

Thermal analysis of metal organic precursors for functional oxide preparation: thin films versus powders

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Abstract

The thermal decomposition of several metal organic precursors, used in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting coated conductors (Cu acetate, Cu, Y and Ba trifluoroacetates and Ce propionate) is analyzed by means of several thermoanalytical techniques (TG/DTA, MS and DSC). In all cases, the metal organic precursors deposited as thin films decompose differently than powders from the same precursors. In thin films, decomposition is facilitated by the easier transport of reactive gas from the surrounding atmosphere and by the easier out-diffusion of volatile products. Consequently, films decompose at lower temperature and are more sensitive to the presence of any residual reactive gas in the furnace. Good thermal contact with the substrate is also shown to minimize overheating in films and avoid combustion processes that are otherwise often observed during the thermal decomposition of powders. Finally, the formation and stability of intermediate products towards the oxide formation, such as metal fluorides, differs in films because of the easier gas exchange. With respect to powders, these compounds are much less stable in films, where their decomposition temperature can be lowered by several hundreds of degrees Celsius. While in some cases the behaviour of films can be predicted by analyzing varying masses of precursor powders, this is not always the case. Therefore, thermal analysis carried out on films is recommended to avoid erroneous conclusions about materials preparation drawn from powders.

Keywords: pyrolysis, thermal decomposition, YBCO

I.- Introduction

Thermal decomposition of metal organic precursors is a current route for the synthesis of metal oxides in the form of powders, thin films or nanostructures [1,2,3,4,5]. Films can be obtained by Chemical Solution Deposition (CSD) techniques. A solution containing the precursor is spread over a substrate and, after solvent evaporation, the film is pyrolyzed. By controlling the precursor concentration and spreading conditions, film thickness can vary from tens of nm to several microns. These techniques allow fabrication of low-cost oxide single or multilayers that find application in microelectronics [6], high-temperature superconductors [7, 8, 9], photovoltaic energy conversion [10], optical layers [11], ferroelectric devices [12], etc.

The oxide quality critically depends on the pyrolysis conditions (heating rate to the isothermal stage, temperature and furnace atmosphere) when metal organic decomposition takes place. At this point, thermoanalytical techniques (notably thermogravimetry (TG) coupled with mass spectrometry (MS) or infrared spectroscopy) are very useful because they give information about the decomposition temperature, decomposition mechanism and kinetics and allow prediction of the evolution of the reaction when the material is submitted to a particular temperature program [13]. Since the signal delivered by any technique is proportional to the sample mass, m_i , thermal analysis experiments are usually done with the precursor in the form of powders (typically, $m_i > 5$ mg) [6], whereas experiments on films are very scarce (typically, $m_i < 1$ mg/cm²). This is so because, for the low masses of films, the TG baseline instability impedes the accurate analysis of the decomposition mass-loss curve. Consequently, the question arises: “Is the information delivered by powders (e.g. decomposition temperature, final or intermediate products and their dependence on the atmosphere) valid for films?”

In this paper, we will show that, in general, one should expect a negative answer whenever the decomposition kinetics is controlled by a transport step. To be more specific, films are expected to decompose differently than powders when the decomposition is controlled by: a) transport of reactive gas (usually O₂ or H₂O); b) evolution of gaseous species (reaction products or solvents) or c) heat transport out of the sample (see the summary given in Fig.1). All these aspects are not exclusive of decomposition processes but are intrinsic to most solid-gas reactions [14]. The fact is that, for most precursors we have analyzed to date, significant differences have been observed between powders and films. So, it is clear that optimization of the pyrolysis step can be hardly achieved with thermal analyses on powders. It is necessary to develop experimental procedures for measuring the decomposition

directly on films or, alternatively, to establish criteria that would help to deduce the behaviour of films from that of powders.

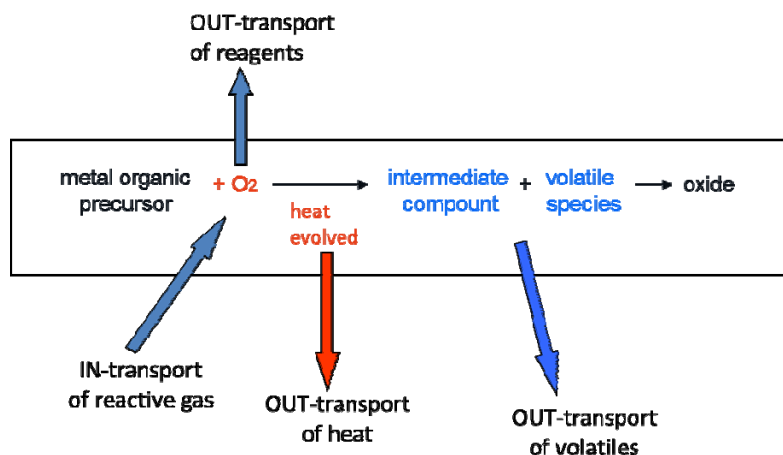


Figure 1.- Scheme showing several transport processes that can have some influence on the formation and microstructural development of oxide powders and films.

