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Synthesis of bismuth/strontium/calcium/copper and yttrium/barium/copper oxide systems from malonate precursors

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Malonate salts of the above metals dissolved in a glycerol/malonic acid polyester have been found to form amorphous oxide systems at relatively low temperatures. Mixtures of the appropriate stoichiometry rapidly form the corresponding 2212 BSCCO and tetragonal YBCO oxide systems on heating to temperatures in the range 750–850 °C. In the case of YBCO, the formation of crystalline barium carbonate can be largely suppressed by an appropriate thermal programme, but whereas the tetragonal $YBCO_{6.5}$ phase can be readily obtained as the sole crystalline phase, oxygen diffusion into this phase is remarkably difficult. This appears to be due to the presence of amorphous intergranular material.

1. Introduction

The discovery of the so-called "warm" superconducting oxide systems has led to a surge of activity in synthetic methods for mixed-metal oxide systems. These have included a number of thermal decomposition routes based on, as examples from the extensive literature, nitrates [1, 2], co-precipitated oxalates [3] sol–gel systems [4, 5], citrate polyester systems [6] and 2-ethyl hexanoate solutions [7].

Co-precipitation methods usually require solutions of different stoichiometry from that of the desired precipitate and careful control of precipitation conditions, principally pH. Heating of the co-precipitates essentially give mixtures of finely divided crystalline oxides. Oxalate-based methods have been developed for yttrium/barium/copper systems but this precursor is unsuitable for bismuth-containing systems. Sol–gel methods are more versatile, but again require close control of gel formation conditions and prior separation of a single metal-containing phase can occur.

Methods based on the total thermal decomposition of a single-phase liquid system have the attraction that (except for volatile metal compounds) the original metal stoichiometry is preserved through to the final product. To minimize the nucleation and growth of crystalline intermediate phases during the thermal decomposition it is desirable to maintain a viscous liquid to a late stage in the decomposition. This is most readily attained by the use of polymeric organic systems. Many metal oxides can be obtained in an amorphous and hence highly reactive form from the decomposition of metal–organic compounds. Thermal decomposition from viscous liquid precursors also holds out the promise of facile formation of films of metal oxide systems on suitable substrates.

The problems associated with the use of organic polymers are mainly associated with carbon formation (leading to possible reduction to the metal, particularly with copper) and carbonate formation. The Group II metals readily form carbonates under such conditions and the decomposition of barium carbonate is widely recognized as the rate-controlling step in the formation of YBCO [8].

The best known and most widely used organic polymer system is the ethyleneglycol/citric acid (EGCA) system originally developed by Pechini for the synthesis of lead titanate and other ferroelectric oxides [9]. This can be used for a range of metals, although care must be taken with copper to avoid forming insoluble basic copper citrate. It also tends to form a relatively large amount of carbonaceous char so that carbon burn-off is not complete until about 600 °C. This formation of carbonaceous char also makes for difficulties in forming continuous layers of metal oxide systems. Veitch [10] developed a variant of this polyester system using glycerol (1,2,3-trihydroxypropane) and malonic acid (propane-1,2-dicarboxylic acid) which has been found to offer significant advantages over the EGCA system in the range of metal ions which can be brought into solution and in the relative cleanness of thermal decomposition. In the EGCA matrices, the polyester formed has pendant carboxyl groups which coordinate metal ions. In the GLMA system the polyester formed has only (possibly) terminal carboxyl groups but has pendant hydroxyl groups along the chain, it will, therefore, not strongly bind metal ions and the GLMA precursors are solutions of metal malonates in a hydroxyl-rich polyester. This paper describes the application of this malonate/polyester precursor to the formation of tetragonal YBCO and the 2212 BSCCO phase.

2. Experimental procedure

The nitrates of bismuth, calcium, strontium, yttrium and copper and barium acetate were used as the sources of metals. Composition of hydrated salts was checked by thermogravimetric analysis. Solutions of individual or mixtures of metal salts were prepared by weighing appropriate quantities and dissolving in glycerol. Solutions were heated to remove water where appropriate.

2.1. Preparation of $YBa_2Cu_3O_{6.5}$

In the preparation of precursor solutions for YBCO, barium acetate was dissolved in glycerol and then appropriate amounts of yttrium nitrate and hydrated copper nitrate were added. This mixture was carefully warmed to produce an emerald green solution. Overheating at this stage can result in precipitate formation. Once prepared, such solutions are generally stable.

