

A Novel Synthetic Method for the Preparation of Oxide Superconductors: Anionic Oxidation-Reduction

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A new chemical method for the bulk synthesis of $\text{Ba}_2\text{YCu}_3\text{O}_7$ powder is described and is applicable to the synthesis of other superconducting oxides. Ionic salt precursors are used which are intimately mixed by spray-drying an aqueous solution of these salts. The anions in the spray-dried mixtures (which in this study are mixtures of nitrate and acetate salts) participate in a low-temperature oxidation-reduction reaction. The exothermic redox reaction and the heat evolved from the reaction completely convert the precursors into their corresponding mixed oxides at temperatures below 300°C in one reaction step. Phase segregation (normally apparent in the decomposition of organic precursors) is not observed in the decomposition of the mixed anion (nitrate/acetate) precursors. The enthalpy of this reaction is strongly dependent upon acetate content in the mixture: $-\Delta H$ (9:4, acetate:nitrate) = 4016 (70) kJ/mole, whereas $-\Delta H$ (5:8, acetate:nitrate) = 890 (70) kJ/mole. These precursors can be reacted at 910°C for 10 min to produce single-phase $\text{Ba}_2\text{YCu}_3\text{O}_x$. Sintered disks of $\text{Ba}_2\text{YCu}_3\text{O}_7$, prepared from $\text{Ba}_2\text{YCu}_3\text{O}_x$ powder, show onset T_c 's of 94-95 K and are fully superconducting by 90.5-91 K. © 1989 Academic Press, Inc.

Introduction

In light of the interest in developing applications for the new cuprate superconductors, the large-scale synthesis of these ceramics becomes desirable. Alternative approaches to the synthesis of these oxides are needed because conventional ceramic methods (1) usually require multiple-step reactions and intermediate grindings. Chemical precursor methods (2-8) usually offer the advantage of shorter firing durations at lower temperatures. They include the evaporation of mixed solutions of nitrates, acetates, and formates or coprecipitation of oxalate and citrate salts. Other chemical methods include (9) precipitation of hydrated oxidized precursors derived from the hydrolysis of organometallic precursors,

as well as the precipitation of hyponitrate precursors from nitrate solutions.

A novel method is reported here for the synthesis of ceramic oxide superconductors. The important aspect of this procedure is a low-temperature oxidation-reduction reaction between anion components of ionic salt precursors which converts the precursors into their mixed oxides at low temperatures. Because of the low temperature of decomposition, the oxide mixture obtained has a high surface area and is therefore very reactive. In this way, firing temperatures and the time required to obtain a single-phase product are reduced. In addition, since the low-temperature decomposition is a one-step reaction, phase segregation is minimized.

The synthesis of $\text{Ba}_2\text{YCu}_3\text{O}_7$ powder was

investigated. Differential scanning calorimetry (DSC) data is presented for the decomposition of the chemical precursors. X-ray diffraction, magnetic (ac) susceptibility, and resistivity data on the superconducting powder and sintered pellets are also presented. Evolved gas analysis (EGA) data is presented for the decomposition by-products.

Experimental

Several stock solutions were prepared containing different ratios of the acetate to nitrate salts but with the correct cation stoichiometry to obtain $\text{Ba}_2\text{YCu}_3\text{O}_7$. These salts were gravimetrically analyzed for hydration. No analysis was required for the barium salts. $\text{Ba}(\text{CH}_3\text{COO})_2$ (Aldrich, 99.9%), $\text{Ba}(\text{NO}_3)_2$ (Aldrich, 99.9%), $\text{Y}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%), $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Alfa, ACS) were used to prepare the stock solutions. Various combinations of the nitrate and acetate salts were used to produce stock solutions containing these salts in the ratios (acetate:nitrate) of 9:4, 7:6, 6:7, 5:8, and 4:9, in addition to a solution consisting of the acetates alone. In all cases, enough precursor to make 250 g of $\text{Ba}_2\text{YCu}_3\text{O}_7$ was dissolved in 4.5 liters H_2O .

