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MOD derived pyrochlore films as buffer layer for all-chemical YBCO coated conductors

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***Abstract*— We report a detailed study performed on LZO pyrochlore material grown by Metal-Organic Decomposition (MOD) method as buffer layers for YBCO coated conductors. High quality epitaxial LZO thin films have been obtained on single crystal (SC) and Ni-5%at.W substrates. Films have been characterized by means of X-ray diffraction analyses (XRD), atomic force microscope (AFM), scanning electron microscope (SEM) in order to evaluate structural and morphological properties. Precursors solutions and heat treatments have been studied by thermal analyses (DSC, TG) and infrared spectra (FT-IR) with the aim of optimizing the annealing process. Thin films of YBCO have been deposited by pulsed laser ablation (PLD) on this buffer layers. The best results obtained on SC showed YBCO films with critical temperature values above 90 K, high self field critical current density values (J_c > 1 MA/cm^2) and high irreversibility field values (8.3 T) at 77 K together with a rather high depinning frequency ν_p (0.5 T, 77 K)>44 GHz as determined at microwaves. The best results on Ni-5%at.W has been obtained introducing in the heat treatment a pyrolysis process at low temperature in air in order to remove the residual organic part of the precursor solution.**

***Index Terms*— Buffer layers, Coated conductors, CSD films, Lanthanum Zirconate, YBCO.**

I. Introduction

YBCO COATED CONDUCTORS with transport performances meeting the requirements of many applications are nowadays commercially available [1]. However, in order to reach a widespread use of coated conductors in applications there are still many features of this technology to be improved [2,3]. One of these, maybe the most important for the market, is the cost per Ampere meter parameter (€/kAm), which sets the ratio between costs and performances of the tape. Chemical Solution Deposition (CSD) techniques for RABiTS (Rolling Assisted Bi-axially Textured Substrates) based technology represent a good chance to reduce this parameter for long length coated conductor production. These techniques, in fact, don't rely with vacuum systems like standard vapor physical deposition methods such as Metal-Organic Chemical Vapor Deposition (MOCVD) or Pulsed Laser Deposition (PLD) [4-7]. Moreover, chemical methods are characterized by high degree of scalability and a precise control of precursors stoichiometry. Among the materials proposed as buffer layers, $La_2Zr_2O_7$ (LZO) represents one of the best candidate because of its structural compatibility and low lattice mismatch with YBCO (≤1.8%) and Ni-5at.%W tapes (7.6%). Many groups [8-13] have recently demonstrated the possibility to grow high quality LZO films with CSD methods. LZO films have also been validated as buffer layer for MOCVD or PLD YBCO [14-16].

We report on a detailed study performed on LZO films deposited by spin coating on both single crystals and metallic tapes starting from pentanedionate precursors. YBCO thin films have also been deposited by PLD on LZO films in order to evaluate the LZO effectiveness as a possible single buffer layer.

II. Experimental

LZO precursor solutions have been prepared by dispersing a stoichiometric mixture of La and Zr Pentanedionate in an excess of propionic acid. The as obtained solution has been treated in an ultrasonic bath at 40 °C for 20 minutes and then rotoevaporated under severe conditions (75 °C - 35 mbar) until the desired concentration is reached. Part of the solution has been powdered in air at 120 °C for several hours. The as obtained powder has been characterized by Differential Scanning Calorimetry and Thermo-Gravimetric (DSC-TG) analyses and Fourier Transform Infrared Spectroscopy (FT-IR).

Spin coated LZO thin films have been grown on both $SrTiO_3$ single crystal and Ni-5at.%W metallic tapes prepared at ENEA or provided by EVICO gmbh. The rotation speed has been set to 3000 RPM for 60 s. After the spinning, films have been dried for 20 minutes at 120 °C in air prior to the heat treatment. The annealing has been performed with a 10°C/min ramp. Background atmosphere (air or Ar/H_2) and annealing temperatures varied for each sample.

LZO films have been characterized by x-ray diffraction, Scanning Electron Microscope (SEM) and Atomic Force

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Microscope (AFM) in order to optimize their structural, morphological and texture properties. On top of LZO layer a thin film of YBCO has been deposited by PLD with deposition parameters optimized for YBCO on single crystal and reported elsewhere [17].