Prior to use, to these solutions (or mixtures of them) 30% by weight of malonic acid was added and the solution heated. Nitrogen oxides were evolved and the resulting solution consisted of metal malonates in a malonic acid/glycerol polyester. For the metal oxide systems discussed here metastable solutions were obtained which are processed by slowly heating, first to remove excess glycerol and then to decompose the glycerol/malonic acid (GLMA) polyester.

Thermal processing of small samples was carried out by building up films on pieces of polycrystalline alumina tile with the initial removal of excess glycerol and partial decomposition of the polyester resin being carried out on a Koffler hotbench, which provides a calibrated temperature gradient up to about 250 °C. Thick films could be built up by repeated application of solutions. Further heating was carried out in a laboratory furnace. Larger samples were processed by slow heating of layers of solution on Petri dishes on a hotplate until a brown/black resin was obtained. This was then scraped off and transferred to alumina crucibles for further heating. Care is required in the decomposition of the organic resin to prevent incandescence. Gram quantities for subsequent pellet formation can be obtained in this way.

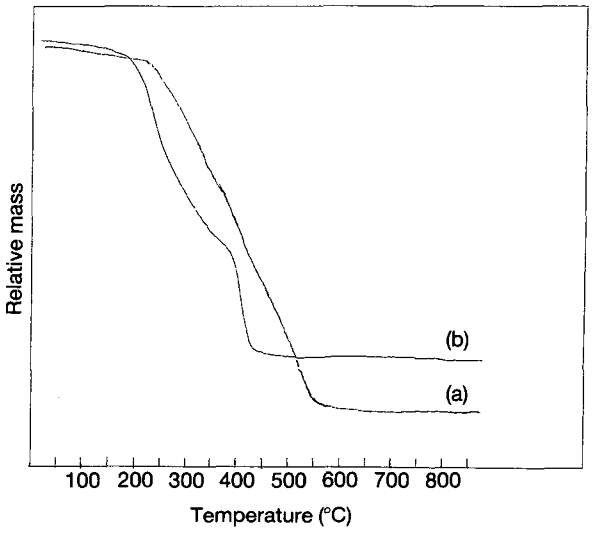

Figure 1 TGA thermograms of (a) EGCA- and (b) GLMA- based precursors of $YBa_2Cu_3O_x$ after heating the original solution and residue to 400 °C. Heating rates, 20 K min^{-1}.

2.2. Preparation of bismuth/strontium/calcium/copper oxide systems

Precursor solutions were prepared by dissolving strontium nitrate in glycerol using heat. Once this solution was obtained, appropriate amounts of bismuth, calcium and copper nitrates were added and brought into solution by gentle warming. Prior to use, 30% malonic acid was added and the solution warmed. Thermal decomposition was carried out as for the yttrium/barium/copper system.

X-ray diffraction (XRD) studies were carried out on thin layers prepared on alumina tiles. Samples for differential scanning calorimetry (DSC) and Fourier transform infrared analysis (FTIR) were initially partially decomposed on Pyrex glass and then in alumina crucibles. FTIR spectra were obtained by diffuse reflectance of crushed material dispersed in potassium bromide.

3. Results and discussion

Visual and infrared studies of the initial stages of the thermal decomposition of metal/GLMA systems show that after evaporation of excess glycerol, the residue consists of metal malonates or nitrates dissolved in a polyester. The decomposition proceeds by decomposition of the polyester and formation of metal carbonates and oxides accompanied by traces of metallic copper. Physically, the system progresses through a liquid stage of increasing viscosity to blackish-brown resins and eventually to black (YBCO) or yellowish-white (BSCCO) solids. Formation of continuous layers was rendered difficult by bubble formation during the decomposition of the polyester.

Thermal decomposition of the organic matrix leaves a residue of amorphous or microcrystalline metal oxides or carbonates which react rapidly on further heating. Comparison with EGCA matrices showed less carbon formation and mass stabilization occurring at lower temperatures. EGCA-based formulations charred extensively in the 300–400 °C region and thermogravimetry indicated that carbon removal was not completed until 600 °C (Fig. 1). It is claimed that GLMA formulations are superior to EGCA formulations in forming less carbonaceous material on thermal decomposition.