A Bowen Engineering, Inc. (North Branch, NJ) conical-type laboratory spray drier was used. The solution was spray dried over a period of 30–40 min. The inlet temperature was 288°C, and the temperature prior to the cyclone apparatus was 105°C. Approximately 75–80% of the light blue powder obtained was collected either in the main chamber or in the cyclone separator attached to the main chamber.

Thermal analysis was performed using the Perkin–Elmer System 7. Differential scanning calorimetry was done in Au pans at a heating rate of $10^\circ\text{C min}^{-1}$ in flowing (50

ml min^{-1}) O_2 . An empty sample pan served as a reference.

The basic EGA apparatus has been previously described (10). The VTI Spectroscan module was combined with an AT&T 6300 Plus personal computer using ASYST software to obtain the relative intensity of selected peaks as the sample was heated at $10^\circ\text{C min}^{-1}$ in a vacuum of 2×10^{-8} to 5×10^{-5} Torr, depending upon the extent of sample outgassing.

Powder X-ray diffraction data were obtained using a Phillips XRD 3600 powder diffractometer with $\text{CuK}\alpha$ radiation using $0.02^\circ 2\theta$ steps and 0.4 sec count time per stop.

The spray-dried powders were reacted in flowing oxygen over a period of 10 min at various temperatures. In all cases, the powders were rapidly quenched in air from high temperatures. Sintered disks of these materials were made to determine the characteristics of the superconducting transition. Sintered pellets were prepared by cold-pressing the decomposed powder at 275 mPa (40,000 psi) into pellets. The pellets were heated to 970°C in flowing oxygen and then annealed at 450°C for 3 hr to maximize the oxygen stoichiometry. Magnetic susceptibility measurements (ac) were made to disks encapsulated in small plastic vials. Measurements were performed during cooling of the sample from room temperature to liquid helium temperatures using a measuring thermometer calibrated to within ± 0.2 K. Resistivity measurements were performed using the four-probe method (10 mA, dc). Contacts were made by soldering indium contacts directly onto the pellet surface.

Results and Discussion

The spray-dried powders were examined by X-ray diffraction, which showed that they consisted of mixtures of $\text{Ba}(\text{NO}_3)_2$ and acetates and nitrates of yttrium and copper.

The presence of $\text{Ba}(\text{NO}_3)_2$ in the spray-dried powder, even though in some cases $\text{Cu}(\text{NO}_3)_2$ was the only nitrate source in the stock solution, is a consequence of the lower solubility in water of the nitrate salts of barium compared to those of yttrium and copper.

Figures 1–6 show differential scanning calorimetry data in which the spray-dried powders are decomposed in flowing oxygen. Heat flow is plotted as a function of temperature.

Figure 1 shows the decomposition of a spray-dried powder in which only the acetate salts were used. The decomposition of the acetates in flowing oxygen is clearly a multiple step process. The three main exotherms correspond to the separate decompositions of copper acetate, yttrium acetate, and barium acetate (at the highest temperature). It is also evident that the decomposition of the acetate mixture is not complete until 400°C . These results are in agreement with previous reports of spray-dried acetate precursors (8).

Figures 2 and 3 show DSC curves of spray-dried powders containing acetate/nitrate salts in ratios of 9:4 and 7:6, respectively. The main decomposition exotherm for the 9:4 mixture is at 326°C , whereas for the 7:6 mixture the main exotherm is evident at 296°C . The lower temperature associated with the lower acetate:nitrate ratio

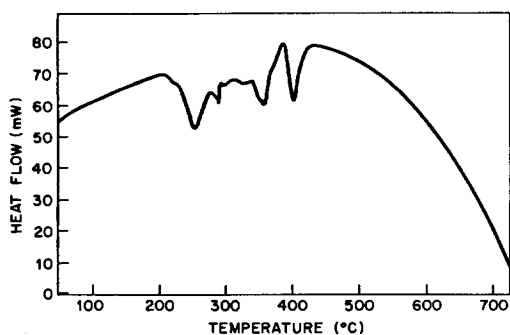


FIG. 1. DSC of all acetate precursors in flowing O_2 .

