

Synthesis and microstructure of bismuth-based mixed metal oxides from organic precursors

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Abstract

A new method for synthesizing homogeneous oxide powders was studied. This paper reports the synthesis of organic precursors using 3,6-dicarboxypyridazine (DCP) as a precipitant. An important advantage of the method is its versatility due to the fact that DCP forms stable complexes for a wide range of elements. Thermogravimetric analysis was used to study the decomposition of the organic precursors and the reaction of the oxide products of pyrolysis.

1. Introduction

Conducting and superconducting ceramics are complex multi-component oxides, in which any chemical inhomogeneity is strongly reflected in the electrical properties.

Most of these compounds are prepared by mixing the elementary oxides or their precursors in the solid state, and then calcining with intermediate grindings. This method requires multiple-step processing in order to obtain a reasonably homogeneous product. Coprecipitation methods have been used successfully for a number of complex oxides, including superconductors [1–3], and have been shown to produce oxide powders of good homogeneity. This technique obviates the numerous cycles of firing and grinding of the starting oxides or carbonates, which are required in the conventional processing.

In this paper, we describe a new aqueous coprecipitation process using 3,6-dicarboxypyridazine (DCP) as a precipitant in the preparation of multi-component oxides; we have tested this technique for the preparation of Bi_2CuO_4 and also for a new perovskite-type mixed oxide $\text{Sr}_3\text{BiO}_{5.5-\delta}$.

2. Experimental procedure

All chemicals were high purity grade purchased from Jansen Chemica and used without further treatment. Deionized water was used for all chemical procedures. The thermogravimetric analysis (TGA) of powder sam-

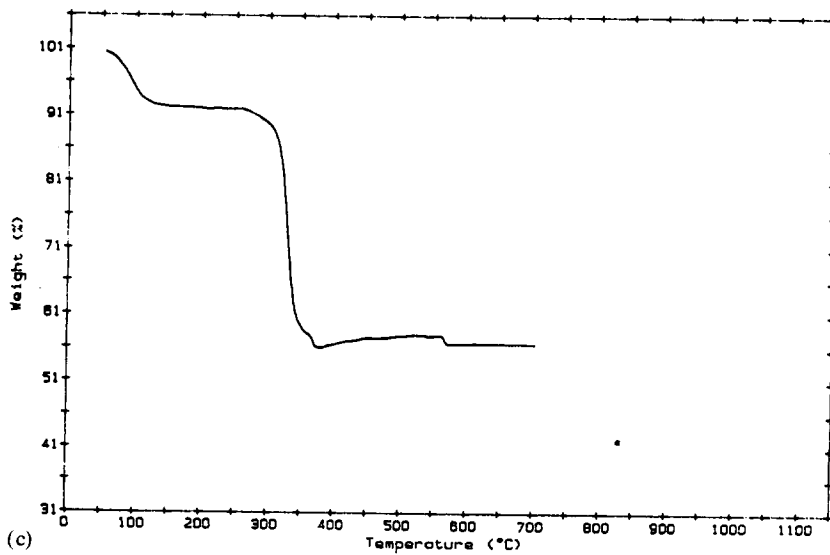
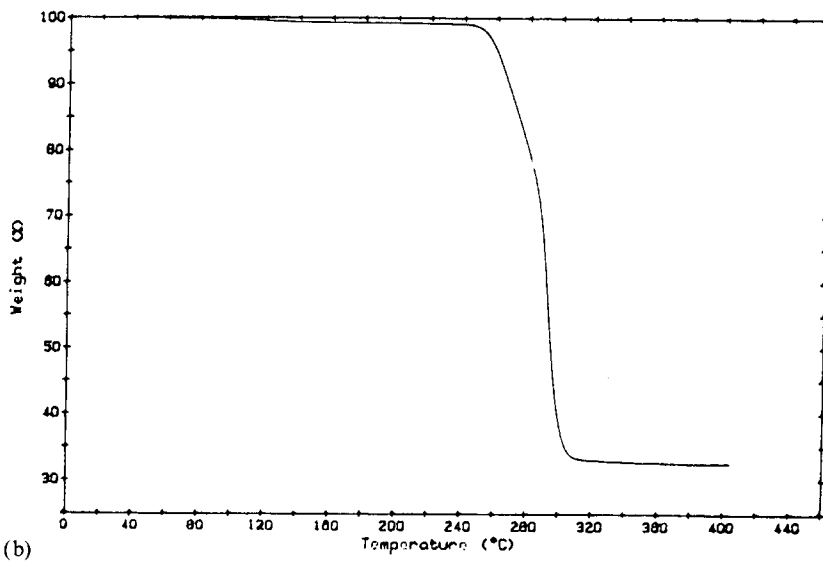
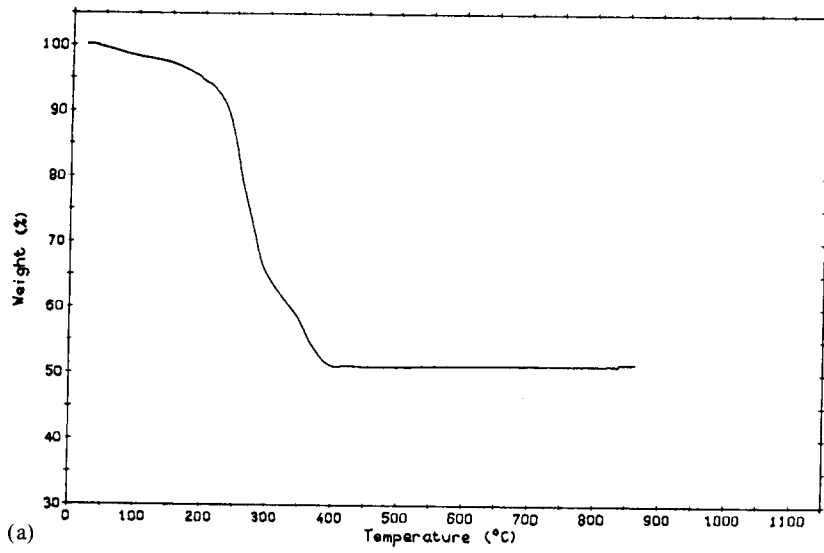
ples was carried out using a Dupont 951 thermal analyzer. DCP was prepared according to a previously reported method [4].

