

Thin film nanocomposites based on YBCO with defects comprised of self-assembled inclusions

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Abstract. The critical current of YBCO superconducting coatings in external magnetic field can be enhanced by incorporating high density of extended nanometer-sized defects to act as pinning centers for magnetic vortices. One particular variant involves the deposition superconducting film with columnar defects comprised of self-assembled BaZrO₃, BaSnO₃ or BaHfO₃ nanoinclusions. Here we report the results of our study of YBCO films with different inclusions prepared by MOCVD. For the first time, we succeeded in growth of YBCO films with oriented nanoinclusions of BaCeO₃ phase and demonstrate that it does not reduce T_c of YBCO, in contrast to BaZrO₃ or BaSnO₃. The best composite thin films revealed the T_c value of about 88K and critical current density at 77K above 1MA/cm² in self-field and around 0.3 MA/cm² in 1 T (B//c).

1. Introduction

Many potential applications of high temperature superconductors (HTS) imply that critical current density in external magnetic field should be enhanced. This is only possible through more effective pinning of magnetic fluxes in superconductor. Significant research activity of recent years is focused on processing of YBCO (or RBCO) films containing nano-sized non-superconducting inclusions of secondary phases, which can act as pinning centers. Special attention is paid to inclusions of oxides with perovskite structure, such as BaZrO₃ [1], BaSnO₃ [2] and BaHfO₃ [3]. Being grown simultaneously with YBCO, these phases form an array of protruding rods or columns within the matrix of superconducting film, parallel to the c-axis of YBCO structure. The characteristic diameter of perovskite rods lies usually within several nanometers. Being structurally similar to YBCO, these phases tend to form epitaxial relations with superconductor and do not disturb epitaxial growth. It has been demonstrated by numerous reports that introduction of several mol.% of such inclusions effectively increases j_c value in 1-5 T range for B||c magnetic field orientation [4]. This not only

increases critical current value, but also contributes to the decrease of j_c dependence on field orientation, making HTS behavior more isotropic.

In this paper we report on our study of MOCVD-grown YBCO films containing different amounts of BaZrO₃ (BZO) and BaCeO₃ (BCO) inclusions. To the best of our knowledge, there is only one recent report on YBCO films with BCO inclusions published so far [5]. In our work we concentrated on the influence of inclusions on crystal lattice parameter c of YBCO structure and resulting superconducting properties.

2. Experimental details

Thin films of pure YBCO and composite films with BZO or BCO inclusions were grown by MOCVD technique at 800°C under an oxygen partial pressure of 0.5 mbar on (001)STO single crystal substrates. Typical film thickness was around 400 nm. After deposition the films were oxygenated at 450°C for 1 hour in flowing oxygen. The inclusions were introduced into YBCO matrix by simple addition of Zr (or Ce) precursor to the initial precursor mixture. Solid precursor mixture was fed into evaporator in form of small portions 0.1-0.3 mg each with the use of specially developed vibration powder feeder. For all the elements, dipivaloylmethanate complexes were used, except for Zr, for which acetylacetonate was employed. The fraction of inclusions for some of our samples is estimated to lay inside the practically interesting range of few %. At present stage of our study, it was difficult to find out exact content of zirconium or cerium in our films. This task was problematic due to overlapping of lines in EDS spectra, small thickness of films and low total content of Zr and Ce additions. Due to incongruent nature of MOCVD process, the cation composition of film differs significantly from that of precursor mixture. Therefore, to refer to the composition of films we used the molar ratio of Zr and Ce precursors to that of Y in initial mixture, $[Zr]/[Y]$ and $[Ce]/[Y]$, respectively. The phase composition and orientation of the composite films was investigated by X-ray diffraction with Rigaku SmartLab diffractometer with CuK α radiation and Ge monochromator. SEM characterization was performed with JEOL 840A microscope, equipped with KEVEX EDS analyzer and HKL Channel 5 system (Oxford Instruments). Critical current density was determined from ac susceptibility measurements for temperature range of 63-90K in external magnetic field up to 1 T.

