

# **Enhanced self-field critical current density of nano-composite YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> thin films grown by pulsed-laser deposition**

(*Short title:* Enhanced critical current density of nano-composite YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> thin films)

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              68.55.Nq Composition and phase identification

## **Abstract**

Enhanced self-field critical current density  $J_c$  of novel, high-temperature superconducting thin films is reported. Layers are deposited on (001) MgO substrates by laser ablation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (Y-123) ceramics containing Y<sub>2</sub>Ba<sub>4</sub>CuMO<sub>x</sub> (M-2411, M = Ag, Nb, Ru, Zr) nano-particles. The  $J_c$  of films depends on the secondary phase content of the ceramic targets, which was varied between 0 and 15 mol %. Composite layers (2 mol % of Ag-2411 and Nb-2411) exhibit  $J_c$  values at 77 K of up to 5.1 MA/cm<sup>2</sup>, which is 3 to 4 times higher than those observed in films deposited from phase pure Y-123 ceramics. Nb-2411 grows epitaxially in the composite layers and the estimated crystallite size is  $\sim$  10 nm.

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The critical current density  $J_c$  of high-temperature superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Y-123) epitaxial thin films is, typically, in the range of  $10^6$  to  $10^7 \text{ A/cm}^2$  at temperatures  $T \leq 77 \text{ K}$  in self-field, i.e. without external magnetic field. A maximum critical current density of  $\sim 3 \times 10^8 \text{ A/cm}^2$  in Y-123 at  $T = 0 \text{ K}$  is predicted from Ginzburg-Landau theory for the de-pairing of Cooper pairs [1]. Various attempts have been undertaken to modify the chemical composition, microstructure and crystallinity of high-temperature superconducting (HTS) thin films in order to increase the values of  $J_c$ . Substitution of various rare earth elements for yttrium, ion and neutron irradiation, and substrate pre-treatments are improving the superconducting properties of HTS layers. The incorporation of secondary phase nano-particles into films is a promising concept for enhancing  $J_c$  enhancement, since this enables type, density and distribution of such nano-materials to be varied and, consequently, the magnetic flux pinning properties of the films to be optimised. Different types of nano-particles including Ag [2],  $\text{BaIrO}_3$  [3],  $\text{BaSnO}_3$  [4],  $\text{BaZrO}_3$  [5, 6, 7, 8, 9],  $\text{Y}_2\text{BaCuO}_5$  [10, 11],  $\text{Y}_2\text{O}_3$  [12, 13, 14] and  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$  [15] have been shown to increase the  $J_c$  of Y-123 based composite layers compared to that of phase pure Y-123 films.

Here, we report for the first time the deposition of Y-123 based HTS films from composite  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ceramics containing  $\text{Y}_2\text{Ba}_4\text{CuMO}_x$  ( $M$ -2411,  $M = \text{Ag, Nb, Ru, Zr}$ ) nano-particles. The new phase M-2411 has a double-perovskite cubic structure (lattice parameter  $a_{2411} = 8.43 \text{ \AA}$  for Nb-2411) and is chemically very stable with a melting point above  $1700 \text{ }^\circ\text{C}$  [16]. Bulk Y-123 superconductors containing insulating M-2411 nano-particles show strongly enhanced magnetic flux pinning and critical current densities over a range of temperatures and applied magnetic fields [17].

The HTS films in this study were grown on (001)  $\text{MgO}$  single crystal substrates by pulsed-laser deposition (PLD), with the same deposition parameters employed for all samples [18]. Nano-composite M-2411/Y-123 ceramics were used as targets for the laser ablation process. Ceramics of different composition ( $M = \text{Ag, Nb, Ru, or Zr}$ ) and secondary M-2411 phase content (0 - 15 mol %) were employed. The films are patterned into tracks of width  $100 \mu\text{m}$  and length  $1.0 \text{ mm}$  by photolithography and wet-chemical etching for electrical characterisation by a four point technique. Au/Ag contact pads were evaporated onto the films after in-situ plasma cleaning of their surfaces. The HTS layer thickness as measured by atomic force microscopy (AFM) was  $\sim 200 \text{ nm}$  for all samples if not otherwise stated. X-ray diffraction (XRD, Cu  $\text{K}\alpha$ ) analysis showed that all layers were epitaxial and oriented parallel to the crystallographic c - axis.

