ESRF	**Experiment title:** Structural and magnetic characterization of dopant-complexes in functional oxides	**Experiment number:** HE-3574
Beamline: ID12/ID08	**Date of experiment:** from: 20.07. / 11.06.2011 to: 27.07. / 14.6.2011	**Date of report:** 08.08.2011
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Report:

The aim of this experiment was to study the possible formation of dopant cluster formation in doubly doped functional oxides by means of x-ray linear dichroism (XLD) and x-ray magnetic circular dichroism (X-MCD).The beamtime was split between soft (ID08) and hard (ID12) x-ray absorption spectroscopy. One set of samples was 3%N-codoped and undoped 2% Fe:TiO_2. Fig. 1 shows the XLD spectra at the anion sublattice of O and N K-edges, respectively. From the very similar XLD signature it can be directly concluded that the N is substitutionally incorporated in the TiO_2 host lattice. Fig. 2 shows the respective XLD at the Ti K-edge and $L_{3/2}$-edges revealing that there are small changes at the pre-edge features of the Ti K-edge upon N-doping. The corresponding features at the $L_{3/2}$-edges are much less pronounced. XLD and thus also XMCD at

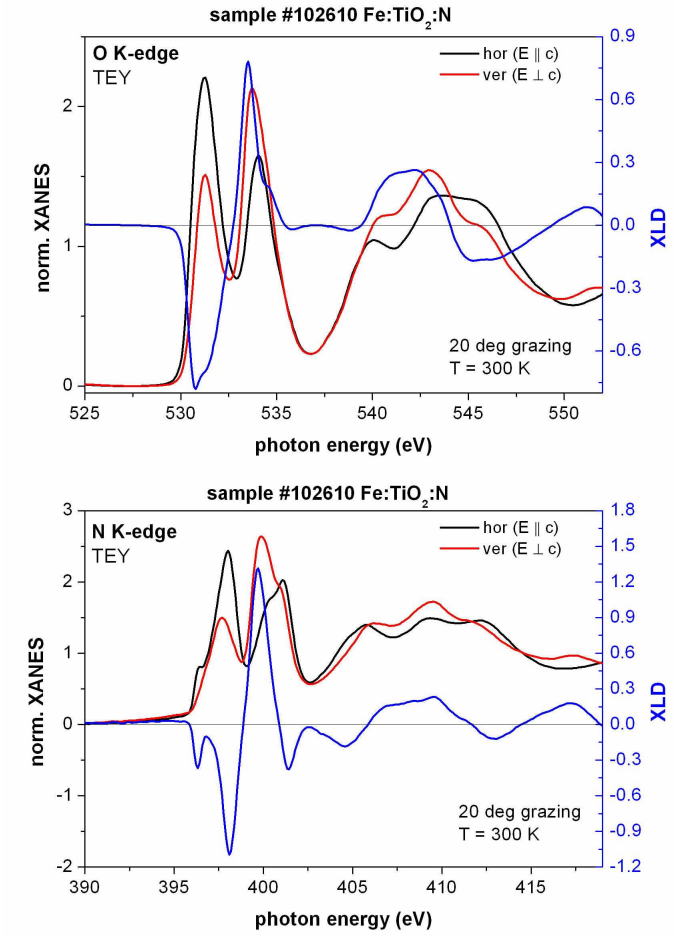

Fig 1: XLD at O and N K-edges of N-doped Fe:TiO_2 (rutile).