3. Results

3.1 Cation composition of films with BZO and BCO inclusions

As already mentioned in Experimental section, we could not determine exact cation composition of composite films with good accuracy by EDS analysis available to us. However, we could reproducibly control the composition of films by changing precursor mixture composition. Fig.1 illustrates gradual change in XRD peak intensities on θ - 2θ -scans originating from admixture oxide and YBCO with the variation of initial precursor composition. Due to the fact that XRD peak intensity of epitaxial films is strongly dependent on degree of crystal perfection, we could not completely rely on such intensity ratio determining the film composition. Nevertheless the result is a good indication of successful growth of composite films with varying content of non-superconducting admixture phase by MOCVD technique.

3.2 XRD study of BZO and BCO inclusions in composite YBCO films

Crystal structure of bulk BaCeO₃ is tetragonal with $a=b=0.6212$ nm and $c=0.8804$ nm [6]. However, the distortion of perovskite cubic lattice is too small to be visible in XRD spectra of inclusions in thin films, therefore, we use further for BCO pseudocubic notation and average cubic lattice parameter of 0.4396 nm. For all the samples studied we revealed c -axis oriented epitaxial growth of YBCO on SrTiO₃ substrate. The inclusions also grow in oriented state in spite of large mismatch with YBCO matrix in ab plane (table 1) with the following epitaxial relations: (001)[100]BMO || (001)[100]YBCO

(M=Zr or Ce). XRD spectra of composite films are given in Fig.2. Except for BZO and BCO inclusions, some admixture of Y_2O_3 and CuO was usually observed in our samples. These secondary phases are expected to appear accordingly to the known phase relations in epitaxial YBCO films, since a part of barium must be consumed by formation of binary oxide with ZrO_2 or CeO_2 [7].

Table 1. Lattice mismatch (%) of YBCO with BZO and BCO.

	in plane ^a	out-of-plane ^b
BaZrO ₃	+8.3	+7.1
BaCeO ₃	+14.0	+12.8

^a determined as $(a_{BMO}-a_{YBCO})/a_{YBCO} * 100\%$.

^b determined as $(3a_{BMO}-c_{YBCO})/c_{YBCO} * 100\%$.

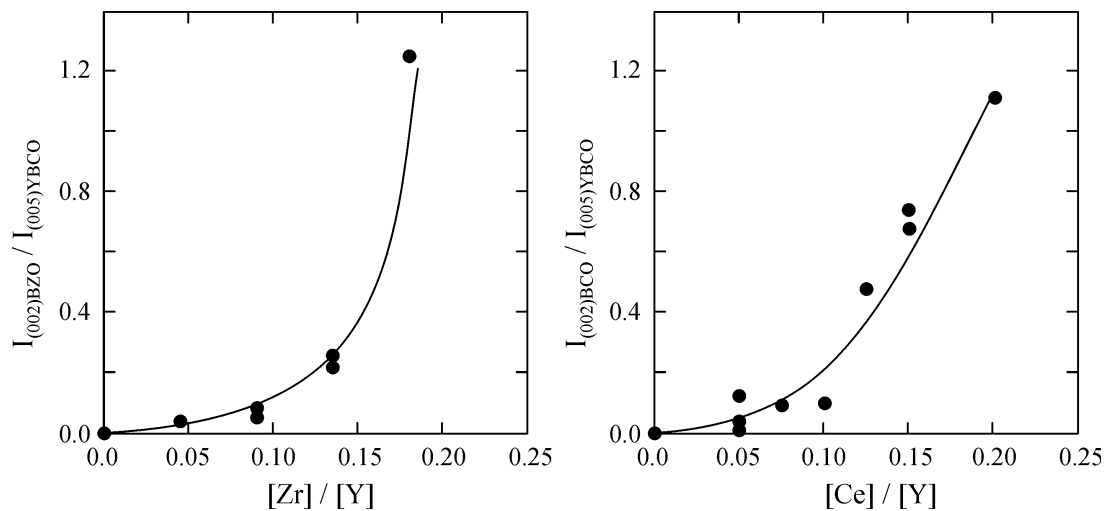


Figure 1. The dependence of relative intensity of BZO and BCO lines in XRD spectra of composite films on precursor composition. Solid lines are guides to the eye.

