Epitaxial superconducting GdBa$_2$Cu$_3$O$_7$–$\delta$/Gd$_2$O$_3$ nanocomposite thin films from advanced low-fluorine solutions

Pablo Cayado$^1$, Bernat Mundet$^1$, Hichem Eloussifi$^2$, Ferrán Vallés$^1$, Mariona Coll$^1$, Susagna Ricart$^1$, Jaume Gázquez$^1$, Anna Palau$^1$, Pere Roura$^2$, Jordi Farjas$^2$, Teresa Puig$^1$ and Xavier Obradors$^1$

$^1$ Institut de Ciència de Materials de Barcelona, ICMAB—CSIC, Campus UA Barcelona, E-08193 Bellaterra, Catalonia, Spain
$^2$ University of Girona, Montilivi Campus, Edif. PII, E17071 Girona, Catalonia, Spain

E-mail: obradors@icmab.es

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Abstract

We have employed the CSD method to synthesize GdBCO and GdBCO–Gd$_2$O$_3$ nanocomposite 250–300 nm thin films. For this we have designed a new low-fluorine solution never used before in the synthesis of GdBCO thin films that allows us to reduce the HF release by 80% and increase the reproducibility of the pyrolysis process. The growth of these thin films required a new thermal process to be designed, which we refer to as ‘flash-heating’, where the heating rate is extremely fast (∼600 °C min$^{-1}$). The structure and the superconducting properties of the pristine GdBCO films are excellent, showing a (001) epitaxial orientation of the GdBCO grains and $T_c$ values that reach 92.8 K, which means an enhancement of more than 1 K with respect to standard YBCO films. The calculated $J_c$ inside the grains ($J_c^G$) also presents remarkable values: $J_c^G$(5 K) $\sim$ 40 MA cm$^{-2}$ and $J_c^G$(77 K) $\sim$ 3.3 MA cm$^{-2}$. Finally, the GdBCO–Gd$_2$O$_3$ nanocomposites films, with a 20% mol of Gd$_2$O$_3$, exhibit superior superconducting properties and pinning performances with respect to GdBCO pristine films.

Keywords: GdBCO, low-fluorine solution, chemical solution deposition, nanocomposites, flash-heating process

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

1. Introduction

Nowadays, there is a major interest in developing high temperature superconducting (HTS) materials with high performance owing to their potential applications in novel devices. Their properties, especially the high values of critical temperature, $T_c$, and critical current density, $J_c$, open up the possibility of using them in devices working at high temperatures (in the range of liquid nitrogen) and at lower temperatures under very high magnetic fields. Among the HTS materials, REBa$_2$Cu$_3$O$_7$–$\delta$ (REBCO) compounds (RE = rare earths), which belong to the family of cuprates, have attracted the attention of the scientific community due to their excellent current capabilities at high magnetic fields [1–6]. Probably the most well known and studied REBCO compound is YBa$_2$Cu$_3$O$_7$–$\delta$ (YBCO). However, in recent years, studies have been conducted involving the replacement of Y$^{3+}$ in YBa$_2$Cu$_3$O$_7$ by other RE ions (e.g. Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$ or Gd$^{3+}$) to form alternative REBCO compounds because some of these compounds can display enhanced superconducting performances [7–9]. The differences in the physical properties are linked mainly to variations in the structure related to the modified ionic radius of the RE ions [10–13]. The modified RE size influences the distances between different planes in the structure and, therefore, the interaction between the orbitals of different atoms, which leads to a change in the properties of the different compounds. Additionally, the change in the RE ions modifies the thermodynamic phase
diagrams and so specific changes are required in the synthesis and processing conditions of these REBCO materials. An additional difficulty is that large RE ions can display a partial substitution into the Ba$^{2+}$ sites, hence deeply influencing the superconducting properties and reducing the stability of the 123 phase in some REBCO compounds [7, 14, 15].

