Detection of nm-Scale Displacements at Frequencies down to 1 mHz by Differential Laser Doppler Vibrometry

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Summary: The displacement of the surface of a sample is detected contact-less by Differential Laser Doppler Vibrometry (D-LDV) at elevated temperatures. The time signal contains the phase difference of the measurement and reference laser beams, already greatly reducing noise from, e.g., length fluctuations, heat haze, and mechanical vibrations. In postprocessing of the data, anharmonic signal contributions are identified and extracted to show the correct thickness changes of thin films and related sample bending. The approach is demonstrated on a $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ (PCO10) thin film sample.

Keywords: Laser Doppler Vibrometry, chemical expansion, thin films, SOFC materials, data processing

Introduction and Motivation

Many active materials which are exposed to varying chemical environments alter their stoichiometry, which is often accompanied by a change in lattice parameter called chemical expansion [1]. Chemical expansion of thin films is of great interest because materials in high-temperature applications such as sensors, fuel cells, and catalysts are often implemented as thin films [2]. The expansion of a thin film adhering to a non- or differently expanding substrate is constrained, which leads to the build-up of great mechanical stress, deformation and, ultimately, delamination or cracking, one of the main failure reasons [3]. Chemical expansion is coupled to the formation and diffusion of oxygen vacancies or interstitials, resulting in an oxygen non-stoichiometry δ. These are slow processes, often requiring long equilibration times. Therefore, new approaches are required to study this directly, especially when the expansion over time is not harmonic and information is partially stored in higher harmonics.

State of Research

When an oxide is exposed to reducing conditions, it exhibits an oxygen non-stoichiometry δ, that reflects the oxygen vacancy concentration $V_O^{\cdot\cdot}$. In case of PCO, the relation at high oxygen partial pressure p_{O2} is [1]

$$[V_O^{\cdot\cdot}] \propto p_{O_2}^{-1/6} \qquad (1)$$

and becomes nearly constant at intermediate p_{O2} [4]. With the chemical expansion ε_C or strain ε

being proportional to δ, it is also constant at intermediate p_{O2} [4]. In other words, the maximum strain is p_{O2} independent at intermediate p_{O2} ranging from about 10^{-17} to 10^{-5} bar. Therefore, Fig. 1 shows essentially the temperature dependent maximum stain provided that the samples reached nearly equilibrium and that the data evaluation adequately takes into account nonlinear effects. The former is fulfilled for slow (periodic) changes of p_{O2} in the mHz range. The latter, i. e. the correct consideration of nonlinear effects, is the main objective of this work.
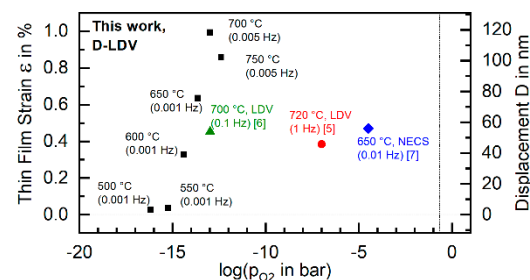

Fig. 1. _Literature data and data from this work for the chemical strain in PCO10 thin films vs p_{O2}._

Experimental Procedure

The sample is comprised of an oxygen-ion conducting substrate [5–7] which acts as a pumping cell. On the substrate, a thin film of PCO10 is deposited. Electrodes are deposited on the film and the backside of the substrate. The sample is excited electrochemically by applying a sinusoidal voltage. According to (1), $V_O^{\cdot\cdot}$ strives toward equilibrium with the effective oxygen partial pressure $p_{O2,eff}$ given by the Nernst relation (2). Here, $p_{O2,air}$ is the ambient p_{O2}, e_0 the elementary charge, k_B

Boltzmann's constant, and T the absolute temperature:

$$p_{O_2,\text{eff}} = p_{O_2,\text{air}}\, e^{-4\,e_0\,U/k_B\,T} \qquad (2)$$

By pumping the sample sinusoidally, the chemical expansion is driven, bending the sample [5–7]. The full displacement, which is the sum of the bending and film-thickness change, can be detected by D-LDV (developed by the authors), and its value extracted from the Fourier transform of the time signal [8]. When entering the range of constant nonstoichiometry, the displacement becomes constant for a portion of the excitation period. Here, some of the information is contained in higher harmonics at the multiples of the excitation frequency, which must be taken into account to extract the true displacement value.

Evaluation of the Data and Results

A fast Fourier Transform (FFT) [8] is done on the high-pass [9] filtered time signal, yielding the spectrum containing delta-shaped peaks at the multiples of the excitation frequency (Fig. 2).
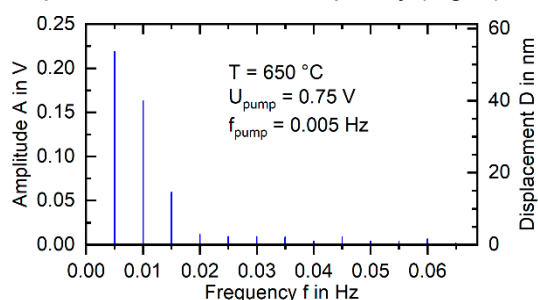
Fig. 2. The filtered spectrum for the inverse FFT.

Because the information is stored in these peaks only, the noise between them can be discarded before transforming the filtered spectrum back into a time signal, from which the displacement is extracted. It is taken as the difference between the minimum of the back transformed signal and the average of the constant range (Fig. 3).
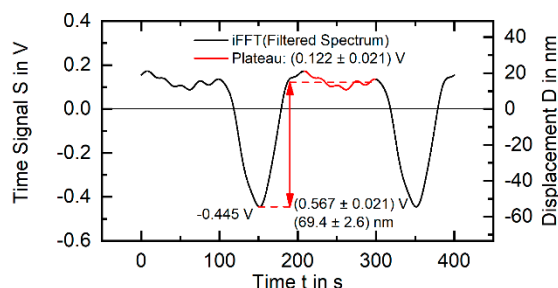
Fig. 3. The extraction of the full displacement.

Conclusions

The applicability of the method is confirmed by comparing two datasets acquired with different pumping voltages (Fig. 4). If higher harmonics taken into account as demonstrated here, the datasets are agreeable with one another, as the

theory predicts. If only the first harmonic at the excitation frequency is evaluated, an increase in excitation voltage results in a decrease in displacement, which contradicts theory. The new evaluation method presented here is, therefore, considered as a valuable tool for the correct detection of chemical expansion.
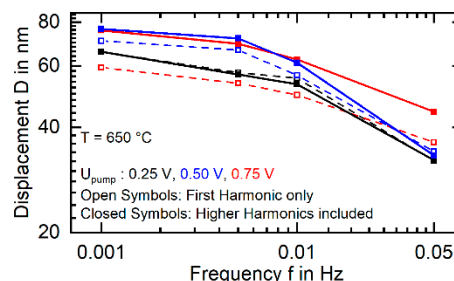
Fig. 4. Comparison of the displacements extracted from first harmonic only and from full spectrum.

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