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Synthesis of $Ba_2YCu_3O_7$ by the SCD Method Using Amino Acid Salt Reducing Agents

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The anionic oxidation–reduction or SCD method relies on an internal oxidation–reduction reaction which converts spray-dried precursors into intimately mixed and highly reactive metal oxide powders. Earlier studies focused on precursor mixtures containing oxidizing components such as NO_3^- salts with reducing salts ($RCOO^-$, where R is H, CH_3, or CH_2CH_3) which react to form $Ba_2YCu_3O_7$ powder. In this work, amino acid reducing agents are used. The impact of the functional group change, in the reducing agent of the NO_3^-/amino acid precursors, is shown by DSC to result in sharp (and therefore rapid) oxidation–reduction reactions which occur at lower temperatures. The trend in reaction temperature correlates inversely with the expected basicity of the amino group in the series (numbers in parentheses represent mole ratios): $CH_3CH(NH_2)COO^-/NO_3^-$ (4/9) = 206°C > $NH_2CH_2COO^-/NO_3^-$ (4/9) = 195°C > $NH_2CH_2CH_2COO^-/NO_3^-$ (4/9) = 191°C. The mixed oxide product is highly reactive and can be converted to single-phase $Ba_2YCu_3O_x$ when fired at 900–910°C for 10 min in flowing oxygen. © 1990 Academic Press, Inc.

Introduction

In recent work (*1*, *2*) a new chemical method for synthesizing homogeneous oxide powder has been reported. In this process, an aqueous solution containing oxidizing and reducing salts is spray dried into an intimately mixed powder. An oxidation–reduction reaction, occurring between the anions in the powder, converts the precursor into mixed oxides at temperature <300°C. Because the precursor is intimately mixed, the energy released during this low-temperature redox reaction drives any remaining decomposition reactions to completion in one step. Thus, this process is called self-propagating chemical decomposition. The mixed metal oxide formed is homogeneous on a fine scale and can be reacted to form the final oxide powder in much shorter times than those using the usual ceramic methods. For instance, single-phase (by X-ray diffraction) $Ba_2YCu_3O_x$ powder can be formed at 910°C in 10 min.

In previous reports, we have described precursors in which strong oxidizers, such as ionic salts containing NO_3^-, react with salts of $RCOO^-$ (where R is CH_3CH_2, CH_3, and H) which act as reducing agents. In this series, the formate/nitrate precursors (where R is H) possess the lowest temperature decomposition, 210°C. The acetate/nitrate (R is CH_3) and propionate/nitrate (R is CH_3CH_2) precursors decompose approximately at 260–270°C. Hence, by making a relatively simple change in the reducing agent (where R is changed to H from CH_3CH_2 or CH_3), the precursor decomposi-

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tion temperature (and reaction enthalpy) (*3*) is significantly altered. Assuming that the carboxylate group is the reactive center, there are several mechanisms by which the reactivity of the carboxylate group is affected by the nature of the hydrocarbons chosen. These could include steric effects as well as variation of the electron density at the carboxylate carbon. In order to change the reactive center in the oxidation–reduction reaction, and perhaps the temperature at which reaction occurs, the hydrocarbon group (in $RCOO^-$) was replaced with a different functional group. Because reducing agents are electron-donating, the electron-rich amino functional groups were thought to be good candidates. In this study, we investigate the anionic redox reaction of nitrate salts with glycinates ($NH_2CH_2COO^-$), β-alanides ($NH_2CH_2CH_2COO^-$), and α-alanides ($CH_3CH(NH_2)COO^-$). The relationship between the expected basicity of the NH_2 groups in the amino acid salt and the decomposition characteristics of the nitrate/amino acid salt precursors is discussed.

Differential scanning calorimetric (DSC) measurements on the spray-dried precursors are reported. X-ray diffraction data for $Ba_2YCu_3O_x$ powder and $Ba_2YCu_3O_7$ pellets, as well as magnetic (ac) susceptibility measurements are presented.

