ESRF	**Experiment title:** **Local atomic structure of nanoadditives in composite YBCO and GdBCO thin films**	**Experiment number:** HC-2421
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Report:

1. Introduction

The use of high-temperature superconducting (HTSC) materials in the energy sector, transport, industrial physics involves the creation on their basis the long winding conductors. These conductors, first of all, should have a high critical current density J_c, which is ensured by the presence in the material of either natural or artificial effective magnetic flux pinning centers.

One of the possible and convenient from the technological point of view methods of creation the additional pinning centers and, consequently, increasing the transport characteristics of HTSCs is the introduction to the volume of HTSCs on the stage of their synthesis of nanosized nonsuperconducting additives (NSA) of inorganic materials which are inert with respect to the superconducting matrix. Here it is necessary to choose the impurities, which on the one hand would not lower the critical temperature of the superconductor and on the other hand would play the role of the effective pinning centers. There are works that deal with the introduction to the HTSCs of the nanoscale additives of magnesium oxide, carbides of niobium, tantalum, titanium, silicon and hafnium nitride.

However, the question still remained unsolved is about the optimal average size (dispersion) of particles of the introduced impurities. The task is complicated by the fact that during the process of chemical vapor deposition of $REBa_2Cu_3O_{7-\delta}$ (REBCO, RE = Y, Sm, Gd) films is changing not only the initial size of the introduced nano-additives, but also their local

environment in the matrix material. In this regard, the aim of research is to determine by means of EXAFS the influence nano-additives embedded in the YBCO and GdBCO matrix on the local atomic structure of matrix, so as the local environments inside the nano-additives.

2. Experiment

EXAFS-spectra were measured at high-quality epitaxial YBCO and GdBCO films with $BaZrO_3$ and $BaSnO_3$ nano-additives above the *K*-Cu (8979 eV), *K*-Zr (17998 eV) and *K*-Sn (29200 eV) edges, using a fluorescence detector at 20, 60, 90, 140, 190, 240, 2170 and 300 K at beamline BM-23. The low concentrations of embedded additives (5-20 mol. %) required the use of the high photon flux source and multi-channel fluorescence detector (Ge, 13 elements) with high sensitivity what should provide the collection of the high-quality spectra with the high signal/noise ratio up to 16 $Å^{-1}$ in momentum space, which in turn allow to conduct the analysis of the absorbing atoms local environment up to 6 Å in real space. The temperature dependence of Debye-Waller factors allowed us to determine the stiffness of interatomic bonds in the nearest environment of absorbing atoms inside the HTSC matrix, so as inside the nano-additives. One of the important parts of our investigations was to understand the local YBCO (GdBCO) matrix distortions around the artificial pinning centers. It is very important to know how these distortions are changing with matrix oxidation during synthesis and to connect it with the type and size of nanoparticles.

3. Results

Among the whole variety of pinning inclusions used in REBCO films our attention was focused on Zr addition in YBCO [1-4], as one of the most technologically advanced solutions. Industrial (SuperOx Inc.) 2G MOCVD $YBa_2Cu_3O_{7-y}$ tapes containing 0, 5, 10, 20 mol % of $BaZrO_3$ nano-additives used as artificial pinning centers were investigated. The optimal $BaZrO_3$ doping level for critical current performance is established to be 5 mol %.

3.1. $BaZrO_3$ nano-additives incorporation in $YBa_2Cu_3O_{7-y}$ MOCVD films

Obtained XANES spectra at Zr K absorption edge demonstrate similarity with rather unique doublet of bulk $BaZrO_3$ (Fig. 1a). It leads to conclusion that the studied nano-additives in our films are $BaZrO_3$ nano-crystallites.

EXAFS further confirms it. It is evident (Fig. 1b) that presence and position of FT maxima for case of Zr nano-additives also coincides with $BaZrO_3$ standard. The observed difference in amplitudes of signal corresponds to the fact of existing structural disorder in nano-additives. Moreover, the disorder achieves maximum and reaches a certain saturation in the case of high concentration of Zr inclusions > 10 mol %. FT maxima offset towards smaller radial coordinate R for the sample with 5 mol % Zr indicates that nano-additives are in compressed state there.

Demonstrated results are qualitatively similar to those described in [5], however, reveal the special behavior for 5 mol % concentration of $BaZrO_3$ inclusions, correlating to critical current performance.

3.2. Influence of $BaZrO_3$ nano-additives on the local structure of $YBa_2Cu_3O_{7-y}$ matrix

Cu K-edge temperature EXAFS measurements at 20, 60, 90, 140, 190, 240, 270 and 300 K allowed us to study local environment of Cu, specially establish the stiffness of Cu-O bonds.

Processing EXAFS spectra was carried out according to standard procedure using FEFF [7] and VIPER [8] programs.

It is seen from Fig. 2 that the inclusion of nano-additives does not lead to any noticeable change in bond lengths of $YBa_2Cu_3O_{7-y}$ matrix, because FT peaks are not displaced relatively to each other. The main impact of the pinning centers is manifested in Cu bonds disordering, characterized by Debye-Waller factor σ. The temperature behavior of σ is described by Einstein's model [9]:

$$\sigma^2 = \sigma_{stat}^2 + \frac{\hbar^2}{2k\mu}\frac{1}{T_E}\coth\left[\frac{T_E}{2T}\right], \quad (1)$$

where σ^2_{stat} – static factor, T_E – Einstein temperature, μ – reduced mass of atoms in bond. Values of T_E enables to judge of bond stiffness k_{bond} ($T_E \sim \sqrt{k_{bond}/\mu}$) [10].

