ESRF	**Experiment title:** Antisite population and phase relationships in kesterite related materials	**Experiment number**: 08-01-1033
Beamline: BM08	**Date of experiment**: from: April 26th, 2017 to: May, 2nd, 2017	**Date of report**: 10/09/2017
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Report:

Introduction

The focus of this proposal was targeted on the identification of the concentration of antisite defects in phases belonging to the stannite-kesterite-kuramite pseudoternary field, a task which represents a specific crystal chemical topic related to the application of the "kesterites" as materials for the solar energy conversion in the field of the renewables. From a spectroscopic point of view, we were aimed at registering high quality X-ray Absorption Spectroscopy (XAS) spectra at the different K edges of the metal ions involved in the crystal chemistry of the pseudoternary field, i.e. Fe, Cu and Zn

Materials

The samples analysed during the experiments were belonging to the following groups:

- 3 natural stannite, i.e. Fe-rich $Cu_2(Fe,Zn)SnS_4$, and kesterite, i.e. Zn-rich $Cu_2(Fe,Zn)SnS_4$ specimens
- 12 microcrystalline synthetic terms belonging to the stannite kesterite join, including the end-members
- 2 nanocrystalline kuramite and kesterite

Of course, taking into account the relatively high absorbance of each sample, and the relative amount of each element (Cu, Fe, Zn) contained in it, the samples were analysed only at the edges where the Transmission mode was easily achievable. This posed a limit, experimentally determined during the experiment, of ~ 0.2 atoms per formula unit of the considered element.

Experimental set up

The experiment was scheduled half way the refurbishment of the LISA BM08 beamline, i.e. immediately after having commissioned the new monochromator, but before having mounted the new set of mirrors. For the

experimental work plan, this represented only a minor problem, as all materials were analysed in the Transmittance mode, prepared as half inch pellets, and the defocused beam (approximately 8 x 1 mm^2 in size) well averaging eventual inhomogeneities in the mineral distribution within the pellet. All measurements were carried out in vacuum, at 80 K. For all samples, repeated measurements were acquired.

Preliminary results

Exemplar spectra, together with the preliminary best fit are shown in the Figure, here below:

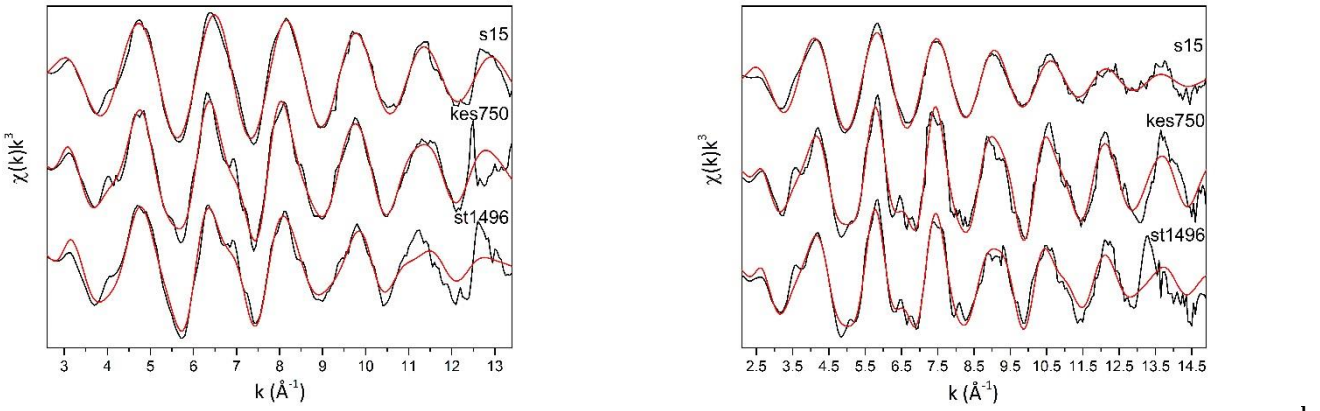

Figure 1 – $k^3\chi$ versus k patterns, in black, of three selected samples (one nanocrystalline, S15; one microcrystalline, kes750; one natural, st1496) together with the best fit simulations, in red. The a) and b) graphs refer to the Cu and Zn K edges, respectively.

The graphs in Figure 1 apparently point out the good signal-to-noise ratio obtained in most of the spectra, which allows a very reliable modelling, with particular reference to the first shell bond distances and Debye-Waller parameters.

As an example, fit results for the three samples in Figure 1 are reported in the following table.

	Cu	Amp	Shell	R(Å)	σ^2(Å^{-2})	D.T. (K)	Zn	Amp	Shell	R(Å)	σ^2(Å^{-2})	D.T. (K)
kes750		0.71(5)	**4 S**	2.311(5)	0.005(1)	-		0.79(8)	**4 S**	2.339(5)	0.003(1)	-
			8 (Cu,Zn)	3.883(8)	-	143(9)			**8 (Cu,Zn)**	3.847(8)	-	155(13)
			4 Sn	3.883(8)	-	//			**4 Sn**	3.847(8)	-	//
			4 S	4.50(1)	-	189(18)			**4 S**	4.46(1)	-	245(37)
			8 S	4.58(1)	-	//			**8 S**	4.54(1)	-	//
st1496		0.84(9)	**4 S**	2.311(2)	0.009(1)	-		0.89(9)	**4 S**	2.340(7)	0.005(1)	-
			8 (Cu,Zn)	3.881(4)	-	137(10)			**8 (Cu,Zn)**	3.85(1)	-	210(28)
			4 Sn	3.883(4)	-	//			**4 Sn**	3.85(1)	-	//
			4 S	4.502(5)	-	161(17)			**4 S**	4.47(1)	-	156(12)
			8 S	4.582(5)	-	//			**8 S**	4.55(1)	-	//
s15		0.75(5)	**4 S**	2.300(5)	0.006(1)	-		0.92	**4 S**	2.339(5)	0.007(1)	-

Notes: D.T.=Debye Temperature

Data were fitted through the ARTEMIS software in the Fourier-Transform (FT) space. No clear II shell signal is observable in sample s15.