3.1. $YBa_2Cu_3O_x$

In the case of the YBCO formulation, XRD examination indicated the material was amorphous up to 200 °C. At this temperature weak reflections at 43.48 ° and 50.52° 2Θ (CuK_α) indicated the presence of metallic copper. Crystalline CuO was evident at 300 °C. Samples heated to 420 °C and examined after short periods of time at that temperature (10 min) show no reflections for crystalline barium carbonate, but samples heated for 2 h showed the presence of crystalline barium carbonate. All samples heated to 440 °C showed the presence of crystalline barium carbonate. Differential scanning calorimetry of the residue obtained from a barium/GLMA system (Fig. 2) showed an exothermic peak in the 420–450 °C region which probably corresponds to the crystallization of barium

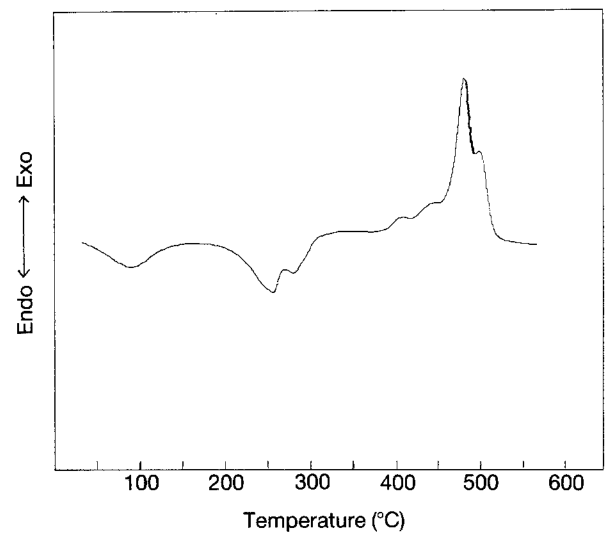

Figure 2 DSC thermogram of residue from a barium/GLMA solution heated to 400 °C. Heating rate, 20 K min^{-1}.

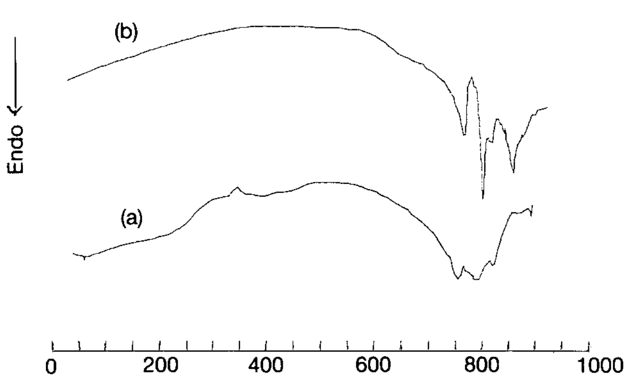

Figure 3 DSC thermograms of (a) YBC/GLMA and (b) BSCCO/GLMA precursors after prior heating to 400 °C. Heating rates, 20 K min^{-1}.

carbonate. This exotherm is, however, not evident in the DSC thermogram of YBC/GLMA (Fig. 3a). FTIR examination of various stages of the decomposition showed evidence of carbonate formation at 350 °C and as a barium/GLMA system is mass stable at this temperature, this is attributed to the presence of amorphous barium carbonate.

It was thus apparent that the formation of crystalline barium carbonate could be minimized and complete decomposition of the organic matrix achieved by halting the thermal decomposition at 420 °C. The strategy adopted for YBCO formulations was to heat the organic precursor to 420 °C under controlled conditions and then transfer it directly to a furnace preheated to a selected temperature. It was hoped in this way to circumvent the slow reaction of crystalline barium carbonate with the other metal oxide components.

The first indications of crystalline $YBa_2Cu_3O_{6.5}$ are obtained on brief heating at 720 °C and single-phase $YBa_2Cu_3O_{6.5}$ with no evidence of crystalline barium carbonate could be obtained by heating for 1 h at 800 °C. The identified phases obtained by heating a YBC/GLMA solution at 10 K min^{-1} are summarized in Table I and XRD diffractograms of materials heated to 420 and 420 °C and then transferred to 750 and 800 °C are shown in Fig. 4.