Experimental

The procedures used are similar to those described previously (*1–3*). An aqueous solution, containing the correct cation stoichiometry to produce $Ba_2YCu_3O_x$, is prepared from $Y(NO_3)_3 \cdot xH_2O$ (Aldrich), $Cu(NO_3)_2 \cdot xH_2O$ (Alfa), $BaCO_3$ (Fisher), and glycine (Aldrich, 99+%), α-alanine (Aldrich, 99%), or β-alanine (Aldrich, 98+%). The copper and yttrium nitrates were gravimetrically analyzed as described previously (*1*). The $BaCO_3$ and amino acids were added such that their stoichiometric ratio was always 1/1. One difficulty encountered in completely dissolving the amino acid precursors was that the basic amino group, in the case of α- and β-alanindes, can raise the solution pH. Most probably, the higher pH precipitates insoluble copper and yttrium hydroxides, as well as preventing the complete digestion of the carbonates. For the alanine derivatives, significant cloudiness in the solution was observed. To circumvent this problem, small amounts of nitric or acetic acid were added to bring the solution pH to approximately 5. [Since the higher nitrate fractions lower the pH when dissolved in water, the mole ratio 4/9 (amino acid/nitrate salt) composition ratio was investigated.] Solutions containing ratios of amino acid/nitrates greater than 4/9 could be prepared with the addition of more acid, although the presence of significant quantities of nitric (or acetic) acid might alter the composition of the spray-dried precursor. The solution might also be made more concentrated in cations by the addition of excess acid.

Enough solution to prepare 125 g of $Ba_2YCu_3O_x$ (4.2 liters H_2O) was spray dried in 30–45 min. A Bowen Engineering, Inc. (North Branch, NJ) conical-type laboratory spray drier was used. The inlet temperature was 300°C. The temperature prior to the cyclone apparatus was 145–152°C. A light purple powder was produced in approximately 65–70% yield.

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 $CuK\alpha$ radiation using 0.02° 2θ steps and 0.4 sec count time per step.

The spray-dried powders were reacted in flowing oxygen over a period of 5–10 min at

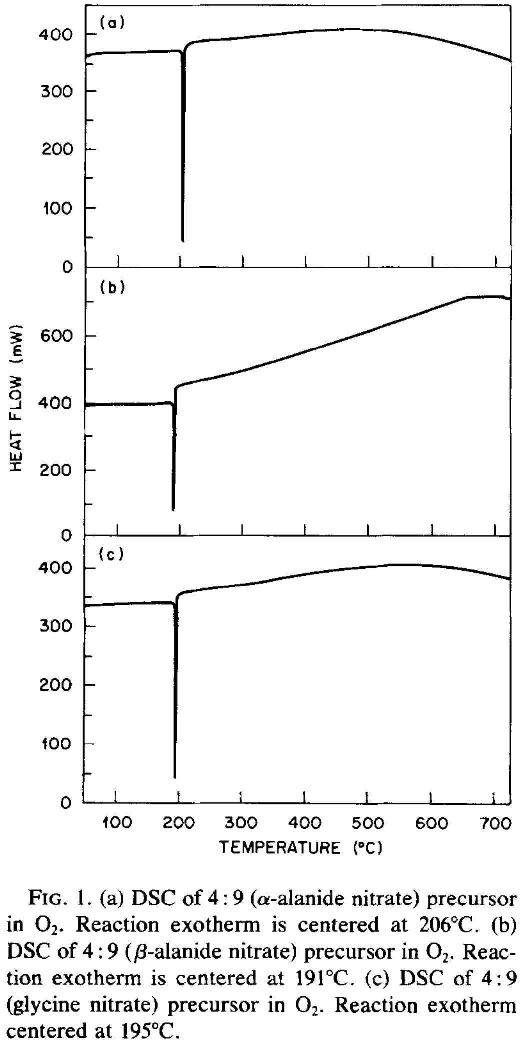


FIG. 1. (a) DSC of 4 : 9 (α-alanide nitrate) precursor in O_2. Reaction exotherm is centered at 206°C. (b) DSC of 4 : 9 (β-alanide nitrate) precursor in O_2. Reaction exotherm is centered at 191°C. (c) DSC of 4 : 9 (glycine nitrate) precursor in O_2. Reaction exotherm centered at 195°C.

various temperatures. The powders were rapidly quenched from high temperatures. Pellets were prepared by cold-pressing precursors, which had been decomposed into their mixed metal oxides (and perhaps some $BaCO_3$) or $Ba_2YCu_3O_x$, at 260 MPa (40,000 psi) into pellets. The pellets were sintered by heating to 945–975°C in flowing oxygen and annealing at 450°C for at least 6 hr in order to maximize the oxygen stoichiometry. Magnetic (ac) susceptibility measurements were made on disks encapsulated in small plastic vials. Measurements were performed during cooling of the sample from room temperature to liquid helium temperatures using a thermometer calibrated to within ±0.2 K.

