Solution design for low-fluorine trifluoroacetate route to YBa$_2$Cu$_3$O$_7$ films

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Abstract
We present our work in the preparation of metallorganic precursor solutions with reduced fluorine content, able to fulfill the requirements for high-performance superconducting YBCO epitaxial layers as a promising approach to low cost and scalable coated conductors. Six different solutions using different quantities of fluorine and non-fluorine carboxylate precursors with a total amount of fluorine from 10 to 50% that of standard trifluoroacetic acid (TFA) solutions. For stabilization purposes different coordinating agents have been used and the solution rheology has been modified for proper substrate wettability. Thermal decomposition analysis and infrared spectroscopy performed directly in films, have revealed that the decomposition takes place in two consecutive stages around 265 and 310 °C respectively, and nuclear magnetic resonance (NMR) analysis could unveil the chemical reactions taking place in the solution. Using the solutions with 20% fluorine and upon optimization of the growth process parameters, YBCO layers with $T_c$ and $J_c$(77 K) of 90 K and 4 MA cm$^{-2}$ are obtained.

Keywords: YBCO films, chemical solution deposition, coated conductors, low-fluorine solutions

(Some figures may appear in colour only in the online journal)

1. Introduction

Chemical solution deposition is a competitive technique to obtain epitaxial films. In particular, metallorganic decomposition has been established as the versatile methodology to grow low-cost, scalable, high-performance epitaxial YBa$_2$Cu$_3$O$_7$ films for coated conductors [1–5]. The trifluoroacetate approach (TFA-MOD) has been the process mainly used for the preparation of YBCO layers [6]. This barium fluoride process, although currently used for industrial companies in the development of long-length biaxially textured coated conductors is still intensively studied, particularly to better understand the underlying decomposition and growth mechanisms and to be able to further improve growth rates, thickness, throughputs and performance [6]. This includes, among others, the study of the deposition, evaporation, shrinkage and decomposition step, especially for thick layers and to correlate them with the use of modified starting solutions [7, 8]. In addition, the intermediate phase evolution and the nucleation and growth mechanisms for these modified solutions should be further analyzed to ensure best performance [9]. The modification of the solutions is intended to reach more environmentally friendly processes, enhanced thickness, planarized final HTS layers and generation of artificial pinning centers by growing nanocomposites [10, 11]. For those reasons, different additives in the precursor solutions have been used in the form of organic molecules (monomers or polymers) or inorganic salts [12, 13].

An important drawback in the use of TFA-YBCO solutions is the need to carefully control the water content of the solution and solution handling during preparation and storing.
to avoid environmental contamination. If the atmospheric absolute humidity exceeds $15\,\text{g}\,\text{m}^{-3}$ [14], inhomogeneous layers are obtained, and even cracks and buckling can be generated as a source of stress release before the decomposition step. An adequate solution design gives us a route to produce more environmentally robust solutions, as we will present in this work.

The use of fluorine in the TFA-MOD approach to YBCO layers is justified by two main reasons: the suppression of barium carbonate by the formation of barium fluoride and the control of the growth process by the HF evolving rate. By utilizing the presented low-fluorine solutions, we are able to accomplish the new requirements concerning environmental safety by the reduction of fluorine content. At the same time the much needed robust designed metalorganic solution (stable, reproducible, low water content and less hygroscopic) is also achieved. Previous studies have reported high-performance layers from low-fluorine solutions [15, 16].

By analyzing the behavior of the precursor salts in the solutions we demonstrate the possible use of different metal-trifluoroacetate salts ensuring an adequate combination of oxyfluorides after the decomposition step. The only requirement is the presence of enough overall fluorine in the precursor solution to produce the desired barium fluoride intermediates.

Solutions with low-fluorine precursors with different solvents (methanol and propionic acid) and an amount of additive (triethanolamine) have been stabilized and their rheology adapted to the deposition technique. Nuclear magnetic resonance (NMR) studies confirmed the conversion yield from acetate to propionate reactions taking place in the solution. Thermal decomposition analysis and IR spectroscopy performed directly in films, revealed that the decomposition of the precursor is completed at $350\,^\circ\text{C}$ and that no BaCO$_3$ is formed despite the fact that trifluoroacetate acid (TFA) salts decompose at high temperature. Upon optimization of growth process parameters, $T_c$ and $J_c(77\,\text{K})$ of $90\,\text{K}$ and $3–4\,\text{MA}\,\text{cm}^{-2}$ are reached for $300\,\text{nm}$ layers.

