Axiotaxy in oxide heterostructures: preferential orientation of BaCeO₃ nanoparticles embedded in superconducting YBa₂Cu₃O_{7- δ} thin films

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1. Introduction

Texture analysis describes the statistical distribution of the orientation for the different grains forming a polycrystalline material. Several different types of texture can be identified: *random*, *epitaxial*, *fiber* and *axiotaxial* [1] alignment. These different types can be explained in relation to the degrees of freedom available to an ensemble of grains with such texture. For random oriented grains, no limitations are present and each grain has three orientation degrees of freedom (e.g. the three Euler angles). By contrast, an epitaxial texture fixes the orientation of each grain, resulting in zero rotational degrees of freedom. Intermediate between these two textures type are the fiber and the axiotaxial texture, which pin the orientation of one specific crystalline direction of the grain (e.g. a crystal's plane normal). As this eliminates two degrees of freedom, the fixed crystal normal acts as a rotational symmetry axis. These two textures differ from one another in terms of the driving force causing them. The fiber axis originates from a minimization of the surface energy by stacking closed-pack planes on top of the host substrate. The axiotaxial texture occurs due to a continuation of crystal planes through the interface between a grain and the underlying substrate for a polycrystalline thin film or between a precipitate and the surrounding matrix. As a consequence, the rotational axis of symmetry is always observed perpendicular to the substrate for a fiber texture, whereas the axiotaxial texture does not have this limitation.

Up to now, the axiotaxy texture has been observed in different materials mainly based on thin films of semiconductors such as in silicide/silicon, germanide/germanium interfaces investigated in previous works [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Interested readers are referred to the recent review papers by De Schutter et al. [13, 14]. This texture was also observed in MnP nanoclusters present in GaP thin films [15]. More recently, semiconductors on top of

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an oxide matrix [16] were demonstrated to have an axiotaxy grain texture. Nevertheless, no evidence of axiotaxy for oxide nanocomposite has been reported.

Aiming to enhance the properties of Cu-based superconducting materials, e.g. YBCO, large efforts have been made to understand and control the vortex anchorage phenomenon, which is a critical factor behind the superconducting performance [17, 18, 19, 20, 21]. As such, vortex pinning is currently one of the promising methodologies to enhance the superconducting capabilities [22, 23]. This technique is based on the blockage of the magnetic vortex movement by non-superconducting regions present in the YBCO structure.

Previous works demonstrated that incorporated secondary phases by *ex situ* (i.e. embedding preformed nanostructures within the superconducting matrix) [24, 25, 26] or *in situ* (i.e. generating controlled heterogeneities during the YBCO fabrication) [27, 28, 29] can act as incorporated vortex pinning centers which increase the critical currents and thus the superconducting performances [18, 30, 20, 31, 32, 33]. The additional structural strain in the YBCO, caused by the incorporation of the nanoparticles and the defects they induce within the material, is claimed to be mainly responsible for the vortex pinning enhancement [34, 35, 36, 37]. As such, the strain generated by these defects can be linked with the degree of alignment of these embedded phases with the surrounding YBCO [38, 39, 40]. In one case, randomly oriented embedded phases produced the desired lattice strain in the host structure due to the larger degree of incoherent interface, intensifying the superconducting properties of the nanocomposite. For epitaxially textured defects, the strain and the associated vortex anchorage phenomenon can be lower due to the better interplanar distance matching. Thus, the investigation of the crystal orientation of the grains forming the pinning centers is of crucial importance, aiming a better understanding and optimization of their effect on the vortex anchorage and the related superconducting performance.

The present research aims to demonstrate the existence of axiotaxial texture for oxide nanoparticles (BaCeO_3) embedded within an oxide matrix ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$). Texture studies on this functional material can lead, in ultimate instance, to the production of optimized thin films with enhanced properties, i.e. to the fabrication of superconducting thin films with better transport capabilities, which are of interest for high power applications through the scalable fabrication of long hybrid superconducting tapes. In addition, this work demonstrates the importance of in-depth texture analysis by proving the existence of an axiotaxial texture in an oxide heterostructure, having an impact in the investigation and fabrication of new oxide-based materials with anisotropic properties in other scientific and technology fields.

2. Experimental Section

Sample preparation

BaCeO_3 (BCO) nanoparticles embedded within the YBCO matrix were produced by the *ex situ* Chemical Solution Deposition (CSD) methodology based on a work recently published [28]: first, preformed CeO_2 nanoparticles (2-3 nm) were suspended into the YBCO chemical solution, followed by a thermal treatment to finally obtain the superconducting BCO-YBCO nanocomposite. The details are given hereafter.

CeO_2 nanoparticles were synthesized by a chemical methodology based on a modified and adapted polyol route [41], as described elsewhere [28, 42]. First, 2.25 mmol of Ce(IV) acetylac-

tonate were added to 12.5 mL of triethylene glycol (TREG), followed by a homogenization of the suspension in an ultrasonic bath. Then, the mixture was placed into a reflux system and thermally heated (1 °C/min) to 280 °C, keeping the temperature constant during 2h30min. After the dwell time, the nanoparticles were cooled down naturally to room temperature. The resulting CeO₂ nanoparticles were washed three times with a mixture of ethylacetate:ethanol 4:1 with the aim to remove the excess of TREG and byproducts of the reaction, while maintaining the superficial TREG acting as capping ligand. A centrifugation system was used to recover the nanoparticles from the cleaning solution. Finally, the nanocrystals were dispersed in 25 mL of absolute ethanol, obtaining a final CeO₂ concentration of 90 mM. The obtained nanoparticles were examined using Transmission Electron Microscopy. Results evidenced a high nanoparticle monodispersity without agglomerates and an average CeO₂ particle diameter of 2.6 nm, as reported elsewhere [42].

