

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>

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: Charge transfer processes in Cr ³⁺ doped persistent phosphors	Experiment number: HC2736
Beamline: BM26A	Date of experiment: from: 16/11/2016 to: 21/11/2016	Date of report:
Shifts: 15	Local contact(s): Dipanjan Banerjee	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Olivier De Clercq (*) Jonas Joos (*) Katleen Korthout (*) Dirk Poelman Philippe Smet Reinert Verstraete (*)		

Report:

1. Performed measurements

All measurements were performed at the Cr K edge at the DUBBLE beamline (BM26A), ESRF, Grenoble, France.

2. XANES results

All spectra were aligned and merged using the *Athena* software to improve the S/N ratio.
The XANES spectra of the samples are displayed in Figure 1.

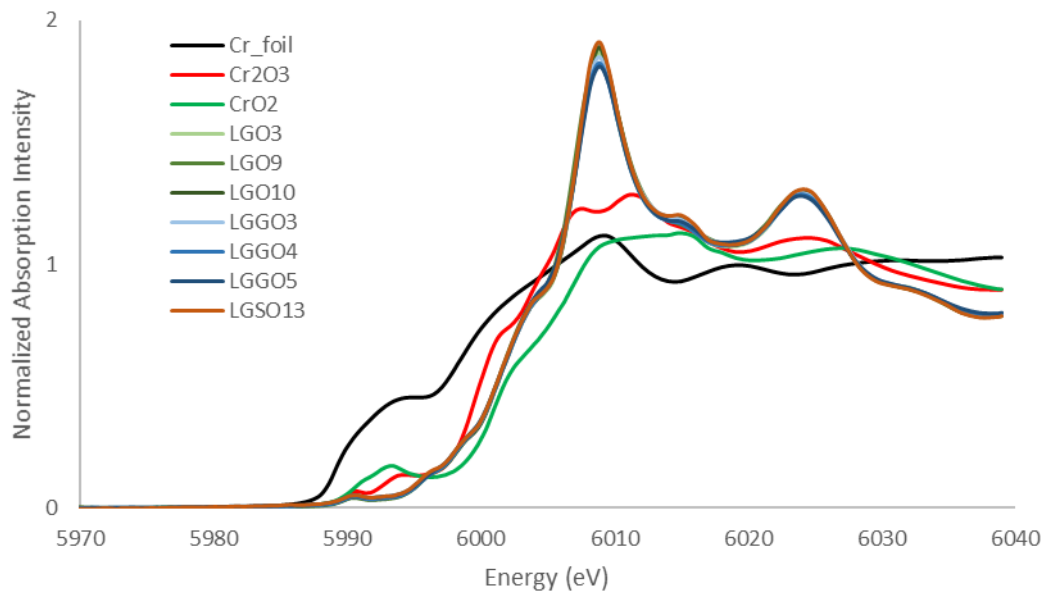


Figure 1: XANES spectra of the LG(G,S)O samples measured at the Cr K edge together with the spectra of some reference compounds: Cr foil (metallic), Cr₂O₃ (trivalent chromium octahedral site) and CrO₂ (tetravalent tetrahedral site).

From these spectra we can observe two things:

- The pre edge region of the measured samples shows one pre edge which coincides with the pre edge peak of Cr₂O₃. In Cr₂O₃ the Cr ions are octahedrally coordinated. Suggesting a preferential octahedral coordination for the Cr ions.
- The absorption step of the real samples is located between the absorption step of Cr₂O₃ and CrO₂. This observation suggests the presence of the Cr ions as well in trivalent as tetravalent oxidations state.

3. EXAFS results

The EXAFS spectra were analysed using the *Artemis* software. The spectra of the samples were analysed together using MDS (multiple data set fitting). This approach is often used if parameters are expected to be the same in different data sets. As such the number of used parameters can be maintained low.

For all spectra a Hanning window was used [2.683 \AA^{-1} , 10.84 \AA^{-1}] and [1 \AA , 4.236 \AA]. The structure of LGO was introduced to generate the scattering paths; both the Ga1 as the Ga2 site were used as possible sites for the Cr ion in the lattice. The scattering paths were calculated up to 4.5 \AA in R space. Besides the possible substitution of two sites also the possible presence of two oxidation states has to be evaluated (Figure 2).