The HTS thin films deposited in this investigation exhibit very different surface morphologies, depending on the ceramic target used for ablation. Figure 1 shows scanning electron micrographs of films produced from Ag-2411 (3 mol %) / Y-123 ceramics (Fig. 1a) and from phase pure Y-123 (0 mol %) ceramics (Fig. 1b). The composite layers are free from micrometer sized

particulates and have a smooth surface with average roughness of 4 – 6 nm (AFM scan range 20 × 20  $\mu\text{m}^2$ ). Particulates are present in the pure Y-123 films, however, which exhibit an increased roughness of ~ 10 nm. Ceramics of higher M-2411 content yield films that exhibit particulates of different size, shape and surface density.

All composite layers exhibit metallic resistivity in the normal state with a sharp transition to the superconducting state. Films grown from Ag-2411/Y-123 and Nb-2411/Y-123 ceramics (1 - 3 mol %) have an in-plane resistivity  $\rho(300 \text{ K}) \approx 0.2 \text{ m}\Omega \text{ cm}$ , which is similar to that observed for Y-123 single crystals ( $\rho_{ab} \approx 0.15 \text{ m}\Omega \text{ cm}$ ), and critical temperatures  $T_{c0} > 88 \text{ K}$  and  $T_c^{\text{onset}} > 90 \text{ K}$ . By comparison, Y-123 thin films deposited from phase pure ceramics have  $T_{c0} \approx 93 \text{ K}$  and  $T_c^{\text{onset}} \approx 95 \text{ K}$ . Film samples of reduced critical temperatures and higher resistivity are produced from ceramics with higher M-2411 content.

The self-field transport critical current density  $J_c$  of HTS layers deposited under identical conditions (laser fluence  $\Phi \approx 2.7 \text{ J/cm}^2$ ) is summarized in Figure 2. The  $J_c$  of films shows a strong and non-monotonic dependence on composition and secondary phase content of the target ceramics. A pronounced maximum of  $J_c(77 \text{ K}) = 3.4 \text{ MA/cm}^2$  and  $4.2 \text{ MA/cm}^2$  is observed for layers deposited from ceramics containing 2 mol % Ag-2411 and Nb-2411, respectively. Films grown from phase pure Y-123 ceramics have  $J_c(77 \text{ K}) = 1.05 \text{ MA/cm}^2$ . Ceramics with high secondary phase content do not yield high-quality layers and the critical current densities are  $\leq 0.3 \text{ MA/cm}^2$  (Ag-2411 and Nb-2411, 10 - 15 mol %) and  $< 0.05 \text{ MA/cm}^2$  (Ru-2411 and Zr-2411, 5 – 15 mol %) at 77 K. Multi-layer samples of Y-123//Ag-2411/Y-123//Y-123 were grown by sequential ablation of pure Y-123 and Ag-2411 (10 mol %)/Y-123 ceramics. The number of laser pulses employed was 3000 (Y-123) and 1000 (Ag-2411/Y-123). The amount of secondary phase ablated for such samples was the same as that in the single layer films fabricated from Y-123 ceramics containing 1.43 mol % Ag-2411. The multi-layered samples have enhanced critical current density ( $2.2 \text{ MA/cm}^2$ ) and similar values of  $T_{c0} = 89 \text{ K}$  and  $\rho(300 \text{ K}) \approx 0.2 \text{ m}\Omega \text{ cm}$ . Films deposited at higher fluence ( $\Phi \approx 3.2 \text{ J/cm}^2$ ) from Ag-2411 (2 mol %)/Y-123 ceramics exhibit similar enhancement of  $J_c$ , with a highest achieved value  $J_c(77 \text{ K}) = 5.1 \text{ MA/cm}^2$ . HTS layers deposited on (001)  $\text{SrTiO}_3$  substrates do not show increased values of  $J_c$  using Ag-2411 (2 mol %)/Y-123 ceramic targets compared to pure Y-123. The variation of  $T_c$  and  $J_c$  of these films is strikingly different to the properties of nano-composite ceramics. The critical temperature  $T_{c0} = 91 \pm 0.5 \text{ K}$  for bulk Y-123 superconductors is independent of the secondary phase and the  $J_c(77 \text{ K})$  values increase monotonically up to 30 mol % content of Ag-2411 [16].

