Preparation of Superconducting $YBa_2Cu_3O_{7-\delta}$ from Carbon-Free Precursors*

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Iodates of yttrium, barium and copper have been studied as possible carbon-free starting materials for the superconducting $YBa_2Cu_3O_{7-\delta}$ compound. TG and EGA experiments on the individual iodates show that while the copper and yttrium iodates readily decompose to oxides, the decomposition of $Ba(IO_3)_2$ to BaO is incomplete up to 1050 °C owing to the thermal stability of $Ba_5(IO_6)_2$. However, when a three-component, mechanical mixture is heated in flowing air a complete reaction occurs by 900 °C, yielding the $YBa_2Cu_3O_{7-\delta}$ phase. A coprecipitation method to produce the starting material was studied as well but found difficult to optimize owing to different solubilities and possible double iodate formation. The resulting products were characterized by XRD for phase purity and crystallinity, by TG for oxygen release and uptake behaviour as well as by resistivity measurements for superconducting properties.

A variety of precursors, including the carbonates, oxalates and citrates, have been used to synthesize the new oxide-based superconductors in bulk form. All these compounds decompose at moderate temperatures, yielding the oxides, but traces of carbon left in a superconductor may be detrimental to its electrical and magnetic properties. During our search for new carbon-free precursors with low solubility we have investigated the iodates as possible starting materials for the $YBa_2Cu_3O_{7-\delta}$ superconductor.

While the thermal behaviour of the rare-earth iodates has been investigated recently by several groups,[2-4] studies on the corresponding copper and barium compounds have not been as frequent. The reaction product between copper salts and iodic acid or alkali iodates was long considered to be a monohydrate, but a more recent study indicates that its composition is identical with that of the mineral bellingerite, *viz.* $Cu(IO_3)_2 \cdot 2/3\ H_2O$,[5] which dehydrates at 290–300 °C and forms the oxide above 500 °C. The anhydrous rare-earth iodates are also stable up to 450–550 °C, at which temperature they decompose in a rather complicated manner,[2,6,7] as shown in reaction (1). According to

$$10\ Ln(IO_3)_3 \rightarrow 2\ Ln_5(IO_6)_3 + 12\ I_2 + 27\ O_2 \qquad (1)$$

Nassau *etal.*[3] this reaction scheme applies only to lanthanum, however. In all other cases only mixtures of oxide and anhydrous iodate are formed.

Barium iodate appears to be thermally more stable, yielding the orthoperiodate at 600–700 °C via the Rammelsberg reaction[8] [reaction (2)]. There are controversial

$$5\ Ba(IO_3)_2 \rightarrow Ba_5(IO_6)_2 + 9\ O_2 + 4\ I_2 \qquad (2)$$

reports regarding the stability of the periodate: according to Peltier and Duval its stability range extends over some tens of a degree,[9] while Várhelyi and Kékedy[10] indicate the formation of BaO first at 1050 °C, in agreement with the data of Gantarz and Górski.[11] Both the decomposition of barium iodate [reaction (2)] and periodate release oxygen and iodine.

In view of these conflicting thermoanalytical data, the thermal decompositions of the individual iodates were studied initially before attempting the synthesis of $YBa_2Cu_3O_{7-\delta}$ from the iodates. Special attention was paid to $Ba(IO_3)_2$ because of its high decomposition temperature.

Experimental

The individual iodates of yttrium, barium and copper, as well as the coprecipitates of these metal ions, were precipitated from aqueous solutions (0.2–0.3 M) of the corresponding nitrates by saturated potassium iodate solution. In the case of copper iodate an excess of KIO_3 had to be avoided because of the possible contamination of the precipitate. After ageing, the precipitates were filtered, washed with distilled water and dried either at room temperature over calcium chloride or in air at 80 °C. The coprecipitations were performed from stoichiometric mixtures of the individual nitrate solutions. Before washing, the mixtures were boiled up to minimize the undesirable change in

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stoichiometry owing to the different solubilities of the iodates.

In order to prepare superconducting oxide samples, either mechanically mixed individual iodates in stoichiometric amounts or coprecipitated mixtures were annealed in a tube oven in flowing air at 950 °C for 3 h and then cooled slowly to room temperature. The phase purity and the crystallinity of the resulting products were studied by X-ray diffraction analyses using Philips MPD 1880 equipment, and the superconductivity was confirmed by resistivity measurements.

