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In-Situ Synchrotron X-ray Study of the Phase and Texture Evolution of Ceria and Superconductor Films Deposited by Chemical Solution Method

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Abstract

In situ synchrotron x-ray diffraction is used to study the phase and texture formation of ceria based films and superconductor films deposited by the chemical solution method on technical substrates. Combined analysis using in situ synchrotron x-ray diffraction, thermogravimetry/differential thermal analysis and Fourier transform infra-red (FTIR) spectroscopy allows to study the details on the decomposition and crystallization processes of ceria based in form of bulk and film. The success of this work demonstrates the possibility of studying chemical reaction pathway and texture evolution of oxides starting from solution precursors using non destructive method.

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1. Introduction

Owing to interface effects, oxide thin films exhibit a much broader range of functional properties in terms of semiconductivity, high-temperature superconductivity and colossal magnetoresistance than bulks samples. Chemical solution deposition (CSD) methods, being among the main thin film growth techniques with low cost and possibility of easy scale-up, have been widely investigated during the last two decades. A successful example is the realization of hundred meter long coated conductors, where a metallic substrate is covered by ceramic buffer layers and finally coated with a layer of $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ ($\text{RE} = \text{Y}$ and rare-earth) [1]. As the importance of such activities has grown, obtaining a better understanding of the chemical reaction pathways, kinetics and mechanisms is becoming crucial. However,

most studies [2, 3] either focus on *ex-situ* characterization or are limited by the need of destructing the samples, which might show different phase and texture evolutions due to newly created surfaces and structural changes during sample preparation processes. It is therefore of great interest and a challenge to conduct *in-situ* studies by non-destructive techniques.

On the other hand, the transition from amorphous state of the as-deposited film to the desired crystalline state in the final film is a common feature of chemical solution deposition techniques. Such processes are of great importance and heavily impact the structural properties and the performance of the film. Knowledge of kinetics with respect to grain growth and texture development during the amorphous-crystalline transition, in particular on technical substrates, is scarce. Further investigations of film and bulk material in terms of nucleation and growth processes is necessary from a fundamental point of view, as they are expected to facilitate the establishment of the correlation between the structural characteristics of the amorphous intermediate and final products.

In this work, ceria based films (10% La doped CeO₂, noted as CLO) and GdBa₂Cu₃O₇ (GBCO) film grown on technical substrates by CSD were selected. Comparative study of the CLO material in form of film and bulk was carried out, in order to enhance the understanding of the reaction path way. Taking advantage of high energy synchrotron x-rays as well as a 2-dimension detector, both the phase and texture evolution of the films were investigated.

2. Experimental details

The experimental procedures for producing CLO and GBCO films by a chemical solution route were reported previously [4, 5]. Commercial Ni-5at.%W (Ni5W) alloy tapes (from Evico GmbH) and Gd₂Zr₂O₇ buffered Ni5W substrates are used as technical substrates for deposition CLO and GBCO, respectively. For the CLO bulk studies, the powder was obtained after slow evaporation of the precursor solution at room temperature. Then it was packed into a tube made of a piece of textured Ni5W piece, following by a gentle pressing to get a tape with two parallel surfaces enabling to position the sample plane perpendicular to the incident beam. This tape with unreacted dry powder is about 2 mm thick. *In-situ* experiments were carried out at the BW5 and P7 beamline at HASYLAB using a high temperature furnace. The experimental setup is similar to that described previously for studies of Power In Tube superconducting wires [6]. For CLO studies, coated films or wrapped powder is clamped in a quartz tube with flowing reducing gas. For GBCO film studies, the coated GBCO film was pyrolyzed up to 500°C in wet flowing O₂, and flowing dry Ar with 100 ppm O₂ is used during *in-situ* study. A heating rate of 5 °C min⁻¹ is used for CLO bulk and film studies, while 20 °C min⁻¹ is used for the GBCO film crystallization. The Ni (200)/(020) reflections are used for alignment before heating. The incident beam, perpendicular to the sample surface, is set to 80 keV ($\lambda = 0.155 \text{ \AA}$), allowing it to penetrate the furnace and the samples. The diffraction patterns are recorded on a plate detector (MAR345). A lead pinhole screen is placed between the sample and the detector to hide the diffraction spots from the Ni (200) reflection. A beam size of 1 mm² is used in all the studies so thousands of grains in the technical substrate are illuminated, providing statistical results for phase and texture analysis of the crystallographic texture in the sample. The two dimensional scattering data are handled by the fit2D and EVA programs, by which the intensity as a function of d-spacing and as a function of azimuth angle are integrated to identify the phases and to evaluate the in plane texture quality, respectively.