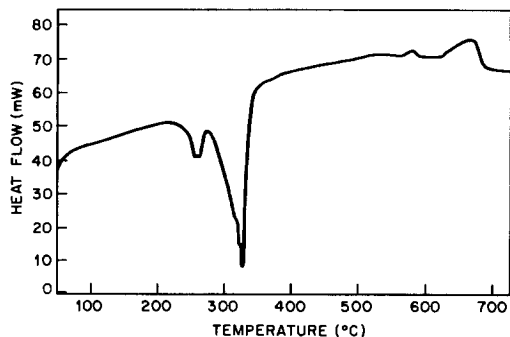


FIG. 2. DSC of the 9:4 (acetate:nitrate) precursor in flowing O_2 .

is noteworthy. In addition, the decomposition appears to be a two-step reaction because a shoulder appears on the main exothermic peak.

A DSC curve of the 6:7 (acetate:nitrate) composition is displayed in Fig. 4. It is evident that the decomposition is now a sharp, exothermic reaction occurring at 270°C . No other exothermic peaks are visible up to 725°C . Therefore, the decomposition of the acetate/nitrate mixtures into their corresponding oxides is complete at this temperature. In Figs. 5 and 6, DSC plots for powders containing these salts in 5:8 and 4:9 (acetate:nitrate) ratios are shown. Sharp exotherms occurring at 270°C are also visible in these figures. In addition, no other peaks are visible up to 725°C .

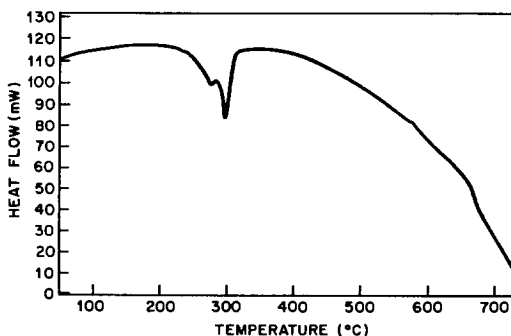


FIG. 3. DSC of the 7:6 (acetate:nitrate) precursor in flowing O_2 .

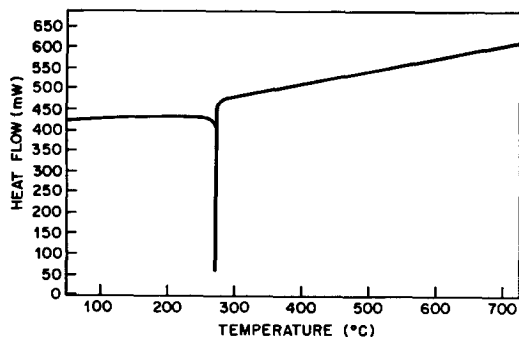


FIG. 4. DSC of the 6:7 (acetate : nitrate) precursor in flowing O_2 .

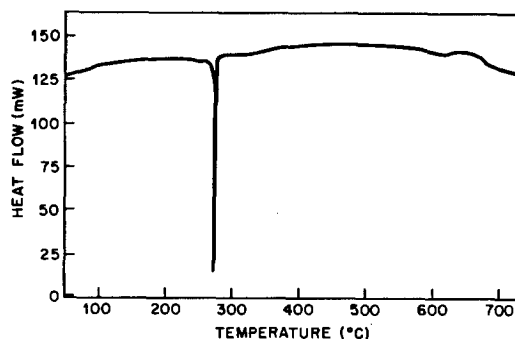


FIG. 6. DSC of the 4:9 (acetate : nitrate) precursor in flowing O_2 .

The DSC data clearly indicate that the introduction of ionic nitrate salts into the organic salt mixture changes the decomposition from a multiple-step reaction (all acetates) to a single-step reaction, as shown by a sharp exotherm in the DSC graph for the 7:6 to 5:8 (acetate : nitrate) precursors. This sharp decomposition at 270°C is at least 130°C lower than that required for the decomposition of the nitrate or acetate salts alone. It appears that the ionic NO_3^- salts, which are more potent oxidizers than molecular oxygen, participate in a low-temperature oxidation-reduction reaction with the organic salts.

