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Preparation of $YBa_2Cu_3O_{7-x}$ by thermal decomposition of coprecipitated oxalates

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Yttrium, barium and copper oxalates are coprecipitated quantitatively from metal acetate solutions with oxalic acid in water–acetone mixtures. The particle-size distribution of the precipitate can be controlled by the precipitation conditions. Thermal decomposition of the coprecipitate leads to single-phase $YBa_2Cu_3O_{7-x}$. Despite the intermediate formation of $BaCO_3$, the minimal reaction temperature (770 °C) is clearly lower than that for the solid-state reaction. Results of differential thermal analysis and isothermal thermogravimetry are discussed. The products are characterized by X-ray diffraction and infrared spectroscopy.

1. Introduction

In connection with the synthesis of $YBa_2Cu_3O_{7-x}$, the conventional solid-state reaction along with several other routes, especially the thermal decomposition of coprecipitated precursors prepared in aqueous solution, were investigated. The synthesis of ultrapure, homogeneous and ultrafine powders is one way to lower reaction temperature and time with regard to the solid-state reaction. Most of these coprecipitated powders contain carbon, so that during the thermal treatment barium carbonate is formed as an intermediate compound. Another problem is in the simultaneous and stoichiometric precipitation: different solubilities and the influence of complex equilibria lead to losses, especially of barium and copper. There have been several attempts to reduce these effects by choosing an optimal pH value, the initial concentration of the metal salts and the precipitating agent [1, 2].

In connection with the estimation of different coprecipitation procedures for the synthesis of $YBa_2Cu_3O_{7-x}$, and their possible advantages in comparison with the conventional route of firing a mixture of Y_2O_3, $BaCO_3$ and CuO, we studied the coprecipitation of the oxalates. The investigations described aimed not only at the preparation of a pure, fine-grained and stoichiometric precursor, but also at the analysis of relations between precipitation conditions, properties of the precursor and its decomposition behaviour. Concerning the conditions for the preparation of phase-pure $YBa_2Cu_3O_{7-x}$, we also included the solid-state reaction.

2. Experimental procedure

As preliminary treatment for the solid-state reaction, weighed amounts of Y_2O_3, $BaCO_3$ and CuO were ball-milled in agate mortar in dry *n*-heptane in a planet mill ("Pulverisette 5", Fritzsch GmbH, Idar-Oberstein, Germany). After drying, the powders were treated thermally as described below.

Coprecipitation was carried out by quick addition of oxalic acid solution to a solution containing the metal acetates. Both the metal salt and the oxalic acid solution contained the same volume of acetone. The particle-size distribution of the resulting powders was measured by a laser particle sizer ("Analysette22", Fritzsch GmbH, Idar-Oberstein, Germany). The thermal decomposition was monitored by differential thermal analysis (DTA) by the "Derivatograph Q 1500 D" (System Paulik-Paulik-Erdey, Budapest, Hungary). X-ray diffraction (XRD) and IR spectroscopy were used for characterization of the coprecipitated powders and determination of the phase content of the reaction products after thermal treatment.

3. Results and discussion

3.1. Precipitation of the individual oxalates and coprecipitation

Based on calculations of the solubility of Y, Ba and copper oxalate, and satisfactorily coinciding with experimental results, Caillaud *et al.* [1] found an optimal pH range for coprecipitation between 2.38 and 2.58. Below this range, barium oxalate is not completely precipitated ($pK_L = 6.83$). Increasing the pH to values above this range led to losses of copper, as it formed a very stable bisoxalato-complex, while the barium and yttrium oxalate yield were quantitative.

Despite the optimization, the maximum yield in [1] only reaches the unsatisfactory value of 90% ($\alpha = 0.9$). Following our investigations, a quantitative precipitation of the three compounds ($\alpha > 0.99$) from metal acetate solutions by precipitation with oxalic acid in water/acetone mixtures becomes possible. The yield of barium is also increased in aqueous solutions by the use of barium acetate as the initial compound. In the case of barium chloride, the precipitation causes the formation of HCl as a strong acid, while the acetic acid formed if barium acetate is used is only weakly

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acidic. So the pH reaches values in the above-mentioned optimal range, depending on the initial metal-salt concentration.

The factors influencing the yield are complex and include, for example, at a given temperature

initial metal concentration;
type of metal salt;
initial concentration of oxalic acid;
pH of the solution;
addition of other solvents.

The influence of a possible excess of oxalic acid on the barium yield is shown in Fig. 1. (The applied excess of acetic acid corresponds to the resulting concentration when Y, Ba and copper oxalate in stoichiometric amounts (1:2:3) are precipitated from acetate solution.)

