

# Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> PHASE TRANSFORMATIONS STUDIED BY REAL TIME SYNCHROTRON RADIATION

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## ABSTRACT

The goal of this paper is to investigate the phase transformations of thin multi-layer structures from High Temperature Superconductor - Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> (YBCO) and manganate - La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSMO, both deposited on different substrates by means of real-time synchrotron X-ray scattering. The phase formations and phase interaction process were in situ examined in oxygen atmosphere and high temperature. The latter was only possible using SR at Rossendorf Beam Line (ROBL), because the process demands short measuring times in order to follow the process adequately. The temperature ranges of the superconducting phases were also described analyzing the lattice parameter and the peak evolutions. The formation of new un-expected phases was registered. We established the general temperature range of the superconducting YBCO phase formation. To attain this purpose a special vacuum chamber was constructed to fit the goniometer and to work in oxygen atmosphere at elevated temperatures.

## 1. INTRODUCTION

The theory by Bardeen, Cooper and Schrieffer (BCS) [1] provided the basis for understanding superconductivity at a microscopic level, superseding previous phenomenological approaches. Central to the BCS theory is the complex coupling between a pair of electrons of opposite spin and momentum through an interaction with the lattice phonons. The electrons that normally repel each other develop a mutual attraction, forming a Cooper pairs, so that they condense into a single state that flows like a frictionless fluid. The average maximum length at which the phonon-coupled attraction can occur is known as the coherence length- $\xi$ . Since the electron coupling is weak, the energy difference between normal and superconducting state is small with the latter laying a distance  $2\Delta$  below the former. Thus, a forbidden energy gap of width

$$2\Delta = 3.5kT_C,$$

appears in the density of states centered about the Fermi level at 0K. When the temperature is raised, the amplitude and frequency of lattice atomic motion increase, interfering with the propagation of phonons between correlated Cooper

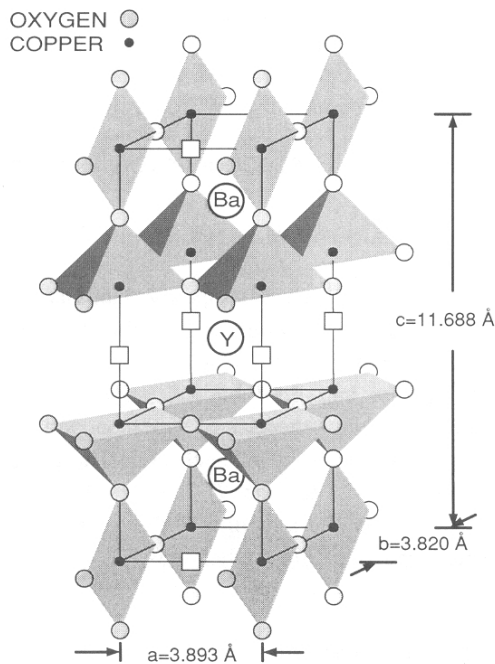
pairs. The attraction between electrons is diminished and  $2\Delta$  decreases. At  $T = T_C$   $\Delta = 0$ . Any perturbation in structure or composition extending over the coherence length can alter  $T_C$  or  $2\Delta$ , placing a practical limit on useful superconducting behavior. Superconductivity apparently persists to film thickness of about 10 Å, lower limits are difficult to establish because the films of such thickness are generally discontinuous. The dependence of critical temperature  $T_C$  on deposition conditions and film thickness has been studied for a long time, though not easily predictable or explainable effects have been reported – e.g. the critical temperature and current depends not only on the film thickness, but also on the magnitude and sign of the film stress, impurities, lattice imperfections, and grain size in generally inexplicable ways. When either  $\lambda_s$  (called penetration depth where both magnetic and current fluxes are confined at the surface) or  $\xi$  becomes comparable to the film thickness, deviation from bulk superconductivity properties may be expected.