For the thermogravimetric (TG) analyses a Perkin–Elmer System 7 thermobalance was used. The thermal decomposition of the individual iodates as well as the mechanical or coprecipitated mixtures was studied up to 1100 °C in dynamic air, oxygen and argon atmospheres using heating rates from 2 to 20 °C min^{-1}. The sample size was typically 10–30 mg. With some of the TG measurements simultaneous evolved gas analysis (EGA-MS) curves were recorded by means of a coupled Leybold–Heraeus IQ 200 quadrupole mass analyser.[12] In those experiments sample sizes up to 150 mg were used. Furthermore, the oxygen release and uptake of the final products during subsequent heating and cooling cycles was studied.

Results and discussion

Individual iodates. Yttrium, barium and copper iodates may be precipitated from aqueous solution as hydrates. TG measurements revealed that yttrium and barium iodates precipitated as the tetra- and monohydrate, respectively, and became partially dehydrated when dried at 80 °C. The water content of copper iodate varied between 3.0 and 3.4 % in repeated experiments, slightly exceeding the theoretical value of 2.83 %, corresponding to the bellingerite, $Cu(IO)_3)_2 \cdot 2/3\ H_2O$, but being clearly below the theoretical value of 4.17 % calculated for a monohydrate.

The thermal decomposition of $Y(IO_3)_3 \cdot 4\ H_2O$ is practically similar in all the atmospheres studied (Fig. 1). The dehydration starts below 100 °C, and the resulting anhydride is stable up to 500 °C. A further heating leads to the oxide as final product at 700–800 °C, but decomposition does not occur in a single step. The plateaus observed in the thermograms at 550–600 °C do not, however, correspond to any stable or stoichiometric intermediates. It should be noted that the final experimental weight loss was in all experiments slightly lower than that calculated for pure Y_2O_3 (cf. Fig. 1). This may be due to the presence of small amounts of thermally fairly stable YOI.[13,14]

The monohydrate of barium iodate loses its water of crystallization by 100 °C. Decomposition of the anhydrous iodate to BaO takes place via $Ba_5(IO_6)_2$. The stability range of barium orthoperiodate formed around 600 °C is remarkably wide, extending up to 1050 °C in air. In an inert atmosphere the decomposition starts at 850 °C, however, but it does not result directly in BaO as is the case in the oxidizing atmosphere (Fig. 2).

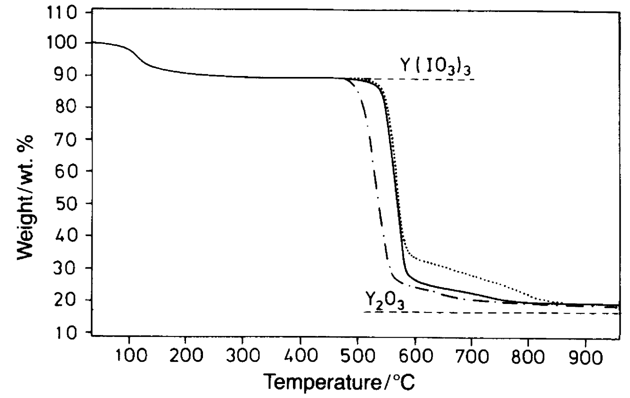

Fig. 1. TG curves for $Y(IO_3)_3 \cdot 4\ H_2O$ recorded in dynamic air (solid line), oxygen (dotted line) and argon (broken line) atmospheres at a heating rate of 5 °C min^{-1}.

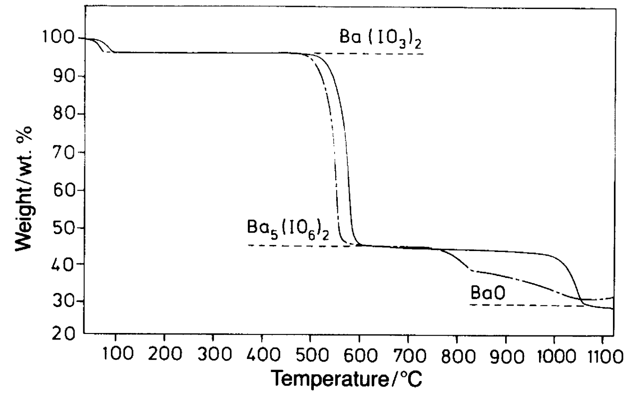

Fig. 2. TG curves for $Ba(IO_3)_2 \cdot H_2O$ recorded in dynamic air (solid line) and argon (broken line) atmospheres at a heating rate of 5 °C min^{-1}.

