EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

# Experiment Report Form

ESRF

**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*

## 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 form 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.

| ESRF | **Experiment title:** relation between the charge state of the Cr dopant in beta-Ga2O3 and the pinning of the Fermi level induced by deep traps created by either protons or X-rays irradiation | **Experiment number**: HC-4497 |
|---|---|---|
| **Beamline**: BM30 - FAME | **Date of experiment**: from: 06-09-2021 to: 06-14-2021 | **Date of report**: |
| **Shifts: 15** | **Local contact(s)**: Olivier PROUX | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

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NB: This experiment was originally numbered 30-02-1148 before becoming HC-4497

**Report:**

**Relation between the charge state of the Cr dopant in beta-Ga2O3 and the pinning of the Fermi level induced by co-dopants and deep traps created by either protons or X-rays irradiation**

Overall, our experiment was successful with enough beamtime on a performant and easily-tuned beamline that is well-equipped. Specifically for this experiment, we were able to simultaneously record the X-ray induced photo-emission of Cr doped β-$Ga_2O_3$ samples with X-ray fluorescence spectra. X-ray induced photoluminescence was of sufficiently high intensity to record very good quality spectra with a state-of-the-art Hamamatsu C10027 photonic multichannel analyser (PMA) that was specifically lent to us by Hamamatsu for evaluation purposes.

This experiment has revealed to us two completely unexpected results:

- Firstly, there is no evolution under X-ray beam of neither xanes nor photoluminescence spectra. This indicates that the Cr oxidation state does not change with X-ray whereas it was observed by our group when Eu is used as a dopant inside GaN.
- Secondly, the xanes spectra between as-grown and proton-irradiated samples are identical (see figure 1a) while the photoluminescence spectra obtained simultaneously during the xanes measurements are completely different (see figure 2).

This is especially true for the set of samples doped with Cr and co-doped with Mg and Si (sample A and B). The photoluminescence spectra of the co-doped sample with Mg is dominated by a red broad emission at around ~725 nm. This band is assigned to the intraionic emission of $Cr^{3+}$ in the octahedral Ga site, associated with transitions from the $^2E$ and $^4T_1$ excited levels to the ground state $^4A_2$. Regarding the sample co-doped with Si, the photoluminescence spectra is dominated by a strong blue emission at ~350 nm assigned to intrinsic β-$Ga_2O_3$ self-trapped excitons and donor-acceptor pair transitions.

As a conclusion, although we observe a dramatic change in the photoluminescence of Cr when irradiating with protons (figure 2), its oxidation state remains constant (figure 1a) and dominated by the charge state 3+. Therefore, the difference on optical properties of Cr depends mainly on the process of excitation and recombination and not on its oxidation state. Different models based on secondary dopant/contaminant whose oxidation state could change with proton irradiation, such as Fe or other defect complex involving intrinsic defects, have been suggested by other authors to explain the dependency of Cr emission with the Fermi level location in β-$Ga_2O_3$. Indeed, taking advantage of the remarkable easiness of tuning of the beamline to probe another energy edge, we could check this hypothesis about the potential role of Fe as a charge transfer channel.

Figure 1 b) shows a detailed study of xanes in the region of the Fe K-edge, for both samples A and B, both as grown and irradiated. The Fe xanes spectra are found to be similar, suggesting that the dominant charge state for both samples is 3+. This result clearly suggests that other defect complex than single Fe should be considered as a channel of energy or charge transfer to explain the distinct Cr optical properties observed in β-$Ga_2O_3$ samples. Complementary investigations using particle inducing X-ray emission (PIXE), Raman Spectroscopy and X-ray diffraction are currently ongoing in our lab to quantify and qualify this secondary dopant that will be the object of either a dedicated proposal or a publication.

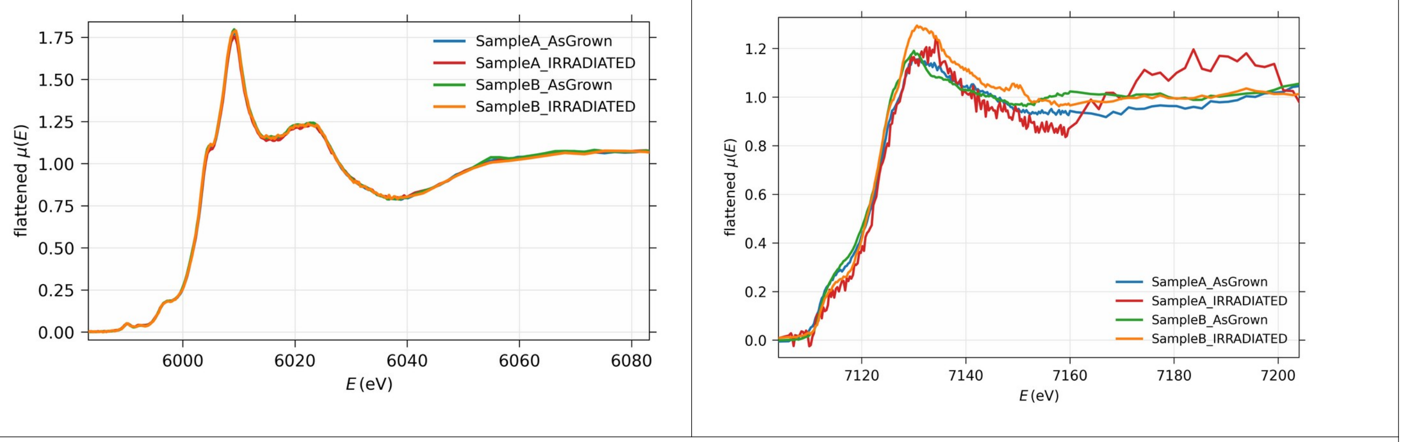


Figure 1: comparison of the xanes part of the two sets of samples A and B, either as as-grown or proton-irradiated. a) region of Cr K-edge b) region of Fe K-edge. No significant xanes modification with the proton or X-ray irradiation is present.

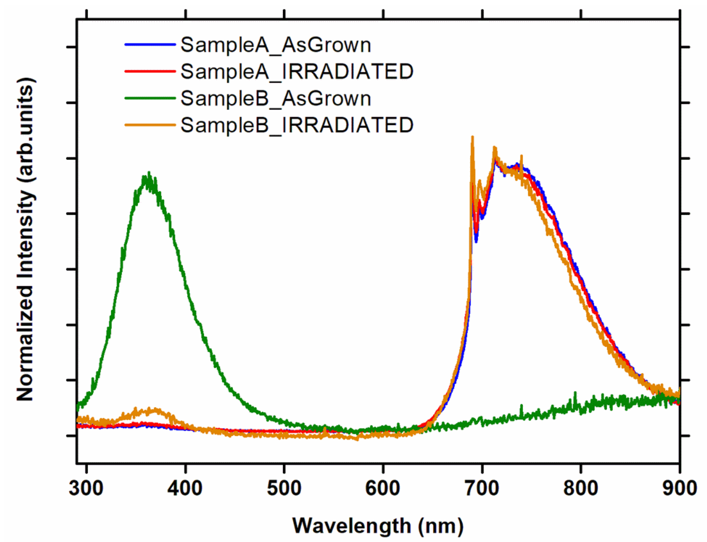


Figure 2: comparison of the X-ray beam induced photoluminescence of the two sets of samples A and B, either as as-grown or proton-irradiated. As-grown samples display a single blue emission band at ~350 nm while proton irradiated display a single red emission around ~725 nm. No evolution was observed during the exposure to the X-ray beam.