Fine-grained high- T_c superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders through a modified citrate method

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Abstract. Synthesis and thermal decomposition characteristics of acetate-modified citrate precursor have been investigated. The intermediates of thermal decomposition exhibit enhanced reactivity. Quantitative estimation of the intermediate phases above 1125 K has been carried out and a directed reaction between $\text{Y}_2\text{Cu}_2\text{O}_5$ and BaCuO_2 phases is postulated for the formation of pure 1–2–3 phase. Isothermal calcination of the precursor at 1175 K for 9 h is sufficient for the complete conversion of the intermediate phases to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The particles thus obtained are nearly spherical and monosized to give a BET surface area of $3\text{ m}^2/\text{g}$. The oxygenated powder shows T_c onset at 97 K for magnetic susceptibility and a narrow hysteresis for magnetization with H_{c1} and J_c values of 105 Oe and $6 \times 10^4\text{ A/cm}^2$ respectively at 77 K. EPR and EDAX techniques confirm the phase purity. Electron diffraction studies confirm XRD results. For oxygenated powder the excess charge (p^+) on square planar copper site $[\text{Cu-O}]^{p^+}$ is estimated to be 0.28.

Keywords. Citrate precursors; ceramic powder processing; high T_c superconductors; fine powder characteristics.

1. Introduction

Synthesis of pure high- T_c oxide superconductors by chemical methods has attracted a great deal of interest in recent years. Studies on these high purity materials enable a better understanding of the physico-chemical characteristics in the normal and superconducting states. The conventional ceramic preparation techniques always yield small quantities of undesirable phases either due to incomplete reaction or high temperature calcination because of a narrow stability range of the 1–2–3 phase in the ternary phase diagram (Roth *et al* 1987; Frase and Clarke 1987; Wang *et al* 1987; Neveh and Pelley 1989).

Though the citrate method has been successfully employed to synthesize ultrafine highly-homogeneous superconducting oxides (Chu and Dunn 1987; Blank *et al* 1988; Pankajavalli *et al* 1988; Sanjines *et al* 1988; Lee *et al* 1989; Yang *et al* 1989), the earlier citrate precursors have two drawbacks. As metal nitrates were used invariably as starting materials, the resultant precursor is hygroscopic and during its decomposition yields well-crystallized BaCO_3 intermediate, which in turn requires a relatively higher final temperature for the formation of 1–2–3 phase.

Hence a modified citrate precursor is reported in the present paper, which overcomes to a large extent the above constraints. The intermediates of decomposition have been identified and a directed reaction observed at the final stages of solid-state reaction to form the 1–2–3 phase. Two other citrate precursors have also been investigated to throw some light on the effect of the nature of the precursor on the course of decomposition.

2. Experimental procedure

Y_2O_3 was of 99.99% purity and all the other chemicals were of Analar grade. Solutions (0.1 M) of citric acid and acetates of yttrium, barium and copper were prepared. Requisite volumes of the solutions were mixed so that $\text{Y}:\text{Ba}:\text{Cu} = 1:2:3$ and the mole ratio of total metal ions to citric acid was 1. The pH of the resultant mixture was adjusted to 6.5–7.00 by adding aqueous ammonia. The solution was first evaporated on a boiling water bath to a homogeneous viscous mass. Further evaporation was carried out at 10^{-2} torr pressure at 355 K. This gave a non-hygroscopic solid residue (precursor A).

Two other precursors were also prepared to study the effect of the nature of precursor on the course of decomposition; One by following the same procedure as above but without pH adjustment. In this case a slight segregation of copper acetate was observed on partial evaporation. Hence after complete drying the resultant mixture was ground well to a uniform consistency (precursor B). The third precursor (precursor C) was prepared from metal nitrates and citric acid following the procedure employed by Blank *et al* (1988).

Thermal studies were carried out using a commercial Ulvac TA-1500 simultaneous TG-DTA-DTG thermal analyser with a heating rate of $20^\circ/\text{min}$ on 5–8 mg of samples. Powder X-ray diffraction was recorded on a Philips PW 1050/70 diffractometer employing nickel-filtered copper radiation and a scan rate of 2° per minute. Transmission electron microscope (Philips EM-301 model) was used for electron diffraction (ED) studies. Surface area was measured with a Micromeritics Accusorb (2100E) instrument. EPR spectra were recorded on a Varian X-band spectrometer model E-109. IR spectra in the $200\text{--}4000\text{ cm}^{-1}$ region were recorded in alkali halide pellets on a Perkin Elmer-597 spectrometer. Vibrating sample magnetometer (VSM) (EG and G Princeton Applied Research, model-155) was used for susceptibility and magnetization studies.

