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THERMAL TREATMENT OF A MODIFIED ALKOXIDE GEL PRECURSOR FOR THE PREPARATION OF THE $YBa_2Cu_4O_8$ SUPERCONDUCTOR

M. K. Van Bael, J. Mullens, R. Nouwen, J. Yperman and L. C. Van Poucke*

Laboratory of Inorganic and Physical Chemistry, Limburgs Universitair Centrum
B-3590 Diepenbeek, Belgium

Abstract

A precursor of Y–Ba–Cu oxides was prepared by a modified alkoxide sol-gel method and its thermal decomposition in air was studied by on-line coupled TG-FTIR and High Resolution Thermogravimetric measurements. A continuous more or less stepwise weight loss was observed between room temperature and 600°C at which all organic compounds had evolved and were progressively oxidized as the temperature increased leaving only Y and Cu oxides and bariumcarbonate. Between 700 and 800°C a final weight loss was observed due to the decomposition of bariumcarbonate into oxide.

Keywords: sol-gel, TG, thermal decomposition, Y–Ba–Cu superconductors

Introduction

Y–Ba–Cu superconducting oxides are usually obtained by heating mechanically mixed oxides or carbonates. The major difficulty encountered in this 'dry' synthesis method is obtaining homogeneous powders. Repeated grinding and heating is required and calcination and sintering times are generally long. Better control of the chemistry and morphology can improve the superconducting properties of the ceramic powders. Therefore, extensive investigations have been performed on 'wet' chemical synthesis methods for superconducting ceramics such as precipitation-filtration [1, 2] and sol-gel techniques for they allow chemical homogeneity and stoichiometric control through molecular level mixing. In the sol-gel method [3], molecular starting compounds are mixed into a homogeneous solution 'sol' which is then turned into a three dimensional metal-oxo polymeric 'gel' by hydrolysis and polycondensation reactions of the molecular precursors. Metal alkoxides $M(OR)_n$ [4] are very suitable starting materials because they have adjustable steric properties, they are able to form oxo-bridges and their rather labile M –O bonds make it possible to modify the properties of the precursor [5, 6]. Moreover, they can easily

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* Author to whom all correspondence should be addressed.

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be removed from the precursor by heating because of their high organic character. However, in the case of Y–Ba–Cu oxides, the starting alkoxides are difficult to obtain and are very expensive. In addition they are very sparingly soluble in organic solvents and are readily hydrolysed even by ppm amounts of water. To increase their solubility and decrease their reactivity towards hydrolysis, alkoxides are often modified by chemical additives [6].

To produce the ceramic powder, decomposition and oxidation of the gel precursor is required. Thermal analysis experiments can be very useful at this stage because they can provide information on the mechanism of decomposition of the gel into oxide [7]. On-line coupling with FTIR measurements [8] allows to qualitatively identify volatilized organic molecules during gel decomposition. When more is known about the decomposition mechanism of the precursor gel, the control and the modification of an appropriate precursor can be improved. In this work, an Y–Ba–Cu precursor is prepared by a modified alkoxide based sol-gel method and its thermal decomposition in air is studied using TG-FTIR and High Resolution Thermogravimetric measurements.