D.C. superconductive properties have been measured in the four-probe configuration. Patterned samples (50 μm wide 1 mm long stripes) were mounted in a He flow cryostat provided with a 12 T superconducting magnet in helium bath. A criterion of $1\mu Vcm^{-1}$ has been used to extract critical current value from the current-voltage characteristics recorded as a function of temperature, applied magnetic field and applied field direction (keeping the maximum Lorentz force configuration).

III. Results and Discussion

DSC and TG analyses have been performed on powdered LZO solution in flowing (1.5 s.c.f.h.) mixture Ar + 5%H_2 with a ramp rate of 10 K/min in order to reproduce the typical heat treatment used for LZO films on metallic tapes (figure 1). As previously reported by other groups [8], the decomposition process of LZO can be divided in 4 steps. The first step is characterized by a weight loss of 2.4%, which can be ascribed to the evaporation of some residual water in powders. Almost all the precursor solution decomposition occurs during the second step, which is characterized by a huge weight loss. According to previously reported studies [18, 19], in this range

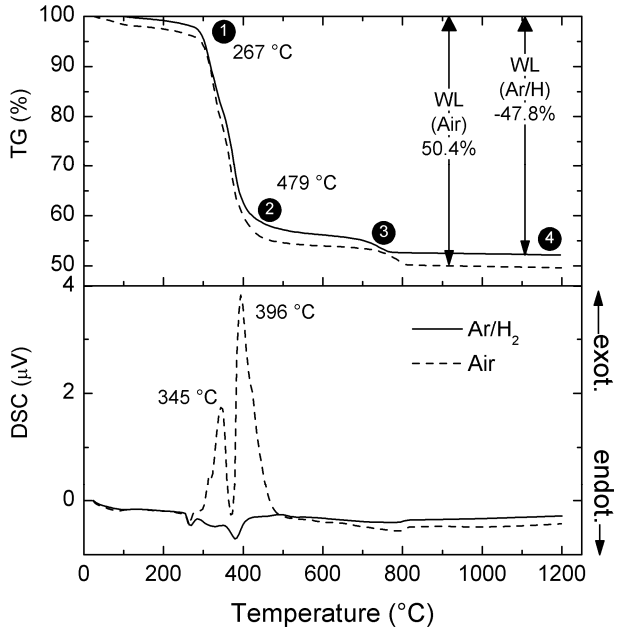

Fig. 1. DSC and TG curves of powdered LZO soultion acquired in flowing Ar/H_2 (continous lines) and Air (dashed lines) atmospheres with a ramp rate of 10 °C/min. Numbers in the upper panel identify the LZO decomposition steps.

of temperatures almost all the Zr should be decomposed in ZrO_2 while La in $La_2O(CO_3)_2$. The decomposition of La-carbonate and the formation of LZO phase are completed in the last two steps. The total weight loss measured in the process is 47.8%. Assuming that the starting powder contains only La and Zr proprionates (as confirmed by IR spectra performed on the solution and not shown here) the total weight loss expected for the LZO decomposition process is 61.4 %, very far from the measured value. The difference between the theoretical value and the measured value has been ascribed to the presence of residual organic component in the treated powders. In order to establish if the reducing atmosphere influences the decomposition process of LZO powders, the same heat treatment has been repeated in flowing air. The results of DSC-TG analyses are shown in figure 1 and revealed a completely different thermal response. Two exothermic peaks at 345 and 396 °C are clearly noticeable, which can be ascribed to carbon combustion. The total weight loss measured is increased to 50.4%, still far from the expected value. This result suggests that, although the presence of oxygen during the heat treatment promotes the carbon removal, a large amount of carbon is still present after the annealing in air. The amount of carbon can be estimated in 6.2 moles per La mole, in agreement with ICP mass measurement results obtained by other groups [10].

With 0.16 M concentrated (with respect to La ion) coating solution, LZO thin film has been deposited by spin coating method on $SrTiO_3$ single crystal substrates. The annealing temperature has been fixed at 950 °C for 30 minutes. Both flowing Ar/H_2 and air have been used as treatment atmosphere. X-ray spectra performed on as grown films, revealed that in both cases only the LZO phase can be