The respectively large width of (002)BZO peaks in XRD spectra is possibly due to small inclusion size, strain and/or solid solution formation. (002)BZO reflexes tend to become narrower as admixture content increases. The observed out-of-plane lattice parameter of BZO (0.414-0.415 nm) is smaller than that of bulk standard ($a = 0.4193$ nm) by almost 1% of value, that is most probably caused by a significant strain. The probable chemical substitution of Zr by Y can be ruled out, since the cubic lattice parameter of $Ba(Zr,Y)O_3$ is known to increase with the increase of yttrium content [8]. It is possible however that zirconium is partly substituted by smaller copper cation.

The width of XRD lines from BCO is constant for all the samples studied revealing similar crystallite size or strain. The lines are also significantly narrower than those of BZO. The BCO lattice parameter is increasing from 0.432 to 0.436 nm on increasing Ce doping, approaching the average bulk value of 0.4396 nm. It can be supposed that BCO in films with low cerium content is doped with yttrium. The crystalline quality of YBCO, if judged by FWHM of (00*l*) peaks, is more deteriorated in case of films containing large amount of BCO inclusions, as compared to the YBCO+BZO composite films. The appearance of admixture of undesirable a-axis orientation is also evident in this case.

From rocking curve measurements performed for films with [Zr]/[Y] and [Ce]/[Y] ratio around 0.10 one can conclude that the type of inclusion has only slight influence on YBCO crystallinity.

However, large difference in crystallinity of nano-inclusions is evident, since rocking curve for BCO is significantly narrower than that for BZO inclusions. This observation is in correspondence with narrower BCO peaks in θ - 2θ -scans (Fig.2). It can be probably related to larger mismatch between BCO and YBCO, resulting in larger extent of strain relief in this case. Another possible reason is the larger size of BCO inclusions; to find out if it is true or not, detailed HREM study is necessary.