2.1. Typical procedure for preparation of the DCP complexes

Aqueous solutions of the different cations were prepared separately, starting from the corresponding metal nitrate salts and water. Dissolution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was carried out using a 2 M nitric acid solution. DCP was dissolved in the minimum amount of water. This solution was vigorously stirred to ensure complete dissolution and heated at about 50 °C. The solution of the metal salt was added dropwise to the DCP solution in a 1:1 molar ratio, except for bismuth where a 2:3 metal to ligand molar ratio was used; in all cases a slight excess of the diacid was used systematically. During the mixing, a powder is gradually formed. The mixture was stirred at 50 °C for 14 h; after cooling, using an ice-water bath, the mixture was filtered and the precipitate dried at 120 °C for 3 h under vacuum. The $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were weighed in the appropriate proportions and dissolved in the minimum of 2 M nitric acid. The solution of the metal nitrates was added to the DCP solution which was prepared with 10% excess of diacid. After stirring for 14 h at 50 °C, water was removed, and the solid residue was suspended into methanol, filtered and dried under vacuum.

2.2. Thermograms of the precipitates

Thermal analysis was used to provide information on the temperature at which volatile matter is lost from the



(continued)

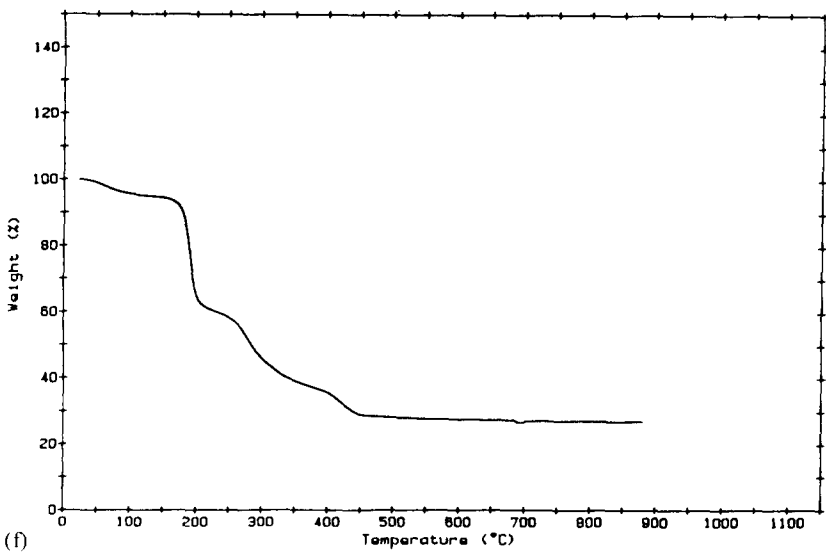
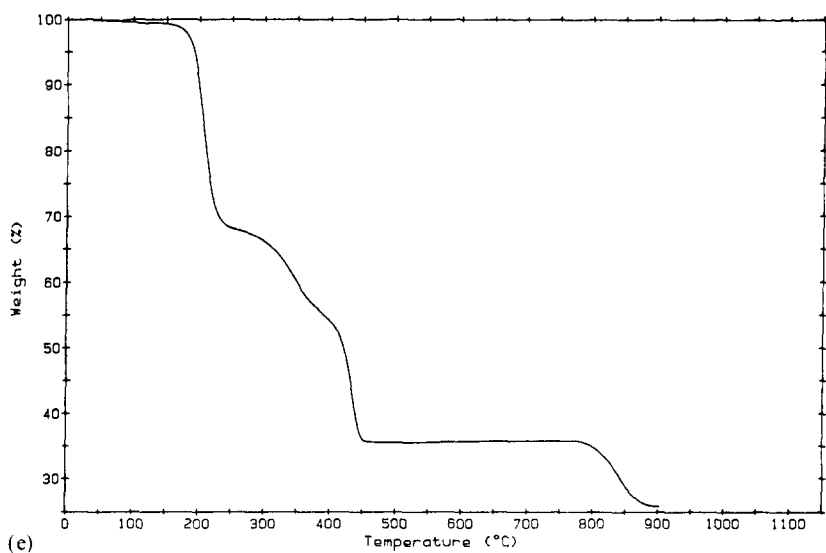
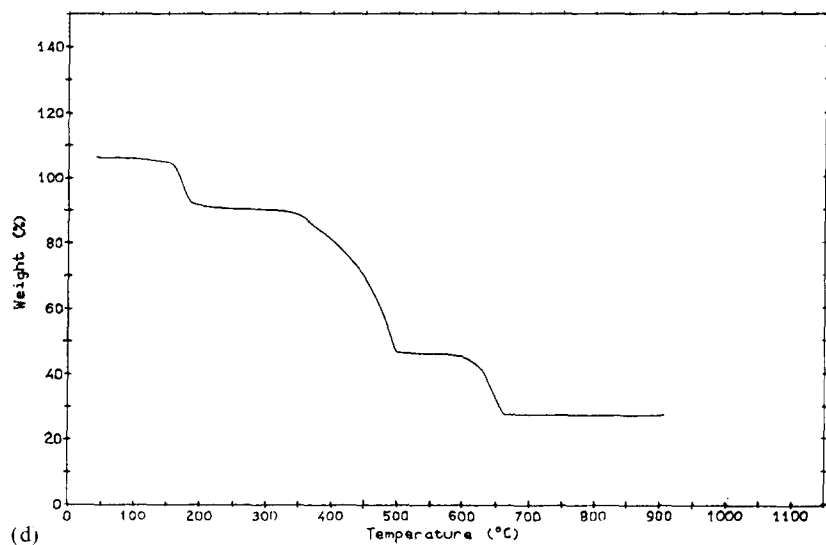


Fig. 1. TGA thermograms of DCP complexes: (a) bismuth, (b) copper, (c) lead, (d) calcium, (e) strontium, (f) bismuth–strontium coprecipitated.

