ESRF	**Experiment title:** Valence to core X-ray emission study of photocatalytically active ferrites	**Experiment number**: CH-5027
Beamline: BM20	**Date of experiment**: from: 29 Nov 2017 to: 05 Dez 2017	**Date of report**: 27/02/18
Shifts: 18	**Local contact(s)**: Dr. Kristina Kvashnina **(kristina.kvashnina@esrf.fr)**	*Received at ESRF:*

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Report:

Ternary iron-based materials like spinel ferrites MFe_2O_4 (M=Ca, Mg, Zn) have drawn a lot of attention in recent years due to their optimum band gap (1.8-2.0 eV) for water splitting. However, contradictory reports about band structure and positions have raised questions about their applicability. As an alternative to electrochemical measurements, valence to core X-ray emission spectroscopy enables determination of occupied and unoccupied electronic states, and not solely the band edge positions. Thus, we wanted to investigate the band structures and electronic states of spinel ferrites to find the correct values for band edge positions in order to understand their photocatalytic and photoelectrochemical performance by comparing it with their underlying electronic structure.

Moreover, the aim of the present experiment was to investigate the degree of inversion of the spinel ferrites prepared at different temperatures, since we want to correlate the inversion degree with photocatalytic activity of spinel ferrite nanoparticles. Therefore, the results will be topic of a forthcoming publication.

XANES, RIXS, XES and valence-to-core (VTC) measurements at the Fe K-edge were performed during 18 shifts of beamtime at the European Synchrotron Radiation Facility on the Rossendorff beamline BM20. During the experiments, 24 different samples were analysed (62 measurements) whose preparation, main features and compositions are summarized in the table below (Table 1).

XANES spectra of spinel ferrite nanoparticles synthesized in the microwave and calcined at different temperatures were recorded from 7090 to 7220 eV and are shown in Figure 1. Only Fe^{3+}-ions are expected, except in the reference material magnetite ($FeFe_2O_4$). The spectra show pre-edge-features at excitation energies of about 7112 to 7116 eV and the main edge beginning at about 7120 eV. The pre-Edge signal is attributed to electron excitations from Fe 1s to empty 3d states. For iron in octahedral coordination spheres only quadrupole transitions are expected here while for iron in tetrahedral sites also dipole transitions should be possible at the same excitation energy which would lead to an increased signal intensity (F. De Groot, G. Vankó, P. Glatzel, *J. Phys. Condens. Matter* **2009**, *21*.). This is in accordance with the trend shown in Figure 1 where the signal intensity increases with the degree of inversion ($ZnFe_2O_4$ is a normal and $NiFe_2O_4$ a fully inverse spinel, $MgFe_2O_4$ can show varying degrees of inversion).

