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Analysis of defects in epitaxial oxide thin films via X-ray diffraction technology

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Abstract

It is demonstrated that a careful X-ray diffraction analysis represents an effective way to determine imperfections and their density in complex oxide epitaxial thin films. A method for simulating X-ray intensities of the (00ℓ) reflexes is developed and demonstrated for the model system $YBa_2Cu_3O_{7-\delta}$. In a first step, the δ dependence of the intensities of the different (00ℓ) reflexes is simulated and compared to literature data of perfect $YBa_2Cu_3O_{7-\delta}$ thin film and bulk samples with different oxygen content. In a second step, it is demonstrated that the δ dependence of the intensities of the different (00ℓ) reflexes depends strongly on the type of defects in case of imperfect $YBa_2Cu_3O_{7-\delta}$. Different types of defects (e.g., cation disorder, cation substitution, Cu deficiency) are discussed. Finally, the method is applied to low-pressure sputtered $YBa_2Cu_3O_{7-\delta}$ thin film. It is shown that according to this analysis and in contrast to previous assumptions, Cu(1) deficiency seems to be responsible for the elongation of the *c*-axis and the reduction of the superconducting transition temperature.
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1. Introduction

The physical properties of complex cuprites are usually strongly affected by their compositions, their structures, and, last not least, their structural (im-)perfections. This is for instance evident in the cases of the critical properties of oxide superconductors or the Curie temperature of ferroelectric oxides [1,2]. Since the discovery of high-T_c (HTS) superconductors in 1988, more than 50 different variations of layered superconducting cuprites are known. These are among others the extensive class of Perovskites of the form Ln–M–Cu–O with Ln representing Y or a lanthanide (Ce, Pr, Pm, or Tb), and M representing an alkaline earth metal (Ba, Sr, or Ca), respectively [3].

The most intensively studied class of HTS is the system $YBa_2Cu_3O_{7-\delta}$ (YBCO). In the easiest case, defects in YBCO are introduced by lack of the oxygen O(1) in the Cu–O chains. This leads to a slight elongation of the crystallographic *c*-axis that is accompanied by a severe reduction of T_c (Fig. 1). The correlation of the O(1) content δ of the phase $YBa_2Cu_3O_{7-\delta}$ can be obtained from measurements of the *c*-axis lattice parameter [4]. However, many more types of defects, substitutions or disorder are known for this material. Alternative or additional to oxygen or Cu deficiency, substitution of the Re component (Y or rare-earth elements) or cation disorder can lead to significant changes in superconducting properties, especially the transition temperature T_c. Fig. 1 displays an example of a less understood dependence of T_c on the elongation of the *c*-axis length that is observed for YBCO thin films. Especially films deposited at low oxygen partial pressure have the tendency to show reduced transition temperatures at strongly elongated *c*-axis lengths [5– 7].

With the renewed interest in thin film deposition of oxide materials, in general, and the development of deposition processes for oxide thin films for applications it becomes increasingly important to be able to characterize the kind and density of defects in these complex epitaxial oxide films in a nondestructive way. In this paper we show that careful X-ray diffraction (XRD) analysis represents a nondestructive and effective way to analyze imperfections and their density in oxide materials. We demonstrate the applicability of the method for the system YBCO.

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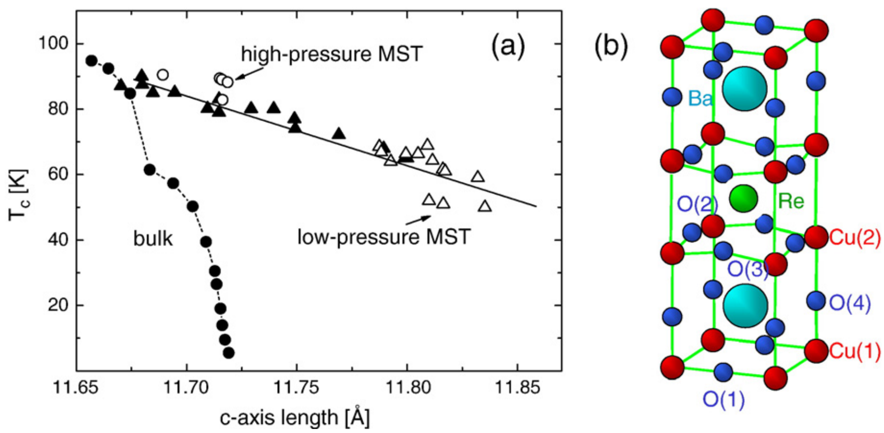

