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YBa₂Cu₃O_{7-x} films with Ba₂Y(Nb,Ta)O₆ nanoinclusions for high field applications

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Abstract— Structural and transport properties of YBa₂Cu₃O_{7-x} films grown by pulsed laser deposition with mixed 2.5 mol.% Ba₂YTaO₆ (BYTO) and 2.5 mol.% Ba₂YNbO₆ (BYNO) double-perovskite secondary phases are investigated in an extended film growth rate, $R = 0.02 - 1.8$ nm/s. The effect of R on the film microstructure analyzed by TEM techniques shows an evolution from sparse and straight to denser, thinner and splayed continuous columns, with mixed BYNO+BYTO (BYNTO) composition, as R increases from 0.02 nm/s to 1.2 nm/s. This microstructure results in very efficient flux pinning at 77 K leading to a remarkable improvement of the J_c behaviour, with the maximum of the pinning force density $F_p(\text{Max}) = 13.5$ GN/m³ and the irreversibility field in excess of 11 T. In this range, the magnetic field values at which the F_p , is maximized varies from 1 T to 5 T being related to the BYNTO columnar density. The film deposited with $R = 0.3$ nm/s exhibits the best performances over the whole temperature and magnetic field ranges achieving $F_p(\text{Max}) = 900$ GN/m³ at 10 K and 12 T. At higher rates, $R > 1.2$ nm/s, BYNTO columns show a meandering nature and are prone to form short nanorods. In addition, in the YBCO film matrix a more disordered structure with a high density of short stacking faults is observed. From the analysis of the $F_p(H, T)$ curves it emerges that in films deposited at the high R limit, the vortex pinning is no longer dominated by BYNTO columnar defects, but by a new mechanism showing the typical temperature scaling law. Even though this microstructure produces a limited improvement at 77 K, it exhibits a strong J_c improvement at lower temperature with $F_p = 700$ GN/m³ at 10 K, 12 T and 900 GN/m³ at 4.2 K, 18 T.

Keywords: Artificial Pinning Centers; Ba₂Y(Nb,Ta)O₆ double perovskite, Pulsed Laser Ablation deposition, YBa₂Cu₃O_{7-x} epitaxial films

1. INTRODUCTION

The improvement of the current-carrying capability through the controlled introduction of material defects able to pin magnetic flux vortices, i.e., artificial vortex pinning centers (APCs), in superconducting

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3 REBa₂Cu₃O_{7-x} (REBCO, RE = Y or rare earths) films has attracted great interest in the last two decades from
4 both scientific and technological point of views. Several strategies have been successfully developed mainly
5 based on substrate surface modification, rare-earth substitution, inclusions of nanoscale secondary phases
6 with remarkable improvement of the critical current density, J_c , properties of REBCO films [1 - 4]. Among
7 them, one of the most studied and scalable methods is based on the incorporation of secondary phases
8 segregated within the REBCO matrix during the film growth stage. This was firstly demonstrated on YBCO
9 films by pulsed laser deposition (PLD) technique by the addition of BaZrO₃ and, since then, replicated with
10 many other Ba-based perovskites APCs and other film deposition techniques such as Metal-Organic
11 Chemical Vapour Deposition (MOCVD) and Chemical Solution Deposition with Metal-Organic salt
12 precursors (CSD MOD) [3 – 8] (a comprehensive review can be found in [9]). In PLD nanocomposite films,
13 secondary phases are typically incorporated as columnar or nanorod defects aligned along the YBCO c -axis
14 by a self-assembly process driven by strain minimization mechanisms [10]. This 1D-like feature has been
15 extensively proven to be very effective for J_c improvements in the high temperature LN₂ (80 – 60 K) range.
16 Nowadays, most of the REBCO coated conductor manufacturers have incorporated the APC technologies in
17 their production lines so that REBCO conductors with optimized performances at high temperature and
18 intermediate magnetic fields are available on the market [11]. More recently, the emerging interest in HTS
19 materials for nuclear fusion and high energy physics high field applications motivate new research activities
20 on REBCO in higher fields ($B > 13 - 20$ T) and lower temperature conditions ($T < 50$ K) [12 – 15].
21 However, at low temperature conditions REBCO has been poorly investigated so far and thus there is
22 insufficient understanding of the most suitable defect landscape, neither of the required optimum pinning
23 centres nor of the materials engineering needed to create them. Certainly, more in-depth studies are needed
24 in order to fulfill the lack of knowledge in the low temperature- high field regime.

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38 The first available data has shown that with the same approach of secondary phase additions, very
39 remarkable improvements in J_c performance can be achieved at low temperature down to 4.2 K [16 - 20]. It
40 appears that a high density of secondary phases can produce very effective secondary effect pinning centres
41 of a complex fine nature [10, 20]. At low temperatures, small sizes (with respect to the superconducting
42 coherence length, for YBCO at $T = 0$ K, $\zeta(0) \approx 0.3$ nm and 1 nm along c -axis or ab - plane, respectively
43 [10]), point – like, 0 D defects are expected to play a major role in the vortex pinning contribution, and so the
44 secondary effect pinning centres appear to produce this complex, very fine defect landscape. In fact, by
45 optimized MOCVD process, very fine BZO column size (≈ 3.7 nm) with dispersed Y₂O₃ nanoprecipitates
46 landscape can be developed in heavy doped Zr (15 mol.%) REBCO achieving the record values of $J_c = 12$
47 MA/cm² at 14 T or, equivalently, $F_p = 1.7$ TN/m³ [18]. Similar record performances ($F_p = 1.4$ TN/m³ at
48 17.5 T and 4.2 K) have been recorded for PLD SmBCO with 3.8 vol.% BaHfO₃ addition by low temperature
49 growth (LTG) method which allows the development of fan shaped columnar system and a high density of
50 low temperature effective random vortex pin points [17]. By the CSD method the successful incorporation of
51 very small nanoparticles (5 nm) has led to a large improvement in low temperature performances due to the
52 synergetic contribution of strain and core pinning by the nanoparticles themselves being their size close to
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3 the coherence length [21]. A possible origin of low temperature effective pin points for vortices have been
4 identified in local oxygen strain-induced non stoichiometry, cation disorder or Cooper pair density
5 depression localized at the YBCO/BZO nanorod interface [16, 22 - 25].
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8 In this paper, the mixed 2.5 mol.% Ba_2YTaO_6 (BYTO) and 2.5 mol.% Ba_2YNbO_6 (BYNO) double
9 perovskite secondary phases in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films deposited by PLD are investigated by varying the film
10 growth rate over two orders of magnitude $R = [0.02 - 1.8]$ nm/s. It is reported in previous works that mixed
11 BYTO + BYNO phases incorporated into the YBCO film matrix as dense and fine columnar system exhibit
12 very remarkable improvements in J_c behavior not only at 77 K but also in lower temperature down to 10 K
13 [26 - 29]. By combining structural investigations by XRD, TEM analyses and J_c transport measurements
14 carried out in a wide temperature and magnetic field ranges, two effective microstructural landscapes have
15 been identified. Slow deposition (low R) gives rise to a well-defined columnar system which is very effective
16 in the high temperature range. This contrasts with the fast limit (high R) in which splayed nanorods,
17 meandering of columns and high density of short stacking faults are promoted resulting in more effective
18 pinning at low temperature temperatures. These two defect populations are developed in the optimal mix in
19 the YBCO-BYNTTO nanocomposite film deposited at $R = 0.3$ nm/s. This film exhibits very dense columns
20 ($n_{\text{col}} \approx 2500 \mu\text{m}^{-2}$) corresponding to an equivalent magnetic flux density $B_{\text{eq}} = n_{\text{col}} \Phi_0 \approx 5.2$ T. Also the
21 BYNTTO columns have low diameters ($d_{\text{BYNTTO}} = 5 \pm 1$ nm) leading to remarkable performance over the
22 whole temperature and magnetic field range. At 77 K, $F_p = 13.5$ GN/m³ and an irreversibility field in excess
23 of 11 T, with maximum $F_p = 900$ GN/m³ at 10 K and 12 T. At higher rates, $R > 1.2$ nm/s, even though a
24 limited improvement in J_c properties at 77 K are observed, a valuable J_c improvement at lower temperature
25 with $F_p = 700$ GN/m³ at 10 K, 12 T and 900 GN/m³ at 4.2 K, 18 T is achieved. These results point the way to
26 yet further improvements at low temperature and high magnetic field conditions, namely by further tuning
27 and refining the YBCO nanocomposite growth conditions.
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42 2. EXPERIMENTAL

