Analytica Chimica Acta xxx (2017) 1–7

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Online-LASIL: Laser Ablation of Solid Samples in Liquid with online-coupled ICP-OES detection for direct determination of the stoichiometry of complex metal oxide thin layers

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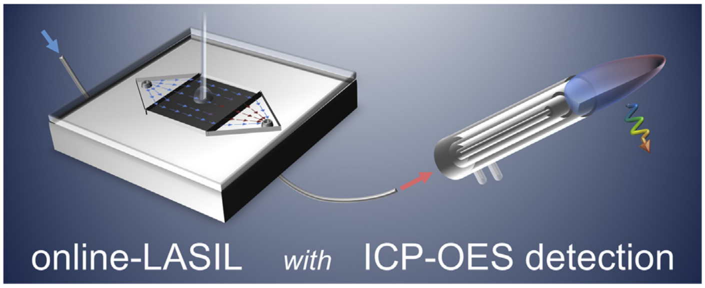
HIGHLIGHTS

- Ablation of a solid sample in a liquid.
- Online connection to a detection device – no manual sample handling.
- Quick and simple analysis with accurate quantification.
- Especially for materials which are hard to dissolve.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 August 2017
Received in revised form
18 October 2017
Accepted 22 October 2017
Available online xxx

Keywords:
Laser Ablation
Flow Injection
ICP-OES
Stoichiometry determination

ABSTRACT

Advanced materials such as complex metal oxides are used in a wide range of applications and have further promising perspectives in the form of thin films. The exact chemical composition essentially influences the electronic properties of these materials which makes correct assessment of their composition necessary. However, due to high chemical resistance and in the case of thin films low absolute analyte amounts, this procedure is in most cases not straightforward and extremely time-demanding. Commonly applied techniques either lack in ease of use (*i.e.*, solution-based analysis with preceding sample dissolution), or adequately accurate quantification (*i.e.*, solid sampling techniques).

An analysis approach which combines the beneficial aspects of solution-based analysis as well as direct solid sampling is Laser Ablation of a Sample in Liquid (LASIL). In this work, it is shown that the analysis of major as well as minor sample constituents is possible using a novel online-LASIL setup, allowing sample analysis without manual sample handling after placing it in an ablation chamber. Strontium titanate (STO) thin layers with different compositions were analyzed in the course of this study. Precision of the newly developed online-LASIL method is comparable to conventional wet chemical approaches. With only about 15–20 min required for the analysis per sample, time demand is significantly reduced compared to often necessary fusion procedures lasting multiple hours.

1. Introduction

The most commonly used way for determination of the elemental composition of inorganic materials is transfer into a clear

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https://doi.org/10.1016/j.aca.2017.10.025
0003-2670/

Please cite this article in press as: M. Bonta, et al., Online-LASIL: Laser Ablation of Solid Samples in Liquid with online-coupled ICP-OES detection for direct determination of the stoichiometry of complex metal oxide thin layers, Analytica Chimica Acta (2017), https://doi.org/10.1016/j.aca.2017.10.025

liquid solution (*e.g.*, by acid digestion, fusion) and subsequent investigation with elemental analysis techniques such as electrothermal (ET) or flame (F) absorption atomic spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), or inductively coupled plasma-mass spectrometry (ICP-MS). The bottleneck of this approach is the sample dissolution step; usually, it involves a series of manual preparation steps which are often not straightforward. For instance when dissolving complex ceramic samples or metal oxide mixtures, laborious digestion steps mostly involving highly toxic reagents have to be carried out [1,2]. For chemically very resistant materials, even fusion (*e.g.*, using Li or Na-borate) might be the only way for adequate sample preparation [3]. Besides the problem of extensive sample preparation, the necessary dilution steps decrease the method sensitivity, especially when thin films are to be analyzed. To circumvent such problems, solid sampling methods like x-ray fluorescence (XRF), electron probe microanalysis (EPMA), glow discharge-optical emission spectroscopy/mass spectrometry (GD-OES/MS), or Laser Ablation-ICP-MS (LA-ICP-MS) can be applied [4]. Depending on the chosen technique, any one of them is to some extent prone to so-called matrix-effects, leading to a discrepancy between observed signal intensitites and the actual sample composition; to ensure reliable quantification, matrix-matched standards have to be employed for accurate signal quantification. Favourably, certified reference materials should be used but are in many cases not available – especially for novel materials. Alternatively, in-house prepared standards offer higher flexibility, but additional workload and one more source of uncertainty make this approach not very attractive especially when high accuracy of the results is required. Additionally, precision of most solid sampling approaches is usually not below 5%, which is significantly higher than values obtained in solution-based analysis (below 1%).