Nanocomposite 6% BaCeO₃-YBa₂Cu₃O_{7-δ} superconducting layer was fabricated via Chemical Solution Deposition (CSD) technique, following the route already reported [28]: A methanolic solution containing the compensated and stoichiometric Y, Ba and Cu trifluoroacetate chemical precursors [43] (total YBa₂Cu₃O_{7-δ} concentration of 1.5 M) was mixed 1:1 with the 90 mM solution of the preformed CeO₂ nanoparticles. The new solution (6 % of CeO₂/YBa₂Cu₃O_{7-δ}) was deposited on a LaAlO₃ (001) cubic single crystal substrate. The spin-coated thin film was thermally treated [28, 44], forming the epitaxial YBCO with embedded nanoparticles. During this second growth step, the CeO₂ nanoparticles react with the controlled excess of Ba²⁺ added to the chemical precursor solution to form BCO nanoparticles [45], which after the complete process can be found embedded within the YBCO matrix. Transmission electron microscopy proved the presence of embedded and coarsened BCO nanoparticles of ~20 nm, while transport measurements showed a J_c^{77K} of 4.3 MA/cm² [28, 42]. X-ray diffraction studies were employed to calculate the YBCO coherent crystal thickness, obtaining a value of 102 nm using the Williamson-Hall plot method already reported [46].

X-ray diffraction

The resulting samples were investigated by X-Ray Diffraction (XRD) for the crystal phase identification and characterization, as well as for texture analysis.

The XRD measurements were carried out at DiffAbs beamline, Synchrotron SOLEIL (Gif-sur-Yvette, France). The X-ray beam (available energies in the 4-23 keV range) is monochromatized ($\Delta E/E \sim 10^{-4}$) using a Si(111) double crystal monochromator; its second crystal can be bended in the sagittal direction for horizontally focusing. Two Si mirrors, Rh-coated and bendable in the longitudinal direction, are used for harmonics rejection and vertical focusing. The result at the sample position is an almost round shape X-ray beam of about 300 μm in size (full width at half maximum, FWHM). The beam divergence is $0.01^\circ \times 0.08^\circ$ (vertical $\times$ horizontal directions respectively), with a photon flux of several 10^{12} ph./s in the spot for most of the energies mentioned above. A 6-circles diffractometer in kappa geometry (angular resolution of the rotations is $\sim 0.002^\circ$) was used together with a point-detector. The slit system placed in front of the detector is motorized and consists of two pairs, including a scatter slit. The angular opening (acceptance) can be thus adapted depending on the type of measurement performed; it was $0.02^\circ \times 0.2^\circ$ (V $\times$ H) for the XRD measurements and $\sim 0.2^\circ \times 0.2^\circ$ for

measuring the texture (via pole figures). The X-ray beam energy was set to 8.048 ± 0.001 keV for all measurements.

The XRD data reported hereafter were recorded using two geometries of measurement. The standard $\theta - 2\theta$ scans (co-planar geometry) and the grazing incidence configuration resulted in the out-of-plane and in-plane patterns respectively, monitoring diffraction from planes parallel to the LaAlO_3 (LAO) substrate (i.e. $(0\ 0\ 1)_{\text{LAO}}$) or to the in-surface plane e.g. $((1\ 0\ 0)_{\text{LAO}})$ orientation. However, these measurement do not give reliable information for textured samples, being only sensitive to a narrow region in the reciprocal space. This limitation is overcome during a *pole-figure* measurement by rotating the sample around its surface normal (azimuth angle) and around the incident X-ray beam direction (elevation angle) (respectively the angles φ and χ) while keeping the diffraction angle 2θ fixed, thus probing the spatial orientation of the same $(h\ k\ l)$ plane of a specific crystal structure. In this way, the different orientations of the crystal plane under investigation can be brought into Bragg diffraction condition; the diffraction intensity scales with the number of grains (i.e. crystalline volume) with that specific orientation. The pole figures are presented in this paper with an equal-area projection, a logarithmic intensity gray-scale (white (low) to black (high intensity)) and are aligned in respect to the LAO orientation as displayed in Fig. 1, where we also define the angles φ and χ . These pole figures were analyzed using the *GUSTAV* [47] software package in order to reproduce the observed diffraction intensities in respect to the underlying textures.

Figure 1: The alignment (orientation using the diffractometer) of measured samples was chosen so that the LaAlO_3 diffraction poles of the single crystal substrate are located at the displayed positions.

3. Results and discussion

The aim of this paper is to report the existence of axiotaxial-oriented grains of BaCeO_3 within a superconducting YBCO thin film, illustrating the importance of detailed texture analysis for this kind of promising nanocomposite materials. In fact, an axiotaxial texture has never been reported before for oxide nanomaterials embedded in a second oxide structure. This is mostly due to the limited area (and number of grains) analyzed when using electron microscopy

based techniques for texture analysis. The changes in their respective crystalline orientation in the case of complex textures might mislead towards a polycrystalline interpretation. To this end, a set of in- and out-of-plane $\theta/2\theta$ measurements were first performed on a sample without nanoparticles embedded, obtaining a clear image of all crystal structures present in the samples which are not originating from the BCO-grains. Thereafter, the same measurements were performed on the sample with BaCeO_3 nano-inclusions. Finally, a selected number of pole figures were acquired at specific 2θ angles of the most intense BaCeO_3 diffracting planes, determining the preferential texture of these embedded nanoparticles.

