Microwave-assisted $YBa_2Cu_3O_7$ precursors: A fast and reliable method towards chemical precursors for superconducting films

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Abstract. Highly stable, pure and anhydrous organometallic $YBa_2Cu_3O_{7-\delta}$ (YBCO) precursor solutions were prepared by dissolving commercial YBCO powder in acetone by trifluoroacetic anhydride (TFAA) or a mixture of TFAA with propionic acid for low fluorine precursors. The reaction is 72 times faster via microwave heating, compared to conventional oil bath heating. More importantly, the formation of by-products is suppressed, as shown by Nuclear Magnetic Resonance (NMR) and Mass Spectrometry (MS). This approach allows a highly reproducible preparation of superconducting coatings which is of interest for a low-cost manufacturing processes capable of large-scale production of the coated conductors via Chemical Solution Deposition (CSD). This technology requires reliable and stable precursor solutions for continuous deposition. In this work, we obtained YBCO thin films on single-crystal substrates (*(100)*-$LaAlO_3$) with a high critical current density (J_c) of 3-4

MA/cm² in self-field at 77 K using TFA-based YBCO precursors and J_c of 5-6 MA/cm² using low fluorine YBCO precursors.

1. Introduction

$YBa_2Cu_3O_{7-\delta}$ (YBCO) coated conductors are considered very promising materials for a variety of technological applications such as motors, generators, transmission cables and other power systems.[1-3] Over the last decades, several methods have been developed to enable the continuous deposition of biaxially textured YBCO films onto long-length flexible metallic substrates, including rolling-assisted biaxial textured substrates (RABiTS), ion-beam-assisted deposition (IBAD) and inclined substrate deposition (ISD).[4-6] An efficient and low-cost process is crucial for the commercial implementation of superconducting power applications. The vacuum methods, i.e. pulsed laser deposition (PLD) and metal-organic chemical vapor deposition (MOCVD), produce YBCO thin films with excellent properties, yet are considered expensive due to the required high vacuum system, hampering the applicability on industrial scale.[7] In contrast, chemical solution deposition (CSD) has gained a lot of interest over the last years due to their low-cost and easy scalability with high efficiency.[3, 5, 8-11]

The most established CSD approach is based on the *ex-situ* BaF_2 process and uses trifluoroacetate (TFA) salts typically dissolved in an organic solvent such as methanol. Several researchers have already demonstrated that this TFA route is a suitable metal-organic-deposition (MOD) method to produce low-cost epitaxial YBCO thin films without the requirement of a high-vacuum system.[7, 12-14] The TFA-MOD process is based on the formation of BaF_2 as an intermediate phase, which is believed to be beneficial over the formation of $BaCO_3$, as the latter can disrupt the YBCO formation due to its high decomposition temperature.[15] BaF_2 on the other hand is stable up to high temperatures, but can be decomposed at 650 °C by the addition of a water vapor to the processing atmosphere.[14] This approach has expanded to one of the most successful growth methods of epitaxial YBCO films with a high critical current density J_c in self-field at 77K on single crystal substrates.[5, 16]

Nevertheless, some potential drawbacks can be identified in the YBCO solution preparation which could hamper the commercial implementation. Several authors have shown that the YBCO precursor can be converted into high quality YBCO thin films by heat treatment under controlled conditions.[17-19] Afterwards, critical current densities J_c of >1 MA/cm^2 were obtained. Thus, a very important feature in TFA-based YBCO processing is controlling the growth of YBCO during thermal treatment. However, the presence of possible impurities in the solution can degrade the final microstructure and superconducting properties of the YBCO thin film due to the improper decomposition of the precursor.[5, 20] Araki *et al.*[21] have shown that the synthesis procedure for the preparation of TFA salts starting from acetates and trifluoroacetic acid (TFAH), as described by Gupta *et al.*[14] exhibits an uncontrolled amount of water (> 3 wt%) and other chemical impurities (a.o. acetic acid). Thus, they developed a purified YBCO precursor solution with a refining process and obtained a high J_c after a long pyrolysis step of ~12 hours.[21] Therefore, several authors made large efforts towards the optimization of the TFA precursor synthesis procedure and the pyrolysis.[4, 22-24] The synthesis procedure of Roma *et al.*[22] starts from YBCO powder, which is dissolved in a mixture of excess trifluoroacetic acid anhydride (TFAA) and a small amount of TFAH (10 vol%) as catalyst resulting in the TFA metal-salts. This procedure typically generates an almost "anhydrous" TFA precursor with a water content of less than 1 wt%. However, this synthesis procedure still suffers from some disadvantages such as a long reaction time of 72 hours and off-stoichiometry of TFAA. Additionally, the use of a conventional heat source (oil bath heating) results in an inefficient thermal energy transfer which may result in a temperature gradient in the reaction volume. The combination of these disadvantages may result in the formation of by-products other than the TFA metal-salts.

