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Materials Characterization

Raman imaging and principal component analysis-based data processing on uranium oxide ceramics

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ABSTRACT

A ceramic sample of uranium dioxide is probed by Raman imaging followed by a combined Lorentzian fitting – Principal Component Analysis process. This allows to evidence structural or chemical inhomogeneities of the material, which affect Raman line intensities but also line positions, evidencing local symmetry lowering. The inhomogeneities were observed not only between grain cores and boundaries, but also inside grain cores themselves. Only a part of these intensity inhomogeneities is as expected due to different orientations of the ceramic grains. Besides, a zone noticeably differing from others has been distinguished, presumably due to local strains or to chemical nature (oxygen stoichiometry), showing the sensitivity of the analysis. This underlines the importance to perform Raman analysis in such ceramic materials at least on several points and better, in imaging mode.

1. Introduction

UO$_2$ is one of the most well-known-oxides not only due to its wide use as nuclear fuel but also as a model compound with high-symmetry simple structure. This deep knowledge allows probing and studying even extremely tiny effects, *e.g.*, those associated with oxygen stoichiometry or with irradiation damages that are of primary importance for applications in power plants and for the spent fuel recycling. Besides this, Raman spectroscopy is known to be a reliable and non-destructive technique to probe inhomogeneities in various materials, through its imaging mode, due to its sensitivity to chemical bonds, structural modifications, or to anisotropic strains in solids. Raman spectroscopy was already frequently used for analysis of uranium oxides, allowing for the detection of stoichiometry changes in their structure and providing important information on the successive stages of the nuclear fuel cycle, from material elaboration up to spent fuel and nuclear waste processing in model compounds [1–4] as in highly active materials including heavier actinides [5–8] or even real nuclear spent fuels [9]. In the last years, Raman scattering is more and more extensively used to characterize UO$_2$, up to various conditions of temperature and pressure [10,11] and this even extents to some *in situ* measurements in ion-beam

facilities [12–15], or environmental sciences for detection of contaminated soils [16].

Stoichiometric UO$_2$ is characterized by a fluorite structure with a face-centered cubic unit cell for which group theory predicts one Raman-active (T$_{2g}$) and one infrared-active (T$_{1u}$) phonons [17]. The Raman band associated to the T$_{2g}$ phonon arises at 445 cm^{-1}, and normally no additional peaks appear up to $\sim$1150 cm^{-1} where the second-order 2LO T$_{1u}$ signature lies, as shown by Livneh and Sterer through high-pressure and multi-wavelength measurements [18]; this 2LO band is of resonant character for red and mostly green excitation lines. The 2LO origin was later confirmed by Jégou et al. [19] and Sarsfield et al. [20] on isomorphous (U,Pu)O$_2$ and PuO$_2$, ruling out some previous assignments of crystal-field (*CF*) transitions.

Thus, UO$_2$ should exhibit a homogeneous 1st-order Raman response with a single T$_{2g}$ phonon band, the wavenumber and intensity of which remain constant within the sample surface of a single crystal. Besides phonons, electronic excitations (*CF* transitions) are known to contribute also to the Raman spectra [7,21–23]. The present paper is focused on ceramic UO$_2$, with elaboration characteristics similar to UO$_2$-based nuclear fuels, leading to similar grain sizes. In the Raman spectrum, it is expected that the position of the T$_{2g}$ mode be independent on the grain

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orientation, while the intensity of the Raman line depends on the relative orientation of Raman incident and scattered beam polarizations with respect to the crystallographic axis [24,25]. However, in the case of UO$_2$ ceramics, a weak supplementary broad line (the so-called U* band) has recently been observed at ~550 cm^{-1} in the Raman spectra, of not yet clear origin apart from the fact that it comes from grain boundaries [13]. Besides this, ionic irradiation induces some new lines called U$_n$ ($n = 1,2,3$) due to creation of defects [13,14]. Some inhomogeneities can therefore be present in this system, and Raman imaging can provide an overview about their distribution within the sample surface and shed some light on their origin. Owing to its high spatial resolution (about 1 μm), performing Raman imaging on an inhomogeneous sample surface gives access to local composition and spatial arrangement of various molecular or solid species. Besides, some recently developed *in situ* measurements, under ion beam irradiation, require an accurate and deep understanding of these inhomogeneities, as these experiments are the most often performed at one single point of the sample surface. Recent *ex situ* measurements highlighted the effect of chemical changes [26–34] (oxidized phases, effect of trivalent rare earth doping) which can also contribute to these inhomogeneities. The goal of this paper is therefore to characterize an UO$_2$ ceramic surface *via* Raman imaging and to extract the information about surface inhomogeneities by means of numerical data processing. For this purpose, an original combined Lorentzian fitting – Principal Component Analysis data processing was developed and is presented here.