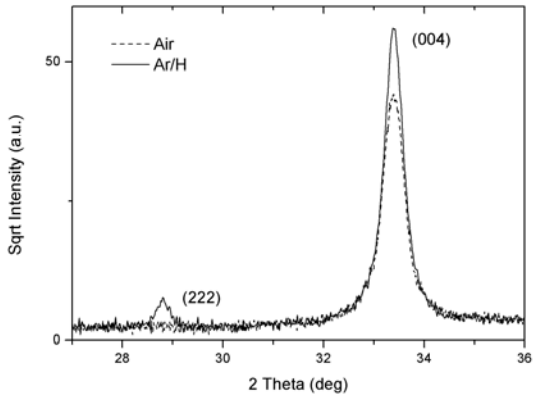

Fig. 2. X-ray diffraction spectra in θ-2θ configuration showing the (400) component and (222) component of LZO films.

detected. As shown in figure 2, sample annealed in air exhibit only (400) peak corresponding to the right *c*-axis orientation while for the sample produced in Ar/H_2 flow also the (222) component is clearly visible. This feature can be ascribed to residual carbon promoting undesired orientations, although the influence of residual organic component on the film growth has not been clearly understood. Taking the peak intensity ratio between *c*-axis and (222) components, β, as a measure of the film orientation quality, we evaluated β=0.99 and β=0.95 respectively for sample annealed in air and Ar/H_2. These values indicate that, in both cases, films are highly *c*-axis oriented and suitable as YBCO deposition template.

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On LZO film annealed in air a 200 nm thin film of YBCO has been deposited by PLD. YBCO film shows good critical temperature values as high as 91 K and good D.C. transport properties. As shown in figure 3, a better in field retention of the critical current density (J_c) and a higher irreversibility field value (H_{irr} = 8.3 T) if compared with standard YBCO/STO have been measured. Preliminary results of J_c measurements as a function of applied field intensity and direction, suggest the presence of correlated defects along YBCO/LZO *c*-axis direction, which can be responsible for the observed transport properties. This result has been also confirmed by microwave measurements [20] performed on the same samples, which

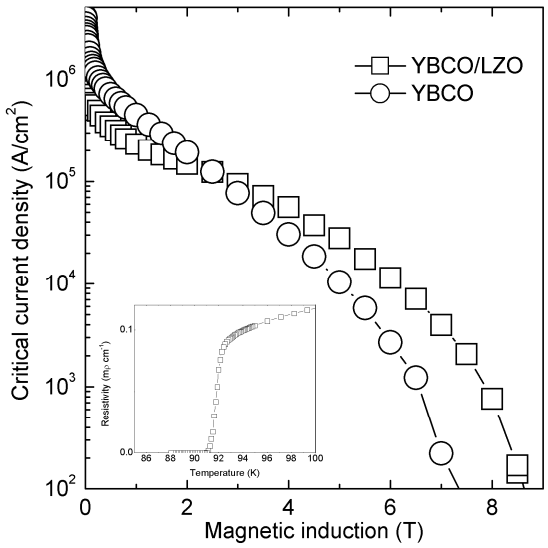

Fig. 3. Critical current density as a function of applied magnetic field recorded in PLD YBCO grown on MOD LZO buffered STO (squares) and PLD YBCO grown directly on STO (circles). In the inset the superconductive transition of YBCO/LZO film is showed.

revealed pinning as strong as in YBCO with $BaZrO_3$ nano-inclusions.

A more concentrated LZO coating solution (0.35 M) has been used to deposit 120 nm thick films on Ni-5at.%W tapes with a single spin coating process. In this case the annealing temperature has been set to 1050 °C for 40 minutes and the heat treatment has been performed in flowing (1.5 s.c.f.h.) Ar/H_2. Films obtained with this process showed a high degree of *c*-axis orientation (β=0.99) and crack-free surfaces. As grown samples have been analyzed by means of Auger spectroscopy depth profiling before and after an annealing simulating PLD-YBCO deposition (850 °C in 300 mTorr oxygen atmosphere) in order to evaluate the effectiveness in blocking metal diffusion from the tape. Results obtained on as grown films showed the presence of a small inter-diffusion region (about 20 nm) where Ni diffuses inside LZO film. After the annealing (see figure 4), the inter-diffusion region remains unaltered, while deep oxygen diffusion into the tape can be clearly seen. The presence of Ni at film surface can't be detected confirming that 120 nm thick LZO film acts effectively as Ni diffusion barrier, in agreement with results obtained with similar techniques by other groups [21, 22]. It is