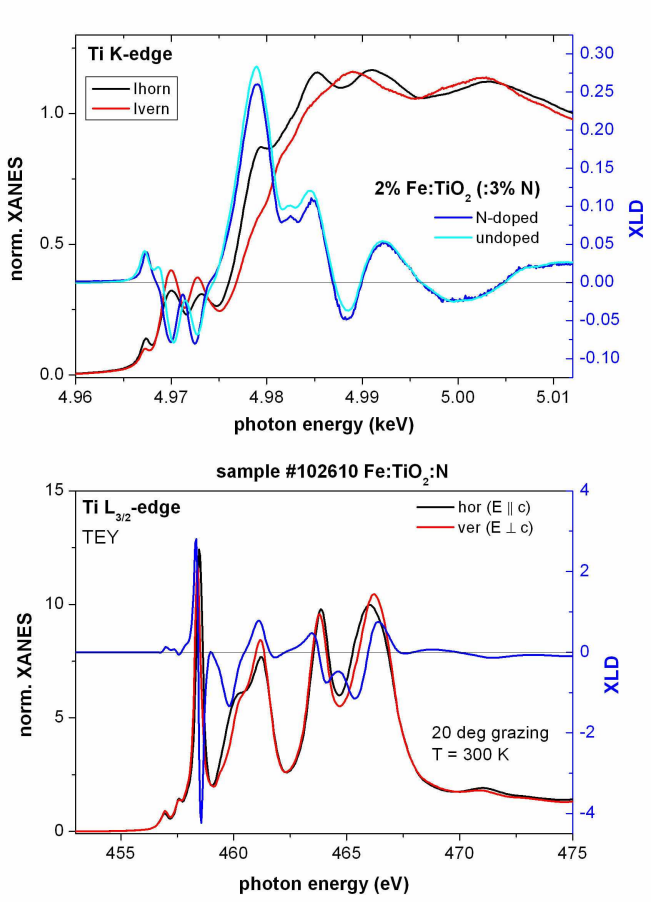

Fig 2: XLD spectra of N-doped and undoped Fe:TiO_2 (rutile) at the Ti K-edge and the $L_{3/2}$-edges.

the Fe absorption edges were impossible to be recorded, the strong Ti K-absorption because of the rutile substrate precluded any measurement at the Fe K-edge and the Fe $L_{3/2}$-edges suffered from large background artifacts in TEY and hardly any signal in FY.

The second set of samples consists of a series of N-codoped Co:ZnO samples with a range of different N as well as Co concentrations. XMCD measurements at ID12 were limited due to the breakdown of the magnet power supply of the 17 T magnet, which made measurements of the magnetic anisotropy by M(H) curves impossible. Fig. 3 shows XLD measurements at the Co and O K-edges, respectively. The signatures reflect the overall trend also seen at the Zn K-edge (not shown) reflecting the variety of structural perfection depending on the preparation conditions. Fig. 4 shows the XLD at the N K-edge in fluorescence yield for most of the samples in Fig. 3. Comparing the XLD of the O K-edge and the N K-edge is becomes obvious that the N is not substitutionally incorporated into the ZnO lattice. The N K-edge exhibits one pronounced peak with sizable XLD which is characteristic for molecular N_2. Since both total electron yield as well as XP did not show any significant amount of N, one has to conclude that these N_2 molecules may be incorporated in the ZnO matrix. Either it can be found at grain boundaries or the molecules may substitute for O vacancies which can be found due to the low amount of O in the sputter gas. Nonetheless, the XLD spectra at all four constituents do not show any indication for the formation of dopant complexes in Co:ZnO:N. In addition, the N data point towards molecular N_2 rather than substitutional doing which may also explain why N-codoping did not lead to the expected p-type conductivity in these samples yet. In contrast, the Ti K-edge of Fe:TiO_2:N shows indications of changes in the electronic structure of the host crystal upon N-doping; however, this could not be corroborated at the Fe K-edge due to the large fluorescence background of the rutile substrate.

Finally, Fig. 4 shows exemplarily two XMCD spectra and the corresponding M(H) curves at the Co K-edge in plane and out of plane, respectively. For this 1µm thick reference film the small anisotropy of the M(H) curves could be recorded with sufficient signal to noise ratio; four other samples were tried as well. The obtained five M(H) curves will be compared to those at the Co $L_{3/2}$-edges (not shown).

In summary, a large set of XLD and some XMCD spectra could be recorded for different doubly doped functional oxides. While for Fe:TiO_2:N substitutional incorporation of N was found the Co:ZnO:N only show signs of the incorporation of molecular N_2 into the host matrix.