Figure 2: (a) Out-of-plane $\theta/2\theta$ XRD (8.048 keV) of the reference YBCO sample, taken at $\chi = 0^\circ$. The epitaxial $(001)_{\text{YBCO}}// (001)_{\text{LAO}}$ growth was verified. (b) Epitaxial $(010)_{\text{YBCO}}// (010)_{\text{LAO}}$ and $(100)_{\text{YBCO}}// (010)_{\text{LAO}}$ growth was proved, together with the indication of a secondary orientation where $(001)_{\text{YBCO}}// (010)_{\text{LAO}}$ (YBCO-AB) and the tertiary $(103)_{\text{YBCO}}// (010)_{\text{LAO}}$ (YBCO-AB'). (c) X-ray diffraction pattern of the 6% BaCeO_3 -YBCO nanocomposite. Note the logarithmic intensity scale in all these measurements. (d) Scheme of the different YBCO growth orientations: the main YBCO-C (c-axis normal to the surface) and secondary YBCO-AB and YBCO-AB' types are represented.

Texture analysis

The phase composition and texture of the YBCO without any artificial secondary phase embedded was used as a reference measurement. Firstly, the out-of-plane (Fig. 2(a)) and in-plane (Fig. 2(b)) XRD patterns were acquired, identifying the main crystallographic phases and orientations. The YBCO and the LaAlO_3 substrate structures were clearly identified in both diffractograms. The Bragg signals corresponding to the presence of BaF_2 ($2\theta = 27.8^\circ$ (200), 42.3° (220)) as impurity were also found [48]. The most intense YBCO orientation was identified as $(001)_{\text{YBCO}}// (001)_{\text{LAO}}$ & $(010)_{\text{YBCO}}// (010)_{\text{LAO}}$ (YBCO-C) from respectively the out-of-plane and in-plane scan. However, due to the pseudo-tetragonal structure of YBCO, this orientation showed a $\varphi=90^\circ$ twinned disposition ($(001)_{\text{YBCO}}// (001)_{\text{LAO}}$ & $(100)_{\text{YBCO}}// (010)_{\text{LAO}}$) because of the small difference between the a (0.3821 nm) and b (0.3887 nm) crystal cell parameters [49, 50]. In practice, both directions can be considered as equivalent, thus considering the YBCO structure as pseudo tetragonal. A secondary growth orientation, denoted as YBCO-AB, was characterized by probing the YBCO c -axis visible in the in-plane scan (i.e. $(001)_{\text{YBCO}}// (010)_{\text{LAO}}$), which is possible when the $a(b)$ -axis is perpendicular to the substrate: $(100)_{\text{YBCO}}// (001)_{\text{LAO}}$ or $(010)_{\text{YBCO}}// (001)_{\text{LAO}}$. A third YBCO orientation is also detected having the (103) and (206) YBCO diffracting planes in the in-plane scan. Thus, the YBCO-AB' orientation is related with the YBCO-AB by a rotation of 45° around the $(0\ 0\ 1)_{\text{LAO}}$ pole: $(010)_{\text{YBCO}}// (001)_{\text{LAO}}$, $(001)_{\text{YBCO}}// (011)_{\text{LAO}}$. Differences of the peak intensity for the different diffracting planes proved that the majority of the YBCO has the c -axis perpendicular to the surface (YBCO-C), with the YBCO-AB and YBCO-AB' as minority orientation. Figure 2(d) represents schematically these three identified orientations of the YBCO on the LAO substrate.

Hereafter, the same approach was used to investigate the phase composition and texture of the nanocomposite formed by the BCO nanoparticles embedded in the oxide YBCO matrix. Fig. 2(c) shows the out-of-plane diffraction pattern, which was similar to the YBCO reference sample, with the expected epitaxial $(001)_{\text{YBCO}}// (001)_{\text{LAO}}$ growth. In addition, the crystalline cubic BCO structure of the embedded particles was evidenced by the extra diffraction peaks situated at $2\theta = 28.7^\circ$ (110), 40.05° (200) and 59.4° (220) (note the very low intensity of these peaks), assigned after comparing with a reported BCO structure (PDF card BaCeO_3 : 01-089-8272). The preferential orientation of these oxide nanoparticles was further investigated by pole figures recorded at an angle corresponding to the diffraction peaks situated at 2θ of 28.7° and 40.05° , which are the highest-intensity diffracting planes of the BCO phase.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ - BaCeO_3 pole figure analysis

The recorded pole figures, displayed in figure 3(a) and 4(a), clearly show several features indicating non-random orientation of the embedded BCO particles. The intensity distribution on circular trajectories indicate the presence of fiber or axiotaxial texture. Intense local spots situated along these circular features indicated various types of epitaxial alignment which we will address after discussion of the circular features.

Identification of the axiotaxial components. The circular features can be distinguished in two groups: the most intense circles were concentric, with the center of rotation coinciding with the normal to the substrate, $(0\ 0\ 1)_{\text{LAO}}$ plane (figure 3(b) and 4(b)), whereas a second group with lower intensity can be found with a center at the LAO $\{100\}$ ($\chi = 90^\circ$, $\varphi = 0, 90, 180, 270^\circ$;

Figure 3: Pole-figure measured at $2\theta = 29.5^\circ$ of the $(1\ 1\ 0)_{BCO}$ plane: (a) $(110)_{BCO}$ raw pole figure. (b) $(110)_{BCO}$ concentric axiotaxy. (c) $(110)_{BCO}$ off-normal axiotaxy. (d) $(110)_{BCO}$ off-normal axiotaxy.

Table 1: Identification of axiotaxial features for both recorded pole figures, represented in Fig. 3 & 4.