Adding excess, oxalic acid influences not only the yield, but also the phase content of the precipitation product. Slight excess leads to a higher solubility of barium oxalate (lower yield) by decreasing the pH value. When the concentration of excessive oxalic acid is further increased, solubility is again lowered (yield increases) and the resulting product consists of barium-hydrogen oxalate. At an excess of $[H_2C_2O_4] = 0.2\,\text{M}$, the composition of the product corresponds to the formula

$$Ba(HC_2O_4)_2 * 2H_2O$$

The precipitation products were characterized by chemical analysis after drying in air (barium and oxalate content) and IR spectroscopy.

These effects have already been described by Kurashvili [3]. The barium yield for an initial concentration of 0.03 M reaches values of $\alpha > 0.9$ in the investigated region. A higher yield should be possible from a higher initial concentration, but this is limited by the solubility of yttrium acetate for coprecipitation. Another method is the addition of solvents with lower dielectric constants such as ethanol [4].

In Fig. 2, the influence of additional acetone on the solubility and yield of barium oxalate is shown under conditions which simulate coprecipitation and for different excess concentrations of oxalic acid.

When the acetone content reaches 50%, the barium yield is practically complete ($\alpha > 0.99$). The yield of copper and yttrium under the same circumstances is also complete. In order to study the coprecipitation, we applied the following method. A solution of the metal acetates was added to a solution of oxalic acid at room temperature, so that the following initial concentrations resulted: $[Y^{3+}] = 0.015$; $[Ba^{2+}] = 0.030$; $[Cu^{2+}] = 0.045$; $[H_2C_2O_4] = 0.1075\,\text{M}$. This causes an excess of oxalic acid of 0.01 M at complete precipitation. Acetone was added in equal amounts to the metal salt and the oxalic acid solution. Analysis of the filtrates shows that complete precipitation is reached ($\alpha > 0.99$) when the acetone content is greater than 50%. The addition of acetone not only ensures a higher yield, but also influences the particle size of the powders produced by raising the

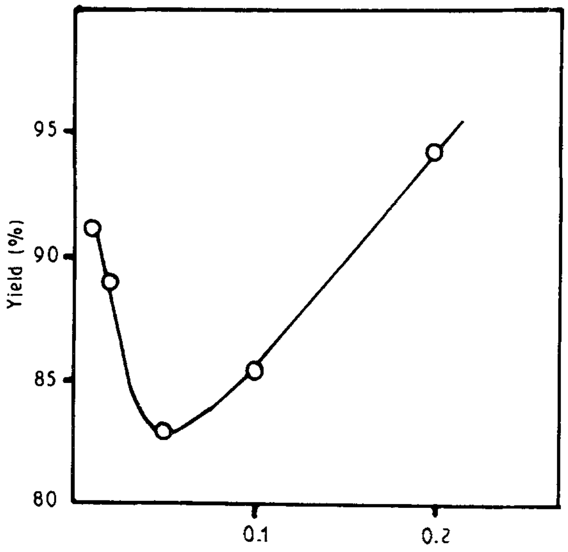

Figure 1 Yield of barium oxalate depending on applied excess oxalic acid at room temperature. $[Ba^{2+}]_0 = 0.03$ M.

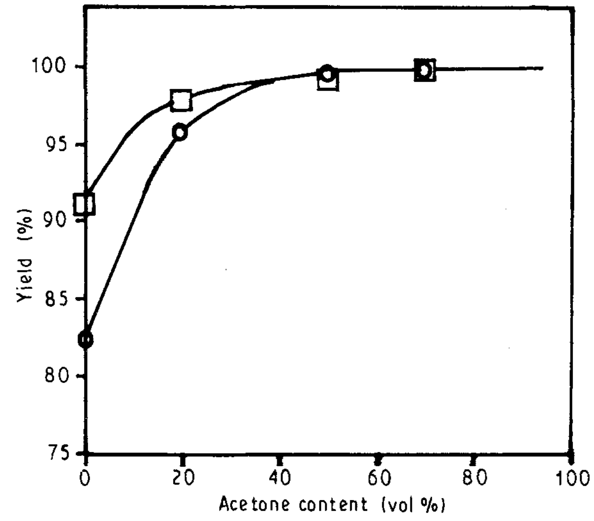

Figure 2 Influence of acetone content of the solution on yield of barium oxalate for different excess concentrations of oxalic acid (□, 0.01; ○, 0.05 M). $[Ba^{2+}]_0 = 0.03$ M.

