EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

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.

ESRF	**Experiment title:** **Local structure of lanthanides in ZnO**	**Experiment number**: CH- 3328
Beamline: BM25	**Date of experiment**: from: **28 April 2011** to: **02 May 2011**	**Date of report**:
Shifts: 9	**Local contact(s)**: Jon Ander Gallastegui	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Dr. Eugenio Otal, *Alexandra Mägli, *Bartosz Penkala, Dr. Davide Ferri - Empa, Laboratory for Solid State Chemistry and Catalysis, CH-8600 Dübendorf, Switzerland**

Dr. Felix Jimenez-Villacorta, College of Engineering, Northeastern University, United States of America

Report:

During this beam time ZnO nanoparticles (NPs) doped with lanthanides and transition metals were characterized. K edges were measured for transition metals (Mn:6539eV, Co:7709eV and Cu:8979eV) and L_3 for the lanthanides (Er: 8358eV and Yb:8944eV). Energy was calibrated with a metallic foil of the metal element for the transition metal doped samples and with a metallic foil of Ni and Cu for Er and Yb, respectively. The measurements were performed in fluorescence mode due to the low concentration of dopants (~2-3 at%). The fluorescence detector was a one element solid state detector because the multielement detector which was required in the proposal to detect low concentration of dopants in the samples was with technical problems at that the moment of the measurements.

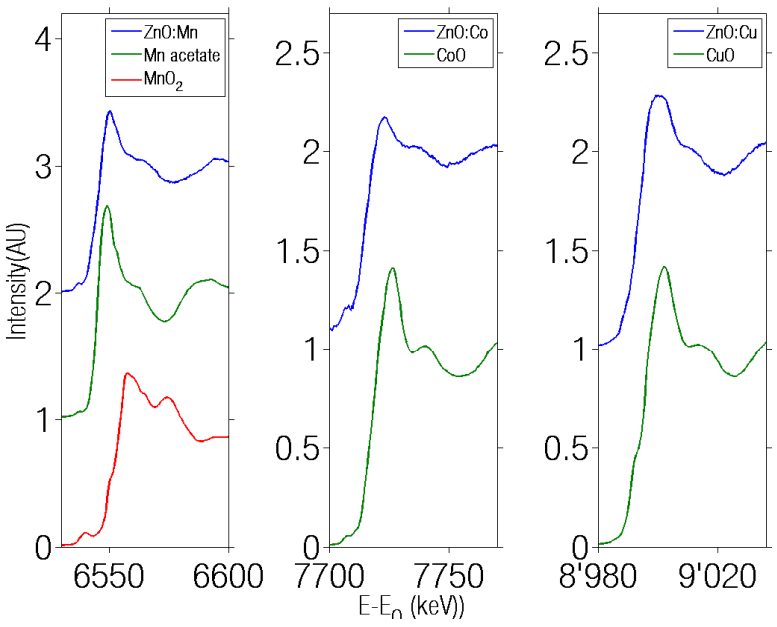

Fig 1 – XANES spectra of doped samples and references

All samples were prepared by forced hydrolysis as described in ref [1]. Dopants were added in the form of divalent acetates to the initial solution.

The low sensibility of the fluorescence detector reduced the amount of studied samples to the transition metals doped ones. Fig 1 shows the XANES spectra of ZnO:Mn, ZnO:Co and ZnO:Cu. The comparison of E_0 shift with respect to the divalent references shows that all dopants remain in a divalent state.

Additionally, the XANES spectra of ZnO:Co and ZnO:Cu exhibit clear

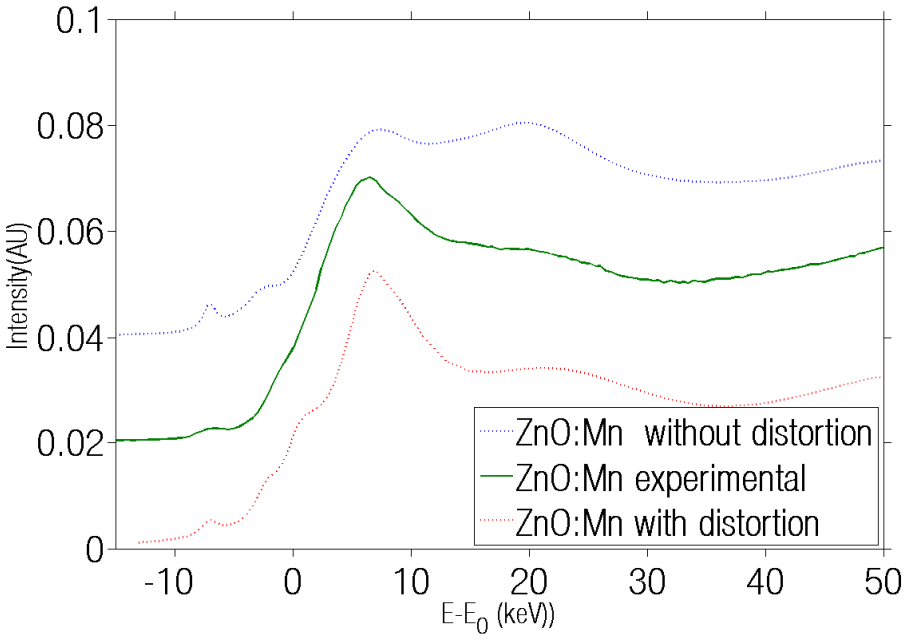

Fig 2 – Comparison of experimental (full line) and simulated (dash line) Mn K edge spectra of ZnO:Mn.

differences compared to the spectra of the respective divalent oxides, indicating that the dopants are not segregated in the form of divalent oxides. With respect to this aspect, i.e. the position of the doping elements in the ZnO host, it was reported that a substitutional position is normally adopted by this elements due to the similar ionic radius with Zn [2][3][4].

To evaluate the distortion caused in the environment of the dopants, EXAFS will provide only average distances in the first coordination shell and no information about the bonding angles On the other hand, XANES will provide more accurate information about distances and angles. Unfortunatelly, XANES is not suitable for fitting, only for modelling.

To clarify this, the simulation of XANES spectra of Mn in ZnO with no distortion was performed using the FDMNES code [6]. Figure 2 shows the comparison of our simulation with experimental spectra and reported simulation by Smolentsev et al. for ZnO:Mn with distorted simmetry [7].

The comparison of the spectra of Figure 2 suggests that the Mn ions in the ZnO host are in a distorted environment compared to the ideal tetrahedral coordination of the Wurtzite structure.

References

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