2. Experimental details

2.1. Preparation and characterization of precursor solutions

Several Y, Ba, Cu metalorganic precursor solutions have been investigated with different contents of fluorine using several salts, solvents and concentration of additives. We identify (a) the standard TFA solution (with 100% fluorine content) using yttrium, barium and copper trifluoroacetates as precursor salts and methanol as a single solvent and prepared as previously described [17], from those with a reduction of fluorine (listed below as (b)). In these fluorine-reduced solutions, as is reported in table 1, the precursors for the low-fluorine CSD process were yttrium trifluoroacetate (Y-TFA, Aldrich), yttrium acetate, barium trifluoroacetate (Ba-TFA, Aldrich), barium acetate (Ba-Ac, Aldrich), and ethylhexanoate (Ba-Eth Aldrich) and/or copper acetate (Cu-Ac, Aldrich). A stoichiometric amount (Y:Ba:Cu = 1:2:3) of the precursors was dissolved in methanol (Solutions 1, 2, 3), methanol-propionic acid ($\text{CH}_3\text{OH}:\text{C}_2\text{H}_5\text{COOH} = 75:25$, solution 4) and propionic acid (solution 5). To these solutions triethanolamine (TEA, Aldrich) was added in 10, 20 and 5% volume (solutions 2, 3 and 4, respectively). Solution 6 was also prepared with just 10% fluorine as specified later.

The systematic analysis of these solutions was carried out by measuring the viscosity with a Haake RheoStress 600 rheometer (ordinary interval around 12–16 mPa·s at $22^\circ\text{C}$), the contact angle with a DSA 100 analyzer (ordinary interval around 30–35° on LAO substrates), the metal stoichiometry was checked by a volumetric assay and this was balanced to the 1:2:3 stoichiometry if necessary by the addition of metal salts, and the water content in the solutions was

| Solution | Metalorganic salts 1:2:3 stoichiometry | Solvent | Conc. | [F content] | Additives |
|----------|----------------------------------------|---------|-------|-------------|-----------|
| 1        | YAc, BaAc, CuTFA                       | Methanol/acetic acid | 1.5 M | 50%         | —         |
| 2        | YAc, BaTFA, CuAc                       | Methanol | 1.5 M | 30%         | 10%TEA    |
| 3        | YTFA, BaEth, CuAc                      | Methanol | 1.5 M | 20%         | 20%TEA    |
| 4        | YTFA, BaAc, CuAc                       | Methanol/Propionic acid | 1.5–2 M | 20% | 5%TEA    |
| 5        | YTFA, BaAc, CuAc                       | Propionic acid | 1 M | 20% | —         |
| 6        | YTFA, YAc, BaAc, CuAc                  | Methanol/Propionic acid | 1.5 M | 10% | 5%TEA    |

| Solution | Viscosity (mPa.s) | Contact Angle | Water content (%wt) | pH (in water) |
|----------|------------------|---------------|---------------------|--------------|
| 1        | 2–5              | 20            | <1                  | 2.5          |
| 2        | 12–14            | 28            | 1.3                 | 5.8          |
| 3        | 12–14            | 35            | 0.8                 | 7            |
| 4        | 9                | 27            | <2                  | 7            |
| 5        | 1.5–2            | <10           | 0.5                 | 4.2          |
| 6        | 6–7              | 25            | <2                  | 4.2          |

Table 1. Solutions with partial reduction of fluorine content.

Table 2. Rheological properties of the TFA and low-fluorine solutions.
measured by the Karl–Fischer method [18]. The thermogravimetric (TG) analysis was done with the TGA/DSC1 apparatus and the masses at room temperature where measured with the XS3DU balance, both from Mettler Toledo. Evolved Gas Analysis (EGA) was performed with a Spectra Quadrupole (Micro Vision Plus) from MKS Instruments. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded in CDCl3 on a Bruker ARX 300 (300 and 75.5 MHz) spectrometer. Chemical shifts are given in ppm relative to TMS (\(^1\)H \(\delta = 0.0\) ppm) or CDCl3 (\(^{13}\)C \(\delta = 77.0\) ppm).

