

Structural characterization at atomic level and optical properties on the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ ($3 \leq k \leq 13$) system.

Supplementary Information:

Detailed experimental condition for HAADF and ABF imaging techniques:

The atomically-resolved study of the microstructure of IZO compounds has been performed in a JEOL-JEMARM200 microscope using two different techniques operating in Scanning Transmission Electron Microscopy (STEM) mode. These techniques are: High Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF).

HAADF implies the collection of the electrons scattered at high angles resulting in incoherent imaging. HAADF provides images which contrast can be qualitative interpreted as chemical information since the intensity is approximately proportional to Z^2 (Z =atomic number). Therefore, brighter contrast corresponds to heaviest elements (Indium) while less bright contrast corresponds to those elements with lower Z (Zinc). The incorporation of spherical aberration correctors allows acquiring HAADF images with atomic resolution, making possible to resolve and locate atomic columns with different composition. HAADF images do not reveal the presence of light elements due to the dependence of their intensity with Z .

Simultaneous acquisition of ABF images allows acquiring phase-contrast images from electrons scattered at low angles. The required system consists of a bright field detector in which the central area is blanked with a beam stopper. By modifying the camera length, the appropriate solid angle enhance the contrast of the oxygen atomic columns is optimized. The resulting image allows the visualization of light and heavy atomic columns, but the intuitive identification of the heaviest element is not directly achievable.

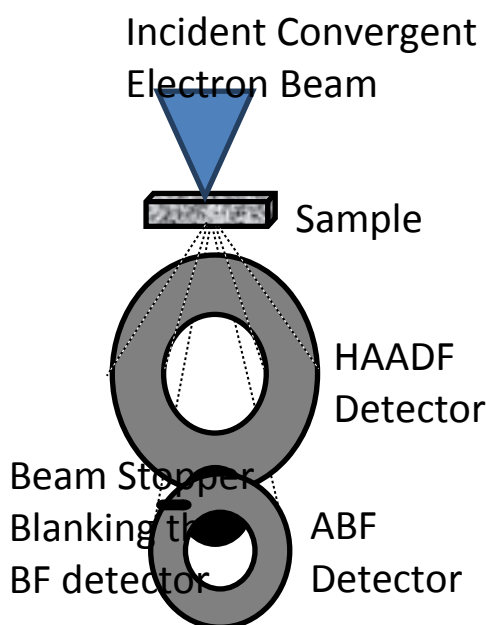


Figure S1. HAADF and ABF-STEM schematic configuration.

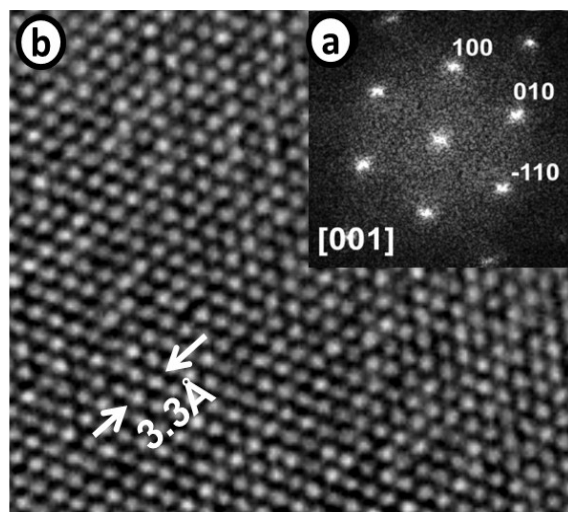


Figure S2. (a) SAED pattern along the zone axis $[001]$ of the hexagonal structure of the $k=3$ term (b) corresponding HRTEM image where a parameter is indicated.

