



Experiment title:

Origin of the luminescence emissions in Zn₂GeO₄/SnO₂ Nanowire Heterostructures

Experiment number:

MA-4877

Beamline:

ID16B

Date of experiment:

from: 24/09/2021 to: 28/09/2021

Date of report:

Received at ESRF:

Shifts:

15

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Report:

Here, we report a correlative hard X-ray study of Zn₂GeO₄/SnO₂ nanowire heterostructures. Complex wide bandgap nanowire based heterostructures deliver a suite of interesting properties that enable key opportunities for future integration of nanophotonics and electronics. The prediction and tailoring of their performance require a joined-up knowledge of their local structure, optical properties and chemistry at the nanoscale. Unique nanowire systems were synthesized by an effective catalyst-free thermal evaporation method using Plateau-Rayleigh (PR) instability that causes a skewer-shaped (SK) architecture¹ (see Figure 1). Our perspective reflects on how these recent developments could be coupled with correlative X-ray characterization to bring together multiple hyperspectral imaging modalities and maps of the local chemistry, structure and functionality to form rich multimodal datasets. We complete the material picture through correlative characterization by nano-X-ray fluorescence and nano-X-ray excited optical luminescence in combination with nano-X-ray absorption.

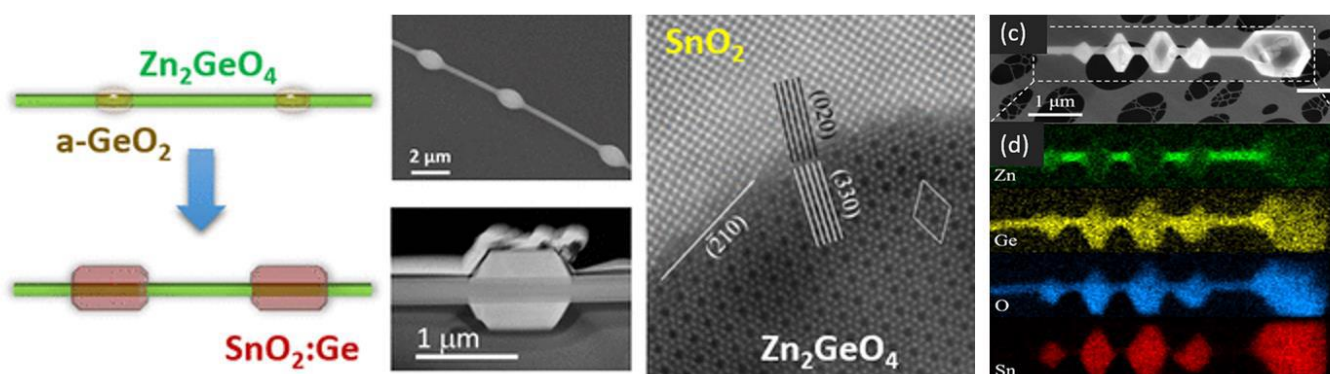


Figure 1: Zn₂GeO₄/SnO₂ nanowire-heterostructures grown by a single step method. Atomic resolution annular dark-field in the scanning transmission electron microscope (ADF-STEM) image of the nanowire–particle interface. The (210) and (120) surface facets for the Zn₂GeO₄ nanowire have been marked, as well as the (330) planes for Zn₂GeO₄ and the (020) planes for SnO₂. A unit cell of Zn₂GeO₄ is shown for reference. (c) The white dashed box in SEM images indicates the area where the EDS maps were taken, showing the elemental distribution of Zn (green), Ge (yellow), O (blue), and Sn (red) elements.¹

A $\text{Zn}_2\text{GeO}_4/\text{SnO}_2$ nanowire-heterostructure were studied at the nanoanalysis beamline of ID16B at the ESRF. The experiments were carried out using a beam lateral resolution of $80 \times 60 \text{ nm}^2$. The XRF maps were taken at 11.25 keV (excitation energy above the Ge K-edge located at 11.1031 keV) with a pixel size of $50 \times 50 \text{ nm}^2$ over a $3 \times 5 \mu\text{m}^2$ sample area and 1s/point integration time. We have also exploited the optical contrast to record spectrally and spatially resolved XEOL signals simultaneously to XRF data for each sample point. The spatially resolved XANES data were acquired in XRF detection mode around the Ge K-edge.

