



**Experiment title:** Structural characterization of piezoelectric distortions and its interplay with magnetism in functional doped oxides

**Experiment number:**  
HE-3781

<b>Beamline:</b> ID 12	<b>Date of experiment:</b> from: 10.07.2012 to: 17.07.2012	<b>Date of report:</b> 13.02.2013
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## Report:

The aim of this experiment was to study the local structural and magnetic properties of Co-doped ZnO epitaxial films on sapphire substrates. The XLD as well as the XMCD should have been recorded in an applied electric field. During the beamtime two different Co:ZnO samples which were furnished with Au top electrodes were measured: a ~2 micron thick 5% Co:ZnO sample as well as a ~1 micron thick 20% Co:ZnO sample. First the usual XLD spectra were recorded at the Zn and the Co K-edges, respectively. Due to the self-absorption and the Au top electrode the absolute size of the XLD could not be analyzed on an absolute scale, however, the spectral shape of XANES and XLD together with the pre-characterization using SQUID (which revealed paramagnetism of both samples) indicate that the Co predominantly substitutes for Zn in both samples. In addition thinner films of both types of samples grown under identical conditions could be quantitatively analyzed using XLD revealing that indeed Co substitutes for Zn. In the following we will thus assume, that Co is exclusively located on Zn lattice sites in both samples. Two different types of XANES and XLD measurements were carried out in applied electrical field: (i) using linear polarized light and switching the external E-field on/off and (ii) using the quarter-wave plate to flip the linear polarization at each photon energy to record XLD either with or without E-field. It turned out that the effects of the E-field were so small that recording full XLD spectra with and without E-field leads to small signals on top of large backgrounds. Therefore most of the experiments were recorded using method (i). In contrast to what was expected, no significant changes of the XLD spectra stemming from the E-field could be demonstrated. However, it turned out that taking the difference between the XANES recorded with and without E-field results in a derivative-like signal. Therefore, the effect of the E-field is a rigid band-shift due to electrostriction.

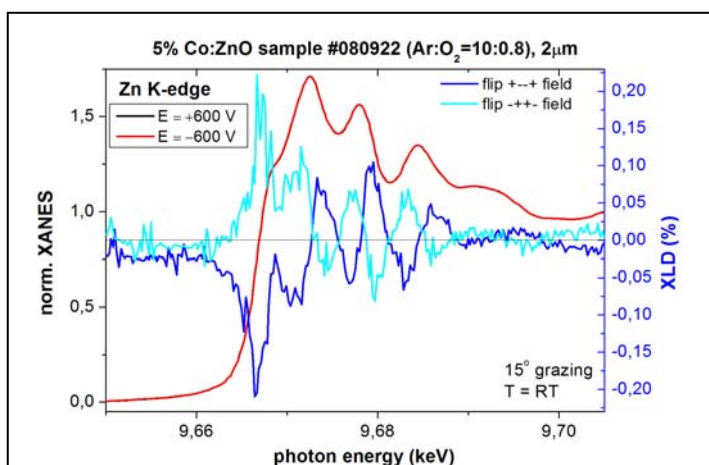


Figure 1: XANES at the Zn K-edge for 5% Co:ZnO recorded with linear horizontal light while flipping the E-field from 600V to -600V and back at each energy point.

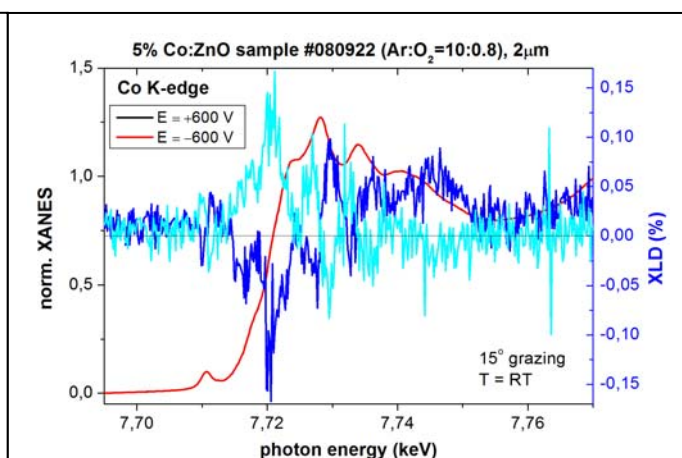


Figure 2: XANES at the Co K-edge for 5% Co:ZnO recorded with linear horizontal light while flipping the E-field from 600V to -600V and back at each energy point.

