Elemental distribution in (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) nanocrystals synthesized via the solid-state nitridation of ZnO and ZnGa$_2$O$_4$

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Abstract: A solid solution of ZnO and GaN, (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$), is a visible-light absorbing semiconductor that is of interest for applications in solar photochemistry. Value of $x$ is typically determined by elemental analysis of ensemble sample, providing only the average composition of the material. But in a solid state reaction, average $x$ and local composition at the single particle level can be quite different. In this work, we aim to better define the value of $x$ by measuring the elemental distribution of (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) nanocrystal samples at the single particle level using energy-dispersive X-ray spectroscopy in scanning transmission electron microscopy to map the elements at a sub-nm level. We combine these experiments with ensemble elemental analysis, powder X-ray diffraction, TEM imaging to create a comprehensive picture of the elemental distribution and its mechanistic origin. We find that the (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) samples are highly heterogeneous, consisting of two types of particles: small ($\sim$5 nm) homogeneous particles of ambiguous crystal structure that contain most of the Ga and N, and large ($\sim$20 nm) single wurtzite crystals that have enrichment in Ga and N near the surface. Those larger particles always have $x$-values of 0.8-0.9 regardless of the ensemble $x$-value.

Keywords: Elemental distribution; Nanocrystals; Oxynitride; Solid state; STEM-EDS