Substrates can also have a catalytic effect on decomposition reactions through their chemical terminations (e.g. H^+ terminations on the surface of glass substrates enhance the decomposition of $Y(TFA)_3$ [15]) or by promoting epitaxial growth of the oxide. Film deposition requires the preparation of a solution that may in turn modify the molecular structure of the precursor. However, such an effect is absent in this present study because of the chemical similarity between solvents and salts (e.g. acetic acid and acetates). Furthermore, a surface energy difference between films and powders may also exist. Nevertheless, as these effects are not related to any transport mechanism they will not be analysed here.

The examples given below correspond to metal organic precursors used for the fabrication of $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting tapes. These tapes consist in the active superconductor layer (1-2 μm thick) separated from the metallic substrate by one or several oxide thin buffer layers such as ceria (CeO_2) or other oxides [16, 17]. Additional examples published in a shorter format can be found in ref. [18].

II.- Experimental

Most precursors were used in their commercial form of powders: anhydrous $Y(TFA)_3$ and $CuAc_2$, and $Cu(TFA)_2$ hydrated were supplied by Aldrich. Ce propionate was synthesised from Ce acetate (see details in [19]) and $Ba(TFA)_2$ from Ba carbonate [20]. The powders were analysed inside alumina pans without cover to facilitate gases exchange (crucible section area, 0.2 cm^2). To obtain thin films, the

precursor salts were dissolved in acetic or propionic acid and, then, a microdrop was spread on an appropriate substrate and dried below 100°C or, alternatively, a spin coater was used. Thin glass discs, platinum foils or silicon and (001)LaAlO₃ single crystalline substrates were used depending on the experiment (typical area of one substrate side was 1 cm²). To increase the mass of the samples, films were deposited on both substrate sides and several (usually two) substrates were kept some mm apart inside the TG furnace, to allow gas exchange with the furnace atmosphere. The quoted thickness of the films is their “nominal thickness”, i.e. the thickness the film would have if transformed into a dense oxide. In our studies we have found two kinds of films: a) aggregates of particles [15] and b) dense films [21]. However, the different behaviour between powders and films does not depend on this structural feature but on the fact that gas and heat transport is easier in films (see next section).

TG analyses were done with a TGA851[°]LF apparatus from Mettler Toledo and a Setsys Evolution apparatus from Setaram under continuous flow of high-purity gases (usually 40 mL/min). The TG curves were corrected by the apparatus baseline, measured during a consecutive measurement under the same conditions. Additionally, the final mass of the sample was always measured and compared with that deduced from the TG curve. Significant discrepancies led us to discard experiments. These precautions were essential for the experiments on films. These apparatus simultaneously delivered the differential thermal analysis signal (DTA). For the differential scanning calorimetry (DSC) measurements, the DSC822 from Mettler Toledo was used. And, finally, mass spectroscopy (MS) measurements were taken simultaneously to the TG curves with an MKS Spectra Quadrupole (Micro Vision Plus), which detects molecular fragments with $m/z < 300$ amu.

Several apparatus were used for the X-ray diffraction experiments (XRD): a) Smart Apex diffractometer of Bruker AXS (with Mo x-ray source) where collection of the diffracted photons was done with a CCD detector that increases the experimental sensitivity at the expense of resolution; b) conventional D8 Advance diffractometer from Bruker AXS in the $\theta - 2\theta$ configuration (Cu x-ray source); and c) thin film diffractometer PANalytical model X’pert PRO MRD (Cu x-ray source). XRD spectra were analyzed using eva software from SOCABIM and the JCPDS database from the International Centre of Diffraction Data.

III.- Results and discussion

III.1.- Transport of reactive gas: decomposition of Ce propionate

The dependence on m_i is easily understood due to the reactive gas consumption at the sample surface. Higher m_i implies faster gas consumption and, consequently, a less reactive atmosphere near the sample because of the higher concentration gradient between the sample surface (at the bottom of the crucible) and the free atmosphere (at the top of the crucible). Thus, T_{dec} must move towards the value for inert conditions when m_i increases. In the case of films, a higher mass corresponds to a thicker film. Consequently, the reactive gas must diffuse over a greater distance through the solid precursor and as a result decomposition will be slower (higher T_{dec}) for thicker films. Finally and given the same precursor mass for powders and films, because the crucible section is usually much smaller than the substrate area, the reactive gas will reach the film surface more easily than the powder and thus T_{dec} will be minimal for thin films.

These predictions are aptly illustrated by the TG curves corresponding to the decomposition of Ce propionate in air and N_2 (Figs. 2 and 3) [11, 19]. Notice that powders decompose in air at a lower temperature when m_i diminishes, and that decomposition begins at the same temperature as in the inert atmosphere when m_i is high enough (see asymptotic behaviour in Fig. 3). Similarly and as to be expected, films decompose in air at a lower temperature when they become thinner (Fig. 2). The most interesting fact for our discussion is that, for the same initial mass T_{dec} is lower for thin films than for powders (Fig. 3). This behaviour is mainly due to the lower mass per unit area (substrate area for films and crucible section for powders) of films. The thinnest film we measured ($0.17 \mu\text{m}$) decomposed at around 120°C below the decomposition temperature of 10 mg of powders. This difference provides us with an insight into the enormous errors that could be made if one applied the information obtained from powders to thin films.

