

# SUPPORTING INFORMATION

## Insights into the effect of iron and cobalt doping on the structure of nano-sized ZnO

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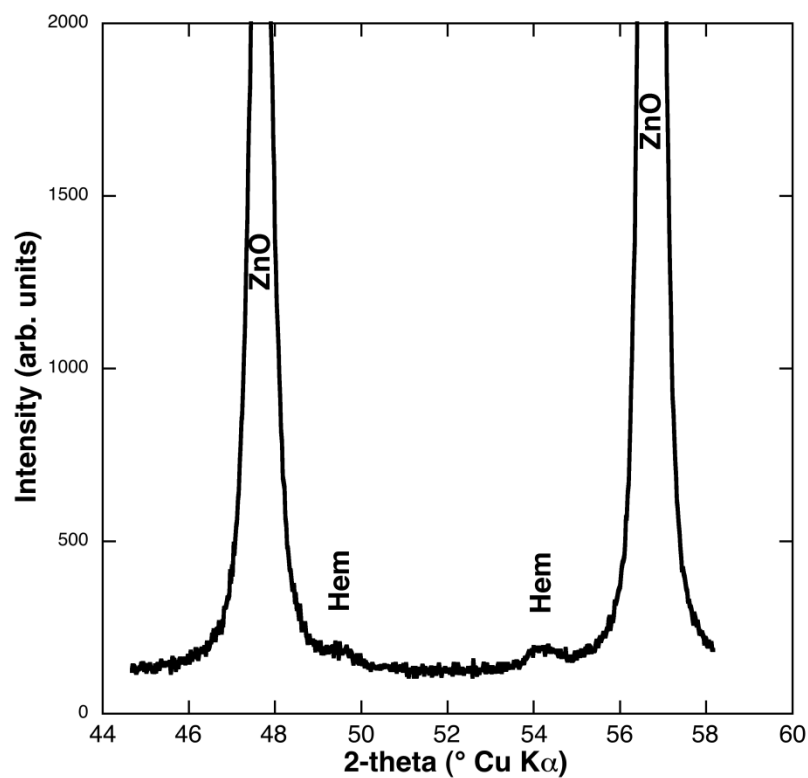
