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Improved REBa₂Cu₃O_{7-x} (RE = Y, Gd) structure and superconducting properties by addition of acetylacetone in TFA-MOD precursor solutions

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For developing commercially utilized high-performance high-temperature superconductors, the fabrication of biaxially textured (RE)Ba₂Cu₃O_{7-x} (REBCO, RE = Y, Gd) coated conductors *via* metal-organic decomposition of trifluoroacetate precursors (TFA-MOD) has become an interesting strategy for industrial scale-up due to low costs and simple operation. However, the hygroscopic nature of commonly used precursor solutions makes them very sensitive to water pollution through air humidity. This can lead to a degradation of the final microstructure, which in return deteriorates critical current densities. Here, we present a new method to overcome that problem by using a moderator of 2,4-pentanedione (acac) in a pre-existing REBCO precursor solution. Our results show that even initially low-performance solutions can be enhanced to such an extent that they finally outperform standard high-performance solutions and the temperature window for their optimal growth widens significantly. Scanning electron microscopy gives evidence of considerable microstructural improvements, *e.g.* avoidance of pore formation and grooves, reduction of buckling and surface granularity. X-ray investigations indicate texture improvements, and electrical measurements reveal that transport critical current densities (J_c) increase in self-field and applied magnetic fields. For YBCO, a molar ratio of acac/RE = 0.64 is most effective and leads to an increase of the maximum pinning force density $F_p^{\max}$ from 1.0 to 2.4 GN m⁻³ at 77 K. For GdBCO, a broad window of annealing temperatures (790–840 °C) is possible for films with J_c values above 2.9 MA cm⁻² and $F_p^{\max}$ above 3 GN m⁻³ at 77 K.

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Introduction

In order to introduce (RE)Ba₂Cu₃O_{7-x}-based superconductors (REBCO, RE = rare earth, *e.g.* Y, Gd) into commercial applications, a reliable low-cost manufacturing process has to be developed leading to high current carrying capabilities of the material – also in applied magnetic fields. The TFA-MOD process is a chemical solution deposition (CSD) method based on metal-organic decomposition (MOD) of trifluoroacetate (TFA) precursors¹ which form the final superconducting film on a substrate as a biaxially textured coated conductor. This process is not only simple and inexpensive, but since more and more knowledge has been accumulated towards higher reproducibility, owing to extensive investigations by many groups,²⁻⁸ it has become a suitable way for upscaling to industrial

production. Yet, there are a few drawbacks in the process that should be overcome.

One very important issue is the high sensitivity of precursor solutions and as-deposited films to humidity, which can induce tremendous degradation of the final thin film microstructure and superconducting properties.^{2,9} This is promoted by the strong hygroscopic character of solutions based on polar organic solvents, *e.g.* short-chained alcohols. In particular, increasing pore formation and surface roughness seem to be due to water retained within the solutions or reabsorbed into as-deposited films as a result of a large surface/volume ratio.

There are several possibilities to get those problems under control, but most of the approaches involve drastic process complication or extension. For example, additional time-consuming effort is necessary to achieve highly anhydrous solutions¹⁰ and high demands are made on their storage and handling. Consequently, the long-time stability of the solutions is affected considerably, for they degenerate with every exposure to a humid atmosphere. Just as well, the handling of as-deposited films requires a thorough, laborious shielding from environmental humidity. But there are also several approaches concerning the thermal decomposition process. *Inter alia*, massive film porosity can be avoided by very slow heating rates.

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Thus, first attempts to grow REBCO thin films by TFA-MOD required extremely long decomposition times of up to 22 h.² Those times could be shortened significantly after the harmful influence of moisture had been identified and reduced.^{4,11} Meanwhile, pyrolysis times of a few minutes have been reported for solutions with very low water contents.¹⁰ Another interesting approach to improve the film microstructure is found in controlling decomposition kinetics by lowering the oxygen partial pressure during the incineration of the organics.¹² Films obtained that way showed an incredible densification when pyrolyzed in a nitrogen atmosphere with simultaneously high texture quality. Yet, critical current densities demanded further optimization. And also solution modifications by high-boiling-point solvents¹³ or solution additives like diethanolamine¹⁴ proved to be very promising for structural improvements and drastically shorter decomposition times could be implemented.

In the present work we introduce another very simple way to avoid long solution processing and refinement times by adding a small amount (<2.2 vol%) of 2,4-pentanedione – also known as acetylacetone (acac) – to the precursor solutions. Those solutions are ready to use in less than 7 hours, lead to a significant improvement of the microstructure and, accordingly, enhance critical current densities (J_c) – even in applied magnetic fields – without the need to take a lot of care on the absolute absence of water and – even better – on the thin film firing temperature, too.

Experimental section

The general principle of CSD processing comprises the preparation of a precursor solution, the coating process on a substrate, and finally the heat treatment. As a foundation for the investigations, we used REBCO (RE = Y, Gd) precursor solutions quite similar to those previously published by our group in ref. 4 – based on the preliminary work of Araki *et al.*⁹ In the following sections, these solutions will be referred to as “standard”, and their preparation is described in detail below.

Preparation of the precursor solutions

The “standard” solutions consist of the metal cations RE(III), Ba(II) and Cu(II) in a 1 : 2 : 3 ratio, which are weighed out as acetate salts (purity $\geq 99.99\%$, Alfa Aesar) and dissolved in deionized water. Through the addition of excess trifluoroacetic acid (TFAH, 99.5+%, Alfa Aesar) the acetates are transformed into trifluoroacetates. Water and other impurities are removed by a rotary evaporator, and the highly viscous residue is rediluted in absolute methanol (99.9%). In order to further reduce the undesired remaining water, methanol is evaporated again in a vacuum and the refilling-evaporation procedure is repeated two more times. The final concentration of 0.25 mol l⁻¹ in yttrium is adjusted with anhydrous methanol. All processing is carried out in a dry argon atmosphere in order to maintain high reproducibility by preventing the influence of atmospheric moisture on the solutions.

For both rare earth elements Y and Gd, one such standard batch solution is prepared and split into portions of 2 ml. For YBCO, four such portions are taken and provided with acac

amounts leading to acac/RE molar ratios of 21.4%, 42.8%, 64.1% and 85.5%, respectively. This corresponds to approximately 0.56, 1.11, 1.66 and 2.19 vol% acac in the YBCO solution. All solutions need a dissolution period in an ultrasonic bath after acac addition, whereby the necessary time increases up to half an hour for 85.5%. Amounts above 90% were also tried but could not be dissolved in an hour and tended to precipitate afterwards. Therefore, they were not used for sample preparation. For GdBCO, only an acac/RE ratio of 64.1% was chosen for further investigations.

