Nano-stripe structures in light rare-earth high-$T_c$ superconductors

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Abstract. Topographic investigations of surfaces of melt-textured GdBa$_2$Cu$_3$O$_x$ (GdBCO) samples were performed by means of AFM and STM at ambient conditions. Pure GdBCO is found to exhibit mainly nanoclusters, while GdBCO doped with ZnO nanoparticles reveals the nanostripe patterns as observed earlier in other high-$T_c$ cuprates. Details of the nanostripe patterns are investigated. Using the electron backscatter diffraction technique and polarization microscopy, we could determine the crystallographic orientation of the nanostripes and their interaction with the always present twin boundary structure.

1. Introduction
The surfaces of light rare-earth-element-based high-$T_c$ superconductors with the composition (LRE)Ba$_2$Cu$_3$O$_x$ (with LRE = light rare earths, e.g. Nd, Eu, Gd, Sm) revealed the presence of pronounced nanostripe structures with periodicities varying between 10 and 60 nm [1-4]. In this contribution, we present a comparison of topographical investigations performed on GdBa$_2$Cu$_3$O$_x$ (GdBCO) and the ternary compound (Nd,Eu,Gd)Ba$_2$Cu$_3$O$_x$ (NEG) by means of atomic force microscopy (AFM) and scanning tunneling microscopy (STM) under ambient conditions. As samples, we employ melt-textured samples and melt-textured samples with nanoparticle additions. The LRE-type of high-$T_c$ superconductors are characterized by their high critical current densities, especially in elevated applied magnetic fields [1], which makes these materials ideal candidates for applications. Nanostripe patterns of GdBa$_2$Cu$_3$O$_x$ samples are presented here for the first time. The goal of this study is to determine details of these structures and their relation to the twin arrangement, which is always present in the (LRE)Ba$_2$Cu$_3$O$_x$ superconductors. For this purpose, we combine AFM/STM analysis with polarization images and high-resolution electron backscatter diffraction (EBSD) measurements [5].

2. Experimental procedure
We employed Digital Instruments Nanoscope III and IV controllers in atomic force microscope (AFM) mode and scanning tunnelling microscopy (STM) mode at ambient conditions. For comparison, AFM scans were performed in contact mode and tapping mode using micro-machined, doped Si cantilevers (Nanoworld Services). A Q-control unit was used to improve the signal-to-noise ratio in the tapping mode. EBSD analysis was carried out using a dual-beam microscope (FEI Inc.)
equipped with an EBSD analysis unit as described in Ref. [6]. The melt-textured (LRE)BCO samples were produced using the standard procedure as described elsewhere [7]. Melt-textured GdBa$_2$Cu$_3$O$_x$ samples without and with ZnO$_2$ nano-particle addition were prepared according to Ref. [8]. Since the as-grown surfaces of the samples were usually too rough to achieve good scanning results, the samples were mechanically polished prior to scanning, either dry from 12 µm to 0.5 µm diamond paper or wet from 320 grain SiO$_2$ paper to 4000 grain SiO$_2$ paper and then from 3 µm diamond polishing solution down to 40 nm colloidal silica (OP-S) [9]. After that, the samples were cleaned for several minutes in acetone in an ultrasonic bath and then for several minutes in an isopropanol bath.

3. Results and discussion

Nanostripes or nanoclusters were found by means of AFM and TEM investigations in a variety of (LRE)Ba$_2$Cu$_3$O$_x$ superconductors; namely in NdBa$_2$Cu$_3$O$_x$, SmBa$_2$Cu$_3$O$_x$, and ternary compounds like NEG or (Sm,Eu,Gd)Ba$_2$Cu$_3$O$_x$ (SEG) [3,10]. The nanoclusters represent regions where the LRE atoms may substitute for Ba, thus leading to a spatial variation of the superconducting properties within the sample. In turn, this spatial variation may be responsible for the extraordinary performance of the (LRE)BCO superconductors. The stoichiometric variation was already demonstrated by EDX analysis [10] in TEM measurements.

Melt-textured GdBa$_2$Cu$_3$O$_x$ samples were up to now only rarely investigated with respect to the nanolamellae structures. Figure 1 shows that the pure GdBCO samples reveal the presence of nanoclusters with a size between 10-20 nm (a) similarly to NdBa$_2$Cu$_3$O$_x$ and only on some places on the sample surface nanolamellae with a width between 60-100 nm (b) are observed. In contrast to that, ZnO$_2$-doped GdBa$_2$Cu$_3$O$_x$ presents again a clear nano-lamellae structure with a width of 20 nm (c). The ZnO$_2$-particles, however, are not detected in the sample. Embedded Gd$_2$BaCuO$_5$ (Gd-211) particles, which are commonly found in the melt-textured bulk samples, are not disturbing the orientation of the lamellae as seen in (c). However, a closer inspection of the lamellae structure reveals a clear difference to the very homogeneous nanolamellae found in SmBa$_2$Cu$_3$O$_x$, NEG or SEG [2,3].