3. Results and discussion

3.1. Phase evolution of CLO bulk

Fig 1a shows the phase evolution of the CLO bulk during heating under reducing atmosphere. Four steps are clearly observed during the decomposition and crystallization processes. At the beginning, the most prominent peak is located at $d = 6.7 \text{ \AA}$, and corresponding well to the other rare earth propionates [7]. $\text{Ce}(\text{C}_2\text{H}_5\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$ probably formed after exchange reaction between the $\text{Ce}(\text{acac})_3 \cdot x\text{H}_2\text{O}$ precursor and propionic acid solvent. With the rise of temperature, minor changes are observed over the temperature interval from room temperature to 130°C . Then, the reflections of cerium propionate disappear rapidly and decomposition products with complex structures are formed in the sample. The decomposition products exist from 134°C to 225°C . However, Debye ring can be detected until the $\text{Ce}_{0.9}\text{La}_{0.1}\text{O}_2$ phase presents at 365°C . The evolution of main reflections involved in the whole process is plotted in Fig 1b.

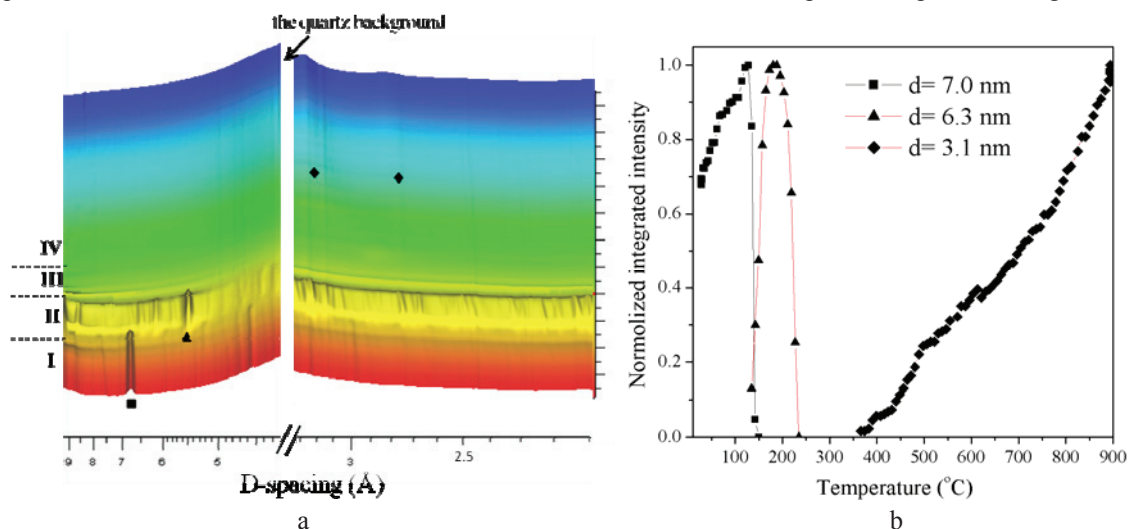


Fig. 1 a) time resolved d-spacing Vs. Intensity, b) Evolution of normalized integrated intensity of three representative reflections marked as ■, ▲, ◆, respectively.