2.2. Thin film growth and characterization

The different metallorganic solutions were deposited by spin coating on (001) LaAlO3 single crystal substrates (5 mm \(\times\) 5 mm) at a spinning rate of 6000 rpm for 2 min. The coatings were pyrolyzed in humid oxygen atmosphere to form precursor films. The heating rate was kept at 3 K min \(^{-1}\) in the temperature range from 100 to 500 \(^\circ\)C. The humid gas was injected by bubbling the dry gas through deionized water (dew point 25 \(^\circ\)C) into the furnace when the furnace temperature was higher than 110 \(^\circ\)C. Subsequently, the YBCO precursor layers were crystallized at 820 \(^\circ\)C in humid N2/0.02% O2. In the last stage the crystallized coatings were pyrolyzed in humid oxygen atmosphere to form precursor layers were crystallized at 820 \(^\circ\)C in humid N2/0.02% O2. In the last stage the crystallized films were annealed at 450 \(^\circ\)C for 4 h in a dry oxygen atmosphere.

Cross-section images were performed by using dual beam (SEM, FIB) Zeiss 1560 XB. Film thickness was determined either by surface profilometry or from FIB images and they were in the range of 250–350 nm.

X-ray diffractometry (XRD) \(\theta/2\theta\) scans were performed on thin film samples using a Siemens D5000 diffractometer with Cu–K\(\alpha\), \(\lambda = 1.5418\) Å. Phi scans were taken on a 2D general area detector diffraction system (GADDS) and a thin film diffractometer PANalytical model XPert PRO MRD. In both cases the x-ray beam wavelength was 1.5418 Å (Cu–K\(\alpha\)). IR spectrosocopy was measured with a Spectrometer Perkin-Elmer Spectrum One in the energy range from 450–4000 cm\(^{-1}\).

The inductive critical current density of the superconducting films, at self-field, was determined from inductive measurements performed with a SQUID magnetometer and calculated accordingly with the Bean Model [19]. We have used the equation \(J_c = 3\Delta M/2a\) [20] valid for thin films, where \(3\Delta M\) is the width of the saturated hysteresis loop at zero field and \(a\) is the sample radius.

Angular transport critical current measurements were carried out in a PPMS Quantum Design system. We patterned the sample with 30 \(\mu\)m width bridges, in the standard four-probe geometry, by using standard photolithography with a Durham Magneto Optics Std MicroWriterTM. The transport current was sent parallel to the ab planes and the magnetic field was applied in the maximum Lorentz force configuration and rotated with an angle \(\theta\) from the c-axis (\(\theta = 180^\circ\)) to the ab plane (\(\theta = 0^\circ\)). The critical current density was determined by using a 10 \(\mu\)V/cm \(^{-2}\) criterion.

3. Results and discussion

3.1. Solution formulation

The fluorine in the metallorganic solutions is introduced by the fluorinated compounds used (trifluoroacetates, TFA). During the pyrolysis thermal treatment, the C-F bond is broken generating F anions or radicals that react with the Ba ions present in the mixture [21] thus generating the Ba, Y fluorinated compounds (scheme 1).

The minimum amount of fluorine necessary for the formation of barium fluoride is deduced from this reaction and corresponds to 2 atoms of fluorine per 1 atom of barium. On the other hand, if we consider the formation of barium, yttrium fluoride intermediate (Ba\(_{1-x}\)Y\(_x\)F\(_{2+x}\) \((x \leq 0.5)\) BYF) the maximum amount of fluorine necessary is 2.5 atoms of fluorine per 1 atom of the solid solution (Ba\(_{1-x}\)Y\(_x\)). Therefore, taking into account the number of F atoms for all the TFA radicals present (i.e. 39 F atoms for the production of 1 equivalent of YBa\(_2\)Cu\(_3\)O\(_7\)), there exists a large excess of fluorine (39 atoms/2 Barium atoms) in the TFA solution.