The microwave processing method that we are introducing in this work can offer a solution to a number of problems stated above. Microwave radiation provides rapid and uniform heating of the reagents and solvents by directly coupling to the molecules, hereby resulting in a more efficient energy transfer and an enhancement of the reaction rate.[25-28] By applying microwave radiation, we were able to dissolve commercial YBCO powder in a TFAA-acetone mixture, yielding extremely pure TFA salts. When comparing our microwave-assisted acid dissolution with conventional oil bath heating, it is clear that the drastic shortening of the synthesis time by a factor of 72 and the high purity of the precursor solution led to significant advances towards more viable YBCO solution processing. This fast and reliable method can equivalently be used for the preparation of a low fluorine (LF) YBCO solution by changing the ratio of trifluoroacetic and propionic acid.

2. Experimental details

3.1. Preparation of YBCO precursor solution

The TFA- and LF-YBCO precursor solution were prepared by dissolving commercial $YBa_2Cu_3O_x$ powder (yttrium barium copper oxide, x ~ 6.7-9.5, Sigma Aldrich) with a controlled stoichiometry of TFAA (Aldrich 99%) and propionic acid (Roth ≥99.5%) in acetone (Panreac PA) as solvent. First, the YBCO powder was dried in a vacuum oven at 150 °C for 24h to remove any adsorbed water. The 0.75 mmol dried YBCO powder was mixed with 6.5 equivalents TFAA and 3 mL dry acetone in 10 mL microwave vial for the preparation of TFA-YBCO. The preparation of LF-YBCO (with 66% reduction of fluorine) can be tuned by modifying the stoichiometric ratio between TFAA and propionic acid and is prepared as follows: 0.75 mmol YBCO powder was mixed with 2.15 equivalents TFAA and 8.7 equivalents propionic acid in 3 mL dry acetone. These mixtures were subjected to microwave heating under an inert atmosphere (Ar) for 30 minutes at 100 °C using a Discover SP CEM microwave operating at 2.45 GHz with a maximum power of 20 W. After the dissolution, a dark blue-green solution is obtained, which is centrifuged for 2 minutes at 3000 rpm. The supernatant is filtered and transferred to a 10 mL boiler flask and the solvent was evaporated under vacuum using a rotary evaporator. The desired mixture of TFA- or LF-YBCO became a viscous dark blue-green gel and is diluted with anhydrous methanol (Aldrich 99.9%) to obtain a total metal ion concentration of 1.5 M. This solution is kept in sealed vials and can be stored for several months under an inert atmosphere without precipitation.

3.2. Characterization of YBCO precursor solution

The metal ion concentration and stoichiometry of Y:Ba:Cu were verified by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis (SPECTRO Genesis) while viscosity measurements were performed with a Brookfield DV-E viscometer (25 °C and 100 rpm). The water content was determined by the Karl-Fischer method.[29] To understand the thermal decomposition of the

TFA-YBCO precursor, thermogravimetrical analysis (TGA) and differential thermal analysis (DTA) were used with a Netzsch Model STA 449 F3 Jupiter system with the heating rate of 10 °C/min under air atmosphere.

3.3. Characterization of solution without YBCO powder

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) were performed on a Perkin-Elmer FT-IR spectrometer spectrum 1000, equipped with a HATR module, Nuclear Magnetic Resonance (NMR) equipment and gas chromatography-mass spectrometry (GC-MS) device are used to analyze the by-products after the synthesis. Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance II Spectrometer operating at a ^{1}H and ^{13}C frequency of 500.13 MHz and 125.77 MHz respectively and featuring a ^{1}H, ^{13}C, ^{31}P TXI-Z probe. The sample temperature was set to 298.15 K. One dimensional (1D) ^{1}H and 2D ^{1}H-^{13}C Heteronuclear Single-Quantum Correlation (HSQC), 2D ^{1}H-^{13}C Heteronuclear Multiple-Bond Correlation (HMBC) and COSY (Correlation spectroscopy) spectra were acquired using standard pulse sequences from the Bruker library. For the 1D ^{1}H measurements, 64k data points were sampled with the spectral width set to 16 ppm and a relaxation delay of 30 s. For 2D processing, the spectra were zero filled to a 4096×2048 real data matrix. Before Fourier transformation, the 2D spectra were multiplied with a squared cosine bell function in both dimensions, the 1D spectra were multiplied with an exponential window function. GC-MS was conducted on an Agilent HP 6890 series with a HP 5972A single quadrupole mass spectrometer. 1 µl of sample was injected into a split/splitless liner with single taper, heated at 250 °C using splitless injection. Separation was performed using a Restek Rxi-5Sil MS column (30 meter long x 0.25 mm internal diameter x 0.25 µm film thickness) and helium as carrier gas at a constant flow rate of 1 mL/min. The oven was programmed as followed: starting at 40 °C where it was held for 2 minutes, followed by a gradient of 10 °C/min to 320 °C holding this temperature for 5 minutes. Transferline to the MS was held at 300 °C. The MS was set to scan for m/z ratios between 41 and 400, after a 3 minute solvent delay.