The structural water is more tightly bound to copper iodate than to yttrium or barium iodates, as the loss of water does not occur until 230 °C when $Cu(IO_3)_2 \cdot 2/3\ H_2O$ is heated. The iodine and oxygen evolution starts around 450 °C, resulting in copper(II) oxide at 500 °C (Fig. 3). In an argon atmosphere the reaction proceeds a step further, and CuO is reduced at 900 °C to Cu_2O, which is also visible in the EGA-MS ^{32}O spectrum.

Precursor mixtures for $YBa_2Cu_3O_{7-\delta}$. The experimentally found total weight loss at 950 °C for mechanical mixtures, containing yttrium and barium iodates in the ratio 1:2 or yttrium and copper iodates in the ratio 1:3, corresponded to the formation of yttrium oxide and barium orthoperiodate or yttrium and copper oxides, respectively. When barium iodate and copper iodate were mixed in the ratio 2:3 the weight loss up to 800 °C indicated the formation of barium orthoperiodate together with copper oxide. Above 800 °C, however, an additional weight loss occurred, the final value of which corresponded to the formation of the

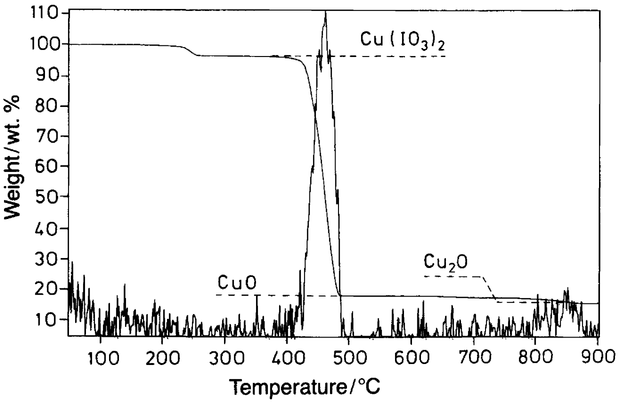

Fig. 3. TG curve for $Cu(IO_3)_2 \cdot 2/3\ H_2O$ recorded in a dynamic argon atmosphere at a heating rate of 5 °C min^{-1} and a simultaneously measured mass spectrum for oxygen evolution.

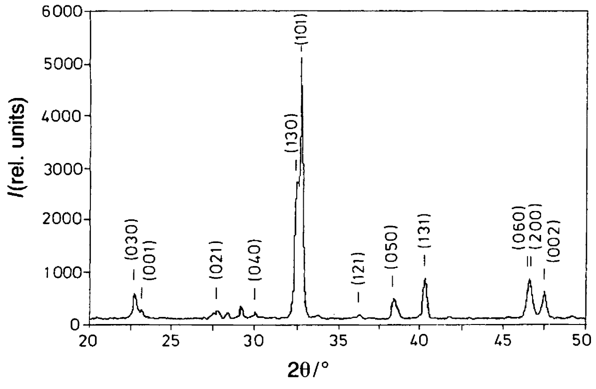

Fig. 5. X-Ray powder diffraction pattern (Cu*K*α radiation) of a mechanically mixed and annealed (flowing air, 950 °C, 3 h) $YBa_2Cu_3O_{7-\delta}$ sample.