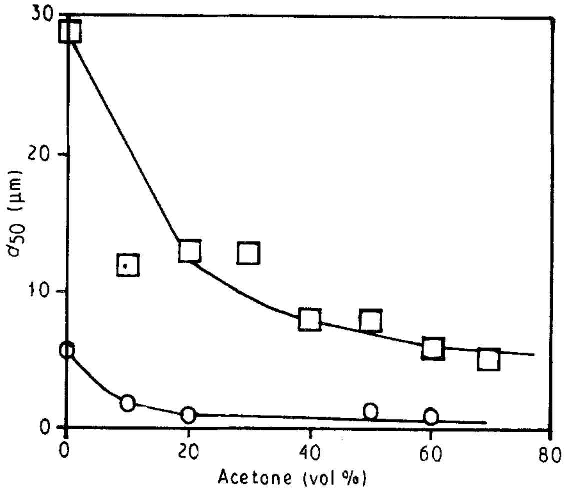

Figure 3 Particle size (d_{50} μm) depending on acetone content of solution. $[Ba^{2+}]_0 = 0.03$ M. $[\text{Oxalic acid}]_{\text{excess}} = 0.01$ M/BaC_2O_4; $[\text{Oxalic acid}]_{\text{excess}} = 0.04$ M/coprecipitation. □, Ba oxalate; ○, 123 oxalate.

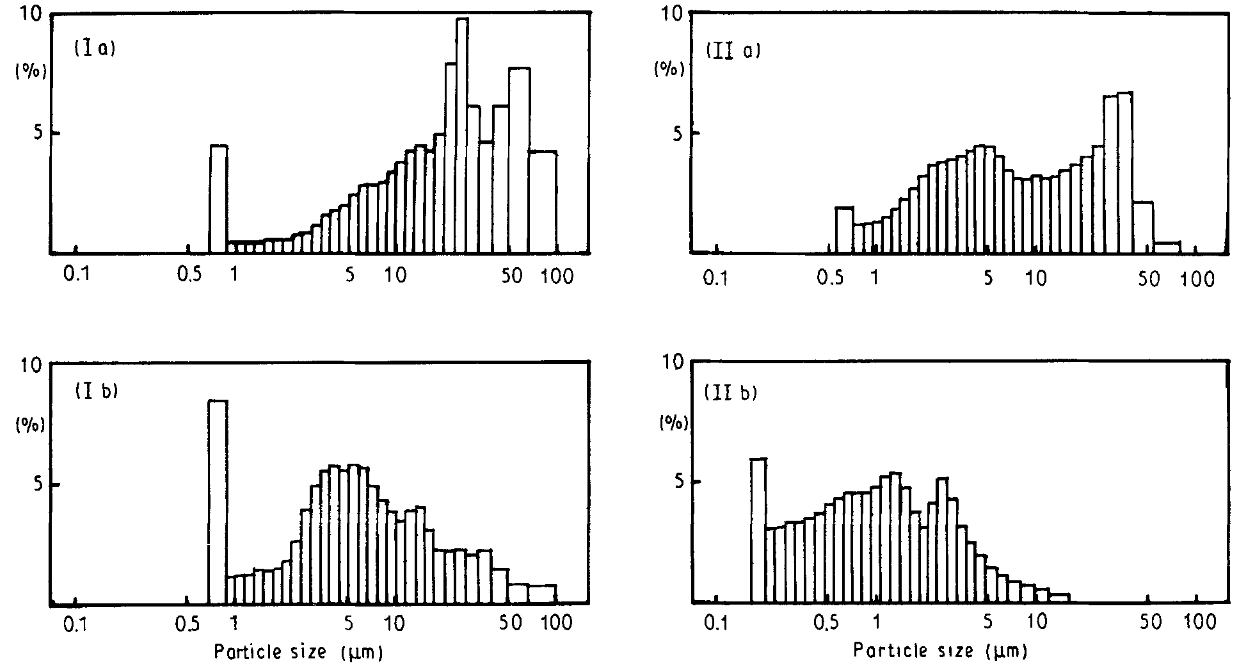

Figure 4 Particle-size distribution of BaC_2O_4 (I) and the coprecipitate (II) produced in (a) water and (b) 60% acetone. $[Ba^{2+}]_0 = 0.03$ M. $[\text{Oxalic acid}]_{\text{excess}} = 0.01$ M.

oversaturation. Fig. 3 shows the particle size (d_{50} µm) in comparison with that of barium oxalate in dependence on the acetone content.