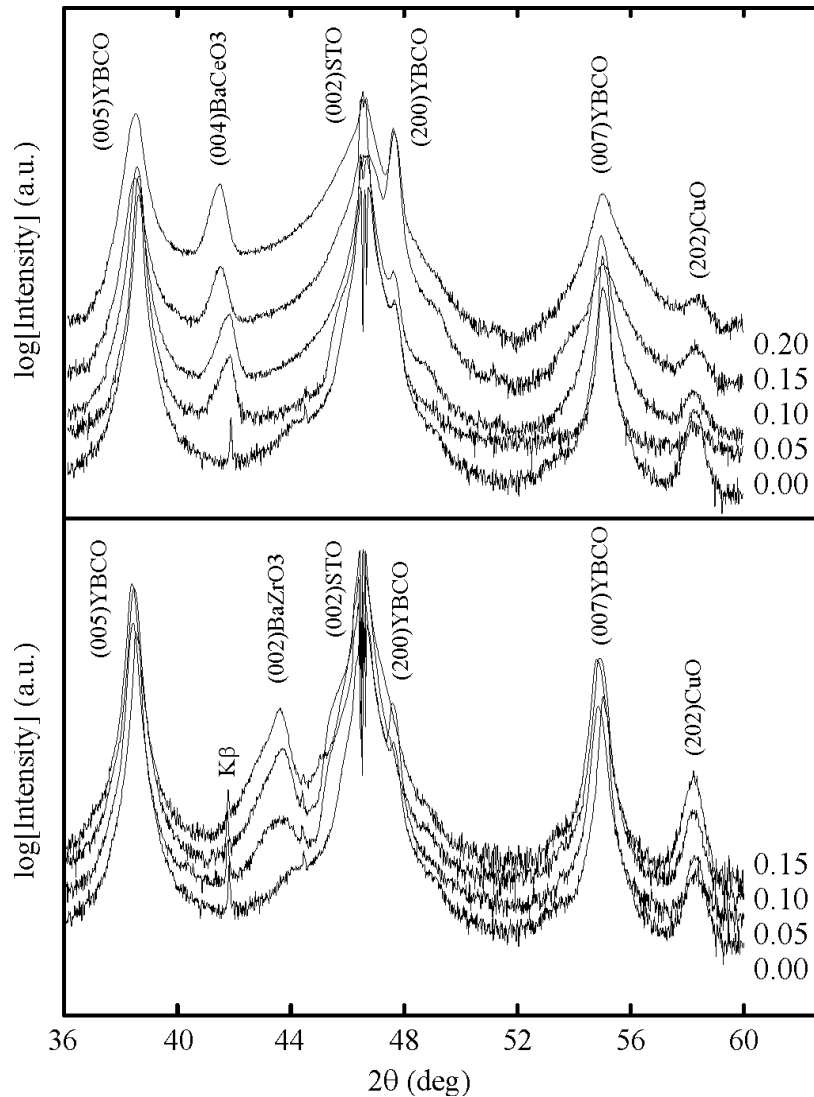


Figure 2. XRD spectra of YBCO films with varying amount of BaCeO_3 and BaZrO_3 inclusions. The ratio of molar amount of Ce or Zr precursor to that of Y precursor is indicated on the right side of spectra.

3.3 The influence of inclusion type on YBCO crystal structure

We have observed that doping of YBCO films with Zr is accompanied by remarkable increase of its c -axis lattice parameter. Interestingly, considerable amounts of Ce doping did not result in any change of this lattice constant (Fig.4). The strain of YBCO lattice can be ruled out, since strain relief in YBCO occurs easily with the formation of misfit dislocations. The reason for the increases of c -axis length may possibly be Zr substitution for copper atoms in the YBCO structure. The same effect was previously reported for YBCO- BaSnO_3 [9] and ErBCO- BaNb_2O_6 [10] systems. The behaviour can be

explained by ionic radii for coordination number 6, typical for B-position of perovskite structure: Ce^{4+} (0.087 nm) > Cu^{2+} (0.073 nm) > Zr^{4+} (0.072 nm) > Sn^{4+} (0.069 nm) > Nb^{5+} (0.064 nm) > Cu^{3+} (0.054 nm) [11]. Cerium cation is considerably larger than copper, making this kind of chemical substitution impossible, while ionic radii of Zr^{4+} nearly equals that of Cu^{2+} . The supposition of chemical substitution is supported by gradual decrease of T_c of YBCO on increasing Zr substitution. In our study, the film with $[\text{Zr}]/[\text{Y}]$ ratio of 0.13 and YBCO c-axis lattice parameter of 1.172 nm has been found to have T_c value equal to 86.5K. In contrast, the addition of BCO inclusions into YBCO matrix did not show any significant T_c reduction.