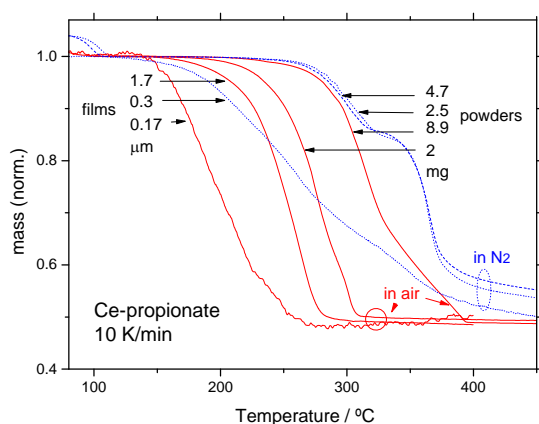


Figure 2.- TG decomposition curves of Ce propionate films and powders in air (solid lines) and in N_2 (dashed lines). Quoted film thicknesses refer to the expected thickness of dense CeO_2 films.

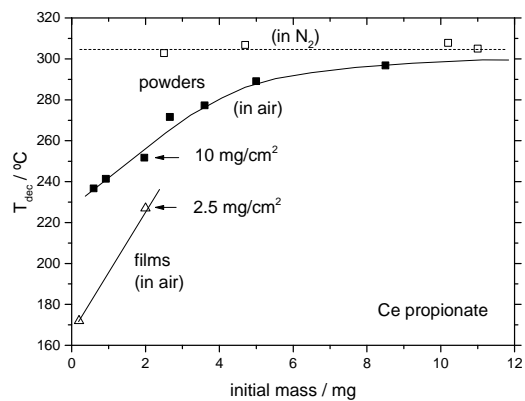


Figure 3.- Decomposition temperature (defined as the temperature where $m/m_i = 0.9$) extracted from the TG curves of Fig. 2 (for clarity, only selected curves were shown).

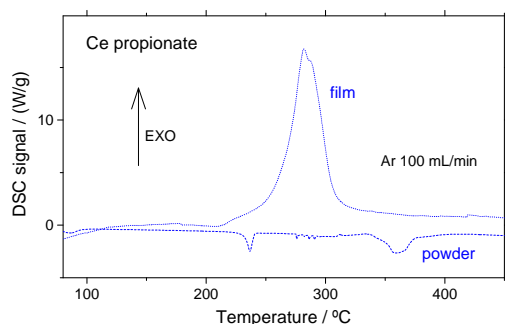


Figure 4.- DSC curves measured in a nominally inert atmosphere.

For experiments carried out in an inert atmosphere, T_{dec} should be independent of m_i and share the same value for films and powders. In Fig. 2 the curves of the powders coincide above 2.5 mg. However, and surprisingly, a thin film begins to decompose at a much lower temperature. We consider that, in this case, the partial pressure of the residual oxygen in the furnace was high enough to enhance the decomposition rate of the film, whereas it was not able to modify the inert conditions near the powders. This explanation is consistent with the complementary DSC experiments carried out on the powders and the one film tested. Fig. 4 depicts that when treated under the same conditions (100 mL/min of Ar), the film reacts with the oxygen giving rise to a highly exothermic peak, whereas the decomposition of powders is endothermic as if the atmosphere were completely inert. In other words, we can conclude that thin films are much more sensitive to traces of oxygen or any reactive gas during pyrolysis than powders are.

Before closing this section, we ought to remark that the different behaviour reported in this and the subsequent section, applies to films that are “thin enough”. The trend observed in T_{dec} as the film mass (thickness) increases (Fig. 3) indicates that Ce propionate films with $m_i > 4$ mg (> 3.5 μm) would decompose at a higher temperature than would be required for the same amount of powders. This is because oxygen has to diffuse through the film to reach the unreacted precursor and while it may not be completely dense, it will always be denser than the aggregates of particles in the powders. Consequently

for thick films, the lower diffusivity through the film will balance the easier gas transport from the furnace atmosphere to the film surface.

III.2.- Evolution of gaseous species: decomposition of $Ba(TFA)_2$

Local atmosphere composition near the sample can also be affected by the volatiles that result from decomposition and, due to the reverse reaction, a higher concentration of products may reduce the overall reaction rate. This effect is very common in carbonates, whose decomposition temperature is lowered by hundreds of degrees when the sample mass is reduced, due to the lower local concentration of CO_2 . It has also been reported in the studies devoted to determine the decomposition temperature of YBCO at very low oxygen partial pressures [22]. The reduction of T_{dec} in $Ba(TFA)_2$ films with respect to powders (Fig. 5) can be explained in a similar way.