If we only want to introduce the fluorine necessary to form the fluorine intermediates, we would require 10% as compared to the 100% assigned to the standard TFA solution. The reduction of the fluorine content in the solution can be done by combining fluorinated and non-fluorinated salts and we have investigated solutions with 10, 20, 30 and 50% fluorine content. By keeping just the Y(TFA)\(_3\) metallorganic salt as the only salt containing fluorine in the solution, we already get 20% of F, i.e., much more than that required to form the desired (barium,yttrium) fluoride.

In an attempt to further decrease the F content, a moderately stable solution could be prepared with 10% F. In this case a mixture of YTFA, YAc (1:1), 2 BaAc, and 3 CuAc in methanol/propanic acid solution has been prepared. Without further optimization, pyrolyzed layers with similar crystalline phases than those in the case of the all-TFA process were obtained although no Y was incorporated in the BaF\(_2\) phase (see figure 1).
The different formulations for the low-fluorine solutions are presented in table 1.

Although there are different alternatives for the formulation of the starting metallorganic salts (see scheme 2), in this work carboxylates are used for the following reasons: they are stable, commercially available and easy to prepare compared to alkoxides, and they have lower carbon backbone content than acetylacetanates.

Taking into account the wettability requirements of the solutions for their deposition on the substrates, medium polar solvents like alcohols were used in their preparation. In the standard TFA approach the solvents used the most are short-chain alcohols like methanol or ethanol. In the preparation of low-fluorine solutions methanol and short length carboxylic acids are used.

Metal acetates are carboxylates with a low amount of carbon atoms in the chain. As a consequence, their solubility, even in short-chain alcohols (medium polar solvents, with medium hydrogen bonding and low-dispersion forces according to Hansen parameters [22]) will be rather low, particularly in the case of barium acetate. Then, taking into account the principle of ‘like dissolves like’ we need to use different additives or solvent mixtures, which are able to change the solutes solubility parameters, for the stabilization of the solutions. These additives are mainly composed of carbon backbone molecules functionalized with alcohol, amine, ether carbonyl and carboxyl groups, isolated or mixed together [8, 23]. Possible reactions of the additives with the YBCO precursors need to be considered because the stability of the resulting solutions is clearly related to the solubility of products or complexes formed. After an initial screening of the stability of the solutions with a set of different additives and solvents, triethanolamine (TEA) and propionic acid in different quantities were used for the formulation of the solutions.

3.2. Solution characterization

All solutions presented with reduced fluorine content are stable for more than two weeks. The control of their rheological properties has enabled us to identify the requirements for the growth of YBCO superconducting layers. We should take into account, however, that these requirements will strongly defer depending on the deposition methodology we intend to use (spin coating, dip coating, inkjet printing) [24, 25].

At this point, our concern is to reach homogeneous solutions with low water contents and rheological properties close to those from the standard TFA solution.

Rheological properties for all the solutions prepared have been evaluated for their use in CSD. Solutions with viscosity in the range of 10 mPa.s can easily be spin coated giving rise to homogeneous pyrolysis. Solutions 2 and 3 with higher viscosities produced nonhomogeneous layers after deposition. The right values for the contact angle are clearly dependent on the substrates used (single crystals or tapes). The values presented here corresponded to LAO single crystal as substrate. The solutions with the contact angle <30 exhibit good wetting. The water content is an important parameter which we propose to be <2%. Higher contents in water produced nonhomogeneous layers after pyrolysis.

It is well known that alcohol solutions are hygroscopic. This is because the hydrogen bond formations easily enable water absorption from the atmosphere. However, a careful control of the preparation protocols and solution handling using inert atmosphere, keeps the water content below 2%wt in all cases. In our case we prepared the solutions under nitrogen atmosphere and the storage is in inert atmosphere in sealed vials at low temperature (4 °C). Using these precautions the solutions remain stable for three months without changes in their rheological properties.

3.3. Use of coordination compounds

In the preparation of low-fluorine solutions some additives or solvent mixtures are used for the stabilization of the solutions, to change the solutes solubility parameters. These ligands are mainly stabilizers for copper. The formation of complexes of Cu(II) carboxylates with triethanolamine has been described previously by different groups [26, 27].