Coating

Subsequently, the precursor solutions are spin-coated on $10 \times 10 \times 1$ mm³ (100)-oriented LaAlO₃ (LAO) single crystal substrates, which have been cleaned for 5 min with 2-propanol in an ultrasonic bath before. The coating settings comprise a rotation speed of 6000 rpm attained in 1 s and maintained for 30 s. During the coating process and in the pre-heat-treatment period, it is essential again to prevent air humidity from entering the highly hygroscopic gel-like films. For that reason, the whole coating process is performed in a glove box under dry nitrogen with a dew point below -25°C .

Thermal treatment

Finally, the precursor films are exposed to a heat treatment (see Fig. 1) in a quartz tube with a gas supply inside a tubular three-zone furnace. For the present investigations, the heat treatment has been subdivided into two parts – pyrolysis and crystallization/oxygenation (left and right pictures in Fig. 1) – but could be executed in a single process with similar results, which would omit the furnace cooling time after the pyrolysis. The bisection of the thermal process is useful due to the possibility to pyrolyze up to six samples in one step, but to crystallize them separately in the crystallization/oxygenation step at different growth temperatures (T_{growth}) in order to optimize T_{growth} . The first part of the pyrolysis is run in dry O₂ (99.998%) up to a sample temperature of 60°C . This short step serves as the evaporation stage for unbound solvent. At 60°C , gas humidification is started to hinder copper trifluoroacetate from sublimation.² The dew point (T_{dew}) of the gas is then adjusted to 19°C and the gas speed increased from 3.4 to 6.8 cm s⁻¹. The incineration of the organics, which has been studied in detail in ref. 12, is finished at 400°C , and the humidification is stopped for the furnace cooling. Prior to the second part, the combined crystallization and oxygenation steps, the quartz tube containing the pyrolyzed samples is flushed with the crystallization gas mixture at a speed of 6.8 cm s⁻¹. This gas mixture comprises humidified nitrogen (99.999%, $T_{\text{dew}} = 19^\circ\text{C}$) containing 100 ppm O₂. After about 30–40 minutes of flushing, the furnace temperature is raised to T_{growth} within 10 min and kept for about an hour.

For all YBCO samples, only one annealing temperature $T_{\text{growth}} = 780^\circ\text{C}$ was used, since this temperature had been determined to be the optimum for YBCO on LAO before. For GdBCO, the T_{growth} series was run in a temperature range from 780°C to 840°C to determine the temperature leading to the

Fig. 1 Heat treatment profiles of pyrolysis (left) and crystallization/oxygenation (right). Pyrolysis takes place in wet oxygen, crystallization in wet nitrogen + 100 ppm oxygen, oxygenation in dry O_2 .

best properties for GdBCO on LAO. The oxygenation follows in dry O_2 with a gas speed of 3.4 cm s^{-1} at 450°C for about two hours with subsequent furnace cooling of the samples.

Characterization

The solutions were analyzed by UV/Vis spectroscopy using an MPC-3100 dispersive two-beam spectrometer (Shimadzu) with methanol as a reference in a range 200–1000 nm using 10 mm QS cuvettes suitable for the ultraviolet region. The thermal decomposition of the solutions was studied by thermogravimetry (TG) combined with differential thermal analysis (DTA) using a Netzsch STA 409 PC/PG. Samples of 17–19 mg were filled into Al_2O_3 crucibles, flushed with wet compressed air (150 ml min^{-1}) and heated from room temperature to 520°C at a rate of 2 K min^{-1} .

Investigations of the structural characteristics of thin film samples were carried out by scanning electron microscopy (SEM; XL20, Philips, secondary electron detector, 20 kV acceleration voltage) and X-ray diffraction (XRD; PW3020, Philips, Co-K_α radiation). For all samples, the superconducting quality was controlled by inductive techniques, *i.e.* the critical current density J_c^{sf} (77 K) (Cryoscan, Theva; sf = self field, $50 \mu\text{V}$ criterion) and the critical temperature T_c . Thereby, inductive J_c uses the third harmonic of the self-induction signal of a small coil directly above the film submerged in liquid nitrogen. The Cryoscan was calibrated with a 300 nm thick standard YBCO sample grown by PLD; the $50 \mu\text{V}$ criterion equals the $1 \mu\text{V cm}^{-1}$ criterion of transport J_c measurements. Additionally, some of the samples were investigated by electrical transport measurements in a four-probe configuration, *i.e.* $J_c(B, 77 \text{ K})$. For that, a physical properties measurement system (PPMS; Quantum Design, $1 \mu\text{V cm}^{-1}$ criterion) was used, which allows in-field measurements up to 9 Tesla. Prior to that, the samples were lithographically masked and structured by wet-chemical etching to give bridges of $50 \mu\text{m}$ width and $800 \mu\text{m}$ length. Those bridges were further used to precisely determine the layer thickness by atomic force microscopy (AFM; Dimension 3100, Digital Instruments, with silicon tips by Nanosensors), as well as for cross sectional SEM analysis after a focused ion beam

(FIB) cut (Helios NanoLab 600, FEI, in-lense detector, 3 kV acceleration voltage).

Results and discussion

Solutions

General considerations. The solutions contain a very low amount of water, but should not be described as anhydrous, since water coordinated to the metal cations is assumed to be very hard to remove completely by simple evaporation, and as a result of the preparation route all the metal cations were initially fully hydrated. Yet, Araki *et al.* described the solvent methanol to be able to substitute for a large amount of water in the coordination spheres of the metals – in particular for yttrium – and thus, postulated the possibility to achieve solutions with water contents of 0.2 wt%.¹¹ Though, long ligand exchange periods have been depicted and therefore, we assume our solutions to be rather in the range of 1 wt%, although we use a similar approach. Yet, the water amount in the solutions is not the only cause of possible film degradation, but particularly the as-deposited precursor films tend to absorb a massive amount of water from humid atmospheres due to their large surface/volume ratio and the strongly hygroscopic character of the gel-like films. Regarding this point, we paid very special attention by coating in a glove box with a permanent atmosphere of dry nitrogen ($T_{\text{dew}} < -25^\circ\text{C}$) and transferred the samples into the dry-flushed furnace within a dry, sealed vessel.