Discussion

Figures 1, 2, and 3 show DSC data for the decomposition of the glycinate/nitrate (4/9), β-alanide/nitrate (4/9), and α-alanide/nitrate (4/9) precursors. Very sharp exotherms are evident which are centered at 206, 195, and 191°C for the α-alanide/nitrate ($CH_3CH(NH_2)COO^-/NO_3^-$), glycinate/nitrate ($NH_2CH_2COO^-/NO_3^-$), and β-alanide/nitrate ($NH_2CH_2CH_2COO^-/NO_3^-$) precursors, respectively. The conversion of these precursors into their corresponding oxides (and perhaps some $BaCO_3$) is complete at these low temperatures. This is shown by the fact that following reaction in flowing oxygen, no unreacted nitrates such as $Ba(NO_3)_2$ were detected by X-ray diffraction. $Ba(NO_3)_2$ ordinarily decomposes at 650°C (*4*) and is visible in the X-ray patterns of the spray-dried precursors before decomposition.

It is interesting to compare the trend in decomposition temperature for this series with that of the $RCOO^-/NO_3^-$ precursors (where R is CH_3CH_2, CH_3, or H), which is shown in Table I. In all cases, the reaction temperature of the amino acid/nitrate salt precursors is significantly lower than that of the $RCOO^-/NO_3^-$ precursors. For instance, glycine, NH_2CH_2COOH, can be derived from propionic acid, CH_3CH_2COOH, by replacing the terminal methyl group by an amino group. The change of functional group results in a decomposition temperature (for the ionic salt precursors) of 195°C, which is 65°C lower than that of the propionate/nitrate precursors. Since the amino group is electron-rich (due to the availability of the lone electron pair) it is a more potent reducing agent toward the ionic ni-

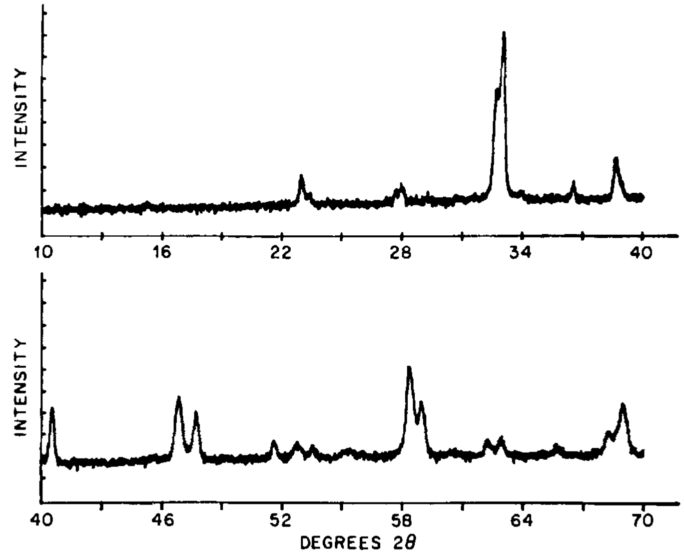


FIG. 2. X-ray diffraction pattern of 4 : 9 (glycine : nitrate) precursor following reaction at 910°C for 10 min. This material is single-phase $Ba_2YCu_3O_x$ (>95%).

trate oxidizers. By changing from the amine-free reducing agents ($RCOO^-$) to the amino acid salts, it appears that the reactive center (in the redox reaction) has been changed from the carboxylate carbon to the amino group.

TABLE I

DECOMPOSITION DATA FOR SCD IONIC SALT PRECURSORS

Precursor mole ratio	Decomposition temperature	Comments
Formate : nitrate		
9:4	210°C	Broad DSC peak
8:5	221°C	Broad
6:7	253°C	Broad
4:9	—	
Acetate : nitrate		
9:4	>270°C	Sharp, two peaks
7:6	>270°C	Sharp, two peaks
6:7	270°C	Sharp
5:8	270°C	Sharp
4:9	>270°C	Sharp, excess $Ba(NO_3)_2$
Propionate : nitrate		
4:9	264°C	Sharp DSC peak
7:6	289°C	Sharp
Amino acid : nitrate		
4 : 9 (α-alanide : nitrate)	206°C	Sharp DSC peak
4 : 9 (glycinate : nitrate)	195°C	Sharp
4 : 9 (β-alanide : nitrate)	191°C	Sharp