In order to achieve reliable performance of spin-injection devices based on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) - La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSMO) double layers, it is essential to reproducibly control not only the individual film growth, but also to form a stable interface region, which is of critical importance for the device characteristics. For deposition of the high-temperature superconducting (HTS) films, a DC faced-target off-axis magnetron sputtering technique was used, while for the ferromagnetic films, RF off-axis magnetron sputtering was employed. The magnetic and electric properties of S/F double-layers are strongly affected by the deposition conditions, lattice mismatch with the substrate, and by the thickness of the films [2]. Different combinations (YBCO/LSMO and LSMO/YBCO) with varying parameters were characterized by X-ray diffraction and Rutherford Backscattering Spectrometry (RBS). The contact-less measurements gave  $T_C \sim 86$  K and  $J_c \sim 0.7 \cdot 10^6$  A/cm<sup>2</sup> for YBCO as a bottom layer, and  $T_C \sim 88$  K and  $J_c \sim 1.7 \cdot 10^6$  A/cm<sup>2</sup> for YBCO as a top layer.

The unit YBCO cell shown in Fig.1 is a variation of the class of oxygen-defect perovskites involving a tripling of unit cells. Perovskites have the property of reversibly absorbing or losing oxygen and are therefore nonstoichiometric with respect to this element. Much effort has been expended in correlating crystal structure and oxygen content with  $T_C$ . As the oxygen content increase from 6.3 to close to 7 atoms per cell  $T_C$  is observed to increase from 30 to  $\sim 90$  K. Concurrently both the  $a$  and  $c$  lattice constant decrease,

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whereas that for  $b$  increases – each by approximately 1% [3].



**Figure 1 - Structural model of the unit  $\text{YBa}_2\text{Cu}_3\text{O}_7$  cell.**  
Squares are vacant sites.

Current transport is believed to occur along the Cu-O ribbons ( $b$ -axis). The pyramidal  $\text{CuO}_2$  sheets perpendicular to the  $c$  axis reflect the layered structure of this as well as other high- $T_c$  oxide materials. Through its effect on atomic spacing oxygen necessarily also modifies the valence of Cu as well as the Cu-O bond length; increasing O decreases the former and increases the latter. Since Cu appears to be an essential ingredient in high  $T_c$  oxides, it has been argued that its valence state and nature of bonding to O critically influence superconducting properties. In fact, loss of oxygen with attendant lowering of  $T_c$  is a major degradation mechanism in thin films. An overall oxygen stoichiometry of very nearly to 7 is required for optimal properties. The oxygen diffusion process has been extensively studied [4].

The goal of this paper is to investigate the phase transformation of thin multi-layer structures from High Temperature Superconductor- $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) and manganate  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) both deposited on different substrates by means of real-time synchrotron X-ray scattering.

## 2. EXPERIMENTAL

Within the scope of the present work we intended to investigate the influence of the spin-polarized quasiparticle injection from manganite  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) layer on the suppression of the supercurrent flowing in a high temperature  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) layer, the both separated by a thin dielectric film ( $\text{CeO}_2$  either  $\text{SrTiO}_3$ ). HTSC devices are more sensitive to quasiparticle injection. The effect of the injection of spin-polarized quasiparticles from ferromagnetic  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) gate leads to a greater current

gain with respect to those attained from un-polarized quasiparticles. So, spin injection devices offer the potential for increased speed and gain compared to existing devices.

During the temperature treatment the crystalline YBCO films were analyzed by real-time synchrotron X-rays scattering. The study of diffraction spectra during annealing at different temperatures allows determining the time needed to form the superconducting phase. Similarly, one can follow up the stability range by extending the experiment over longer time. By recording spectra at different temperatures for a time series each, we found the general existence range of the superconducting state in your layer system.