A number of attempts were made to increase the oxygen content and form the Cu(III)-containing orthorhombic phase of composition $YBa_2Cu_3O_{6.5+x}$ by slow cooling in air and oxygen and by annealing in oxygen atmospheres at temperatures between 350 and 450 °C. In all cases XRD examination of the materials obtained showed no or only slight splitting of the reflections in the 33.5 °–34.0 ° 2Θ range corresponding to the {0 3 1} and {1 3 0} planes, indicating that incorporation of oxygen into the lattice and consequent formation of the orthorhombic phase was not being achieved to any significant degree. The most probable reason for this is that there remained a layer of amorphous barium carbonate or other material around the crystalline regions and that this prevented oxygen diffusion. Some evidence for this is that a sample previously showing only the XRD pattern for tetragonal YBCO showed low-intensity reflections associated with $BaCO_3$ after heating for 24 h at 450 °C in flowing oxygen. The importance of porosity or microcracks in achieving high oxygen stoichiometries has

TABLE I Crystalline phases identified during the thermal decomposition of yttrium/barium/copper/GLMA

Temperature (°C)	Identified crystalline phases
200	Amorphous polyester with metal carboxylates and trace of metallic copper
300	Metal carboxylates, trace crystalline CuO
350	Amorphous $BaCO_3$, trace crystalline CuO
420	Trace crystalline $BaCO_3$, CuO
440	Crystalline CuO, $BaCO_3$
720	Tetragonal $YBa_2Cu_3O_{6.5}$, $BaCO_3$
800	Single-phase tetragonal $YBa_2Cu_3O_{6.5}$

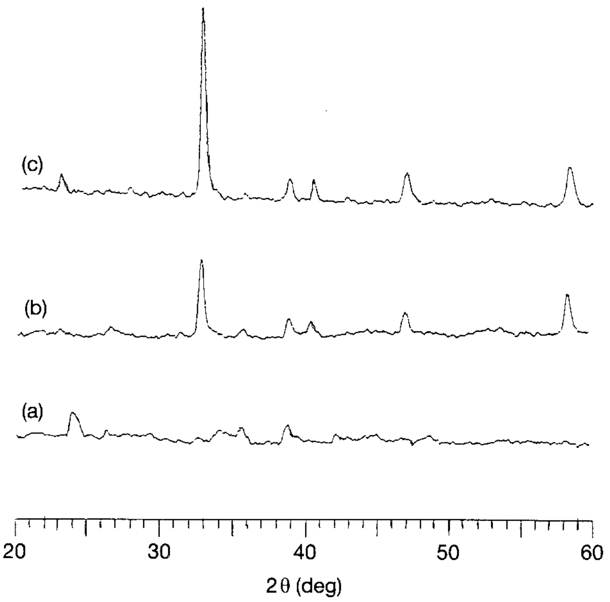

Figure 4 XRD diffraction patterns of residues from YBC/GLMA precursors heated to 420 °C and then individually at (a) 420 °C for 15 min, (b) 750 °C for 2 h, (c) 800 °C for 2 h. CuK_α radiation.

been noted by a number of workers in this field [11, 12].

Attempts to circumvent this problem by extended heating times at around 800 °C were not successful and heating to temperatures above 900°C led to reaction with the alumina substrate. These problems negate the apparent advantages of the GLMA precursor system as a preparatory route to superconducting YBCO but use of less reactive substrates may allow high-temperature processing and more complete reaction of the amorphous material.

TABLE II Crystalline phases identified during the thermal decomposition of 2212 BSSC/GLMA

Temperature (°C)	Identified crystalline phases
350	Bi_2O_3, Cu
450	Bi_2O_3, CuO, $CaCO_3$
550	CuO, $CaCO_3$, $SrCO_3$, (no Bi_2O_3)
700	2201 BSCCO, CuO
750	2201 BSCCO, CuO
800	2212 BSCCO, trace 2201 BSCCO

3.2. Bismuth/strontium/calcium/copper oxides

Studies were carried out using the so-called 2212 formulation i.e. designed to produce $Bi_2Sr_2CaCu_2O_{8+x}$. Thermogravimetric analysis of a 2212/GLMA precursor showed that mass loss proceeded in three distinct stages followed by a slow mass loss which was not complete until 850 °C. FTIR showed that carbonate persisted up to 750 °C but was not detected at 800 °C. The crystalline phases identified by XRD in samples heated to the indicated temperatures are summarized in Table II and the XRD patterns obtained after heat treatment at a range of temperatures is shown in Fig. 5. The phase purity and degree of crystallinity compare favourably with those reported by Okano *et al.* [13] for films obtained from glycerol solution of the metal nitrate.

