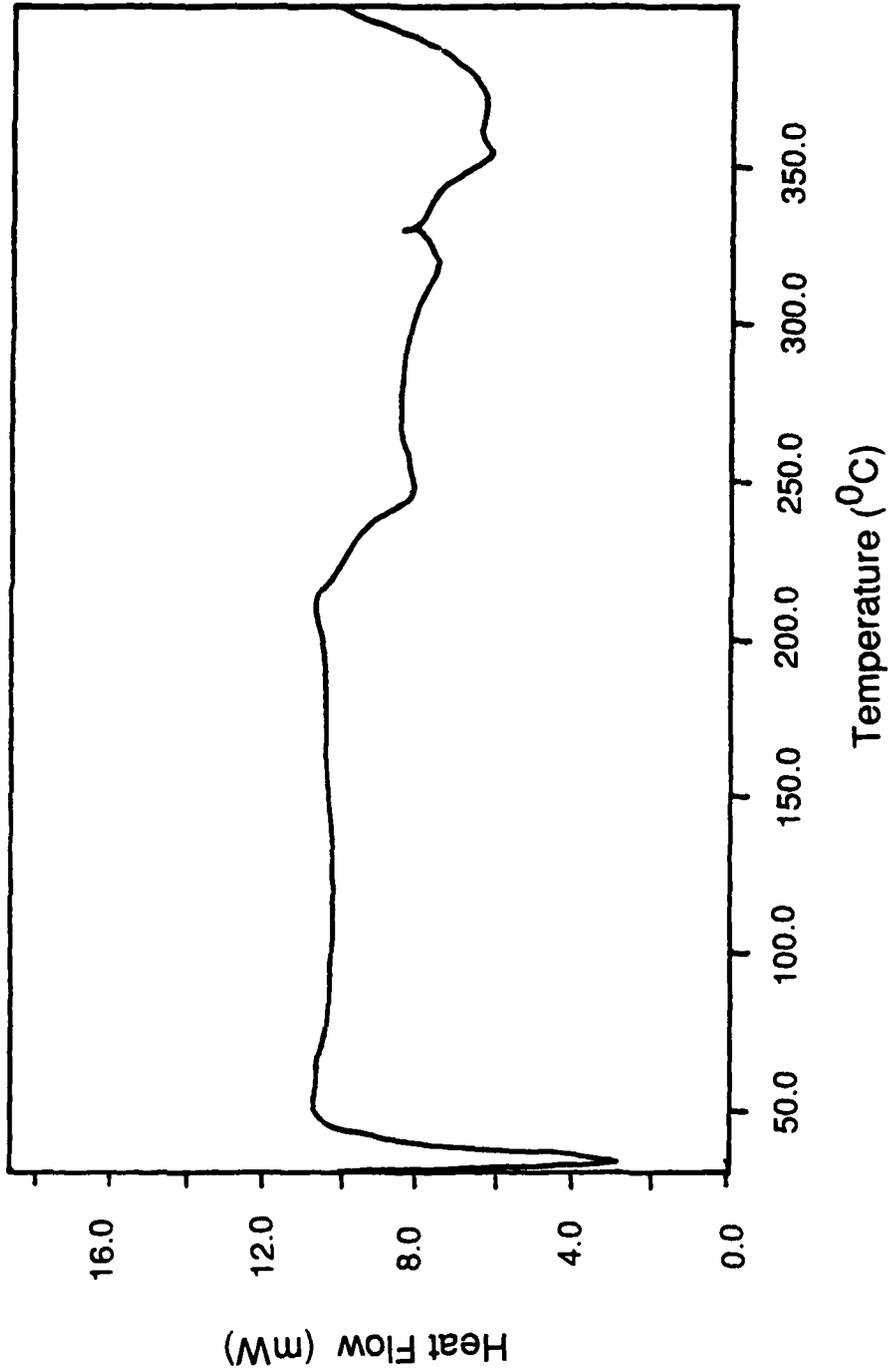