It is important to know the minimum amount of ligand necessary for the stabilization of the non-fluorinated copper salt in the solution. Considering the stoichiometry of these complexes, two equivalents of TEA are necessary to stabilize two or three equivalents of copper depending on the coordination type. Then, for copper stabilization in the solution it would be necessary to use 10% volume of TEA when no other competing ligands are present (Solutions 2 and 3). However, we need up to 20% volume of TEA to obtain a completely stable solution. That can be accounted for through the yttrium and barium stabilization. Yttrium or Barium salts can interact with TEA forming stable and soluble intermediates as previously described [28].

Although solutions with a high content in TEA (around 20% volume in solution 3) are promising and the first trials showed the production of good superconducting layers on LAO single crystal, its high viscosity (three times higher than the standard TFA solution) is the reason for the irreproducibility problems observed in the deposition step. Layers with...
inhomogeneous pyrolysis and non-uniform distribution of liquid along the substrate are obtained after deposition by spin coating from this highly viscous solution.

Solutions 1 and 2 are adequate from the point of view of their rheological characteristics. However, solutions 4 and 5 are proposed as an alternative to 2 due to their lower fluorine content. The latter solutions present a combination of aminoacohol ligands and carboxylates like propionic acid. Carboxylic acids can act in two ways: (a) forming carboxylates in the solution by scrambling with acetates giving salts with longer organic chains compatible with the methanol solvent and (b) acting as a bidentate ligand interacting in the free positions of the structure (scheme 3) and preventing water absorption [29].

To confirm some of these hypotheses we have studied their behavior by NMR studies. For that purpose and due to the difficulty in measuring copper-based solutions in NMR, we have prepared a solution containing only the binary mixture of barium and yttrium salts with the same combination of methanol, propionic acid and TEA used in Solution 4. After evaporation of the solvents until constant weight, $^1$H- and $^{13}$C-NMR spectra of the remaining residues were obtained. From the $^1$H-NMR spectra we observe the transformation of barium acetate to barium propionate in more than 80%. The quadruplet at 2.18 ppm (2H) and triplet at 0.98 ppm (3H) indicate the presence of the propionate moiety being the singlet at 1.89 ppm of the remaining acetate. This is confirmed by $^{13}$C-NMR spectra (singlet at 28.1 and 8.2 ppm for CH$_3$CH$_2$ and at 21.9 ppm for CH$_3$ from the acetate) where the presence of trifluoroacetate is also observed by the signals at 116.0 and 161.7 ppm as quadruplets indicating the presence of fluorine atoms in the carbon chain (see figure 2). This result confirms our initial assumption of the scrambling between propionate and acetate radicals in the solution.

Therefore, the NMR study confirms the evolution of acetates to propionates and the permanence of fluorinated moieties in the layer.

Water is strongly absorbed during the deposition and drying (evaporation) process. The content of water increases very quickly for dried layers, because the evaporation of the solvent causes the highly hygroscopic salts to easily coordinate with the hydroxyl groups. This process renders a safe handling quite difficult. In the case of TFA solution 1, this phenomenon leads to the necessity to work in a controlled atmosphere with environmental absolute humidity below 15 gr m$^{-3}$ up to the pyrolysis process. When this value is surpassed the deposited layers strongly suffer an unwettability process accumulating the solution to the center of the substrate.

We have observed that the use of additives can strongly inhibit the water absorption phenomenon occurring in the deposited layers. Figure 3 shows the rate of water absorption on the deposited layers produced from solutions 4 and 5 and from the standard TFA solution. The measurements were carried out with a microbalance in layers previously dried at 70°C.

Our results demonstrate that low fluorine solutions produce less hygroscopic layers than TFA solutions. The absorption of water is reduced from 18% for the TFA solution to 4% for the low-fluorine solutions 4 and 5. These results can be explained by the presence of coordination compounds (TEA or propionic acid) of the metal salts, which therefore prevents their coordination with water molecules (Scheme 3). The presence of dimeric systems in solution for copper and yttrium [30] favors free coordination positions to be occupied by water molecules.

