



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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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: Bimetallic alloys or intermetallic compounds on the surface of (La,Sr,Ce)(Me,Ti)O ₃ formed via topotactic ion-exchange exsolution	Experiment number: A08-1-1098
Beamline: LISA	Date of experiment: from: 20.09.2022 to: 24.09.2022	Date of report: 23.12.2022
Shifts: 12	Local contact(s): Francesco D acapito (email: dacapito@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Beata Bochentyn , Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland Agata Ducka , Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, 80-233 Gdańsk, ul. Narutowicza 11/12, Poland		

Report:

A wide set of ceramic samples has been synthesized via the Pechini method. The following compositions with single metal have been given:

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}TiO_{3-δ} (LSCT) - reference

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Co_{0.1}Ti_{0.9}O_{3-δ} (Co-doped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Cu_{0.1}Ti_{0.9}O_{3-δ} (Cu-doped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Fe_{0.1}Ti_{0.9}O_{3-δ} (Fe-doped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Ni_{0.1}Ti_{0.9}O_{3-δ} (Ni-doped LSCT)

and bimetallic compositions:

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Co_{0.05}Cu_{0.05}Ti_{0.9}O_{3-δ} (Co,Cu-codoped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Co_{0.05}Fe_{0.05}Ti_{0.9}O_{3-δ} (Co,Fe-codoped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Ni_{0.05}Co_{0.05}Ti_{0.9}O_{3-δ} (Ni,Co-codoped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Ni_{0.05}Cu_{0.05}Ti_{0.9}O_{3-δ} (Ni,Cu-codoped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Ni_{0.05}Fe_{0.05}Ti_{0.9}O_{3-δ} (Ni,Fe-codoped LSCT)

(La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Fe_{0.05}Cu_{0.05}Ti_{0.9}O_{3-δ} (Fe,Cu-codoped LSCT)

Moreover, a set of reference samples was also analysed: NiO, Co₃O₄, CuO, Cu₂O, Fe₂O₃, Fe₃O₄, CeO₂, Co-foil, Cu-foil, Fe-foil.

The samples were in a powder form in both as-prepared and reduced state. The reduction of as-prepared powders was performed in home laboratory in hydrogen for 10h at 900°C.

The measurements at LISA beamline were performed in the transmission and fluorescence modes at 80K (cooled down with liquid nitrogen). The proper weight amount of particular powders was mixed with cellulose and pressed into pellets before the analysis. The measurements were taken at the near-edge and in the extended range spectra (up to 500 eV above the edge energy). The K-edges of Ce, La and transition metals were collected, as well as CeL₃ edge in few compositions was measured for comparison.

The exemplary figures presenting the obtained results are given below:

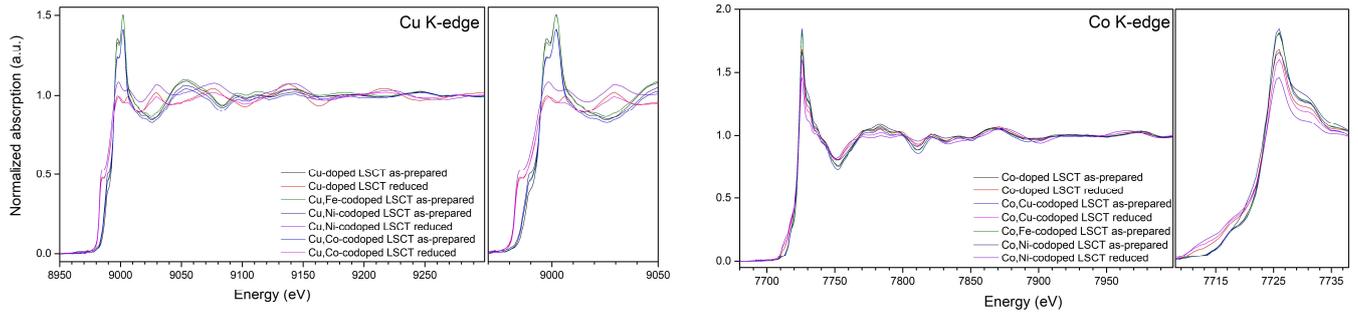


Fig.1: Cu K-edge (*left*) and Co K-edge (*right*) XANES spectra of samples with different dopants in both as-prepared and reduced states.

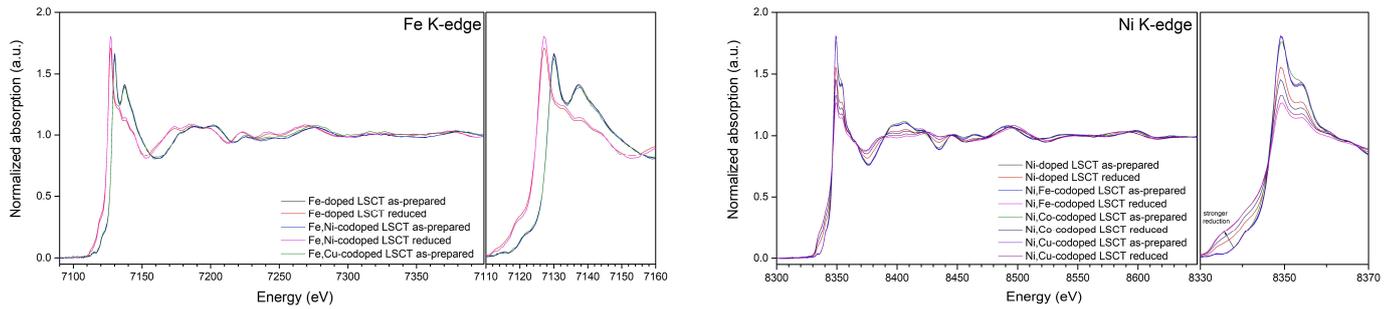


Fig.2: Fe K-edge (*left*) and Ni K-edge (*right*) XANES spectra of samples with different dopants in both as-prepared and reduced states.