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44 YBCO-BYNTTO composite films were deposited using a composite target with nominal 2.5 mol.%
45 Ba_2YTaO_6 (BYTO) and 2.5 mol.% Ba_2YNbO_6 (BYNO) composition, by pulsed laser ablation (PLD)
46 technique using two excimer laser sources, XeCl and KF, emitting at wavelength $\lambda_L = 308$ and 248 nm,
47 respectively. The dependence of the YBCO absorption coefficient upon the laser wavelength induces
48 differences of about a factor 3 in the growth rate per laser pulse at the given laser source λ_L values, being the
49 smallest film growth at wavelength $\lambda_L = 308$ nm [30]. YBCO film growth rate has been further tuned by
50 changing the laser repetition rate in the range $f_L = [1, 15]$ Hz. The film growth rates, R , have calculated from
51 the actual thickness of films measured by atomic force microscopy after patterning and/or by TEM cross
52 sectional view. The calculated film growth rates span over two orders of magnitude from $R = 0.02$ nm/s to
53 1.8 nm/s. The nanocomposite target has been prepared by mixing and grinding the precursor oxides BaO,
54 Y_2O_3 , and Nb/Ta₂O₅ in stoichiometric quantities with pure YBCO powder and sintering in flowing oxygen at
55 950 °C. For all films depositions occurred at the same conditions of temperature (840 °C), oxygen pressure.
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3 The thickness of the films is in the range 150 – 230 nm. For only one film the thickness has been increased to
4 900 nm. Films are deposited on (001) SrTiO₃ single crystal substrate. The deposition process and target
5 preparation details can be found elsewhere [28, 31].
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8 All samples have been analyzed by X-ray diffraction techniques with a Rigaku SmartLab diffractometer
9 equipped with a 9 kW rotating anode and with a primary beam monochromator that grants CuK α 1 radiation.
10 The parallel beam geometry is used to record $\theta - 2\theta$ measurements and $\omega -$ scans across the (005)YBCO
11 peak, and by using a Eulerian-Cradler polar figures and φ -scans have been acquired. Lattice parameters have
12 been estimated by the Nelson-Riley extrapolation method assuming as uncertainty the error in the Nelson-
13 Riley linear regression fit [32].
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17 Critical current measurements were carried out on strips with defined geometry obtained after patterning
18 with the usual optical photolithographic procedures. The strip widths used for this study are 30 – 50 μ m.
19 Critical current is defined with the electric field threshold $E_c = 1 \mu$ V/cm. The critical current density (J_c) is
20 simply obtained dividing the critical current value by the cross-sectional area of the strip. Pinning force is
21 calculated as $F_p = J_c \times \mu_0 H$, while the irreversibility field values, H_{irr} , as the field above which the normalized
22 pinning force density $F_p/F_p(\text{Max})$ is below 10^{-2} . For the angular dependence of the critical current density
23 $J_c(\theta)$, the angle θ was defined as the angle between the magnetic field direction and the substrate normal
24 direction, i.e., YBCO $c -$ axis. Samples are mounted into two cryostats equipped with 12 T and 18 T
25 superconducting magnets. More details can be found in [31].
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31 For TEM measurements, cross-section and plan view lamellas were produced by focused ion beam (FIB,
32 FEI Dual Beam Helios NanoLab). High- and low-angle annular dark field scanning transmission electron
33 microscopy (HAADF STEM and LAADF STEM) imaging, STEM energy dispersive X-ray spectroscopy
34 (STEM EDX) mappings were carried out on both on an FEI Titan probe Cs-corrected ChemiSTEM [33] and
35 QU-Ant-EM “cubed” electron microscopes operated at 200 kV and 300 kV acceleration voltage respectively.
36 Some of STEM EDX mappings were carried out on a Tecnai Osiris TEM operated at 200kV equipped with a
37 “Super-X” EDX detector operated at 200 kV.
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45 2. RESULTS AND DISCUSSION

48 3.1 Structural analyses

49 The effect of the growth rate R spanning over about two orders of magnitude from $R = 0.02$ to 1.8 nm/s on
50 the resulting film microstructure has been firstly analyzed.
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52 As widely reported in previous works, BYNTO doping forms a dense a fine columnar system with BYNTO
53 phase segregated as columns aligned along the YBCO c -axis [19, 26, 27]. In Fig. 1 the cross-sectional view
54 of samples deposited at the lowest ($R = 0.02$ nm/s) and highest ($R = 1.8$ nm/s) limits of the investigated film
55 growth rate range are shown. At low values of R (Fig. 1a), well defined and straight BYNTO columns are
56 formed perfectly parallel to the film growth direction (corresponding to the YBCO c -axis). Columns are
57 grown from the STO substrate interface to the film surface across the entire film thickness. From the planar
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view investigation, the column diameter, d_{BYNTO} , and the density, n_{col} , have been accurately measured as $d_{\text{BYNTO}} = 12 \pm 2$ nm and $n_{\text{col}} = 540 \mu\text{m}^{-2}$, corresponding to an equivalent magnetic flux density $B_{\text{eq}} = n_{\text{col}} \Phi_0 = 1.1$ T (Φ_0 is the magnetic flux quantum).

As often reported, BYNTO columns are decorated by few Y_2O_3 nanoparticles (about 20 nm in size, fig. 1a right side and fig. 1b yttrium EDX map) [27, 28]. Figure 1b shows STEM EDX mapping, revealing that distributions of Ta and Nb elements are uniformly distributed within the columns and confirming BYNTO columns composition. Figure 1c demonstrates simultaneously acquired high-resolution HAADF and LAADF STEM plan view images showing the cross section of a BYNTO column. The BYNTO column is well faceted with semi-coherent interface with YBCO. The occurrence of misfit dislocations at the BYNTO/YBCO interface can be very easily identified through geometric phase analysis (GPA) map analysis producing local peaks in the strain distribution (see Fig. 1c, right image). Accumulation of strain is not revealed within the BYNTO column and YBCO matrix indicating that these dislocations, generated at the interface to accommodate the lattice misfit, are an effective mechanism for the elastic strain release. On the other hand, the dark sharp contrast in the HAADF STEM image around BYNTO nanocolumn (see Fig. 1c, left image) is consistent with a lower YBCO oxygenation localized at the interface region. A strain-induced local oxygen nonstoichiometry has been invoked to explain the reduction of the c -axis strain of YBCO lattice close the interface of YBCO/BZO nanocolumns [22, 34]. Although it provides an efficient strain relief mechanism, the oxygen deficiency in the YBCO layer surrounding the APC nanocolumns can lead to a local T_c depression. The overlap of nonstoichiometric YBCO layers, which easily results in samples with increasing doping levels, could be responsible for the observed progressive reduction in T_c typically observed in YBCO nanocomposite. A similar microstructure is recognized for samples deposited at increasing growth rates up to $R = 0.3$ nm/s [19], the main difference being related to the size and the density of the columns which get denser and finer as R increases. In addition, Y_2O_3 nanoparticle density shows an increasing trend with R together with a reduction in size (from ≈ 20 nm to 5 nm in film deposited at $R = 0.3$ nm/s) even though any quantitative estimates have not been carried out [28].

TEM investigations of the film deposited at $R = 1.8$ nm/s reveal a different microstructure as shown in Fig. 2. From cross sectional view (Fig. 2a), the presence of splayed nanorods and meandered columns uniformly distributed within the YBCO matrix are observed together with a high density of stacking faults. The presence of yttria in the form of small segregated nanoparticles is confirmed. Nanorods are preferentially aligned to the YBCO c -axis and exhibit an average length of about 50 nm. In addition, BYNTO nanocolumns meandering from the substrate to the film surface (one example is highlighted by yellow dotted path in Fig. 2a can be recognized. Stacking faults consist of an extra Cu-O chain inserted between two Ba-O planes along the YBCO c -axis resulting in a local variation of the stoichiometry ($\text{Y}_2\text{Ba}_4\text{Cu}_8\text{O}_{16}$, Y248 or Y124). This defect, created during the film growth stage in order to accommodate the strain along the c -axis, is promoted in extremely severe strain conditions as in CSD YBCO with APC nanoparticles or in pristine YBCO films close to the substrate interface region [35]. The presence of stacking faults have been reported often in previous works on YBCO with APC doping systems and BYNTO [26, 28,

36]. By comparing Figs 1a and 2a, an increase in the density of stacking faults with increasing R can be easily recognized. As can be seen in Fig. 2a, stacking faults extend even more than 50 nm and most of them are induced by the BYNTO nanorods being generated from, or terminated at, the BYNTO interfaces. On the other hand, very short stacking faults can be even observed as clearly seen in Fig. 2b. In that image, the diffraction contrast visualizes the strain in the sample as brighter contrast features localized around the short Y124 intergrowths and BYNTO nanocolumn. The chess plate-like contrast in the BYNTO nanocolumns corresponds to periodically spaced misfit dislocations. From plan view images the BYNTO nanorod/column density has been estimated as $n_{\text{col}} \approx 1530 \mu\text{m}^{-2}$, corresponding to $B_{\text{eq}} = 3.2$ T. The column diameter appears even smaller than the values reported for the other samples reaching a very remarkable size of $d_{\text{BYNTO}} = 3$ nm. However, some spread in the column diameter value has been observed with d_{BYNTO} up to 6 nm.