Figure 1 and 2 show the Zn and Co K-edges of the 5% Co:ZnO sample, respectively. The spectra were recorded with linear polarized light with the polarization being parallel to the c-axis of the wurtzite ZnO and thus being parallel to the direction of the applied external E-field. At each photon energy the E-field was flipped from +600V to -600V and back and the corresponding XANES are recorded separately (shown in black and red). The difference between the two XANES is of the order of less than 0.2%. Upon reversing the field sequence to -600V to +600V and back the sign of the difference spectrum reverses as well thus demonstrating that temporal drifts in the beamline cannot be responsible for the observed behavior. In addition, it can be seen that Zn and Co behave qualitatively the same consistent with the fact that Co substitutes for Zn. For a more in-depth analysis, the 20% Co:ZnO sample is studied in more detail. Like for the 5% Co sample, the influence of the E-field on the XANES is a rigid energy shift of the entire spectrum, no matter if measured at the Zn (Fig. 3) or at the Co (Fig. 4) K-edge. To estimate the stability of the experimental setup, an identical difference is recorded without applying any E-field and the resulting difference is shown in Figs. 3 and 4 in cyan for the Zn and Co K-edge, respectively. One can see that temporal or energy instabilities are much smaller than the actual difference signal induced by the E-field. Note, that also the reversal of the difference signal as shown in Figs. 1 and 2 was studied (not shown). In addition the difference is also recorded for different magnitudes of the E-field and all signatures decrease with decreasing E-field (not shown). To summarize the E-field dependence, the photon energy was fixed to the maximum difference signal and the size of the difference signal was measured as a function of decreasing and increasing electrical field sequences (not shown). The optimum sequence is to start at 0 V increasing to maximum field in one direction, e.g. to +600V and then decreasing all the way to -600V and back, i.e. record a full “hysteresis” including “virgin curve”. The resulting E-field dependence of the difference signal for Zn and the Co is shown in the respective insets of Figs. 3 and 4 and is found to be linear in both cases. This linear behavior points towards an electrostrictive behavior. Finally, a quantitative estimate of the observed difference signal shall be made. For that two measured XANES spectra recorded at -600V and +600V are manually shifted along the energy axis and the resulting difference is analyzed as a function of shift. While the XANES are recorded in steps of ThB (angle of the crystal of the monochromator) of 12, the spectra were interpolated to steps of ThB=1 and then shifted in steps of 0.02 in ThB. The resulting difference signal has still the same shape as the experimental ones in the Figs. but with altered amplitude. By that the smallest possible difference was taken resulting in a nominal E-shift. For the Zn K-edge a rigid band shift of about 3 meV was found while for Co only 2 meV were deduced. This implies that the electrostrictive effect is locally smaller for the Co ions compared to the Zn ions which was an unexpected result which needs further investigations. The small size of the observed shift shall be stressed.

In summary, the electrostrictive effect of an external E-field on the piezoelectric wurtzite compound Co:ZnO has been studied. It has been found that the E-field induces a rigid band shift both at the Zn as well as at the Co K-edges. No changes in the XLD which would result from an altered local symmetry could be detected. The size of the band shift depends linearly on E-field at both edges. The size of the actual energy shift is found to be of the order of a few meV at photon energies of about 10 keV. The possibility to reliably measure such tiny energy shifts (of the order of  $10^{-7}$  !!!) highlights the extreme stability of beamline ID12 and offers new perspective to study electrostrictive effects in multicomponent sample with element specificity.

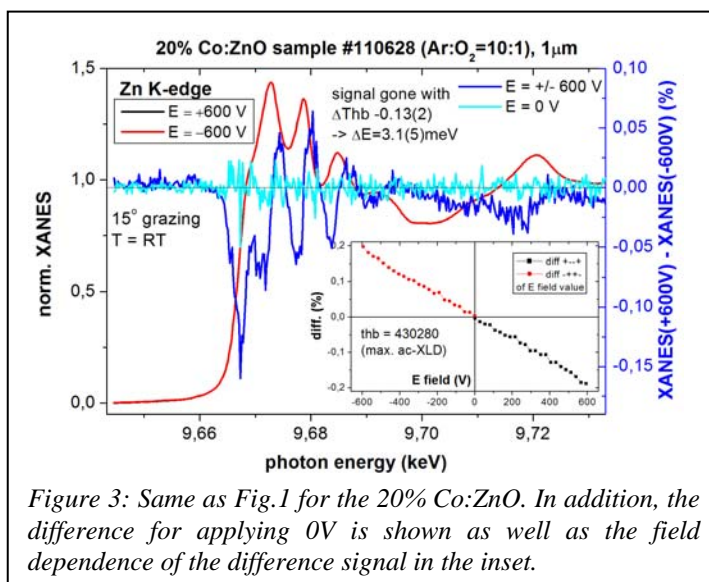


Figure 3: Same as Fig.1 for the 20% Co:ZnO. In addition, the difference for applying 0V is shown as well as the field dependence of the difference signal in the inset.

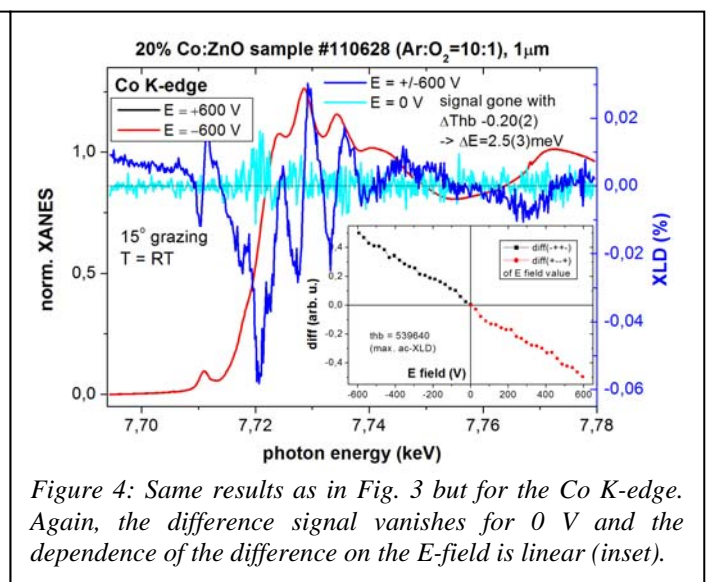


Figure 4: Same results as in Fig. 3 but for the Co K-edge. Again, the difference signal vanishes for 0 V and the dependence of the difference on the E-field is linear (inset).