Experimental

The preparation of the Y–Ba–Cu precursor gel is based on the method described by Katayama *et al.* [9]. They designed a heterometallic alkoxide for preparing a homogeneous and viscous sol through modified alkoxides. The starting alkoxides are $Y(O^iC_3H_7)_3$ 25% solution in toluene (Johnson Matthey), $Ba(OC_2H_5)_2$ 10% solution in ethanol (Johnson Matthey, 99.5%) and $Cu(OCH_3)_2$ powder (Aldrich, 97%). In a nitrogen-filled (Air Liquide N57) glovebox, $1\cdot10^{-3}$ mol $Cu(OCH_3)_2$ powder is dissolved in 2-butoxyethanol (ACROS, 99%) with $2\cdot10^{-3}$ mol ethylenediamine (en) (Aldrich, 99%) at 50°C. Thus, a more stable and soluble modified copper alkoxide $Cu(OCH_3)_2(en)_2$ is formed. A modified yttrium alkoxide is prepared by adding $0.25\cdot10^{-3}$ mol $Y(O^iC_3H_7)_3$ solution in toluene to a mixture of $0.25\cdot10^{-3}$ mol ethylacetoacetate (EAA) (ACROS, 99%) and 2-butoxyethanol. One isopropoxy group is substituted by an EAA to form a chelate compound $Y(O^iC_3H_7)_2(EAA)$ which reduces the reactivity of one of the OR groups [9]. After partially hydrolysing the modified copper alkoxide with equimolar water (deionised) in 2-butoxyethanol at 50°C under stirring, a heterometallic mixture is prepared by adding the $Y(O^iC_3H_7)_2(EAA)$ solution and $0.5\cdot10^{-3}$ mol $Ba(OC_2H_5)_2$ solution in ethanol respectively. The mixture is stirred for two hours and then hydrolysis is carried out with a water/2-butoxyethanol mixture at a H_2O/M –O ratio of 1. The resulting dark blue mixture is stirred for another few hours at 50°C and thereafter exposed to ambient atmosphere at room temperature. After two weeks, the dark blue mixture has turned into a viscous dark khaki-coloured solution and is further dried until a paste like substance was formed.

The conventional TG equipment used in this work is a TA instruments TGA 951–2000 on-line coupled with a Bruker IFS 48 FTIR apparatus with a resolution of 8 cm^{-1}. The on-line coupling has been described in detail previously [8]. The used carrier gas is an air like mixture (Air Liquide) of O_2 and N_2 at a flow rate of 50 ml min^{-1} and the heating rate is set at 10°C min^{-1}.

High resolution thermogravimetric measurements were performed with a TA Instruments Hi-Res TGA 2950 thermogravimetric analyser. The equipment uses a furnace purge of 80 ml min^{-1} dry air. The experiments were carried out in the high resolution option in which, dependent on resolution and sensitivity parameters. The heating rate is dynamically and continuously modified in response to changes in the rate of weight loss of the sample. The maximum heating rate was set at 10°C min^{-1}.

Results and discussion

TG curves and their respective DTG curves were used to study the thermal behaviour of the Y–Ba–Cu precursor gel in dry air.

Figure 1 shows the conventional TG and DTG curves using a 10°C min^{-1} heating rate from room temperature to 1000°C. As can be seen from the TG curve, a continuous mass decrease occurs until about 600°C. At 800°C there is a final minor mass loss.

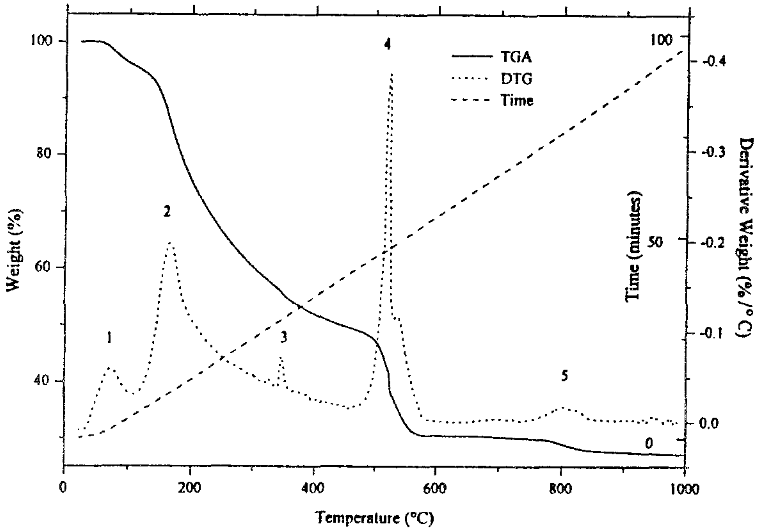

Fig. 1 TG of the precursor gel in dry air. Heating rate: 10°C min^{-1}

The shape of the DTG curve suggests a not completely resolved stepwise decomposition. The maxima of the DTG curve are listed in Table 1. The significance of the maximum value temperatures should however be put in perspective since they depend on experimental conditions like heating rate. As an example, the DTG maxima of the conventional 10°C min^{-1} heating rate experiment are compared (Table 1) with those of a measurement recorded with the high resolution apparatus (Fig. 2). The temperatures of the DTG maxima are indeed reduced by increasing the resolution of the measurement. This effect is normal because the high resolution option constrains the mass loss to lower rates which can only by maintained at lower temperatures. The slower heating rates due to the high resolution settings can clearly be seen in the time curve on Fig. 2. The shape of the high resolution curves is simi-