Addition of small amounts of acac to such a “standard” solution should not lead to a significant change of the over-all water concentration but leads to a spontaneous change of the solution colour from intensive blue to deep green. Therefore, it is apparent that an interaction with the copper(II) species occurs. Plenty of such interaction mechanisms between the transition metal and the bidentate ligand are conceivable, since a manifold of complex geometries solely for copper(II) carboxylates have been reported to date.^{15–21} This is due to the fact that structural characteristics not only depend on the carboxylate group itself but also on the availability and sort of neutral ligands. Also acac is well-known to form very stable complexes, but it could be either a neutral ligand exchanging

for water or methanol molecules, or expelling the trifluoroacetate groups as a monocharged ligand. That is because the β -diketone structure leads to a weak acidity of the proton in the α -position – between the two keto groups – since a resonance effect for the negative charge is enabled in the conjugated system. This is the basis for the keto–enol–tautomerism of acac and other β -diketones, whereby the keto species is favoured in polar solvents such as methanol. But even more, it is the basis for its strongly nucleophilic character.

However, the literature on copper(II) complexes is very focused on solid state investigations, and much less is reported on their behaviour in solutions, although the solvent is very likely to have a severe influence on structural characteristics as well – in particular when a coordinating solvent is considered. Yet, there is a strong tendency from binuclear complexes for solid copper acetate¹⁵ and propionate²² to mononuclear structures for haloacetates, since the halogen atoms – and in particular multiple fluorine atoms – weaken the Cu...Cu interactions considerably, which is reflected in a drastic increase of the Cu...Cu bond lengths.¹⁸ Thus, for the tetrahydrate of solid Cu(TFA)₂ the preference of the mononuclear species has been demonstrated.¹⁸ Furthermore, Grasdalen *et al.* showed for Cu(Ac)₂ (Ac = acetate) that the well-established solid-state dimer is also very stable in solutions of acetic acid, but collapses to a certain extent in ethanol and even more in methanol solutions.^{23,24} Accordingly, the already destabilized Cu...Cu bond in solid anhydrous²¹ or monohydrated¹⁹ Cu(TFA)₂ is very likely to dissolve in methanol and a monomer is formed analogous to the tetrahydrate. And since TFA is a bidentate ligand similar to Ac and acac, it is also more than reasonable to assume coordination in the basal plane of the copper complex, while the neutral ligands methanol and/or water fill up the axial positions leading to the most desirable octahedral coordination.

Grasdalen *et al.*²⁴ also investigated acac additions in methanolic solutions of Cu(Ac)₂ and showed that they lead to an exchange of Ac by acac – although the hydrated salts of the acetates were used. This is due to the fact that the Cu–acac bond has a significantly more covalent character than the Cu–Ac bond.²⁵ Depending on the amount of acac added, Cu(Ac)₂ was progressively replaced by two new species – a mixed ligand complex Cu(Ac)(acac) and the fully transformed Cu(acac)₂, whereby the latter is assumed to reach nearly 100% at very high acac concentrations. Unfortunately, the mixed ligand species could not be isolated as crystals, but their existence was underlined by ESR and UV/Vis investigations and could be clearly determined to form monomeric molecules exclusively – just as Cu(acac)₂ does.^{26–28} This is a clear sign for the acac group to rather have a chelating than a bridging function. Especially in UV/Vis spectroscopy, the progressive exchange character became obvious.

Thus, it is even more likely for Cu(TFA)₂ to lose the TFA groups in exchange for acac in a similar way, since the nucleophilic character of TFA is even weaker than that of Ac due to the electron-withdrawing effect of the fluorine atoms. This is supported by the fact that we see precipitation of a blue powder, when a certain molar acac/Cu ratio has been surpassed, which is only approximately 0.3 – corresponding to 4 drops of 2,4-

pentanedione in 2 ml REBCO–TFA solution. We could clearly identify this powder by XRD to be Cu(acac)₂ with no signs of other phases, which underlines the existence of a comparable intermediate Cu(TFA)(acac) species and shows the pure acetylacetonate to be less soluble than Cu(TFA)₂. Though, in a pure Cu(TFA)₂ solution with a lower initial concentration of Cu²⁺ (<0.2 M) both species Cu(TFA)(acac) and Cu(acac)₂ remain dissolved when the acac addition is increased, which is accompanied by a change of the solution colour *via* green back to rather bluish in the presence of very high acac concentrations. Naturally, the growing Cu(acac)₂/Cu(TFA)(acac) ratio is responsible for that, since the pure acetylacetonate also gives a blue solution in methanol – although not as intense as does the trifluoroacetate. Table 1 gives an overview of the copper(II) complexes discussed above.

UV/Vis investigations. The diverse colour change of Cu(TFA)₂ solutions is the striking difference compared to Cu(Ac)₂, since solutions of the latter do not show such a behaviour, when increasing amounts of 2,4-pentanedione are added. Therefore, we performed UV/Vis spectroscopy on pure solutions of Cu(TFA)₂ in methanol with and without acac additions (Fig. 2) in order to find proof for the assumptions illustrated above. Thereby we investigated highly diluted solutions in order to resolve the strong-intensity absorbance bands in the ultraviolet range of the spectrum, but measured solutions with rather high Cu²⁺-concentrations of approximately 0.02–0.05 mol l^{−1}, too (inset). This was necessary to enable an examination of the very weak-intense absorbance in the visible range, which is a result of the forbidden d → d electronic transitions, whereby a transformation of the absorbance into the absorption proved to be helpful for clearness.

On the one hand, the inset in Fig. 2 shows a slight shift of the absorption edge typical for Cu²⁺ in the red region of the spectrum towards shorter wavelengths when acac is added to the trifluoroacetate solution, which is similar to that observed by Grasdalen *et al.* in the case of Cu(Ac)₂. It is quite reasonable to attribute this to a stronger ligand field splitting by acac in a presumed mixed-ligand complex of a similar geometry as a result of the greater electron density located at the oxygen atoms, but cannot be responsible for the massive colour change. However, we see an additional absorption band in the visible range at about 390 nm emerging as a very weak-intense shoulder from a strong band in the UV region having its maximum at 300 nm. Such a shoulder is not found in pure Cu(TFA)₂ solutions, but a comparative measurement of Cu(acac)₂ in methanol reveals a slight tailing effect in exactly this range of the spectrum.