Preferred alignment	Resulting angle of circular features		Color in Fig. 3 & 4
	$(1\ 1\ 0)$ diffraction	$(2\ 0\ 0)$ diffraction	
$(0\ 0\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	45°	$0, 90^\circ$	yellow
$(1\ 1\ 0)_{BCO} // (0\ 0\ 1)_{LAO}$	$0, 60, 90^\circ$	54°	green
$(2\ 1\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	30°	45°	blue
$(1\ 1\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	35°	66°	red

Figure 4: Pole-figure at $2\theta = 41.05^\circ$ of the $(2\ 0\ 0)_{BCO}$ plane: (a) $(200)_{BCO}$ raw pole figure. (b) $(200)_{BCO}$ concentric axiotaxy. (c) $(200)_{BCO}$ off-normal axiotaxy. (d) $(200)_{BCO}$ off-normal axiotaxy.

figure 3(c) and 4(c)) or the LAO $\{110\}$ ($\chi = 90^\circ$, $\varphi = 45, 135, 225, 315^\circ$; figure 3(d) and 4(d)). This latter group suggested that the grain texture is not fiber, since only concentric circles would appear in this case, pointing towards an axiotaxial disposition of the BCO grains in the YBCO structure.

To explain the observed features as axiotaxy, it suffices to first identify the axis of rotation for the diffracting grain and subsequently verify if this axis of rotation allows plane continuation through the interface between the BCO and its surrounding. Table 1 summarizes the identification of the axiotaxial features observed in the pole figures (Fig. 3 & 4) and is detailed in the following.

The radius of the circular features ($\chi = 0^\circ$) is indicative of which crystal plane normal is

the axis of rotation. As such, the $(110)_{BCO}$, $(001)_{BCO}$, $(112)_{BCO}$ and $(111)_{BCO}$ plane normals can explain all concentric features for both pole figures when taken as axes of rotation, as indicated by the simulated curves in the Fig. 3 & 4. Therefore, the identified BCO planes were found to be preferentially parallel to the $(001)_{YBCO-C}$, since both structures presented the same orientation.

In addition, the exact same circular radii were present for those features with an off-normal axis of rotation, and are thus explained with the same BCO planes as axis of rotation with two in-plane orientations ($\chi = 90^\circ$) of this axis instead of being perpendicular to the substrate normal ($\chi = 0$). These two in plane orientations are related with each other by a 45° rotation of φ around the surface normal ($(001)_{LAO}$). Therefore, the two in-plane orientations were parallel to the $(001)_{YBCO-AB}$ and $(001)_{YBCO-AB'}$. Hence, the BCO planes forming the axis of rotation resulted to be parallel to the $(001)_{YBCO}$ plane, independently on its disposition with respect to the substrate.

The physical origin of the axiotaxial texture is related to a continuation of the crystallographic planes across the interface with a low mismatch, and in this case, between the YBCO and the BCO grains independently on their orientation around the rotation axis (Fig. 5a). We have found that this condition is fulfilled for all observed axiotaxial features described here. In order to simplify the explanation, we give here the example of the plane continuation for $(001)_{BCO} // (001)_{YBCO}$ orientation. Figure 5b shows the BaO plane continuation (at scale) for a 20 nm BCO nanoparticle surrounded by a YBCO matrix. The similar BaO interplanar spacing ($4.377\text{\AA}$ in the BCO crystal and $4.298\text{\AA}$ & $7.386\text{\AA}$ in the YBCO lattice) facilitates the plane continuation with a mismatch less than 1%. Thus, by extending the crystallographic structure along the interface, matching will occur after 3 YBCO and the corresponding 9 BCO cells (33 % of matching occurrence), producing the systematic continuation of two matching BaO planes across the interface (Fig. 5c). Additionally, we should note that the YBCO matrix accommodates the stacking faults to decrease the strain associated to these lattice mismatches.

A similar approach was done for the other BCO axis of rotation to study the crystallographic plane continuation from the embedded grains towards the matrix, always referred to the continuation of BaO planes and not to secondary matching possibilities which would favor even more the axiotaxial texture. Results proved that more than 30% of the BaO planes from the YBCO crystal structure continue across the interface to the BCO grains. Table 2 reports the overview of the mismatch and continuation frequency of the BaO planes for the distinct BCO grain orientations observed.

Figure 5: (a) The continuation of crystalline planes, characteristic of the described axiotaxial texture, occurs across the interface independently on the orientation of the BCO grains respect to the rotation axis. (b) For the $(0\ 0\ 1)_{BCO} // (0\ 0\ 1)_{YBCO-C}$ orientation, some BaO planes continue from the BCO grains (orange) to the YBCO (blue) matrix, as represented (at scale) for an average 20 nm BCO nanoparticle. (c) A closer look revealed some BaO and secondary atomic planes continuation through the interface, favoring the axiotaxial orientation. (d) Identification of the crystallographic planes (green) perpendicular to the rotation axis. To facilitate the understanding of the $BaCeO_3$ crystal orientation, the unit cell is also represented (blue).

Table 2: Mismatch and periodicity of the BaO-BaO plane continuation between the YBCO and BCO grains. The mismatch is averaged for all the possible BaO planes matching along 100nm of interface. Other crystallographic planes matching at the interface are also possible.

