



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.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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: XAS Study of oxygen-deficient hexagonal polytype

Experiment number:
CH-2981

Beamline:
BM25A

Date of experiment:
from: 17-9-2009 to: 20-9-2009

Date of report:
18-2-2010

Shifts: 9

Local contact(s): Félix Jiménez Villacorta

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Dr. María Hernando-González

Dr. Felix Jimenez-Villacorta

Ms. Laura Miranda Pérez

Dr. German R. Castro

Dr. Marina Parras

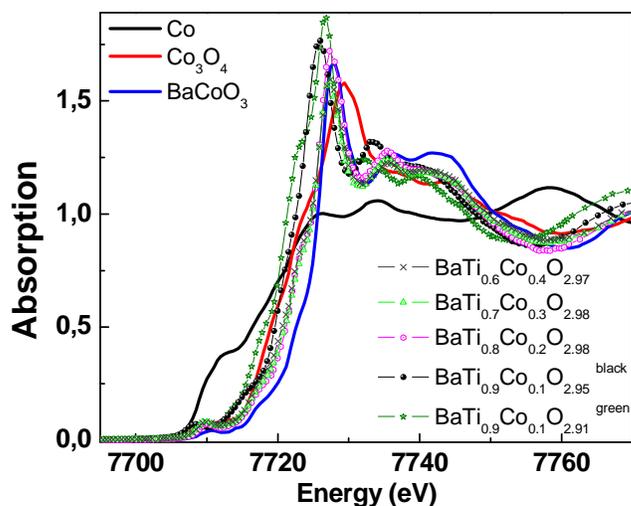
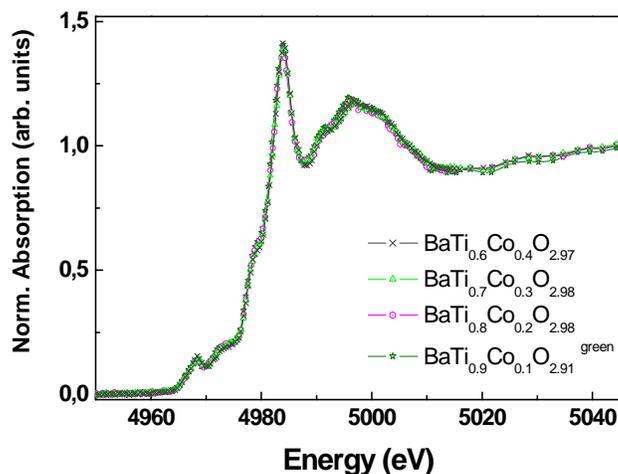
Report:

A set of hexagonal $\text{BaTi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ close-packed perovskites, with $x=0.1-0.4$ have been measured. Due to the large absorption coefficient provided by the A cation ($A=\text{Ba}$) at these energies, a preliminary study suggests the collection of the XAS spectra in the fluorescence yield mode.

In order to estimate the oxidation state of the B cations of such set of samples, X-ray absorption spectroscopy measurements at the Co K-edge and the Ti K-edge have been performed in the Spanish CRG beamline (SpLine) at the European Synchrotron Radiation Facility. XANES spectra have been collected in the fluorescence yield mode using a 13-element Si(Li) detector. A Co foil and a Co_3O_4 mesh have been used as reference. Several scans per sample have been measured in order to improve the signal-to-noise ratio. Data treatment of the experimental XANES spectra has been performed with the ATHENA software.ⁱ

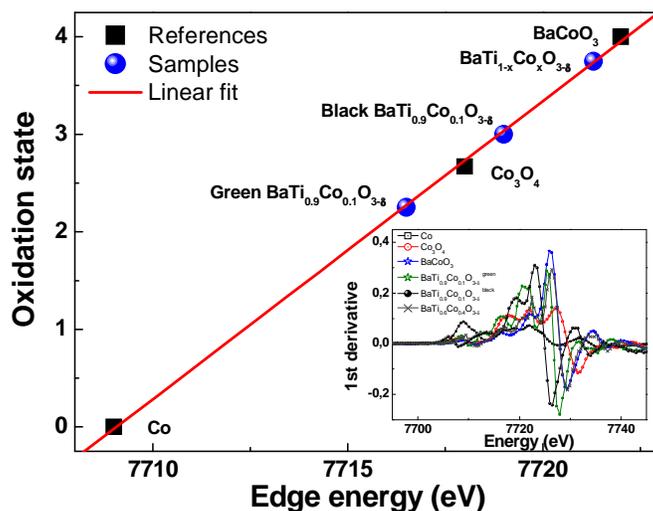
Ti K-edge and Co K-edge XANES spectra are shown in the figure. The Ti K-edge XANES spectra do not exhibit any relevant modification in edge position and spectral shape, being the spectral shape similar to BaTiO_3 compounds measured in other works.^{ii,iii} This confirms an oxidation state of Ti^{+4} in all the samples. On the other hand, Co K-edge XANES spectra of the BTCO samples present very slight differences in their spectral shape, as a very