As shown in Fig. 4, the particle-size distribution of powders precipitated in water is relatively broad and bimodal, while in water/acetone mixtures more homogeneous products are obtained. The fine-grained fraction of coprecipitates from aqueous solution predominantly contains Y and Cu oxalate; the fraction of a particle size above 10 µm corresponds to barium oxalate. These facts were not surprising, because the individual oxalates do not form solid-solution crystals.

Comparing the particle size of barium oxalate and of the coprecipitate, a tendency to lowering of the particle size is seen. This effect increases for precipitations in acetone containing solution (Fig. 4; I, II). The presence of yttrium and copper oxalate which may serve as a heteronucleus for barium oxalate could be the reason. XRD reveals that the coprecipitated powders are of a much lower crystallinity than the individual oxalates prepared under the same conditions. The IR spectrum shows a superposition of the vibrations of the compounds.

Concluding, we can state that the coprecipitated powders consist of a mixture of the individual oxalates as a fine-grained powder ($d_{50} = 1$ µm) of high homogeneity and exact stoichiometry. The homogeneity may also be seen by SEM photographs.

3.2. Thermal decomposition of the coprecipitation products

In order to monitor the decomposition, DTA was applied. Fig. 5 shows the results for typical powders, prepared from 60% acetone solution. Up to 150 °C, dehydration of the oxalates takes place. The exotherm reaction between 250 and 300 °C corresponds to the

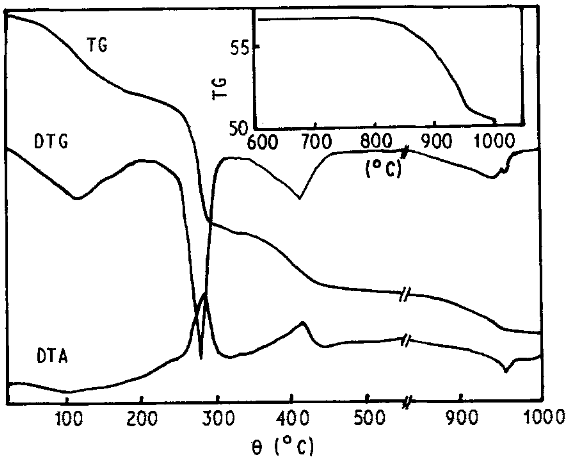

Figure 5 DTA of the coprecipitate (heating rate = 5 K min^{-1}).

oxidation of CO, which is formed by the decomposition of Y and copper oxalate. Barium oxalate decomposes in the temperature range of 400–500 °C and forms $BaCO_3$, which reacts with Y_2O_3 and CuO at temperatures above 800 °C. In a sector of Fig. 5 the thermogravimetry in the temperature range of 600–1000 °C can be seen. It thus becomes clear that the reaction to $YBa_2Cu_3O_{7-x}$ takes place at temperatures above 800 °C. More detailed information with regard to the reactivity of the Y_2O_3, $BaCO_3$ and CuO mixture obtained can be gained if isothermal thermogravimetry is used. Measuring the mass loss, it becomes possible to give values for the inversion, i.e. the reaction yield (Fig. 6). The reaction yield of a powder produced by coprecipitation after 3 h at 835 °C (ambient atmosphere) is 100% (3 in Fig. 6), while the values for the conventionally prepared powder are only 40% (1). The high homogeneity and reactivity of

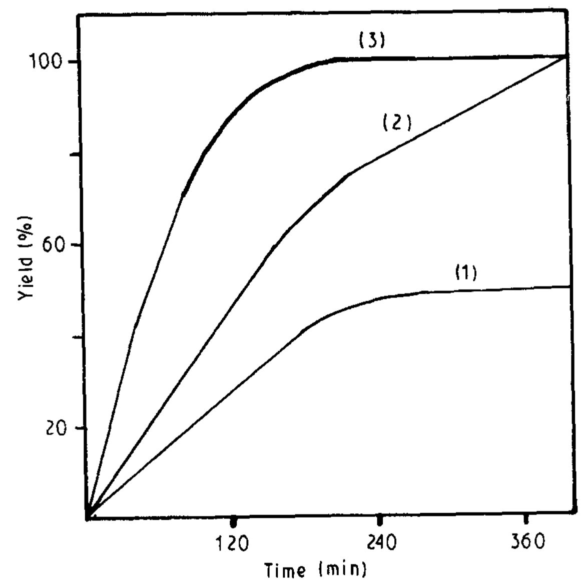

Figure 6 Reaction yield for the solid-state reaction (1) at 835 °C and for the coprecipitate at 770 °C (2) and 835 °C (3); heating rate 20 K min^{-1} to the final temperature.