3.4. Chemical solution deposition and characterization of the thin layers

The TFA- and LF-YBCO solutions were deposited on *(100)*-$LaAlO_3$ (LAO) single crystal substrates (Crystek GmbH) by means of spin-coating. Prior to coating, the substrates were chemically cleaned before the deposition to remove adsorbed organics.[30] The YBCO thin films were deposited using a spin coater model CHEMAT (6000 rpm with time of 2 min). The deposited layer was preheated at 65 °C for 3 minutes to evaporate the solvent. The coated gel films were pyrolyzed in a humidified oxygen atmosphere. The typical heat treatment of TFA-YBCO thin film on LAO was described by Roma *et al.*[22] For the pyrolysis, the sample temperature was increased from room temperature at a heating rate of 3-5 °C/min to 310 ºC with a dwell time of around 30 min at 310 °C. The inlet gas was humidified by passing it through a water bubbler at a dew point of 25 °C. In the case of LF-YBCO, the final pyrolysis temperature is 400 °C. Subsequently, the pyrolyzed thin film of YBCO on LAO undergo a high temperature thermal treatment (sintering and annealing) at 800 °C in a humid 200 ppm oxygen/nitrogen atmosphere and was switched to dry oxygen at 450 °C for 2 hours during the annealing step to change the YBCO crystal structure from tetragonal into orthorhombic to obtain good superconducting properties.

Characterization of the texture and phase composition of the YBCO thin films was performed by means of X-ray diffraction (XRD) on a Bruker D8 diffractometer with the Cu K_α line as the primary X-ray source. The thin films microstructure was analyzed by a FEI Nova 600 Nanolab Dual Beam FIB-SEM and a Cs-corrected JEOL JEM-2200FS TEM operating at 200 kV. The samples for TEM investigations were prepared using ion milling techniques where a cross-sectional lamella was obtained via the FIB *in-situ* lift-out procedure with an Omniprobe™ extraction needle and top cleaning.[31] The superconducting properties of the YBCO thin films were determined with inductive measurements of the critical current density J_c in self-field at 77K (Cryoscan™ by THEVA).

3. Results and discussions

3.1. TFA-YBCO precursor characterization

In this work, a TFA-YBCO precursor is prepared starting from desiccated commercial YBCO powder mixed with TFAA in acetone using a microwave-assisted treatment. This preparation method leads to a yield of about 98 %, thus the YBCO powder almost completely dissolved in a stoichiometry of Y:Ba:Cu = 1±0.01:2±0.01:3±0.01 as confirmed by ICP-OES analysis (Appendix A). Compared to the conventional synthesis procedure as described by Roma *et al.*[22], we only used a stoichiometric amount of TFAA and removed the TFAH catalyst because microwaves themselves can be used to overcome high activation energies for product formation by selectively coupling to intermediates in the transition states.[27] Due to this efficient energy transfer of microwave heating, the preparation time of this dissolution takes 1 hour. It results in a reduction of preparation time by a factor of 72 compared to conventional heating by oil bath as described by Roma *et al.*[22] Instead, the chemical reaction of YBCO powder with TFAA via the microwave-assisted treatment is given in Eq. 1

$$YBa_2Cu_3O_x + 6.5\,TFAA \rightarrow Y(TFA)_3 + 2\,Ba(TFA)_2 + 3\,Cu(TFA)_2 \qquad \text{Eq. 1}$$

Indeed, the great advantage of this chemical reaction is the lack of water. Consequently, the water content is now dependent on the use of solvents and starting precursors. Therefore, this microwave-assisted approach leads to a precursor solution with a very low H_2O content (<0.5 wt%, determined by Karl Fischer) when high purity starting products are used. Moreover, the microwave-assisted dissolution of YBCO powder always delivered highly stable TFA precursors with a low water content, suitable for the deposition of YBCO films and potentially interesting for their industrial scalability.