Fig. 3 shows ABF and LAADF STEM cross sectional images on a thicker YBCO-BYNTO layer. This film has been deposited at the intermediate rate $R = 1.2$ nm/s, increasing the film thickness up to about 900 nm in order to analyze the evolution of the defect landscape in thicker films. In Fig. 3a, a cross-section overview of the sample is reported from which the development of a very dense and columnar structure all over the film section can be recognized. Looking in more detail, it can be observed that this sample exhibits an intermediate character between lower and higher rate limits. In particular, there are bundles of columns that are partially interrupted at a certain film height (different from region to region) leaving some regions of the film cross section free of columnar structures. This feature can be an anticipation of the formation of nanorods instead of continuous columns observed for higher growing rates. The density of BYNTO columns remains rather constant across the film thickness. The presence of small yttria crystals decorating BYNTO columns or nanorods is still observed as confirmed by EDX map shown in Fig. 3b.

From the TEM investigations it is determined that the d_{BYNTO} size varies from about 12 nm, down to about 3 nm (see Table 1). As already reported in our previous work, d_{BYNTO} is affected by f_L [19] independently of the laser wavelength adopted for the film growth. This behaviour indicates that, under the present investigated growth conditions, the column size is mainly determined by the surface diffusion time $t \propto 1/f_L$. Adatoms within the spatial range $\sqrt{(D_S t)} \approx \sqrt{(D_S/f_L)}$, with D_S being the diffusion coefficient of BYNTO elements at the YBCO surface, will be able to migrate to the growing BYNTO nuclei before the new incoming materials arrive on the film surface. From that time on, the nuclei lateral growth will proceed only through bulk diffusion process, which is orders of magnitude slower than surface diffusion [10], thus BYNTO preferential growth along the c -axis will result. The dependence of d_{BYNTO} upon the deposition temperature, T_g , has often been reported for BaZrO₃ and BaHfO₃ APC systems [37, 38]. In those cases, an increase in column size was reported with T_g , which is consistent with the accelerated surface diffusivity of the elements due to increase in the diffusion coefficient D_S with temperature. Moreover, it can be observed that the column or rod diameters exhibit a similar value and same range of variability ($\approx 5 - \approx 15$ nm) indicating that this might be a general property of the Ba-based perovskite APC systems.

In Fig. 4a, the XRD θ - 2θ spectra recorded on films deposited at different growth rates are shown. As can be seen, all spectra reveal good c -axis oriented YBCO growth as determined by the presence of sharp YBCO

(00 l) peaks and without any traces of peaks related to other YBCO grain orientations. The presence of a minor peak centered at 34 ° suggests that the formation and segregation of crystallites of Y₂O₃ occurred during the growth. The presence of minor fraction of yttria inclusions in YBCO films is not surprising being widely reported in high quality YBCO films [39]. The calculated c -axis lattice parameters do not reveal any clear dependence with R , whose values range between 1.169 nm to 1.171 nm (\pm 0.001 nm) (see Table 1), similar to the values measured for pristine YBCO epitaxial films on STO substrates deposited in the same film growth rate range.

BYNTO particles grow cube-on-cube with respect to the YBCO lattice as recognized by the presence of only the (002) and (004) peaks in the θ - 2θ patterns. However, the (004) BYNTO peaks exhibit a broad and smeared structure as can be more clearly discernible in Fig. 4b. This structure clearly depends on the growth rate: at low R , an asymmetric peak at about 43.6 ° can be recognized with a broad low angle tail. The peak weakens with increasing R eventually disappearing or being incorporated in a broader band centered at about 43.2 °. Interestingly, (004) BYNTO is shifted to higher angles with respect to the bulk values (about 42.86 °, continuous line in Fig. 4b) of either BYNO or BYTO phases. Similar features were observed in a previous study on mixed niobate/cuprate Ba₄Y₂CuNbO_y secondary phase additions into YBCO films. In that case, the shift and the broadening of the peaks in the XRD pattern were attributed to the formation of Ba₂YNbO₆ with variable yttrium content [40]. By analogy, in the present work, the formation of Ba₂Y_x(Nb,Ta)_{2-x}O₆ ($0 \leq x \leq 1$) can be assumed, with some loss of yttrium responsible in the phase being responsible for the observed peak shift and the broadening feature due to the inhomogeneous distribution of the yttrium content in the BYNTO segregated particles. In this framework, the increasing Y loss induces a shift in the peak towards higher angle values. In Fig 4b, the positions of (002) peaks for BaNbO₃ and BaTaO₃ are also marked by dashed-dotted lines as reference for $x = 0$ limits [41]. As can be seen, the peaks in the case of films deposited at $R = 0.02$ and 0.1 nm/s are comprised within these limits, with the low angle side of the (004) reflections smeared over the whole angular range up to the BYNTO bulk value ($x = 1$) suggesting that an inhomogeneous distribution of Y into BYNTO particles incorporated within the YBCO matrix has been achieved during the film growth spanning the full $0 \leq x \leq 1$ range. From these features, at low R , considerable Y loss in BYNTO is derived being $x \approx 0$ the largest components. The increase in R hinders the tendency of the loss in yttrium as suggested by the shift of the band peak to lower angles approaching the $x \approx 1$ limit. The loss of Y can be justified on the basis of reduction of strain at the BYNTO/YBCO interface. The lattice misfit between YBCO and BYNTO along the c -axis can be calculated as $(3 \times c_{\text{BYNTO}} - 2 \times c_{\text{YBCO}})/(2 \times c_{\text{YBCO}}) = -0.083$, whereas the misfit with respect to BaNbO₃ (or BaTaO₃) is ≈ -0.065 (calculated as $(3 \times c_{\text{BYN(TO)}} - c_{\text{YBCO}})/c_{\text{YBCO}}$), thus a great benefit in terms of reduction of interfacial strain would derive by the Y release from BYNTO lattice. The resulting excess of Y likely causes dense Y₂O₃ nanocrystals to form, decorating the BYNTO columns in the samples.

3.2 YBCO dc transport properties

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3 In Fig. 5 the $J_c(H)$ curves measured at 77 K for YBCO-BYNT0 samples deposited at different growth
4 rates are shown. As can be seen, the growth rate mainly affects the in-field behaviour, rather than J_c self-field
5 values. All samples show improved performances with respect to pristine YBCO film. Only the sample
6 deposited at $R = 1.8$ nm/s (the upper limit of the investigated range) does not exhibit any valuable increase
7 over the whole magnetic field range. In the low growth rate range ($R \leq 0.3$ nm/s), $J_c(H)$ curves show a better
8 in-field behavior in the low field region with the occurrence of a marked plateau whose extension increases
9 with the growth rate from ~ 0.5 T to ~ 4 T for $R = 0.02$ nm/s and 0.3 nm/s, respectively. The irreversibility
10 field $\mu_0 H_{irr}$ largely increases reaching, for the sample at $R = 0.3$ nm/s, the record value of ~ 11 T. As already
11 pointed out, the J_c plateau can be related to the occurrence of the matching field effect, the result of a co-
12 operative action of the columnar system characterized by the very favourable and pinning-effective condition
13 in which each vortex line is individually pinned by a single BYNT0 column. This effect, whose extension is
14 proportional to the column density, has been already observed in BYNT0 films [27, 28]. Interestingly, the
15 thicker sample grown at $R = 1.2$ nm/s exhibits very similar magnetic field dependence if compared to the
16 sample grown at $R = 0.3$ nm/s, consistent with the similar BYNT0 column density revealed by TEM. This
17 trend is confirmed for increasing growth rates ($R = 1.4$ and 1.8 nm/s), where the low field plateau
18 progressively disappears and the J_c in-field behaviours weaken, becoming similar to pristine YBCO for $R =$
19 1.8 nm/s. As observed by TEM investigations, for these high rate values, BYNT0 is preferably assembled as
20 short splayed nanorods system, and this likely reduces the effective contribution to vortex pinning provided
21 by columnar systems when $\mu_0 H$ is parallel to the YBCO c -axis.