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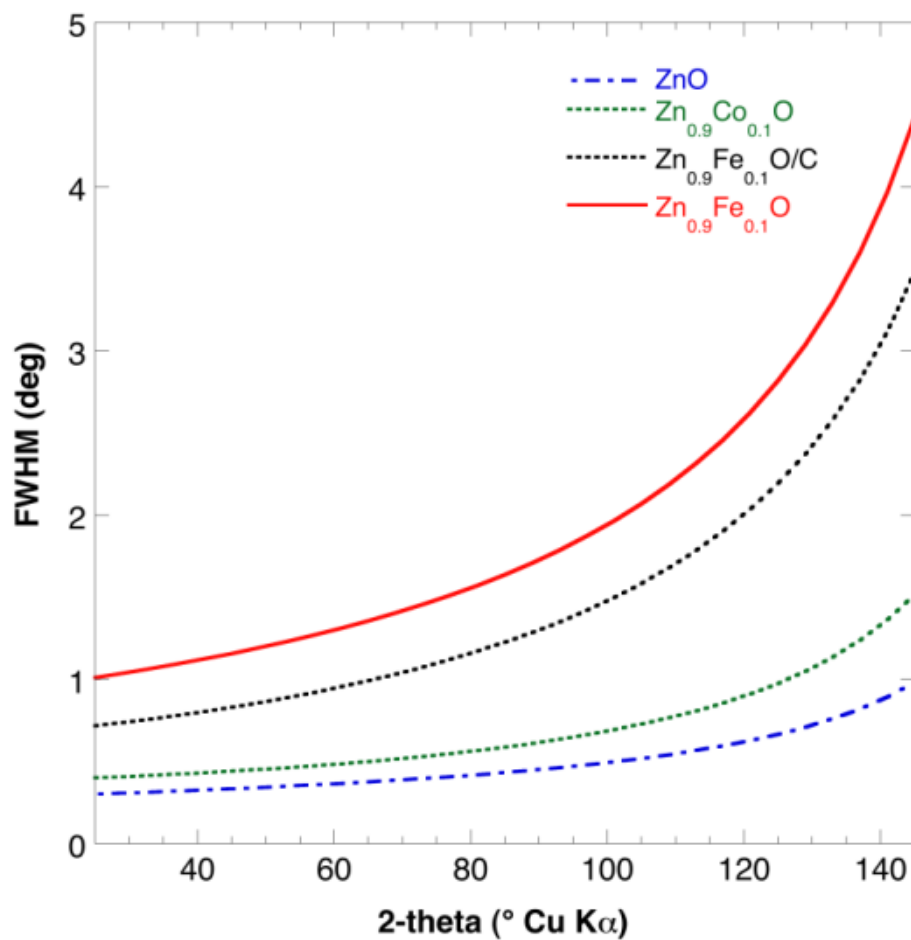
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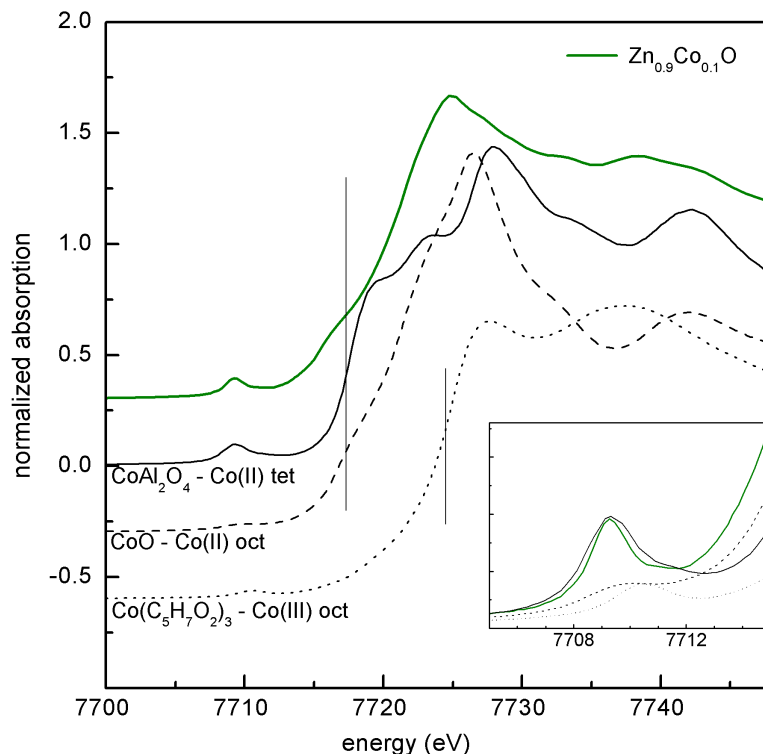


