ESRF	**Experiment title:** Cation ordering in $AgBiS_2$ nanoparticles, a new material for high efficiency thin film solar cells	**Experiment number**: HC3035
Beamline: BM 08	**Date of experiment**: from: 15/6/2017 to 20/6/2017	**Date of report**: 25/2/2020
Shifts: 15	**Local contact(s)**: F. d'Acapito	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Alexandros Stavrinadis, ICFO, Barcelona, Spain

Francesco d'Acapito, CNR-OGG, c/o ESRF

Federico Boscherini, Universityof Bologna

Gerasimos Konstantatos, ICFO, Barcelona, Spain

Report:

The original focus of this experiment was to probe the cation ordering in a set of specially deposited $Ag_xBi_{1-x}S_2$ samples. The EXAFS measurements were successful, high quality data were obtained. Despite the apparently simple EXAFS signal (Fig. 1) the analysis posed considerable problems and an intriguing issue arose. Briefly, the EXAFS measurements indicated a local structure similar to a monoclinic phase while XRD patterns indicated a hexagonal crystallographic structure. This apparent contradiction was solved by using a combination of DFT and MD simulations.

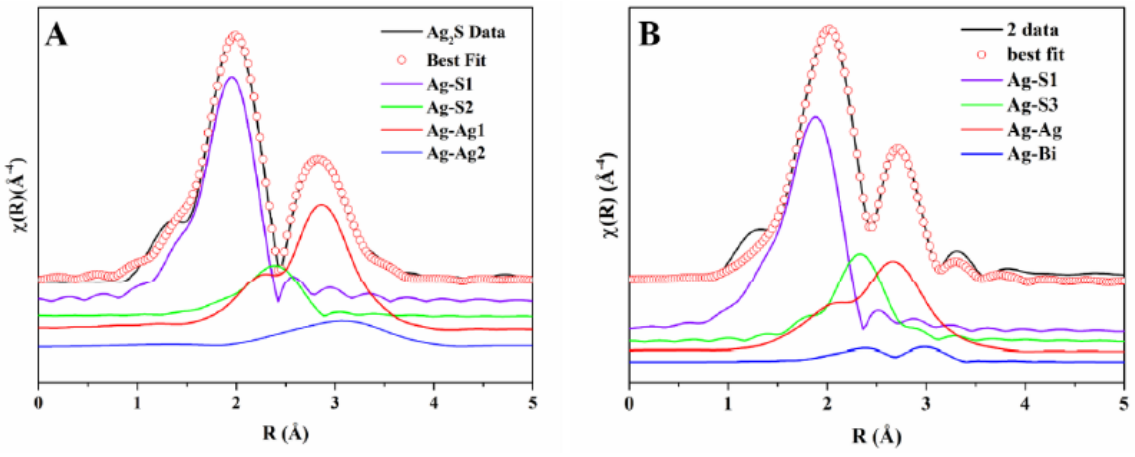

Fig. 1: FTs of Ag K-edge spectra with components used in the fitting for Ag_2S (A) and sample 2 (B).

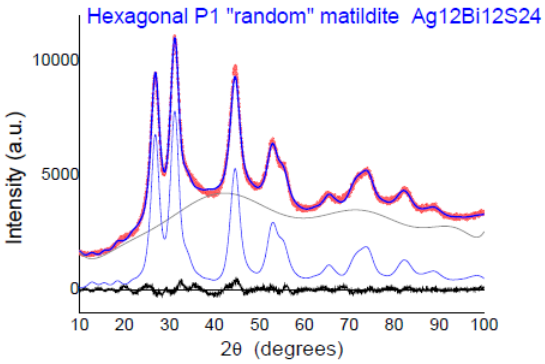

Fig. 2: Comparison between the experimental XRD pattern of a sample (red points) and the simulation based on atomic coordinates obtained from the density functional theory (DFT)–MD simulations (blue line), including an amorphous-like background.

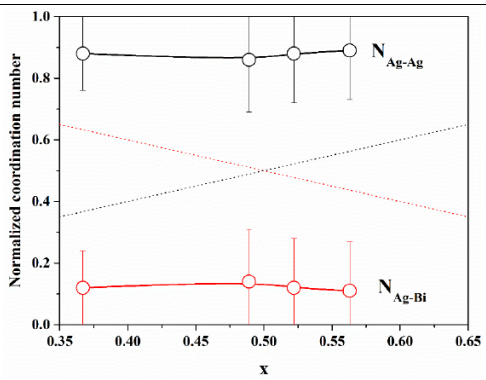

Fig. 3: No rmalized coordination numbers in the cation coordination shell as a function of Ag concentration. The dashed lines correspond to a random distribution of cations.

DFT–MD simulations showed that a random distribution of Ag and Bi in the cation sites of the hexagonal matildite structure gives rise to "short" Ag–S bonds detected experimentally by EXAFS; at the same time, the lattice remains hexagonal, providing a good comparison to the XRD patterns (Fig. 2). The EXAFS analysis indicated that the distribution of cations around Ag is not actually random, but a preference for Ag–Ag correlations is present (Fig. 3). However, more than 10% Bi is always found in the local cation environment of Ag, enough to induce strong local distortions in the Ag–S, producing short bond lengths that are not present in the bulk matildite structure. It is possible that these local distortions are related to electronic defects that affect the photovoltaic properties, a subject worthy of further investigation. Finally, these results illustrate the power of combined experimental–simulation studies of complex structures found in nanostructured materials.

These results have been published in the paper J. Kopula Kesavan, F. d'Acapito, P. Scardi, A. Stavrinadis, M. Z. Akgul, I. Burgues, G. Konstantados and F. Boscherini,, Nanomaterials 2020, 10, 316; doi:10.3390/nano10020316

nanomaterials

MDPI

Article

Cation Disorder and Local Structural Distortions in $Ag_xBi_{1-x}S_2$ Nanoparticles

Jagadesh Kopula Kesavan [1], Francesco d'Acapito [2], Paolo Scardi [3], Alexandros Stavrinadis [4], Mehmet Zafer Akgul [4], Ignasi Burgués-Ceballos [4], Gerasimos Konstantatos [4,5] and Federico Boscherini [1,2,*]