

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Progress in the understanding of structural and electronic properties of codoped N,Nb-TiO ₂ nanopowders as transparent conducting oxides for optoelectronic applications	Experiment number: MA1979
Beamline:	Date of experiment: from: 26 feb 2014 to: 01 mar 2014	Date of report: 17 Jul 2014
Shifts:	Local contact(s): Paula M. Abdala	<i>Received at ESRF:</i>
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Report: This study represents a step forward of previous experiments performed at ESRF concerning the location of N species in N-doped TiO₂ nanoparticles.^[1,2] More in detail, the present work aims at investigating the crystallographic structure and the local distortions of the coordination geometry of Nb and Ti in TiO₂:Nb and TiO₂:Nb,N nanostructured powders. In the Literature, single-doped TiO₂:Nb materials were extensively studied during the last decade. It is well established that their conduction states are dominated by hybridized 3d-4d orbitals of both the transition metals.^[3] However, their electronic properties are known to be also dramatically influenced by the titania crystallographic^[4] and defect structure.^[5] Clearly, all these aspects must be accounted for when the final aim is to find suitable strategy to engineer the band gap of prototype materials for photoelectrochemical applications. Adding a non-metal (*e.g.* N) as a codopant could be a suitable strategy to push deep mid-gap states of guest transition metals lower into the band gap. In this way, the electron-hole recombination rate is expected to be slowed down. Recently, TiO₂:N,Nb materials recently claimed interest in the titania community,^[6,7] as the combination of Nb and N dopants was reported to significantly enhance the photocatalytic response under visible irradiation with respect to single-doped (N or Nb) analogues. However, the reasons underlying these evidences are still far to be fully understood. The experiments we performed at ESRF are intended to contribute bridging this gap.

We operated at the bending magnet BM01B station of the Swiss-Norwegian beamline. We performed high-resolution powder X-ray diffraction (HR-XRPD) and extended X-ray absorption fine structure (EXAFS) experiments on two series of doped TiO₂:D (D = N and/or Nb) nanostructured systems. The first one collected powders synthesized by the sol-gel (SG) method in the nominal 0.5-5% D/Ti molar ratio, while in the other series the dopant were added by impregnation (IMP) in the nominal D/Ti range 8-14 %. HR-XRPD diffractograms were recorded from 4° to 50° in 2 θ at 0.9 °/min in Debye-Scherrer capillary geometry using Si-111 monochromated X-rays with $\lambda = 0.50494(3)$ Å. The Rietveld method as implemented in the GSAS program suite^[8] was utilized to fit experimental diffractograms. X-ray absorption curves were then collected around both Ti K and Nb K edges at room temperature. Ti spectra were recorded in transmission mode after carefully diluting the powder in cellulose to avoid thickness effects. Nb-centred spectra were on the contrary collected in fluorescence mode, as the signal in transmission geometry was partly contaminated by a spurious Bragg reflection due to the crystal monochromator. A Si (111)-monochromated beam was employed in the 4.88 – 6.00 (Ti K edge) and 18.9 – 20.0 keV (Nb K edge) energy ranges.

From the HR-XRPD analysis, it turns out that the investigated samples always contain anatase (*I4₁/amd*) and a non-negligible minority of brookite (*Pbca*), whose specific signature is the (211) reflection at ≈ 10.0 deg. The only exception was the SG-N,Nb/Ti = 0.05 material, as it also shows a segregated α -NbO₂ phase (*I4₁/a*). The latter is recognizable by the secondary peak at 2 $\theta \approx 8.9$ °, attributable to (4 0 0) and (0 4 0) equivalent reflections of the contaminating Nb oxide (Figure 1).

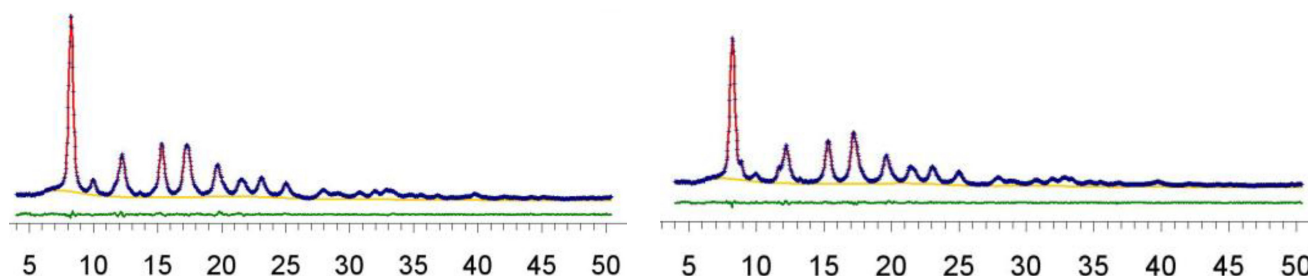


Figure 1. Diffractograms of an intermediate (1%, left) and a heavily (5 %, right) doped SG-N,Nb materials. Intensities are in arbitrary units. 2θ angular values are expressed in degrees. Blue crosses: observed data. Red curve: Fitting. Yellow curve: Background. Green curve: Point-by-point residuals.

