ESRF

Experiment title:
XAS study of kesterite-like quaternary chalcogenide nanopowders and thin films

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Report:

Aim of the experiment

Investigation of the local symmetry and valence state of Cu, Fe and Zn metal ions in kesterite-like ternary and quaternary chalcogenides, $Cu_2(Zn,Fe,Cu)SnS_4$, 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 Cu, 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 synthetic nanocrystalline powders, polycrystalline reference compounds, and, namely, thin films. Owing to the

Table 1 – list of the investigated samples

Sample label	edge	details	Sample label	edge	details
Cu_xS_y	Cu	Thin film	14968	Fe, Cu, Zn	natural
$Cu_xZn_yS_z$ (1:1)	Cu, Zn	Thin film	Ant	Fe	Synthetic, nano
$Cu_xZn_yS_z$ (1:5)	Cu, Zn	Thin film	St1499/51	Fe, Zn	natural
$Cu_xZn_yS_z$ (1:9)	Cu, Zn	Thin film	st1495	Fe, Zn	natural
Zn_xS_y	Zn	Thin film	enf4	Fe, Zn	natural
904	Fe, Cu, Zn	natural	enperu	Fe, Zn	natural
958	Fe, Cu, Zn	natural	15859	Fe, Zn	natural
961	Fe, Cu, Zn	natural	985	Zn	natural
971	Fe, Cu, Zn	natural			

fact that nanocrystalline and polycrystalline materials were analysed in a dedicated experiment (MA1783), we focussed our characterisation on thin films, which were analysed in grazing incidence. The list of the analysed samples is shown in Table 1.

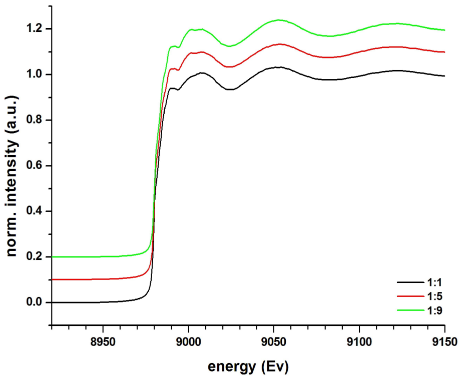

Figure 1 – Cu K- edge XANES spectra of $Cu_xZn_yS_z$ thin film samples

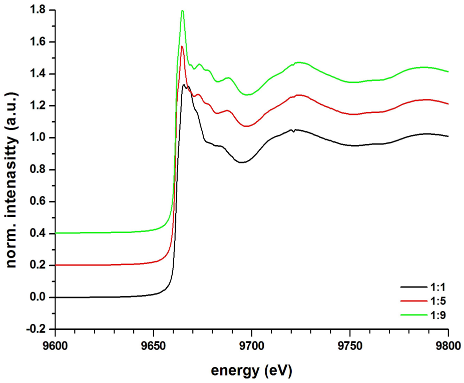

Figure 2 – Zn K- edge XANES spectra $Cu_xZn_yS_z$ thin film samples

Preliminary results

The XAS spectra, shown in the Figures 1 and 2, confirm that the adopted experimental procedure is able to obtain relevant information on the thin films, which have a thickness <50 nm. Spectra, in fact, are of good quality and EXAFS information can be studied up to 12 $Å^{-1}$ in the k space.

A preliminary survey of the Cu K-edge spectra reveals an homogeneous structural environment of Cu in the films. Cu in the three samples is characterised by a poorly symmetric environment, as in an "amorphous state". Conversely, the survey of the Zn K-edge spectra reveals an highly ordered structural environment for the three samples, and a marked difference between the 1:1 films and the other two films. This difference, at a first insight, can be attributed to a partial oxidation of the film.

These contrasting results are planned to be interpreted on the light of the complex film morphology revealed by the SEM investigations (also performed at the ESRF facility), shown in Figure 3a. The apparent presence of nanowhiskers on the film surface is, in fact, proven by SEM investigation. The nanowhiskers are not present in all the samples. According to the scheme of Figure 3b, we want to sort out the physical reason, depending on the film composition and structure, which drive the deposit from the element-by-element architecture induced by the ECALE synthesis towards the structured sulphide film (consisting of an epitaxial body with nanowhiskers on top).

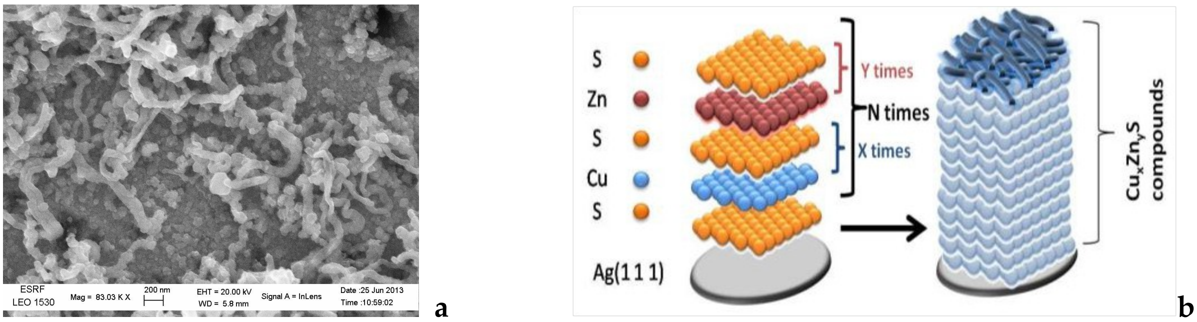

Figure 3 – a) SEM micrograph of the 1:1 sample, evidencing the presence of nanowhiskers on the film surface; b) schematic representation of the procedure followed in realising the film through the ECALE procedure.