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33 The corresponding maximum of pinning force density, $F_p(\text{Max})$, with $F_p = J_c \times \mu_0 H$, values, plotted in Fig.
34 6a, increases from ~ 4 GN/m³, showed by pristine YBCO films, to 7.1 GN/m³ for 0.02 nm/s sample and up
35 to a plateau value of 12 – 13 GN/m³ showed in the rather wide R range from 0.1 up to 1.2 nm/s. This three-
36 fold increase with respect to the pristine YBCO confirms the effectiveness by BYNT0 related defects as
37 strong pinning sources at 77 K. In the low R range and up to $R = 0.3$ nm/s, the position of the maximum
38 pinning force value, $\mu_0 H_{F_p(\text{Max})}$, show a progressive increase and a close correspondence with B_{eq} calculated
39 by TEM for the BYNT0 column density, as can be seen very easily in Fig. 6a. This is a clear confirmation
40 that, in this R range, the pinning force mechanisms are dominated by the efficient interaction of vortices with
41 BYNT0 columnar system and thus can be ultimately tuned by the film growth rate as preliminarily reported
42 in a previous work [19]. The decrease in both $F_p(\text{Max})$ and $\mu_0 H_{F_p(\text{Max})}$ values observed in the higher rate limit
43 is consistent with the reduced vortex pinning capability of the columnar system with increased splaying and
44 the resulting loss of the matching field effect.

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53 Angular J_c curves, shown in Fig. 7, are also consistent with these results. Samples deposited with $R = 0.3$
54 and 1.2 nm/s exhibit very intense and broad bands centred at $\theta = 0^\circ$ ($H // c$ -axis) revealing the high efficiency
55 of the BYNT0 related defect landscape in the moderate and high field region (see Figs 7b and 7c for 3 T
56 and 5 T, respectively) which dominate the vortex pinning in almost the whole angular range (excluding the
57 regions around $\theta = \pm 90^\circ$ where ab -plane intrinsic pinning is active).

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60 On the other hand, samples deposited at lower R ($= 0.02$ nm/s is shown in Fig. 7) develop sharper peaks in

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3 $J_c(\theta)$ curves, clearly discernible even for magnetic field values much greater than the equivalent field B_{eq} .
4 The different behaviour can be attributed to the effect of the more splayed character of columnar structure
5 already starting for samples grown at $R = 0.3$ and 1.2 nm/s with respect to $R = 0.02$ nm/s, as already reported
6 in previous works on BYNTO and other APC systems [19, 42, 43]. As R is increased and the microstructure
7 moves from columnar towards splayed nanorods, the J_c peak coherently gets weaker as observed for the
8 sample at $R = 1.4$ nm/s.
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12 These results show that, at 77 K, the mixed BYTO+BYNO doping provide a robust pinning contribution
13 in a rather wide range of film growth rates between $R = 0.3$ and 1.2 nm/s, reproducibly improving J_c in both
14 moderate and high field regions through the occurrence of a matching field effect.
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17 The temperature behaviour of the J_c properties can be analysed in Fig. 8a and 8b in which the $J_c(H)$ curves
18 measured at 50 K and 10 K, respectively, are shown. As can be seen, as the temperature is reduced from
19 77 K, a strengthening of the J_c in-field performances of the samples deposited in the high rate limit is
20 observed. At $T = 50$ K, the $J_c(H)$ curve recorded for sample grown at $R = 1.4$ nm/s approaches the ones of
21 samples at 0.3 and 1.2 nm/s and, at $T = 10$ K, all the YBCO-BYNTO nanocomposite films in the high rate
22 limits, $R \geq 0.3$ nm/s, exhibit very similar performances achieving J_c values between 7.5 and 6.0 MA/cm² at
23 12 T. On the other hand, films deposited with lower growth rates show a worse magnetic behaviour with a
24 larger depression in J_c in the mid to high field region in both temperature conditions, 50 K and 10 K. In
25 particular, the $J_c(H)$ curves for the samples deposited at the lowest growth rate $R = 0.02$ nm/s largely overlap
26 the J_c recorded for pristine YBCO films.
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33 Further indications on the temperature behaviour of YBCO-BYNTO samples can be obtained from the
34 maximum of the pinning force density $F_p(\text{Max})$ plotted, in Fig. 6b, as a function of the temperature. As can
35 be seen, high rate samples ($R > 0.3$ nm/s) exhibit a sharp increase in $F_p(\text{Max})$, as the temperature is reduced,
36 resulting in higher $F_p(\text{Max})$ values for $T \leq 50$ K if compared with other samples. In the whole temperature
37 range inspected, the optimal pinning strength is achieved for the YBCO-BYNTO film deposited with $R =$
38 0.3 nm/s, achieving about 900 GN/m³ at 10 K and 12 T. For this sample, an extrapolated $F_p(\text{Max})$ at 4.2 K in
39 excess of 1 TN/m³ can be predicted, approaching the performance limits already reported for other APC
40 systems [17, 18, 44]. On the contrary, the sample deposited at the lowest investigated growth rate value
41 (0.02 nm/s) shows improved pinning performances only at 77 K, whereas for $T \leq 65$ K, $F_p(\text{Max})$ the values
42 are very close to the ones calculated for pristine YBCO down to 10 K, further supporting the notion that, in
43 this low rate conditions, the incorporation of BYNTO columns provides a limited benefit in the low
44 temperature flux pinning.
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52 The origin of this reduced effect of the temperature on the pinning efficiency can be ascribed to the
53 dominant pinning mechanism active in these films, the matching field effect. Similar evidence of weak and
54 limited temperature behaviour of the matching field-related improvement has been previously reported for
55 YBCO films with 5 mol.% BZO addition [31] having similar BZO n_{col} . Even in that case, the influence of
56 APC columnar defects at low temperatures was discernible only in a low magnetic field range close to the
57 B_{eq} . In this view, the higher $F_p(\text{Max})$ values at low temperatures, achieved by increasing R , can be only partly
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3 explained by the higher columnar density. In high rate YBCO-BYNTTO samples, it is a different
4 microstructure and pinning landscape which play an effective role in improving the pinning efficiency at
5 lower temperatures.
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8 A deeper insight can be gained with the analysis of Fig. 9a – 9c, where the pinning force density $F_p(H)$
9 curves are plotted for selected samples deposited with $R = 0.02, 0.3$ and 1.4 nm/s. $F_p(H)$ curves for pristine
10 YBCO films are also shown in Fig. 9a, for comparison. As can be clearly recognized in Fig. 8a, the low R
11 YBCO-BYNTTO film improves the F_p of the pristine sample at $T = 77$ K but, as T is reduced, the
12 improvements in F_p are limited to the field region close to $B_{eq} = 1.1$ T. This result, together with the
13 temperature independent maximum of F_p appearing at $\mu_0 H_{F_p(\text{Max})} = 0.8$ T, are a direct evidence of the
14 matching field effect. Thus, for this low growth rate sample two contributions to the vortex pinning can be
15 identified: one related to the presence of the BYNTTO columnar system, very efficient up to $\mu_0 H \approx B_{eq}$, which
16 is superimposed to a pristine YBCO-like contribution.
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19 The sample deposited at $R = 0.3$ nm/s shows the best F_p performance in the whole temperature and
20 magnetic field ranges. The $F_{p(\text{Max})}$ values are shifted to higher values approaching 5 T at lower temperatures
21 (50 and 30 K) which is close to the estimated n_{col} for this sample ($B_{eq} \approx 5.2$ T), indicating that even for this
22 samples the interaction of flux lines with the BYNTTO columnar system dominates the pinning force (Fig.
23 9b). However, in this case, differently from the low rate deposited film, the pinning force contribution from
24 BYNTTO do not produces a well defined peak in a limited range of H , but leads to an effective increase of F_p
25 in the whole magnetic field range investigated.
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28 Finally, for the YBCO-BYNTTO sample deposited at the highest growth rate $R = 1.8$ nm/s, even though the
29 effective contribution of the BYNTTO pinning centres is discernible by the remarkable improvement of
30 transport properties, the F_p curves are more similar in shape to pristine YBCO films (Fig. 9c). This can be
31 recognized in Fig. 10a and 10b, showing that, in both pristine YBCO and 1.8 nm/s grown YBCO+BYNTTO,
32 the F_p curves can be described by the usual temperature scaling law $F_p = A(T) f_p(h)$, with f_p a function of the
33 reduced magnetic field $h = H/H_{F_p(\text{Max})}$, $f_p(h) = h^\beta (1-h)^\gamma$ [45 , 46]. The scalability of the F_p curves implies that
34 a single mechanism of vortex pinning is active in the investigated temperature range. The same features are
35 recognized for sample deposited at $R = 1.4$ nm/s. On the contrary, for samples grown with $R \leq 1.2$ nm/s, the
36 F_p scaling law cannot be applied due to the presence of two pinning contributions with comparable strength
37 having different temperature dependences, as shown in Fig. 10c. Therefore, the introduction of the mixed
38 BYNO+BYTO secondary phases generates different vortex pinning effective defect landscapes depending
39 on the growth rates: at low rates a strong correlated pinning related to the columnar system is superimposed
40 on an isotropic mechanism; at high growth rates, the mechanism cannot be identifiable with BYNTTO
41 columns or c -axis correlated nanorods but with a more complex scenario related to the presence of BYNTTO.
42 The peculiar feature of this complex pinning landscape is its strong effectiveness at low temperatures.
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45 This is fully consistent with what has been observed by TEM investigations: by increasing R , BYNTTO
46 defects change from sparse and relatively large columns to denser and thinner columns with increased
47 density of decorating Y_2O_3 nanoparticles. By further increasing R increase, the BYNTTO columns start to form
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nanorods and meandered columns with extremely low size down to 3 nm, as well as an increased number of stacking faults. It is likely that these two defect landscapes are present in the optimal YBCO-BYNT0 nanocomposite film deposited at $R = 0.3$ nm/s, leading to a superior performances of that sample over the whole temperature and magnetic field ranges.