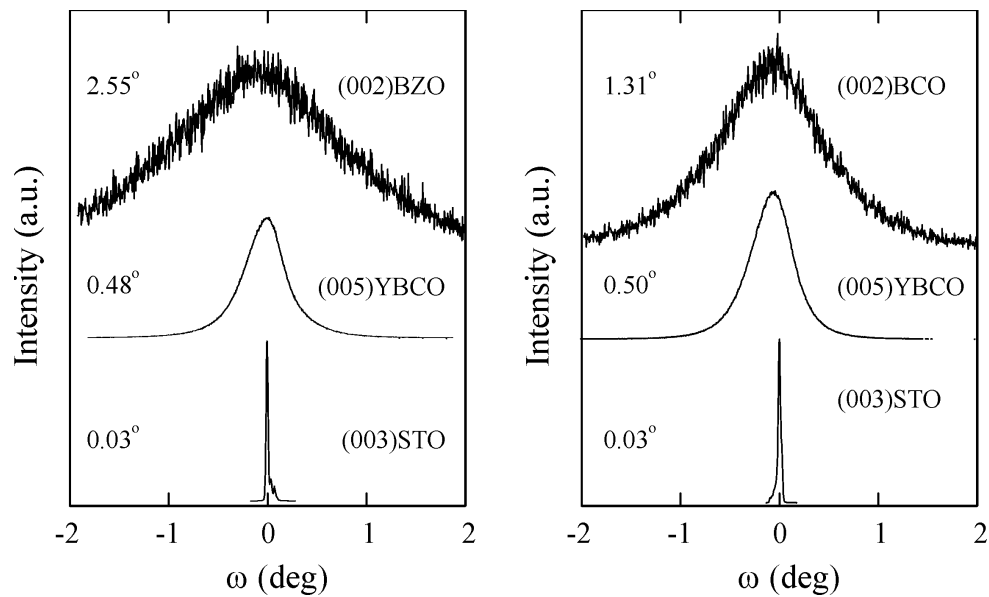


Figure 3. Rocking curves of substrate, YBCO superconducting matrix and inclusions. On the left, corresponding peak FWHM values are given.

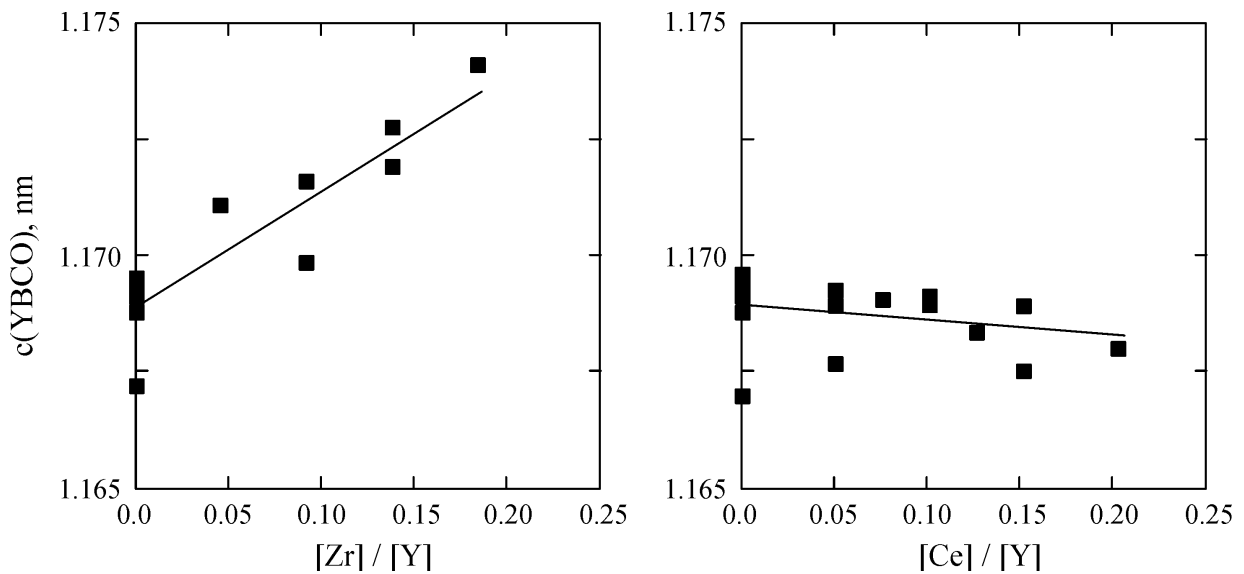


Figure 4. YBCO c-axis lattice parameter dependence on content of Zr or Ce in the sample.