3. Results and discussion

The thermal decomposition of precursor A is found to proceed through several stages to finally form the 1–2–3 phase viz (i) formation of individual oxides of yttrium and copper(II) along with BaCO_3 in the temperature range 300–825 K by a multistep decomposition of the precursor, (ii) formation of 1–2–3 phase along with $\text{Y}_2\text{Cu}_2\text{O}_5$ and BaCuO_2 phases in the temperature range 1025–1125 K and (iii) the formation of phase pure 1–2–3 oxide in the temperature region 1125–1175 K by a directed reaction between the oxides $\text{Y}_2\text{Cu}_2\text{O}_5$ and BaCuO_2 .

The main features of the thermal decomposition of precursor A are shown in figure 1. The removal of adsorbed water occurs below 375 K. The initial decomposition is an overlapping multistep process as inferred from the three distinct endotherms at 490 K, 565 K and 605 K for a sharp weight loss step. Formation of CuO at the initial stage of the precursor decomposition is inferred from isothermal heating of the precursor for 7 h at 575 K. Further decomposition is exothermic as seen from the intensely sharp exothermic differential peak centred around 720 K. A complete combustion of the organics occurs at this stage and a minimum temperature of 825 K is sufficient for the formation of BaCO_3 and Y_2O_3 along with CuO.

Figure 1. TG and DTA trace of precursor A.

It is interesting to note that the pH-adjusted nitrate-citrate precursor shows the presence of traces of BaCO_3 even after the calcination at 1170 K while the citrate precursor polymerized with ethylene glycol does not contain BaCO_3 at the same temperature (Lee *et al* 1989). This emphasizes the fact that the reactivity of the intermediates of decomposition depends strongly on the choice of the precursor though the extent of the dispersion of metal ions is the same in all the precursors. This has been further substantiated from the present investigation where BaCO_3 is not observed for the acetate-citrate precursor calcined at 1123 K. The influence of the nature of precursor on the course of reaction and reactivity of the products is brought out in table 1. The most significant observation is the continued presence of BaCO_3 to higher calcination temperatures for precursors (B) and (C).

The residue after calcination of the acetate-citrate precursor at 1125 K for 17 h shows the presence of only three phases: 1-2-3, $\text{Y}_2\text{Cu}_2\text{O}_5$ and BaCuO_2 . The green phase has not been observed at any stage. The above three phases present in the mixture were estimated quantitatively by the procedure reported by Itoh *et al* (1988). A maximum of 30 mol% of BaCuO_2 was found for the residue obtained by calcining the precursor at 1135 K for 12 h and the amount of $\text{Y}_2\text{Cu}_2\text{O}_5$ was found to be 8 mol%. The reflections employed for the quantitative estimation of the phases are (103) + (110) of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$, (600) of BaCuO_2 and (211) of $\text{Y}_2\text{Cu}_2\text{O}_5$.

The mole ratios of the three phases $\text{Y}_2\text{Cu}_2\text{O}_5$: BaCuO_2 : $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$ were 1:4:8:3 at this stage. There were no BaCO_3 reflections in the XRD of this residue. In addition the IR spectrum does not show any characteristic ionic carbonate absorptions including the strongest absorption ν_{as} at 1445 cm^{-1} .

Table 1. Comparison of the products of isothermal decomposition of different citrate precursors

Decomposition temperature (K)	Precursor (A) acetate-cit.	Precursor (B) acetate cit.	Precursor (C) nitrate-citrate
575	CuO	CuO	CuO
825	BaCO ₃	BaCO ₃	BaCO ₃
	CuO	CuO	CuO
	Y ₂ O ₃	Y ₂ O ₃	Y ₂ O ₃
1075	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}
	BaCO ₃	BaCO ₃	BaCO ₃
	Y ₂ Cu ₂ O ₅	Y ₂ BaCuO ₅	Y ₂ Cu ₂ O ₅
	BaCuO ₂	Y ₂ Cu ₂ O ₅	BaCuO ₂
		BaCuO ₂	
1135	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}
	Y ₂ Cu ₂ O ₅	BaCO ₃ (trace)	BaCO ₃ (trace)
	BaCuO ₂	Y ₂ Cu ₂ O ₅	Y ₂ Cu ₂ O ₅
		Y ₂ BaCuO ₅	
		BaCuO ₂	BaCuO ₂
1175	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}
		Y ₂ BaCuO ₅ (trace)	
		BaCuO ₂ (trace)	
1205	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}	YBa ₂ Cu ₃ O _{6.5+δ}

By increasing the calcination temperatures from 1135 to 1155 K, a gradual reduction in the intensities of BaCuO₂ and Y₂Cu₂O₅ has been observed with a corresponding increase in the intensity of the strongest reflection of YBa₂Cu₃O_{6.5+δ}. At 1165 K, only traces of Y₂Cu₂O₅ and BaCuO₂ were observed. Calcining the residue obtained at 1165 K to a temperature of 1175 K for 8 h resulted in the pure 1–2–3 phase formation. The progress of the different stages of decomposition of the precursor was followed by XRD and the XRD traces are presented in figure 2.