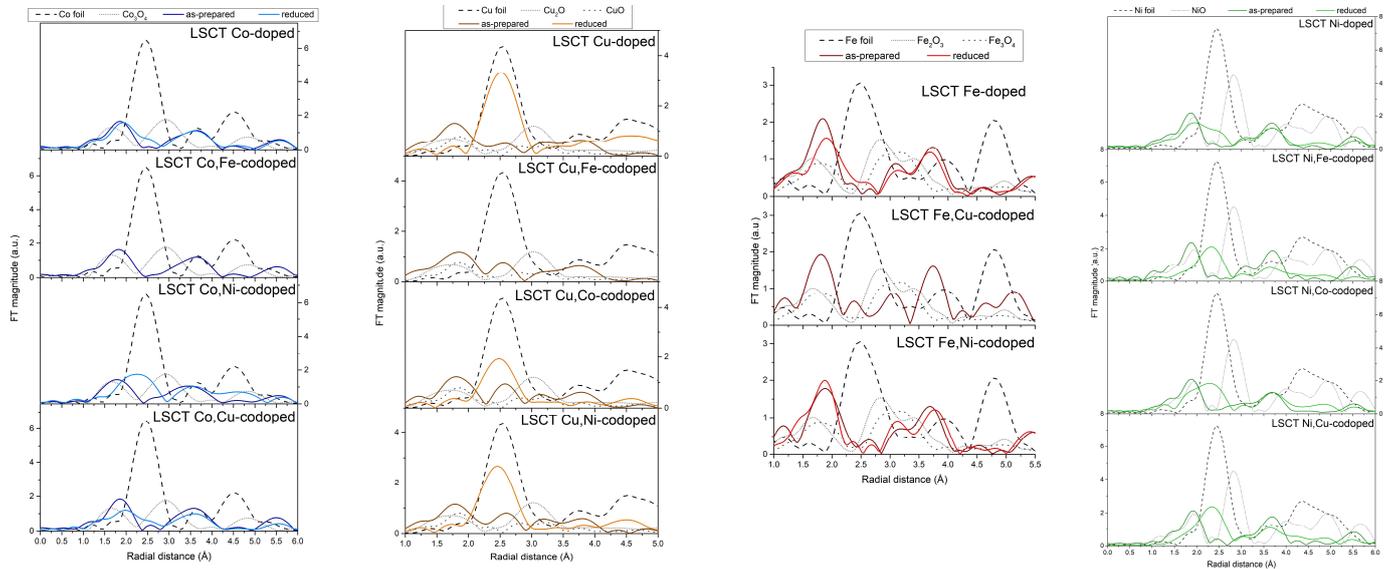


Fig.3: Fourier transformed EXAFS spectra of LSCT samples doped with different metals collected as K-edges of Co, Cu, Fe and Ni (*from left to right*), respectively.

The metallic dopants were added to $(\text{La}_{0.3}\text{Sr}_{0.6}\text{Ce}_{0.1})_{0.9}\text{TiO}_{3-\delta}$ (LSCT) perovskite structure in order to perform the exsolution process of metallic nanoparticles on the surface of the host material in reducing conditions.

The K-edge XANES of all analysed samples (Figs 1 and 2) confirm that a high-temperature reduction in hydrogen shifted the edge position towards lower energies than it was observed for as-prepared samples. It's a consequence of a decreased oxidation state of particular metals. The most significant shift (up to 4 eV) was found for Fe-containing samples. It seems that metals other than iron are in a partially reduced state even in as-prepared samples, in order to provide the electroneutrality condition. Thus the edge shift to lower energies after a high-temperature reduction in H_2 is not so significant.

Moreover, the pre-edge behaviour allows to distinguish a reduction efficiency depending on the co-doped metals. For example, if one focuses on the results given for Ni K-edge XANES (Fig.2 right), then it is clear that the absorption edge of LSCT doped only with nickel occurs for the highest energy. Co-doping nickel with cobalt decreases this energy, whereas co-doping nickel with copper and iron improves this effect to the highest extent.

EXAFS was used to study the local geometry of the metallic centres. The FT EXAFS (Fig. 3) of particular compositions confirm that in consequence of the reduction process the local geometry remains oxides with metals at lower oxidation state or even a metallic foil. It indirectly confirms that the exsolution process occurred, leading to the formation of metallic particles on the host material. The effect is even stronger when two properly selected metals are added to the structure (e.g. Ni-Fe or Ni-Cu). Due to the high complexity of the system (at least 6 elements), this EXAFS analysis is rather of qualitative character.