Table 1 Mass loss regions and DTG maxima during thermal decomposition of the Y–Ba–Cu precusor gel in dry air

	Region	10°C min^{-1} heating rate		High resolution	
		mass change/ %	maximum/°C	mass change/ %	maximum/°C
1	20–100°C	100–96	73	100–92	20
2	100–300°C	96–57	165	92–53	121
3	300–400°C	57–52	346	53–48	339
4	450–600°C	50–30	523	46–28	509
5	700–850°C	30–27	805	28–25	763

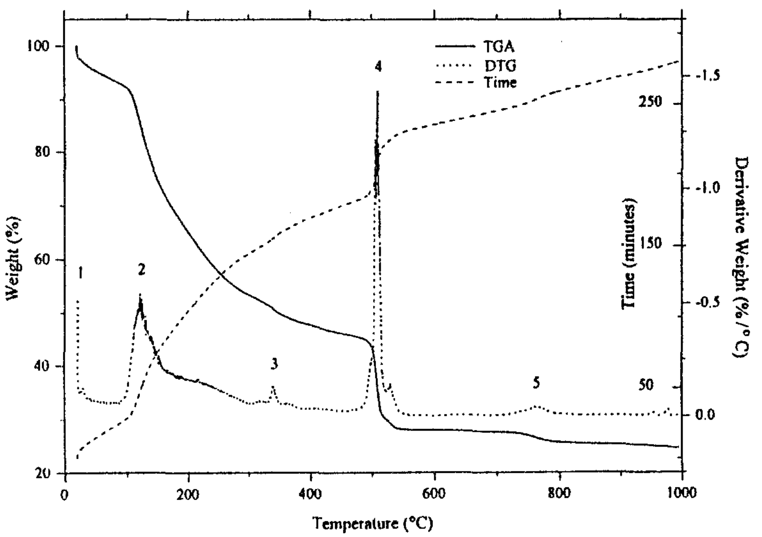

Fig. 2 TG of the precursor gel in dry air. High resolution measurement

lar to those recorded with the conventional equipment confirming the above mentioned stepwise decomposition. The first maximum in the DTG curve has moved to room temperature and is therefore not completely seen. This is a result of the high resolution option: since the mass decrease starts already at room temperature, heating will not go on until the accompanying reaction has come to an end. Because high resolution and sensitivity settings do not very much improve the separation of overlapping decomposition steps, they also confirm that the decomposition reactions between 100 and 600°C occur simultaneously and that this is a property inherent to the precursor.

The more or less stepwise thermal decomposition can also be seen from the online coupled FTIR measurements of the evolution of the evolved gases during thermal treatment in dry air. The integrated absorption resolves five regions of increased absorption corresponding with the regions of mass loss in the TG curves (Tables 1, 2). A characteristic FTIR spectrum is observed in each of these regions.

From the FTIR absorptions, functional groups present in the evolved gases can be detected. Our intention is to assign these functional groups to evolved products of the decomposition, but since the precursor consists of a mixture of various starting compounds, the system is very complex and a lot of possible assignments can be made. Table 2 lists the observed absorptions during the different stages of mass loss.

Table 2 Overview of the observed functional groups in the FTIR spectra of the evolved gases during the thermal decomposition of the Y–Ba–Cu precursor gel in dry air