![Figure 1](image_url)

**Figure 1.** Tapping AFM-images of melt-textured GdBa$_2$Cu$_3$O$_x$ samples. Figures (a) and (b) show pure GdBa$_2$Cu$_3$O$_x$ samples exhibiting nanoclusters [as marked by arrows in (a)] and nanostripes (b). Image (c) gives the well-developed lamellae structure around a Gd-211 inclusion in GdBa$_2$Cu$_3$O$_x$ with embedded ZnO$_2$ nano-particles.
In Fig. 2, a 3D representation of a tapping-mode AFM image of this nanolamellae structure is presented. The profiles taken parallel and perpendicular to the lamellae clearly illustrate the irregularity of these nanolamellae, which are better characterized as dense strings of nanoclusters. These nanoclusters have a height of about 4 Å; the width along the lamellae is about 50 nm and across about 10 nm. This observation is very important for the understanding of the nanolamellae formation: The nanoclusters, representing areas of several unit cells where a LRE/Ba substitution has taken place, do exist in all (LRE)BCO superconductors. In samples with a higher melting temperature a longer cooling time is required allowing the formation of nanolamellae out of these clusters. Obviously, the doping with nanoparticles is influencing this process via a change of the melting temperature of the system.

**Figure 2.** 300 × 300 nm$^2$ 3D-representation of a tapping-AFM image of ZnO$_2$-doped GdBCO. Profiles taken along (lower graph) and perpendicular (upper graph) to the nanolamellae illustrate the irregularity of the lamellae structure. The individual nanoclusters forming the lamellae structure have heights of up to 4 Å. The widths of the nanoclusters along the lamellae is about 50 nm.

In contrast to this, the most homogeneous nanolamellae structures were observed in SmBa$_2$Cu$_3$O$_x$ and NEG melt-textured samples. Figure 3 compares the modulation height across the nanolamellae to the unit cell height of NEG, measured using tapping AFM (a) and STM (b). The lamellae height is found to be of the order of 5 – 6 Å, whereas voids and steps within the lamellae exhibit a height of 1.2 nm, corresponding to the unit cell height of NEG. Figure 3 (b) illustrates how several sets of lamellae are oriented parallel to each other on different height levels, which also correspond to an unit cell height.

The essential result of the AFM/STM measurements performed here is the determination of the relation of the twin boundaries and the nanolamellae structures. Adding a polarization filter foil to the optical microscope of the AFM setup enables to visualize the twin patterns of the samples investigated as illustrated in Fig. 4 (a). In the (LRE)BCO samples, the twins run in [1 1 0] and [1 -1 0] directions, which clearly defines the crystallographic orientation. Figure 4 (b) shows the twin structure as dark stripes within the AFM image of the nanolamellae structure. This enables us to determine the angle between the lamellae and the twins to be about 33° to one of the twin directions. With this angle, the nanolamellae are not related to any crystallographic orientation, which is also confirmed by electron backscatter diffraction (EBSD) analysis [5,6]. Here, it is possible to determine the orientation of the twin structure in detail, but there is no misorientation observed in between the individual twins which would correspond to the nanolamellae [11].
Figure 3. Comparison of the modulation height across the nanolamellae to the unit cell (uc) height in NEG samples. (a) gives a tapping-mode AFM image, (b) a STM image in ambient conditions. It is clearly visible that defects within the nanolamellae structure correspond to a unit cell height.

Figure 4. (a) 400 × 400 µm² polarized light image of twin boundaries in NEG, (b) contact AFM image of the nanolamellae structure above the twin boundary arrangement. The dark stripes in (b) are twin boundaries. The nanolamellae are found to run in angle of 33° to one of the twin directions (dark stripes).
In summary, we have presented an analysis of the nanolamellae structures found in GdBCO and NEG high-$T_c$ superconductors. The nanolamellae found in GdBCO samples consist of chains of nanoclusters, while in NEG homogeneous nanolamellae are formed. Possible reasons for this behaviour are discussed. Furthermore, we determine the angle between the nanolamellae and one of the twin directions to be $33^\circ$.

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