The decomposition of the metal organic precursor is one of the critical steps in CSD-based growth of high quality ceramic films. TGA-DTA analysis can give detailed insights in the temperature dependency of the decomposition. Early works affirmed that TFA metal-salts start to decompose at the range between 200-250 °C.[7] From the TGA-DTA analysis (full black line) shown in Fig. 1, it can be seen that the weight loss starts at 100 °C and the precursor is fully decomposed at 340 °C with a total mass loss of around 70 %. The mass loss as a function of temperature can clearly be divided in three separate stages.[20] The first stage (from 50 to 100 °C) shows the dehydration and evaporation of organic solvents with a very small mass loss of around 2 %, which is lower compared to the mass loss of 8 % for non-purified TFA-YBCO precursor obtained via the conventional preparation method,[4, 21, 22] confirming the small water content. The second stage between 100 and 210 °C was previously attributed to the evaporation of coordinated solvents and results in a mass loss of approximately 10 %. Starting at 210 °C, the thermo-oxidative decomposition of the TFA metal-salts takes place with a broad exothermic peak in the DTA signal which indicated the successful decomposition of the three TFA-precursors, $Y(TFA)_3$, $Cu(TFA)_2$ and $Ba(TFA)_2$, leading to a large mass loss (~60 %). As this can induce a large shrinkage during thin film processing the third stage is considered to be the critical step in the decomposition of TFA precursors.[4, 22, 24]

The TGA analysis of both microwave-assisted (full black line) and conventional (blue dotted line) heated TFA precursors shows a difference in the decay in the second stage (between 100 and 210 °C), as seen in Fig. 1. We hypothesized that the mass loss in the sample prepared by conventional heating, is due to high boiling impurities, formed during the dissolution. To facilitate the analysis of the organic content, both dissolution methods (microwave and conventional) were repeated in the absence of YBCO powder. After the microwave-assisted dissolution of the TFAA-acetone mixture, a yellow solution was obtained compared to a dark orange-brown solution after the conventional heating treatment, confirming the occurrence of by-products in the latter. The resulting solutions were evaporated at 80 °C, reissolved in acetone and investigated via ATR-IR spectroscopy, given in Fig. 2. The microwave-assisted solution (full black line) shows no characteristic peaks which means that all the volatiles (acetone and TFAA) were removed during evaporation and no high boiling molecules were formed during the microwave heat treatment. The IR spectrum of the conventional heated solution (blue dotted line) contains characteristic peaks. The C=O stretching (marked with symbol *) peak at 1780 cm^{-1} is related to an unsaturated ketone. Moreover, the C=C stretch (marked with symbol $^{\#}$) is clearly visible on the spectrum at 1684 cm^{-1}. NMR analysis is used to determine the structure of unknown by-products in the conventional heating solution.

From the ^{1}H-NMR spectrum of the solution prepared via conventional heating without adding YBCO powder (Fig. 3(A)), the predominant compound 4-methylpent-3-en-2-one or mesityl oxide (MO) is recognized. This is also confirmed by 2D NMR techniques such as HSQC (Fig. 3(B)) and HMBC

(Appendix B). It confirms the presence of characteristic peaks of unsaturated ketone shown on ATR-IR spectrum (Fig. 2).

Thus, the conventional heating mainly leads to the formation of MO which originates from the aldol condensation of acetone. As described by Nikolopoulos *et al.*[32], acetone condensation does not only lead to MO but also to 4-hydroxy-4-methylpentan-2-on or diacetone alcohol (DAA). To clarify the condensation reaction using conventional heating, GC-MS was investigated to identify other by-products. It is clear in the GC spectrum (Fig. 4) and MS-spectra (Appendix B) that other products than MO are formed, namely DAA, phorone (2,6-dimethylhepta-2,5-dien-4-on) and isophorone (3,5,5-trimethyl-2-cyclohexene-1-one) and the relative ratio of these by-products is given in table 1. Actually, MO is the predominant compound with the relative ratio of 77.9 % and is also confirmed by NMR analysis. This elucidates the next reaction pathway in the acetone condensation process (Fig. 5). The first step is the self-condensation of acetone to DAA and the second step is the dehydration of DAA to MO. The condensation of acetone to DAA can be catalyzed by either basic or acidic sites while the dehydration of DAA to MO is acid-catalyzed. Here, we study the dissolution of YBCO powder to metal salts using TFAA, because TFAA is the acid anhydride of TFA and can act as a catalyst. Thus, the MO is mainly formed via the condensation of acetone acid-catalyzed by TFAA with DAA as an intermediate product which is quickly converted to MO. The minor by-products phorone and isophorone are formed due to over-condensation. However, these by-products are not observed in the microwave-assisted solution without TFA metal salts, and thus the microwave-assisted method provides a highly stable TFA precursor solution with less impurities. Furthermore, a viscosity of 3.5±0.1 cP for 1.5 M TFA-YBCO solution is obtained for the microwave-assisted solution. This is lower compared to the viscosities of 4 cP for 0.75 M TFA-YBCO reported by Roma *et al.*[22] using conventional heating. This could be explained by the absence of the condensation by-products in microwave-assisted method which could influence the viscosity of the total solution. Although, higher viscosities can be desirable for the preparation of thicker YBCO films, a more accurate control over the rheological properties can be obtained as one can start from a high purity YBCO precursor solution.[1]

