

Report on the experiment HS-2718: Fe-doped lithium niobate crystals: depth-dependence of the Fe²⁺/Fe³⁺ ratio by reflEXAFS measurements.

The EXAFS-reflEXAFS experiment was performed at the Fe K-edge ($E=7112$ eV) at the Italian beamline GILDA of the European Synchrotron Radiation Facility. The monochromator was equipped with a couple of 311 Si crystals and it worked in dynamical focusing mode; the harmonic rejection was achieved by a couple of Pd-coated mirrors, working at an incidence angle of 3 mrad. Due to low Fe concentration, the x-ray absorption spectra from the samples were measured in fluorescence mode with a 13-element high-purity Ge detector; the EXAFS spectra of metallic Fe, Fe₂O₃ and hercynite (Fe²⁺-containing only) crystalline powders were also recorded as a standard references.

The experiment was divided into 4 different parts:

- The EXAFS spectra of some standard compounds were recorded either in transmission mode (Fe foil, Fe₂O₃ crystalline powder) or in fluorescence mode (hercynite).
- The EXAFS spectra of the samples were recorded in fluorescence mode; the incidence angle was about 45 deg, so that the probed depth was about 40 μm . The samples were mounted onto a vibrating sample holder, to reduce the effect of possible x-ray standing waves from the LiNbO₃ crystal.
- The EXAFS spectra of the samples were recorded in fluorescence mode; the incidence geometry was properly chosen to have a large component (about 80-90%) of the x-ray beam polarization parallel or perpendicular to the c-axis of the crystal. In this case, due to standing wave effects, only the XANES part of the absorption spectrum was recorded for most of the samples.
- The EXAFS spectra of the samples were recorded in fluorescence mode in the reflEXAFS chamber; the incidence angle α was slightly higher than the critical one ($\alpha=\alpha_c+0.06$ deg, with $\alpha_c\sim 0.35$ deg), to probe a thickness of ~ 200 nm of the Fe-doped layer; for the z-cut samples the c-axis was then almost perpendicular to the polarization vector, while for the x-cut samples, the absorption spectra were recorded using two configuration (c-axis parallel or perpendicular to the polarization vector). The absorption spectrum of a Fe-layer deposited on kapton was measured at the same time, in order to have an absolute energy calibration. This last measure did not affect the reflEXAFS one. Due to standing wave effects, for most of the samples only the XANES part of the absorption spectrum was successfully recorded.

The analysis of the EXAFS spectra was performed by the FEFF8-FEFFT 2.98 package [20, 21]: the Fe-O and Fe-Nb backscattering phase and amplitude were calculated from a LiNbO₃ cluster with one Fe atom replacing either Li or Nb site; the calculation was also extended for different interatomic distances of the Fe-O couple, from 2.00 Å to 2.60 Å. The EXAFS analysis was based onto a multiparameter single scattering fit into the R-space of the first Fe-O coordination for the spectra of x800 and z800 samples, of the first two Fe-O coordinations and the Fe-Nb coordination for the spectra of x1000 and z1000 samples; the S_0^2 parameter of the standard EXAFS formula was set to the value obtained by fitting the Fe foil spectrum.

In the first figure the EXAFS signals of the samples, recorded with a 45 deg geometry, are shown; correspondingly, in the second figure the Fourier transform moduli are reported. A first peak, corresponding to a Fe-O coordination, is evident for all the spectra; on the other hand, only for the samples heated at 1000 C is evident a second correlation peak, located at about 3 Å. The results of the samples heated at 800 C indicate that the local order around Fe atoms is similar in the two cases: Fe atoms are surrounded by about 4 O atoms at a distance of 2.00 ± 0.01 Å, the Debye-Waller factor is about 45×10^{-4} Å². As far as the samples heated at 1000 C are concerned, the EXAFS signal that in the Fourier transform modulus corresponds to the range $R=1.3-3.4$ Å can be reproduced with two shell of O atoms and one shell of Nb atoms. For the x-cut sample the Fe-O distances are 2.00 ± 0.02 Å and 2.63 ± 0.04 and the Fe-Nb one is 3.14 ± 0.02 Å; the corresponding values for the z-cut samples are 2.00 ± 0.02 Å, 2.68 ± 0.04 Å and 3.11 ± 0.02 Å, respectively. As a comparison, the first three shells of atoms around Li in the LiNbO₃ crystal are composed of 3 O atoms at a distance of 1.92 Å, 6 O atoms at 2.77 Å and 6 Nb atoms at 3.17. This result shows that the Fe site is very similar to the Li one in the crystal even if some differences in the interatomic distances are evident. The coordination numbers of the three analyzed shells are strongly affected by the orientation of the crystal with respect to the x-ray polarization vector, so that in this case they cannot be directly compared to the corresponding values of the Li site.

The preliminary XANES analysis evidenced that the pre-edge peak, evident in all the spectra of the Fe-doped LiNbO₃ samples, is located in the region 7113.0-7114.4 eV; for comparison, the corresponding peak in Fe₂O₃ (Fe³⁺) and hercynite spectra (Fe²⁺) are located at 7113.4 eV 7112 eV, respectively. This observation suggests that Fe ions into the LiNbO₃ crystal are mostly in the oxidation state 3+; work is in progress to further test these preliminary results, and to investigate if different Fe oxidation states are present near the sample surface.