Grain orientation	BaO plane d-spacing		% of BaO_{YBCO} planes across the interface	Average mismatch
	BCO	YBCO		
$(001)_{BCO} // (001)_{LAO}$	4.377 Å	4.298 Å & 7.386 Å	33	0.088 %
$(110)_{BCO} // (001)_{LAO}$	3.095 Å	4.298 Å & 7.386 Å	32	0.077 %
$(111)_{BCO} // (001)_{LAO}$	2.527 Å	4.298 Å & 7.386 Å	36	0.045 %
$(211)_{BCO} // (001)_{LAO}$	1.787 Å	4.298 Å & 7.386 Å	50	0.023 %

Epitaxial features. Both pole figures (Fig. 6) also show local epitaxial spots with high diffraction intensity, situated at specific locations along the axiotaxy pattern (i.e. for specific rotation angles around the axiotaxy axis). They can be explained by considering the possibility of *double axiotaxy*. An individual BCO grain with a specific axiotaxial orientation in respect to a YBCO host lattice (e.g. the $(0\ 0\ 1)_{BCO} // (0\ 0\ 1)_{YBCO-C} // (0\ 0\ 1)_{LAO}$ axiotaxial condition), still has a degree of freedom around the axiotaxial rotation axis. As a consequence, it is not unlikely that a BCO-grain crystallizes at the border of two different-oriented YBCO grains (e.g. between the majority YBCO-C and a minority YBCO-AB grain). Such a grain can be expected to "select" or "lock in" at a preferred rotation angle around the axiotaxy axis, when this angle results in a favorable plane alignment between the BCO particle and both neighboring YBCO grains (e.g. $(0\ 0\ 1)_{BCO} // (0\ 0\ 1)_{YBCO-C} // (0\ 0\ 1)_{LAO}$ and $(1\ 0\ 0)_{BCO} // (0\ 0\ 1)_{YBCO-AB} // (1\ 0\ 0)_{LAO}$). This would result in a fixed orientation of the BCO grain, i.e. an epitaxy-like orientation, which we refer to as a "double axiotaxy" due to its orientational origin. A total of seven different double axiotaxies could be observed in the measured pole-figures, as highlighted in figure 6 and listed in table 3, explaining all of the observed high intensity spots along the axiotaxy lines.

4. Conclusions

This study reports an axiotaxial texture in an oxide heterostructure. Pole figures, recorded using synchrotron X-ray diffraction, allowed to study the $BaCeO_3$ grain texture when embedded into an epitaxial $YBa_2Cu_3O_{7-\delta}$ superconducting matrix. The data analysis revealed a preferential axiotaxial orientation of the BCO grains having the $(0\ 0\ 1)_{BCO}$, $(1\ 1\ 0)_{BCO}$, $(2\ 1\ 1)_{BCO}$ and $(1\ 1\ 1)_{BCO}$ crystallographic planes parallel to the $(0\ 0\ 1)_{YBCO}$. In addition, the YBCO crystal growth orientation presented one out-of-plane and two secondary in-plane preferential orientations with respect to the $(0\ 0\ 1)_{LAO}$ sample substrate, consequently defining the three distinct rotation axis directions of the axiotaxial texture. As a consequence, some of the epitaxial features found in the pole-figures correspond to a double-axiotaxial disposition, i.e. a BCO crystal satisfying at the same time the conditions related to two differently oriented YBCO grains, being thus locked in a preferred orientation around the axiotaxial rotation axis.

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Figure 6: BCO grains can satisfy multiple axiotaxial conditions at the YBCO grain boundaries. The seven individual components of the resulting epitaxy are displayed (various symbols) in this figure and tabulated in the table 3.

Table 3: Overview of the observed “double axiotaxy” (i.e. which satisfy multiple axiotaxial conditions). Due to the symmetry of the LAO substrate and the pseudo-tetragonal YBCO, all h and k indexes can be interchanged. Note that α_1 & α_2 are rotated by 45° around $[0\ 0\ 1]_{LAO}$ due to the angles between YBCO-AB and YBCO-AB’ (similar for β and γ).

Symbol (Fig. 6)	YBCO-C axiotaxy	YBCO-AB axiotaxy	YBCO-AB’ axiotaxy
α_1 (●)	$(0\ 0\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	$(1\ 0\ 0)_{BCO} // (1\ 0\ 0)_{LAO}$	$(1\ 1\ 0)_{BCO} // (1\ 1\ 0)_{LAO}$
α_2 (▼)	$(0\ 0\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	$(1\ 1\ 0)_{BCO} // (1\ 0\ 0)_{LAO}$	$(1\ 0\ 0)_{BCO} // (1\ 1\ 0)_{LAO}$
β_1 (●)	$(1\ 1\ 0)_{BCO} // (0\ 0\ 1)_{LAO}$	$(-1\ 1\ 0)_{BCO} // (1\ 0\ 0)_{LAO}$	-
(equivalent)	<i>idem</i>	$(0\ 0\ 1)_{BCO} // (1\ 0\ 0)_{LAO}$	-
β_2 (▼)	$(1\ 1\ 0)_{BCO} // (0\ 0\ 1)_{LAO}$	-	$(-1\ 1\ 0)_{BCO} // (1\ 1\ 0)_{LAO}$
(equivalent)	<i>idem</i>	-	$(0\ 0\ 1)_{BCO} // (1\ 1\ 0)_{LAO}$
γ_1 (●)	$(1\ 1\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	$(1\ -1\ 0)_{BCO} // (1\ 0\ 0)_{LAO}$	-
(equivalent)	<i>idem</i>	$(2\ -1\ -1)_{BCO} // (1\ 0\ 0)_{LAO}$	-
γ_2 (▼)	$(1\ 1\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	-	$(1\ -1\ 0)_{BCO} // (1\ 1\ 0)_{LAO}$
(equivalent)	<i>idem</i>	-	$(2\ -1\ -1)_{BCO} // (1\ 1\ 0)_{LAO}$
δ_1 (●)	$(2\ 1\ 1)_{BCO} // (0\ 0\ 1)_{LAO}$	$(0\ -1\ 1)_{BCO} // (1\ 0\ 0)_{LAO}$	-
(equivalent)	<i>idem</i>	$(1\ -1\ -1)_{BCO} // (1\ 0\ 0)_{LAO}$	-