3.2. Generalization for the preparation of the YBCO precursor

Currently, CSD research is evolving towards the use of an YBCO precursor with a lower fluorine content to reduce the release of fluorinated compounds during the thermal process.[23] In general, complex additives or solvent mixtures are necessary during the preparation of low fluorine solutions to improve the stability of metal ions (mainly for copper).[33, 34] Especially, the stabilization of the metal ions can lead to an improved growth mechanism, resulting in thin films with high quality.[35, 36] In this work, the fabrication of a LF-YBCO precursor solution with a 66 % reduction in fluorine content, using microwave irradiation, results in the formation of highly pure metal salts with less impurities as confirmed on ATR-IR spectrum (Fig. 2, red dashed line) of purified solution without the presence of YBCO powder. Thus, the aldol condensation is not catalyzed by the presence of propionic acid. This microwave-assisted method also results in stable YBCO precursor solution without the formation of precipitates and remains stable for several weeks without additives (Appendix A). It shows that the microwave-assisted method can result in YBCO precursor solutions with different contents of fluorine by adjusting the ratio between TFAA and propionate acid.

3.3. Growth and characterization YBCO thin film

In this section, we only focus on the TFA-YBCO and LF-YBCO (66% fluorine reduction) precursors as the thermal process of different contents of fluorine YBCO is still not completely understood and it is not the aim of this research to elucidate this process. The deposited TFA-YBCO precursor was thermally treated according to Roma *et al*.[22] The standard pyrolysis results in a layer without any inhomogeneities such as buckling or cracks. Subsequently, the pyrolyzed layers were crystallized at 800 °C for 2 hours to epitaxial YBCO film. The epitaxial quality of the YBCO thin film was analyzed by θ-2θ diffraction patterns. The XRD spectrum of TFA-YBCO (Fig. 6) shows very strong *(00ℓ)* YBCO reflections (2θ = 22.8 *(003)*, 30.6 *(004)*, 38.5 *(005)* and 46.6 *(006)*) without any sign of random YBCO or impurities. Next, the thin film should exhibit a smooth and homogeneous microstructure in order to achieve a high critical current density, J_c. FIB-SEM analysis shows that the thickness of the YBCO film is 50-100 nm determined from the cross-sectional view (not shown). However, a thickness of 200-250 nm is obtained of a TFA-YBCO precursor prepared via conventional heating. The relatively low thickness of the microwave-assisted TFA-YBCO layer is believed to be caused by the low viscosity of the precursor solution. Thicker films can, however, be achieved by enhancing the viscosity and/or metal concentration of the precursor and by controlling the wetting behavior and the deposition parameters.[30, 37] In this paper, we focused on the latter parameters. The substrates were first rinsed with isopropanol and afterwards heated to 400 °C on a hot plate in air, instead of ultrasonic cleaning, while the spin rate was decreased to 2000 rpm compared to Roma *et al.*[22] These modifications lead to a thickness of 250-300 nm after the crystallization step as confirmed by the cross-section determined via FIB-SEM (see inset Fig. 7(A)). More importantly, it is also clear from this cross-section that the film is homogeneous and crack-free without the presence of any *a/b* -oriented grains. In Fig. 7(B), the LAO/YBCO interface was studied by HRTEM, which confirms that the YBCO layer grows fully *(00ℓ)*-oriented without the formation of secondary phases. The selected area electron diffraction (SAED) pattern is shown in the inset of Fig. 7(B) which further confirms the excellent biaxial alignment and the cube-on-cube orientation relationship between YBCO and LAO. These excellent structural properties yielded YBCO films with critical current densities J_c up to 3.5 MA/cm² in self-field at 77 K (Fig. 8, full black line), similar to the results obtained via the conventional TFA precursors by Roma *et al.*[22], showing the high potential of these novel microwave-assisted TFA solutions due to the reduced preparation time with the factor of 72 times.