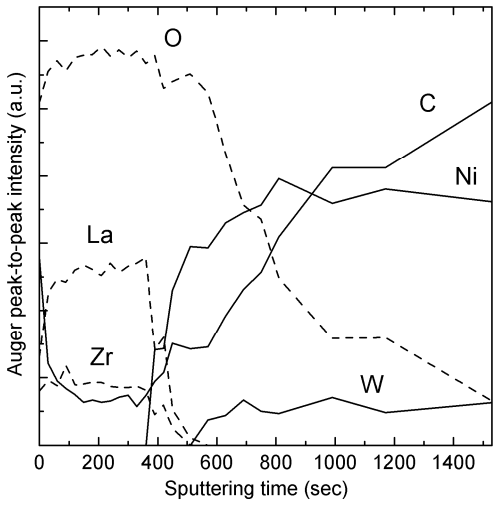

Fig. 4. Auger depth profile for a LZO film grown on Ni-5at.%W tape subjected to thermal treatment simulating YBCO PLD deposition. Signals intensity ratio does not represent elements relative concentration.

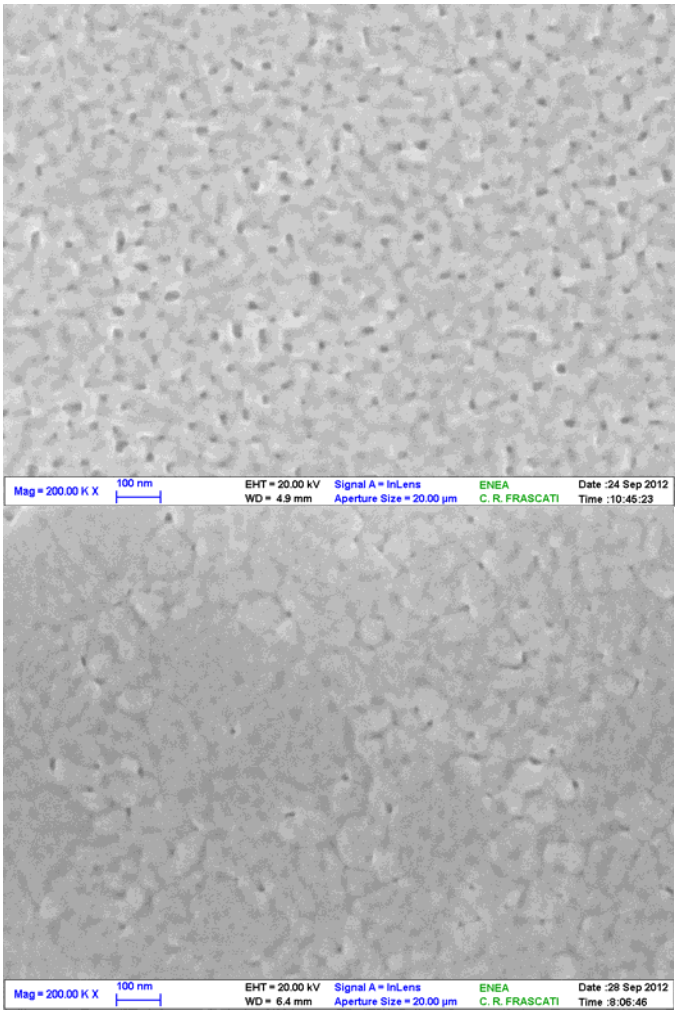

Fig. 5. Scanning Electron Microscope (SEM) images of LZO films surface grown on Ni-5at.%W metallic tapes. Upper panel: film grown with standard heat treatment; lower panel: film grown with two step heat treatment (see text for details).

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worth noting that Auger spectroscopy revealed the presence of residual carbon into the LZO film even after the annealing simulating YBCO deposition.

SEM investigations shown in figure 5 (upper panel), revealed that films exhibit a porous surface, characterized by a high density of 10-30 nm sized voids. The presence of such nano-voids on the LZO film surface (and also inside the film) have been reported by several groups [21] and is usually ascribed to the evaporation of the residual organic component inside the unconverted film. Over such LZO film a 200 nm thick YBCO film has been deposited by PLD, but YBCO showed poor superconductive properties. As shown in figure 6, the resistive transition was characterized by a low onset temperature (about 80 K) and incomplete transition to the

