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:** Chromium oxides in pigments and glazes from the French manufacture of Sèvres	**Experiment number**: HG-43
Beamline: ID21	**Date of experiment**: from: 4th October 2014 to: 8th October 2014	**Date of report**: 21/06/2016
Shifts: 12	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Louisiane Verger, [1,2] Olivier Dargaud, [2] Laurent Cormier [1]

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Report:

12 shifts on beam line ID21 were granted from the 4th to the 8th of october 2014 to the study of pigments and glazes by X-Ray absorption near edge spectroscopy (XANES) at the Cr K edge. The pigments studied are crystallised compounds synthesized at the "Manufacture of Sèvres". The mixture of these pigments with a colourless frit is applied on the porcelain and fired at high temperature (1280°C) to form a glaze, *i.e.* a glassy layer.

A focus was given to a particular pigment, mainly composed of a spinel $ZnAl_2O_4$:Cr^{3+}. In this investigation we understood the mechanism of colour change occurring during the thermal treatment of glazes composed of this kind of pigments. The aim was to follow the environment and the oxidation state of chromium from the pigment to the glaze. The spatial resolution of the X-Ray beam available at ID21 enabled us to characterize by µ-XANES spectroscopy the grains of pigment embedded in the uncoloured glass. The analysis is focused on the investigation of pre-edge features which are sensitive to both the redox and coordination.

This work leads to two articles, one already published and one under review. The abstract of the two articles are given below.

Article 1: Spectropic properties of Cr^{3+} in the spinel solid solution $ZnAl_{2-x}Cr_xO_4$

L. Verger, O. Dargaud, G. Rousse, E. Rozsályi, A. Juhin, D. Cabaret, M. Cotte, P. Glatzel and L. Cormier. *Physics and Chemistry of Minerals*, 2015, DOI:10.1007/s00269-015-0771-8.

The evolution of the structural environment of Cr^{3+} along the solid solution $ZnAl_{2-x}Cr_xO_4$ has been investigated using a multi-analytical approach. X-ray diffraction confirms that the system follows Vegard's law. Diffuse reflectance spectra show a decrease of the crystal field parameter with the Cr content, usually

related to the increase of the Cr-O bond length in a point charge model. This interpretation is discussed and compared to the data obtained by first-principle calculations based on density functional theory (DFT). X-ray Absorption Near Edge Structure (XANES) at the Cr K-edge spectra show a pronounced evolution in the pre-edge with the Cr content, characterised by the appearance of a third feature. Calculations enable to assign the origin of this feature to neighbouring Cr. The colour change from pink to brownish pink and eventually green along the solid solution has also been quantified by calculating the L*, a*, b* and x, y coefficients in the system defined by the International Commission on Illumination.

Article 2: The stability of gahnite doped with chromium pigments in glazes from the French manufacture of Sèvres

L. Verger, O. Dargaud, G. Rousse, M. Cotte and L. Cormier *(submitted, under review).*

The french manufacture of Sèvres, famous for its production of fine porcelain artefacts, has been synthesising pink pigments mainly composed of the spinel phase $ZnAl_{2-x}Cr_xO_4$ with x varying from 0.25 to 0.41 since the middle of the 19^{th} century. This kind of pigment is mixed with an uncoloured frit to obtain decorations for porcelain artefacts. However, the pink colour of the pigment is altered in a particular uncoloured frit and a brownish colour appears. The mechanism of this colour change was investigated. Observations under a scanning electron microscope revealed the formation of a phase rich in Cr resulting from reactions between the uncoloured frit and the pigment during firing. X-Ray Diffraction combined with Rietveld refinements and X-Ray Absorption Near Edge Structure at the Cr K-edge measurements showed that the new formed phase belongs to the same spinel phase $ZnAl_{2-x}Cr_xO_4$ than the pigment, but with a higher Cr content x. We showed that its formation and thus the stability of the pigment is driven by the Al content in the uncoloured frit.