The following scheme can be formulated to represent the decomposition of the acetate-citrate precursor to form the 1–2–3 phase.

+ gaseous decomposition products.

The powder sample YBa₂Cu₃O_{6.5+δ} was oxygenated at 1175 K for 2 h and slowly cooled down to 655 K and annealed in flowing oxygen again for 12 h. The temperature was slowly brought down to 300 K and the sample subjected to various investigations employing different physicochemical techniques. The oxygen content of the sample was

Figure 2. Progress of thermal decomposition of precursor A with temperature (a) 575 K (b) 825 K (c) 1075 K (d) 1125 K and (e) 1175 K.

determined from iodometric titration and by reducing a known quantity of the sample at 1075 K with a 1:4 mixture of H_2 and Ar. The δ value has been found to be 0.42 for the oxygenated powder, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$. For the same sample a complete absence of EPR signal has been observed as an indication of its phase purity.

XRD clearly shows the orthorhombic splittings and the observed cell dimensions are in good agreement with the reported single-crystal data. Orthorhombicity is further confirmed from ED along [100] zone axis which clearly shows a b^*/c^* value of 3.00. Splitting of spots in ED is due to twinning about (110) planes. The particle size is around $0.3\ \mu\text{m}$ from transmission electron micrograph. The relevant electron micrographs are shown in figure 3. The non-porous crystalline nature of the powder is shown up by its low surface area of $3\ \text{m}^2\text{g}^{-1}$.

The sample exhibits an almost temperature-independent susceptibility in the normal state $T_c < T < 300\ \text{K}$ as shown in figure 4. Meissner effect has been observed at T_c (onset) = 97 K, which is a slightly improved superconducting characteristic compared to previous reports. This observation agrees with earlier conclusions that T_c enhancement is observed with increase in p^+ of $[\text{Cu}-\text{O}]^{p+}$ (Tokura *et al* 1988). For our sample the value of p^+ was calculated to be 0.28.

Magnetization studies were performed at 77 K to obtain H_{c1} and J_c values. Figure 5 shows the narrow M-H hysteresis, a characteristic feature of fine-grained superconducting oxides at $T < T_c$. The irreversibility of magnetization is attributed to strong flux-pinning effects. An estimate of the lower critical magnetic field H_{c1} of 105 Oe is obtained from the linear portion of the initial magnetization. The minimum field at

Figure 3. Transmission electron micrographs of (a) Isolated primary particles, (b) ED along [100] zone axis and (c) splitting of spots about (110) planes indicating twinning.

Figure 4. Magnetic susceptibility vs temperature of $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$.

Figure 5. M-H hysteresis at 77 K for $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$.

Figure 6. XRD of $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ powder.

Table 2. Physicochemical characteristics of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$ powder prepared from acetate-citrate precursor (A)

Characteristics	Typical value
Lattice parameter	$a = 3.82 \text{ \AA}$, $b = 3.89 \text{ \AA}$ $c = 11.68 \text{ \AA}$
Composition (after oxygen annealing)	$\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$
Onset of superconductivity (from susceptibility measurement)	97 K
Volume fraction superconducting	35%
BET surface area	$3 \text{ m}^2/\text{g}$
Particle size (from TEM investigation)	$0.3 \text{ }\mu\text{m}$
H_{c1} at 77 K (from magnetization measurement)	105 Oe
J_c at 77 K (from magnetization study)	$6 \times 10^4 \text{ A/cm}^2$

which the magnetization changes its slope is chosen as H_{c1} . The critical current density J_c obtained by using the Bean model (Bean 1964), $J_c = 30 \times M/d$ for equiaxed grains of average diameter d ($0.3 \text{ }\mu\text{m}$) is found to be $6 \times 10^4 \text{ A/cm}^2$. The value of ΔM , the change in magnetization for increasing and decreasing fields, is calculated from the hysteresis at 5 kOe and found to be 0.06 G. The J_c value is in good agreement with previously reported values of the order of 10^4 – 10^6 A/cm^2 and theoretically-predicted maximum critical current densities (Larbalestier *et al* 1987; Stancil *et al* 1988). The ΔM value of the citrate derived powder is 350 times smaller compared to a single crystal (Jin *et al* 1989). The physicochemical characteristics of the powder are given in table 2.

4. Conclusions

The hygroscopic nature of the nitrate-citrate precursors could be reduced to the minimum by choosing metal acetates instead of nitrates. Enhanced reactivity of the intermediates of decomposition has been observed for the modified citrate precursor. Quantitative estimation of the intermediate phases was performed and a directed reaction is found responsible for the formation of pure 1–2–3 phase. Improved superconducting characteristics have been achieved for the acetate-citrate-derived fine-grained $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$ powders.

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