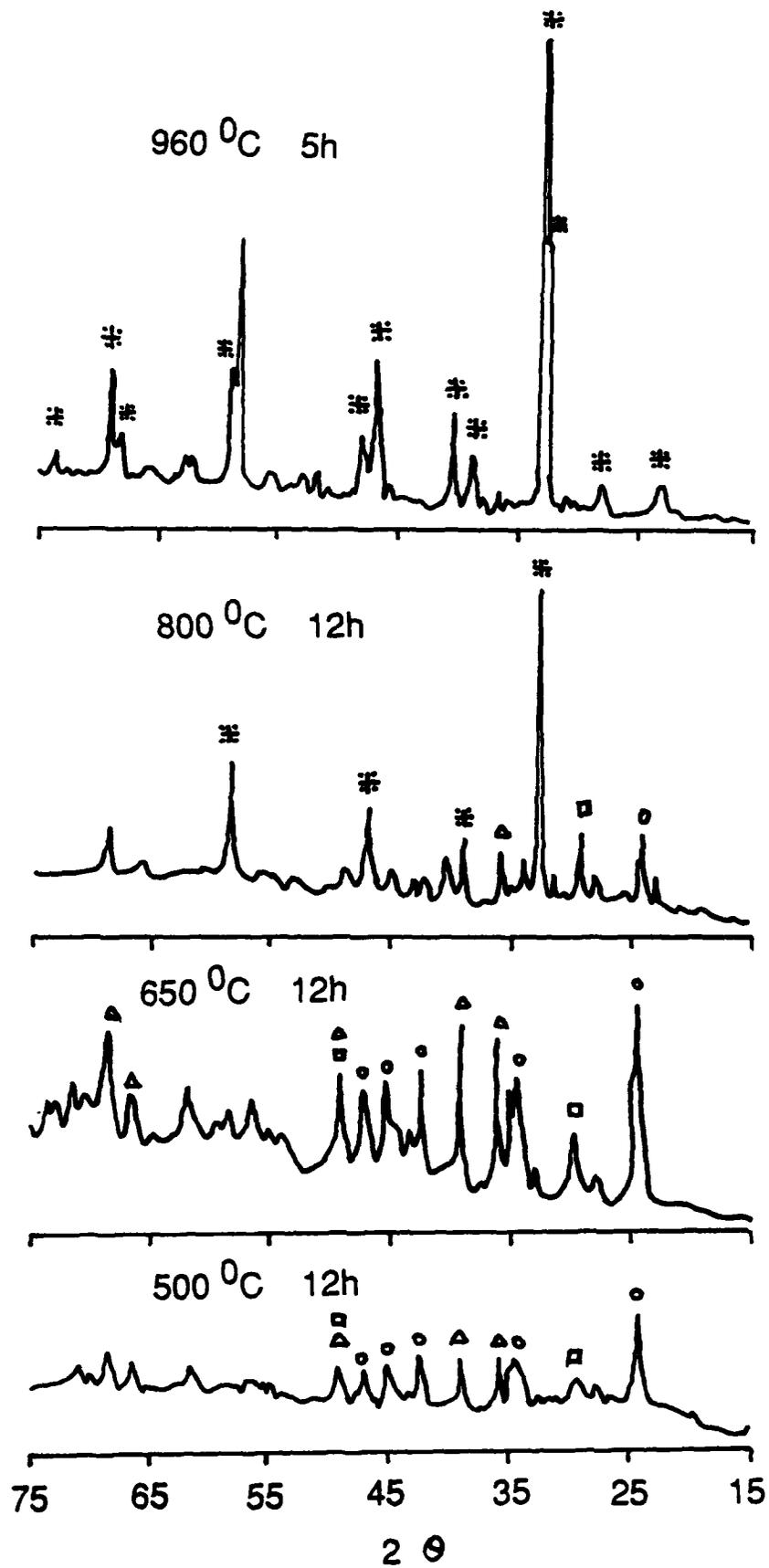
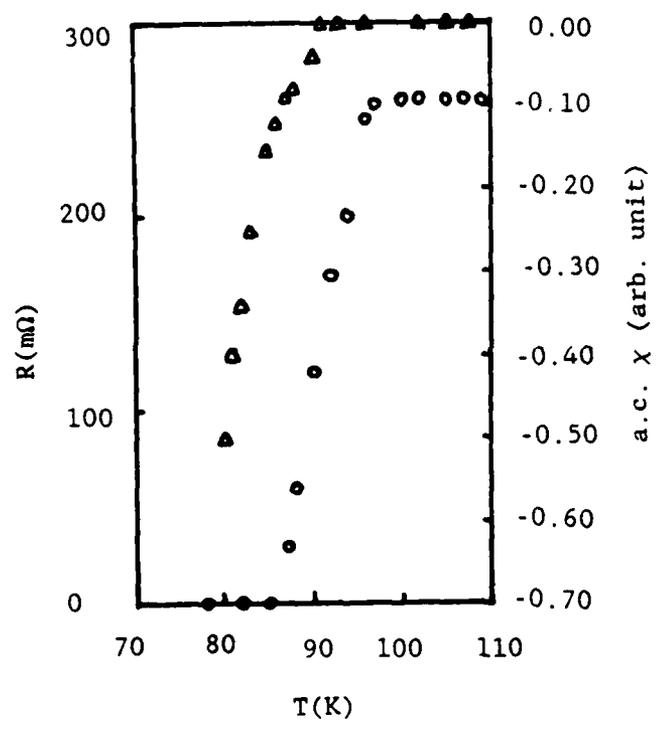