First all four virtual spectra were calculated to evaluate if one of the possibilities was preferential. The largest coincidence was found when the Cr ions occupy the octahedral Ga1 sites in the lattice. Subsequently the spectra were fitted using MDS with only this site and one oxidation state for the Cr ions. An R-factor of $R=0.03$ was found.

Subsequently the presence of another Cr absorber on the Ga1 site was introduced. The fit significantly improved and an energy shift of 0.82 eV was found. This energy shift indicates the different oxidation state for both Cr absorbers: Cr³⁺ and Cr⁴⁺. Furthermore it was found that $(69 \pm 1)\%$ of the Cr ions is in the trivalent state and the other $(31 \pm 1)\%$ in the tetravalent state (the exact values of all fitting parameters are tabulated in Table 1 with their respective errors). The R factor of the fit was in this case well below 0.020 .

All the spectra are within the error margins similar, so no direct indication for the presence of Ge ions in the direct neighbourhood (within 4.5 \AA from the absorber) could be found. There are two possible reasons for this phenomenon: (1) no incorporation of Ge in the direct neighbourhood of the Cr ions, or (2) the similar atomic scattering factors of Ge and Ga make it difficult to differentiate between them.

Besides the preferential substitution of the Cr ions on the Ga1 sites, it is also observed that the Cr-O distance is smaller than the Ga1-O distance. This effect can be caused by the preferential shorter distance Cr-O (e.g. Cr₂O₃ and CrO₂).

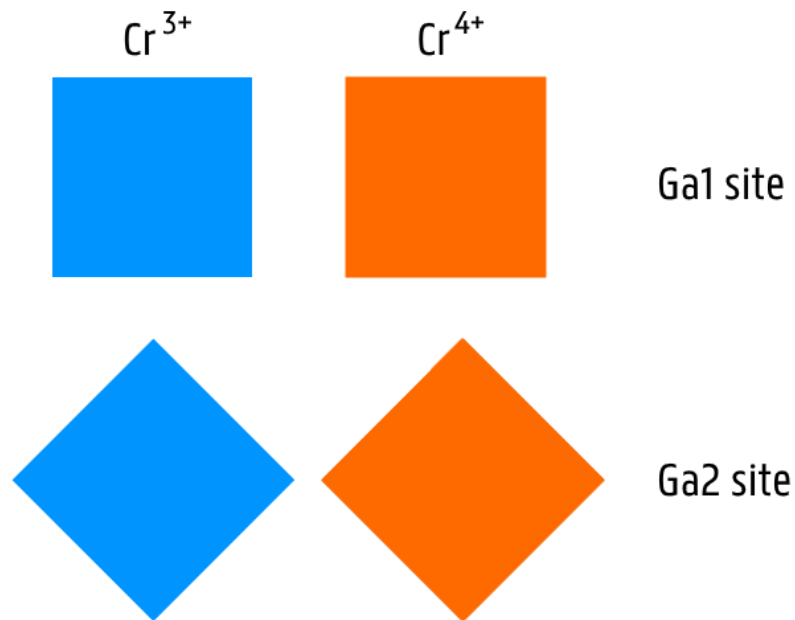


Figure 2: Graphic representation of the possible substitutions of the Cr atoms on the cationic sites in LGO.

Table 1: (top) Influence of Cr incorporation on the equilibrium distances with the nearest neighbours. $R(Axx)$ is the equilibrium distance as derived from the XRD pattern; $\Delta R(Axx)$ is the change as derived from the EXAFS spectra. (bottom) Debye-Waller factors for each type of scattering path, i.e. the parameter is only dependent on the type of scatterer.

	Cr^{3+}	Cr^{4+}
$\Delta R(021)/R(021)$	-4.03(11)%	-4.41(26)%
$\Delta R(022)/R(022)$	5.21(28)%	-1.48(52)%
$\Delta R(023)/R(023)$	-1.35(19)%	-2.94(47)%
$\Delta R(\text{Ga11})/R(\text{Ga11})$	1.945(53)%	-0.62(12)%
$\Delta R(\text{Ga21})/R(\text{Ga21})$	0.01(4)%	3.57(10)%
	Oxygen	Gallium
σ^2	0.00456(24)	0.00103(21)