Among REBCO compounds, GdBa$_2$Cu$_3$O$_{7-\delta}$ (GdBCO) offers an appealing potential over YBCO [16–18]. In particular, the increase in the $T_c$ that is observed in the GdBCO bulk [7, 18] and thin films [19, 20], reaching up to 94–95 K, causes an upward shift of the irreversibility line which makes GdBCO a very promising material for some applications.

The first GdBCO samples studied were in the form of single crystals [21] and in bulk samples [7, 22]. These initial samples already revealed the great properties of GdBCO compared with other REBCO compounds. The GdBCO thin films have been prepared over many years by in situ growth techniques, i.e. sequential deposition and growth. The properties of the thin films synthesized by sputtering [23–26], PLD [27] or MOCVD [28] have confirmed the results obtained in the case of single crystals and bulk samples. However, in the search for a scalable and low-cost technique for the preparation of coated conductors, some researchers have focused on chemical solution deposition (CSD) as an attractive option for thin film growth [29–31]. This technique can be defined as ex situ growth because the deposition and growth are two separate steps. The case of GdBCO films is not an exception and different works have explored the CSD method to prepare GdBCO films. Most of these works were based on the well known trifluoroacetate (TFA) route [32], resulting in a $J_c$ of 2–4 MA cm$^{-2}$ and a $T_c$ of 93–94 K [16, 19, 33, 34], in good agreement with GdBCO thin films prepared by in situ growth methods [17, 20, 35, 36].

In order to enhance the in-field performance, we introduced secondary phases in our films forming GdBCO nanocomposites. The insertion of different secondary phases to prepare the nanocomposites has been extensively investigated by many groups, showing that the in-field properties of REBCO films can be vastly improved by both ‘in situ nanocomposite’ and ‘ex situ nanocomposite’ approaches [37–42]. In the first case, complex metal–organic solutions are prepared which contain all the elements required to form the nanocomposite and the secondary phases are spontaneously segregated. In the second case, preformed nanoparticles (NPs) are added to form a colloidal solution [40, 41]. We have opted here for the ‘in situ nanocomposite’ approach, in which the NPs are spontaneously segregated in the superconducting matrix during the growth process to include Gd$_2$O$_3$ NPs in the GdBCO films.

Despite the fact that the TFA route is an extended and well-controlled process, the fact that HF is released into the environment during the processing of TFA-derived films has led to a search for alternative solutions. The so-called ‘low-fluorine’ solutions (LF) offer the possibility of reducing the F content and, therefore, HF release, maintaining the same BaF$_2$ route for the REBCO formation than in the case of the TFA route which facilitates the processing [43]. The LF precursors have been recently investigated for the preparation of YBCO thin films, but little work has been done to grow GdBCO [33, 44].

In this work we report the preparation of thin GdBCO films using a new formulation of LF solution. The advantages of using LF over TFA (apart from the reduction of F content) are as follows: the new LF solution is less sensitive to environmental humidity and also leads to films with enhanced viscoelastic properties which then results in improved homogeneities after the pyrolysis process.

The film growth process has also been investigated in relationship to superconducting properties. It will be shown that an improved epitaxy is achieved using a new growth process called ‘flash-heating’, as an alternative to the standard one used in TFA-derived films. This process minimizes the nucleation of undesired grain orientations in the GdBCO–LF films during the heating ramp and leads to high critical currents, although some granularity effects still limit the superconducting performances. GdBCO + 20 mol% Gd$_2$O$_3$ films have been synthesized using the ‘in situ nanocomposite’ approach and we have shown that a smooth magnetic field dependence of the critical currents, similar to YBCO nanocomposites, is achieved.