precipitate and the key temperature at which the decomposition is complete. The TGA thermogram of the bismuth complex (Fig. 1(a)) shows a gradual weight loss from 40 to 220 °C. A second weight loss between 220 and 400 °C is observed, which is indicative of the loss of organic moieties. The TGA thermogram of the copper complex (Fig. 1(b)) shows an abrupt weight loss between 250 and 310 °C which corresponds to the simultaneous loss of coordinated water and organic moieties. The TGA thermogram of the lead complex (Fig. 1(c)) also shows a sharp weight loss between 320 and 420 °C; it is characteristic of the loss of organic ligands. High temperature X-ray diffraction patterns show the decomposition of the complex giving a mixture of the two forms of PbO. Subsequent oxidation gives Pb₃O₄ with intermediate formation of nonstoichiometric phases. At 450 °C the final product is the orthorhombic form of PbO (Fig. 2). The thermal decomposition of the calcium complex (Fig. 1(d)) shows the loss of two water molecules between 150 and 200 °C; like most DCP compounds, it decomposes between 320 and 500 °C. This second weight loss is due to the break up of the complex into carbonates. The last weight loss between 600 and 660 °C is related to the decomposition of CaCO₃ into CaO. Thermal decomposition of the strontium derivative (Fig. 1(e)) exhibits three distinct decomposition steps. The first major weight loss, occurring between 180 and 450 °C, is due to the break up of the DCP compound into carbonates. The last weight loss between 780 and 880 °C is indicative of the loss of CO₂. The thermal decomposition of the Bi–Sr coprecipitated complex shows a weight loss between 180 and 450 °C in several steps (Fig. 1(f)), corresponding to the sum of the individual decompositions of the bismuth and the strontium complexes in that temperature range. Furthermore, in the temperature range 780–880 °C, the last step of the SrCO₃ decomposition is not observed, and it

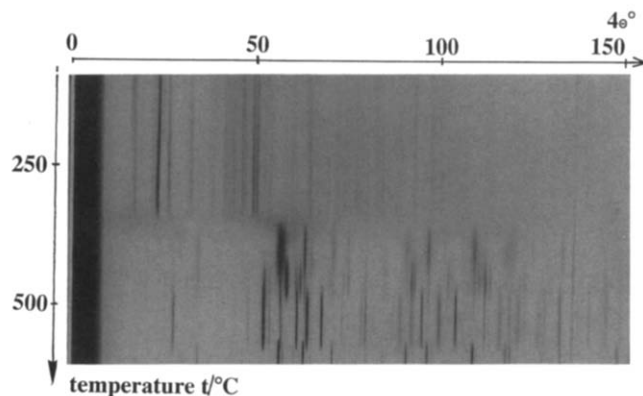
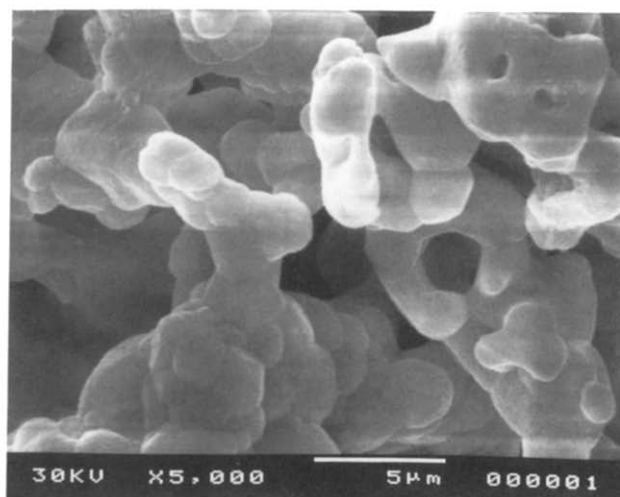


Fig. 2. High temperature X-ray diffraction pattern of the DCP lead complex.

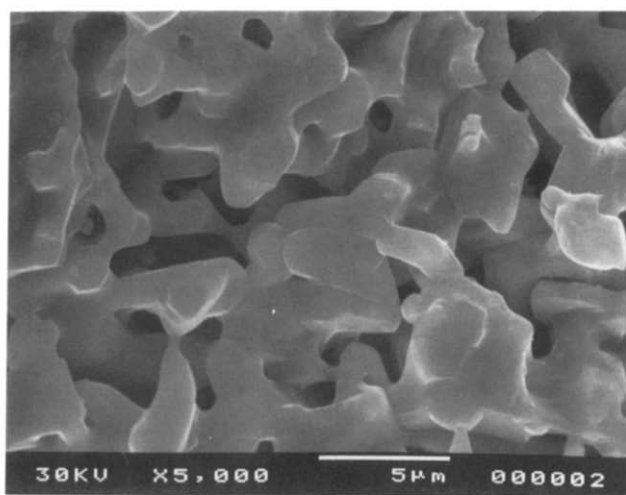
proves the direct formation of the mixed oxides at a lower temperature.

