Synthesis of highly textured superconducting NdBa$_2$Cu$_3$O$_{7-y}$ thin films using an aqueous inorganic sol-gel dip coating technique.

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Abstract. In general, the sol-gel method is a very attractive route for ceramic synthesis because it permits direct fabrication of multi-component ceramics in different configurations without powder intermediates. This diversity, in which materials can be formed, has made the sol-gel method an important synthesis route in several domains of research. For (RE)Ba$_2$Cu$_3$O$_{7-y}$ superconducting thin film development, chemical solution deposition (CSD) techniques starting from sol-gel precursors can offer a cost-effective and more flexible large-scale alternative synthesis route in comparison to the common used vacuum techniques. This work describes the deposition of thin NdBa$_2$Cu$_3$O$_{7-y}$ layers on SrTiO$_3$ single crystals based on a new sol-gel dip coating process using aqueous precursor solutions. Two inorganic aqueous sol-gel routes were investigated, a metal nitrate – citric acid based and a metal acetate – triethanol amine based solution.

1. Introduction.
For the development of coated conductors with high $J_c$ performances, REBa$_2$Cu$_3$O$_{7-y}$ (REBCO) superconductors still remain the materials of choice due to their ability to operate in high magnetic fields. NdBa$_2$Cu$_3$O$_{7-y}$ (NBCO) is a particularly very promising material because the superior conductive properties in comparison to the well-known YBCO system. It has the highest superconducting transition temperature $T_c$ and exhibits an enhanced critical current density $J_c$ in intermediate magnetic fields [1]. In addition we have noted an increased rate of crystal growth of the Nd-homologue e.g. in flame spraying applications relative to the Y-member of this double perovskite family [2, 3].

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Although different vacuum based techniques produce high quality thin films for use as coated conductors, problems arise in view of high costs, high throughput and scalability \[4\]. Thus, alternative low cost and non-vacuum processes for the production of REBCO coated conductors need to be developed in order to facilitate their introduction into broad fields of application. One of the most promising chemical solution deposition routes for the production of industrial long length superconducting tapes by a continuous system is the dip coating technique, using aqueous sol-gel precursor solutions.

In the sol-gel method, the initial metal salts are mixed at a molecular level in an aqueous solution and should therefore lead to more homogenous end products that can be prepared at lower temperatures and/or in shorter times \[5\]. To deposit the thin layer of the liquid precursor on the substrate, the dip coating technique has the advantage that it can be applied to any kind of substrate, no matter its shape or size.

Amongst the multitude of possible sol-gel methods, we have selected an aqueous inorganic route where the metal salts are dissolved in water and kept in solution by chelating with a complexing agent \[6\]. This inorganic metal-chelate sol-gel route possesses real advantages over the other sol-gel routes which are mainly investigated by others for the time being (alkoxides, TFA) \[7\]: the metal salts used in this method are cost effective starting products and can be easily dissolved in water and the method is environmentally friendly because the use of toxic metal fluorides and the formation of very aggressive HF as well as the use of organic solvents can be avoided \[8\].

In this paper, two different inorganic sol-gel solutions for the deposition of thin films are studied, with special attention to the resulting microstructure and morphology. It has become clear that a judicious selection of both, the most appropriate metal salts and the most appropriate complexing agents, is a prerequisite in order to obtain the deposition of crack free coatings.

2. Experimental.

2.1. Sol-gel chemistry

Two different sol-gel formulations were developed in this study. The first solution is based on the amorphous citrate gel method (ACM), which we have already investigated earlier \[9\]. Here, to an aqueous solution of stoichiometric metal nitrates (M) with total concentration of 0.6 M, a diluted aqueous solution of 1.8 M citric acid (CA) was added under stirring in air. After the addition, the pH was adjusted to a value of 5 using aqueous ammonia solution.

For the preparation of the second type precursor we started with the dissolution of metal acetates in 0.6 M concentration in a 2.5 : 1 water-acetic acid mixture at 60 °C. After refluxing this mixture during 12h, pure tri-ethanol amine (TEA) is added dropwise as a complexing agent in a metal : TEA proportion of 1 : 3. The pH of this mixture is equal to 7 and no further adjustment is necessary. For both routes we obtained clear blue precursor solutions, which can be stored in a closed container for several months without any noticeable change.