In order to further interpret the process of the decomposition behaviour of CLO, thermogravimetry/differential thermal analysis (TG/DTA) trace and Fourier transform infrared (FTIR) spectra were acquired and are shown in Fig. 2. Four steps of weight loss are observed in the TG curve, which are also evidenced in the DTG curve by four peaks. The first weight loss occurs between room temperature and 140°C . According to the typical FTIR spectrum recorded in-situ during this step, this process corresponds to the loss of absorbed water and crystal water. Additionally, the increasing intensity of the strongest XRD reflection in this step also provides evidence of crystallinity improvement. The second step with a small weight loss finishes at 228°C . A small endothermic peak observed in this step is associated with the melting of the propionate [8], which is also proved by the abrupt disappearance of Debye rings at 225°C . The third step starts from the the end of instable thermal signal in the DTA trace. The weight loss of about 30% and an intense endothermic peak indicate that vigorous decomposition takes place. The FTIR spectra show that the gases evolved during this step are mainly CO_2 and 3-pentanone, suggesting that elimination of unoxidized propionate fragment of the propionate ligand is the primary way of decomposition in a inert atmosphere. The fourth stage of the TG curve consists a smooth weight loss up to 1200°C , corresponding

to the releasing of a small amount of CO_2 (as shown in Fig. 2b). This process is associated to an amorphous-crystallization transition as the CLO phase appears at the beginning of this stage, as early as 365°C . Note that no Ce_2O_3 is detected over the whole process, and oxygen from the atmosphere is probably insufficient to have significant influence on the bulk. So it is reasonably deduced that Ce^{3+} ion has already been oxidized into Ce^{4+} in the decomposition stage probably due to the oxygen provided from the carboxyl groups. However, the carbonaceous residue seems to still contribute to a relatively large weight loss of 12% from the appearance of CLO phase up to 1200°C . For film preparation, the significance of this study lies not only in determining the decomposition process of CLO, but also in elucidating the role of the atmosphere and the carbonaceous residue.

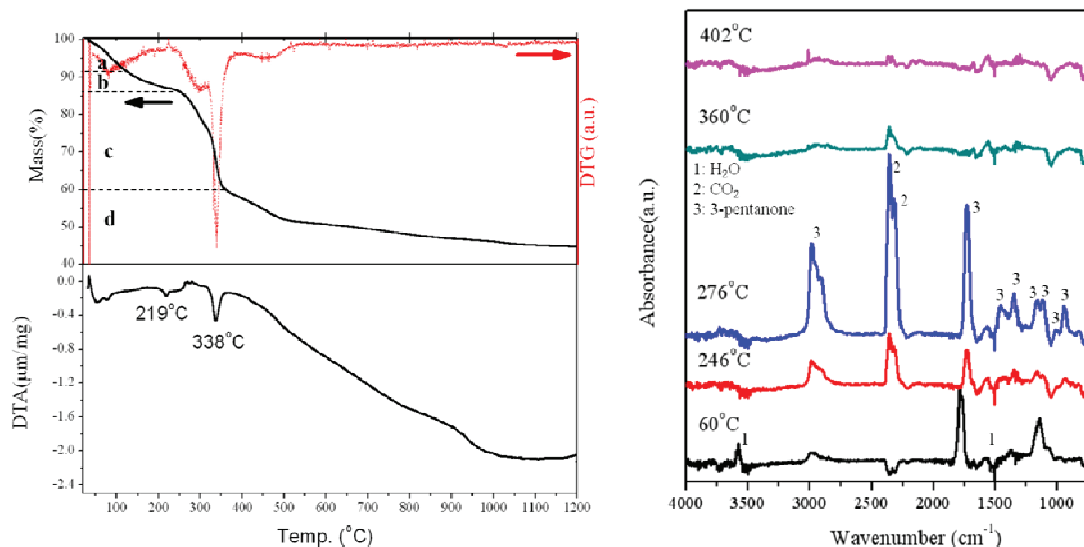


Fig. 2 a) Upper panel: TG curve (solid line corresponding to left vertical axis) recorded in flowing argon, and the first derivative of the TG curve (dash line corresponding to rightY axis). Lower panel: DTA curve of the propionate recorded in flowing argon. b) FTIR spectra of the gas phase evolved from the sample at different temperatures during decomposition.