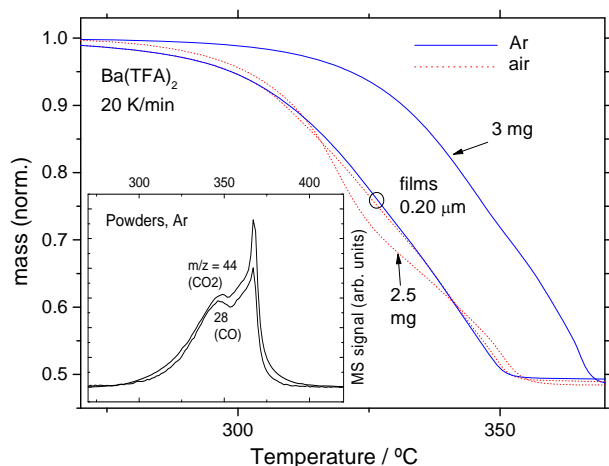


Figure 5.- TG curves of $Ba(TFA)_2$ powders and films decomposition in Ar and air. Inset: MS curves of CO and CO_2 measured during powder decomposition in Ar.

First of all, notice that $Ba(TFA)_2$ powders decompose at a lower temperature in air than in Ar (Fig. 5). Although this fact may induce to think that decomposition is triggered by reaction with oxygen, this is not the case. DSC measurements show that the decomposition enthalpy is more exothermic in air by just the heat evolved during the oxidation of one mol of CO to CO_2 [20]. In other words, oxygen molecules do not participate in the primary decomposition reaction but in a secondary reaction with CO out of the sample. This fact, together with MS results, notably the equal amounts of CO and CO_2 detected in inert atmosphere (inset of Fig. 5), led us to propose the following overall decomposition reaction:



So, in air oxygen reacts with CO and reduces its concentration near the sample, thus reducing the inverse reaction rate and enhancing the decomposition rate in powders (i.e., lowering T_{dec}).

On the contrary, experiments carried out in films show that their T_{dec} is identical in air and Ar [21] and lower than for powders in Ar (Fig. 5). This result is consistent with reaction (1) if gas exchange is so easy in films that CO concentration is so low that the reverse reaction can be neglected even in the absence of oxygen.

This example tells us that, even if T_{dec} clearly depends on the presence of reactive gas species (usually O_2) in powders, this dependence may be lost when dealing with films.

III.3.- Heat transport: combustion of Cu(II) acetate

When decomposition of metal organic compounds takes place in air or in pure oxygen, the process is highly exothermic. Consequently, the sample temperature will be higher than that measured by the TG apparatus and indicated on the x-axis of a mass-loss curve. This sample overheating will depend on the heat dissipation paths [23]. For large samples in powder form, the process will be more adiabatic and, eventually, combustion can occur. Combustion begins with a local overheating that leads to local thermal runaway (ignition) that propagates all along the sample as a combustion front. This phenomenon can be identified in a TG curve by an abrupt mass loss (solid curve in Fig. 6) that often begins with a slope discontinuity. Decomposition reaches completion in few seconds indicating that the local temperature at the combustion front is hundreds of Celsius above the measured temperature [24].

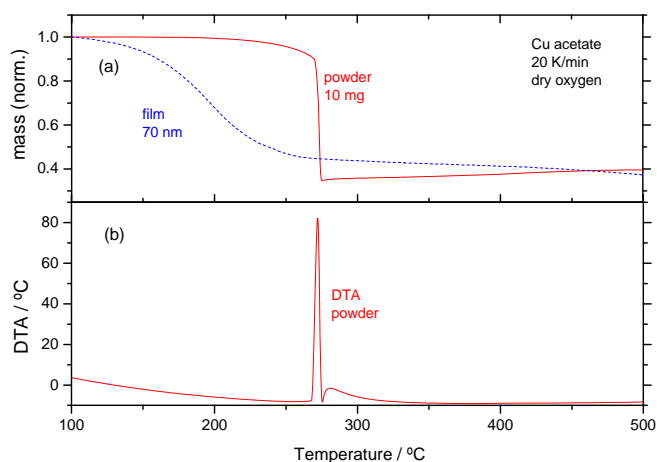


Figure 6.- a) TG decomposition curves of Cu acetate in dry oxygen for powders and one film; b) the corresponding DTA curve for the powder showing that its decomposition entails high overheating of the sample leading to combustion (the DTA signal from the film was below the apparatus sensitivity).

Combustion synthesis has been recently proposed as a general route for the low-temperature fabrication of oxide thin films [6]. However, calculations shown that the very high thermal conductance between the substrate and the film makes it very difficult to reach the overheating needed for combustion and, consequently, we think that combustion of thin films (say, below 1 μm) is very unlikely [25]. In fact, we have observed combustion in several precursor powders but this phenomenon was always absent for the corresponding films. The case of Cu acetate in dry oxygen constitutes a nice example (Fig. 6).