2. Solution synthesis and film preparation and characterization

2.1. GdBCO–LF solution synthesis

The solution is prepared using three different precursor salts: gadolinium trifluoroacetate (Gd-TFA), barium acetate (Ba-OAc) and copper acetate (Cu-OAc). First, the Ba-OAc (Sigma-Aldrich $\geq99.5\%$) is dissolved in a mixture of methanol and propionic acid (Sigma-Aldrich $\geq99.5\%$). The amount of propionic acid added to the mixture is 26% of the final volume of the prepared solution. Once the Ba-OAc is dissolved, an amount of triethanolamine is added (TEA, Sigma-Aldrich 98%) which is 5% of the total volume of the final solution, and is homogenized for 10 min. After homogenization, Cu-OAc (Alfa-Aesar $\geq98\%$) is added. After 15–20 min, the Cu-OAc is completely dissolved and, finally, the Gd-TFA is added to complete the solution. The solution is adjusted to the desired concentration with methanol and then placed in sealed vials under an Ar atmosphere. Similar procedures have been used in previous works [43–45].

In this work we have used 0.25 M GdBCO–LF solutions (with respect to Gd content of the solution) leading to films with a thickness of ~250–300 nm after the conversion step, as measured by profilometer analysis. The rheological features of the 0.25 M GdBCO–LF solutions are also very similar to those recently reported for YBCO in similar solutions (solution four in [43]). This solution is also used to prepare the GdBCO–Gd$_2$O$_3$ nanocomposite. In this case, an excess of Gd-TFA is added to promote the spontaneous segregation of Gd$_2$O$_3$. 

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2.2. Thin film preparation

GdBCO and GdBCO + 20 mol% Gd2O3 films were studied in this work. The films were prepared by depositing the precursor solutions on 5 × 5 mm LaAlO3 (LAO) single crystal substrates via spin coating (6000 rpm, 2 min). The subsequent standard pyrolysis and growth processes are also described elsewhere [40, 46]. The flash-heating process (described in detail in section 3) is also used to obtain an improved texture and superconducting properties.

2.3. Thin film characterization

The microstructure and phase analysis of the grown GdBCO and 20%M Gd2O3 films were performed by two-dimensional (2D) x-ray diffraction (XRD) using a Bruker AXS GADDS diffractometer. This diffractometer has the same geometry as a conventional 4-circles diffractometer where the circle is associated with a 2D detector. This allows a wide range of reciprocal space, thus allowing us to simultaneously analyze the coexisting random and epitaxial crystalline phases. The radiation used is CuKα (λ = 1.5406 Å). The microstructure of the films at the atomic scale was analyzed with a FEI-TITAN low-base operated at 300 kV equipped with a CEOS aberration corrector. The morphology of the films after pyrolysis and after the growth was analyzed by a Leica DM 1750 M optical microscope and a SEM Quanta 200 ESEM FEG, respectively. The granularity measurements and the superconducting properties (Tc and Jc) of the films were obtained with a Quantum Design PPMS and XL-7T SQUID. Electrical contacts were prepared by evaporating silver pads and subsequently annealing under flowing oxygen, ensuring contact resistances below 10 μΩcm².

3. Results and discussion

3.1. Pyrolysis process: TFA versus LF solutions

The pyrolysis process used to remove the organic content of the as-deposited metal–organic solution is a critical step in CSD [47]. As demonstrated in the case of YBCO films, the inhomogeneities that appear during the pyrolysis process due to the strong shrinkage, resulting from solvent evaporation and decomposition of the precursors, degrade the final film properties [46, 48, 49]. To achieve smooth and defect-free films after pyrolysis is not straightforward. In the YBCO–TFA films, this shrinkage can be as high as 50% of the initial thickness [46]. An additional limitation of the TFA solutions is their high hygroscopicity [50]. Even the as-deposited films are very sensitive to humidity [16]. It is suggested that this effect is due to the fact that fluorine–water bonds are formed and are stronger than fluorine–methanol bonds, thus causing water absorption. This fact, together with a large difference in the values of vapor pressure (PV) at room temperature and the surface tension of methanol and H2O (PV = 3173 and 162 65 Pa, and γ = 72.9 and 22.5 mN m⁻¹ for H2O and methanol, respectively), cause aggregation of the precursor species creating inhomogeneous stress in the films. This stress is likely to cause mechanical instabilities that result in film buckling or cracking, thus reducing film homogeneity after pyrolysis [46, 47, 51].

