ESRF	**Experiment title:** A simultaneous multiedge fit to probe antisite population in kesterites: contribution of the Sn edge	**Experiment number**: MA4274
Beamline: BM08	**Date of experiment**: from: July 27th, 2018 to: July, 30th, 2018	**Date of report**: 09/09/2020
Shifts: 9	**Local contact(s)**: Giovanni Orazio Lepore	*Received at ESRF:*

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Report:

Introduction

The main focus of this project is 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 Sn K edge. Obtained data will be then integrated with the Cu/Zn K edge data-set measured during exp. 08011033 and with the S K edge data obtained at PHOENIX beamline (SLS-PSI).

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

Cu, Fe and Zn K edges had already been analysed in experiment 08-01-1033. Sn K edge measurements were performed on the same pellets in fluorescence mode.

Experimental set up

The experiment fully benefited from the refurbishment of BM08 "LISA". Measurements were performed using the new monochromator and focusing mirrors. 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:

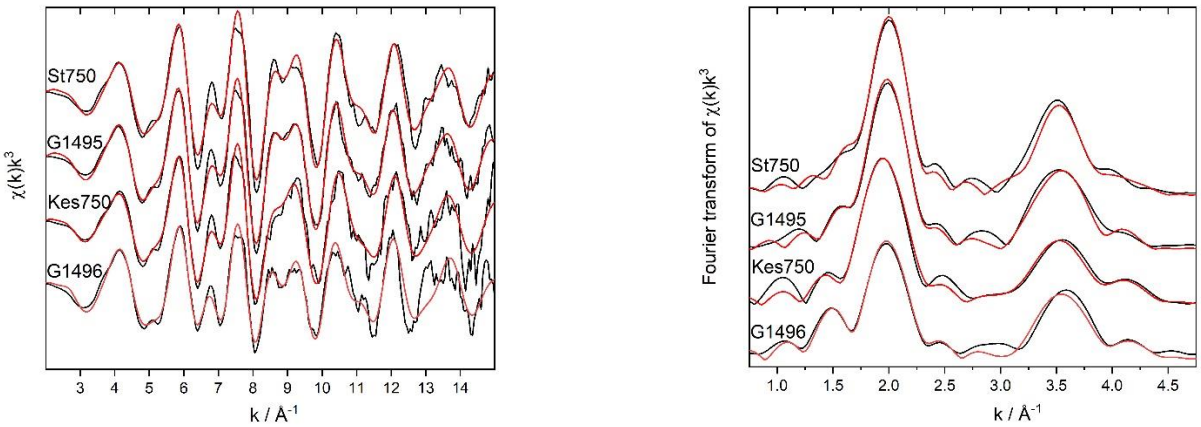

Figure 1 – $k^3\chi$ versus k (left) and its Fourier transform (right) patterns and relative EXAFS fits of four selected samples (G1496=natural kesterite, G1495= natural stannite, Kes750= synthetic kesterite, St750= synthetic stannite).

The graphs in Figure 1 point out the good signal-to-noise ratio obtained in most of the spectra, which allows a reliable modelling, with particular reference to the first shell bond distances and Debye- Waller parameters. As an example, fit results for the four samples in Figure 1 are reported in the following table.

	Amp	Shell	R(Å)	σ^2(Å^2)		Amp	Shell	R(Å)	σ^2(Å^2)
G1496	1.1(1)	**4 S**	2.412(4)	0.0034(7)	**Kes750**	1.0(1)	**4 S**	2.407(4)	0.0028(5)
		12 (Cu,Zn)	3.86(1)	0.008*			**12 (Cu,Zn)**	3.84(1)	0.01*
		4 S	4.48(1)	0.009*			**4 S**	4.45(1)	0.009*
		8 S	4.52(1)	0.009*			**8 S**	4.49(1)	0.009*
G1495	1.1(1)	**4 S**	2.419(2)	0.0031(3)	**St750**	1.1(1)	**4 S**	2.415(4)	0.0030(4)
		12 (Cu,Zn)	3.86(1)	0.009*			**12 (Cu,Zn)**	3.85(1)	0.009*
		4 S	4.47(1)	0.013*			**4 S**	4.46(1)	0.013*
		8 S	4.51(1)	0.013*			**8 S**	4.51(1)	0.013*

Notes: *estimated using the correlated Debye model (Sevillano, et al., *Phys. Rev. B* **20**, 4908, 1979). Data were fitted through the ARTEMIS software in the Fourier-Transform (FT) space.

Measurements were time efficient and all samples spectra were aquired in the assigned shifts. Data quality was good, with spectra showing low noise up to k= 13 Å^{-1}. Some of the samples show sign of minimal oxidation. No signs of beam damage were observed during repeated XANES scans on the same sample, therefore the oxidation should be attributed to the presence of a minimal amount of host phases (in the case of natural samples) and/or to the a chemical degradation of the samples with time.

Fits according to the kesterite/stannite model are extremely satisfying since, in the same data-set, differences in the order of the third decimal digit can be appreciated on first shell distances and Debye-Waller factors.

The obtained data-set will be compared and joined with data obtained during exp. 08-01-1033 and during an experiment in PHOENIX beamline (PSI) which dealt with the measurement of the S K edge with the double aim of improving the reliability of the structural analysis and investigating the distribution of Cu and Zn (other than Sn) around S atoms.