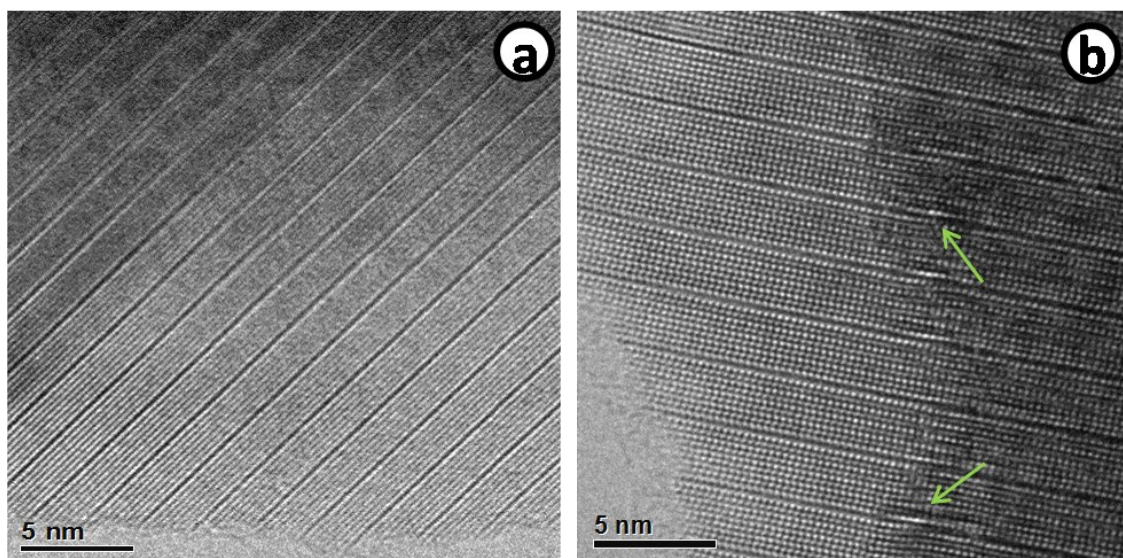


Figure S3. (a) HRTEM image along $[1-10]$ of $k=5$ (b) HRTEM Image along $[010]$ of $k=7$. Dislocations and stacking faults (marked with green arrows) are present in the thicker areas of the crystal. In both samples a high degree of crystallinity is observed.

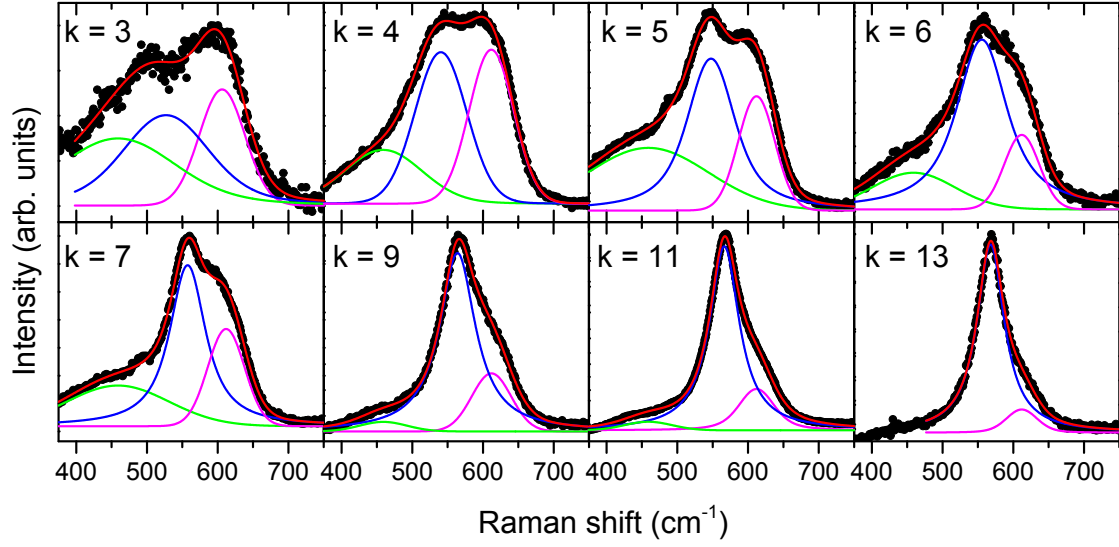


Figure S4. Enlargement of the resonant Raman spectra ($\lambda_{\text{ex}} = 325 \text{ nm}$) of the different synthesized IZO compounds showing the 517-635 cm^{-1} band and its fit to three Voigt profiles. The intensity for the 459 cm^{-1} peak of the term $k = 13$ is too low to be included in the fit. The position for the peaks at 459 and 612 cm^{-1} has been fixed according to the average values of the corresponding peaks of the reference Raman spectra of $\text{In}_2\text{O}_3(\text{F}^{(7)}_{2g}/\text{F}^{(8)}_{2g})$ and $\text{E}^{(4)}_g/\text{F}^{(11)}$ modes respectively), weighted to their relative intensities (see text in the manuscript).