Due to the oxygen depletion effect discussed above, decomposition of Cu acetate powders begins at a temperature higher than that of films. For the experiment reported in Fig. 6, decomposition of powders becomes unstable at 270°C where the abrupt mass loss indicates that combustion occurs. This mass-loss event is accompanied by a sharp differential thermal analysis (DTA) peak indicating a sudden heat evolution (Fig. 6b). Although, the DTA gauge recorded a sample overheating of 80°C, the local temperature at the combustion front is much higher. The interesting point here is that, in contrast with powders, the film TG curve is smooth (dotted curve in Fig. 4a), i.e. no combustion takes place. Comparison of both curves in Fig.6a tells us that TG experiments on powders that experience combustion to analyse the thermal evolution of films is nonsense and, probably, a common error [6, 26].

The first three examples discussed so far (Ce propionate, Ba(TFA)₂ and Cu acetate) lead us to point out that, in general, films decompose at a temperature lower than powders. Therefore, researchers interested in low-temperature processing of CSD films should take it into account. We have recently shown that ceria films can be obtained at a temperature as low as 160°C from Ce propionate [11]. Similarly, CuO nanocrystalline films can be obtained at 180°C through isothermal decomposition of Cu acetate. The XRD curves of powders and a thin film treated at 180 °C for 1 h are shown in Fig. 7. Whereas Cu acetate remains the dominant phase (perhaps the only phase) in the powders, the film has been decomposed into CuO.

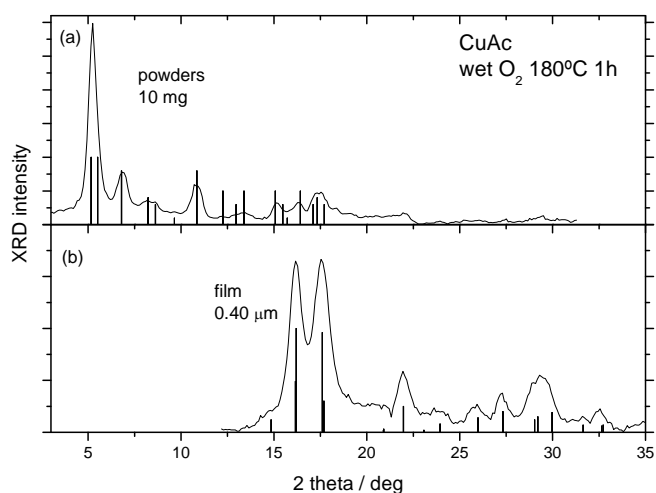


Figure 7.- XRD of the product of Cu acetate after heat treatment at 180°C lasting 1 h in wet O₂. The curve of powders (a) has the characteristic peaks of Cu acetate (i.e. no decomposition has occurred), whereas, the curve of one film (b) corresponds to CuO.

The two last examples that follow deal with the differences between films and powders with respect to the formation and stability of intermediate decomposition products.

III.4.- Gas exchange and combustion: reduction of Cu

In some cases, decomposition of metal organic precursors entails a change in the metal oxidation state. Decomposition of Au [27], Ni [28] and Ag acetates [29] in an inert atmosphere leads to the formation of metallic nanoparticles, whereas oxidation of Ce(III) into Ce(IV) is usually observed for ceria precursors even in an inert atmosphere [19]. The effect of oxidizing or reducing species produced during decomposition or coming from the furnace atmosphere will depend, in general, on their transport across the sample. Since this transport is easier in films than in powders, differences of the oxidation state may be expected between films and powders. This point will be analyzed for the particular case of Cu acetate decomposition in dry oxygen.

Let us analyze first the TG curves measured on varying amounts of powder that are plotted together in Fig. 8. To deduce the nature of the decomposition products, the masses of CuO, Cu₂O and metallic Cu are indicated as horizontal lines. Note that at 600°C where the mass becomes stable (no further increment is observed above this temperature), all the curves lay below the mass of CuO (the only thermodynamically stable state in dry oxygen at this temperature). This means that some Cu has been lost during decomposition due to precursor evaporation. This effect is well known in YBCO thin film growth processes by CSD, where an initial excess of Cu precursor to compensate for it is used or decomposition is done in a wet atmosphere to avoid the evaporation of the Cu precursor [30] and has also been reported for other metal oxide precursors [31]. Anyway, the feature we are interested in is the smooth mass gain observed in powders after decomposition. It corresponds to the oxidation of Cu₂O or metallic Cu into CuO [32]. This process indicates that, despite the highly oxidative furnace conditions, copper becomes partially (or highly) reduced during decomposition. Recently, in situ XRD measurements during heating ramps have shown the successive states of oxidation that Cu acquires during decomposition on Cu acetate powders [33].