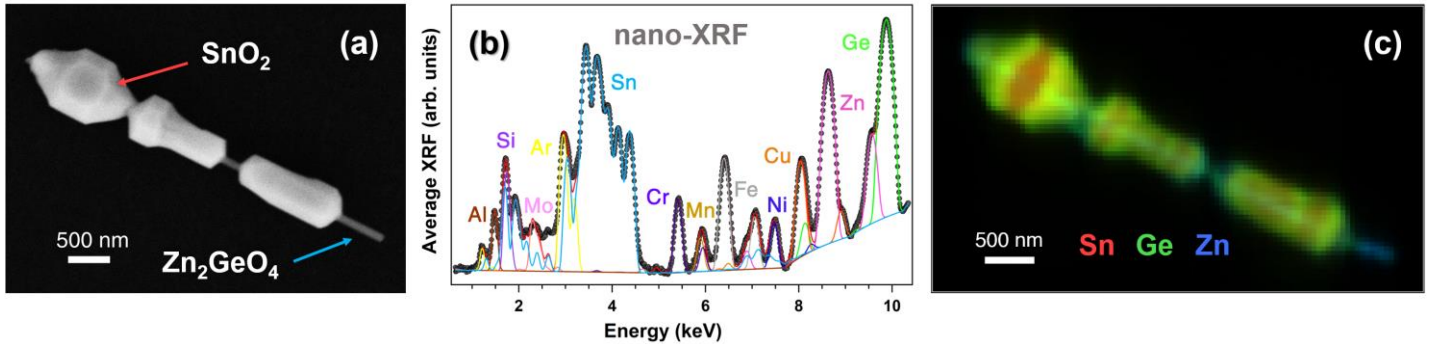


Figure 2: (a) SEM image of SK-structure. (b) Average XRF spectrum recorded over the SK-structure shown in (a) at 11.25 keV. (c) XRF map in RGB visualization that depicts the XRF intensities of Sn (red), Ge (green), and Zn (blue). Their colour brightness (light represents high counts, dark low counts) indicates the intensity ranges.

Figure 2 shows the XRF nanoimaging results obtained by raster-scanning the SK-structure in the X-ray nanobeam. Our results point to the formation of a $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ solid solution which keeps the rutile crystal structure. Likely, the faceted areas present a lower amount of Ge (and a higher amount of Sn) because the Ge out-diffusion to the Zn_2GeO_4 nanowire surface (which is arranged in periodic droplets due to PR-instability) acts as nucleation sites for the Sn crystallites. The more faceted the $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ crystallites is, the more Sn replaced Ge to form the rutile crystal phase.