The rather large energy gap suggests that this observation could result from a charge transfer, but the very weak intensity points to a forbidden transition. Thus, it discards t_{2g} → π^* (metal–ligand) and π → e_g (ligand–metal) transitions, since both of them are allowed, but it promotes the probability of an intraligand n → π^* transition. This transition was also expected to show up at the longer wavelength side of the π → π^* transition in trivalent metal–acac complexes caused by the keto form of the acac ligands.²⁹ Though, the extremely high intensity of the neighboring π → π^* usually covers this forbidden

Table 1 Overview of copper(ii) complexes and their established or presumable structures and colours in methanol

Copper compound	$\text{Cu}(\text{Ac})_2$	$\text{Cu}(\text{TFA})_2$	$\text{Cu}(\text{acac})_2$	$\text{Cu}(\text{Ac})(\text{acac})$	$\text{Cu}(\text{TFA})(\text{acac})$
Structure in methanol	Both dimeric and monomeric	Very likely monomeric	Monomeric	Monomeric	Most likely monomeric
Colour in methanol	Blue	Intensive blue	Blue	Blue	Deep green

Fig. 2 UV/Vis spectra of three different types of solutions: dotted black lines represent solutions of pure $\text{Cu}(\text{TFA})_2$ in methanol; striated red lines contain an amount of acac comparable to the amount starting the precipitation in REBCO solutions ($\text{acac}/\text{Cu} \approx 0.3$), solid green lines give a comparison to pure $\text{Cu}(\text{acac})_2$ in methanol. The major graph is recorded at highly diluted solutions; the solutions presented in the inset were of rather high Cu^{2+} -concentrations ($\approx 0.02\text{--}0.05\text{ M}$).

transition, but it can become visible in 3,3-substituted metal-acetylacetonate complexes due to the fact that the keto form is the only coordinating species in this case.²⁹ However, the symmetry descent and the consequential increase of vibrationally induced transitions can also be the reason for extraordinarily high intensities of forbidden transitions.²⁶ Thus, the occurrence of this shoulder in acac-containing $\text{Cu}(\text{TFA})_2$ can be considered to be another strong indication of a highly asymmetric coordination in a mixed ligand species. Thereby, the asymmetry of the presumable mixed $\text{Cu}(\text{TFA})(\text{acac})$ complex should be significantly greater than in $\text{Cu}(\text{Ac})(\text{acac})$ due to the stronger difference of the electron densities located at the oxygen atoms of both the different ligands. In any case, the additional absorption of violet and blue light causes the green colour of the solutions.

All the transitions visible in the ultraviolet range of the spectrum arise from $\pi \rightarrow \pi^*$ transitions within the ligands. The strong-intensity absorption at 235–240 nm is caused by the TFA groups and is visible in both solutions of the trifluoroacetate – with (240 nm) and without (235 nm) acac additions. Accordingly, the lower energy transition at 300 nm in the acac-containing solution belongs to acac – the ligand with the more expansive electronic delocalization. In the pure acetylacetonate complex, this transition occurs at slightly lower wavelengths (290 nm), and three more bands occur at higher energies (205, 213 and 240 nm). All of them are related to a quadruple splitting of the $\pi \rightarrow \pi^*$ transition within the ligand by π -bonding to the central ion, only the absorption band at around 290 nm is

unaffected by that.³⁰ These bands are also visible in the acac-containing $\text{Cu}(\text{TFA})_2$ solution, but with drastic shifts of the intensity ratios indicating a mixed ligand species to be present rather than the $\text{Cu}(\text{acac})_2$ complex itself. Particularly, the extraordinarily high intensity of the 205 nm absorption band despite the low acac concentration supports that idea. However, π -bonding is also likely in the pure TFA complex and could be the reason for the doublet of the 240 nm band. The finding of nearly identical transition energies (apart from the 10 nm shift from 300 $\rightarrow$ 290 nm) in the pure $\text{Cu}(\text{acac})_2$ and the mixed ligand solutions point to a very low mutual interference of the π molecular orbitals of the ligands, but yet, the severe intensity shifts support the idea of a mixed ligand species, because complex symmetry aspects and the subsequent changes of skeletal vibrations can lead to such a drastic change of transition probabilities.²⁷

Charge density reallocation and a basically new bonding situation within the copper complex might influence the thermal decomposition and, in particular, the gelation process in the precursor films due to a different behaviour towards hydrolysis and condensation, and as a consequence, the properties of the resulting REBCO thin films might be affected fundamentally. Yet, we would like to emphasise at this point that the present gelation process is not equivalent to sol-gel processing of metal alkoxides and is very likely to a large extent caused by incomplete crystallization due to fast solvent evaporation. However, in particular for $\text{Cu}(\text{TFA})_2$ it has been demonstrated before that the transition metal cation tends to hydrolyse³¹ and the hydrolysed species react to form oligomers by condensation reactions.³² In contrast to sol-gel, these processes will occur to a minimum extent at room temperature, since the acidity of TFAH is rather large ($\text{p}K_{\text{a}} = 0.2$) and, thus, the free TFA anion will keep the equilibrium for hydrolysis reactions very much on the side of the educts. On the other hand, the low boiling temperature of TFAH should lead to a change of the equilibrium position, as soon as the acid leaves the film. We would also like to stress that we do not fully exclude acac interacting with either Ba or RE as well, but our results strongly suggest that the main interactions are related to the Cu species. Though, our results concerning REBCO-TFA solutions with varying RE elements point to an influence of RE on the water sensitivity in non-acac solutions, as will be demonstrated further down.

Thermal investigations. In order to determine such a possible impact on thermal decomposition, two types of solutions were investigated by thermal analysis in a wet air atmosphere (Fig. 3). One is a standard precursor solution of GdBCO without additions (thin/black lines), the other the same

Fig. 3 Thermal analysis of two different solutions: standard GdBCO solution (thin/black lines) and the same solution with 64.1% acac per Gd (thick/red lines). Solid lines show the mass loss of the solutions over the applied temperature, dotted lines correlate with the heat of reactions. Both solutions show very similar curve progressions apart from a delay from 115 °C to 140 °C for the acac solution due to inhibited Cu condensation kinetics.

solution containing 64.1% acac per Gd (thick/red lines). Up to a temperature of 115 °C, both solutions show very similar curve progressions for both the TG and the DTA signals. A huge mass loss of nearly 40% occurs below 59 °C, just before the second step is observed, where less than 5% of the mass leaves. The beginning of the third step at 77 °C (mass loss ~5%) is nearly invisible in TG, but becomes clearer by a comparison of the DTA curves. The first big mass loss is very likely due to the evaporation of unbound solvent. The large scale of evaporation below the actual boiling point of methanol ($T_B = 65$ °C) is due to the very high vapour pressure of 130 h Pa at 20 °C. The second mass loss could be caused by a small fraction of weakly coordinating solvent. However, this assumption would need clarification, *e.g.* by exhaust gas analysis. The same applies for the third step, which starts at a temperature slightly higher than the boiling point of TFAH ($T_B = 72$ °C). Thus, it might be free or liberated acid due to hydrolysis in the wet atmosphere. At 115 °C the curves of the two solutions split. At this temperature, only the pure GdBCO solution shows a mass loss of up to 8%, whereas the beginning of this fourth step seems to be delayed to 140 °C in the acac-containing solution.