Functional group	Wavenumber/ cm^{-1}	Band assignment	Decomposition region				
			1	2	3	4	5
H_2O	3900–3600	$\nu(HOH)$	+	–	–	++	–
	1750–1450	$\delta(HOH)$	+	–	–	++	–
OH	3700–3600	$\nu(OH)$	–	++	?	–	–
CH_2/CH_3	3000–2800	$\nu_{as}(CH_n)$, $\nu_s(CH_n)$	–	++	+	–	–
	1470–1370	$\delta_{as}(CH_n)$, $\delta_s(CH_n)$	–	++	+	–	–
C–O–C ether	1130	$\nu(C–O)$	–	++	+	–	–
C–O–H	1060	$\nu(C–O)$	–	++	+	–	–
C–O–C ester	1040	$\nu(C–O)$	–	++	+	+	–
O–C=O	1263	$\nu(C–O)$	–	++	+	+	–
C=O	1750	$\nu(C=O)$	–	++	+	–	–
NH_3	968/932	$\nu_2(NH_3)$ [14]	–	+	++	+	–
CO_2	3750–3600	$(\nu_{as}+\nu_s)(OCO)$, $(2\delta+\nu_{as})(OCO)$	–	+	+	++	+
	2400–2300	$\nu_{as}(OCO)$	–	+	+	++	+
	618–721	$\delta(OCO)$	–	+	+	++	+
CO	2180–2110	$\nu(CO)$	–	–	+	+	–
N_2O	2260–2190	$\nu_1(N_2O)$	–	–	–	++	–
NO	1840–1920	$\nu(NO)$	–	–	–	++	–
NO_2	1650–1550	$\nu_2(NO_2)$	–	–	–	++	–

++ Absorption is mainly present in the above decomposition region
+ Absorption is present but not predominant in the above decomposition region
– Absorption is not present in the above decomposition region

In the first region of mass loss, from room temperature to 100°C, only bands at 3900–3600 cm^{-1} and 1450–1750 cm^{-1} due to water are detected by FTIR. The mass loss is therefore attributed to evaporation of absorbed water or water that is formed during condensation reactions.

In the temperature domain from 100 to 300°C, in which the second mass decrease is observed, the FTIR spectra (Fig. 3a) contain typical absorptions of alkyl-groups (3000–2800 cm^{-1} and 1470–1370 cm^{-1}), alcohols (3700–3600 cm^{-1} and 1060 cm^{-1}), ether (1130 cm^{-1}), O–C=O (1263 cm^{-1}), ester (1040 cm^{-1}) and carbonyl (1750 cm^{-1}) functions. H_2O, NH_3 gas (968 and 932 cm^{-1} [10, 11]) and a considerable amount of CO_2 (3750–3600 cm^{-1}, 2400–2300 cm^{-1} [12] and 618–721 cm^{-1} [13]) are detected as well.

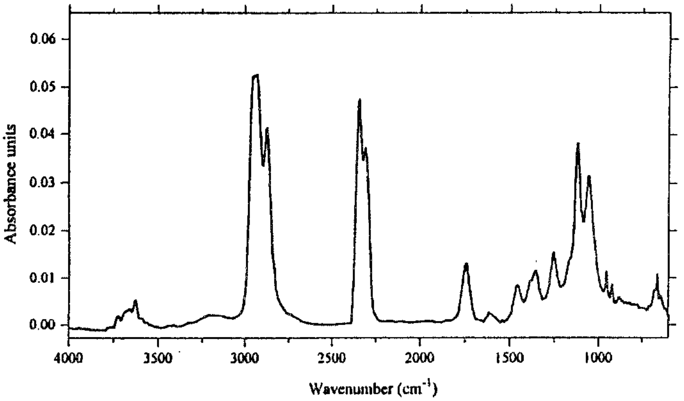

Fig. 3a FTIR spectrum of gases released by heating the precursor gel during decomposition region 2 (100–300°C)

This mass loss is mainly attributed to the evaporation of the solvent butoxyethanol which explains the observed alkyl, alkohol and ether absorptions. They carbonyl, ester and O–C=O absorptions can be due to evaporation of ethylacetoacetate (boiling point: 180.1°C) in the gel. The appearance of NH_3 and CO_2 absorptions results from decomposition reactions of ethylenediamine and ethylacetoacetate respectively.

Between 300 and 400°C a small but distinct mass decrease occurs. The FTIR spectrum of the evolved gases in this domain (Fig. 3b) differs from the spectrum recorded during the mass loss between 100 and 300°C indicating that other kinds of reactions are involved. Absorptions of alkylgroups, etherfunctions and alkohols are much less pronounced and some CO(2180–2110 cm^{-1} [14]) is detected in addition.

It is assumed that up to this temperature, the precursor has lost the largest amounts of free organics and from now on decomposition of the gel-matrix is the predominant cause of gas evaporation.