3.2. Comparison study of crystallization of CLO bulk and film

Besides the investigation of the phase evolution during crystallization, the texture formation can also be studied simultaneously thanks to the two-dimensional detector. First, let's move to the crystallization behaviour of the CLO film annealed in a strongly reducing atmosphere. Detailed studies are published in [9]. Briefly, we have determined the onset temperature of CLO phase formation, which is as early as 860°C . After a short dwell time of 15 min, the (020)/(200) CLO reflection intensity saturates. Furthermore, it is interestingly found that excellent in-plane texture forms as soon as the CLO phase is present, and the FWHM value of the (020)/(200) reflection remains at a nearly constant value of 4.0° throughout the crystallization process. These results imply that the interfacial nucleation with preferential orientation is a predominating mechanism occurring during the amorphous-crystallization transformation. It is well known that removal of carbonaceous residue produced during pyrolysis process in reducing atmosphere is a critical issue for oxide films prepared by chemical solution method [10]. Previous papers [8, 11] reported the importance of oxygen partial pressure on the oxides formation in form of film or powder. However, detailed studies on how the PO_2 affects oxide films grown on metallic substrates is

scarce. That is due to the complexity resulting from the interactions between the O_2 and the substrate, which might occur before oxide nucleation. In this case, even though the desirable phase could be obtained eventually, the texture is highly affected by the oxide layer forming on top of metallic substrates (i.e., NiO or $NiWO_4$ when using NiW as substrate). In this study, a preliminary investigation on the effect of PO_2 on the phase and texture evolution was performed. An atmosphere with a high PO_2 was also used for CLO crystallization for comparison study. Surprisingly, the onset temperature of CLO phase formation is reduced to 550 °C, i.e. 300 °C lower than that of the film crystallized in strongly reducing atmosphere with low PO_2 . On the other hand, strong spots corresponding to the NiO phase are also visible in the sample annealed at a high PO_2 , indicating that a textured NiO film forms at the interface in such conditions. Although several issues are not clarified, such as the consequence of NiO formation and nucleation in the film, or the effect of the substrate interface change on the film growth, the results provide evidence that PO_2 in the reducing gas does play a important role on the onset temperature of texture formation, and the crystallization temperature for CLO film could be much lowered.

3.3. Preliminary in-situ study on the crystallization of a GBCO film

As shown in Fig. 3, the GBCO (001) reflection starts to appear at 740 °C, and becomes intense at 760 °C, while the same trend is also found in the reflections GBCO (103)/(013), (006) and (123)/(116) which are the strong reflections of a GBCO powder sample. This result indicates that no clear preferential nucleation and growth occurring in the film, in agreement with the ex-situ morphology observation and the conventional XRD θ -2 θ scan, which show that a polycrystalline film forms during crystallization. The reason must be due to the film thickness larger than 1 micrometer. Furthermore, no Ni-based oxide is detected during the in-situ measurement, most probably because of the texture. We also noticed that there

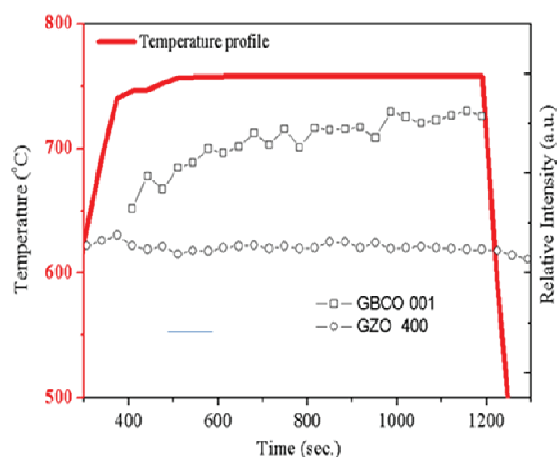


Fig. 3 Integrated intensity of the reflections GBCO(001) and GZO (004), as a function of temperature and dwell time.

is no obvious change in neither the integrated intensity nor the texture quality of the GZO buffer layer, which is an indication of its high stability in the atmosphere used for superconductor layer heat treatment.

4. Conclusion

The crystallization behaviour of ceria based bulks and thin films starting from chemical solutions can be studied by means of in-situ synchrotron X-ray diffraction. Several important issues during the amorphous-crystallization transition, such as the decomposition process of precursors, the correlation between phase and texture formation are addressed in this work. Combined analysis with other techniques gives insight into the decomposition and crystallization processes. It is demonstrated that in-situ synchrotron X-ray diffraction as a non destructive method is a powerful tool to study structural evolution of solution derived films and has the potential of being applicable to most types of oxide thin films.

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