References

- [1] C. Detavernier, A. Özcan, J. Jordan-Sweet, E. Stach, J. Tersoff, F. Ross, C. Lavoie, An off-normal fibre-like texture in thin films on single-crystal substrates, *Nature* 426 (December) (2003) 641–645.
- [2] C. Detavernier, C. Lavoie, J. Jordan-Sweet, A. S. Özcan, Texture of tetragonal α -FeSi₂ films on Si(001), *Phys. Rev. B - Condens. Matter Mater. Phys.* 69 (17) (2004) 174106.
- [3] A. S. Özcan, K. F. Ludwig, C. Detavernier, C. Lavoie, J. L. Jordan-Sweet, Axiotaxy of *CoSi*₂ thin films on Si(100) substrates and the effects of Ti alloying, *J. Appl. Phys.* 95 (12) (2004) 8376–8381.
- [4] S. Gaudet, C. Detavernier, C. Lavoie, P. Desjardins, Reaction of thin Ni films with Ge: Phase formation and texture, *J. Appl. Phys.* 100 (3) (2006) 034306.
- [5] M. Falke, H. Scheletter, O. Filonenko, A. Mogilatenko, G. Beddies, S. Schulze, M. Hietzschold, A. Bleloch, K. De Keyser, C. Detavernier, Axiotaxy of CrSi₂ on Si(001); from the micrometer- to the Angstrom-scale, *Microsc. Microanal.* 3 (001) (2007) 6–7.
- [6] S. L. Liew, B. Balakrishnan, C. S. Ho, O. Thomas, D. Z. Chi, Phase and texture of Er–Germanide formed on Ge(001) through a solid-state reaction, *J. Electrochem. Soc.* 154 (1) (2007) H9–H12.
- [7] C. Detavernier, J. Jordan-Sweet, C. Lavoie, Texture of NiSi films on Si(001), (111), and (110) substrates, *J. Appl. Phys.* 103 (11) (2008) 113526.
- [8] K. De Keyser, C. Van Bockstael, R. L. Van Meirhaeghe, C. Detavernier, E. Verleysen, H. Bender, W. Vandervorst, J. Jordan-Sweet, C. Lavoie, Phase formation and thermal stability of ultrathin nickel-silicides on Si(100), *Appl. Phys. Lett.* 96 (17) (2010) 4–6.
- [9] K. De Keyser, C. Detavernier, J. Jordan-Sweet, C. Lavoie, Texture of CoSi₂ films on Si(111), (110) and (001) substrates, *Thin Solid Films* 519 (4) (2010) 1277–1284.
- [10] K. De Keyser, R. L. Van Meirhaeghe, C. Detavernier, J. Jordan-Sweet, C. Lavoie, Texture of cobalt dermanides on Ge(100) and Ge(111) and its influence on the formation temperature, *J. Electrochem. Soc.* 157 (4) (2010) H395.
- [11] F. A. Geenen, W. Knaepen, J. Demeulemeester, K. De Keyser, J. L. Jordan-Sweet, C. Lavoie, A. Vantomme, C. Detavernier, On the formation and structural properties of hexagonal rare earth (Y, Gd, Dy, Er and Yb) disilicide thin films, *J. Alloys Compd.* 611 (2014) 149–156.
- [12] F. A. Geenen, W. Knaepen, K. De Keyser, K. Opsomer, R. L. Vanmeirhaeghe, J. Jordan-Sweet, C. Lavoie, C. Detavernier, Formation and texture of palladium germanides studied by in situ X-ray diffraction and pole figure measurements, *Thin Solid Films* 551 (February) (2014) 86–91.