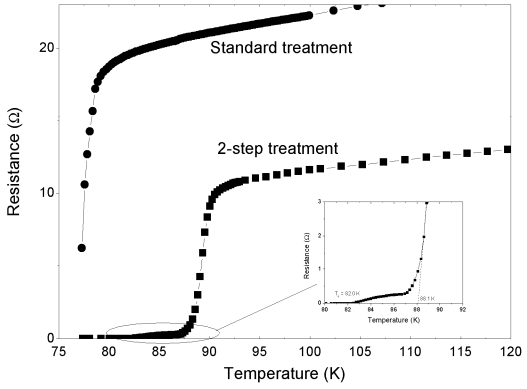

Fig. 6. Superconductive resistive transition measured on PLD YBCO films grown on LZO buffered Ni-5at.%W tapes treated with the standard annealing (circles) and the modified two steps annealing (squares). In the inset a magnification of the transition region for the sample obtained with the two steps annealing is shown.

superconductive phase down to 77 K. The surface morphology of YBCO film revealed the presence of several holes (100-200 nm sized), which have been correlated with the high density on nano-voids observed on LZO surface. This is direct evidence that the presence of residual carbon into LZO films affects film texture and morphology with severe drawbacks on YBCO properties. For this reason we developed a modified heat treatment for LZO film growth with a low temperature pyrolysis step performed in air. The temperature of the pyrolysis step was set at 350 °C, high enough to promote carbon combustion without compromising metallic tape through oxidation. Pyrolysis is followed by the standard annealing at 1050 °C in flowing Ar/H_2. As shown in the lower panel of figure 5, the surface morphology of LZO film obtained with the modified heat treatment is different. It is characterized by a very low density of nanovoids and by the presence of big islands (300-400 nm diameter) due to the coalescence of smaller grains. The surface is very compact and smooth as revealed also by AFM analyses which evaluated the root mean square value for the roughness in a 2x2 μm area in R_{rms} = 3.5 nm (R_{rms} = 6.5 nm for LZO films obtained with standard heat treatment). YBCO film deposited by PLD method on this LZO film showed improved superconductive properties, with high transition onset temperature (> 90 K). The measured value for the critical temperature T_c = 82K, does not completely reflect the improvement obtained with the two step heat treatment. As shown in the inset of figure 6, at least 90% of the transition was completed at 88 K. These promising results indicate that LZO surface, and consequently, YBCO properties can be improved by optimizing the low temperature pyrolysis process.

IV. Conclusions

We reported on spin coated LZO films grown on STO single crystals and Ni-5at.%W metallic tapes starting from coating solution with La and Zr pentanedionate. DSC-TG characterizations performed on powdered solution revealed a large amount of residual carbon in treated solution. Residual carbon strongly influences the microstructural and texture quality of buffer layer both on single crystal and metallic tape. For LZO film on STO, the heat treatment performed in oxidizing atmosphere promotes carbon removal allowing high quality buffer layers. PLD YBCO grown on these films exhibits very good superconductive properties. On the contrary, LZO films grown on tape show poor surface morphology due to the reducing atmosphere used during the heat treatment. These features directly affect superconductive properties of PLD YBCO final layer. The use of a pyrolysis treatment performed in air followed by standard annealing in Ar/H_2 improves buffer quality with direct positive consequences on YBCO properties.

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References

[1] Some of the major companies producing YBCO coated conductors are Superpower (www.superpower-inc.com), American Superconductor
[2] (www.amsc.com), Brucker (www.brucker-est.com), Sunam (www.sunam.com) and Fujikura (www.fujikura.co.jp).
[3] D. Larbalestier, A. Gurevich, D. M. Feldmann, and A. Polyanskii, “High-Tc superconducting materials for electric power applications” *Nature*, vol. 414, p. 368, 2001.
[4] T. G. Holesinger, L. Civale, B. Maiorov, D. M. Feldmann, J. Y. Coulter, D. J. Miller, V. A. Maroni, Z. Chen, D. C. Larbalestier, R. Feenstra, X. Li, Y. Huang, T. Kodenkandath, W. Zhang, M. W. Rupich, A. P. Malozemoff, "Progress in Nanoengineered Microstructures for Tunable High-Current, High-Temperature Superconducting Wires"*Adv. Mater.* vol. 20, p. 391, 2008.
[5] X. Obradors *et al*., "Chemical solution deposition: A path towards low cost coated conductors", *Supercond. Sci. Technol*. vol. 17, p. 1055, **??**.
[6] R. W. Schwartz, "Chemical solution deposition of perovskite thin films", *Chem. Mater.* vol. 9, p2325, 1997.
[7] F. F. Lange, "Chemical solution routes to single-crystal thin films", *Science* vol. 273, p903, 1996.
[8] M. Paranthaman *et al., J.Am.Ceram.Soc.* Vol. 84**,** p27, 2001.
[9] K. Knoth, R. Huhne, S. Oswald, L. Schultz, B. Holzapfel, "Detailed investigations on $La_2Zr_2O_7$ buffer layers for YBCO coated conductor by chemical solution deposition", *Acta Materalia* vol. 55, p517, 2007.
[10] Z. M. Yu *et al.*, "Deposition of $La_2Zr_2O_7$ film by chemical solution deposition", *J. sol-gel Sci. Technol.* vol. 54, p.363, 2010.
[11] X. B. Zhu *et al.*, "Seed layer, solution concentration and thickness effects on CSD-derived $La_2Zr_2O_7$ buffer layers for coated conductor", *Phys.C* vol. 467, p. 73, 2007.