Combining the positive characteristics of solution-based analysis (calibration with aqueous standards, accuracy/precision of the obtained results) with the ease of use and unneccessity of sample preparation of a solid sampling technique can tremendously simplify the characterization of newly synthesized technologically relevant materials. One very promising approach to fulfill these requirements is Laser Ablation of a Sample in Liquid (LASIL). When firing the focused laser beam on the sample surface, a local plasma plume is formed which will immediately expand into the liquid. Compared to Laser Ablation (LA) under ambient pressure and in gas atmospheres, the liquid covering the sample will induce strong confinement of the formed plasma plume resulting in extremely high temperatures and pressure conditions. During plasma expansion, the formation of micro-jets supports particle ejection from the ablation site. LA of materials submerged in liquids is currently predominantly used for the production of nanomaterials. The mechanisms occurring during the irradiation of the liquid-covered sample surface have been studied closely; a detailed discussion is beyond the scope of this work. Further information can be found elsewhere [5,6]. Besides, this technique has been shown to be suitable for use in chemical analysis. Douglas et al. [7] and Okabayashi et al. [8] already presented this possibility; in short, the nanoparticle suspensions formed by laser irradiation of the sample material were analyzed using conventional solution-based ICP-MS. Quantification was performed using external calibration. Machida et al. [9] recently presented more detailed studies about particle size distributions and elemental fractionation effects of volatile elements in such laser-generated nanosols with detailed focus on the feasibility for chemical analysis. All these works highlight the fact that the benefits of solid sampling can be successfully combined with those of solution-based analysis. However, in all of the previously published work, laser ablation in liquid has been performed without direct transfer of the sample material to the detection device. A manual step (*i.e.*, pipetting) was necessary to transfer the generated particle suspension to the measurement device. Besides hampering the routine applicability of the analytical approach, this operation step might induce systematic errors due to particle agglomeration and sedimentation, as well as unwanted sample contamination.

As shown in multiple previous studies, manual steps can be completely automated with the use of flow injection (FI) systems [10–12]. Besides reducing time demand, reproducibility of sample measurement can be considerably improved. On-line coupling of the FI-System with the element specific detection device provides further advantages compared to those of conventional batch procedures in which sample pretreatment and the actual measurement are separated [13,14]. For example, FI-Systems with online detection allow improvements in sensitivity since unnecessary sample dilution could be avoided. Furthermore, the risk of sample losses or contamination could be minimized with online-detection systems. In the last years we published a variety of FI applications with on-line ICP-OES or ICP-MS detection, including procedures for sample enrichment [15], matrix or analyte separation [16], sample fractionation [17], dynamic sample extraction [18] and dynamic etching of surface layers [19]. Based on this previous experience we were able to develop an online-LASIL system which consists of a liquid-purged LASIL compartment directly coupled to an ICP-OES instrument as detection device. This setup gives the opportunity to transfer the ablated sample material directly into the ICP torch without the necessity of manual sample handling.

The applicability of the developed online-LASIL system is demonstrated by the analysis iron-doped strontium titanate (Fe:STO) layers produced by pulsed laser deposition (PLD). As polycrystalline material, STO is used in a wide range of applications, *i.e.* as oxygen sensor, as solid oxide fuel cell (SOFC) electrode or as varistor to mention only a few. In all these applications the electrochemical properties are defined by the defect chemistry which is well understood for $SrTiO_3$ bulk material [20–22]. Novel technologies, *i.e.* memory devices based on memristors, tend to implement the material as thin layers. In this field of application STO is among the most intensively investigated materials [23–26], although the observed effects are not entirely understood. Therefore, a carefully executed analytical characterization is a promising way to gain a better understanding of the observed electrochemical effects, not only for $SrTiO_3$ but for oxide thin films in general.

2. Experimental section

2.1. Chemicals

Ultra pure water was before every experiment freshly dispensed from a Barnstead EASYPURE II water system (ThermoFisher Scientific, Marietta, OH).

Single element standard solutions (for ICP, 1 g L^{-1} in HNO_3) for Sr, Ti, Fe, and Eu were purchased from Merck, Darmstadt, Germany. Concentrated acids – 37% (v/v) HCl, 40% (v/v) HF, and 68% (v/v) HNO_3 – were all of p.a. quality and also purchased from Merck, Darmstadt, Germany.

Sodium tetraborate (p.a.) was supplied by Acros Organics B.V.B.A., Geel, Belgium.

2.2. Preparation of $SrTiO_3$ thin layers

Undoped and Fe-doped $SrTiO_3$ thin films were prepared by pulsed laser deposition (PLD) using a KrF excimer laser with a wavelength of 248 nm (Coherent, The Netherlands). Nominal Fe concentrations in the target material were 1% and 5% of the B site cations in the perovskite-type $SrTiO_3$ (ABO_3), respectively. The thin

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