77 °C and 140 °C are characteristic temperatures, when studying the decomposition of copper trifluoroacetate, as done by Mosiadz *et al.*³³ This group investigated the behaviour of solid $\text{Cu}(\text{TFA})_2 \cdot 1/2\text{H}_2\text{O}$ in three different atmospheres (dry argon, dry and wet oxygen) and came to the conclusion that TFAH is eliminated stepwise – depending on the atmosphere – at 77 (83, 87) °C and at 143 (143, 149) °C, forming $\text{Cu}_2(\text{TFA})_3\text{OH}$ and $\text{Cu}(\text{TFA})_2 \cdot \text{CuO}$ in the accordant steps. Thereby, the first product results from a simple hydrolysis, whereas the second step could be described as a condensation reaction.

Obviously, the hydrolysis step runs in both our solutions – with and without acac additions – without any hindrance at a similar temperature of 77 °C. This is not too surprising, for the molar acac/Cu ratio is only 0.21 and thus a large amount of the trifluoroacetate species exists unaffected by acac. However, the condensation occurs rather early in our non-acac solutions

compared to the trifluoroacetate investigated in ref. 33. On the one hand, this indicates a clear difference between pure, solid $\text{Cu}(\text{TFA})_2 \cdot 1/2\text{H}_2\text{O}$, which is very likely existing as a solid-state dimer,^{19,21} and the rather monomeric species existing in the precursor film. On the other hand, it is also plausible that the difference is simply caused by the weak hydration of the pure trifluoroacetate – or by the low degree of ligation in general. Unfortunately, it is not at all trivial to determine the number and kind of ligands of the copper species at different temperatures present inside the multi-component system of the precursor thin films, and since it is not useful to consider the copper species separately, we have to leave this question unanswered at this point. Though, the initial water amount of the solutions of roughly 1 wt% and the fact that we expose an initially hygroscopic solution to a humidified atmosphere encourages us to assume a certain percentage of water molecules to persist up to 115 °C in the coordination spheres of the Cu^{2+} cations leading to an accelerated condensation at this temperature. Unfortunately, omitting the humidification of the gas is not an option, since the $\text{Cu}(\text{TFA})_2$ species needs to be hydrolysed to a certain extent – at least in the superficial region of the thin films – in order to counteract sublimation by the formation of a less volatile copper species.^{31,32}

An explanation for the temperature shift after acac addition is simply given by the fact of a lower tendency for acac-containing copper species to hydrolyze and oligomerize. Only at the boiling point of acac ($T_B = 140$ °C) a thermolytic reaction is forced. Such effects are well known for 2,4-pentanedione in the sol-gel chemistry of metal alkoxides. Several examples were reported in the literature, *e.g.* in ref. 34 and 35, where acac was described to be advantageous due to the possibility to control hydrolysis and condensation kinetics. In the case of metal alkoxides, acac substitutes for alkoxy groups and is then more difficult to be hydrolysed. Depending on the degree of substitution, condensation can even be disabled completely, which keeps colloidal particles small in diameter and prevents precipitation. The same articles report that even a partial exchange of alkoxy groups for different alkoxy groups can lead to a complete change of charge distribution within the metal alkoxide, which can speed up or slow down hydrolysis and condensation. In many cases, mixed alkoxides behave completely different compared to the respective parent compounds.

However, quantitative calculations from our TG-DTA results were not performed due to the high volatility of methanol, which precluded a determination of the initial masses with sufficient precision. Yet, the observed mass losses at 77 and 115/140 °C are very well in the expected order of magnitude for a partial hydrolysis and condensation of $\text{Cu}(\text{TFA})_2$ beyond 50%. Hence, the results of the thermal investigations point to a moderated behaviour for the decomposition process in the low temperature range when acac is added to REBCO-TFA precursor solutions. On the one hand, this might prevent extended segregation of copper species by condensation and thus maintain a well-homogenized distribution of all metal cations within the film, which is crucial for the conversion into homogenous REBCO. On the other hand, the task of moderators like acac is to promote equilibrium reactions and therefore enable back

reactions, which can lead to broad healing of defects in the microstructure. Further, the slowdown of the release of volatile species in acac solutions could have positive effects on the microstructure in a more macroscopic scale, too, which will be investigated in the following section.

Thin film samples

Microstructure. The present study of REBCO trifluoroacetate precursors demonstrates that acac has an advantageous influence on the microstructure – as illustrated in Fig. 4 for YBCO in the form of SEM plan-view and cross-sectional images. All samples shown here have been exposed to the same complete conversion process (pyrolysis, formation at 780 °C, post-annealing in oxygen). The first two pictures (a) and (b) in the upper row show samples derived from a standard fresh solution (a) and from the same solution aged for three months with a high-frequent usage (b), respectively. Both samples exhibit a very granular surface in the plan view, whereas the aged solution seems to have additional problems with buckling and deep grooves – very likely due to the effect of progressive water pollution mentioned before. Besides, the cross sections reveal pore formation beneath the surface. All those features are undesired, because they can lead to a reduction of critical current densities. The next four pictures ((c)–(f)) show how the microstructure changes with increasing amounts of acac. For

those samples, the same “aged” precursor solution as in (b) was used. While 21.4% (c) and 42.8% (d) acac/RE already show a clear reduction of the surface granularity as well as a significant smoothing of the layer as a whole without subsurface pores, there is still a certain degree of buckling observable in the plan view images. The smoothest layer was obtained for 64.1% acac/RE (e) with no obvious buckling. For higher concentrations (f) the microstructure clearly degraded again, which becomes mainly visible in the cross sections. However, all amounts of acac point to a substantial levelling of the surface and avoidance of the pores beneath.

In order to verify the beneficial effects of acac found for YBCO, similar investigations were performed for GdBCO precursor solutions. In contrast to YBCO, pure solutions for GdBCO seem to show a much higher sensitivity to pollution with moisture, which might indicate hydrolysis and/or condensation to be an issue not only of copper, but of rare earth species, too – and apparently with different severity depending on the RE element. Though, there is another possible explanation. Different rare earth elements might simply retain different amounts of water in their coordination spheres and hence in the as-deposited films, speeding up water-related reactions of the copper species without being affected by hydrolysis themselves. At present, we have not investigated this entirely, but we clearly favour the second possibility, since both thermal analysis and X-ray investigations provide no evidence for a

Fig. 4 Plan-view and cross-sectional SEM images for six different YBCO samples: (a) from a fresh “standard” solution; (b) from the same solution after three months aging; (c)–(f) from the aged solution containing different amounts of acac from 21.4–85.5% acac/Y. Pure solutions (a) and (b) show very grainy surfaces and pores beneath. For the old solution (b), additional buckling is observed. Acac additions suppress pore formation completely and lead to smoothest layers for 64.1%.

hydrolysis of the RE species. However, the whole GdBCO preparation process seems to need an even more elaborate screening from air humidity in order to achieve similar high-performance samples every time. So whenever the influence of moisture could be eliminated to the best possible extent, GdBCO did exceed YBCO in J_c performance, as expected from the slightly higher GdBCO transition temperature ($\sim 2\text{--}3\text{ K}$). Then, superconducting layers were very compact, smooth and free of pores (compare Fig. 5(a)). For less careful handling, it can happen easily that samples show massive buckling with grooves almost down to the substrate interface, as well as misorientations – even for fresh solutions (Fig. 5(b)).