3. Results and discussion

We first applied this technique to the synthesis of a new mixed oxide Sr₃BiO_{5.5}; it is normally obtained [5] by solid state chemistry of a Bi₂O₃–SrCO₃ mixture reacted at 850 °C, the completeness being obtained after several intermediate grindings and refiring at the same temperature. The thermogram of a mixture of bismuth and strontium organic complexes shows that the decomposition is obtained between 780 and 850 °C. A comparison of samples obtained by both synthesis



(a)



(b)

Fig. 3. Scanning electron micrographs of Sr₃BiO_{5.5}: (a) mixture of Bi₂O₃ and SrCO₃; (b) mixture of bismuth and strontium DCP complexes.

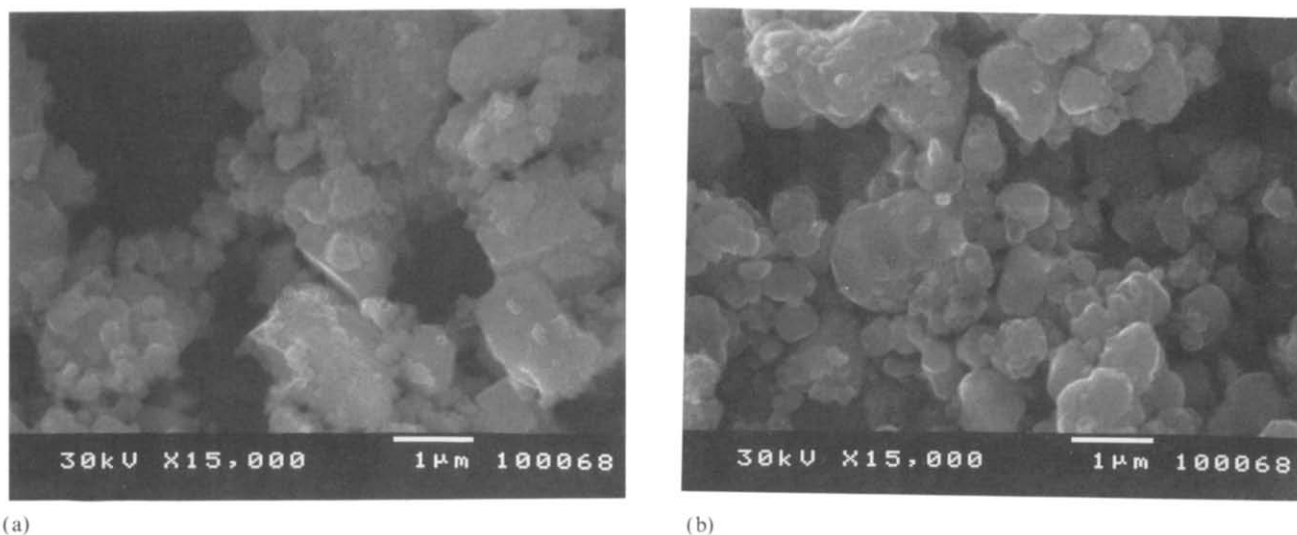


Fig. 4. Scanning electron micrographs of Bi₂CuO₄: (a) sample heated at 600 °C; (b) sample heated at 750 °C.

routes, clearly shows that the grain size is identical when the same temperature treatment is used. The organic route yields better crystallinity (Fig. 3).

The synthesis of Bi₂CuO₄ proves the validity of the coprecipitation technique. The solid state synthesis is performed at 750 °C from a Bi₂O₃, CuO mixture, but the organic route shows the formation of the same compound, identified by its X-ray diffraction pattern, as soon as 550 °C. Scanning electron micrographs of samples synthesized at 600 and 750 °C by the organic route prove the dependence of the grain size upon the selected temperatures (Fig. 4).

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