- [13] B. De Schutter, K. De Keyser, C. Detavernier, Visualization and classification of epitaxial alignment at hetero-phase boundaries, *Thin Solid Films* 599 (2016) 104–112.
- [14] B. De Schutter, K. De Keyser, C. Lavoie, C. Detavernier, Texture in thin film silicides and germanides: A review, *Appl. Phys. Rev.* 3 (3) (2016) 031302.
- [15] S. Lambert-Milot, S. Gaudet, C. Lacroix, D. Menard, R. A. Masut, C. Lavoie, P. Desjardins, MnP nanoclusters embedded in GaP epitaxial films grown by organometallic vapor-phase epitaxy: A reciprocal space mapping and transmission electron microscopy study, *J. Vac. Sci. Technol. A* 30 (6) (2012) 061510.
- [16] A. Danescu, J. Penuelas, B. Gobaut, Surface Science Texture of Ge on $SrTiO_3$ (001) substrates: Evidence for in-plane axiotaxy, *Surf. Sci.* 644 (2016) 13–17.
- [17] J. L. MacManus-Driscoll, S. R. Foltyn, Q. X. Jia, H. Wang, A. Serquis, L. Civale, B. Maiorov, M. E. Hawley, M. P. Maley, D. E. Peterson, Strongly enhanced current densities in superconducting coated conductors of $YBa_2Cu_3O_{7-x} + BaZrO_3$, *Nat. Mater.* 3 (7) (2004) 439–443.
- [18] J. Gutiérrez, A. Llordés, J. Gázquez, M. Gibert, N. Romà, S. Ricart, A. Pomar, F. Sandiumenge, N. Mestres, T. Puig, X. Obradors, Strong isotropic flux pinning in solution-derived $YBa_2Cu_3O_{7-x}$ nanocomposite superconductor films., *Nat. Mater.* 6 (5) (2007) 367–73.
- [19] T. Puig, J. Gutiérrez, A. Pomar, A. Llordés, J. Gázquez, S. Ricart, F. Sandiumenge, X. Obradors, Vortex pinning in chemical solution nanostructured YBCO films, *Supercond. Sci. Technol.* 21 (2008) 034008.
- [20] K. Matsumoto, P. Mele, Artificial pinning center technology to enhance vortex pinning in YBCO coated conductors, *Supercond. Sci. Technol.* 23 (1) (2009) 014001.
- [21] X. Obradors, T. Puig, S. Ricart, M. Coll, J. Gázquez, A. Palau, X. Granados, Growth, nanostructure and vortex pinning in superconducting $YBa_2Cu_3O_7$ thin films based on trifluoroacetate solutions, *Supercond. Sci. Technol.* 25 (12) (2012) 123001.
- [22] A. Crisan, V. Dang, P. Mikheenko, Nano-engineered pinning centres in YBCO superconducting films, *Phys. C Supercond. Appl.* 533 (2016) 118–132.
- [23] T. Horide, N. Matsukida, M. Ishimaru, R. Kita, S. Awaji, K. Matsumoto, Pin potential effect on vortex pinning in $YBa_2Cu_3O_{7-\delta}$ films containing nanorods: Pin size effect and mixed pinning, *Appl. Phys. Lett.* 110 (5) (2017) 052601.
- [24] N. M. Strickland, N. J. Long, E. F. Talantsev, P. Hoefakker, J. A. Xia, M. W. Rupich, W. Zhang, X. Li, T. Kodenkandath, Y. Huang, Nanoparticle additions for enhanced flux pinning in YBCO HTS films, *Curr. Appl. Phys.* 8 (3-4) (2008) 372–375.
- [25] A. Frolova, N. Pompeo, F. Rizzo, K. Torokhtii, E. Silva, A. Augieri, G. Celentano, V. Pinto, A. A. Armenio, A. Mancini, A. Rufoloni, A. Vannozzi, G. Sotgiu, L. Ciontea, T. Petrisor, Analysis of transport properties of MOD YBCO films with $BaZrO_3$ as artificial vortex pinning centers, *IEEE Trans. Appl. Supercond.* 26 (3) (2016) 8001205.

- [26] V. Pinto, A. Angrisani Armenio, L. Piperno, A. Mancini, F. Rizzo, A. Vannozzi, A. Ruffoloni, A. Augieri, V. Galluzzi, A. Frolova, G. Sotgiu, E. Silva, F. Fabbri, R. Lamanna, G. Celentano, Aging of precursor solutions used for YBCO films chemical solution deposition: Study of mechanisms and effects on film properties, *IEEE Trans. Appl. Supercond.* 26 (3) (2016) 7500405.
- [27] I. Bretos, T. Schneller, M. Falter, M. Bäcker, E. Hollmann, R. Wordenweber, L. Molina-Luna, G. Van Tendeloo, O. Eibl, Solution-derived $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting films with $BaZrO_3$ (BZO) nanodots based on reverse micelle stabilized nanoparticles, *J. Mater. Chem. C* 3 (2015) 3971–3979.
- [28] P. Cayado, K. De Keukeleere, A. Garzón, L. Perez-Mirabet, A. Meledin, J. De Roo, F. Vallés, B. Mundet, H. Rijckaert, G. Pollefeyt, M. Coll, S. Ricart, A. Palau, J. Gázquez, J. Ros, G. Van Tendeloo, I. Van Driessche, T. Puig, X. Obradors, Epitaxial $YBa_2Cu_3O_{7-x}$ nanocomposite thin films from colloidal solutions, *Supercond. Sci. Technol.* 28 (12) (2015) 124007.
- [29] K. De Keukeleere, P. Cayado, A. Meledin, F. Valles, J. De Roo, H. Rijckaert, G. Pollefeyt, E. Bruneel, A. Palau, M. Coll, S. Ricart, G. Van Tendeloo, T. Puig, X. Obradors, I. Van Driessche, Superconducting $YBa_2Cu_3O_{7-\delta}$ nanocomposites using preformed ZrO_2 nanocrystals: growth mechanisms and vortex pinning properties, *Adv. Elect. Mat.* 2 (10) (2016) 1600161.
- [30] M. Vélez, J. Martín, J. Villegas, A. Hoffmann, E. González, J. Vicent, I. K. Schuller, Superconducting vortex pinning with artificial magnetic nanostructures, *J. Magn. Magn. Mater.* 320 (21) (2008) 2547–2562.
- [31] A. K. Jha, K. Matsumoto, T. Horide, S. Saini, P. Mele, Y. Yoshida, S. Awaji, Tailoring the vortex pinning strength of YBCO thin films by systematic incorporation of hybrid artificial pinning centers, *Superconductor Science and Technology* 28 (2015) 114004.
- [32] L. Opherden, M. Sieger, P. Pahlke, R. Hühne, L. Schultz, A. Meledin, G. V. Tendeloo, R. Nast, B. Holzapfel, M. Bianchetti, J. MacManus-Driscoll, J. Hänisch, Large pinning forces and matching effects in YBCO thin films with $Ba_2Y(Nb/Ta)O_6$ nano-precipitates, *Sci. Rep.* 6 (2016) 21188.
- [33] J. Huang, L. Li, X. Wang, Z. Qi, M. A. P. Sebastian, T. J. Haugan, H. Wang, Enhanced flux pinning properties of YBCO thin films with various pinning landscapes, *IEEE Trans. Appl. Supercond.* 27 (4) (2017) 8000305.
- [34] D. C. van der Laan, T. J. Haugan, P. N. Barnes, D. Abrahimov, F. Kametani, D. C. Larbalestier, M. W. Rupich, The effect of strain on grains and grain boundaries in $YBa_2Cu_3O_{7-\delta}$ conductors, *Supercond. Sci. Technol.* 23 (2010) 014004.
- [35] P. Abellán, F. Sandiumenge, M.-J. Casanove, M. Gibert, A. Palau, T. Puig, X. Obradors, Interaction between solution derived $bazro_3$ nanodot interfacial templates and $yba_2cu_3o_7$ films leading to enhanced critical currents, *Acta Materialia* 59 (5) (2011) 2075 – 2082.

