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Synthesis of $Ba_2YCu_3O_7$ Powder by Anionic Oxidation (NO_3^-)–Reduction (RCOO$^-$, where R Is H, CH_3, and CH_3CH_2)

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A new method for synthesizing homogeneous oxide powder, reported earlier, is studied. This technique involves spray drying a solution containing an oxidizing and reducing salt into an intimately mixed powder. The spray-dried powder undergoes an internal oxidation–reduction reaction which completely converts it into the mixed oxide at <300°C. The resulting powder is homogeneous on a fine scale and can be reacted to form the final oxide compound at much shorter times than those using the usual ceramic methods. Single phase (>95%) $Ba_2YCu_3O_{7-x}$ is formed in 10 min at 910°C. Previously, mixtures of nitrate (oxidizing) and acetate (reducing) salts were studied. This is now extended to include other organic reducing agents such as formates and propionates and comparisons are made for RCOO$^-$, where R = H, CH_3, and CH_2CH_3. The formate/nitrate and propionate/nitrate precursors are completely converted into their oxides at temperatures as low as 210° and 260°C, respectively (as opposed to 270°C for the acetate/nitrate precursors). The enthalpy of the low-temperature reaction is dependent on the organic fraction in the mixture. In addition, the reaction enthalpies of the formate/nitrate precursors are less than that of the propionate/nitrate or acetate/nitrate precursors: $-\Delta H$ (7 : 6, propionate : nitrate) = 3184, $-\Delta H$ (7 : 6, acetate : nitrate) = 3473, and $-\Delta H$ (8 : 5, formate : nitrate) = 958 kj/mole. Hence, control over both the reaction enthalpy and the decomposition temperature can be achieved by the choice of organic ligand reducing agent and the nitrate/reducing agent ratios. © 1989 Academic Press, Inc.

Introduction

In a previous paper (*1*), a novel chemical method for the bulk preparation of homogeneous oxide powders was described. A chemical process which can be used for large-scale synthesis is desirable because ceramic methods (*2*) require multiple-step processing with intermediate grindings. Chemical methods can decrease the firing duration and temperatures required to produce single-phase materials. The chemical method described (*1*), which is further investigated in this study, involves mixing oxidizing and reducing salts in an aqueous solution. This solution (which can contain nitrate and organic salts) is spray dried to form an intimately mixed powder. The spray-dried precursors can be completely decomposed into their mixed metal oxides (and in some cases some $BaCO_3$) at temperatures as low as 270°C. This is a consequence of an internal (or anionic) oxidation–reduction reaction which occurs between the nitrate and the organic salt ligands. Since the oxidizing and reducing agents are intimately mixed, this exothermic reaction, once initiated, drives any remaining reactions to completion in one reaction step. Thus, this technique is called

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self-propagating chemical decomposition (SCD). Because the decomposition occurs in one reaction step, as opposed to a multiple-step decomposition for organic precursors, phase segregation in the resultant oxide powder is minimized. For instance, single-phase $Ba_2YCu_3O_7$ can be formed in 10 min at 910°C (as opposed to several hours via the ceramic route).

In addition, we have noted that some control over the reaction enthalpy (*1*) as well as over the reaction temperature, can be achieved by varying the ratio of acetate/nitrate salts in the spray-dried precursor. Control of these parameters can have a significant impact on grain growth and therefore on particle size of the superconductor oxides.

In this study, we explore the effect of organic reducing agents other than the acetates. Precursors containing propionate ($CH_3CH_2COO^-$) and formate ($HCOO^-$) salts are used. The impact of the organic reducing agent carbon chain length (in the series $RCOO^-$, where R is H, CH_2, and CH_3CH_2) on the enthalpy of reaction and on the (redox) reaction temperature will be discussed.

Experimental

Stock solutions were prepared with the correct cation stoichiometry to produce $Ba_2YCu_3O_7$. Several combinations of the nitrate and formate salts were used to produce solutions containing these salts in the ratios (formate : nitrate) 9 : 4, 8 : 5, 6 : 7, and 4.9. $BaCO_3$ (Fisher, ACS) and, where necessary, $CuCO_3$ (Fisher) were converted into their corresponding soluble formates by reactions with a minimum of formic acid. Y_2O_3 was used instead of $Y_2(CO_3)_3 \cdot xH_2O$ to form yttrium formate. Yttrium carbonate is too hygroscopic to be manipulated and accurately weighed in air. Instead, Y_2O_3 is converted into the carbonate by placing it in boiling water. Formic acid is then added to convert the carbonate into the soluble formate. $Ba(NO_3)_2$ was used for the 6 : 7 (formate : nitrate) composition, and $Y(NO_3)_3$ for the 4 : 9 compositions. The propionate/nitrate precursor solutions were prepared using the same procedure, except that propionic acid was used instead of formic acid.