This is further demonstrated by DSC data which shows a dependence of the de-

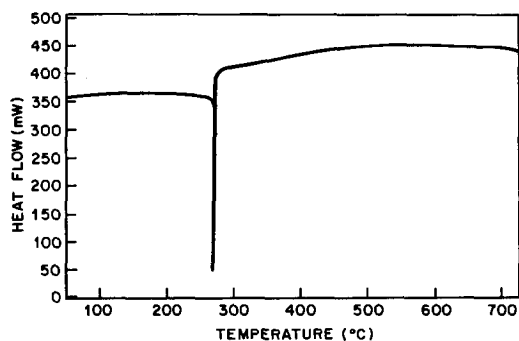


FIG. 5. DSC of the 5:8 (acetate : nitrate) precursor in flowing O_2 .

composition characteristics on the nitrate/acetate ratio. One expects that an ideal precursor composition related to the stoichiometry of the redox reaction (in O_2 atmosphere) should exist. The DSC data show that as the nitrate concentration increases along the series 9:4 (acetate : nitrate), 8:5, 7:6, and 6:7, the decomposition changes from multiple peak exotherms to a single lower temperature exotherm at 270°C for the 6:7 (acetate : nitrate) ratio. At even lower nitrate compositions, such as that found in the 5:8 (acetate : nitrate) precursors, the temperature of the sharp exotherm does not vary from 270°C . In this case, it is likely that the redox reaction of the fraction of the precursor containing the "ideal" acetate/nitrate ratio evolves enough heat to decompose nitrates in excess of that ideal ratio. X-ray diffraction of the decomposed precursors following reaction at $270\text{--}300^\circ\text{C}$ in flowing oxygen indicates that the decomposition is indeed complete. $\text{Ba}(\text{NO}_3)_2$, which is present in these precursors and which normally decomposes at 650°C in oxygen, was not detected after the low-temperature reaction. Hence, for these compositions the entire precursor mixture has been converted in the mixed oxides at 270°C . The 4:9 (acetate : nitrate) precursor seems to have slightly exceeded the limit where the redox reaction can de-

compose all of the excess nitrates at 270°C. Some Ba(NO₃)₂ is still present after a low-temperature reaction of this precursor, as determined by X-ray diffraction.

Another noteworthy trend is shown in Table I. Here, the enthalpies of reaction for the different compositions are obtained by integrating all of the decomposition peaks, including those occurring at temperatures higher than 270°C. The total enthalpy of reaction is shown to decrease as the acetate content in the spray-dried powder decreases. For instance, from the 9:4 acetate:nitrate composition one obtains $-\Delta H$ to be approximately 4016 (70) kJ/mole, whereas $-\Delta H$ obtained from the decomposition of the 4:9 (acetate:nitrate) precursor is 721 (70) kJ/mole. Therefore, it appears that a large portion of the reaction energy results from combustion of the acetate group (or its hydrocarbon component). Hence, the heat of reaction can be manipulated by varying the acetate:nitrate ratio in the spray-dried precursor.

Evolved gas analysis was performed on the precursor mixture which contains the acetate and nitrate salts in a ratio of 6:7. The product gases of the decompositions

are, in addition to H₂O, a mixture of N₂, N₂O, NO, and NO₂ as well as CO, CO₂, and O₂. The decomposition of the precursors for the EGA, however, was performed in vacuum. The precursors were normally reacted in flowing oxygen, so that the effluents for the EGA analysis may be different from those obtained under normal conditions. In particular, the lower oxides of nitrogen and CO which were detected may not be present when the precursors are reacted in flowing oxygen.