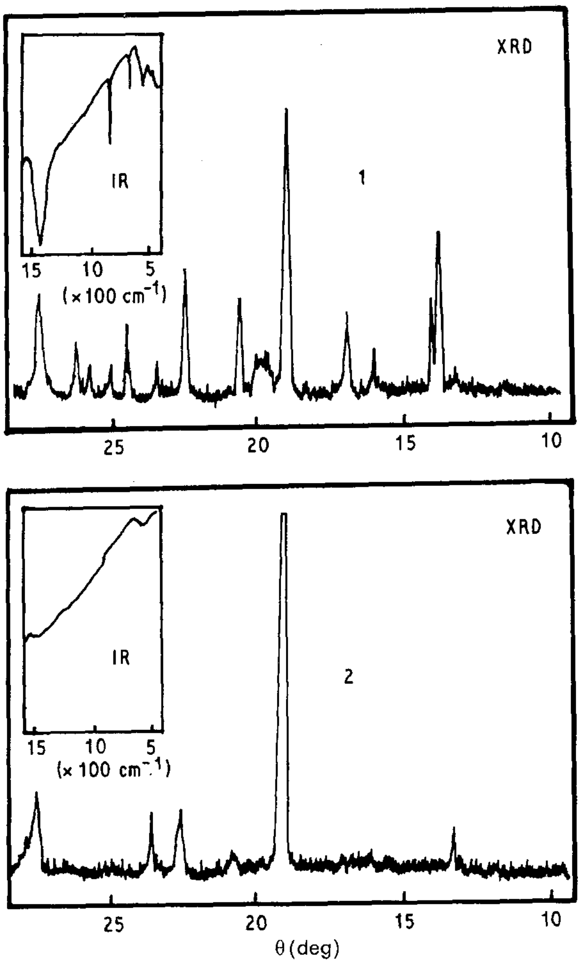

Figure 7 XRD pattern and IR spectra of the physical mixture (1) and the coprecipitate (2) after firing at 820 °C for 2 h at ambient atmosphere (preheated furnace).

the wet chemical powder allows the reaction temperature to be reduced to 770 °C (2). Within 7 h, the reaction is complete and single-phase powders result. For a single-phase powder in the case of the conventional method, temperatures up to 900 °C are required. For this reaction, reactivity depends to a great extent on particle size, i.e. the preliminary treatment or the 'history' of the powder. The results presented were obtained for a powder of relatively broad particle-size distribution and of an average particle size of 5 μm.

Consequently, reducing the particle size leads to a higher reactivity. Jaeger and Aslan [5] observed a complete reaction within 30 min at 900 °C for ultrafine powders of a particle size of 0.3 μm.

Despite the intermediate formation of $BaCO_3$, an advantage of the oxalate method is the production of a homogeneous mixture of Y_2O_3, $BaCO_3$ and CuO during the reaction, which is of a high reactivity allowing a reduction of temperature and time.

3.3. Characterization of the decomposition products

In Fig. 7, typical sectors of the XRD pattern and the IR spectra of the reaction products are shown. After 2 h, the oxalate precursor is completely decomposed into $YBa_2Cu_3O_{7-x}$, while the conventional method leads only to reaction yields of 10%. The XRD pattern and IR spectra of the solid-state reaction product show Y_2O_3, $BaCO_3$ and CuO.

6. Conclusions

Based on the above results, we can state that the coprecipitation of metal acetate solutions containing acetone allows the production of homogeneous, stoichiometric, fine-grained powders of high reactivity. The particle size of these powders can be controlled by the precipitation conditions. The coprecipitates decompose at 770 °C to phase-pure $YBa_2Cu_3O_{7-x}$. These results agree with those of Negishi *et al.* [6], who also studied thermal decomposition.

Despite the intermediate formation of $BaCO_3$, the reactivity is higher than that of a physical mixture. To decrease the reaction temperature for these mixtures below 850 °C, long periods of milling time are required, leading to impurities. Despite the low reaction temperature required for our powders, grain growth already takes place. Hence the particle size of the products does not correspond to that of the precursor. Using a precursor of a particle size (d_{50}) of 1 μm after 4 h at 820 °C, we obtained a powder with a size (d_{50}) of 30 μm.

Zhuang *et al.* [7] reported a low-temperature process applying nitrate precursors. The required temperatures are in the range of 750–800 °C and the product is not a single-phase one. In this context, our method is advantageous with regard to this carbon-free synthesis.

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