3.4 Superconducting properties of YBCO composite films

The best composite films produced demonstrated critical current density (j_c) values above $1\text{MA}/\text{cm}^2$ at self field and 77K and around $0.3\text{ MA}/\text{cm}^2$ in 1 T and 77K ($B\parallel c$). The normalized critical current density of YBCO films with BZO inclusions versus applied magnetic field ($B\parallel c$) is shown in Fig.5. It was observed that BZO addition allows to increase the critical current density stability and the optimal amount of BZO particles is achieved at $[\text{Zr}]/[\text{Y}]$ around $0.05\text{-}0.10$. The optimum most probably results from the competition of three processes: the enhancement of pinning force, the decrease of T_c and degradation of YBCO crystallinity films with increasing concentration of inclusions. The measurements of critical current of the YBCO film with BCO inclusions with $[\text{Ce}] / [\text{Y}] = 0.10$ has shown that this addition did not increase critical current at 77K . This could be due to non-optimal amount of inclusions, their large size or large misfit between YBCO and BCO structures leading to considerable strain in superconducting film. Further investigations are under way to clarify this issue.

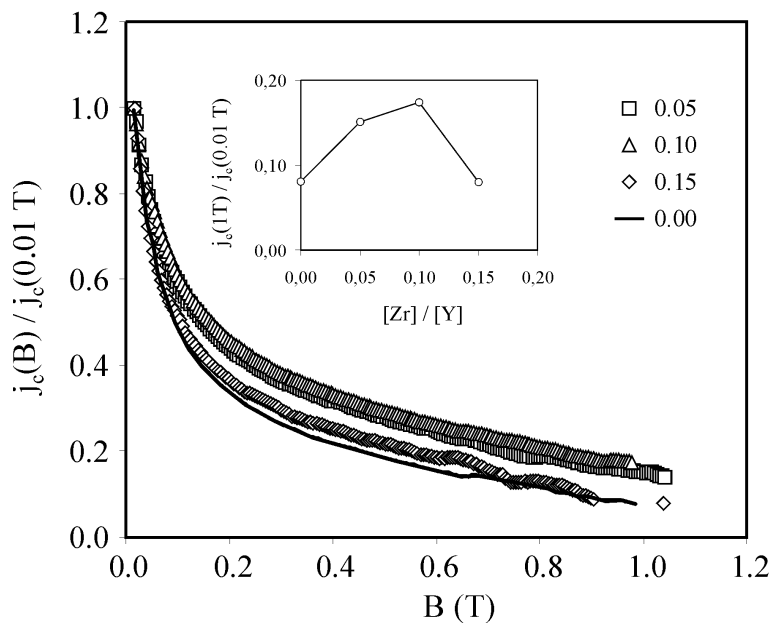


Figure 5. Magnetic field dependences of j_c/j_c^{sf} at 77K for the YBCO+BZO films. The $[\text{Zr}]/[\text{Y}]$ ratio is indicated in right corner. The inset demonstrates effect composition on the j_c/j_c^{sf} of thin films in external magnetic field of 1 T ($B\parallel c$).

4. Conclusions and future work

We succeeded in MOCVD growth of high quality superconducting YBCO films containing nanoinclusions BaZrO_3 and BaCeO_3 phases. XRD study of composite films reveal complex behavior of these systems and critical differences between Zr and Ce substitution. It is argued that Ce substitution leads to possibly larger perovskite particle size, than in case of Zr doping. On the other hand, critical temperature is not reduced in YBCO+BCO composites, while T_c gradually decreases with increase of Zr doping. The results obtained on BZO inclusions are consistent with observations of other authors, while detailed study of BCO admixture phase is reported here for the first time.

Future work will be focused on characterization of current-carrying properties of composite films and investigation of their microstructure by means of transmission electron microscopy.

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