2. CONCLUSIONS

In this work, over the whole temperature range down to 4.2 K, the influence of the film growth rate, R , on the structural and J_c properties of YBCO epitaxial films with incorporated 2.5 mol.% BYTO and 2.5 mol.% BYNO double perovskite secondary phases have been investigated. It is found that the nanocomposite microstructure is strongly affected by the variation of the film growth rate within the range $R = 0.02 - 1.8$ nm/s. In particular, from TEM analyses, it was observed that in the low R limit the microstructure is characterized by straight BYNT0 columnar structure that switch to meandered and truncated nanorods in the opposite high rate limit, with the cross over value being between $R \approx 0.3 - 1.2$ nm/s. The different nature of the BYNT0 segregation is observed by XRD measurements which reveal a change in the shape and shift in the angle position reflection peak. A possible explanation for this feature of a reduction of strain at the BYNT0/YBCO interface, through Y loss into the BYNT0 lattice ($\text{Ba}_2\text{Y}_x(\text{Nb,Ta})_{2-x}\text{O}_6$ ($0 \leq x \leq 1$)) is proposed. The BYNT0 columnar microstructure results in very efficient in flux pinning at 77 K providing the chance of tuning the extension of the plateau in the $J_c(H)$ curves and, correspondingly, the maximum in the pinning force density by varying the film growth rate up to 0.3 nm/s. An F_p as high as 13.5 GN/m^3 and an irreversibility field in excess of 11 T is obtained in these films. The film deposited at a middle rate, $R = 0.3$ nm/s, exhibits the best performances over the whole temperature and magnetic field range, achieving the maximum $F_p = 900 \text{ GN/m}^3$ at 10 K and 12 T. From the analysis of the $F_p(H, T)$ curves, it is shown that in YBCO-BYNT0 films deposited in the high R limit a different vortex pinning is set up which is not dominated by BYNT0 columnar defects. Here, a microstructure characterized by BYNT0 nanorods and meandered columns together with short stacking faults is generated which, even though it produces a limited improvement in J_c properties at 77 K, it exhibits a strong J_c improvement at lower temperature with F_p values of 700 GN/m^3 at 10 K, 12 T and 900 GN/m^3 at 4.2 K, 18 T. This is a promising result in view of the development of REBCO based coated conductors for applications requiring high field conditions such as large magnets for nuclear fusion reactors and particles accelerators. Finally, as a general remark, this study points out that the complex defects landscape developed in nanocomposite YBCO with APCs requires complete temperature characterization of the J_c behaviour to understand the subtleties of the different operative pinning mechanisms in the obtained complex pinning landscape.

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Laser repetition rate (Hz)	Film growth rate (nm/s) \pm 10 %	d_{BYNTO} (nm)	$n_{\text{col}} (\mu\text{m}^{-2}) / B_{\text{eq}} (\text{T})$	T_c (K)	c_{YBCO} (nm) \pm 0.001 nm	FWHM (005) YBCO ω -scan
1	0.02	12 \pm 2	540/ 1.1	89.3	1.169	0.12 $^\circ$
5	0.1	8 \pm 1	960/ 2	89.9	1.17	0.12 $^\circ$
10	0.3	5 (*)	2500/ 5.2 (*)	89.2	1.169	0.13 $^\circ$
10	1.2	5 (*)	---/ 5.5 (*)	88.7	---	---
10	1.4	---	---	88.6	1.171	0.14 $^\circ$
15	1.8	3 - 6	1530 / 3.2	87.2	1.170	0.24 $^\circ$

Table 1. Summary of structural parameters on YBCO-BYNT0 obtained by TEM and XRD investigations: d_{BYNTO} = BYNT0 average column diameter, n_{col} = BYNT0 column density, $B_{\text{eq}} = n_{\text{col}} \Phi_0$ is the equivalent magnetic flux density. All values are calculated by plan view images unless marked by (*). Samples deposited by XeCl laser source are highlighted in gray.

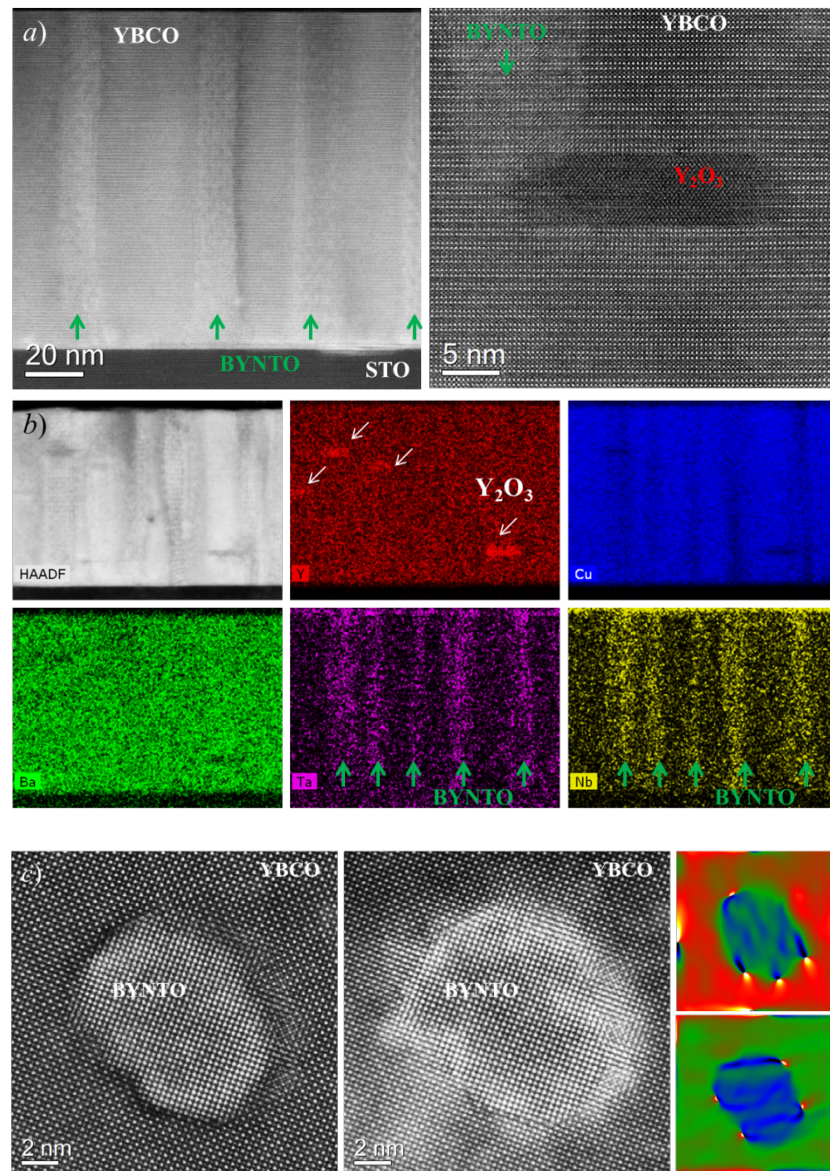


Figure 1. TEM investigations of YBCO-BYNT0 films deposited at growth rate $R = 0.02$ nm/s.

a) cross-section view. *Left panel:* HAADF STEM overview of the film showing the BYNT0 straight columns nucleated at the STO substrate and ended on the film surface (green arrows); *right panel:* high resolution HAADF STEM image showing BYNT0 nanocolumn (marked by green arrow) decorated by Y_2O_3 nanoparticle.

b) cross-section view: HAADF STEM image showing the mapped area together with elemental Y, Ba, Cu, Ta and Nb EDX maps confirming BYNT0 composition of the columnar structures and the Y_2O_3 composition of the decorating nanoparticles.

c) plan view. *Left and central panels:* HAADF and LAADF STEM Z-contrast images. Dark sharp contrast in the HAADF STEM image and bright halos in the LAADF image around BYNT0 nanocolumns are corresponding to the lower oxygenation on the interface and to the local strain, respectively. Interphase dislocations causing local strain can be well visualized by GPA maps (*right panel*).