Such a low-performance solution was used for further experiments and provided with 64.1% acac/Gd – the concentration which had led to optimal results for YBCO. Again, all samples were exposed to a similar heat treatment process but this time with varying T_{growth} because this is the essential parameter for good superconducting performance and needs very precise tuning for every change in the system (*e.g.* RE, substrate type, solution additives). Thus, films were heated up to temperatures from 790 °C to 840 °C, whereby the highest J_c sample is shown in Fig. 5(a) and (b) for the pure fresh and pure aged solutions, respectively. Samples grown from the acac-containing solution at different temperatures are shown in Fig. 5(c)–(f).

The solution with 64.1% acac/Gd leads to very similar microstructural characteristics of the films at all applied growth temperatures, which is in clear contrast to analogue investigations on the growth temperature for solutions without acac additions, which we will publish in a forthcoming paper. Only at the lowest considered temperature (790 °C), a minimal amount of very small, needle-shaped *a*-axis grains is observed. This orientation is undesired in REBCO thin films for it cuts the copper oxide plains, which run parallel to the *a/b* planes of the REBCO elementary cell and carry the supercurrent. Thus, the whole process is focused on realizing a perfect *c*-axis texture (*c*-axis perpendicular to the substrate interface) of the films in order to achieve a good alignment of CuO plains. However, apart from such small misorientations at lowest temperatures, all layers (c)–(f) are very homogeneous and compact, *i.e.* no voids visible in SEM, very smooth surfaces with low granularity and no obvious misorientations above 790 °C. The smoothest layer resulted from annealing at 825 °C. So GdBCO solutions seem to react similarly well to the same amount of acac additions found to be optimal for YBCO solutions. This might be considered to be an indicator that it is indeed the copper complexation being the major mechanism for protection from hydrolysis and structural film degradation. At least, a similar RE-related effect is no longer obvious in acac-containing solutions, and thus the RE element seems to play only a secondary role in moisture sensitivity.

Fig. 5 Plan-view and cross-sectional SEM images for six different GdBCO samples: (a) from a “standard” high-performance solution; (b) from a “standard” solution with low performance; (c)–(f) from the same low-performance solution containing 64.1% acac/Gd grown at different temperatures (790–840 °C). In contrast to the low-performance solution without acac additions, all the other examples show very good microstructure, *i.e.* compact homogenous films without voids and grooves and a very low surface granularity. Only for (a) and (c) small amounts of needle-shaped *a*-axis grains can be identified.

XRD patterns of the YBCO samples are shown in Fig. 6(a). The strong (00 l) reflections of YBCO indicate a good, c -axis-textured growth for all films, but in fact, the reflections are a bit weaker without acac addition. Besides that, some minor signs of phase impurities are observed in all films, but not all of them can be assigned to a certain phase. Only the reflections at around $2\theta = 38.3$ and 39.6° are well-known to be YBCO (103) and Y_2O_3 (400), respectively, and are mainly observed in YBCO films grown on LAO. XRD patterns of GdBCO films from the acac solution (Fig. 6(b)) show a very high quality of texture, too, with a few weak and very diffuse indications of phase impurities – the most obvious reflection at around $2\theta = 49^\circ$ (not identified).

Film thickness. The determination of the film thickness is very important for an evaluation of sample quality because this value is taken as a basis for calculations of critical current densities. Unfortunately, it is often left unclear in the literature how other groups determine their sample thickness and which value (minimum, mean, maximum, or any value determined from local measurements) is used – in particular since local and macroscopic thickness inhomogeneity is often observed in CSD samples. As a result, ambiguities and errors in thickness determination complicate the comparison of sample performances published by different groups. The following considerations of the film thickness are based on statistical evaluations of a population of approximately 140 standard REBCO samples. The mean thickness and standard deviation of the mean thickness of each single sample had been determined from six AFM profiles taken within two different sample spots of $90 \times 90 \mu\text{m}$ size, and both values – mean thickness and standard deviation – have been averaged over those 140 samples, giving the average (mean) thickness and average standard deviation. Thus, the average standard deviation is not the standard deviation of the average thickness, but the average of thickness standard deviations within the samples.

Generally, the standard parameters used for solution preparation, coating and heat treatment result in an average film thickness of around (265 ± 25) nm for solutions without acac modifications. Thereby, the error of 25 nm is dominated by the average standard deviation. Accordingly, this error is closely

related to rather macroscopic thickness inhomogeneity (order of magnitude $>40 \mu\text{m}$) but not to the microscopic surface roughness. A very small reading error of about 1.5 nm is included, too. The negligence of the sample roughness for the determination of this error is motivated by the fact that roughness has actually no direct influence on the mean and the average thickness, since the influence of the roughness on the thickness is rather very local (lateral order of magnitude $<1 \mu\text{m}$). That means that inductive scanning techniques for J_c calculations should not be influenced significantly by surface roughness since one scan point measures in a lateral dimension of $>50 \mu\text{m}$ and, thus, even shielding currents induced in fully isolated structures contribute to inductive J_c . On the other hand, macroscopic thickness variation, like buckling and waviness, can be a significant source of error for inductive J_c calculations, as long as their order of magnitude is in the dimension of $50 \mu\text{m}$ and more. Hence, the mean thickness of a sample is appropriate to be used for inductive J_c -calculations – taking into account the uncertainty of 25 nm (roughly 10%). However, a massive microscopic surface roughness will lead to a disturbance of the transport current without any doubt – due to a reduction of the “effective” (current-carrying) cross section, which might correspond to specific surface roughness values, like *e.g.* the rms value. We will try to make a cautious estimate of the influence of the sample roughness on the “effective” cross section for transport currents in the section on critical current densities further below.

