X-ray Absorption Spectroscopy on crystalline and nano-scale Iron borides

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X-ray absorption measurements for the Fe-K-edge were carried out for several nano-scale samples as well as for reference compounds. Nanoparticles were obtained by reduction of apropriate iron compounds with coordinating solvents present and at low and moderate temperatures [1]. In contrary, reference iron compounds (e.g. FeB, Fe_2B and $FeBO_3$) were synthesized via the high temperature route (ceramic method) [1]. The nano-particles are X-ray amorphous and therefore a combination of different methods e.g. XAS,TEM, EELS and XPS was applied for characterizing them.
Sample preparation for XAS involves preparing 13 mm thin pellets of a mixture of the sample (amount calculated with program XAFS mass) and polyethylen as binding agent. Reduction and analysis of the XAS data was performed using the programs WinXAS [2], ATOMS [3] and FEFF7 [4] and by a standard procedure described in [5].

The position of K-edges depends amongst others on the oxidation state of the absorbing atoms. In Fig. 1a, experimental near edge spectra are displayed that were background corrected and normalised. They show as an example several stabilized Fe-B-particles and crystalline Fe_3BO_6 as reference. Since measurements were done several days after synthesis, it was observed that the samples did not consist anymore from iron borides but contained iron as Fe^{3+} in form of borates like $FeBO_3$ or Fe_3BO_6. Directly after synthesis the oxidation state had been investigated with X-ray photoelectron spectroscopy revealing an oxidation state like in Fe_2B, thus confirming the expected result.

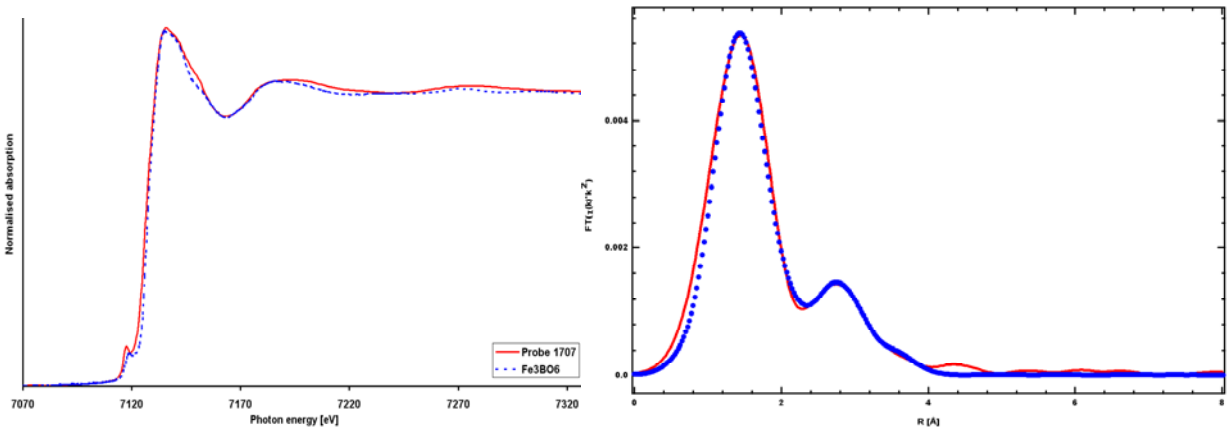

Figure 1: (a) X-ray Absorption Near Edge Fine Structure (XANES) of a nanoscale sample (system Fe-B) more than three days after synthesis, (b) EXAFS fit (blue dashed line) for same sample (more than three days after synthesis) [1].

The parameters of the local structure were fitted from EXAFS spectra using Fe_3BO_6 parameters as a first approximation. The EXAFS fit is shown in Fig. 1b and parameters of the local structure for the first 10 coordination shells are listed in table1.

Table 1: Results of EXAFS fit for sample in Fig. 1.

N	Bond	CN	R [Angström]	σ^2 [Angström]^2	ΔE_0 [eV]
1	Fe-O	1.12	1.86	0.004	2.736
2	Fe-O	0.81	1.89	0.003	2.736
3	Fe-O	1.10	1.93	0.007	0.800
4	Fe-O	1.44	2.02	0.007	0.800
5	Fe-O	3.68	2.08	0.023	-7.000
6	Fe-B	1.56	2.58	0.001	5.948
7	Fe-Fe	1.40	2.74	0.010	-5.308
8	Fe-B	1.38	3.04	0.002	0.802
9	Fe-B	2.33	3.05	0.002	0.802
10	Fe-Fe	6.00	3.08	0.034	2.354

In conclusion, samples from synthesis in coordinating solvents mentioned above are slowly oxidized in air, producing amorphous iron borates with a local structure very close to Fe_3BO_6. A layer of stabilizing ligands protects the sample against immediate oxidation but oxidation takes place within a few days. Currently, additional reference materials are synthesized and characterized in many ways. XAS is being performed, too, in order to test the suitability of them for reference samples for our iron boride nanoparticles. Fig. 2 shows as an example the background-subtracted and normalised absorption for a lot of FeB samples. They were produced either by arc melting or in high frequency furnace and they look very similar.

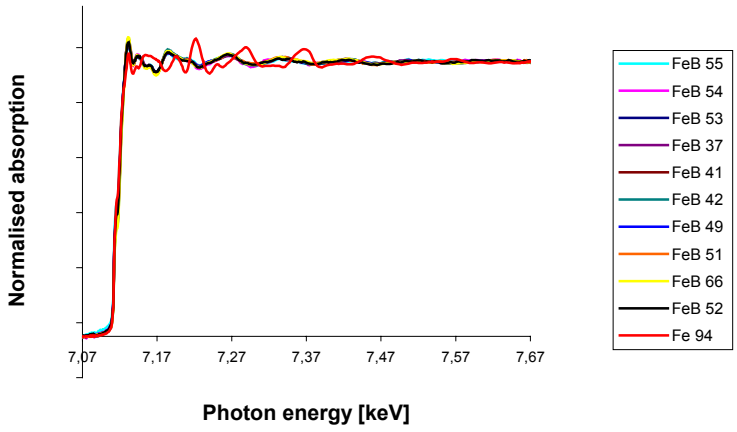

Figure 2: Normalised Absorption of Fe-B samples.

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References

[1] D. Fofanov, PhD thesis, University of Hamburg, 2006
[2] T. Ressler, S.L. Brock, J. Phys. Chem. B, 103, 6407 (1999)
[3] B. Ravel, ATOMS 2.46b, Univ. of Washington (1994)
[4] B. Ravel, FEFF 7.02, Univ. of Washington (1994)
[5] B. Lengeler, P. Eisenberg, Phys. Rev. B 21, 4507 (1980)