This problem can be partially overcome with the use of LF solutions. The LF solutions present important advantages from different standpoints: (i) the use of non-fluorinated compounds is environmentally friendly, (ii) a reduction in the TFA-salt content in the solution, using TEA as a ligand, which coordinates with metal ions, stabilizing them, and also helping to achieve a smooth release of stress in the films during pyrolysis due to its viscoelastic behavior. This is probably the reason why different ligands (TEA, DEA, PEG, etc) are sometimes used to improve the quality of CSD films, with the use of propionic acid as a solvent [16, 43, 52, 53]. Finally, the use of propionic acid instead of TFA also helps to reduce the water absorption of the solution. This will lead to a higher yield of homogenous films after pyrolysis.

We have compared how the TFA and LF solutions (GdBCO–TFA and GdBCO–LF, respectively) absorb water from the ambient air. The GdBCO solutions were spread over glass disks and then the mass change due to water absorption from the surrounding air was measured for each using a microbalance. The results are plotted in figure 1. Notice the very high water absorption of the TFA films (10 wt%) that diminishes to one half for the LF films. These results can be explained by the coordination of metal ions to TEA or propionic acid that prevent their coordination with water molecules.

The reduction of the water absorption in the GdBCO–LF solutions causes an increase in the film homogeneity after pyrolysis (more than 95% of the films without inhomogeneities), even when solutions prepared several weeks before are used. Figure 2 shows optical microscope images of the surface of two pyrolyzed films deposited on LAO substrates from solutions prepared one week before. The film made from the TFA solution presents a large amount of cracks while the film deposited from LF solution exhibits a homogeneous surface with no defects. This difference is attributed to the fact that, usually after one week, the water content in the TFA
YBCO. This suggests that the crystallization of GdBCO lines shift towards higher temperatures as compared to the standard growth process for the YBCO–TFA films [31, 56, 57]. However, increasing the crystallization temperature to 820 °C (dwell time: 180 min) and reducing $P_{O_2}$ to 1.10 $^{-4}$ atm (100 ppm) did not lead to fully satisfactory results. While the obtained $T_c$ values improved when $P_{O_2}$ was reduced, the 2D XRD pattern shown in figure 3(a)) demonstrates that the film is not completely epitaxial—some fraction of polycrystalline grains still remains and the film texture of the c-axis oriented grains is not of high quality. The ring that appears with the spots in the (001) Bragg positions indicates that the c-axis oriented grains tend to grow with a certain degree of misorientation. Also, the presence of a ring corresponding to the (103)GdBCO Bragg peak confirms that randomly oriented grains have also formed. Finally, we also notice the spot associated with (200)GdBCO Bragg’s peak which means that there are also some grains that nucleate epitaxially with the a–b plane perpendicular to the substrate. The Bragg’s peaks associated with (102) reflection, identified with an arrow in figure 3(a)) can be better identified in the integrated pattern shown in figure 3(b)).

The existence of undesirable nucleation under these conditions can also be clearly seen in the SEM image shown in figure 4. In this image, we can see that the nucleation of the a-axis is promoted. This is something not observed in the case of YBCO–LF films which show perfect c-axis oriented films using similar processing conditions [43].

In order to investigate why the films do not crystallize with only c-axis epitaxial orientation, a film quenching study at different temperatures was performed. The results shown in figure 5 provide clues to discern the origin of the problem. Under the currently used nucleation and growth conditions [25–27], the GdBCO phase nucleates at temperatures in the range of 710 °C–725 °C, but at these temperatures the heterogeneous nucleation of GdBCO leads to multiple nuclei orientations oriented perpendicular to the substrate interface (c-axis, a–b plane and maybe even <103> axes) because we are in the region of high supersaturation conditions [31, 58]. We observe that the (103) peak is the first observed when temperature is increased (between 710 °C and 725 °C), thus suggesting that homogeneous nucleation, leading to randomly oriented grains, occurs before the c-axis oriented epitaxial grains ((001) peaks appear between 750 °C and 790 °C). It should not be disregarded, however, that some heterogeneous nucleation of grains with <103> axes perpendicular to the substrate first appear, later leading to randomly oriented grains which contribute to the observed (103)GdBCO Bragg peak. In any case, this suggests that under these particular conditions, the GdBCO crystalline phase forms under an excessive supersaturation where the nucleation barriers for the different crystalline orientations are too close to the c-axis oriented nucleation.

solution was well above 2 wt% (2.9 wt% in this particular case) while, for the LF solution, it remained below 2 wt%.