To attain this purpose a special chamber was constructed to fit the goniometer and to work in oxygen atmosphere at elevated temperatures, shown in Fig.2. The spherical opening for radiation entrance-exit is the polyamid “kapton”, transparent for the X-rays and resistant to high temperatures, leaving no residues. The measured structure was 40 nm quenched in vacuum YBCO deposited on  $\text{SrTiO}_3$  (STO) substrate. The experiment carried out was designed to simulate the process of oxygen uptake and superconducting phase formation such as it take place in the deposition set up. Set of scans was measured from 650°C to room temperature in oxygen pressure of 900 mbar. The oxygen content is correlated with the lattice constants of the YBCO layer.

## 3. RESULTS AND DISCUSSIONS

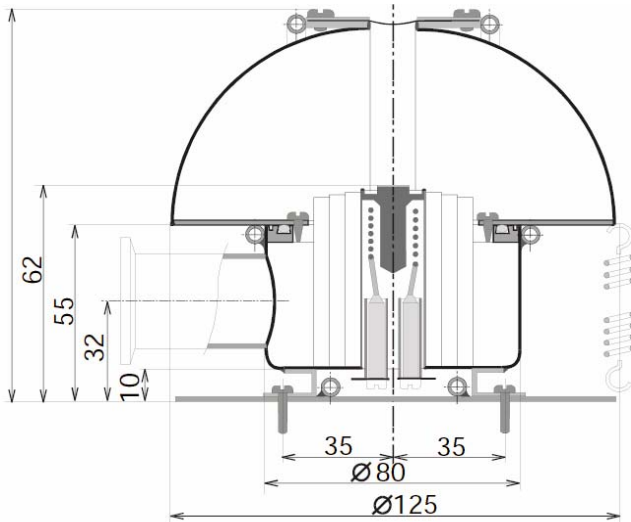
By recording spectra at different temperatures for a time series each, we show the general existence range of the superconducting state in single and double layer systems. We have been mentioned also how important is to form a stable interface region. We have found by high-precision RBS simulation that nevertheless how good is the film quality, an interface region of disorder from 20 to 40 nm is presented in all structures. The width of these regions was only possible to calculate by the channeled RBS spectra (Fig. 3) where they appears as a relatively narrow peaks visible for the barium cations, as well as for the cuprum ones.

The beginnings are denoted as “SD” – surface dislocations, and the ends – “ID” – interface dislocations. We note, that nevertheless how good the superconducting film is, these zones are always present. The interface region is of critical importance when very thin films are demanded and if no other phases (not-superconducting) are detected in such film of width not overcoming 40 nm, these regions exercise considerable stress due to the mismatch with the substrate.

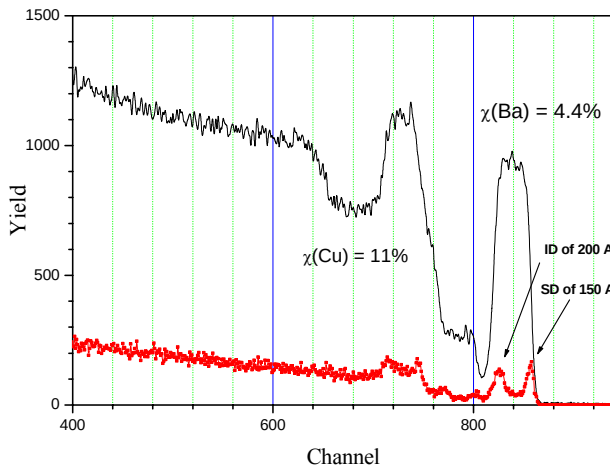
The measured structure was 40 nm quenched in vacuum YBCO deposited on  $\text{SrTiO}_3$  (STO) substrate. Set of scans was measured from 650°C to room temperature in oxygen pressure of 900 mbar. The oxygen content is correlated with the lattice constants of the YBCO layer. Its structure consists of three cubes, with yttrium or barium at the center, copper at the corners, and oxygen at the middle of each edge with the exception of the middle cube, which has oxygen vacancies at the outer edges.

The critical feature in this structure is the presence of two sheets of copper-oxygen ions, located above and below the oxygen vacancies, along which superconduction takes place.