**Figure S1.**

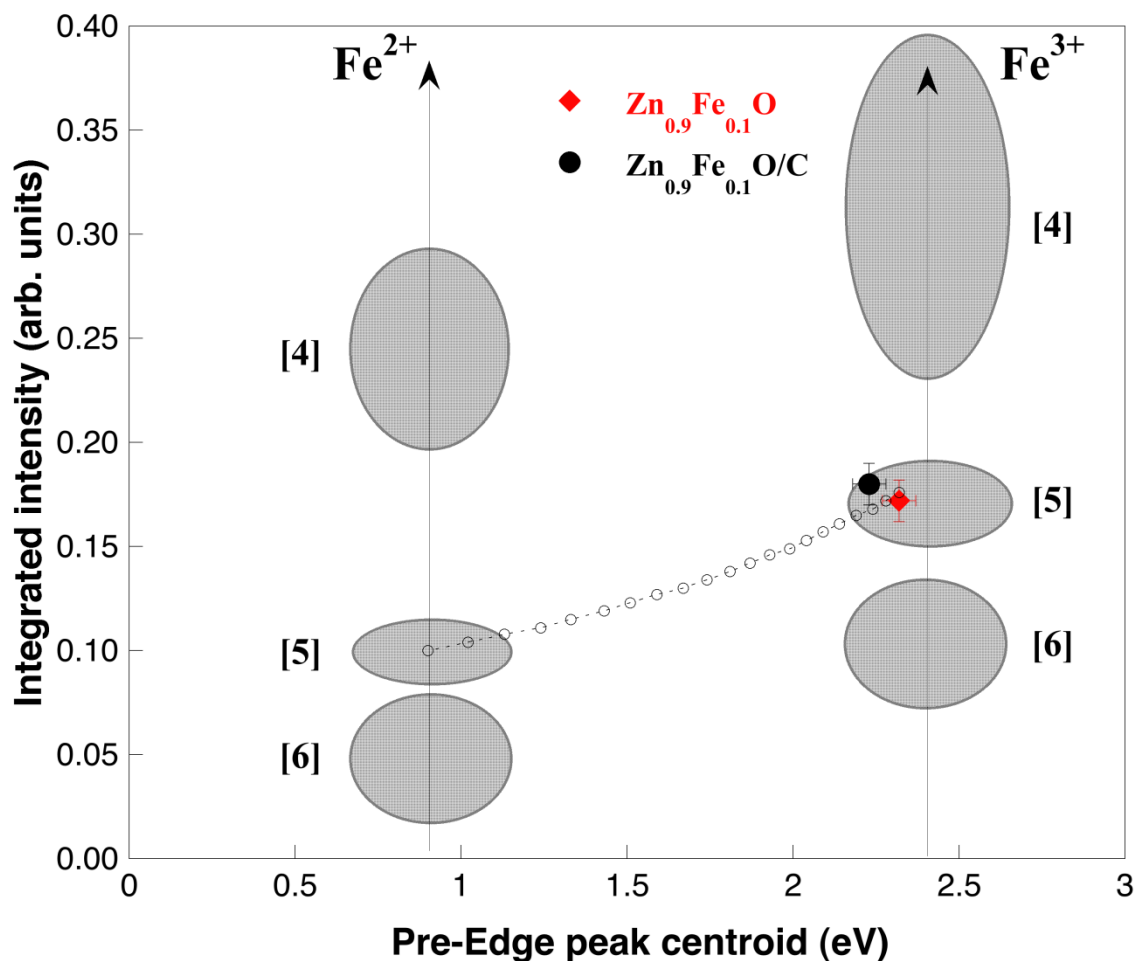
XRD pattern recorded for a 99.5 wt.% ZnO and 0.5 wt.% hematite ( $\text{Fe}_2\text{O}_3$ ) mixture, showing the reflections corresponding to  $\text{Fe}_2\text{O}_3$ . Consequently, it is concluded that crystalline Fe-bearing impurities, if any, are limited to an amount significantly lower than 0.5 wt.%. The reflections related to  $\text{Fe}_2\text{O}_3$  are labeled as ‘Hem’, whereas two other reflections assigned to ZnO are labeled as ‘ZnO’.



**Figure S2.** ‘Full Width at Half Maximum’ (FWHM) of the diffraction reflections as determined by fitting the diffraction reflections profile shape according to a Pseudo Voigt function. It is evident that the FWHM increases from ZnO to Zn<sub>0.9</sub>Fe<sub>0.1</sub>O, indicating that the crystallinity decreases in the order ZnO > Zn<sub>0.9</sub>Co<sub>0.1</sub>O > Zn<sub>0.9</sub>Fe<sub>0.1</sub>O/C > Zn<sub>0.9</sub>Fe<sub>0.1</sub>O.



**Figure S3.** Co K-edge normalized XANES spectrum of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  compared with the spectra of three model compounds containing solely octahedrally coordinated Co(II) [ $\text{CoO}$ ], tetrahedrally coordinated Co(II) [ $\text{CoAl}_2\text{O}_4$ ], and octahedrally coordinated Co(III) [ $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ ]. The absorption edge of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  lies very close to the value 7717.3 eV (marker) found for  $\text{CoO}$  and  $\text{CoAl}_2\text{O}_4$  [26]. In both compounds, Co is divalent although having different coordination. Therefore, the XANES measurements reveal that most of the Co in  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  is present in the 2+ oxidation state. The pre-edge peak of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample is similar in energy position and intensity compared to that of the tetrahedrally coordinated  $\text{Co}^{2+}$  compound ( $\text{CoAl}_2\text{O}_4$ ), compatible with the presence of Co in the tetrahedral site of the wurtzite structure.



**Figure S4.** Pre-edge peak integrated intensity and energy centroid as compared with Fe model compounds (cf. Fig. 4 and Table 2). 0 in the energy axis refers to the edge energy of metallic iron (7112 eV). The grey areas correspond to literature data of Fe model compounds with different oxidation state and coordination geometry, whereas the dotted line is a linear combination between two putative end-members - one with the same centroid energy as the purely trivalent Fe sample and one with the centroid energy typical for purely divalent Fe model compounds. Each small circle is placed at 0.05 step in the  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio.

