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:** Incorporation of Cr and Mn in NIR persistent luminescent phosphors	**Experiment number**: 26-01-1110
Beamline: BM26A	**Date of experiment**: from: 09/03/2017 to: 13/03/2017	**Date of report**:
Shifts: 12	**Local contact(s)**: Dipanjan Banerjee	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jiaren Du(*)

Jonas Joos(*)

Katleen Korthout(*)

Lisa Martine(*)

Dirk Poelman

David Van der Heggen(*)

Report:

Red-emitting phosphors based on fluorides doped by Mn^{4+} can be used in combination with yellow/green emitting phosphors such as YAG:Ce or other garnet compositions to achieve warm white light (CCTs<5000 K on the blackbody locus, color rendering index (CRI) >80) from a blue LED, equivalent to that produced by current fluorescent, incandescent and halogen lamps.

One of these matetials is $K_2SiF_6:Mn^{4+}$, is being produced in the LumiLab research group and investigated for luminescent applications. To improve the production process we decided to study the precursor material: K_2MnF_6, which was (wrongly) assumed to contain only Mn^{4+} ions.

The oxidation state of Mn ions has been investigated in the past using mostly XANES and ELNES. To accurately determine the oxidation state of the Mn ions we measured the XANES spectra of several Mn reference compounds (see Table 1) at the DUBBLE beamline, ESRF, Grenoble, France. Figure 1 shows the XANES spectra of the various reference compounds, besides the dependency on the oxidation state also a dependency on the neighbourhood can be observed.

Table 1: Table with the Mn reference compounds that were measured. This table lists their nearest neighbours and the (assumed) oxidation state of the Mn ions

Compound	Nearest neighbours	(assumed) oxidation state
Mn foil	Mn	Metallic
MnO	O	II
Mn_2O_3	O	III
MnO_2	O	IV
$KMnO_4$	O	VII
MnS	S	II
MnF_2	F	II
MnF_3	F	III
K_2MnF_6	F	IV