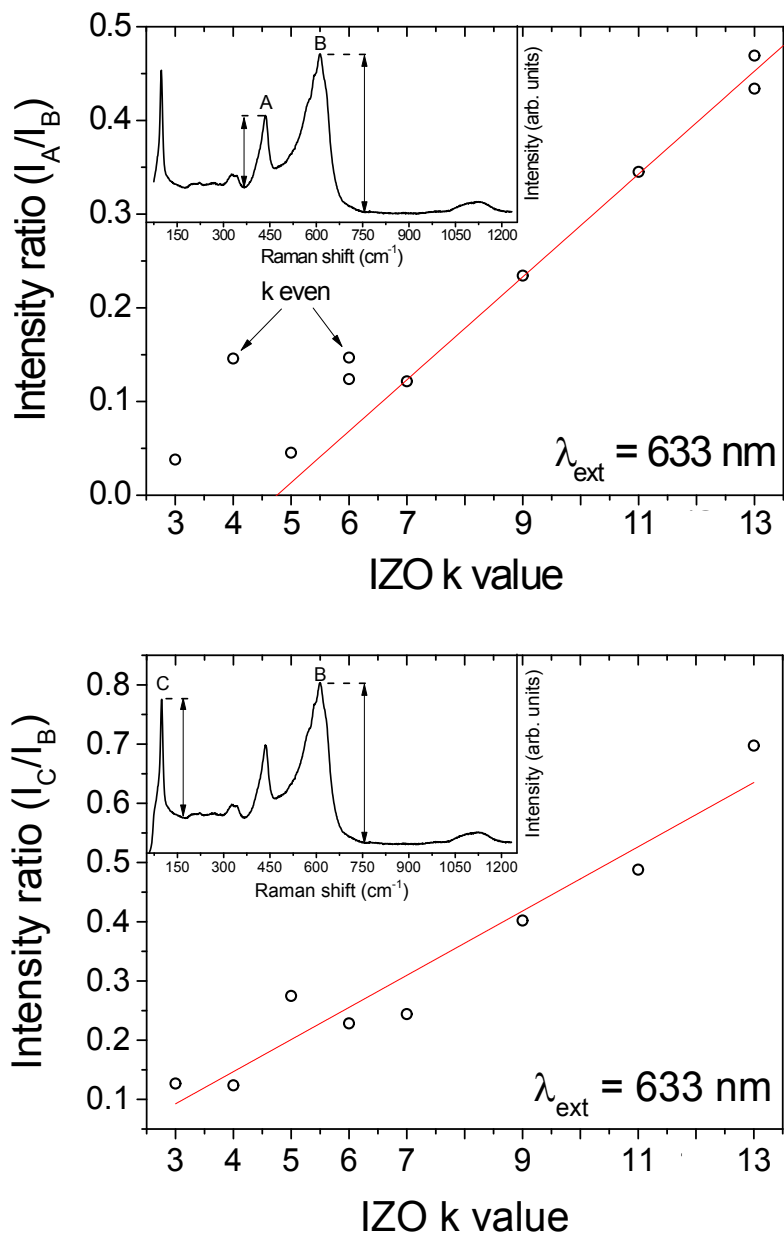


Figure S5. (a) Intensity ratio between the 437 and 612 cm^{-1} peaks (marked as A and B in the inset) vs. k value of the spectra recorded with an excitation wavelength of 633 nm. Inset shows how the intensity of the 437 and 612 cm^{-1} peaks is measured from the onset of each peak. It is worth noting that the values with k even (4 and 6) deviate from the observed trends. This can probably be expected since the crystalline structure of the IZO compounds with k even (hexagonal $P6_3/\text{mmc}$ space group) differs slightly from those with k odd (rhombohedral $R\text{-}3\text{m}$ space group). (b) Same as (a) for the 99 and 612 cm^{-1} peaks, labelled as C and B respectively