The degree of Cu reduction during decomposition of powders can be estimated by the mass-gain that is observed after decomposition, because Cu and Cu₂O will become fully oxidized when the

temperature is raised in an oxidative atmosphere. So, the mass gain measured from the end of decomposition up to 600°C, (see the definition of Δm_i in Fig. 8), is just a measure of the degree of reduction that copper has experienced during decomposition. From the TG curves of Fig. 8, it is clear that Cu reduction is lower for smaller m_i . This result is, as expected, according to the general argument that the out-diffusion of reducing species formed during decomposition [32] and the transport of oxygen into the sample is easier for smaller amounts of powder. In addition, combustion also contributes to this result. Since the decomposition rate is very high at the combustion front, the concentration of reducing volatile species there will be also very high and will partially displace oxygen, making the local atmosphere more reducing than in the absence of combustion. Since combustion (i.e. the abrupt step on the TG curves) accounts for almost the 100% of the mass-loss for the largest sample whereas it accounts roughly for 50% of the mass-loss for the smallest sample, we deduce that copper reduction during decomposition must be more pronounced as m_i increases, as observed.

In the absence of combustion, thin films should experience minimum Cu reduction. Unfortunately, the Cu reduction feature characteristic of the TG curves of powders is absent from the curve of a thin film because decomposition still continues up to around 500 °C (Fig. 8) making it impossible to extract its degree of reduction. We can try to estimate it in thin films by extrapolating the results of powders to $m_i = 0$. From the inset of Fig. 6, it is clear that the degree of copper reduction will be very small in films. We have verified it by XRD measurements on powders and a film treated up to 300°C (Fig. 9). The diffraction curve obtained on 10 mg of powders indicates that CuO is the residual phase whereas it is the only phase detected in the film (i.e. no Cu reduction is observed after decomposition of Cu acetate films in dry oxygen).

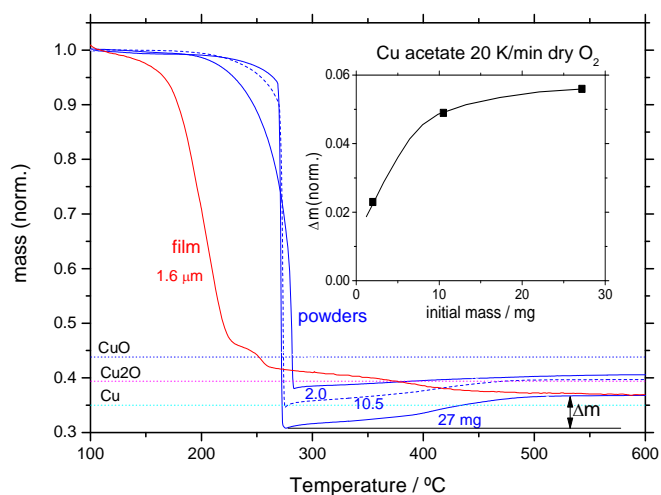


Figure 8.- Comparison between the TG decomposition curves of Cu acetate powders and one film in dry oxygen. The y-axis of the inset corresponds to the mass increment due to complete oxidation of Cu and Cu₂O (see arrow in the main figure) that follows acetate decomposition. The solid curve shows the general trend.

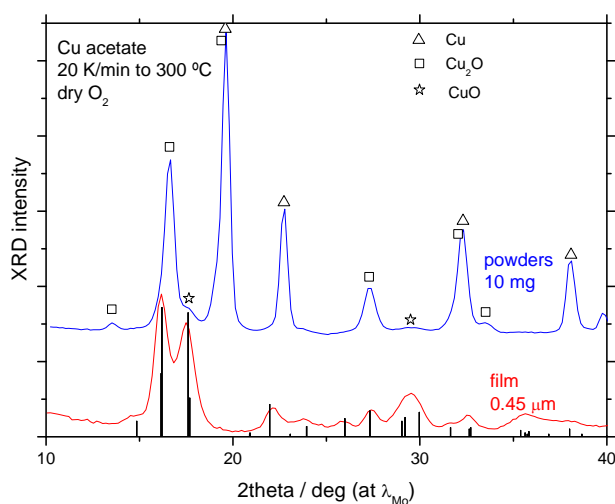


Figure 9.- XRD curves of Cu acetate treated up to 300°C in dry oxygen (vertical bars: expected peaks for CuO). Whereas copper is highly reduced in the powder, it is fully oxidized in the film.

This example illustrates that, when used uncritically, the results on powders can lead to very erroneous conclusions for films (e.g. from any individual TG curve one would deduce a high reduction degree). However, when treated with caution, from the trend of the powders at the limit of zero initial mass we can deduce the approximate behaviour of films.

III.5.- Stability of intermediate products: metal fluorides and YBCO formation

Although the usual aim of CSD is to obtain oxide films, sometimes decomposition of the precursor molecule leads to the formation of intermediate products such as metal carbonates or fluorides [2, 34, 18]. In fact, at present, the most promising precursors for YBCO production are fluorine-based [16, 17]. With this choice, maximum critical currents are obtained. However, if we trusted on the thermal analysis of powders, we should conclude that this solution would be far from satisfactory because of the abundance of BaF₂ in their decomposition product.