The composition and crystallinity of the films was investigated by x-ray diffraction analysis (XRD 3 circle system with 2D detector). The XRD intensity distribution in reciprocal space **for a thin film sample** deposited from Nb-2411 (15 mol %) / Y-123 ceramic is shown in Figure 3a. The

layer thickness of this sample was 400 nm. The diffraction pattern reveals  $(00\ell)$  and  $(10\ell)$  reflections of c-axis oriented Y-123 and the  $(002)$  reflection of the MgO substrate. The additional XRD peak marked by circle (Fig. 3a) corresponds to the  $(220)$  reflection of Nb-2411. This signal is observed with films deposited from nano-composite ceramic targets and is not detected with phase pure Y-123 films (0 mol % M-2411). The  $(220)$  reflection is the most intense diffraction peak of the M-2411 phase [17]. The angular width of the observed  $(220)$  Nb-2411 peak,  $\Delta(2\theta)_{FWHM} = 1.31^\circ$ , is larger than that of the  $(103)$  Y-123 reflection ( $\Delta(2\theta)_{FWHM} = 0.81^\circ$ ). This peak broadening is probably related to size effects and an average Nb-2411 crystallite size of  $10 \pm 2$  nm is estimated from Scherrer's formula. The measured diffraction angles of the  $(220)$  peak,  $2\theta = 30.7 \pm 0.7^\circ$  and  $\chi = 43.9 \pm 1.6^\circ$ , indicate the c-axis orientation and cube-on-cube epitaxy of Nb-2411 crystallites in the Y-123 matrix (calculated angles  $2\theta_{th} = 30.0^\circ$  and  $\chi_{th} = 45.0^\circ$ ). This epitaxial structure is confirmed by XRD  $\varphi$  scans of the  $(103)$  Y-123 and  $(220)$  Nb-2411 reflections (Fig. 3b). Both reflections show maximum intensity at about the same angle  $\varphi$  and a  $\Delta\varphi = 90^\circ$  rotational symmetry (inset of Fig. 3a). The angular width of the Nb-2411 reflection obtained from a fit to the data is  $\Delta\varphi_{FWHM} = 4.7^\circ$ . The lattice mismatch of cubic double-perovskite Nb-2411 ( $a_{2411} = 8.43$  Å) and orthogonal triple-perovskite Y-123 (lattice parameters  $a_{123} \approx 3.85$  Å and  $c_{123} = 11.68$  Å) is  $|(a_{2411} - 2 a_{123}) / 2 a_{123}| \approx 9.5\%$  and  $|(3 a_{2411} - 2 c_{123}) / 2 c_{123}| \approx 8.3\%$ . Epitaxial growth of Nb-2411 in Y-123 is observed also in the nano-composite ceramics and the Nb-2411 crystallite size in the bulk materials is  $\sim 10 - 20$  nm [17, 19].

In order to evaluate the formation of the epitaxial Y-123 phase in thin films, XRD  $\omega$  scans of the  $(005)$  Y-123 reflection were performed (so-called rocking curves). From the measured diffraction intensity  $I(\omega)$  the angular width  $\Delta\omega_{FWHM}$  of the rocking curve was determined by fitting a Pseudo-Voigt peak profile to the data. The epitaxial Y-123 phase was quantified by integrating the diffraction intensity over the relevant angle range (epitaxial phase signal  $E = \int I(\omega) d\omega$ ). A similar procedure was employed to quantify the epitaxial phase formation in other oxide thin film materials [20]. For c – axis oriented Y-123 films with strong out-of-plane texture the angular widths are typically  $\Delta\omega_{FWHM} < 3^\circ$  depending on the type of substrate, film thickness and XRD apparatus and measurement technique. The thin film samples reported in this study revealed  $\Delta\omega_{FWHM} = 0.33^\circ$  and  $\Delta\omega_{FWHM} \leq 1.2^\circ$  for the pure Y-123 (0 mol %) and the nano-composite (1 – 3 mol % Ag-2411 and Nb-2411) layers, respectively. The epitaxial phase signal was  $E = 2.75$  and  $E = 3.09 \pm 0.17$  (in arbitrary units) for the pure Y-123 and the nano-composite films, respectively. Ceramics of higher M-2411 content (10 and 15 mol %, M = Ag and Nb) yielded layers of reduced crystallinity with  $E < 2.4$  and  $\Delta\omega_{FWHM} = 0.6 - 3.2^\circ$ . The XRD results indicate improved epitaxy of Y-123 on MgO in nano-composite films that are laser-deposited from ceramics of low M-2411 content.