3.4. Thermogravimetric and evolved gas analysis

Customarily, TG analysis is done using powders. However, in a recent work, relevant differences were observed when the analysis was performed in films [31]. Films are expected to decompose differently than powders when the decomposition is controlled by: (a) transport of reactive gas, (b) evolution of gaseous species or (c) heat transport out of the sample. All these aspects are not exclusive of decomposition processes but are intrinsic to most solid–gas reactions [32]. In previous papers it has been shown that, for several precursors, significant differences between powders and films arise [33–35]. So, it is clear that optimization of the pyrolysis step cannot be achieved with thermal analyses of powders.

The evolution of the sample mass and of the evolved volatiles during pyrolysis of the dried solution 5 is shown in figure 4. In particular we observe the formation of H$_2$O (m/z = 18), propionic acid (m/z = 29), CO$_2$ and CF$_3$CFO (m/z = 69). In figure 4 only the evolution of the main fragments is shown but volatile identification is based on the complete analysis of the defragmentation pattern. TG curves are normalized to the mass of the sample once dehydrated, m$_0$. Since EGA analysis shows that dehydration is completed at 150°C, the value of m$_0$ corresponds to that of the sample mass at 150°C. The decomposition takes place in two consecutive stages that exhibit a maximum transformation rate at 265 and 310°C respectively (see the time derivative of the TG curve). These two stages entail the decomposition of the propionate salts and the formation of propionic acid. At low temperature, the main volatile is propionic acid while at higher temperature CO$_2$ is the main volatile, mostly related to propionic acid decomposition in the gas phase. In addition, only traces of fragments related to acetic acid were observed.
Assuming that the deposited solution contains YTFA, barium and copper propionates, the mass of the dehydrated solution should be \( m_0 = 406 \text{ mg per 1 ml of solution.} \)

According to figure 1, after pyrolysis the solid residue is mainly BYF and CuO, therefore the mass of the solid residue at 500 °C is 184 mg per 1 ml of solution, i.e., 45.3% after normalization to \( m_0 \). From figure 4, one can verify a nice agreement between the predicted final mass (dashed line at 45.3%) and the measured final mass 45.1%. Note that, in the case of a dried solution of YTFA, barium and copper acetates, the mass of the dehydrated solution would be \( m_0 = 371 \text{ mg per 1 ml and the mass after pyrolysis would be 41.0%}, \) clearly in disagreement with the measured final mass.

To check the influence of the water on the reaction we have compared the TG curves obtained under wet and dry oxygen atmospheres (figure 5(a)). Apart from the fact that the initial water uptake is slightly smaller in dry conditions, the evolution of the reaction is very similar under both conditions, i.e., water does not affect the reaction behavior. Conversely, apart from CO2, the main volatile detected under dry conditions by EGA is 3-pentanone. The main fragment of the fragmentation pattern of 3-pentanone is \( m/z = 57 \), while in the case of propionic acid the intensity of the fragment \( m/z = 57 \) is about half the intensity of fragment \( m/z = 29 \) [36]. In wet conditions, we observe that fragment \( m/z = 29 \) is about twice as intense as fragment \( m/z = 57 \), but in dry conditions the more abundant fragment is \( m/z = 57 \) (figure 5(b)). Actually, it is well known that propionate salts decomposition entails the release of 3-pentanone [37, 38]. Therefore, the formation of propionic acid observed under wet conditions may result from the reaction in the gas phase between the released 3-pentanone and the water present in the atmosphere.

The DSC signal (figure 6) shows two exothermic peaks nicely correlated to the mass loss rate at the two decomposition stages. This result rules out the formation of propionic acid being related to an evaporation reaction of propionic acid and clearly indicates that precursor pyrolysis is an exothermic process.

As for the TFA groups, the EGA curve in figure 4(b) shows a tiny signal around 320 °C that would correspond to the decomposition of YTFA. Note that the formation of BYF involves that 72% of the fluorine atoms initially present in the solution should remain in the film after pyrolysis; therefore, a weak signal related to fluorinated species is in agreement with the formation of BYF.

