Flux pinning improvement of YBCO superconducting films with BaZrO$_3$ nanoparticles prepared by chemical solution deposition method

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Abstract. The aim of this study is to introduce artificial pinning centres into the YBCO structure and to investigate the dependence of the critical current on applied magnetic fields. Chemical solution deposition technique is appearing as a very promising method to achieve thin films at low cost. YBCO films with Zr doping have been prepared successfully by the trifluoroacetate metal-organic deposition (TFA-MOD) method through dissolving different amounts of Zr (IV)-2,4-pentanedionate into the precursor solution. The optimum BaZrO$_3$ concentration for $J_c$ improvement in magnetic fields was investigated. The surface morphology of the films was observed by Scanning Electron Microscope (SEM). Phase analysis of the doped and undoped samples was performed by XRD, critical transition temperature ($T_c$) and critical current densities ($J_c$) were reported as a function of dopant concentration. The correlation of optimum dopant concentration with microstructure, pinning and superconducting properties was investigated.

1. Introduction

Production of long-length and low cost YBCO films has been an essential aim in the field of superconducting processing. Besides, YBCO films need to possess a high critical current density ($J_c$) under high magnetic fields for practical applications as power and high field applications [1, 2]. Improvement of their performance in magnetic fields has become one of the interesting topics on high temperature superconductors (HTS). However, the ability for HTS to carry currents is significantly reduced in the presence of magnetic fields. In order to counteract this effect, various methods to increase the HTS current carrying abilities in magnetic fields by flux pinning have been developed through the pinning of the quantized flux lines by nanoscale crystalline defects and impurities [3, 4]. Vacuum deposition techniques like pulsed-laser deposition (PLD) and metal organic chemical vapour deposition (MOCVD) have been used to produce these nanocomposite YBCO films. However high cost and small exposure area of these deposition techniques have hindered the large scale production [5]. Because of this reason, the more practical and cost effective chemical solution deposition method (CSD) is preferred recently.

The way for flux pinning in the structure can be the use of nanoparticles-modified substrate surfaces, mixing rare earth doping in to the structure and doping with BaMeO$_3$ nanoparticles. Among these approaches, BaZrO$_3$ (BZO) nanoparticles in YBCO thin films are one of the most popular ones which can prevent the vortex motion at high fields. The amount of dopant in the structure needs to be high enough to generate the density of defects, which is needed to enhance flux pinning in magnetic fields. However, excess amounts of this nonsuperconducting content can suppress the self-field and in-field $J_c$ values significantly [6].
In the present work, undoped and BZO doped YBCO thin films were grown with a non-vacuum, cost-effective chemical solution deposition method. Their microstructures and dependence of the critical current on applied magnetic fields were investigated as a function of dopant concentration.

2. Experimental Studies
The precursor solutions of undoped and doped YBCO were prepared by dissolving acetates of Y, Ba and Cu with different amounts of Zr(IV)-2,4-pentanedionate in propionic acid with a quantity of TFA. It is followed by a solution purification process. The concentration of the solution was fixed to 0.25 M with addition of acetone and propionic acid with a certain ratio. Three different doped solutions were prepared with 6, 12 and 18 mol% BaZrO$_3$. Film deposition on 10 mm x 10 mm STO (100) single crystal substrate was performed by spin coating technique at a rotation speed of 6000 rpm and acceleration speed of 6000 rpm s$^{-1}$.

Coated samples were heat treated according to the profile shown in figure 1. During the heat treatment process, dry gas treatment up to 60$^\circ$C prevents the gel film from absorbing humidity that would deteriorate film integrity. Above 60$^\circ$C, humidified O$_2$ is introduced to suppress the sublimation of Cu trifluoroacetate. Metal trifluoroacetates decompose and harmful gaseous residues are removed during the pyrolysis to give a precursor film. After that, the fluoride containing precursor film is fired at a maximum temperature of 780$^\circ$C under humidified N$_2$ mixed with 100 ppm O$_2$ and then oxygenated at 450$^\circ$C to obtain the YBCO superconducting film.

![Figure 1. Heat treatment profile for the production of undoped and BZO doped YBCO films. All films are crystallized at 780°C and oxygenated at 450°C.](image)

X-Ray Diffraction (XRD) was carried out using a Philips diffractometer with Co K$\alpha$ radiation to ascertain the phase purity of the undoped and doped films. Scanning Electron Microscopy (SEM, Philips XL20) was used to characterize the surface morphology of the final films. The critical transition temperature ($T_c$) and critical current density ($J_c$) of the films were measured by an inductive method. Transport measurements up to 6 T at 77 K on bridges of 0.8 mm length and 50 µm width were carried out with a physical properties measurement system (PPMS).