The YBCO thin film, starting from LF-YBCO precursor, was fabricated on LAO substrate with the same deposition and wetting parameters as described above. Fig. 9 shows that the θ-2θ spectrum of LF-YBCO thin film is *(00ℓ)*-oriented without secondary phases. Fig. 10 shows a SEM image of a LF-YBCO thin film which is homogenous and dense layers with the thickness of 250-300 nm (see inset Fig. 10). This film has also a crack-free surface with slightly different surface morphology than the standard TFA-YBCO. Nevertheless, epitaxial growth was observed for the LF-YBCO precursor, giving rise to superconducting performances with critical current densities up to 4 MA/cm^2 in self-field at 77 K (Fig. 8, red dashed line) compared to Palmer *et al.*[33] However, superconducting applications demand even higher critical current densities. This requires an optimization of the thermal treatment using the LF-YBCO precursor to improve the homogeneous nucleation before the growth of epitaxial YBCO.[33, 34] Preliminary results have shown that current densities of 5-6 MA/cm^2 can be reached for the LF-YBCO, indicating that also high-performance YBCO thin films can be obtained starting from a microwave-assisted LF-YBCO precursor. (Appendix C) Further research will aim at confirming and elucidating the thermal process and transferring these results from single crystal LAO to metallic Ni-x%W substrates for the coated conductor architecture.

4. Conclusions

It has been demonstrated that microwave heating is efficient in facilitating the dissolution of YBCO powder to an anhydrous TFA precursor with a reduction in preparation time by a factor of 72 compared to conventional heating by oil bath. Other advantages are the use of only a stoichiometric amount of TFAA and the removal of TFAH, resulting in a highly pure precursor as confirmed by a thorough analytical study. This fast and reliable method can also deliver a modified fluorine content of YBCO precursor by adjusting the ratio between TFAA and propionic acid. After spin-coating and growth of the TFA-based and low fluorine (LF) YBCO thin film, the epitaxial YBCO thin films are obtained with critical current densities (J_c) up to 4 MA cm^{-2} in self-field at 77 K. However, we obtained J_c of 5-6 MA/cm² by the strict optimization on the processing level for LF-YBCO thin film. These properties are very promising and indicate that this microwave assisted procedure can improve significantly the standard TFA-based and LF chemical solution deposition of YBCO thin films.