The above features of the GdBCO–LF solution allow us to obtain reproducible films. So, from now on, we will focus on the LF solution. However, its use requires us to modify the standard thermal process for the pyrolysis of the TFA solutions. We have used a thermal process already reported for YBCO–LF [43]. It is similar to the one used for the TFA solutions but with a higher dwell temperature (500 °C) and a higher gas flow rate (0.121 min $^{-1}$) to favor the complete decomposition of the TEA.

3.2. Growth process: flash-heating process

The phase diagram of GdBCO reported by Iguchi et al and Lee et al shows that the stability [35, 54] and peritectic [55] lines shift towards higher temperatures as compared to YBCO. This suggests that the crystallization of GdBCO films should be optimum at higher temperatures than in the YBCO films. It is also noticeable that in most works devoted to GdBCO film synthesis, lower values of $P_{O_2}$ are used [16, 33, 35]. So we concentrated on exploring the growth conditions shifted to higher crystallization temperatures and lower oxygen partial pressures ($P_{O_2}$), as compared to the standard growth process for the YBCO–TFA films [31, 56, 57].

Figure 2. Optical microscope images of the surface of a pyrolyzed film deposited from a one week old solution of (a) GdBCO–TFA and (b) GdBCO–LF. The water content was much higher in the TFA solution (2.9 wt%), which explains the appearance of cracks which are absent in the LF film.
It is well known that c-axis oriented grain nucleation is more favorable at high temperatures for REBCO structures [31, 58]. This is because, at high temperatures where supersaturation is lower, the difference in the nucleation barriers, and so the nucleation rates, between the a–b axis oriented grains, the randomly oriented grains and the c-axis oriented grains is larger, even if all the nucleation rates are lower [59]. Therefore, it is interesting to accelerate, as much as possible, the transition through intermediate temperatures where non-desirable nucleation events may occur. This will not allow enough time to induce multiple nucleation events at low temperatures, thus reaching the crystallization temperature as fast as possible to favor the nucleation of c-axis grains. With this aim, a ‘flash-heating’ process was designed. This process is similar to the one reported by Erbe et al [16]. The furnace is first pre-heated at the dwell temperature (820 °C in this case) and then the film is introduced directly at this temperature. With this procedure it is possible to reach average heating ramps of ~600 °C min⁻¹, more than 20 times faster than the 25 °C min⁻¹ of the original process. The XRD patterns of the films grown using this type of process are presented in figure 6. A perfect epitaxial (001) GdBCO film with no presence of other orientations or other phases is achieved with our ‘flash-heating’ process.

Despite the fact that the XRD patterns do not reveal the presence of other crystal orientations, in the SEM images (figure 7), it is still possible to observe a small amount of a–b grains (white arrows) and some pores (black spots). This means that the thermal process is still not fully optimized and there is still some room to improve the processing conditions. Healing the porosity in CSD films is a complex issue strongly
dependent on film thickness which may be tuned through annealing the temperature and time; however, it is also necessary to avoid film dewetting which may be promoted at excessive heating temperatures \cite{60}.

Nonetheless, at this stage, the films present \( T_{c, \text{onset}} \) of 92.6 K with \( \Delta T_c = 10.1 \) K (see figure 8(a)) which is similar to the best results previously reported for GdBCO–TFA and GdBCO–LF films \cite{16, 20, 35, 44}. However, moderate values of self-field critical current densities, \( J_{c}^{sf} \) at 5 K \( \sim \)12.5 MA cm\(^{-2}\) and \( J_{c}^{sf} \) at 77 K \( \sim \)1.5 MA cm\(^{-2}\), were registered (see figure 8(b)).