The spray-dried precursors were reacted at 910 and 820°C for 10 min in flowing oxygen to produce Ba₂YCu₃O_x directly. Compositions which had acetate to nitrate ratios smaller than 6:7 produced Ba₂YCu₃O_x with the single-phase materials, as determined by X-ray diffraction. This may be a consequence of the lowest decomposition temperatures (270°C) for these compositions. Figure 7 shows an X-ray diffraction pattern of single-phase Ba₂YCu₃O_x produced from the 5:8 (acetate:nitrate) precursor. The 4:9 (acetate:nitrate) composition showed as a secondary phase 2% CuO in the X-ray diffraction pattern (Fig. 8). Hence, 95% phase purity or greater is obtained under these conditions. At 820°C approximately 85% Ba₂YCu₃O_x is obtained for both compositions after 10–15 min of reaction in flowing oxygen.

Phase segregation is minimized for the nitrate/acetate precursors. This is shown by a comparison with the decomposition of a spray-dried mixture of acetate precursors or nitrate precursors alone. The (entirely) acetate precursors were prepared in the same manner as the acetate/nitrate precursors. The (entirely) nitrate precursors were spray dried from an aqueous solution diluted by 50% in order to dissolve all of the Ba(NO₃)₂. The acetate precursors show >40% secondary phases when decomposed at 910°C for 15–20 min in oxygen (33% BaCO₃, 13% CuO, and other phases), and the nitrate precursors show approximately

TABLE I
REACTION ENTHALPIES OBTAINED FROM DSC DATA
IN FLOWING O₂

Ratio of acetate : nitrate salts in the precursor	$-\Delta H$ (kJ/mole Ba ₂ YCu ₃ O _x) ^a (x = 6–7)
9:4	4016 ± 70 ^b
7:6	3473 ± 70
6:7	>1163
5:8	890 ± 70
4:9	721 ± 70

^a The molecular weight of the precursor mixtures was calculated from the appropriate nitrate:acetate ratios in the precursor. The degree of hydration of the spray-dried precursor was shown by gravimetry (for the 4:9 precursors) to be only ~1% of the total molecular weight.

^b Estimated error based upon multiple DSC runs.

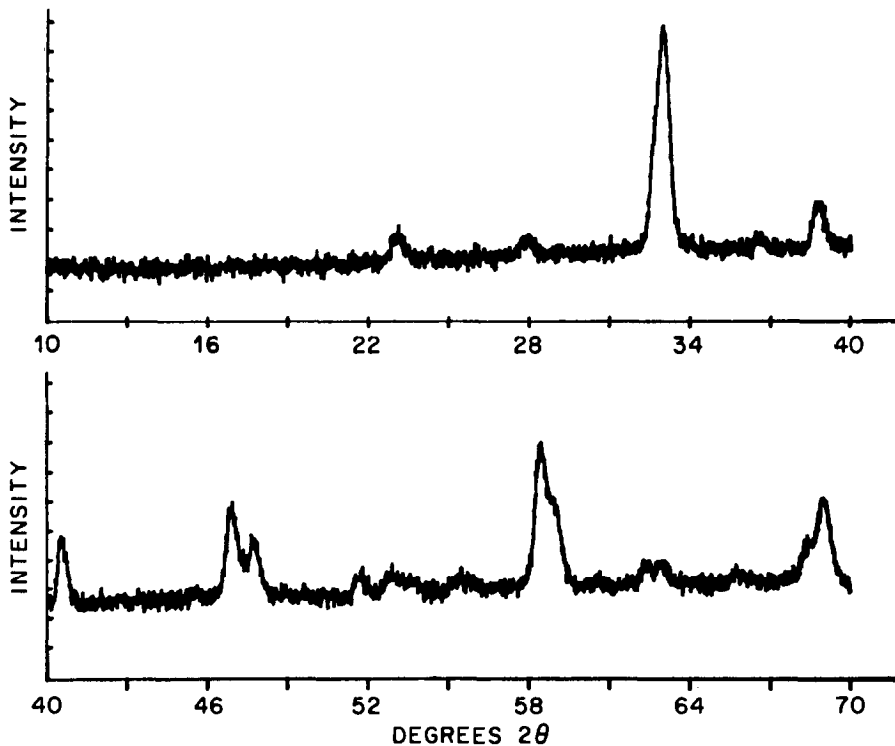


FIG. 7. X-ray diffraction pattern of BaYCu_3O_x obtained from the decomposition of the 5:8 (acetate:nitrate) precursor at 910°C for 10 min in flowing O_2 .