Y(TFA)₃ powders decompose into fluorides and oxyfluorides that are stable up to 1000°C (Fig.10a) [35], a temperature much higher than that of YBCO film formation (around 800°C). The product of Ba(TFA)₂ decomposition (BaF₂) is still much more stable. One can see in Fig. 10b that BaF₂ begins to decompose above 1200°C [20]. Furthermore, we have treated a powder mixture obtained by precipitation from a solution containing the Y and Ba TFA precursors with molar ratio Y:Ba = 1:2, because studies on the mechanism of YBCO formation [17] indicate that Y and Ba fluorides are less stable when obtained from the mixture. The corresponding TG curve of Fig. 8c shows a mass loss step at 750°C. The final mass at 810°C has a value consistent with a mixture of BaF₂, YOF and Y₂O₃. In fact, XRD measurements reveal that the product contains two Ba oxyfluoride phases plus BaF₂ and a complex fluoride of Ba and Y (Fig. 11), i.e., no oxides have been produced at the temperature that is used to obtain YBCO films. Consequently, thermal analysis of powders would lead to the erroneous prediction that YBCO preparation is not possible from TFA precursors.

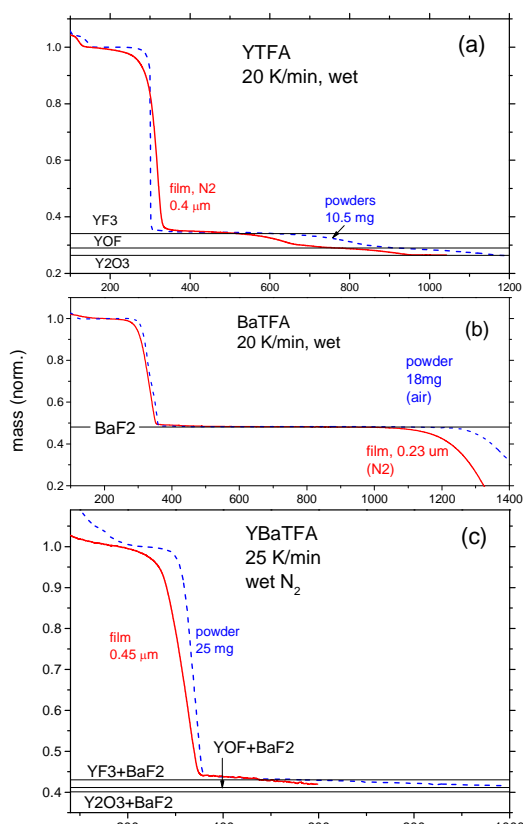


Figure 10.- TG curves of the decomposition of powders and films of $Y(TFA)_3$ (a), $Ba(TFA)_2$ (b) and a binary TFA precursor with molar ratio Ba:Y = 2:1 (c).

If we repeat these experiments with films, the result is quite different. Both BaF_2 and YF_3 films are less stable than powders; their decomposition temperature is lower by more than $100^\circ C$ (Figs. 10a and 10b) [21, 15]. The stability of Y fluoride is still lower if films are obtained from the binary solution. Just after precursor decomposition, above $400^\circ C$, their corresponding TG curve (Fig. 10c) already has a negative slope that continues up to the maximum temperature of this particular experiment ($600^\circ C$ – glass substrate) suggesting that BaF_2 reaches complete decomposition. This point is nicely confirmed by the XRD curve measured on this film, where Y_2O_3 is the only phase containing Y, all the Y fluorinated phases have disappeared and the main Ba-related phase is BaF_2 (Fig. 11).

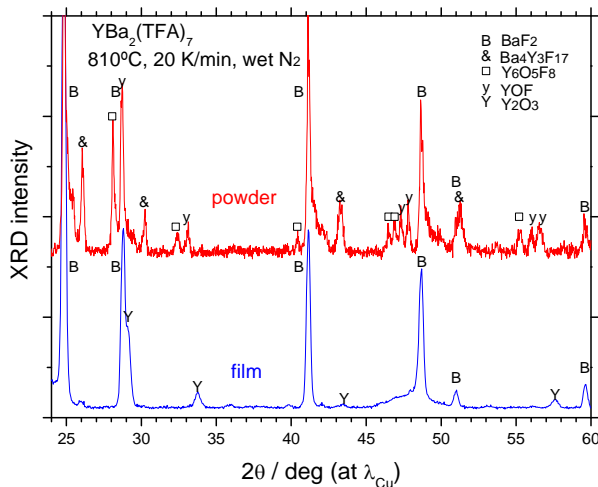


Figure 11.- XRD of the products of decomposition of a binary $Y(TFA)_3/2Ba(TFA)_2$ precursor after heating them up to $810^\circ C$ in wet N_2 .

The different behaviour of films can be explained by the fact that, thanks to the enhanced gas transport of volatiles or reactive gases, intermediate products tend to be less stable in films than in powders. In the particular case of metal fluorides, it has been shown that they decompose by reaction with water vapour and that the rate-limiting step is HF out-diffusion [35]. Therefore, its faster diffusion in films explains their lower decomposition temperature.