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References

1. J. Feys, P. Vermeir, P. Lommens, S. C. Hopkins, X. Granados, B. A. Glowacki, M. Baecker, E. Reich, S. Ricard, and B. Holzapfel, "Ink-jet printing of $YBa_2Cu_3O_7$ superconducting coatings and patterns from aqueous solutions," *J. Mater. Chem.,* **22** [9] 3717-26 (2012).
2. D. Larbalestier, A. Gurevich, D. M. Feldmann, and A. Polyanskii, "High-Tc superconducting materials for electric power applications," *Nature,* **414** [6861] 368-77 (2001).
3. I. Van Driessche, J. Feys, S. C. Hopkins, P. Lommens, X. Granados, B. A. Glowacki, S. Ricart, B. Holzapfel, M. Vilardell, A. Kirchner, and M. Backer, "Chemical solution deposition using ink-jet printing for YBCO coated conductors," *Supercond. Sci. Technol.,* **25** [6] 065017 (2012).
4. X. Obradors, T. Puig, A. Pomar, F. Sandiumenge, N. Mestres, M. Coll, A. Cavallaro, N. Romà, J. Gázquez, J. C. González, O. Castaño, J. Gutierrez, A. Palau, K. Zalamova, S. Morlens, A. Hassini, M. Gibert, S. Ricart, J. M. Moretó, S. Piñol, D. Isfort, and J. Bock, "Progress towards all-chemical superconducting $YBa_2Cu_3O_7$-coated conductors," *Supercond. Sci. Technol.,* **19** [3] S13-S26 (2006).
5. X. Obradors and T. Puig, "Coated conductors for power applications: materials challenges," *Supercond. Sci. Technol.,* **27** [4] 044003 (2014).
6. B. Ma, K. K. Uprety, B. L. Fisher, R. E. Koritala, S. E. Dorris, and U. Balachandran, "YBCO-coated conductors fabricated by inclined substrate deposition technique," *Supercond. Sci. Technol.,* **17** [9] S477-S81 (2004).
7. T. Araki and I. Hirabayashi, "Review of a chemical approach to $YBa_2Cu_3O_{7-x}$-coated superconductors—metalorganic deposition using trifluoroacetates," *Supercond. Sci. Technol.,* **16** [11] R71-R94 (2003).
8. I. Van Driessche, G. Penneman, J. Abell, E. Bruneel, and S. Hoste, "Chemical approach to the deposition of textured CeO_2 buffer layers based on sol gel dip coating," *Mater. Sci. Forum,* **426** 3517-22 (2003).
9. P. Vermeir, I. Cardinael, M. Bäcker, J. Schaubroeck, E. Schacht, S. Hoste, and I. Van Driessche, "Fluorine-free water-based sol–gel deposition of highly epitaxial $YBa_2Cu_3O_{7-\delta}$ films," *Supercond. Sci. Technol.,* **22** [7] 075009 (2009).
10. V. Cloet, J. Feys, R. Hühne, S. Hoste, and I. Van Driessche, "Thin $La_2Zr_2O_7$ films made from a water-based solution," *J. Solid State Chem.,* **182** [1] 37-42 (2009).
11. M. Arin, P. Lommens, S. C. Hopkins, G. Pollefeyt, J. Van der Eycken, S. Ricart, X. Granados, B. A. Glowacki, and I. Van Driessche, "Deposition of photocatalytically active TiO_2 films by inkjet printing of TiO_2 nanoparticle suspensions obtained from microwave-assisted hydrothermal synthesis," *Nanotechnology,* **23** [16] 165603 (2012).
12. P. Mankiewich, J. Scofield, W. Skocpol, R. Howard, A. Dayem, and E. Good, "Reproducible technique for fabrication of thin films of high transition temperature superconductors," *Appl. Phys. Lett.,* **51** [21] 1753-55 (1987).
13. K. Vandaele, M. Mosiadz, S. Hopkins, A. Patel, I. Van Driessche, and B. Glowacki, "The influence of heat treatment parameters on pyrolysed TFA-derived YBCO films deposited by inkjet printing," *MRS Bull.,* **47** [8] 2032-39 (2012).
14. A. Gupta, R. Jagannathan, E. I. Cooper, E. Giess, J. Landman, and B. Hussey, "Superconducting oxide films with high transition temperature prepared from metal trifluoroacetate precursors," *Appl. Phys. Lett.,* **52** [24] 2077-79 (1988).
15. P. Vermeir, I. Cardinael, J. Schaubroeck, K. Verbeken, M. Bäcker, P. Lommens, W. Knaepen, J. D'haen, K. De Buysser, and I. Van Driessche, "Elucidation of the Mechanism in Fluorine-Free Prepared $YBa_2Cu_3O_{7-\delta}$ Coatings," *Inorg. Chem.,* **49** [10] 4471-77 (2010).
16. M. Falter, K. Demmler, W. Hassler, B. Schlobach, B. Holzapfel, and L. Schultz, "Chemical solution deposition (CSD) of $YBa_2Cu_3O_{7-x}$ films and oxide buffer layers by dip coating," *IEEE Trans. Appl. Supercond.,* **13** [2] 2751-54 (2003).
17. P. C. McIntyre, M. J. Cima, and M. F. Ng, "Metalorganic deposition of high-Jc $Ba_2YCu_3O_{7-x}$ thin films from trifluoroacetate precursors onto (100) $SrTiO_3$," *J. Appl. Phys.,* **68** [8] 4183-87 (1990).
18. J. Smith, M. Cima, and N. Sonnenberg, "High critical current density thick MOD-derived YBCO films," *IEEE Trans. Appl. Supercond.,* **9** [2] 1531-34 (1999).
19. A. P. Malozemoff, "HTS wires at commercial performance levels," *IEEE Trans. Appl. Supercond.,* **9** 2469-73 (1999).