Figure 4 shows the XRD angular width and epitaxial phase signal and the critical current density of various thin films and multi-layers deposited from Ag-2411/Y-123 and Nb-2411/Y-123 nano-composite ceramic targets. Samples revealing enhanced current density  $J_c > 2.1 \text{ MA/cm}^2$  showed moderate angular width  $\Delta\omega_{FWHM} \leq 1.2^\circ$  (Fig. 4a) and strong Y-123 epitaxial signal  $E \approx 3$  (Fig. 4b). Such samples were deposited from ceramics containing 1 – 3 mol % M-2411 (thin film samples) and 1.43 mol % Ag-2411 (equivalent content for multi-layer samples) and the corresponding data points are encircled by ellipses in Figure 4. Phase pure Y-123 films had  $J_c = 1.05 \text{ MA/cm}^2$  (triangle symbols, Fig.4). At high M-2411 content (10 and 15 mol %) the films had  $J_c < 0.3 \text{ MA/cm}^2$  and reduced Y-123 phase signals. These results indicate a correlation of  $J_c$  of the nano-composite layers with the crystallinity of the Y-123 matrix.

The mechanism of  $J_c$  enhancement in the nano-composite films remains to be clarified. The M-2411 nano-particles in films may act as artificial pinning centres. The observed improvement of Y-123 phase formation, the modified layer morphology and the possible stabilization of other phases by the non-equilibrium PLD process may contribute also to the enhancement of  $J_c$  in self-field. At 77 K temperature,  $J_c(2 \text{ mol \%}) / J_c(0 \text{ mol \%})$  is 4.0 and 3.2 for Nb-2411/Y-123 and Ag-2411/Y-123, respectively. An enhancement of  $3.8\times$ ,  $\leq 2\times$  and  $\sim 2\times$  was achieved for BaZrO<sub>3</sub>, Y<sub>2</sub>BaCuO<sub>5</sub> and Y<sub>2</sub>O<sub>3</sub> nano-particles in Y-123 [9, 10, 12], respectively. Angle dependent in-field measurements  $J_c(B)$  and transmission electron microscopy investigations are under way to investigate the flux pinning behaviour [21] and the defect microstructure of the novel films. The M-2411/Y-123 nano-composite material might also have potential for the fabrication of improved HTS layers on technical substrates.

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## Figure captions

### FIGURE 1

Surface micrographs of novel Y-123 based thin films (scanning electron microscopy). Layers deposited from Ag-2411 (3 mol %)/Y-123 nano-composite ceramics reveal smooth surfaces without particulates (a). Films fabricated from single phase Y-123 ceramics contain particulates of micrometer size (b).

### FIGURE 2

Self-field critical current density  $J_c$  of Y-123 based thin films on (001) MgO. Layers deposited from Ag-2411/Y-123 and Nb-2411/Y-123 ceramics (1 – 3 mol %) show enhanced  $J_c$  values in comparison to phase pure Y-123 films (0 mol %). Multi-layered Y-123//Y-123/Ag-2411 //Y-123 samples (ML) also show higher  $J_c$  values (diamond symbols).

### FIGURE 3

X-ray diffraction (XRD) of films deposited from Nb-2411 (15 mol %)/Y-123 ceramics. The reciprocal space intensity map shows  $(00\ell)$  and  $(10\ell)$  reflections from c-axis oriented Y-123 and the  $(220)$  reflection of epitaxial Nb-2411 (marked by circle, a). The  $(002)$  MgO substrate peak is indicated by the subscript S. XRD  $\phi$  scans of  $(103)$  Y-123 and  $(220)$  Nb-2411 reflections (b). The solid lines represent fits to the data. The reflections show  $\Delta\phi = 90^\circ$  rotational symmetry (inset).

### FIGURE 4

Self-field critical current density  $J_c(77\text{ K})$ , XRD angular width  $\Delta\omega_{\text{FWHM}}$  and epitaxial phase signal E of nano-composite films pulsed-laser deposited from Ag-2411/Y-123 and Nb-2411/Y-123 ceramics. Samples with enhanced  $J_c > 2.1 \text{ MA/cm}^2$  have small widths of the  $(005)$  Y-123 reflection,  $\Delta\omega_{\text{FWHM}} \leq 1.2^\circ$  (a), and strong Y-123 signals,  $E \approx 3$  (b). Ellipses mark samples produced from ceramics containing 1 – 3 mol % M-2411. Pure Y-123 films (0 mol % M-2411) are marked by triangle symbols. Films deposited from targets with 10 and 15 mol % M-2411 have  $J_c < 1 \text{ MA/cm}^2$  (dashed lines mark  $J_c$  value of 1  $\text{MA/cm}^2$ ).

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