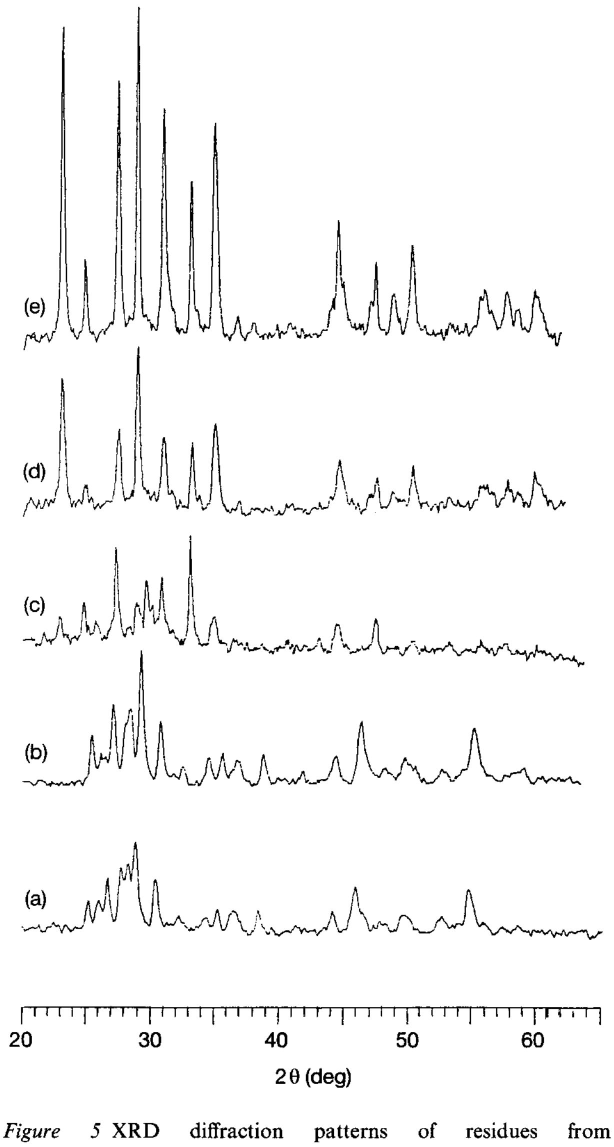

Figure 5 XRD diffraction patterns of residues from 2212BSCCO/GLMA precursor heated to 400 °C and then individually for 2 h at (a) 500 °C, (b) 600 °C, (c) 750 °C, (d) 800 °C. (e) The effect of heating for 17 h at 800 °C. CuK_α radiation.

Studies on 2223 BSCCO formulations in GLMA gave similar results except that removal of carbonate was complete by 750 °C. The 2201 phase is evident at 700 °C and becomes the dominant crystalline phase at 800 °C. Heating above 800 °C caused melting and no satisfactory XRD evidence for the formation of the 2223 phase was obtained. DSC studies on BSCCO formulations gave complex thermograms (Fig. 3b) which were difficult to interpret, but there is evidence of a solid state endothermic reaction to form the 2212 phase at 800 °C.

4. Conclusions

Thermal decomposition of solutions of metal nitrates or acetates dissolved in a glycerol/malonic acid solvent leads to homogeneously mixed and reactive mixtures of amorphous and microcrystalline oxides and carbonates. This matrix provides a convenient route to the preparation of 2212 BSCCO and tetragonal $YBa_2Cu_3O_{6.5}$ with minimal formation of carbonaceous char. The $YBa_2Cu_3O_{6.5}$ material obtained was resistant to oxygen annealing and formation of the superconducting $YBa_2Cu_3O_{6.5+x}$ phase, this resistance to oxygen uptake is presumed to be due to intergranular amorphous material.

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