Fig. 1. (a) Transition temperature as function of the c-axis length of YBCO bulk (solid circle) and YBCO thin films deposited under different conditions (high-pressure dc magnetron sputtered (open circles), low-pressure dc magnetron sputtered (open triangles), radio-frequency magnetron sputtered (solid triangles, data from literature [8]). Whereas O(1) deficiency in the CuO chains is responsible for the change of c-axis length and T_c in case of the bulk material, different physical reasons have been discussed for the much shallower decrease of T_c as function of the c-axis length (indicated by the solid line) in case of the fully oxygenated thin films. The reason for the unusual behavior of the sputtered samples will be discussed in the last part of this paper. (b) Sketch of the structure of the perfect YBCO unit cell with Re representing Y or a rare-earth element. The denotation of the different atoms will be used in this publication.

Applying well-known models, we derive a method to simulate XRD intensities of the reflexes observed for epitaxial YBCO thin films, i.e. the (00ℓ) reflexes with $\ell = 1, 2, \ldots, 7$. First, we develop a method to simulate the XRD intensities of the (00ℓ) reflexes of 'perfect YBCO' as function of the O(1)-content δ. The simulated intensities are compared to experimental data of our high-pressure sputtered thin films [9] and, additionally, literature data obtained for YBCO bulk and thin film samples. Second, it is demonstrated, that the dependence of the XRD intensities on the O(1)-content δ represents an ideal tool to investigate the perfection of sample. On the one hand, the O(1)-content δ is the only parameter, that can easily and reversibly be modified even after preparation and characterization of the sample. At the same time it has a strong impact on the XRD diffraction. On the other hand, this impact of the O(1) dependence on the intensities of the XRD diffraction peaks is affected in different ways by different types of defects. We discuss and simulated the expected δ dependence of the XRD spectra of YBCO with different types of defects (e.g., cation disorder, cation substitution, and Cu deficiency). Finally, we analyze the defect structure in our low-pressure sputtered YBCO films. Different types of defects have been discussed in the literature for low-pressure sputtered films. Especially cation disorder was proposed using indications given by Raman experiments [8]. However, we demonstrate that substantial Cu (1) deficiency is more likely to explain the elongated c-axis and the T_c reduction in our low-pressure sputtered YBCO films (see Fig. 1).

2. Structural defects in YBCO thin films

The orthorhombic as well as the tetragonal YBCO phases are characterized by a superlattice with lattice parameters $a \cong b \cong a_p$ and $c \cong 3\ a_p$, that is based on a Perovskite unit cell with lattice parameter $a_p \approx 3.8$ Å. For the perfect YBCO structure, the periodicity along the c-axis is defined by the regular arrangement of the cations, Y (or Re) and Ba, and the oxygen vacancies in the Y planes and in the Cu(1) planes (Fig. 1b).

The exact position (necessary for the simulation of the XRD diffraction spectra) of the different atoms (Re, Ba, Cu(1–2), and O(1–4) in the perfect unit cell can be obtained from the literature. However, any type of defect in the structure will automatically modify the exact position and, thus, the resulting XRD pattern. A large number of possible defects are known, these are among others:

(i) The orthorhombic to tetragonal distortion is determined by the O(1) occupation δ in the Cu(1) plane of the $YBa_2Cu_3O_{7-\delta}$. The deficiency δ has a large impact on the c-axis length and the transition temperature (see e.g., Fig. 1a).

(ii) The exact positions of the Cu(1) and Cu(2) depend strongly on the oxygen occupancy of the BO_5 — pyramids and BO_6 — octahedral, respectively. Oxygen deficiency as well as lack of Cu are possible reasons for structural modifications that also affect the superconducting properties. For instance Cu(1) deficiencies up to 10–14% (induced during high temperature annealing of YBCO) are reported [10].

(iii) Finally, cation substitution or cation disorder represent possible structural modifications for these Perovskites. Especially for the case of thin films the stoichiometric relation of the cations usually diverges from Re/Ba = 1/2. There are even reports, that Ba-rich films tend to perform better (higher stability and critical currents). However, even for perfect integral stoichiometry reductions of T_c in combination with an enhancement of the c-axis length have been observed (see Fig. 1a). It was suggested, that in these cases the Re and Ba cations could exchange their positions (cation disorder) which would cause an elongation of the c-axis parameter and possibly a reduction of T_c [7].

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