20. X. Obradors, T. Puig, S. Ricart, M. Coll, J. Gazquez, A. Palau, and X. Granados, "Growth, nanostructure and vortex pinning in superconducting $YBa_2Cu_3O_7$ thin films based on trifluoroacetate solutions," *Supercond. Sci. Tech.,* **25** [12] 123001 (2012).
21. T. Araki, H. Kurosaki, Y. Yamada, I. Hirabayashi, J. Shibata, and T. Hirayama, "Coating processes for $YBa_2Cu_3O_{7-x}$ superconductor by metalorganic deposition method using trifluoroacetates," *Supercond. Sci. Technol.,* **14** [9] 783 (2001).
22. N. Roma, S. Morlens, S. Ricart, K. Zalamova, J. M. Moreto, A. Pomar, T. Puig, and X. Obradors, "Acid anhydrides: a simple route to highly pure organometallic solutions for superconducting films," *Supercond. Sci. Technol.,* **19** [6] 521-27 (2006).
23. A. Llordes, K. Zalamova, S. Ricart, A. Palau, A. Pomar, T. Puig, A. Hardy, M. Van Bael, and X. Obradors, "Evolution of metal-trifluoroacetate precursors in the thermal decomposition toward high-performance $YBa_2Cu_3O_7$ superconducting films," *Chem. Mater.,* **22** [5] 1686-94 (2010).
24. K. Zalamova, N. Romà, A. Pomar, S. Morlens, T. Puig, J. Gázquez, A. E. Carrillo, F. Sandiumenge, S. Ricart, N. Mestres, and X. Obradors, "Smooth Stress Relief of Trifluoroacetate Metal-Organic Solutions for $YBa_2Cu_3O_7$ Film Growth," *Chem. Mater.,* **18** [25] 5897-906 (2006).
25. M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa, and T. Tsuji, "Microwave-Assisted Synthesis of Metallic Nanostructures in Solution," *Chem. – Eur. J.,* **11** [2] 440-52 (2005).
26. J.-S. Schanche, "Microwave synthesis solutions from personal chemistry," *Mol. Divers.,* **7** [2] 291-98 (2003).
27. J. A. Gerbec, D. Magana, A. Washington, and G. F. Strouse, "Microwave-Enhanced Reaction Rates for Nanoparticle Synthesis," *J. Am. Chem. Soc.,* **127** [45] 15791-800 (2005).
28. R. Gedye and J. Wei, "Rate enhancement of organic reactions by microwaves at atmospheric pressure," *Can. J. Chem,* **76** [5] 525-32 (1998).
29. A. Calleja, S. Ricart, X. Palmer, R. Luccas, T. Puig, and X. Obradors, "Water determination of precursor solutions with oxidant cations by the Karl Fischer method: the YBCO-TFA case," *J. Sol-Gel Sci. Technol.,* **53** [2] 347-52 (2010).
30. P. Vermeir, F. Deruyck, J. Feys, P. Lommens, J. Schaubroeck, and I. Van Driessche, "Comments on the wetting behavior of non-porous substrates for ceramic coated-conductor applications," *J Sol-Gel Sci Technol,* **62** [3] 378-88 (2012).
31. E. Montoya, S. Bals, M. D. Rossell, D. Schryvers, and G. Van Tendeloo, "Evaluation of top, angle, and side cleaned FIB samples for TEM analysis," *Microsc. Res. Tech.,* **70** [12] 1060-71 (2007).
32. A. Nikolopoulos, B.-L. Jang, and J. Spivey, "Acetone condensation and selective hydrogenation to MIBK on Pd and Pt hydrotalcite-derived Mg Al mixed oxide catalysts," *Appl. Catal. A-Gen.,* **296** [1] 128-36 (2005).
33. X. Palmer, C. Pop, H. Eloussifi, B. Villarejo, P. Roura, J. Farjas, A. Calleja, A. Palau, X. Obradors, and T. Puig, "Solution design for low-fluorine trifluoroacetate route to $YBa_2Cu_3O_7$ films," *Supercond. Sci. Technol.,* **29** [2] 024002 (2015).
34. L. Jin, C. Li, J. Feng, Z. Yu, Y. Wang, L. Lei, G. Zhao, A. Sulpice, and P. Zhang, "Optimization of fluorine content in TFA-MOD precursor solutions for YBCO film growth," *Supercond. Sci. Technol.,* **29** [1] 015001 (2015).
35. U. Hasenkox, S. Hoffmann, and R. Waser, "Influence of precursor chemistry on the formation of $MTiO_3$ (M= Ba, Sr) ceramic thin films," *J. Sol-Gel Sci. Technol.,* **12** [2] 67-79 (1998).
36. G. Pollefeyt, S. Clerick, P. Vermeir, P. Lommens, K. De Buysser, and I. Van Driessche, "Influence of Aqueous Precursor Chemistry on the Growth Process of Epitaxial $SrTiO_3$ Buffer Layers," *Inorg. Chem.,* **53** [10] 4913-21 (2014).
37. W. Wu, F. Feng, K. Shi, W. Zhai, T. Qu, R. Huang, X. Tang, X. Wang, Q. Hu, and J.-C. Grivel, "A rapid process of $YBa_2Cu_3O_{7-\delta}$ thin film fabrication using trifluoroacetate metal–organic deposition with polyethylene glycol additive," *Supercond. Sci. Technol.,* **26** [5] 055013 (2013).