A Bowen Engineering, Inc. (North Branch, NJ) conical-type laboratory spray drier was used. Enough solution to make 250 g of $Ba_2YCu_3O_7$ was spray dried over a period of 30–40 min. The inlet temperature was 288°C. The temperature prior to the cyclone collector was 149–152°C. Approximately 75% of the light blue powder obtained was collected in the main chamber and the cyclone apparatus attached to the main chamber.

Thermal analysis was performed using the Perkin–Elmer System 7. Differential scanning calorimetry (DSC) was done in open Au pans at a heating rate of 10°C min^{-1} in flowing (50 ml min^{-1}) O_2. An empty sample pan served as a reference.

Powder X-ray diffraction data were obtained using a Phillips XRD 3600 powder diffractometer with Cu$K\alpha$ radiation.

The spray-dried powders were reacted in flowing oxygen over a period of 5–10 min at various temperatures. [*Caution: This reaction should be attempted only in an open system with excess flowing oxygen.*] In all cases, the powders were rapidly quenched from high temperatures. Single-phase $Ba_2YCu_3O_x$ could be prepared in this manner, as determined by X-ray diffraction. Pellets were prepared by cold-pressing precursors, which had been decomposed into their mixed metal oxides or $Ba_2YCu_3O_x$, at 276 mPa (40,000 psi). The pellets were sintered by heating to 940–975°C in flowing oxygen and then annealed at 450°C for 6–10 hr to maximize the oxygen stoichiometry. Magnetic susceptibility measurements (a.c.) were made on disks encapsulated in small plastic vials by cooling the samples from room temperature to liquid helium temperatures using a thermometer calibrated to within 0.2 K.

Results

Table I summarizes the decomposition temperatures and thermodynamic data obtained from DSC measurements (Figs. 1–7) of formate/nitrate and propionate/nitrate precursors. Figures 1a–1d show DSC data from formate/nitrate decompositions in flowing O_2. It is striking that the 9 : 4 and 8 : 5 (formate : nitrate) precursors show decomposition exotherms centered at 210°C (9 : 4) and 220°C (8 : 5). This is a marked improvement over the 270°C reaction temperatures of the acetate/nitrate precursors. X-ray diffraction of the precursors, following reaction at 300°C (10 min in flowing oxygen) indicates the decomposition is complete at these temperatures. $Ba(NO_3)_2$, which can be detected by X-ray diffraction in these precursors (*1*), and which normally decomposes at 650°C (*3*), was not detected after this low-temperature reaction.

TABLE I

THERMODYNAMIC DATA FOR THE DECOMPOSITION OF IONIC SALT PRECURSORS

Precursor ratio	Decomposition temperature	$-\Delta H$ (kJ/mole)
Formate : nitrate		
9 : 4	210°C	1036 ± 70
8 : 5	221	958
6 : 7	253	541
4 : 9	Excess of oxidant	—
Acetate : nitrate		
9 : 4	>270°C	4016 ± 70
7 : 6	>270	3473
6 : 7	270	>1163
5 : 8	270	890
4 : 9	>270	721
Propionate : nitrate		
4 : 9	264°C	1073 ± 70
7 : 6	289	3184

Figure 1c shows a decomposition exotherm for the 6 : 7 (formate : nitrate) mixture. Although the onset is low, the decomposition peak is centered at 250°C. Therefore, this precursor mixture is not completely reacted following a low-temperature firing. X-ray diffraction of this precursor, after reaction at 300°C, showed some residual $Ba(NO_3)_2$. In Fig. 1d, DSC data for the 4 : 9 (formate : nitrate) composition is displayed. It is evident that the reaction of this composition at low temperature is also incomplete, since immediately after the exothermic peak, an endotherm is visible. This low-temperature endotherm can be attributed to the decomposition of copper or of yttrium nitrate salts.