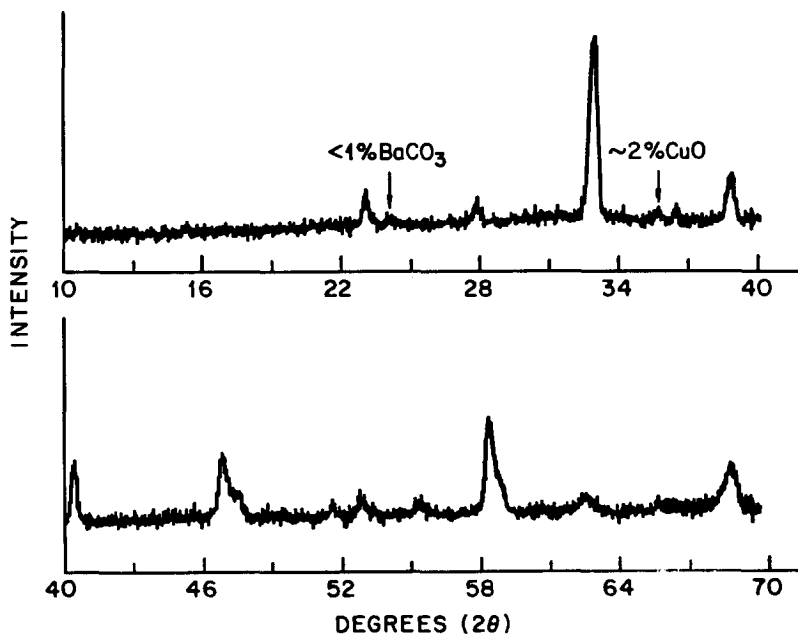


FIG. 8. X-ray diffraction pattern $\text{Ba}_2\text{YCu}_3\text{O}_x$ obtained from the decomposition of the 4:9 (acetate:nitrate) precursor at 910°C for 10 min in flowing O_2 .

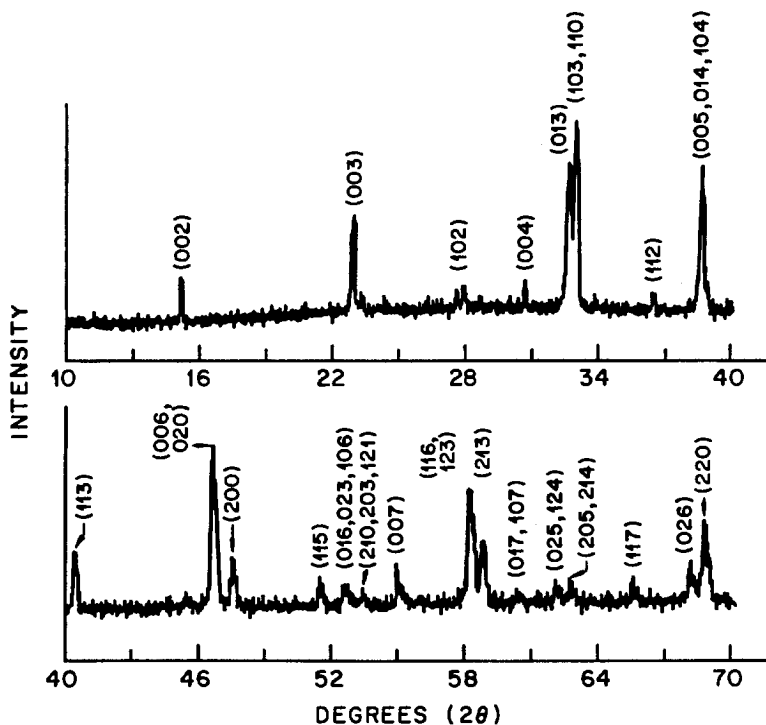


FIG. 9. X-ray diffraction pattern of $\text{Ba}_2\text{YCu}_3\text{O}_7$, obtained from pellets of $\text{Ba}_2\text{YCu}_3\text{O}_x$ sintered at 975°C and annealed at 450°C in flowing oxygen.