The values of \( J_c \) reported in figure 8 are very likely affected by the presence of a small amount of \( a-b \) grains which behave as barriers for percolative current. The presence of these \( a-b \) grains, and also the porosity that is observed in figure 7, produce inhomogeneities in the film that could induce a granular behavior for the current flow \cite{61–64}. Granularity in superconductors is characterized by the existence of two different critical current densities: one inside the grains (\( J_{c}^{G} \)) and another one associated with the grain boundary network (\( J_{c}^{GB} \)). It is possible to determine the \( J_{c}^{G} \) by applying the method reported by

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**Figure 6.** (a) 2D XRD \( \theta-2\theta \) frame, and (b) integrated pattern of GdBCO–LF films grown using the flash-heating process at 820°C.

**Figure 7.** SEM image of a GdBCO film prepared by the flash-heating process showing a small amount of \( a-b \) grains (indicated by white arrows) and some pores (black spots).

**Figure 8.** Inductive measurements on a GdBCO–LF film grown by using the flash-heating process showing (a) the low field magnetizations versus temperature allowing us to determine the \( T_c \), and (b) the measured temperature dependence of the self-field \( I_c(T) \).

3.3. GdBCO–Gd$_2$O$_3$ nanocomposites

The preparation of GdBCO + 20 mol% Gd$_2$O$_3$ nanocomposite films has been carried out following the solution methodology described in section 2.1 and the flash-heating process described in section 3.2.

The XRD patterns of the nanocomposite films after the conversion process are shown in figure 10. They show epitaxial c-axis orientation of the GdBCO grains but the broadening of the (00l) spots suggests some degree of misorientation (figure 10(a)). The peaks corresponding to Gd$_2$O$_3$ can be also observed, both in figures 10(b) and (c). This confirms the formation of the Gd$_2$O$_3$ phase during the growth process. The presence of Gd$_2$O$_3$ NPs within the GdBCO matrix leads to an increased nanostrain, reaching values of 0.24 ± 0.01%, higher than pristine GdBCO–LF films (0.13 ± 0.01%). Also the nanostrain obtained in these nanocomposites is comparable with the values obtained for CSD YBCO nanocomposites [38, 66]. Nevertheless, it should be taken into account that, very likely, this value of strain has, in addition to a contribution from the nanostrain arising from defects, some contribution associated with mesostrain (strain at grain boundaries) owing to the observation of some granularity effects [58].

The TEM analysis shows perfect c-axis oriented GdBCO grains, together with a random distribution of 30–50 nm Gd$_2$O$_3$ NPs (red arrows) in figure 11(a). Also, it is possible to distinguish the presence of stacking faults (SFs) in figures 11(b)–(d) (white arrows) which have been recently shown to have a peculiar defect structure and display ferromagnetic properties [67]. Figure 11(d) shows the presence of superposed Gd$_2$O$_3$ NPs within the GdBCO matrix, causing the formation of SFs at the interfaces.

The superconducting properties of the GdBCO–LF + 20 mol% Gd$_2$O$_3$ nanocomposites are improved with respect to the pristine GdBCO–LF films. The $\rho(T)$ curve shown in figure 12(a) display a $T_c$ (value of $T$ at 50% of the transition) of $\sim$91.7 K with a $\Delta T_c$ $\sim$ 3.5 K ($\Delta T_c = T_{c,90\%} - T_{c,10\%}$).

Figure 12(b) displays the $J_c(T)$ curve in which we can observe that the $J_c^{sf}$ at 77 K reaches 3.2 MA cm$^{-2}$ while the $J_c^{sf}$ at 5 K arrives at 24.7 MA cm$^{-2}$.