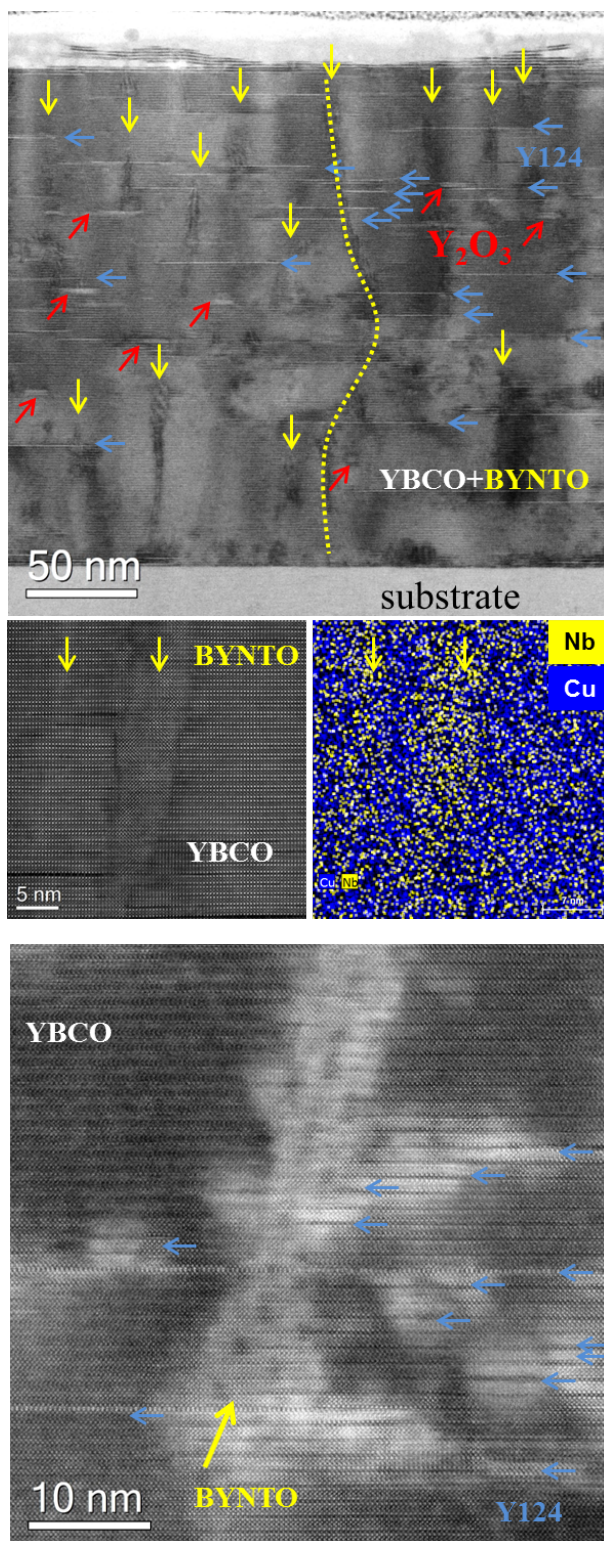


Figure 2. TEM investigations of YBCO-BYNTO films deposited at growth rate $R = 1.8$ nm/s.

a) Top panel: ABF STEM overview of the film showing BYNTO splayed nanorods (yellow arrows) and a BYNTO column meandering through the whole film thickness (yellow dashed line). The presence of Y_2O_3 nanoparticles and stacking faults are identified by red and blue arrows, respectively.; *bottom panel:* high resolution HAADF STEM image showing a BYNTO column in YBCO matrix and corresponding elemental Cu-Nb EDX map.

b) ADF STEM image showing the strain as brighter contrast features around the short Y124 intergrowths (blue arrows) and BYNTO nanocolumn. The chess plate-like contrast on BYNTO nanocolumn is produced by periodically spaced misfit dislocations with the brighter area corresponding to the dislocations strain and darker contrast to areas between the dislocations.

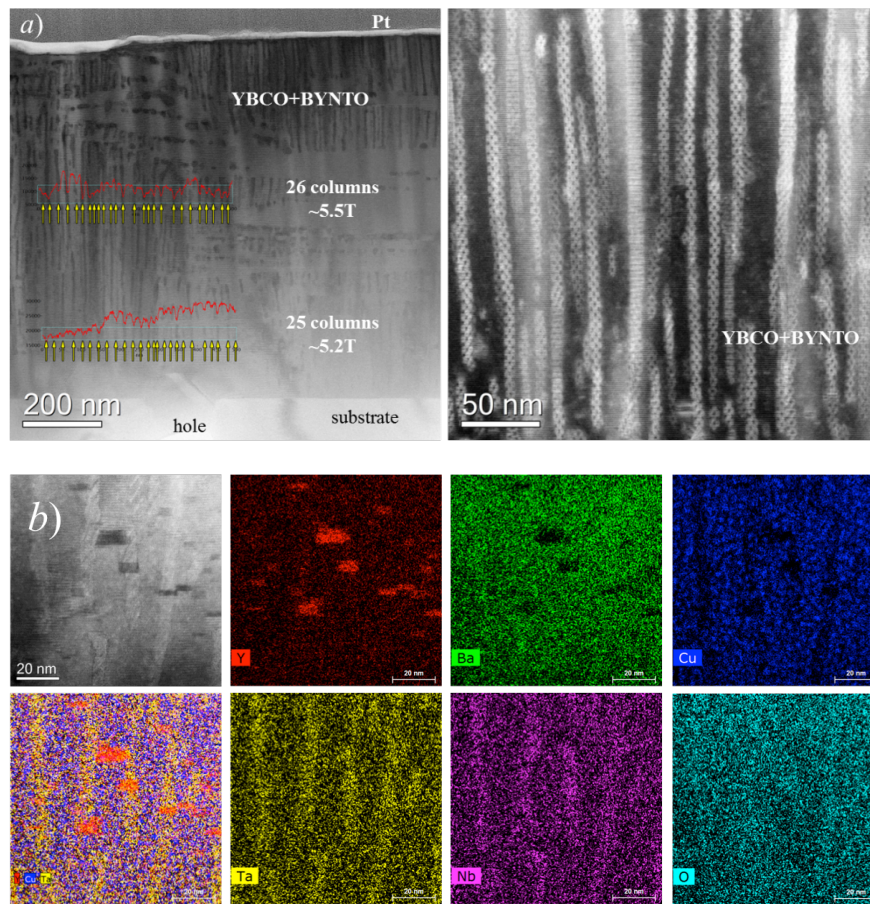


Figure 3. TEM investigations of YBCO-BYNTO films deposited at growth rate $R = 1.2$ nm/s.

a) Left panel: ABF STEM overview of the film showing the BYNTO columnar structures developed across the entire film thickness. Yellow arrows identify BYNTO columns in three different in which the estimate of B has been done; *right panel:* LAADF STEM image showing the bright diffraction contrast around BYNTO columns. Some of nanocolumns appearing truncated.

b) HAADF STEM image together with corresponding elemental EDX maps for Y, Ba, Cu, O, Ta and Nb confirm BYNTO nanocolumns and Y_2O_3 composition.