2. Image Data Processing

Modern Raman systems allow one to obtain spectra maps in several manners [35–38] and the final results essentially depend on the selected parameters for the visualization of the surface state. These parameters are generally intensity, width, or position of the appropriate Raman peak, which can be extracted by a classical fitting procedure. It is widespread and one of the simplest and oldest methods described numerous times in the literature [39–41]. However, the amount of the spectra collected in Raman measurements sometimes reaches hundreds or thousands, or even tens of thousands, and the ordinary fitting procedures become inefficient in the case of very similar or low-contrast signals. Moreover, these algorithms exhibit some difficulties in probing low-intensity signatures (such as the 550 cm^{-1} line above-mentioned) when lying in the tail of a much more intense line. Therefore, additional approaches are required allowing not only a simultaneous treatment of the mapping data but also revealing any small spectral changes. The methods of source separation can be applied for this purpose. They are known for a high efficiency to distinguish the relevant information from noise in the spectral signals and to detect even very tiny difference in data sets, based on the extraction of the entire spectral characteristics. Among such methods which are frequently reported in the literature for spectroscopic imaging data analysis, Principal Component Analysis (PCA) is well-known as an accurate and simple approach [42–45]. It has successfully been applied not only for the treatment of imaging data collected on biomaterials and pharmaceuticals [46–49], but also to classify and isolate samples with different structural features by performing a standard spectroscopic probing of materials [50,51], or, in the nuclear field, for probing the oxidation state of zirconium alloys encompassing the uranium oxide fuel in a power plant [52,53].

The main difference between both methods of data analysis is as follows: PCA is a decomposition procedure where a number of unknown orthogonal spectral sources (Principal Components - PC) are derived from data, while classical fitting procedure is a spectral recombination procedure in which data are described on the basis of known spectral sources, *i.e.*, individual lineshapes in this case. Nevertheless, one method can successfully be sustained by the other one, when treating a giant amount of spectral data.

In the present work, confocal Raman imaging followed by a fitting procedure with Lorentz functions and PCA, as well as the crossed analysis of the outputs of both methods, have been applied. The data processing used here is described in details in the Appendix section, as it simply consists of the application of already known mathematical methods. The PCA development is a rewriting of the whole data set (a spectrum at each (x,y) point of the map), in the form of the product of three matrices, through the so-called singular value decomposition (SVD). The singular value matrix contains the spectral-like information by order of decreasing importance and only the first ones contain relevant information, the following ones are nothing but noisy-like features. This simplifies the problem and allows the spectral-like information to be rapidly extracted out from the whole set of data.

3. Materials, Experiment and Data Treatment

3.1. Sample Preparation

The sample used in this work was a disc of sintered UO$_2$ ceramic (8 mm in diameter, ^{235}U–depleted), polished to achieve a mirror-like surface, and after annealed at 1700 °C in an Ar/H$_2$ atmosphere in order to insure nominal oxygen stoichiometry and to release polishing strains and defects.

3.2. Experiments

Raman imaging measurements have been performed on an InVia Reflex Renishaw system in a point-by-point confocal mode in back-scattering "VV geometry" (Vertical—Vertical, or parallel polarization of incident and scattered light) to achieve an intensity maximum of the Raman signal, according to the polarization characteristics of a T$_{2g}$ mode [24]. An area of 86.9 × 94.6 μm^2 was scanned with a step of 1.1 μm in both dimensions, resulting in $h \ x \ l = 79 \times 86 = 6794$ collected spectra.

The samples have been excited with a 633 nm He-Ne laser. The choice of the laser source is determined by the dependence of Raman activity of uranium oxides on the laser excitation wavelength in order to limit resonance effects [18,21]. Hence some wavelengths can induce the additional resonance-Raman driven band at ~570 cm^{-1} in the Raman spectrum of stoichiometric UO$_2$, which is assigned to the IR-active (LO component) and Raman-silent T$_{1u}$ phonon.

The Raman-scattered light has been collected under a Leica DM 2500 microscope with a 50 × objective, and dispersed by a holographic grating with 1200 grooves/mm. For each of the scans, a spectrum was recorded with an integration time of 5 s in the 300–800 cm^{-1} wavenumber range, and the number of sampled wavenumbers was 391. This corresponds to the spectral cover of the CCD in one window without any wavenumber scanning. In such a way the whole acquisition time remains reasonable (around 10 h) but this precludes accessing to other spectral features of interest, such as the 2LO mode lying at 1150 cm^{-1}.

3.3. Data Processing

The acquired data formed a tri-dimensional (3D) set of spectra, represented by intensity, wavenumber range and point coordinates of each spectrum that needed their special processing (see Appendix A.1 for the details). All treatment procedures were implemented by means of programs developed in the MATLAB platform. The obtained 3D data were transformed into a 6794 × 391 matrix (number of spectra by number of sampled wavenumbers), as explained in Appendix A.1. Data treatment with PCA has been performed in obedience to the model presented by Eq. (A.1) in Appendix A.2. Picturing and interpretation of the PCA components (scores and loadings) were carried out as presented in Appendix A.3. Fitting of the Raman spectra has simultaneously been implemented with Lorentzian profiles on the rows of data matrix, allowing extraction of intensity, position, and half-width of