3. Results and Discussion.
Figure 2 shows the $\theta$-2$\theta$ diffraction pattern of undoped and BZO doped YBCO films. In this pattern, the major peaks correspond to the (00l) reflections of the YBCO phase and STO substrate which indicates that the YBCO film has a strong c-axis texture. Depending on the amount of dopant
concentration, there is a slight increase at the BaZrO$_3$ (200) peak intensity. The structural integrity of the YBCO film can be easily affected by the doping process. In all doped samples (103) orientation of the YBCO phase becomes observable which represents that these small amounts of dopant deteriorate the textured structure of the film. Also, reduction in the (008) YBCO peak intensity with increasing BZO amount is evidence for this structural deterioration. A similar effect was found by J Hänisch et al [7] with nanoscale precipitates of Hf dopant in YBCO films.

Figure 2. X-ray θ-2θ scans of undoped and BZO doped YBCO films with a Co Kα radiation.

Figure 3 depicts surface morphologies of undoped and doped samples. These images show that all films have a smooth, crack free surface and all of them are generally formed by c-axis oriented grains. BZO doped YBCO films present a denser surface structure with decreasing porosity compared with the undoped YBCO films. On the other hand, 18 mol% BZO doped sample surface has bigger sized grains in comparison to the fine grains of 6 and 12 mol% BZO doped sample surfaces.

Figure 3. Surface morphologies of (a) pure YBCO film and YBCO films with (b) 6 mol%, (c) 12 mol% and (d) 18 mol% BZO addition.

The dependence of inductively measured critical transition temperature ($T_c$) on the amount of BZO in the structure is shown in figure 4. The $T_c$ value of 90.1 K for an undoped YBCO film decreases gradually to 88.2 K with the increasing amount of dopant inside. Zr diffusion into YBCO and substitution on yttrium (Y) sites might be the reason for lowered $T_c$. Besides, the transition width of $T_c$ (Δ$T_c$) stays below 1.0 K for undoped, 6 mol% and 12 mol% doped samples but is 2.0 K for 18 mol% doped sample which indicates the higher inhomogeneity of this sample.
Figure 4. Dependence of critical temperature $T_c$ and transition width $\Delta T_c$ on the amount of BZO in YBCO. $T_c$ value is decreasing with increasing amount of BZO.

Figure 5. Inductive critical current density ($J_c$) measurements of undoped and BZO doped YBCO samples at 77K in self-field.

Inductive measurements of the critical current density ($J_c$) at 77 K in self-field was also performed and the results are given in figure 5. The $J_c$ values of samples are 3.15, 2.95, 1.85 and 0.91 MA/cm² for undoped, 6, 12 and 18 mol% doped YBCO films, respectively. As reported by Campbell and Evetts [8], the most accurate quantitative measurements of flux pinning are those of $J_c$ as a function of field and temperature. Therefore, transport measurements were performed up to 6 T at 77 K in order to determine the magnetic field dependence of the critical current density as shown in figure 6.

Figure 6. Field dependence of the critical current density for all samples on a single crystal STO substrate.

It can be seen that the 6 mol% BZO doped YBCO sample has the highest $J_c$ value for all magnetic fields. At fields lower than 4 T, the undoped sample has higher $J_c$ value than 12 mol% doped sample. However, the drop rate of 12 mol% doped sample is slower than the pure YBCO and $J_c$ value of this sample exceeds the value of undoped YBCO sample at fields higher than 4 T. Within all the samples, the 18 mol% doped YBCO film has the lowest $J_c$ value even at high fields which means that the superconducting structure of YBCO film is destroyed; self-field and in-field properties are suppressed with the excess amount of dopants concentration.
4. Conclusions
Barium zirconate (BZO) nanoparticles were introduced into the YBCO structure by the chemical solution deposition (CSD) method. The textured structure of undoped YBCO thin film was deteriorated with increasing dopant concentration. Both critical transition temperature ($T_c$) and critical current density ($J_c$) decreased with increasing dopant concentration. $J_c$ measurements performed at 77 K to 6 T and highest $J_c$ value has been reported for 6 mol% BZO doped sample. Further efforts will focus on improving the $J_c$ value of films under high magnetic fields as well as the application of CSD method with other dopants and REBCO systems.

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