The transport of electrons perpendicular to these sheets is not favored, making the YBCO structure severely anisotropic. One of the challenges in fabricating crystalline YBCO ceramics capable of passing large currents is to align all the grains in such a manner that their copper-oxygen sheets line up. We calculated the lattice parameter "c" in function of the temperature, which is related with the oxygen content.



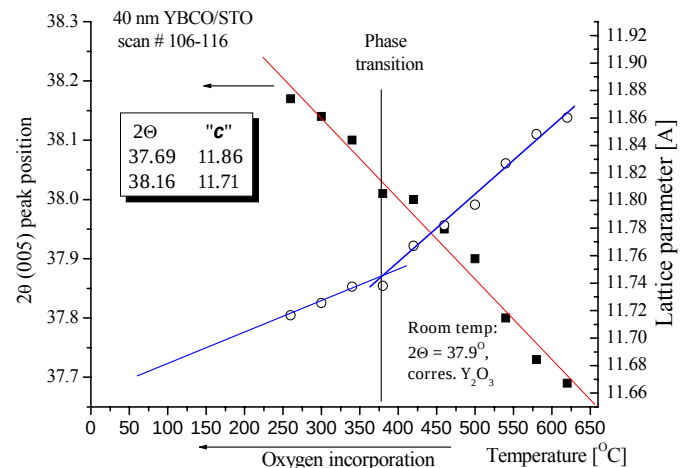
**Figure 2 - Vacuum chamber with heater operating in oxidation atmosphere close to temperature of 800°C designed to fit the goniometer of the SR beam. All units are in "mm".**



**Figure 3 - 1.7 MeV <sup>4</sup>He<sup>+</sup> RBS spectra in random (solid line) and channeling geometry (dots) of YBCO/STO structure annealed in oxygen atmosphere.**

In Fig.4 YBCO (005) peak evolution as a function of the annealing temperature is shown. The straight line, with correlation factor 0.988 refers to the  $2\theta$  positions, which shifts to the higher values. Before raise the temperature, a spectra was taken at room temperature which give  $2\theta = 37.9^\circ$  – characteristic value for the body-centred cubic Y<sub>2</sub>O<sub>3</sub> phase, together with BaCuO<sub>2</sub> phase. The two straight lines representing two one-to-one dependences refer to the calculated lattice parameter "c" via the relation of Nelson-Relay. Here

it is possible to distinguish two very probable transition mechanisms; the first one occurring at the higher temperature region transforming phases (called later fractions) like Y<sub>2</sub>O<sub>3</sub> and BaCuO<sub>2</sub> quenched in the deposition set up. These phases exist together with the oxygen poorest YBCO phase with oxygen content 6.36. Such phase have T<sub>c</sub> in the range 30-40K. The fraction's bonds are subject to high temperature and reactive oxygen atmosphere dissolves in a new YBCO cells. The fraction phases disappear during the process and new YBCO peak (111) appears at 33.74°. The second transition mechanism takes place at lowers than 400° C and is related with subsequent oxygenating of the so formed orthorhombic cell. Most probably by diffusion process oxygen atoms takes the free vacancies places situated between the pyramidal CuO<sub>2</sub> sheets (Fig.1). The experiment was carried down to 260°C and by this temperature the "c" lattice parameter is equal to 11.71 Å corresponding to oxygen content 6.7, according to Jorgenson et al [5]. This value corresponds to a high crystalline quality superconducting film and is the best value obtained in this work. If one follows the trend by the second line up to room temperature an oxygenating process could result in lattice parameter of 11.67° corresponding to Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.