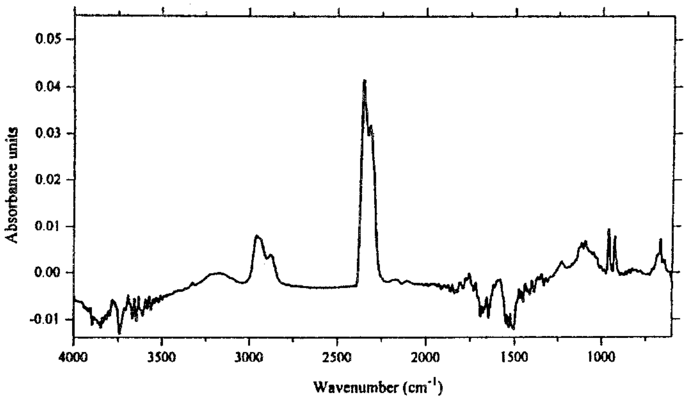

Fig. 3b FTIR spectrum of gases released by heating the precursor gel during decomposition region 3 (300–400°C)

The mass loss between 450 and 600°C is not observed in TG curves recorded in an inert He atmosphere and is therefore attributed to the oxidative burning out of organic residues in the gel, giving rise to mainly CO_2 and H_2O, but also NO_2 (1650–1550 cm^{-1}) [15] and to a less extent N_2O (2260–2190 cm^{-1}) [16] and NO (1840–1920 cm^{-1}) [14] evaporation (Fig. 3c). It is known that in air nitrogen compounds like ammonia decompose into N_2. The metals, present in the gel, can however act as catalysts to give rise to NO (Oswald process) that is readily oxidised to NO_2. The small amounts of NH_3 and O–C=O that are observed can be attributed to release of left organics inside the gel-matrix.

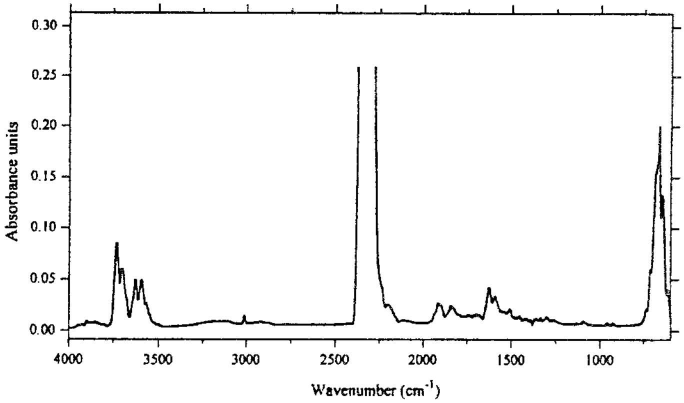

Fig. 3c FTIR spectrum of gases released by heating the precursor gel during decomposition region 4 (450–600°C)

The final minor weight loss from 700 to 850°C with only CO_2 evolvement is typical for the decomposition of $BaCO_3$. Although pure $BaCO_3$ only decomposes at temperatures above 1000°C, it was shown before that during the preparation of Y–Ba–Cu oxides, BaO is already formed at 750°C [17, 18].

Conclusions

The thermal decomposition of a sol-gel precursor for Y–Ba–Cu ceramic oxides can be studied by TG-FTIR and High Resolution Thermogravimetric measurements.

The weight of the sol-gel precursor decreases continuously between room temperature and 600°C. Different decomposition steps can however be distinguished by DTG curves and FTIR spectra of the evolved gases. Due to the structure of the gel, complete separation of the decomposition steps cannot be obtained even by using a High Resolution Thermogravimetric Analyser.

During the whole region of continuous decomposition, organics are released from the precursor and the liberated products become progressively more oxidized as the temperature increases. The different stages of decomposition cannot completely be resolved because solvents and chemical additives can evolve at this broad range of temperature. This is a consequence of the structure of the precursor gel: a metal-oxo polymeric network surrounds and encapsulates the organic solvent system. As the matrix decomposes, progressively more encapsulated organics can evolve but in a higher oxidized state because of the elevated temperatures.

At 600°C all organics are removed from the precursor, now consisting of Y and Cu oxides and bariumcarbonate.

The final minor weight loss, observed between 700 and 850°C is attributed to the decomposition of bariumcarbonate into oxide.

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