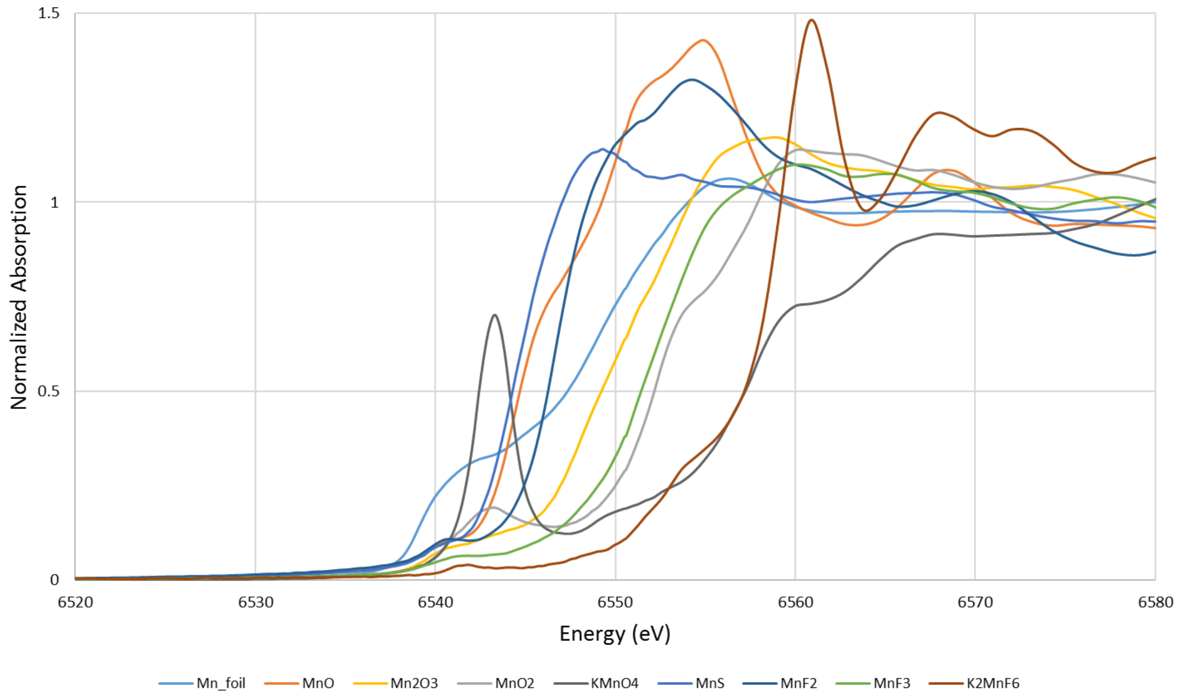

Figure 1: XANES spectra of Manganese reference compounds and K_2MnF_6. The spectra were normalized using the Athena software.

The determination of the oxidation state of Mn using XANES has been reported using several ways: PCA, fingerprinting using (the derivatives of) reference spectra, linear combinations of (the derivatives of) reference spectra,… We chose to determine the oxidation state using linear combinations of the derivatives of reference spectra. It is always preferable to work with this first derivative, since the spectroscopic structure is clearer and possible errors in post edge normalization do not change the shape of $d\chi(E)/dE$.

In Figure 2 the derivative of the fluoride Mn compounds are shown.

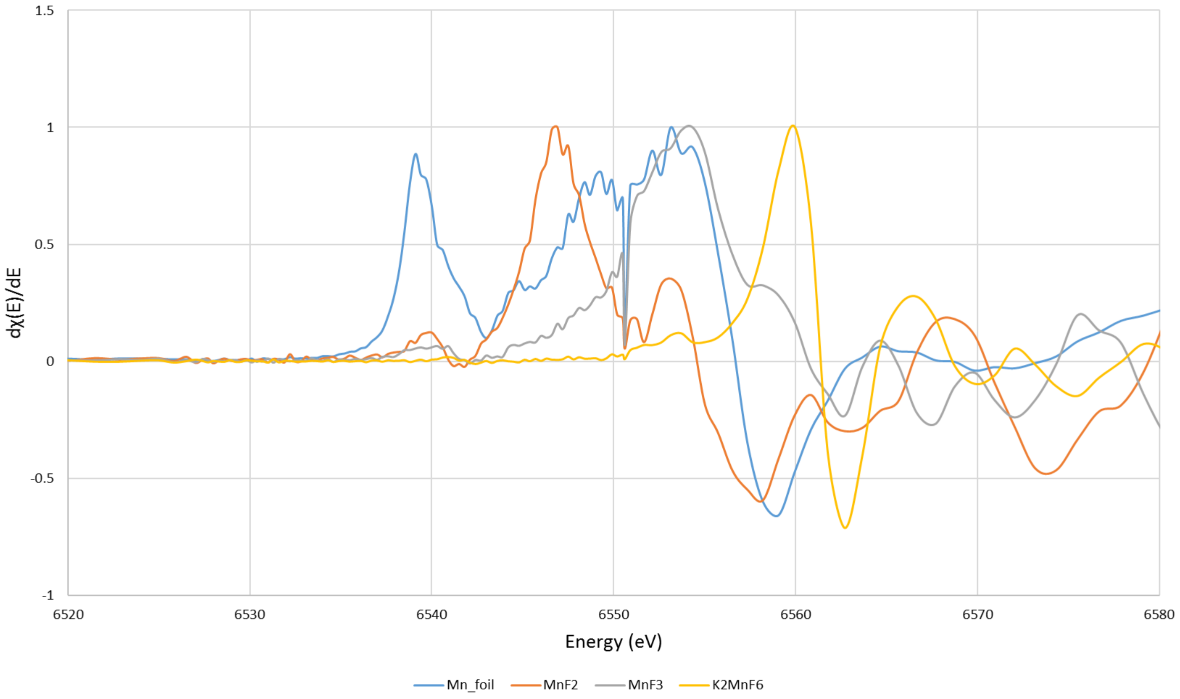

Figure 2: The first derivatives of XANES spectra of the fluoride Mn compounds and the precursor material K_2MnF_6.