**Table S1.** Chemical composition of the synthesized ZnO samples as obtained by ICP and SEM/EDX analysis. The ratios of Zn to Co and Zn to Fe were determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES) utilizing an ULTIMA 2 (Horiba, Kyoto, Japan) with axial plasma viewing. In order to dissolve the as-synthesized samples, hydrochloric acid was used. Table S1 lists the normalized molar fractions measured by ICP-OES. The chemical composition was also verified by EDX analysis performed by means of a FESEM (Zeiss LEO1525, equipped with a Gemini Column and a Bruker EDX detector). Analyses were performed at 20 kV and 10 nA, with 15 minutes counting time. Resulting compositions are expressed as Co/(Co+Zn) or Fe/(Fe+Zn) ratio.

<b>Sample</b>	<b>Zn<sup>a</sup></b>	<b>Co<sup>a</sup></b>	<b>Fe<sup>a</sup></b>	<b>M/(M+Zn)<sup>b</sup></b>
<b>ZnO</b>	1	-	-	1
<b>Zn<sub>0.9</sub>Co<sub>0.1</sub>O</b>	0.90	0.10	-	0.09(1)
<b>Zn<sub>0.9</sub>Fe<sub>0.1</sub>O</b>	0.89	-	0.11	0.11(1)
<b>Zn<sub>0.9</sub>Fe<sub>0.1</sub>O/C</b>	0.89	-	0.11	0.12(1)

<sup>a</sup> molar fractions of Zn and dopants as determined by ICP

<sup>b</sup> molar fraction of the dopant as determined by SEM  
(the error concerning the last digit is reported in brackets)

**Table S2.** Structural parameters obtained by fitting the experimental EXAFS signals measured at the Zn K-edge. R is the average interatomic distance and  $\sigma^2$  the EXAFS Debye-Waller factor (variance of the distance distribution function). The coordination numbers (N) were kept fixed.

Sample	Bond type	N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )
<b>ZnO</b>	Zn-O	4	1.979(3)	0.0057(9)
	Zn-Zn	6	3.209(4)	0.0095(5)
	Zn-Zn	6	3.251(4)	0.0095(5)
<b>Zn<sub>0.9</sub>Co<sub>0.1</sub>O</b>	Zn-O	4	1.977(3)	0.0056(9)
	Zn-Zn(Co)	6	3.207(5)	0.0098(6)
	Zn-Zn(Co)	6	3.248(5)	0.0098(6)
<b>Zn<sub>0.9</sub>Fe<sub>0.1</sub>O</b>	Zn-O	4	1.978(3)	0.0053(8)
	Zn-Zn(Fe)	6	3.208(5)	0.0114(6)
	Zn-Zn(Fe)	6	3.249(5)	0.0114(6)
<b>Zn<sub>0.9</sub>Fe<sub>0.1</sub>O/C</b>	Zn-O	4	1.978(3)	0.0054(9)
	Zn-Zn(Fe)	6	3.208(5)	0.0107(6)
	Zn-Zn(Fe)	6	3.250(5)	0.0107(6)

**Table S3.** Structural parameters obtained by fitting the experimental EXAFS signals measured at the Co and Fe K-edges. R is the average interatomic distance and  $\sigma^2$  the EXAFS Debye-Waller factor (variance of the distance distribution function). The coordination numbers (N) were kept fixed.

Sample	Bond type	N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )
<b>Zn<sub>0.9</sub>Co<sub>0.1</sub>O</b>	Co-O	4	1.968(8)	0.0037(12)
	Co-Zn	6	3.221(7)	0.0097(9)
	Co-Zn	6	3.263(7)	0.0097(9)
<b>Zn<sub>0.9</sub>Fe<sub>0.1</sub>O</b>	Fe-O	4	1.939(9)	0.0080(16)
	Fe-Zn(Fe)	6	3.20(3)	0.0357(47)
	Fe-Zn(Fe)	6	3.24(3)	0.0357(47)
<b>Zn<sub>0.9</sub>Fe<sub>0.1</sub>O/C</b>	Fe-O	4	1.93(1)	0.0087(10)
	Fe-Zn(Fe)	6	3.21(3)	0.0336(39)
	Fe-Zn(Fe)	6	3.26(3)	0.0336(39)