On the other hand, the strength of the vortex pinning of the GdBCO–LF + 20 mol% Gd$_2$O$_3$ nanocomposite films shown in the $J_c/J_c^{sf}$ dependence at 77 K with a magnetic field (figure 13(a)) turned out to be enhanced compared to those of the reference pristine YBCO–TFA films, and similar to the reported values on GdBCO–TFA + BHO nanocomposite films [39]. The GdBCO + 20 mol% Gd$_2$O$_3$ curve shows the typical smoothed field dependence that is commonly observed in the YBCO nanocomposites. Note that the curve for the GdBCO + 20 mol% Gd$_2$O$_3$ film is very similar to the YBCO + 10 mol% BZO nanocomposite films and much smoother than in the case of the pristine YBCO–TFA film. This demonstrates that the GdBCO + 20 mol% Gd$_2$O$_3$ films have enhanced vortex pinning, at least at the same level as the YBCO + 10 mol% BZO nanocomposites in films with similar thicknesses. The calculated $B^\ast$ ($J_c(B^\ast) = 0.9 J_c^{sf}$) reaches a value of $\sim$0.1 T, which is in the range of the values

Palau et al [64]. We investigated, therefore, if granularity could be at the origin of the reduced $J_c^{sf}$ values in our films. How percolative current blocking can be observed in thin films and how this influences the $J_c^{sf}$ values has been widely investigated by several authors. The existence of granularity can be experimentally identified by performing hysteresis loops at different maximum applied fields [63, 64]. Figure 9 displays a set of such hysteresis loop measurements with a maximum magnetic field of 8 T measured at 5 K. It is observed that the maximum value of the magnetization at the reverse branch appears approximately at an applied field of 0.4 T. For a single crystalline superconducting film, this would be expected at zero field. The displacement of the maximum value of the magnetization to higher fields is attributed to granularity effects. The magnetization peak appears when the return internal magnetic field at the grain boundaries is compensated by the applied field [65]. The obtained grain size is 0.5 μm, and the $J_c^G$ values for the GdBCO film measured in figure 9 by applying this method are: $J_c^G(5 K)\sim$ 40 MA cm$^{-2}$ and $J_c^G(77 K)\sim$ 3.3 MA cm$^{-2}$ (determined with the same kind of measurements at 77 K). These results show that, if the granularity could be avoided by optimizing the processing conditions, the performances of the GdBCO–LF films might be largely enhanced.

Figure 9. Hysteresis loops at different fields in a GdBCO–LF film grown with the flash-heating process showing a displacement of the maximum of the magnetization.
reported for the YBCO nanocomposites [41]. Finally, the analysis of the angular dependence of $J_c(\theta)$ and the isotropic collapse of the irreversibility line $H_{irr}(\theta)$ (figures 13(b) and (c)) has provided evidence of isotropic behavior in GdBCO–LF + 20 mol% Gd$_2$O$_3$ nanocomposite films, similar to the YBCO nanocomposites [38, 40, 41, 66, 68]. Also remarkable is the broadening of the peak at 90° ($H\parallel ab$), associated with defects that are effective pinning centers close to the $a-b$ plane and the vanishing of the peak at 0° ($H\parallel c$), associated with a loss of effectiveness of correlated defects parallel to the $c$-axis. We attributed both peak evolutions to the presence of a large density of SFs, as we have seen in figure 11, that favor the accommodation of vortices at a broader angle range around the $a-b$ planes and also cause a strain-driven break of the $c$-oriented twin boundary coherence [69].