Within the series of ionic nitrate/amino acid salt precursors, the trend in decomposition temperature is: $NH_2CH_2CH_2COO^-$ (β-alanide) < $NH_2CH_2COO^-$ (glycinate) < $CH_3CH(NH_2)COO^-$ (α-alanide). This trend correlates with the expected decrease in basicity of the amino group, the most basic amino group being that which has the most available lone pair of electrons to enter into a redox reaction. (The β-alanide/nitrate precursor is more basic, and therefore more reactive, than the glycinate/nitrate precursors because the amino group is one additional carbon removed from the terminal carboxylate group. The slightly electropositive carboxylate carbon tends to draw electron density away from a neighboring amino group.)

The comparison between the glycinate/nitrate and α-alanide/nitrate precursors is also interesting. α-Alanine can be derived from glycine by replacing one hydrogen (in

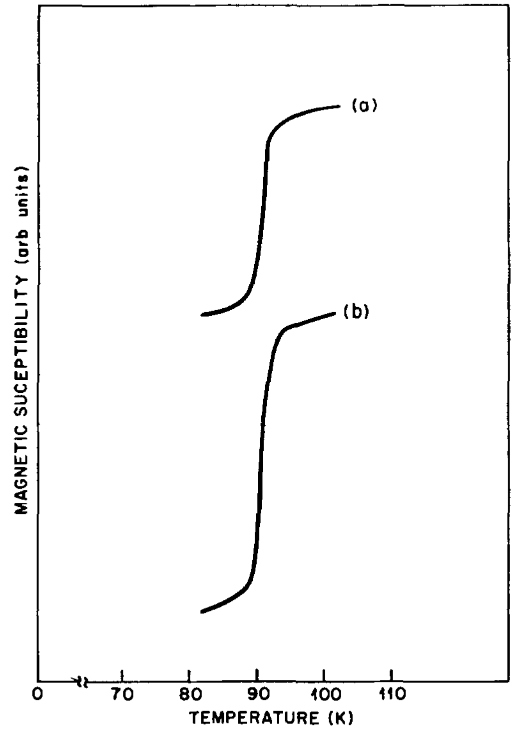
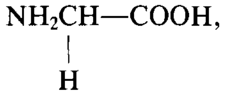
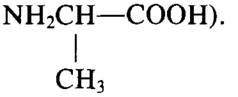


FIG. 3. Magnetic (ac) susceptibility plot of sintered pellets prepared from 4 : 9 (β-alanide : nitrate) precursor. (a) Sintered pellet prepared from mixed oxide; (b) pellet pressed from $Ba_2YCu_3O_x$ and sintered.

glycine,  $NH_2\underset{\substack{|\\ H}}{C}H\text{—}COOH$, with a methyl group  $NH_2\underset{\substack{|\\ CH_3}}{C}H\text{—}COOH$). Undoubtedly, hydrogen is less polarizable than the methyl group, and thus would tend to delocalize electron density away from the amino group to a lesser degree. Hence, the amino group in glycine is more electron-rich and is therefore a better reducing agent with a lower precursor decomposition temperature.

The amino acid/salt nitrate precursors either directly, or when decomposed into the metal oxides in a low temperature reaction step, produce (>95%) single-phase $Ba_2YCu_3O_x$ after reaction at 910°C for 10 min. The powder X-ray diffraction pattern of this product is shown in Fig. 2. Sintered pellets prepared from either the mixed metal oxide (which contains some $BaCO_3$) or $Ba_2YCu_3O_x$ are single phase as determined by X-ray diffraction. Magnetically determined superconducting transitions are sharp (no wider than 4 K) and have onsets of 94–92 K. Figure 3 shows that pellets formed and sintered using $Ba_2YCu_3O_x$ possess transition characteristics which are similar to those obtained from pellets sintered from the mixed metal oxides.

In summary, the functional group on the reducing component of the NO_3^-/organic salt precursors influences the temperature of decomposition. The reactive center on the reducing agent apparently shifts from the carboxylate carbon (in the $RCOO^-$ salts) to the amino group (in the amino acid salts). The amino group, by virtue of a lone electron pair which can enter into a redox reaction with NO_3^- salts, lowers the reaction initiation temperature. In addition to being a simple laboratory procedure, the rapid decomposition which results at low temperatures should be useful as a large-scale processing method for oxide powders.

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