- [36] A. Llordés, A. Palau, J. Gázquez, M. Coll, R. Vlad, A. Pomar, J. Arbiol, R. Guzmán, S. Ye, V. Rouco, F. Sandiumenge, S. Ricart, T. Puig, M. Varela, D. Chateigner, J. Vanacken, J. Gutiérrez, V. Moshchalkov, G. Deutscher, C. Magen, X. Obradors, Nanoscale strain-induced pair suppression as a vortex-pinning mechanism in high-temperature superconductors, *Nat. Mater.* 11 (4) (2012) 329–336.
- [37] S. Awaji, T. Suzuki, H. Oguro, K. Watanabe, K. Matsumoto, Strain-controlled critical temperature in $REBa_2Cu_3O_{7-\delta}$ -coated conductors, *Sci. Rep.* 5 (March) (2015) 11156.
- [38] B. Maiorov, S. A. Baily, H. Zhou, O. Ugurlu, J. A. Kennison, P. C. Dowden, T. G. Holesinger, S. R. Foltyn, L. Civale, Synergetic combination of different types of defect to optimize pinning landscape using $BaZrO_3$ -doped $YBa_2Cu_3O_7$, *Nature Mater.* 8 (5) (2009) 398–404.
- [39] L. Lei, L. Liu, X. Wang, S. Wang, J. Jia, G. Zhao, C. Wu, L. Jin, C. Li, P. Zhang, Strongly improved current-carrying capacity induced by nanoscale lattice strains in $yba_2cu_3o_{7-\delta}$ - $ba_{0.7}sr_{0.3}tio_3$ composite films derived from chemical solution deposition, *J. Mater. Chem. C* 4 (2016) 1392–1397.
- [40] S. Chen, M. A. Sebastian, B. Gautam, J. Wilt, T. Haugan, Z. Xing, J. Wu, Enhancement of isotropic pinning force in YBCO films with $BaZrO_3$ nanorods and Y_2O_3 nanoparticles, *IEEE Trans. Appl. Supercond.* 27 (4) (2017) 4–8.
- [41] E. Solano, L. Perez-Mirabet, F. Martinez-Julian, R. Guzmán, J. Arbiol, T. Puig, X. Obradors, R. Yañez, A. Pomar, S. Ricart, J. Ros, Facile and efficient one-pot solvothermal and microwave-assisted synthesis of stable colloidal solutions of MFe_2O_4 spinel magnetic nanoparticles, *J. Nanoparticle Res.* 14 (8) (2012) 1034–1049.
- [42] A. Garzon-Manjon, Synthesis of metal oxide nanoparticles for superconducting nanocomposites and other applications, Ph.D. thesis, Universitat Autònoma de Barcelona (2016).
- [43] T. Honjo, Y. Nakamura, R. Teranishi, H. Fuji, J. Shibata, T. Izumi, Y. Shiohara, Growth mechanism of YBCO films in metal organic deposition method using trifluoroacetates, *IEEE Trans. Appl. Supercond.* 13 (2) (2003) 2516–2519.
- [44] X. Obradors, T. Puig, A. Pomar, F. Sandiumenge, S. Piñol, N. Mestres, O. Castaño, M. Coll, A. Cavallaro, A. Palau, J. Gázquez, J. C. González, J. Gutiérrez, N. Romà, S. Ricart, J. M. Moretó, M. D. Rossell, G. V. Tendeloo, Chemical solution deposition: a path towards low cost coated conductors, *Supercond. Sci. Technol.* 17 (8) (2004) 1055–1064.
- [45] K. Develos-Bagarinao, H. Yamasaki, Y. Nakagawa, Effect of surface modification of CeO_2 buffer layers on J_c and defect microstructures of large-area YBCO thin films, *Supercond. Sci. Technol.* 19 (8) (2006) 873–882.
- [46] E. Solano, Synthesis and characterisation of ferrite nanoparticles for $YBa_2Cu_3O_{7-\delta}$ - nanocomposite superconducting layers: a neutron and synchrotron study, Ph.D. thesis, Univeristat Autònoma de Barcelona (2013).

- [47] K. De Keyser, C. Detavernier, R. L. Van Meirhaeghe, Characterization of the texture of silicide films using electron backscattered diffraction, *Appl. Phys. Lett.* 90 (12) (2007) 1–4.
- [48] M. Yoshizumi, I. Seleznev, M. J. Cima, Reactions of oxyfluoride precursors for the preparation of barium yttrium cuprate films, *Phys. C* 403 (3) (2004) 191–199.
- [49] J. Brötz, H. Fuess, Detwinning in $YBa_2Cu_3O_{7-\delta}$ films on vicinal $SrTiO_3$ (0 0 1) due to anisotropic strain at the interface, *Phys. C Supercond.* 339 (2000) 75–78.
- [50] H. Zhang, J. Yang, S.-M. Wang, H.-Z. Liu, HRXRD analysis for $YBa_2Cu_3O_{7-x}$ deposited on 001 $LaAlO_3$, *Trans. Nonferrous Met. Soc. China* 21 (12) (2011) 2633–2637.