**Figure 4 - (005) peak shift following the oxygen corporation and the corresponding c-axis parameter variation.**

Fig.5 illustrates YBCO (001) peak amplitude evolution as function of the oxygenation-annealing process. This peak was particularly chosen as far as its plan of reflection is the most simples and less influenced by the substrate or by the oxygen vacancies. It is believed to affirm Cu-O plan formation and the alignment of the "c" axis in larger grains (CDR) [3]. In Fig.5 four temperatures – phase transition region were established. The first called "Fraction phase melting" is characterized by very low peak amplitude in the range of 620-540°C. By this region the quenched YBCO phase and the fraction phases "melt" or exist other cubic cells are submitted to transformation. In the second region noted as "YBCO-reformatting", relatively fast process of YBCO formation is promoted by the increased atom mobility and oxygen diffusion leading the YBCO-cells reformatting free

of other mixed phases. After this temperature region a separation in  $b$  and  $a$  axis take place and the tetragonal-orthorhombic transition stage occurs. The termination of this relatively fast cell-reformatting process perfectly coincides with the two regions referring to a different lattice evolution dynamics (Fig.4). The last region described, as “Oxygen Vacancy Supply” is the most “cooled” part of the process where only slight oxygen incorporation continue to change the lattice, improving so its quality, respectively resulting in increased critical temperature.

If scans are achieved at very grazing angle at specular mode a regular undulating spectrum appears known as Laue fringes. The repetition frequency is directly related with the film thickness and it is typical for high crystalline film quality. Such Laue fringes are observed in the studied spectra YBCO/STO and they begin to clearly appear below 380°C. This special feature, not shown here, perfectly matches to the already defined transition regions, Fig. 5.

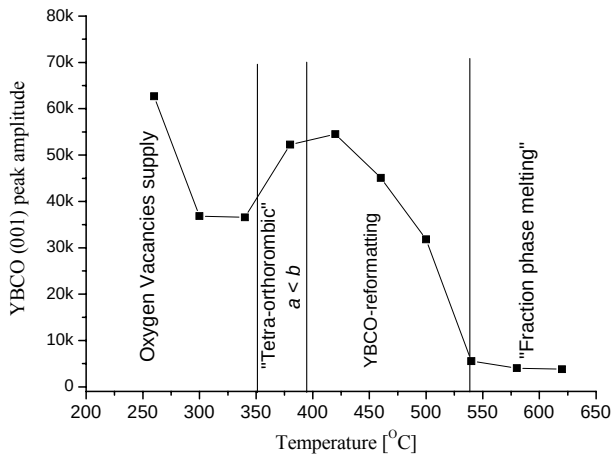


Figure 5 - Temperature variation of the (001) peak amplitude.

In Fig 6 (a, b) are presented extracts from the SR-XRD experiment, referring to the room temperature scan (Fig. 6a) and the last scan from this set registered at the lowest (260°C) temperature, all drawn by constant oxygen pressure of 900 mbar. It is worth noting, that when thin film is growth at insufficient oxygen supply other phases could be formed, such as for ex.  $\text{BaCuO}_2$ ,  $\text{Cu}_2\text{BaO}_2$  and/or  $\text{Y}_2\text{O}_3$ . These phases are indicated with arrows on Fig 6 (a,b). All other YBCO (00l) planes are shifted in left (to lower  $2\theta$ ) in comparison with the orthorhombic superconducting phase. Moreover peak (004) is missing. At the end of the process and the reflections from the  $\text{BaCuO}_2$  phase disappears and (004) YBCO peak appears. The (00l) peak positions correspond to the peak reflections representative for  $\text{Y}_{1.1}\text{Ba}_2\text{O}_{6.68}$  (Pattern: 39-486, orthorhombic lattice,  $a=3.82 \text{ \AA}$ ,  $b=3.889 \text{ \AA}$ ,  $c=11.7 \text{ \AA}$ ).

In the frame of this study we established also that the coherent domain reflection (CDR) size undergoes changes, namely increase from 28 to 38 nm. The increasing CDR sizes, during the oxygen uptake claim that the phase transition into orthorhombic structure unifies the grains into larger domains leading to relaxation the stress and cell mismatches. By this way, the necessities oxygen in the vacant states and the pyramidal Cu-O sheets are supplied from one side, and from other, the Cu-O ribbons get parallel each to other increasing

in this manner the current transport. According this dependency the individual grain could gain dimension up to 38 nm.