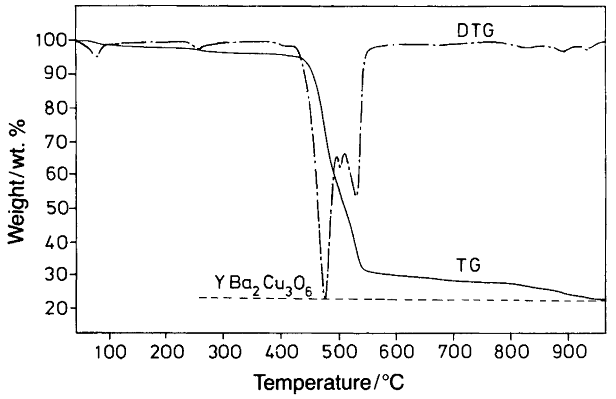

Fig. 4. The thermal decomposition of the 1:2:3 ternary mixture of Y, Ba and Cu iodates. The curve is recorded in a dynamic air atmosphere at a heating rate of 5 °C min^{-1}.

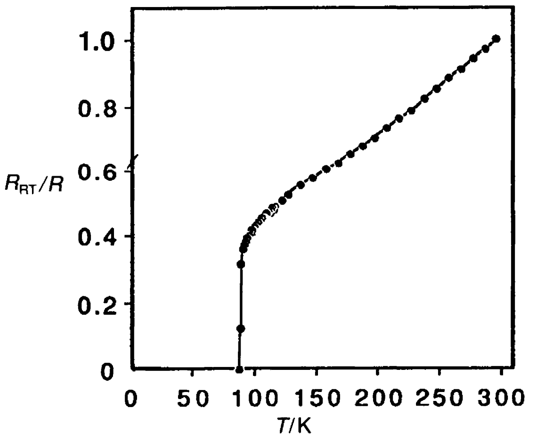

Fig. 6. Resistivity curve for coprecipitated and annealed $YBa_2Cu_3O_{7-\delta}$ sample. Cooling rate 2 K min^{-1} until 200 K and 1 K min^{-1} thereafter.

oxides. In the case of the 1:2:3 ternary mixture of yttrium, barium and copper iodates the total weight loss at 950 °C was also equal to that calculated for the complete reaction (Fig. 4). Similar results were obtained with the coprecipitated samples, although within a reproducibility of 2 % in the total weight loss, as the different solubilities of yttrium, barium and copper iodates may cause small changes in the stoichiometry. In the coprecipitation method there is also the possibility of double iodate formation.

The preparation of the $YBa_2Cu_3O_{7-\delta}$ bulk samples by annealing the mechanical mixtures of yttrium, barium and copper iodates under static air or oxygen yielded, according to X-ray diffraction measurements, besides $YBa_2Cu_3O_{7-\delta}$, also some unreacted barium orthoperiodate and other unidentified impurity phases even after heating at 950 °C for as long as 80 h. However, when performing the annealing in flowing air at 950 °C for 3 h almost pure $YBa_2Cu_3O_{7-\delta}$ was obtained; e.g. the peaks due to $Ba_5(IO_6)_2$ were completely missing in the X-ray diffraction pattern shown in Fig. 5. As seen from the DTG curves in Fig. 4, the reactions between individual iodates take place in four steps. The first three around 500 °C overlap each other and involve the decomposition of the iodates (cf. Figs. 1–3). The last process above 800 °C is due to the decomposition of $Ba_5(IO_6)_2$ and to the complete formation of $YBa_2Cu_3O_{7-\delta}$. The fact that the decomposition of $Ba_5(IO_6)_2$ involves oxygen requires the use of a flowing atmosphere with an oxygen concentration that is not too high.

The oxygen release and uptake behaviour measured for one of the slowly cooled $YBa_2Cu_3O_{7-\delta}$ samples was completely reversible during the heating and cooling cycles in air. The estimated oxygen deficiency δ varied between 0.2 and 1.0 when the temperature was cycled in the range 50–950 °C. Finally, the resistivity curve of the same sample revealed superconductivity with T_c around 90 K (Fig. 6). The above results, together with the XRD data, suggest that the synthesized sample was essentially a single-phase superconducting material.

Conclusion

By using the corresponding iodates as starting materials it is possible to prepare, in a carbon-free process, the yttrium barium copper oxide $YBa_2Cu_3O_{7-\delta}$ as a superconducting powder. It should be noted, however, that although the precursor mixture does not contain any carbon, carbonate ions may be introduced into the $YBa_2Cu_3O_{7-\delta}$ lattice from carbon impurities present even in the most pure commercial oxygen.[15]

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