The previous characterization is consistent with the FTIR ex situ analysis of the solid residue at different temperatures (figure 7). The FTIR spectrum accounts for the presence of TFA ligands in different bonding modes, most notably a strong broad absorption in the 1732–1622 cm\(^{-1}\) region centered at 1685 cm\(^{-1}\) and strong absorptions centered at 1208 and 1150 cm\(^{-1}\) [39, 40]. Propionate ligands exhibit absorption peaks at 2978, 2944 and 2876 cm\(^{-1}\), a strong broad band centered at 1568 and absorption peaks at 1466, 1431, 1371 and 1299 cm\(^{-1}\) [36]. In addition, a broad band in the 3050–3700 cm\(^{-1}\) region centered at 3433 cm\(^{-1}\) is related to water [39, 41]. FTIR spectra show a progressive diminution of the absorption peaks related to propionate groups from
200 up to 300 °C while TFA absorption peaks remain unaffected up to 300 °C, and at 320 °C there is a significant diminution of the amplitude of TFA absorption peaks. Note also that the amplitude of the broad band centered at 3433 cm\(^{-1}\) and related to H\(_2\)O remains roughly constant up to 300 °C. Since FTIR analysis is performed \textit{ex situ} this indicates that up to 300 °C films are very hygroscopic i.e., after a short exposure to ambient films take up water. Since the presence of propionic groups clearly diminishes from 200 to 300 °C while TFA groups remain roughly constant, this would indicate that these solutions are highly hygroscopic mainly due to the presence of YTFA. Indeed, TFA salts and in particular YTFA is very hygroscopic due to its high Lewis acidity [39, 42]. This fact would also account for the lower water uptake of these low-fluorine solutions when compared to standard TFA solutions (figure 2).

It is worth noting that despite the fact that TFA salts decompose at the very end of the precursor pyrolysis, no
Barium carbonate is formed. Indeed, EGA analysis shows that most fluorine remains after precursor pyrolysis and XRD exhibits the formation of BYF and no traces of BaCO$_3$ are detected (figure 8). Moreover, EGA analysis performed up to 830 $^\circ$C shows no traces of CO$_2$, that would result from the decomposition of BaCO$_3$. Instead, at 550 $^\circ$C we observe the formation of fluorine volatiles related to BYF decomposition to form Y$_2$O$_3$ and BaF$_2$. Therefore, the use of BaTFA is not compulsory to prevent BaCO$_3$ formation, so adding the fluorine amount necessary to form BYF may suffice.

3.5. Thermal treatment

After all the analysis performed and reasons exposed up to now for the different solutions investigated, we decided to use mainly solution 4 for the growth of YBCO layers. The solution was deposited by spin coating on LAO single crystal and the decomposition of the metallorganics was achieved at rather low temperature, and then a high-temperature treatment until the maximum growth temperature (800–820 $^\circ$C) was pursued.

The pyrolysis for solutions 4 and 5 was done between 100 and 500 $^\circ$C using humid oxygen atmosphere.

XRD analysis of the solution 4 pyrolyzed sample showed crystalline phases corresponding to copper oxide and (barium, yttrium) fluorides (see figure 8). The reduction of fluorine content in the precursor solution does not seem to affect the final aspect and composition of the pyrolyzed layer. Neither barium carbonate nor other phases was detected. ISCD file numbers for XRD analysis are in the [43].

Smooth pyrolyzed layers are achieved after the thermal treatment at 500 $^\circ$C using humid N$_2$O$_2$ (but also with air atmosphere). The formation of vertical open porosity is observed (figure 9) by FIB analysis. Due to the films morphology and taking into account their poor mechanical properties at this stage [14], this vertical open porosity is attributed to gas escape towards the film surface.

3.6. Characterization of epitaxially grown films

Considering the growth mechanism of YBCO films in the TFA approach which essentially proceeds through the reaction of Ba(O,F)$_2$, CuO and Y$_2$O$_3$, we should not expect major modifications of the optimal processing conditions [44] using the low-fluorine solutions. Therefore, the pyrolyzed films were grown at 820 $^\circ$C, in a humid N$_2$ atmosphere with 200 ppm O$_2$ [17]. After growth, the thickness ranged from...
250 to 350 nm depending on the concentration and viscosity of the solution. The films were systematically analyzed by XRD and SEM (figure 10) for solution 4, to respectively check the epitaxial quality and the morphology at the nanometric scale. The θ–2θ XRD pattern showed that YBCO films only have (00l) reflections and that no secondary phases are present. The films display a sharp texture, as identified by narrow in-plane φ-scan values, Δφ = 0.5° and rocking curves Δω = 0.2°. A typical case for solution 4 is presented in figure 10. All these structural analysis results comparable to those from the standard TFA solution and SEM images showed homogeneous and rather compact layers (figure 10(b)), however a detailed intermediate phase evolution analysis [45] together with a TEM study of the microstructure should be carried out to ascertain if the defect structure is modified [46].