Despite the improved behaviour of films and, in particular, of the binary film, BaF₂ still survives at 800°C, thus precluding YBCO formation. Since YBCO films are prepared at this temperature, we must conclude that BaF₂ stability is lower when Cu(TFA)₂ precursor enters into play. To reveal this effect, a ternary solution of Y, Ba and Cu TFA precursors with molar ratio 1:2:3 has been prepared and, after precipitation, it has been heat treated in wet nitrogen. The complexity of this particular precursor mixture makes it very difficult to reach any conclusion about the nature of the products from the TG curves. So, we have analysed them by XRD.

One film of the ternary precursor with 0.9 μm of nominal thickness was deposited on silicon substrates protected by a nanometric Y₂O₃ film and after treating it at 810°C during 30 min, its product has been compared with that of 9 mg of powders treated at 920°C. We have taken silicon instead of the substrates used for YBCO film production to avoid epitaxial crystallization, so that the observed differences between the film and powders can be unambiguously related to gas transport.

The XRD curve of powders (Fig.12a) shows that BaF₂ is still the only Ba-containing crystalline phase like in the binary precursor; i.e., apparently, copper atoms have not diminished the stability of this phase. On the contrary, one can notice (Fig. 12b) an important diminution of the BaF₂ content in the film. This result on the film is consistent with the interpretation that gas transport makes it easier YBCO synthesis in thin films than in powders even if epitaxial crystallization is prevented by using a silicon substrate.

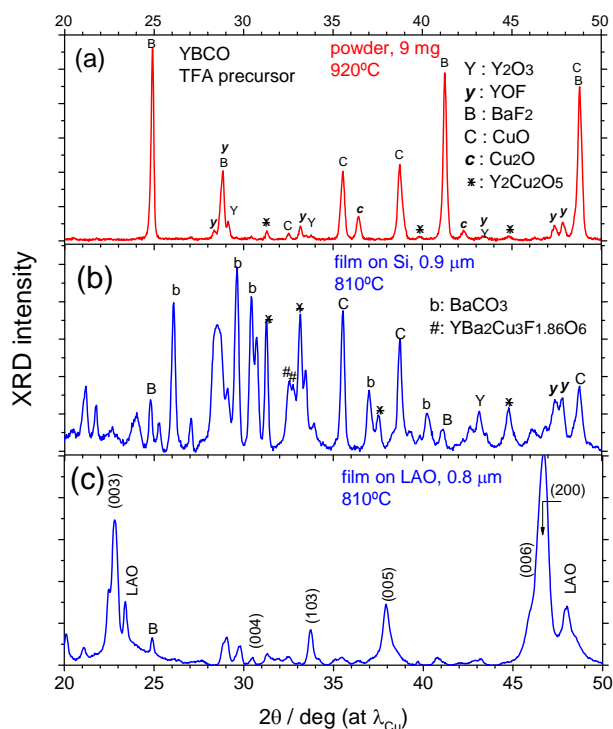


Figure 12.- XRD of the decomposition products of a ternary 1:2:3 Y:Ba:Cu TFA precursor in the form of powders (a), in a film deposited on silicon (b) and on (001)LaAlO₃ (LAO) single crystalline substrate (c). The indexed peaks in (c) refer to YBCO.

Before leaving this section, we should remark that films on LaAlO_3 substrates (where epitaxial crystallization occurs) treated at identical conditions are completely transformed into YBCO (Fig. 12c). This means that lattice match with the substrate does not only make possible epitaxy but it activates the reaction between the component oxides of YBCO.

IV.- Conclusions

The examples given above clearly show that films of metal organic precursors decompose differently than their corresponding powders: a) their decomposition temperature is lower; b) decomposition via combustion does not occur (so far, we have not found a single exception to these two conclusions); c) films are more sensitive to residual amounts of oxygen in the furnace atmosphere and d) the intermediate products obtained before oxide formation are less stable. These differences arise because, in thin films, gas exchange is easier, and the substrate offers an efficient path to heat dissipation and, eventually, promotes epitaxial growth. Our results raise the question about the usefulness of doing thermal analyses on powders for predicting the behaviour of films.

After decades of doing thermal analysis on powders by people that make films, any intention of discrediting this practice is nonsense. We want simply to remark that not only quantitative information may not be accurate enough (e.g. the decomposition temperature) but that even qualitative conclusions may be erroneous (e.g. combustion of films). In those cases where the decomposition evolves with the mass of powders, this evolution can serve to predict the behaviour of films. However, in the absence of such an evolution, the behaviour of films can only be deduced by general rules like those indicated in the previous paragraph.

We thus conclude that thermal analysis on films is very useful for the analysis of the preparation of oxide films and may be unavoidable in some instances. Although the sample mass must be lower than with powders, films of 1 mg may already deliver significant results. This amount of sample can be analyzed without much difficulty by modern TG/DTA and DSC equipment.

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