



	Experiment title: XAS study at Fe and Zn K edges of ternary and quaternary kesterite-like sulfides for photovoltaic applications	Experiment number: MA-1783
Beamline: BM25a	Date of experiment: from: 30/04/2013 to: 06/05/2013	Date of report: 30/12/2013
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Report:

Aim of the experiment

Investigation of the local symmetry and valence state of Fe and Zn metal ions in kesterite-like ternary and quaternary chalcogenides, $\text{Cu}_2(\text{Zn}, \text{Fe}, \text{Cu})\text{SnS}_4$, for use in solar cells. The study is also aimed to fully define the crystal chemistry of the transition metal ions in these innovative materials for the p layer of thin film solar cells.

Experimental procedures

Samples have been investigated by means of X-ray Absorption Spectroscopy (XAS) at the Fe and Zn K edges. Particular care was taken in obtaining high quality data in the pre-edge, XANES and EXAFS regions, due to their complementary information (i.e. valence states and structural features). XAS investigations were run in air, at room temperature, by using a multiple sample holder, both in the Transmission and Fluorescence mode. To this last mode, a multi-element solid state detector was used.

Samples considered for the XAS investigations included nanocrystalline powders and polycrystalline reference compounds. The list of the analysed samples is shown in Table 1. Owing to the configuration of the beamline (in open air) and of the low energies of the elements considered (Fe and Zn K edges) we opted for not analysing thin film devices, which were analysed in an another beamtime, specifically assigned for these very diluted and thin samples (08-01-939, performed at BM08).

Table 1 – list of the investigated samples

Sample label	edge	structure	details	Sample label	edge	structure	details
637	Fe	bornite	synthetic	Dst	Fe	stannite	synthetic
636	Fe	bornite	natural	Td	Fe	tetraedrite	natural
Bn	Fe	bornite	natural	kesold	Zn	kesterite	synthetic
BnMn	Fe	bornite	synthetic	dkes	Zn	kesterite	synthetic
cpy	Fe	calcopyrite	natural	N2	Zn	kesterite	synthetic, nano
N9	Fe	pirite	synthetic, nano	N3	Zn	kesterite	synthetic, nano
py	Fe	pirite	natural	22551	Zn	sfalerite	natural
po	Fe	pirrotina	natural	dos18	Zn	sfalerite	synthetic
22551	Fe	sfalerite	natural	St1499/51	Zn	stannite	natural
dos18	Fe	sfalerite	synthetic	St1499/51 F	Zn	stannite	natural
St1499/51	Fe	stannite	natural	st1495	Zn	stannite	natural
st1495	Fe	stannite	natural	23 F	Zn	stannite	synthetic
stsyn	Fe	stannite	synthetic	N11	Zn	wurtzite	synthetic, nano
23	Fe	stannite	synthetic	dos37	Zn	wurtzite	synthetic
N1	Fe	stannite	synthetic, nano	Td	Zn	tetraedrite	natural
bomba	Fe	stannite	synthetic, nano				

Preliminary results

Nanoparticles obtained by solvothermal methods (i.e. at low temperatures and with short duration of the synthetic runs) are confirmed to crystallise in the kuramite structural model and to uptake a significant, but not abundant, amount of Fe or Zn. Preliminary XANES spectra of Fe-bearing and Zn-bearing kuramite samples are shown in the Figures 1 and 2, respectively.

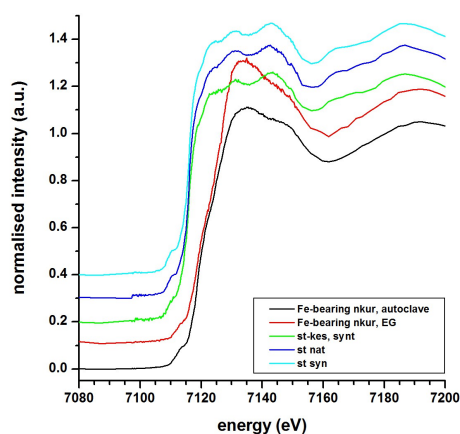


Figure 1 – Fe K- edge XANES spectra of Fe-bearing nanokuramite samples, compared to some natural and synthetic reference compounds

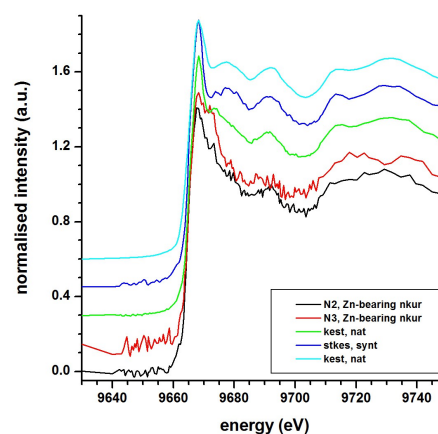


Figure 2 – Zn K- edge XANES spectra of Zn-bearing nanokuramite samples, compared to some natural and synthetic reference compounds

The comparison of the Fe- and Zn-bearing nanokuramite samples with the relevant standards (stannite and kesterite) leads to a preliminary conclusion. It is apparent, in fact, that the fate of Fe and of Zn during the uptake by nanokuramite is different: the former tends to clusterise in limited volumes of the structure, whereas Zn replaces Cu in its site in the structure. No clustering of Zn ions has been observed in samples arising from different syntheses.

Preliminary results

With reference to the aims declared in the proposal, we are able to formulate the following considerations.

1) the occurrence of trivalent Fe in quaternary sulfides

Fe(III) can conceivably coexist in some terms of the quaternary sulfides.

2) the occurrence of random, short-range and long-range ordered distribution in tetrahedral sites

Fe tends to clusterise, whereas Zn attains an ordered replacement in the kuramite structure