The phase composition remains essentially unchanged, with a content in anatase as high as ≈ 69 -73 %, throughout both the IMP and SG single doped samples. On the contrary, the brookite amount was found to rapidly and monotonically decrease in SG codoped powders, down to ≈ 14 %, as the dopant loadings increased. Interestingly, in SG codoped samples, the higher the anatase weight fraction, the smaller the corresponding crystallite volume-weighted average dimensions. A possible mechanism accounting for this evidence is a codoping-induced strong thermodynamic bias towards anatase. This implies a large and negative free energy change associated to the appearing of the $I4_1/amd$ phase, that is larger when N, Nb concentration is increased. According to this scenario, nucleation of anatase should be faster in the codoped case than in single-doped $\text{TiO}_2\text{:N}$ materials due to smaller expected critical radii of the corresponding crystal nuclei.

No changes are detected in the local coordination geometry of Ti ions with respect to the undoped reference by means of the EXAFS analysis. This is not unexpected on the basis of our previous results on single-doped $\text{TiO}_2\text{:N}$ powders^[1], as the dopant loadings here considered are relatively low.

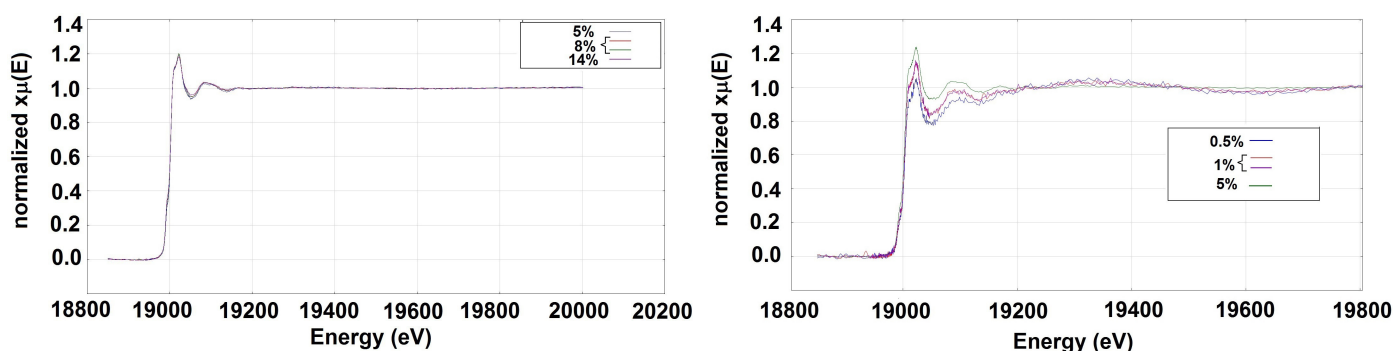


Figure 2. Normalized X-ray absorption curves across the Nb K edge of $\text{TiO}_2\text{:N,Nb}$ codoped samples. Left: IMP series. Right: SG series.

Figure 2 shows the Nb K edge X-ray absorption spectra for the both IMP and SG sample series. While the overall appearance of the latter strongly depends on the amount of dopants included in the material, the former is not influenced by the specific dopant loading. These evidences indicate that different synthetic strategies imply different local environments of Nb ions. For example, the Nb coordination shell in IMP samples should be somewhat isotropic, as it can be inferred from the corresponding scarcely structured signal.

In conclusion, the experiments here discussed allowed us to investigate the effect of N and Nb dopants on the material microstructure in two series of TiO_2 nanopowders, differing for the synthetic method. We demonstrated that N and Nb have an important synergic effect in governing the phase composition and the average crystallite dimensions in SG codoped samples, while the IMP ones are significantly less affected. Accurate fitting of EXAFS data are still required to provide a physical interpretation for the observed spectral changes throughout the SG series. Currently, the present analysis is being complemented by first-principle DFT simulations in the bulk and other experimental characterizations (including EPR and DRS measurements), with the aim of building up a sound interpretative model for the observed doping-induced changes at the nanoscale. A manuscript for submission to Journal of Physical Chemistry C is under revision.

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