Since no reference material for Mn^{4+}in a fluorine environment is present first a trend was made between the single valent Mn compounds and their absorption edge energy. The absorption edge energy was defined as the first maximum in the first derivative of the absorption spectrum. A linear fit was performed, the results are depicted in Figure 3 and Table 2.

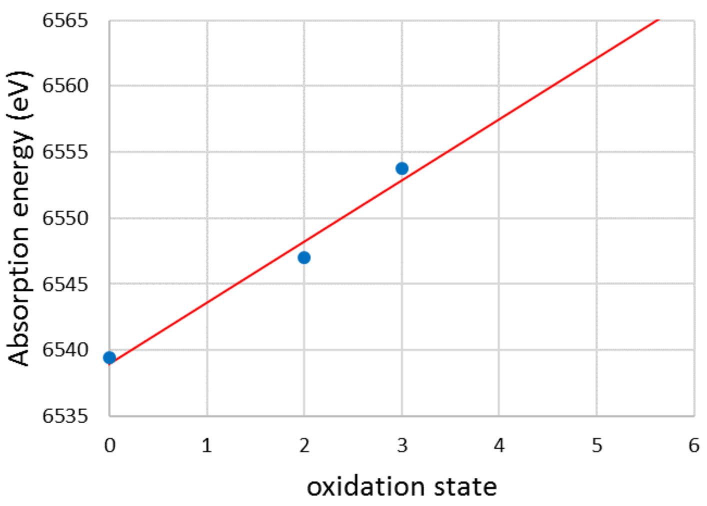

Figure 3: Linear trend between the absorption energy and the oxidation state of Mn in Mn fluorides

Table 2: Parameters of the fit displayed in Figure 3.

Parameter	Value	SE
Y junction	6539.0	1.5
Slope	4.63	0.72

Based on the values displayed in Table 2, we calculate that the absorption edge energy associated with tetravalent Mn in a fluorine environment is 6557.5 ± 4.4 eV. In we take a closer look at Figure 2, we indeed observe a peak around 6559 eV, well consistent with this value.

The next step is calculating the presence of the different oxidations states of Mn in K_2MnF_6. For this purpose all the first peaks in the first derivative of the XANES spectra of the reference compounds were fitted using a Gaussian function:

$$\chi(E) = a * e^{-\left(\frac{(E-b)}{c}\right)^2}$$

A Gaussian was also fitted to the peak in the first derivative of the XANES spectrum of K_2MnF_6 that is located around 6559 eV. The results are depicted in Table 3.

Table 3: Results of the fitting procedure on the first derivative of the XANES spectra.

Compound	A	AE(a)	B	AE(b)	C	AE(c)
Mn foil	0.90	0.33	6539.42	0.71	1.5	1
MnF_2	0.98	0.12	6547.01	0.27	2.51	0.38
MnF_3	0.98	0.081	6553.74	0.29	3.56	0.39
K_2MnF_6	1.04	0.28	6559.51	0.31	1.36	0.44

Subsequently the first derivative spectrum of K_2MnF_6 is fitted using all these four Gaussians to check the presence of other oxidation states. In this analysis the b and c parameters are fixed (values in Table 3), and only the amplitudes of the Gaussians is determined.

Table 4: Results of the components analysis on the XANES results of K_2MnF_6.

	A	AE(A)
Metallic Mn	0.007	0.068
MnF_2	0.002	0.053
MnF_3	0.109	0.061
Tetravalent Mn	1.05	0.12

From the results in Table 4, we can conclude that the fraction of metallic Mn and divalent Mn are negligible. The fractions of trivalent and tetravalent Mn are determined using the fitting results and are 21% and 79% respectively.