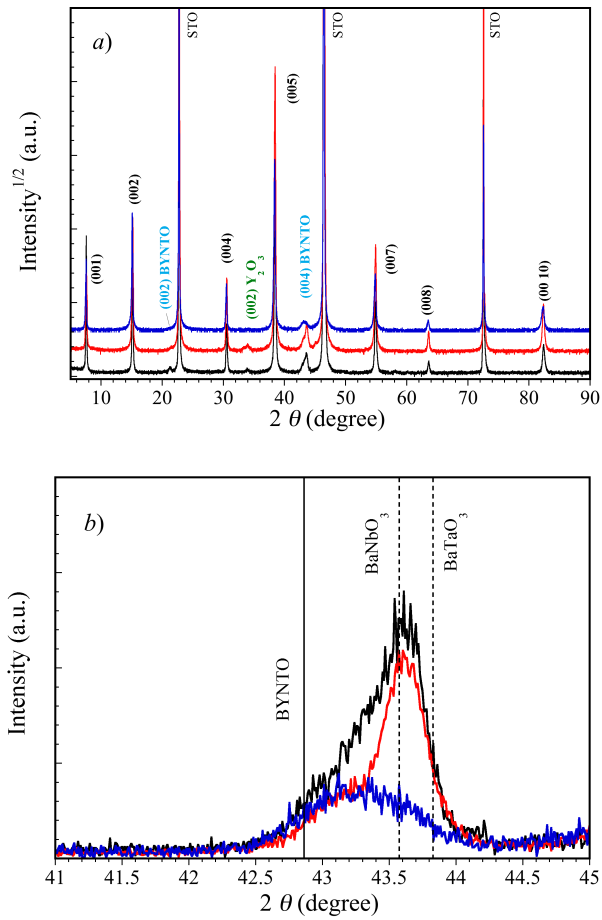


Figure 4. *a)* X-ray θ - 2θ diffraction patterns recorded for YBCO-BYNTO films deposited at different growth rate: $R = 0.02$ nm/s (black line), 0.3 nm/s (red line) and 1.8 nm/s (blue line). *b)* Detail of the (004) BYNTO peak. The continuous line marks the BYNTO bulk peak position whereas dashed lines BaNbO₃ and BaTaO₃ (002) peaks.

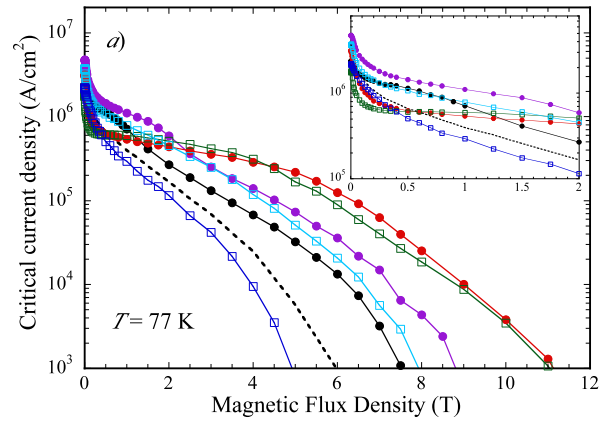


Figure 5. $J_c(B)$ curves collected at 77 K for samples deposited with growth rates $R = 0.02 \text{ nm/s}$ (black circles), 0.1 nm/s (purple circles), 0.3 nm/s (red circles), 1.2 nm/s (green squares), 1.4 nm/s (light blue squares), and 1.8 nm/s (blue squares). In the insert, details of the low field region are emphasized. Pristine YBCO sample curve is also reported for comparison (dashed line).

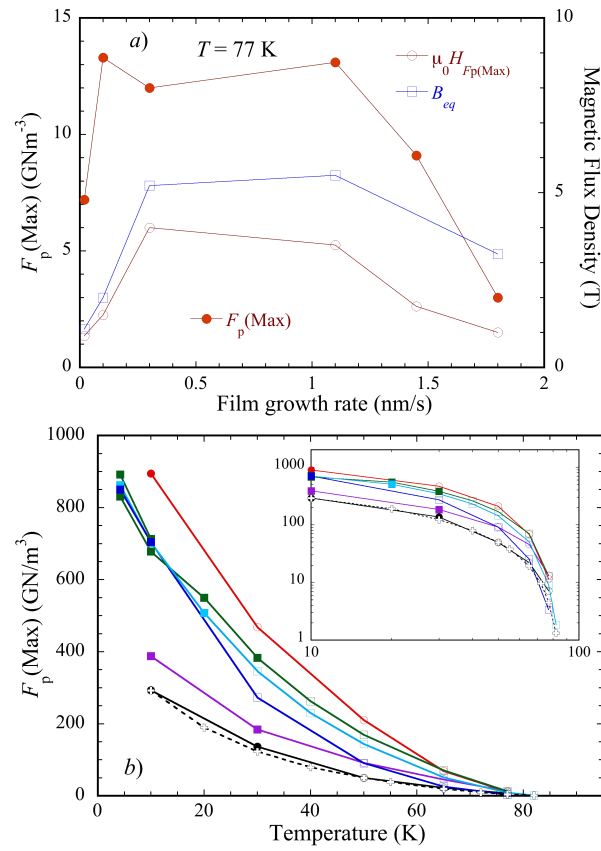


Figure 6. *a)* Maximum of the pinning force density $F_p(\text{Max})$ calculated from $J_c(B)$ curves at 77 K as $J_c \times \mu_0 H$ (red solid circles), magnetic field $\mu_0 H_{F_p(\text{Max})}$ corresponding to $F_p(\text{Max})$ (red empty circles), and equivalent magnetic field $B_{\text{eq}} = n_{\text{col}} \Phi_0$ calculated from TEM analyses (blue empty squares) as a function of the film growth rate; *b)* Temperature dependences of the $F_p(\text{Max})$ (empty symbols) for films deposited at different growth rates. At low temperatures, if the maximum of F_p was not reached, F_p values are calculated at 12 T (full symbols). Pristine YBCO sample curve is also reported for comparison (dashed line)

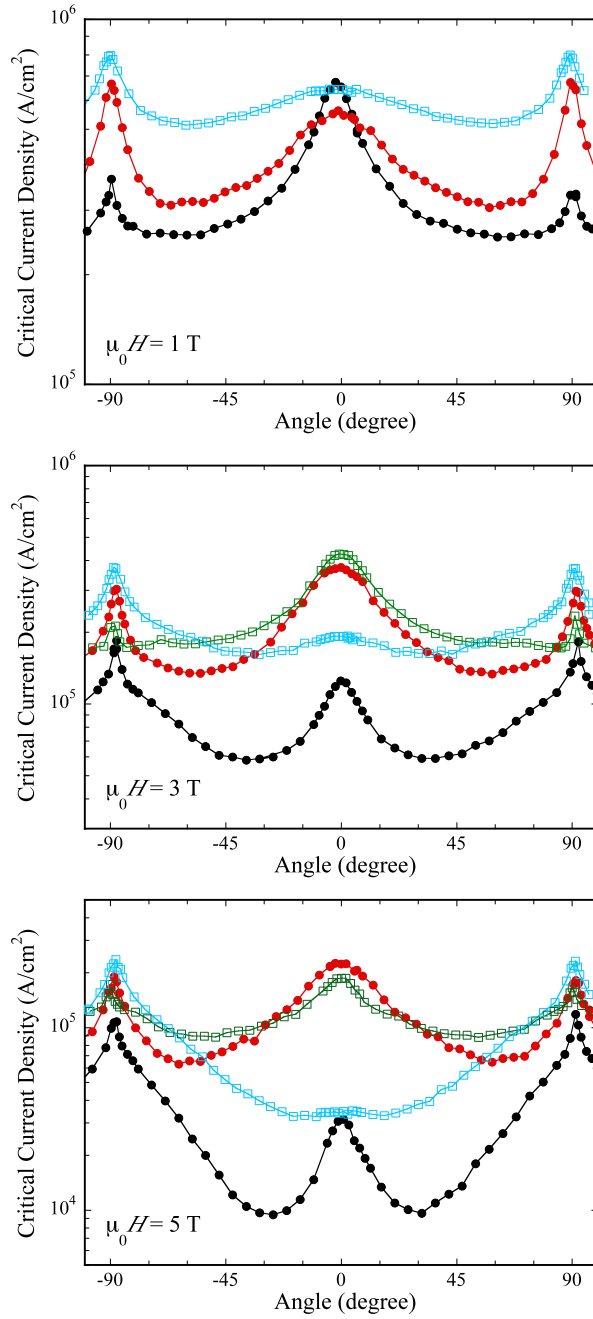


Figure 7. $J_c(\theta)$ curves dependence upon the $\mu_0 H$ direction and YBCO c -axis angle collected at 77 K for samples deposited with growth rates $R = 0.02$ nm/s (black circles), 0.3 (red circles), 1.2 (green squares), and 1.4 nm/s (light blue squares) for $\mu_0 H = 1$ T a), 3 T b), and 5 T c).