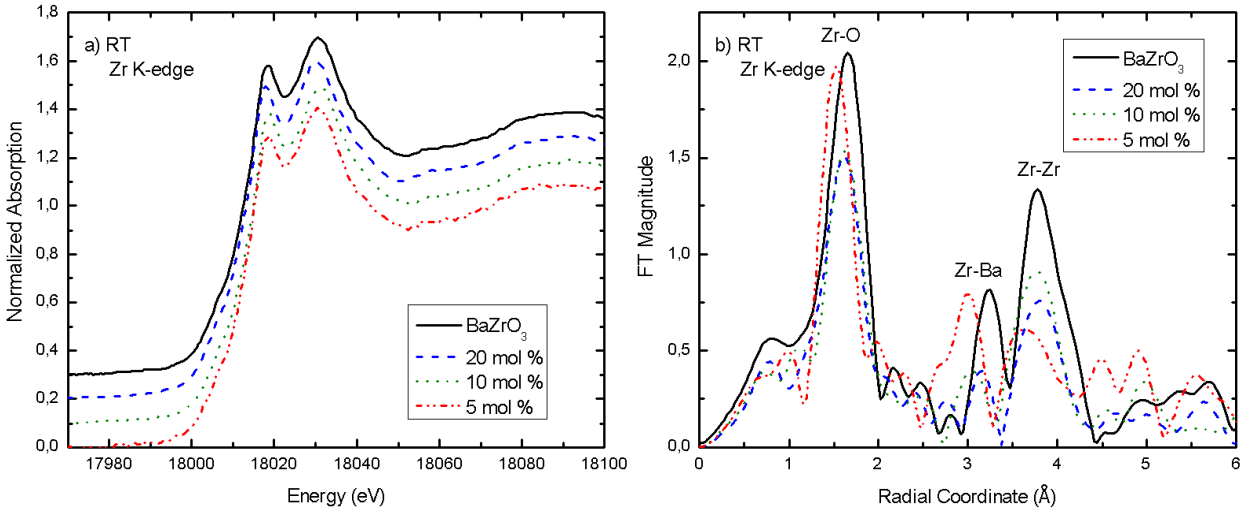

Fig. 1. Zr K-edge XANES (a) and EXAFS FT Magnitude (b) for $YBa_2Cu_3O_{7-y}$ MOCVD films containing 5, 10, 20 mol % of $BaZrO_3$ nano-additives and $BaZrO_3$ standard at RT.

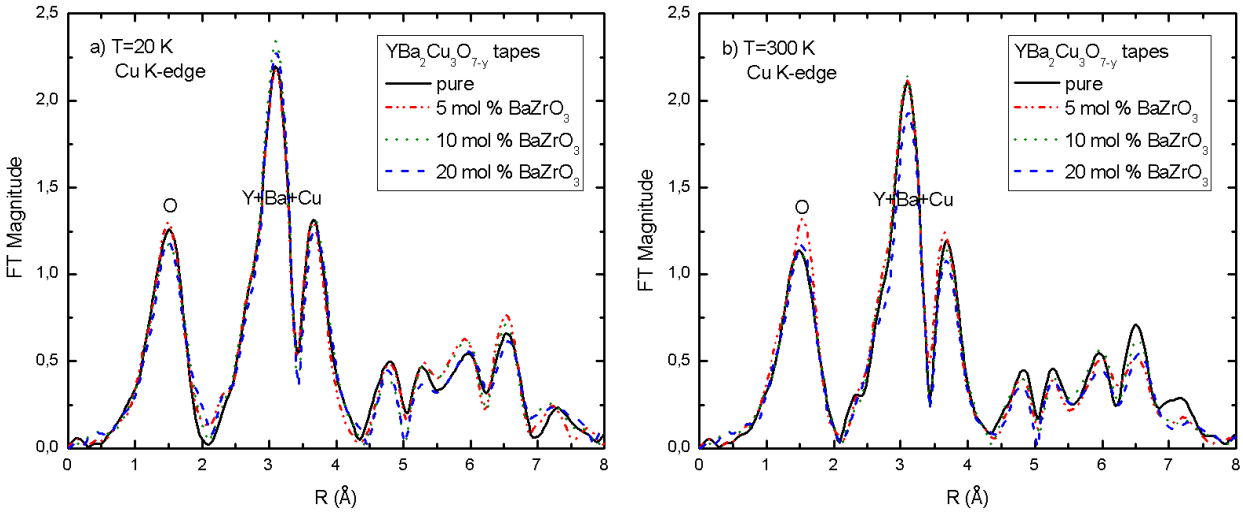

Fig. 2. Cu K-edge FT Magnitude for $YBa_2Cu_3O_{7-y}$ MOCVD films containing 0, 5, 10, 20 mol % $BaZrO_3$ nano-additives at 20 K (a) vs. 300 K (b).

Already from Fig. 2a we can say that a small additive $BaZrO_3$ of 5 mol % slightly arranges Cu-O bond, while large inclusions begin to disorder it (the effect of 10 and 20 mol % $BaZrO_3$ is the same). Nano-additives caused disordering is also observed by EXAFS in [6]. From Fig. 2a,b is also clear that 5 mol % $BaZrO_3$ additive makes Cu-O bond the most stiff (see Table 1), which is in good correlation with the largest observed value of the critical current.

Table 1.

$BaZrO_3$ (mol %)	σ^2_{stat}, 10^{-3} Å^2	T_E, K
0	6.0	409
5	5.9	488
10	6.4	426
20	6.4	438

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