Sample Labelling	Description	analysed species	XANES	RIXS	Site selective XES	VTC
Reference Hematite	hematite reference	a-Fe_2O_3	x	x	x	
Reference Magnetite	magnetite reference	Fe_3O_4	x	x	x	
Kik-ZFO-MW275-3	$ZnFe_2O_4$ prepared @275°C, calcined 300°C	$ZnFe_2O_4$	x	x	x	
Kik-ZFO-MW275-400C-1	$ZnFe_2O_4$ prepared @275°C, calcined 400°C	$ZnFe_2O_4$	x		x	
Kik-ZFO-MW275-500C-1	$ZnFe_2O_4$ prepared @275°C, calcined 500°C	$ZnFe_2O_4$	x		x	
Kik-ZFO-MW275-600C-1	$ZnFe_2O_4$ prepared @275°C, calcined 600°C	$ZnFe_2O_4$	x	x	x	
kik-ZFO-MW275-PVP-1	$ZnFe_2O_4$ prepared @275°C with polymer shell	$ZnFe_2O_4$	x			
Kik-ZFO-B206-CSi-1	ZnFe2O4 prepared @275°C with citrate shell	$ZnFe_2O_4$	x	x	x	
ZFO PLU Gel 300C	porous ZnFe2O4 dried with polymer	$ZnFe_2O_4$	x	x	x	
ZFO PLU 600C 12h	porous ZnFe2O4 calcined@600°C	$ZnFe_2O_4$	x	x	x	x
ZFO PLU 550C 12h	porous ZnFe2O4 calcined@550°C	$ZnFe_2O_4$	x			
ZFO PLU 500C 12h	porous ZnFe2O4 calcined@500°C	$ZnFe_2O_4$	x		x	
Kik-MFO-MW275-PVP-1	$MgFe_2O_4$ prepared @275°C with polymer shell	$MgFe_2O_4$	x	x	x	
ANB_MFO_126 (1)	$MgFe_2O_4$ prepared @200°C	$MgFe_2O_4$	x	x	x	
ANB_MFO_126_400 (2)	$MgFe_2O_4$ prepared @200°C, calcined @ 400°C	$MgFe_2O_4$	x	x	x	
ANB_MFO_126_600 (3)	$MgFe_2O_4$ prepared @200°C, calcined @ 600°C	$MgFe_2O_4$	x	x	x	
ANB_MFO_126_800 (4)	$MgFe_2O_4$ prepared @200°C, calcined @ 800°C	$MgFe_2O_4$	x	x	x	x
ANB_MFO_128 (9)	$MgFe_2O_4$ prepared @250°C	$MgFe_2O_4$	x	x	x	
ANB_MFO_128_T400 (10)	$MgFe_2O_4$ prepared @250°C, calcined @ 400°C	$MgFe_2O_4$	x		x	
ANB_MFO_128_T600 (11)	$MgFe_2O_4$ prepared @250°C, calcined @ 600°C	$MgFe_2O_4$	x		x	
ANB_MFO_128_T800 (12)	$MgFe_2O_4$ prepared @250°C, calcined @ 800°C	$MgFe_2O_4$	x		x	
ANB_MFO_129 (13)	$MgFe_2O_4$ prepared @275°C	$MgFe_2O_4$	x			
ANB_NFO_09 (17)	$NiFe_2O_4$ prepared @200°C	$NiFe_2O_4$	x		x	
ANB_NFO_09_T500 (18)	$NiFe_2O_4$ prepared @200°C, calcined @500°C	$NiFe_2O_4$	x	x	x	x

Table 1- Samples labelling and description

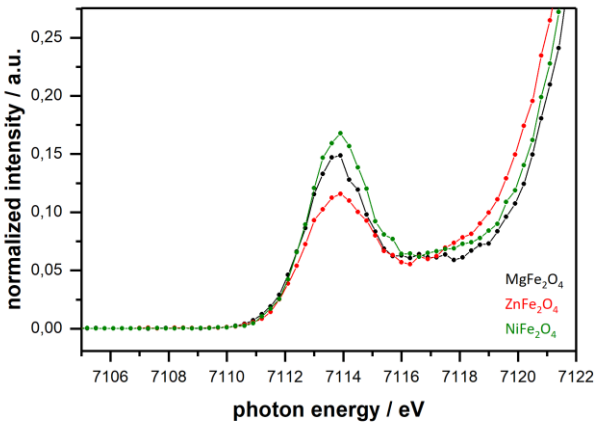

Figure 1. XANES spectra of the pre-edge region of different spinel ferrites

There are also slight differences in the onset of the main edge. The pre-edge region of differently calcined $MgFe_2O_4$ samples prepared in the microwave at 200 °C was also investigated. From the intensity of the pre-edge it could be concluded that the degree of inversion increases up to a calcination temperature of 600 °C and then decreases again upon calcination at even higher temperatures. Interestingly, when the microwave synthesis is performed at 250 °C, the trends in pre-edge intensity and main-edge onset is less pronounced (but still present), indicating that the structural changes upon calcination are smaller for this sample. The exact analysis is currently under progress.

RIXS planes in the pre-edge area of differently calcined $MgFe_2O_4$ all looked pretty much the same and did not show additional features to those seen in the XANES spectra. A cut through the RIXS plane at 7114 eV incident photon energy revealed that there might be a shift in the emission energy dependent on calcination temperature. Site-selective-XES was conducted to investigate the pre-edge signal in greater detail. Emission spectra were recorded over an emission energy range of 6395 – 6415 eV at incident photon energies of 7113, 7114 and 7118 eV.

Valence-to-core X-ray emission spectra were recorded over an emission energy range of 7085 – 7130 eV. The main goal was to determine the valence band edge of the different spinels, and data analysis is currently under way. However, in the 18 shifts not all samples could be measured, which makes forthcoming beamtimes desirable to see the influences of preparation procedure on the electronic structure of our spinel nanomaterials

Conclusion: Degrees of inversion could be quantified depending on the material and preparation, leading to new insights into our developed microwave synthesis. Band gaps were determined by comparing the first deviation of the XANES and the VTC signal.