The anisotropic behaviour of the nanocomposite films can be characterized by a field-independent anisotropy parameter $\gamma_{eff}$ when the anisotropic Ginzburg–Landau scaling behaviour of $J_c(\theta, H)$ at fixed temperatures is studied. As proposed by Blatter et al [70] and applied to REBCO films [68, 71, 72], the isotropic and anisotropic contributions to $J_c(\theta, H)$ and the irreversibility line $\mu_0H_{irr}(T)$ can be extracted from a plot of the effective field $H_{eff} = \varepsilon(\theta)H$, where $\varepsilon(\theta) = \left[\cos^2(\theta) + \gamma_{a+b}^2 \sin^2(\theta)\right]^{1/2}$ and $\gamma_{eff}$ is the mass anisotropy ratio [37, 38, 68, 72, 73]. In our case, the GdBCO–LF + 20 mol% Gd$_2$O$_3$ nanocomposite studied shows an effective $\gamma_{eff}$ value of $\sim$2.3 instead of the $\gamma_{eff} \sim$ 5–7 value obtained for pristine YBCO–TFA films [37, 38]. The $\gamma_{eff}$ value found for our GdBCO–LF + 20 mol% Gd$_2$O$_3$ nanocomposites is in the same range as YBCO nanocomposites.
suggesting that GdBCO nanocomposites display a similar vortex pinning landscape to YBCO nanocomposite films [38, 40, 41, 66, 68]. The origin of this reduction in $\gamma_{\text{eff}}$ by the addition of NPs has been associated with isotropic nanostrain and a novel depairing mechanism related to tensile strain fields in defects formed around the NPs (especially in CSD-grown films) [37, 38, 74]. Other authors have also considered the contribution of geometrical effects for sufficiently small [75], dirty-limit scattering and a change in coherence length anisotropy (discussed especially for PLD-grown films) [76].

4. Conclusions

We have shown that the preparation of high critical current density GdBCO thin films by CSD is challenging, requiring thorough optimization of the precursor solution formulation and the design of a new high temperature thermal process. The sensitivity of the GdBCO–TFA solutions to ambient humidity has led us to the development of a new LF solution to prepare GdBCO thin films by the CSD method. The developed GdBCO–LF solution solves the problem of reaching highly homogeneous films after the pyrolysis process. This novel solution avoids using a high concentration of TFA salts (which are highly hygroscopic), and the presence of propionic acid, while the use of TEA (coordination agents) helps to prevent water absorption that can cause film buckling formation and a degradation of the texture quality. Also, the presence of TEA provides the system with viscoelastic properties that help to release stress generated due to shrinkage during pyrolysis without causing inhomogeneity. The use of this new solution allows us to increase the rate of

Figure 11. (a) LAADF and (b)–(d) HAADF STEM images of a GdBCO–LF + 20 mol% Gd$_2$O$_3$ film grown with the flash-heating process at 820 °C. (a) A random distribution of 30–50 nm Gd$_2$O$_3$ NPs is observed with the matrix of the film causing the presence of SFs marked by white arrows in (b), (c) and (d). (d) Two superimposed Gd$_2$O$_3$ NPs.
homogeneous films after pyrolysis up to a 95% success rate. The growth of epitaxial GdBCO–LF films required us to design a new thermal profile, referred to as the ‘flash-heating’ process, with heating ramps of $\sim 600 ^\circ C \text{min}^{-1}$, to obtain full $c$-axis oriented GdBCO films. The superconducting properties of the resulting GdBCO–LF films are close to the best reported values so far. The $T_c$ reaches 92.6 K while the $J_c\text{sf}$ at 77 K reaches $\sim 1.5 \text{MA cm}^{-2}$. However, this $J_c$ value is still limited by granularity effects and, therefore, the flash-heating growth process should still be further optimized. The value of the $J_c\text{sf}$ at 77 K inside the grains has been estimated to be $\sim 5 \text{MA cm}^{-2}$ which suggests that there is still much room for improvement. The flash-heating process has also been shown to be a useful approach to grow epitaxial GdBCO + $\text{Gd}_2\text{O}_3$ nanocomposite films. These nanocomposite films show typical features already observed for the CSD YBCO nanocomposite films (enhanced nanostrain and a large concentration of SFs) and also improved superconducting properties as compared to pristine GdBCO–LF films reaching $T_{c,50} \sim 91.7 \text{K}$ and $J_c\text{sf}$ at 77 K $\sim 3.2 \text{MA cm}^{-2}$. The critical currents of the nanocomposites are, however, still limited by granularity effects, and so further efforts should be made in order to reach the highest performances.

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ORCID iDs
Pablo Cayado https://orcid.org/0000-0003-7303-6122

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