Figure 3 shows DSC plots for the 4 : 9 and 7 : 6 (propionate : nitrate) precursors. A sharp exotherm is apparent at 264°C for the 4 : 0 precursor and at 289°C (T_{center}) for the 7 : 6 propionate : nitrate precursors. X-ray diffraction shows that the decomposition is complete at these temperatures.

Those precursors which are completely reacted at low temperatures can be directly converted into $Ba_2YCu_3O_x$. For instance, following reaction of the 9 : 4 and 8 : 5 (formate : nitrate) decomposed precursors (the mixed metal oxides) at 910–920°C for 10 min, single-phase (>95%) $Ba_2YCu_3O_x$ was formed. No secondary phases were detected by X-ray diffraction. This pattern is shown in Fig. 2. The 4 : 9 (propionate : nitrate) precursor also yields single-phase materials under these reaction conditions, as shown in Fig. 4.

Sintered pellets prepared from $Ba_2YCu_3O_x$ or the mixed metal oxides are single phase (>95%) as determined by X-ray diffraction. In Table II, the superconducting transitions of some of these pellets are listed. Sintered pellets formed from mixed metal oxides obtained from the 9 : 4 (formate : nitrate) and 4 : 9 (propionate : nitrate) precursors show T_c onsets of 95 and 93 K, respectively, with transition widths of no

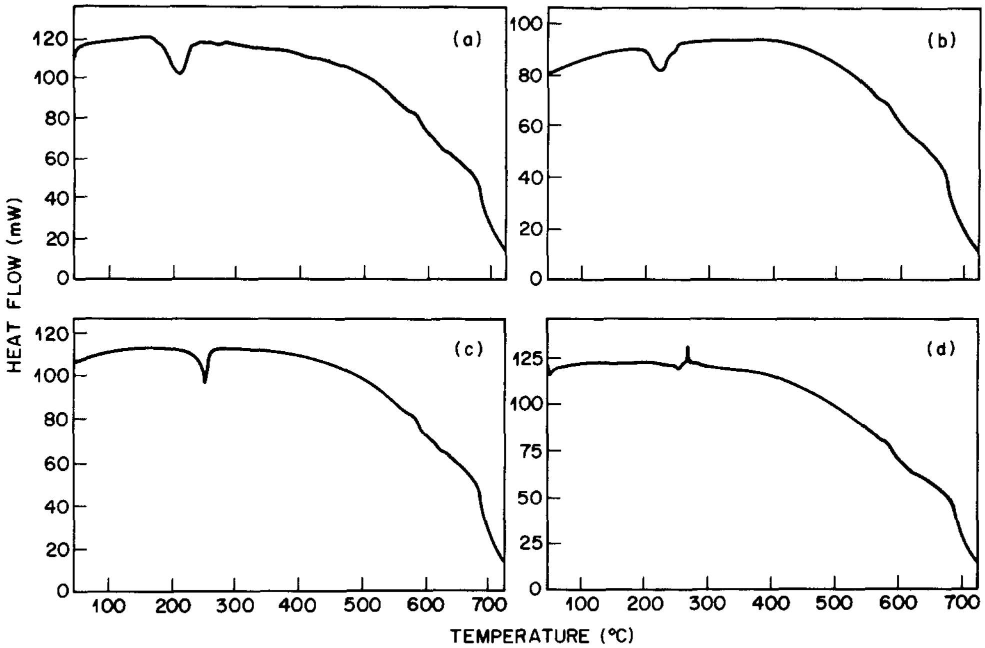

FIG. 1. DSC of formate : nitrate precursors in flowing O_2; (a) 9 : 4 (formate : nitrate), (b) 8 : 5, (c) 6 : 7, and (d) 4 : 9.

more than 4–5 K. In addition, pellets prepared from $Ba_2YCu_3O_x$ formed from the 9 : 4 and 8 : 5 (formate : nitrate) precursors, as well as those from the 4 : 9 and 7 : 6 (propionate : nitrate) precursors, all show onset T_c's of 93–94 K with transition widths of no more than 4–5 K. However, sintered pellets prepared from mixed oxides obtained