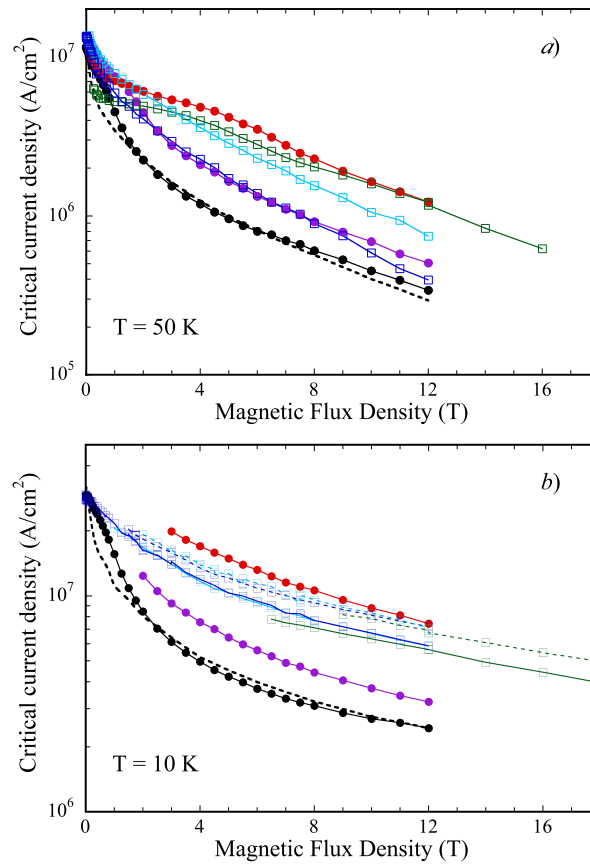


Figure 8. $J_c(H)$ curves collected at 50 K (a) and 10 K (b) for samples deposited with growth rates $R = 0.02 \text{ nm/s}$ (black circles), 0.1 nm/s (purple circles), 0.3 nm/s (red circles), 1.2 nm/s (green squares), 1.4 nm/s (light blue squares), and 1.8 nm/s (blue squares). Pristine YBCO sample curves are also reported for comparison (dashed lines). The dashed curves in b) refer to the $J_c(H)$ curves measured at 4.2 K.

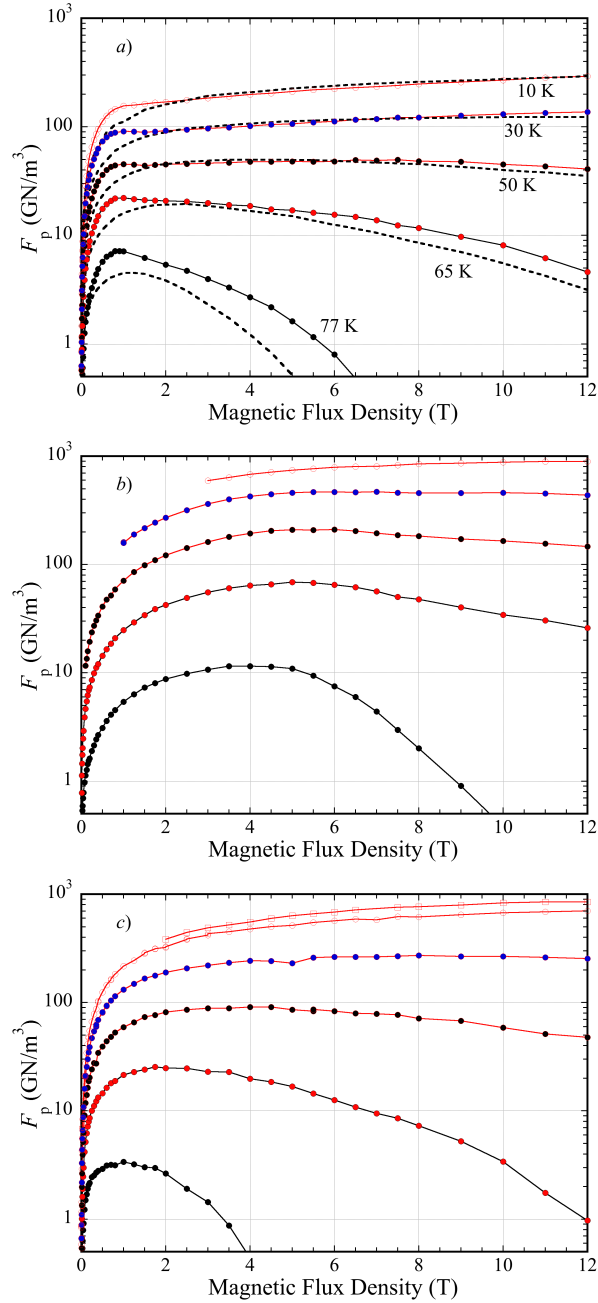


Figure 9. $F_p(H)$ curves collected at different temperatures 77 K, 65 K, 50 K, 30 K and 10 K for samples deposited with growth rates $R = 0.02$ nm/s (a), 0.3 (b), and 1.8 nm/s (c). In a), dashed lines refer to $F_p(H)$ measured on pristine YBCO film. In c), square symbols refer to $F_p(H)$ at 4.2 K.

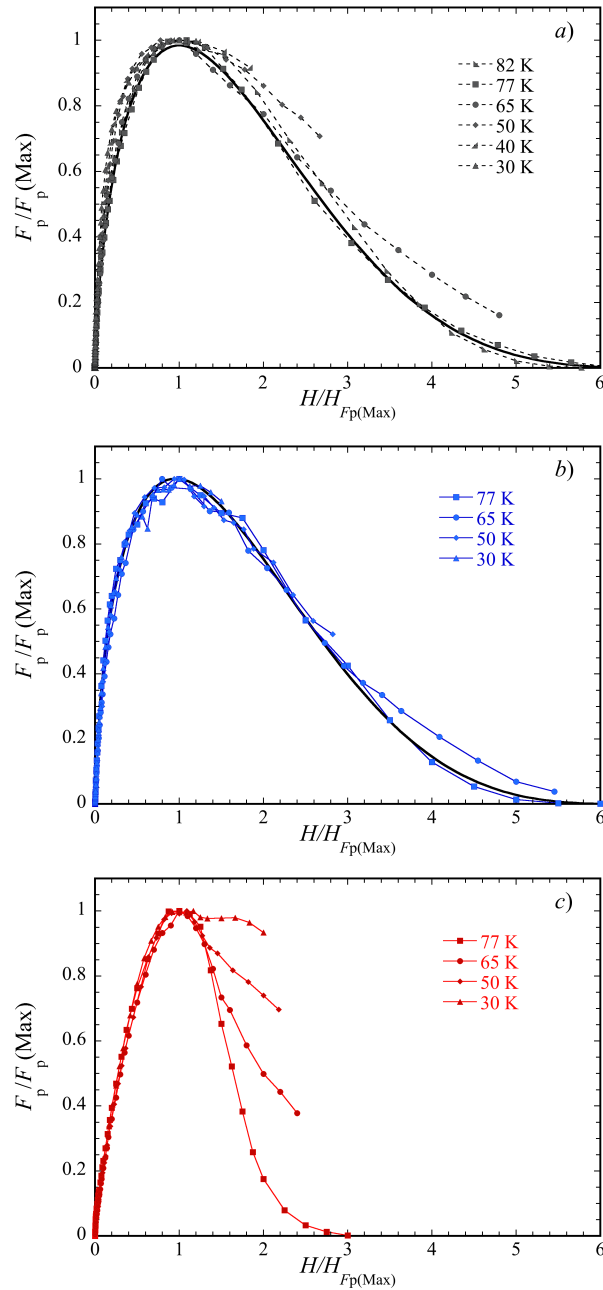


Figure 10. Scaling law for pinning force density $F_p(H)/F_p(\text{Max})$ curves collected at different temperatures for pristine YBCO film (a), YBCO-BYNT0 film deposited with growth rates $R = 1.8$ nm/s (b), and 0.3 nm/s (c). Continuous black lines are the fits with $f_p(h) = h^\beta (1-h)^\gamma$. Best fits are obtained with $\beta = 0.66$ (a), 0.61 (b) and $\gamma = 4$ (a), 3.5 (b). The scaling law in (c) cannot be applied