[12] V. Cloet, P. Lommens, R. huhne, K. De Buysser, S. Hoste, I. Van Driessche, "A study of the parameters influencing the microstructure of thick $La_2Zr_2O_7$ films", *J. Cryst. Growth* vol. 325, p. 68, 2011.

[13] T. Caroff, S. Morlens, A. Abrutis, M. Decroux, P. Chaudouët, L. Porcar, Z. Saltyte, C. Jiménez, P. Odier, F. Weiss, "$La_2Zr_2O_7$ single buffer layer for YBCO RABiTS coated conductors", *Supercond. Sci. Technol.* vol. 21, p. 075007, 2008.

[14] S. Sathyamurthy, M. Paranthaman, H-Y. Zhai, H. M. Christen, P. M. Martin, A. Goyal, "Lanthanum zirconate: a single layer processed by solution deposition for coated conductor", *J. Mater. Res.* vol. 17, p. 2181, 2002.

[15] O. Stadel *et al.*, "MOCVD of coated conductors on RABiTS", *J. Phys.: Conf. Ser.* vol. 97, p. 012158, 2008.

[16] T. Caroff *et al.*, " $La_2Zr_2O_7$ single buffer layer for YBCO RABiTS coated conductors", *Supercond. Sci. Technol.* vol. 21, p. 075007, 2008.

[17] V.Galluzzi *et al.*,"$YBa_2Cu_3O_{7-x}$ films with $BaZrO_3$ inclusions for strong-pinning in superconducting films on single crystal substrate" *IEEE Trans. Appl. Supercond.*, vol. 17, p. 3628, 2007.

[18] L. Ciontea, M. Nasui, T. Petrisor Jr., R.B. Mos, M.S. Gabor, R.A. Varga, T. Petrisor, "Synthesis, crystal structure and thermal decomposition of $[La_2(CH_3CH_2COO)_6(H_2O)_3]3.5H_2O$ precursor for high-k La_2O_3 thin films deposition", *Mat.Res.Bulletin* Vol. 45, p. 1203, 2010.

[19] R. B. Mos, Phd Thesys, Technical University of Cluj-Napoca (2012).

[20] A. Angrisani Armenio, A. Augieri, F. Fabbri, R. Freda, V. Galluzzi, A. Mancini, F. Rizzo, A. Rufoloni, A. Vannozzi, G. Sotgiu, N. Pompeo, K. Torokhtii, E. Silva, E. Bemporad, G. Contini, G. Celentano, "Growth and characterization of $La_2Zr_2O_7$ buffer layers deposited by chemical solution deposition", Phys. Procedia Vol. 36, p1552, 2012.

[21] See for example L. Molina, H. Tan, E. Biermans, K. J. Batenburg, J. Verbeeck, S. Bals, G. Van Tendeloo, "Barrier efficiency of sponge-like $La_2Zr_2O_7$ buffer layers for YBCO-coated conductors", *Supercond. Sci. Technol.* vol. 24, p. 065019, 2011.

[22] V. Narayanan, K. de Buysser, E. Bruneel, I. Van Dressche, "X-ray photoelectron spectroscopy (XPS) depth profiling for evaluation of $La_2Zr_2O_7$ buffer layer capacity", Materials vol. 5, p. 364, 2012.