Investigations of the mean layer thicknesses by AFM on samples relevant to the present work (filled rhombi, Fig. 7(a)) revealed a declining trend with increasing amounts of acac in the aged YBCO precursor solution. The sample without acac-modifications showed the thickest layer of 285 nm. This is slightly above the average of 265 nm usually obtained from standard solutions, yet still within the average standard deviation of our process. But it could also result to a certain extent from solution thickening through solvent evaporation, which is a direct function of storage time and the frequency of usage. Also without usage, solutions show a little solvent loss by time, even for properly sealed vessels, which is due to a certain permeability of the mostly polymeric vessel lids, especially for

Fig. 6 XRD patterns of YBCO films obtained from solutions with different acac concentrations (a) and of 64.1% acac/Gd containing GdBCO films at different growth temperatures (b). Datasets are shifted for clarity. All samples show a good REBCO c -axis texture, but show some weak signs of secondary phases, too.

Fig. 7 (a) Mean layer thicknesses of YBCO thin films (filled rhombi) and viscosities of different REBCO precursor solutions (open symbols) vs. the acac/RE ratio. Dashed/dotted lines act as a guide to the eye. The thickness decreases when acac is added, although the solution viscosities remain unaffected; (b) mean layer thicknesses of acac-modified GdBCO thin films vs. the annealing temperature. No clear thickness dependence is observed. All error bars are based on the average standard deviation of the thickness.

small and highly volatile molecules like methanol. The consequential increase of the metal–organic concentration does not only directly lead to an increase of the layer thickness, but also increases both the solution viscosity η and density ρ . They, in return, influence the layer thickness d , as well, as determined for dip coating techniques in the form of the Landau–Levich equation:³⁶

$$d \propto \eta^{2/3} \rho^{-1/2}.$$

Those parameters, however, cannot explain the decrease in the thickness after acac additions, for the viscosity has been demonstrated to be unaffected for several solutions when acac is added (compare Fig. 7(a)). The density and concentration can be considered nearly constant for such low amounts of acac in 2 ml solution (max. 2 vol%), too. Therefore, there must be another reason for the thickness change with acac additions.

Since it is the sample without acac-modifications which showed the thickest layer, this might be caused by the voids below the surface observed in SEM in such samples. Hence, acac films are simply more compact than non-acac films due to a lower degree of porosity, while in the latter films the presence of pores increased the mean layer thickness only apparently. Yet, the mean “effective” thickness should actually be the same for all films grown from REBCO solutions with a similar concentration, viscosity, and density and applied to the same coating parameters since they should all contain roughly the same mass of the REBCO phase. That means that one should be able to define one mean thickness value for such an entity of films, which can be considered to be valid at least for inductive J_c calculations, where surface roughness plays a less important role. Unfortunately, an increase of pore formation goes hand in hand with an increase of the surface roughness and, as mentioned above, a severe roughness should, in fact, have an impact not on the mean thickness, but on the effective superconducting cross section for transport J_c . In summary, closed pores are assumed to artificially increase the mean layer

thickness determined by AFM, but leave the effective cross section unchanged, while surface roughness is assumed to leave the mean layer thickness rather unchanged, but yet to reduce the effective cross section for transport currents. In any case, those assumptions lead to a certain ambiguity for J_c calculations from “simple” mean thickness values – at least for films with massive pore formation and roughness, and in particular for transport currents, because in this case both features – pores and roughness – would lead to an overestimation of the “apparent” layer thickness in comparison to the less easily accessible “effective” layer thickness.

For GdBCO films obtained from the 64.1% acac/Gd solution, no clear layer thickness dependence on T_{growth} has been observed (Fig. 7(b)). All mean thicknesses lie between 200 and 250 nm and, therefore, do not differ very much from the high-performance solution without acac, which resulted in a very compact 250 nm film. Though, they are a bit thinner than the low-performance solution film of 275 nm. The calculation of an average layer thickness for all films obtained from acac-containing solutions (approximately 40 samples) resulted in (230 ± 25) nm and from the deductions above, this value is assumed to be the average of the “effective” layer thickness for films without acac additions, too, still neglecting the influence of surface roughness. However, this value will be taken as a basis for inductive J_c calculations for all samples grown from 0.25 M solutions, since this value allows the best possible comparability of inductive critical current densities. Furthermore, the uncertainty of the layer thickness is obviously the same as in non-acac films, which demonstrates that macroscopic thickness variations are not affected by this sort of solution modification. The thickness difference of 35 nm between both types of films allows an estimation of the porosity of roughly 15 vol% in non-acac films. Thereby, this value should mainly consist of fully covered pores, but to a smaller part also of surface roughness which cannot be captured by AFM scans due to resolution limits (*i.e.* limits due to the shape and the size of surface features).

Critical current densities. Fig. 8 shows a comparison between inductively and resistively determined J_c values at 77 K

and self-field. The influence of the acac concentration is shown for YBCO in Fig. 8(a); the influence of the growth temperature is demonstrated for GdBCO + 64.1% acac/Gd in Fig. 8(b). In contrast to the inductive J_c values, which required the assumption of an average thickness value of 230 nm to be valid for all samples, the sizes of the bridges used for transport measurements have been precisely determined by AFM for each sample. Therefore, transport J_c values correspond to the “apparent” cross section meaning the superconducting phase plus the pores and neglecting any surface roughness. However, pores and roughness are much more significant at 0% acac concentration, as deduced above from thickness and SEM investigations, while at higher acac concentrations “effective” and “apparent” thickness should more or less coincide within the limits of the thickness error – and this should be reflected in the deviations of the inductive and transport J_c values.

For YBCO, the inductive J_c values indicate a slight increase of the self-field performance from 3.3 MA cm^{-2} to $3.6\text{--}4.0 \text{ MA cm}^{-2}$, when 21.4–64.1% acac/Y are added and suggest deterioration for the highest concentration (3.4 MA cm^{-2}). Within the error of $\pm 10\%$ resulting from the uncertainty of the layer thickness, this curve progression can be considered constant, indeed, which is in good agreement with the fact that T_c is rather unaffected by acac additions. Inductively determined T_c values (50%) are 89.0 K and 89.7 K, $\Delta T_c (= T_c(90\%) - T_c(10\%))$ are 0.7 K and 0.8 K for the samples derived from the fresh and the aged solutions, respectively, while the acac-containing YBCO samples show values in the range 89.2–89.5 K for $T_c(50\%)$ and 0.6–0.9 K for ΔT_c . Thereby, the rather low ΔT_c values indicate a homogeneous T_c over the whole sample size.

Transport J_c values show a stronger increase from 1.8 MA cm^{-2} for 0% acac/Y up to 3.9 MA cm^{-2} for 64.1% acac/Y. Thus, transport and inductive J_c values also coincide within the thickness error for acac-containing samples – the largest deviation for the resistive from the inductive value is -12% at the lowest acac concentration of 21.4%. However, for films obtained from solutions without acac there is a much larger discrepancy between both values – also demonstrated for the fresh solution

in Fig. 8(a) and for the two non-acac GdBCO samples in Fig. 8(b). Those deviations are as large as -40 to -50% ; only the high-performance GdBCO sample displays a slightly lower deviation of around -30% .