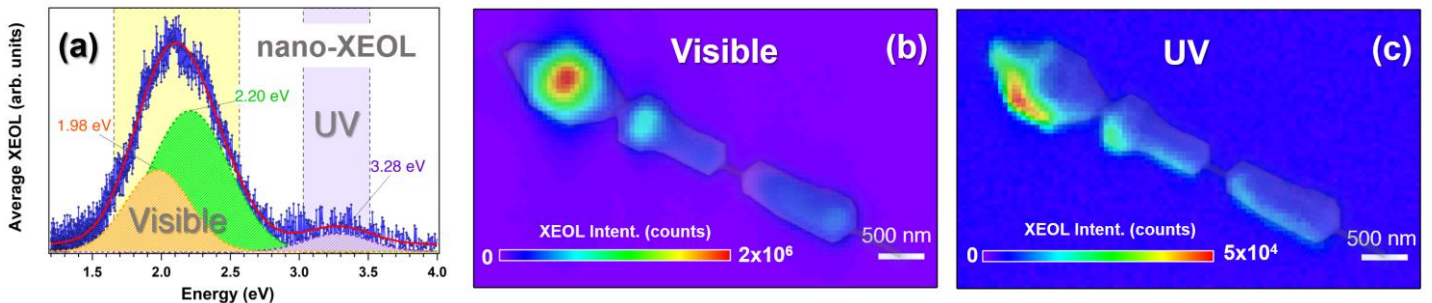


Figure 3: (a) Average XEOL spectrum recorded over the SK-structure shown in Figure 2a. (b) and (c) XEOL integrated intensity maps over the energy ranges defined by the colour bands (visible and UV) in (a).

Figure 3 display the spatial distribution of the respective XEOL bands observed in the SK-structure. The visible emission associated to oxygen vacancies is mostly distributed within the $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ crystallites, becoming particularly stronger where Sn signal is higher. On the other hand, the less intense UV band of unclear origin is only emitted from one side of the $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$, which suggests an orientation dependent effect linked to the crystal structure. This UV emission could come from the preferential incorporation of defects coming from the out-diffusion of Ge or Zn from the Zn_2GeO_4 nanowire, which would result into electronic states within the energy bandgap, leading to the UV emission. Therefore, the inhomogeneous variation of the radiative centres could probably be associated with the different distribution of impurities and/or structural imperfections.

Finally, Figure 4 shows a representative XANES spectrum obtained on the SK-structure, which suggests an octahedral coordination of Ge atoms in the $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ crystallites. No significant differences were found in the XANES spectra around the K-edge of Ge in the different zones of the crystallites. In order to further

investigate the origin of the UV band anisotropy suggested by the results of this experiment, new spatially resolved nano-XRD and nano-XANES measurements were performed on the same SK-structure in the months following this experiment (in-house research). The results suggest a potential interrelation of Zn species with the UV radiative transitions. The degree of optical light and strain produced varies over the $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ crystallites, likely supported by the irregular formation of secondary phases observed by XRD, which could be assisted by the higher concentration of Zn impurities. Finally, nano-XANES measurements around Zn K-edge indicate the octahedral coordination of Zn in the $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ crystallites, which supports that Zn is incorporated into the alloy within the Sn sites, ruling out the possibility to form an isolated compound such as ZnO.

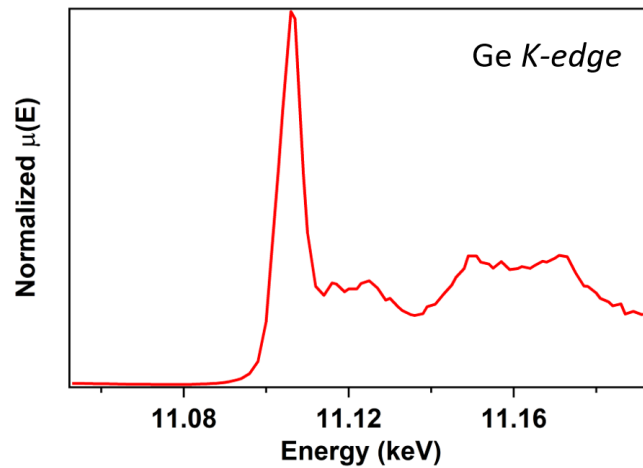


Figure 4: Representative XANES spectrum acquired on the SK-structure.

Therefore, the multi-technique synchrotron approach allowed us to unravel the elemental composition, optical processes and atomic configurations of the $\text{Zn}_2\text{GeO}_4/\text{SnO}_2$ nanowire heterostructures, making it possible to determine them independently and spatially resolved at the nanometer length scale. The analysis of the data has been successfully completed, resulting in a research article which has been uploaded to the arxiv platform ([arXiv:2206.09730](https://arxiv.org/abs/2206.09730)) and has recently been submitted for publication to the journal *Small* (Journal Impact Factor of 15.153, 2021).

References

- [1] J. Dolado et al. *Cryst. Growth Des.*, 20, 506–513 (2020).