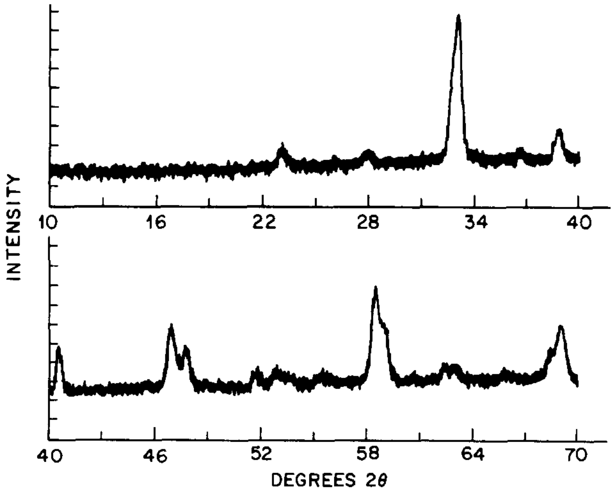

FIG. 2. X-ray pattern of a representative formate/nitrate (8 : 5, formate : nitrate) precursor following reaction at 910°C for 10 min in O_2.

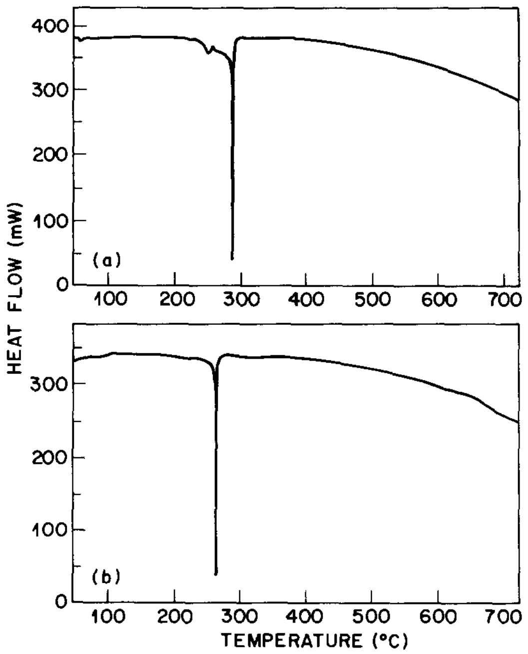

FIG. 3. DSC of propionate : nitrate precursors in flowing O_2; (a) 7 : 6 (propionate : nitrate), (b) 4 : 9.

from the 8 : 5 (formate : nitrate) and 7 : 6 (propionate : nitrate) precursors show broad transition widths with onsets of 92–93 K. For these two compositions, the decomposed precursor's mixed oxides sinter very differently from $Ba_2YCu_3O_x$. The reason for this may be due to the choice of firing cycle, which would influence grain growth during the sintering process.

Discussion

The X-ray diffraction and DSC data for the formate/nitrate precursors appear to indicate the existence of an "ideal" precursor composition. This has been noted (*1*) for the acetate/nitrate precursors as well. For these precursors, it appeared that an ideal acetate/nitrate ratio existed, and that slightly beyond this composition, the energy released from the anionic redox reaction was insufficient to decompose any excess nitrates, especially $Ba(NO_3)_2$. It seems likely that the 9 : 4 and 8 : 5 formate : nitrate compositions also encompass an ideal ratio. This ratio is different from that of the acetate/nitrate precursors, whose ideal ratio appeared to lie within the 6 : 7 to 5 : 8 (acetate : nitrate) range.

The enthalpies of reaction for the propionate/nitrate and formate/nitrate salts, obtained from integrating the peaks obtained from the DSC data, are tabulated in Table I and are shown graphically in Fig. 5. It is

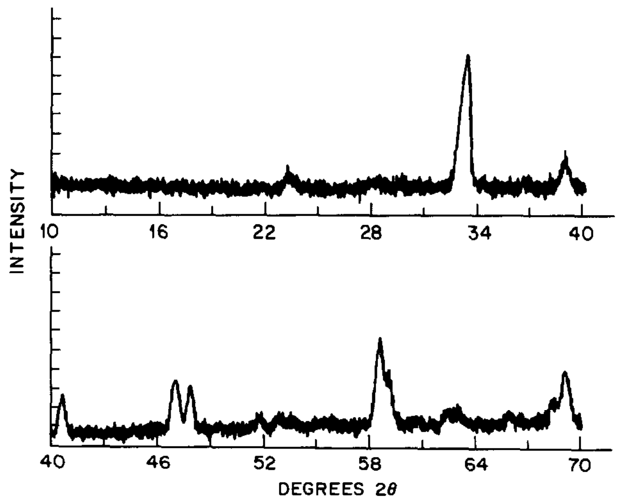

FIG. 4. X-ray pattern of 4 : 9 (propionate : nitrate) following reaction at 910°C for 10 min in O_2.