2.2. Dip-coating and thermal treatment

The NBCO precursor films on STO substrates were dip coated at a withdrawal speed of 170 mm/min. Immediately after dip coating, the liquid layer is converted to a gel in a dust free furnace at 60°C. Subsequently, this amorphous gel is transformed to the desired crystalline superconducting phase by an appropriate heat treatment in a tube furnace. As is well known, the NBCO system exhibits a strong tendency for Nd/Ba substitution with formation of a Nd123(ss) or Nd1+xBa2-xCu3O7-y solid solution phase, which has detrimental effects on the superconducting properties of the obtained layer \[10,11\]. Because this substitution is very sensitive to the applied conditions of temperature and atmosphere during the thermal treatment, an accurate choice of these parameters is very important. Earlier investigation showed that the Nd/Ba substitution in bulk NBCO could be depressed by the use of high sintering temperatures in combination with an atmospheric reduced oxygen pressure \[12\].
2.3. Analysis
The microstructure of the deposited layers was characterized by X-ray diffraction (XRD; Siemens D5000, CuKα) using 0-2θ geometry in combination with pole figures for determination of the degree of biaxial texturation of the layer. The overall morphology of the thin films was characterized by optical microscopy (Leitz) and SEM (Philips 501), while surface roughness and thickness of the layer was determined using an interferometric profilometer (WYKO, UCAM). The critical temperature of the superconductive layers was determined by resistivity measurements using a custom made four-point test device (Keithly).

3. Results and discussion.
Figure 1a shows the SEM image of the NBCO layer deposited from the ACM precursor solution. It can be clearly seen that the layer obtained has a discontinuous and very porous surface morphology. This is undoubtedly related to a vigorous auto combustion reaction between the nitrates and the citric acid. These observations lead us to conclude that the ACM solution-gel method is not the appropriate sol-gel route to deposit thick superconductive layers with high Jc performance. Nevertheless, earlier investigations proved that this ACM method could be used successfully for the deposition of thin CeO2 buffer layers as long as the deposited layer doesn’t exceed the critical thickness of approximately 50 nm [9].

Figure 1b shows the SEM micrograph of the NBCO layer deposited from the acetate-TEA precursor. In stark contrast to the ACM-method, thick homogeneous and crack-free layers are obtained here. The average thickness of the layer, as determined by AFM, was 1 micron with a maximum dip coat speed of 170 mm/min and a viscosity equal to water (1 cP) (Figure 2). The layer showed an average roughness of Rₐ = 318 nm.

Figure 3 shows the 0-2θ XRD spectrum of the sintered and annealed NBCO layer dip coated on a (100) polished STO substrate. From the intensity of the different (00l) peak reflections, a strong c-axis orientation of the layer can be observed. No peaks could be attributed to other orientations of the NBCO phase or to remaining BaCuO₂ phase.

Figure 4a shows the (103) pole figure for this layer and exemplifies a highly in-plane textured NBCO phase. This is confirmed by the very low degree of misorientation angles (2.67°) calculated from the FWHM given in the accompanied phi-scan in figure 4b.
First, NBCO bulk material was synthesised for $T_c$ analysis using the water based acetate-TEA sol-gel route described in 2.1. The resistivity measurement in liquid nitrogen given in figure 5a clearly shows a sharp superconducting transition of the NBCO material at 94 K.

For the thin film deposition, we applied the same synthesis conditions as used for the bulk material. Figure 5b shows the resistivity curve of the acetate-TEA based layer. The drop in resistivity at a $T_c$ of 89 K is too low and too broad probably due to the presence of Nd for Ba substitution in the crystal structure leading to the formation of Nd$_{123}$ solid solution phase [11].

4. Conclusions.
We prepared NBCO thin films of 1 micron thickness by dip coating aqueous sol-gel solutions on polished (100) STO single crystal substrates. Two aqueous inorganic sol-gel routes were explored: a metal nitrate - citric acid based solution and a metal acetate – triethanol amine acid based solution. The thermal decomposition behaviour of both solutions was investigated and correlated to the final morphology of the deposited layers. By adjusting the different parameters during thermal treatment, we were able to get control over the layer morphology. Starting from aqueous based solutions using metal acetates and tri-ethanol amine as a complexing agent, highly textured NBCO films were deposited with in-plane misorientation angle less than 3°. After optimisation of the thermal procedure, a $T_c$ value of 89 K was reached.

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