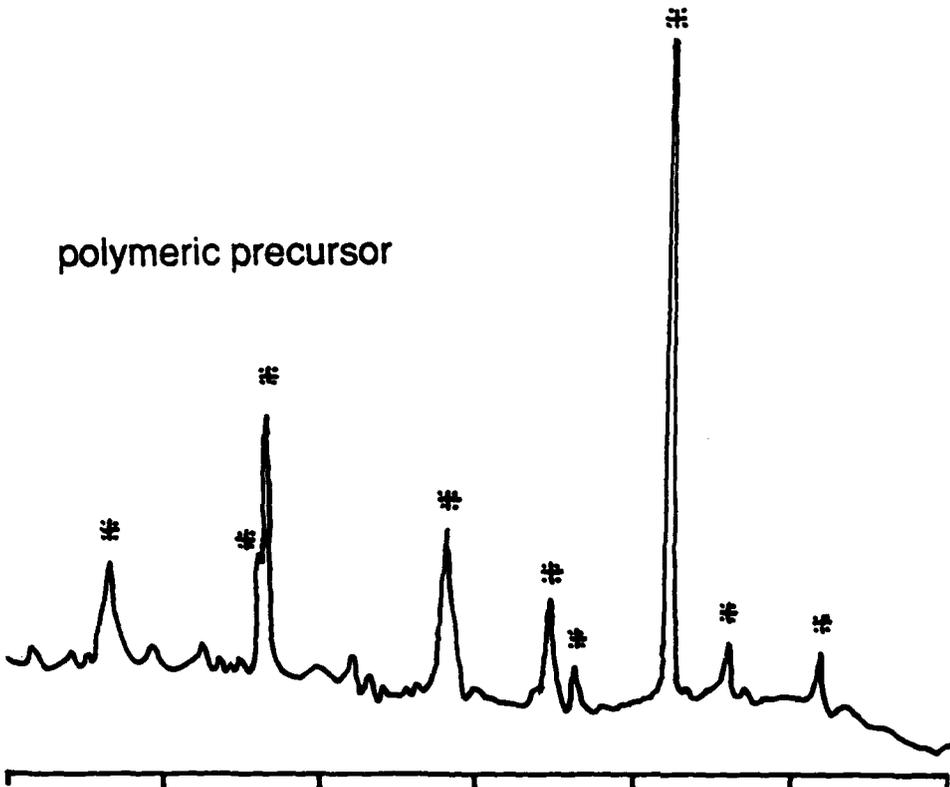