subtle decrease in the white line intensity can be observed. Compared to the BaCoO_3 XANES spectrum used as a reference, a negligible decrease of the pre-edge peak intensity have been observed as the Co content increases.

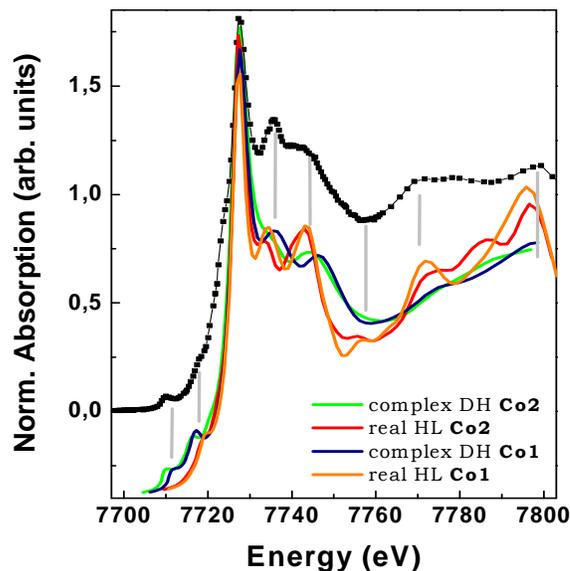


In order to estimate the oxidation state of Co in the samples, the edge position has been determined from the maxima of the 1st derivative. Results show no difference in the edge position for the whole set of $\text{BaTi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ samples, with Co content between $x=0.2$ and $x=0.4$. Results are compared to the references and an oxidation state of $\sim+3.75$ is then deduced, suggesting a combination of both Co^{+3} and Co^{+4} cations. However, samples with $x=0.1$, green- and black- $\text{BaTi}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$, exhibit a Co K-edge spectrum shifted to lower energies, which confirm the enhanced presence of Co^{+2} , apart from more important modifications in the XANES features. The remarkable decrease of the oxidation state in the Co cations of such samples, since Ti cations still present an oxidation state of +4, suggests that the green and black- $\text{BaTi}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$ samples show a noticeable reduction in the oxygen content. In order to corroborate the relative content of Co cations in the $\text{BaTi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ samples, the Co K-edges have been fitted considering contributions from each oxidation state

by means of step functions, and Gaussians to reproduce the spectral features, coming from transitions to $4p$ states (and pd hybridized $3d$ states). Results are in total agreement with the estimated valence obtained from the edge positions.



Two more considerations can be pointed. Firstly, it should be remarked that we obtained the first XANES spectra at the Ti K-edge energy range, lowering the up-to-now operation threshold of the BM25A beamline. Secondly, we would like to point that these results give very valuable information to interpret the physical properties of such hexagonal oxides, and at the present is under submission process in a high-quality peer-reviewed journal. Finally, full multiple scattering XANES calculations are under development (shown below), giving additional information included in a future short report.



i B. Ravel and M. Newville, **J. Synchrotron Rad.** **12**, 537 (2005).

ii A. Caballero, J.P. Espinós, A. Fernández, D. Leinen and A.R. González-Elipe, **Nucl. Instrum. Meth. B** **97**, 397 (1995).

iii M.L. Moreira, G.P. Mambrini, D.P. Volanti, E.R. Leite, M.O. Orlandi, P.S. Pizani, V.R. Mastelaro, C.O. Paiva-Santos, E. Longo and J.A. Varela, **Chem. Mater.** **20**, 5381 (2008).