TABLE II

SUPERCONDUCTING TRANSITIONS OF SINTERED PELLETS

Precursor ratio	From $Ba_2YCu_3O_x$ powder T_c (onset), T_c ($R \sim 0$)	From green oxides T_c (onset), T_c ($R \sim 0$)
9 formate : 4 nitrate	95, 90	93, 88
8 formate : 5 nitrate	92, 89	93, 81
5 acetate : 8 nitrate	94, 91	94, 90
4 propionate : 9 nitrate	93, 88	93, 88
7 propionate : 6 nitrate	93, 89	92, 85

evident that a trend shown for the acetate/nitrate precursors also exists for other organic reducing agents. In Table I and Fig. 5, it is generally true that as the organic component in the mixture is reduced, the enthalpy of the reaction decreases. It is likely that much of the energy released by the reaction results from combustion of the hydrocarbon fragment in the reducing agent. It is also apparent that the reaction enthalpy is closely tied to the choice of organic reducing agent. In general, the acetate/nitrate and propionate/nitrate precursors of a given composition release more energy during the oxidation–reduction reaction than do the formate/nitrate precursors. This also supports the view that a substantial portion of the reaction enthalpy is produced from combustion of the hydrocarbon component in the precursor.

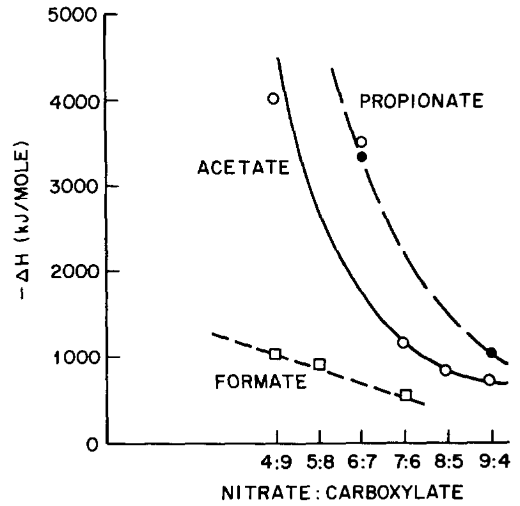

FIG. 5. Reaction enthalpy versus nitrate/carboxylate ratios for various precursors.

The trend in decomposition temperature, obtained from the DSC data, is also noteworthy. In general, for the precursor series $NO_3^-/RCOO^-$, the decomposition temperature trend is $CH_3CH_2 > CH_3 > H$ (for R in $RCOO^-$). If the aliphatic group were the reactive center in this reducing agent, then one would expect the most electron-rich fragment to be the most reactive, with the lowest decomposition temperature. The most electron-rich carbon should be farthest from the (electron-withdrawing) carboxylate group. Since the reducing agent salts of $CH_3CH_2COO^-$ have the highest decomposition temperature and $HCOO^-$ the lowest, then clearly the aliphatic group cannot be the initial reactive center. However, if the redox decomposition involves some carbon–oxygen bond breaking, as well as cation–oxygen bond formation, then the following can be argued. The replacement of R–COO^- (where R is CH_3CH_2 or CH_3) with H–COO^- results in a greater effective (positive) charge on the carboxylate carbon. We think this affects the reactivity by weakening the C–O bond, perhaps by making it less covalent. Consequently, carbon–oxygen bond breaking during the reaction is enhanced and results in the lower decomposition temperatures observed for the formate/nitrate precursors.

Conclusion

These results demonstrate that both the reaction enthalpy and (redox) decomposition temperature can be controlled by the choice of organic reducing agent and the nitrate/reducing agent ratio in the precursor. These precursors can be rapidly converted into single-phase $Ba_2YCu_3O_x$ by virtue of a low-temperature redox reaction which forms a highly reactive mixture of metal oxides and $BaCO_3$. The ease of formation of $Ba_2YCu_3O_x$ and the mixed metal oxides makes these mixed ionic salt precursors ideal for the large-scale synthesis of superconductor oxides.

References

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