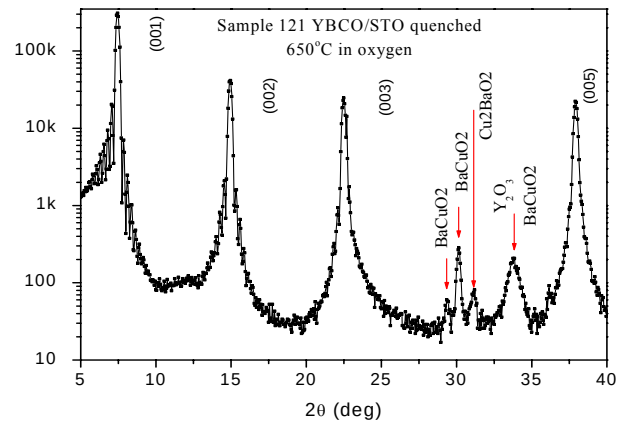


Figure 6a - YBCO/STO scan at the beginning of the oxygen uptake at 650°C.

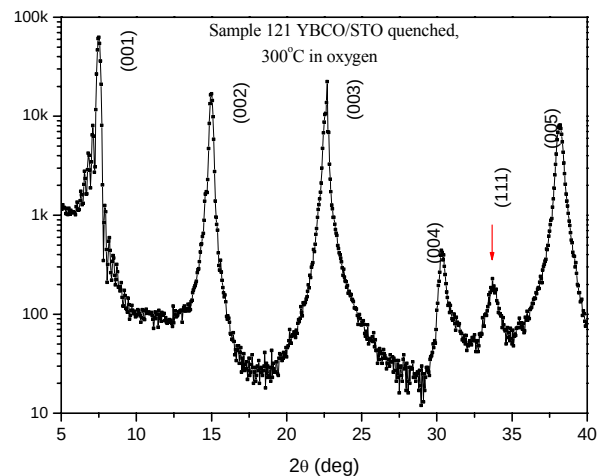


Figure 6b - YBCO/STO scan at the end of the oxygen uptake process. Temperature - 300°C.

#### 4. CONCLUSION

The SR-XRD experiment helps us to establish the temperature range of existence of the superconducting phase by analyzing the lattice parameter and the peak evolutions of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  thin film, simulating so the real growth conditions. The temperature range of the phase's transitions (tetragonal to orthorhombic) was confirmed by both the peak (00l) amplitude evolution and the unit lattice parameter. Moreover, during this process new unexpected oxide phases were observed and confirmed by high precision RBS analyses. These phases have been previously reported in our earlier work and have been localized in interface zone of 20 nm thickness [6].

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## REFERENCES

1. BARDEEN, J.; COOPER, L.N.; SCHRIRFFER, J.R.; *Phys. Rev.* 108 (1957) 1175.
2. CHEN, Z.Y.; BISWAS, A.; ZUTIC, I.; WU, T.; OGALE, S.B.; GREENE, R.L.; VENKATESAN, T, *Phys. Rev. B* 63 (2001) 212508.
3. TARASCON, J.M.; BAGLEY, B.G., *MRS Bull.* XIV (1989) 53.
4. OTTAVIANI, G.; NOBILI, C.; NAVA, F.; AFFRONTI, M.; MANFREDI, T.; MATACOTA, F.C.; GALLI, E., *Phys. Rev. B* 39 (1989) 13.
5. JORGENSEN, J.D.; VEAL, B.W.; PAULIKAS, A.P.; NOWICKI, L.J.; CRABTREE, G.W.; CLAUS, H.; KWOK, W.K., *Phys. Rev. B* 41 (1990) 1863.
6. GRIGOROV, K.; TSANEVA, V.; SPASOV, A.; MATZ, W.; GROETZSCHEL, R.B.H.; REUTHER, B.H., *Vacuum* 69 (2003) 315.