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Atomically resolved structure of luminescent $ZnkIn_2O_{3+k}$

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Indium zinc oxides (IZOs) have attracted the interest due to their physical properties and high chemical stability. These materials constitute a large field of research due to its applications as transparent electrodes in transistors, flat panel displays, solar cells, sensors and photocatalysis properties. In this work, several terms of the homologous series $ZnkIn2O_3^+k$ with $3\leq k\leq 13$ materials were prepared by the ceramic method. The microstructure of the materials has been elucidated by means of X-ray Diffraction (XRD), high-resolution transmission electron microscopy (HRTEM and STEM) and Raman spectroscopy. Additionally, luminescence properties were measured by cathodoluminescence in a scanning electron microscope. The structure can described based on a hexagonal symmetry, with R-3m space group for those terms with odd k, and P63/mmc for k even, although overlap of the diffraction maxima occurs for higher members of the series. HRTEM images show these materials are formed by the ordered intergrowth of layers of InO_2- octahedral sharing edges with InZnkOk+1+ blocks stacked perpendicularly to the c-axis of the crystal, where zinc and indium occupy tetrahedral and trigonal bipyramid sites. The existence of extended defects such as twins, dislocations and disordered intergrowths were also observed. TEM in High Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) modes show the indium and zinc distribution along [1-10] and [010] zones axes. The characteristic modulation of this homologous series (a zigzag pattern) is also visualized. Cathodoluminescence (CL) measurements show the existence of a main emission band centered at 1.75 eV, associated to Zn vacancies. The variation of the intensity and width of the band depends on the chemical composition of the material. These results suggest that physical properties can be tailored for technological applications depending on the material composition.

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