Fig 2

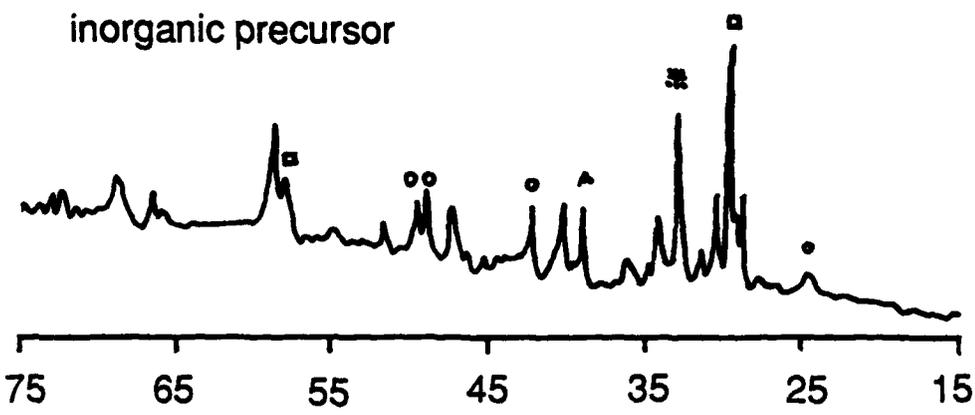




polymeric precursor

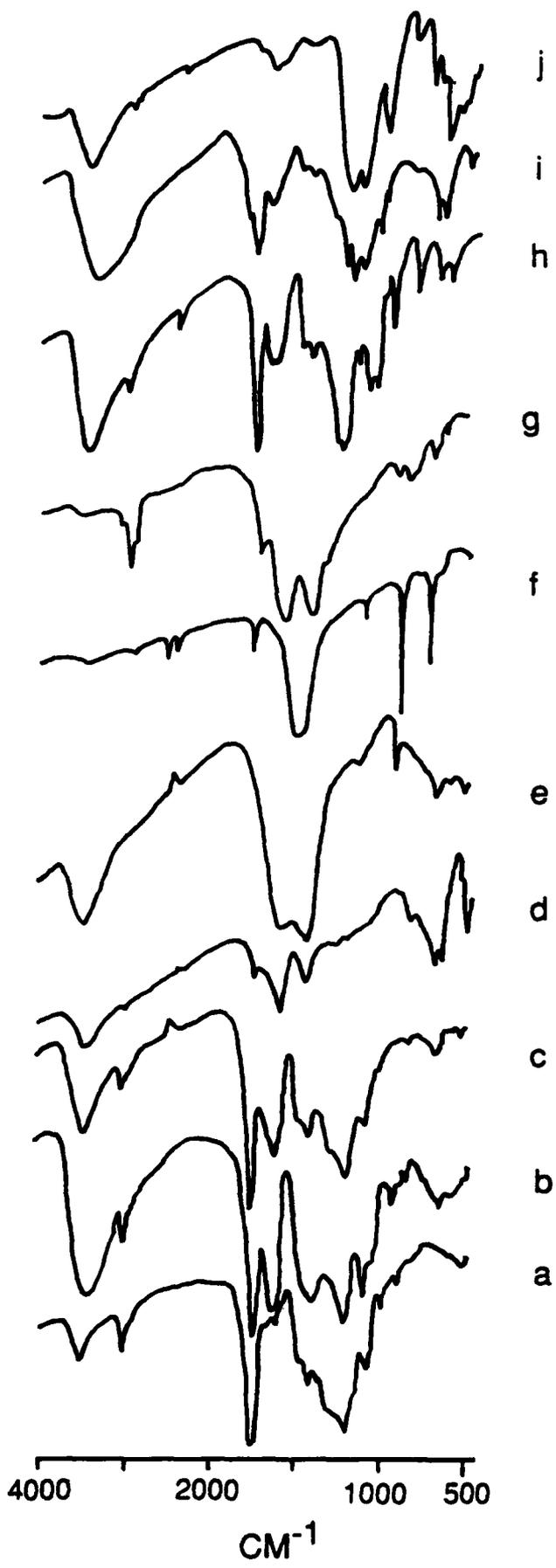


inorganic precursor



2θ

Fig 5



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