10% impurity phases (5% BaCuO_2 , 2% CuO , and 3% $\text{Cu}_2\text{Y}_2\text{O}_5$). This phase segregation is probably a consequence of the fact that the decomposition of these precursors occurs in several steps.

Sintered pellets were prepared from single-phase powders obtained from the acetate/nitrate precursors. The sintered pellets are completely single phase (>95%), as shown by X-ray diffraction in Fig. 9. The X-ray diffraction pattern can be indexed on the basis of an orthorhombic unit cell with $a = 3.823(5)$, $b = 3.886(5)$, and $c = 11.690(5)$ Å. These parameters are in agreement with those reported (1) for $\text{Ba}_2\text{YCu}_3\text{O}_{6.98}$, the composition which is the upper limit of oxygen content and which exhibits the highest superconducting T_c 's. Magnetic (ac) and resistivity measurements of sintered pellets obtained from the 5:8 (acetate:nitrate) composition show the material possesses

an onset of $94\text{--}95^\circ\text{K}$ and is fully superconducting by $90.5\text{--}91^\circ\text{K}$ (Fig. 10). The material obtained from the 9:4 (nitrate:acetate) composition has a magnetically determined onset at $93\text{--}94^\circ\text{K}$ and is fully superconducting by 88°K .

This low-temperature oxidation-reduction technique should be applicable to other mixtures of oxidizing and reducing salt precursors. For instance, organic salts other than the acetates could be good reducing agents. These studies are currently in progress. The ionic nitrate salts appear to be the best choice for the oxidizing components, however. Other strong oxidizers, such as the perchlorate salts, would not be good candidates because they can be explosively reactive, and may leave behind a halide residue following decomposition. These residues would contaminate any $\text{Ba}_2\text{YCu}_3\text{O}_7$ produced.

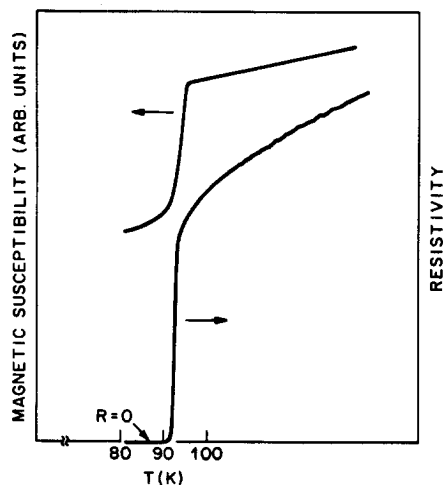


FIG. 10. Magnetic (ac) susceptibility and four-probe resistivity data from pellets of $\text{Ba}_2\text{YCu}_3\text{O}_7$ sintered from $\text{Ba}_2\text{YCu}_3\text{O}_x$ obtained from the 5:8 (acetate:nitrate) precursor.

Conclusion

A new and simple low-temperature reaction between ionic salt precursors which can be used to produce superconductor oxides has been investigated. It has been demonstrated that the nitrate salts, which are potent oxidizers, participate in a low-temperature oxidation-reduction reaction. This is shown by the fact that the temperature of the reaction is at least 130°C lower than the decomposition temperature of either ionic salt separately. This is also supported by the dependence of the reaction temperature on the ratio of the acetate to nitrate salts in the spray-dried precursor. It is noteworthy that within a certain composition range (from 6:7 to 5:8 (acetate:nitrate)), the temperature of complete decomposition does not vary from 270°C . The reaction enthalpy, on the other hand, decreases with decreasing acetate concentra-

tion. This offers the advantage that the reaction enthalpy can be adjusted, by varying the acetate:nitrate ratio within a certain composition range, without compromising the low decomposition temperature of the precursors. The precursors can be decomposed at 910°C to yield single-phase (95% or better) $\text{Ba}_2\text{YCu}_3\text{O}_x$. Sintered disks of these materials are single phase and exhibit superconducting properties which compare favorably with those obtained from ceramic methods.

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