Those J_c deviations of inductive vs. resistive values of roughly 45% in samples grown from non-acac solutions are not only much larger than in any of the acac samples but also larger than both the thickness error of around 10% and the additional error of the thickness caused by porosity of roughly 15%. To a large extent, the massive residual deviation is very likely caused by the strong surface roughness and the resulting reduction of the effective current-carrying cross section. However, there are more factors to consider – e.g. differences in grain sizes, stoichiometric homogeneity and strain, which are indicated by XRD measurements in Fig. 7 through lower (00l) intensities and slightly broader reflections in non-acac samples, but which at present have not been investigated in detail. Further, it is quite reasonable to assume texture deterioration – particularly in the surroundings of porosity and roughness – to contribute to J_c reduction, as well. Differences in secondary phase formations are also indicated by XRD.

For GdBCO grown from acac solutions (filled symbols, Fig. 8(b)), it is also found that the deviation between inductive and resistive J_c values is rather small, only at the highest temperature of 840°C a deviation of $+27\%$ is observed. Such a large deviation cannot be explained by the thickness error only, and the opposite sign indicates that porosity and/or roughness have little to do with that. However, the very high growth temperature gives reason to exclude this sample from current considerations, but demonstrates that further sources of error have to be considered here, too. In particular, the rather large ΔT_c value of 4.4 K points to sample inhomogeneities being responsible for the J_c deviations. Yet, the complete investigated temperature range yielded samples with $J_c \geq 2.9 \text{ MA cm}^{-2}$ (inductive) and $\geq 3.2 \text{ MA cm}^{-2}$ (transport), respectively, while similar T_{growth} investigations on non-acac samples indicated a very narrow window of only 10 K for the growth of samples with J_c higher than 3 MA cm^{-2} ($810\text{--}820^\circ\text{C}$), which will be published

Fig. 8 Critical current densities at 77 K and self-field for (a) YBCO over the acac concentration and (b) GdBCO over the thin film growth temperature. Triangles show the resistively measured J_c , and rhombi the inductively measured J_c . The samples grown from non-acac solutions display a larger discrepancy between inductive and resistive values, which is very likely rooted in microstructural characteristics. Dotted lines serve as guide for the eye only. Error bars are based on 10% thickness uncertainty.

Fig. 9 Pinning force densities. (a) YBCO with different acac concentrations in the aged precursor solution. 64.1% acac/Y show the highest $F_p^{\max}$. (b) GdBCO without acac modifications grown from "high performance" solution 1. The optimum sample is attained when grown at 810 °C. (c) GdBCO with 64.1% acac/Gd grown at temperatures 790–840 °C. All the samples show similar curve progressions, with $F_p^{\max}$ above 3 GN m⁻³ and therefore much higher performance than the original "low performance" solution 2 (open rhombi).

in a forthcoming paper. T_c values (50%) are 92.8 K and 92.4 K, ΔT_c values are 0.5 K and 1.0 K for the samples from the high-performance solution without acac and the acac-derived sample grown at 825 °C, respectively.

Properties in applied magnetic fields. When a type II superconductor like YBCO is in the so-called mixed state, magnetic flux lines penetrate the diamagnetic material. If the flux lines were motile within the superconductor, a transport current would lead to dissipation due to the so-called Lorentz force acting on the vortices surrounding the flux lines. The pinning force F_p is the force necessary to fix a magnetic flux line in a particular spot and, therefore, prevent it from moving when a current is applied. Such pinning centres are preferably non-superconducting (e.g. point defects, dislocations and other imperfections in the crystal structure, or secondary phases), as the energy level for the flux line is lower in such spots compared to the perfectly diamagnetic superconducting phase. Fig. 9 illustrates these pinning force densities calculated from $V(I, B)$ characteristics ($F_p = J_c \times B$). For YBCO (a), those curves show clearly that 64.1% acac/Y is, indeed, the optimum concentration in our standard precursor solutions – as assumed from microstructural features and self-field measurements. The maximum pinning force density $F_p^{\max}$ could be more than doubled in relation to non-acac YBCO thin films from 1.0 to 2.4 GN m⁻³. Fig. 9(b) stands exemplary for a typical trend of non-acac REBCO samples (here: GdBCO) grown at different T_{growth} values. Generally, only one annealing temperature leads to optimal results, whereas a temperature only 10 °C higher or lower significantly deteriorates pinning force densities and consequently current carrying capacities. Fig. 9(c) demonstrates that J_c in magnetic fields of a low-performance solution (open rhombi) can be improved considerably when acac has been added to the solution. Further, all acac samples with different T_{growth} values from 790 up to 840 °C show similarly high $F_p^{\max}$ and similar curve progressions in general, and all samples exceed the best sample from the non-acac route in performance. Thus, acac seems to help overcome the necessity to precisely set T_{growth} in the firing process, which facilitates

operation; respectively it seems possible to grow similarly good samples at lower temperatures, which is an important aspect for energy and cost saving considerations. Even temperatures lower than investigated might still lead to good results, but of course the scope is not infinite. First signs of *a*-axis oriented growth at 790 °C point to limitations. This is because nucleation barriers for both types of orientations are linked to the degree of supersaturation and therefore to the annealing temperature. Hence, in the regime of low temperatures there is an increasing thermodynamical preference for the nucleation and the growth of *a*-axis grains over the *c*-axis orientation.^{37,38}

Conclusions

Small additions of 2,4-pentanedione (acac) in REBCO (RE = Y, Gd) precursor solutions have a very positive effect on both the microstructural characteristics of thin films and, consequently, the critical current densities. Additions of 21.4–85.5% acac in relation to RE elements lead to a complete avoidance of extended pores beneath the surface, as well as a containment of buckling, grooves and surface granularity. Critical current densities were improved not only at self-field, but also in applied magnetic fields, and investigations on the growth temperature of such films revealed a much lower sensitivity to the actual annealing temperature. Moreover, a similar performance to that obtained for non-acac films could be obtained at lower temperatures, which is an interesting aspect with regard to energy input and costs. For YBCO, 64.1% acac/Y leads to the best results, and pinning force densities were increased from 1.0 to 2.4 GN m⁻³. Using the example of GdBCO, we demonstrated that an initially low-performance solution resulting in films with less than 1 GN m⁻³ can be turned to very high performance when acac is added. Then, more than 3 GN m⁻³ was achieved in a T_{growth} window of 50 K.

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