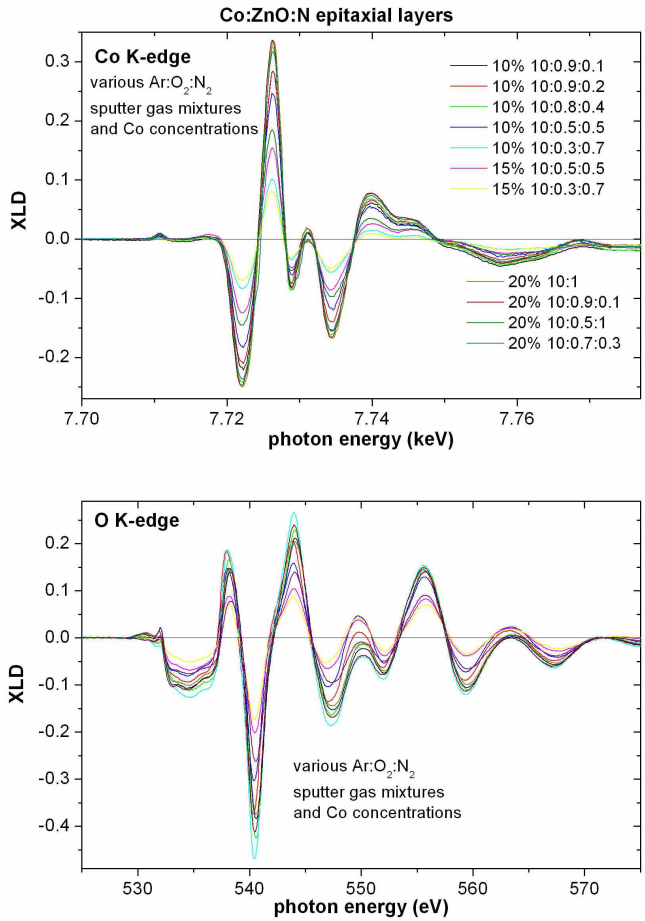

Fig. 3: XLDs of Co:ZnO:N films at the Co and O K-edges.

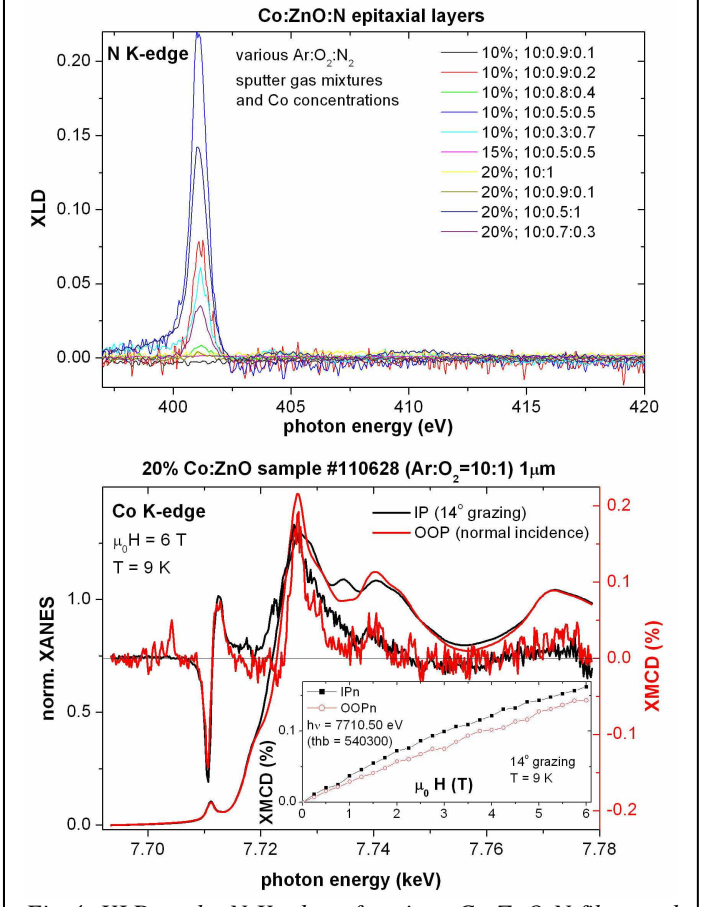

Fig 4: XLD at the N K-edge of various Co:ZnO:N films and XMCD & M(H) in plane and out of plane at the Co K-edge.