The superconducting properties seem to be more sensitive to the particular solution. In general, \( J_c(77 \text{ K}) = 3–4 \text{ MA cm}^{-2} \) at self-field and \( T_c = 92 \text{ K} \), were measured by

![Figure 10.](image)

**Figure 10.** (a) XRD q-2q analysis (b) phi-scan and rocking curve (c) SEM image of the YBCO layer formed from solution 4 after growth on LAO.

![Figure 11.](image)

**Figure 11.** \( J_c(77 \text{ K}) \) of the YBCO films grown via low-fluorine solutions 1 to 5 for different samples. Solution zero corresponds to the TFA standard solution and solutions 1 to 5 are those indicated in table 2.
SQUID magnetometer which are in the same range of values as those obtained using our standard TFA process [6]. In figure 11, a plot of the critical current density, $J_c$(self-field, 77 K) versus different solutions for layers with similar thickness ($\sim$300 nm) is shown. The best results, comparable with the standard TFA solution (0 in the graph) are obtained using solutions 3, 4 and 5. However, we must remember that the reproducibility of solution 3 was rather poor due to the deposition difficulties explained before.

We have completed the analysis of the superconducting properties of a YBCO film at 77 K grown with solution 4 by means of in-field angular transport measurements. Figure 12 shows the comparison between a sample $J_c(H)$ at 77 K $= 4.3$ MA cm$^{-2}$ grown with the standard TFA solution and a sample with $J_c(H)$ = 4.4 MA cm$^{-2}$ grown with solution 4. Very similar results are obtained for both $J_c(H)$ and $J_c(\theta)$ dependencies indicating that they present comparable vortex pinning properties and thus similar microstructural defects. The two anisotropic peaks $J_c(\theta)$ associated to twin boundaries (at $\theta = 180^\circ$ for $H//c$) and mainly stacking faults (at $\theta = 90^\circ$ for $H//ab$) are also very similar. We, therefore, conclude that the low-fluorine solutions, and solution 4 in particular, are able to obtain high-performance YBCO films following a fluorine-based CSD growth.

From all the results presented in this paper, we can suggest that solution 4 is the most suitable one to fulfil all the requirements of environmental safety and robustness, and to reach good structural and superconducting properties.

4. Summary

The chemistry involved in the preparation of YBCO solutions with reduction of fluorine content has been studied and a set of different stable low-fluorine solutions has been proposed (decreasing the fluorine content even down to 10%). These solutions produced layers that after deposition and drying are less hygroscopic and more robust towards environmental conditions. This fact can be related to the presence of coordinating ligands (carboxylic and aminoalcohols) that hampers the absorption of water due to the reduced amount of TFA ligands. Among the solutions analyzed, the ones with 20% fluorine have been more intensively studied. It has been observed that decomposition is an exothermic process and proceeds through two stages that involve the decomposition of propionic salts and the release of 3-pentanone. No volatiles related to acetates have been detected by EGA, i.e., during solution in propionic acid, Ba and Cu acetate transform into Ba and Cu propionates, as also confirmed by NMR analysis. At the end of the last stage, around 320°C YTFA decomposes, the final solid residue after pyrolysis being mainly BYF and CuO. During pyrolysis only small amounts of volatiles containing fluorine have been observed, i.e., after pyrolysis most fluorine remains in the solid residue to form BYF. Pyrolysis is completed at 350°C for all low-fluorine solutions. After deposition on LAO and the growth process, YBCO epitaxial layers layers of around 300 nm were obtained presenting high structural and superconducting properties, similar to those obtained for the standard TFA solution.

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