

## Cation disorder in zinc-group IV- nitride and oxide nitride semiconductor materials revealed through neutron diffraction

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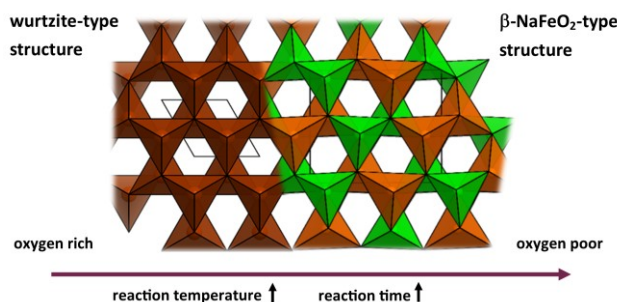
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Zinc-group IV-nitrides are being considered as promising candidates for photovoltaic absorber materials, containing uniquely elements of low toxicity and low resource criticality [1] Further to band gap tuning by alloying group IV elements (Si, Ge, Sn), it has been postulated based on DFT calculations that these compounds possess a second mechanism for bandgap tuning through cation disorder [2]. While this intrinsic cation disorder is not straightforward to tune directly, we found that a degree of oxygen inclusion in the material triggers cation disorder and hence can mimic the effect. [3]

We have studied  $\text{ZnGe}(\text{N},\text{O})_2$  as a model system, in which a large range of compositions can be accessed conveniently as bulk powder samples through ammonolysis reaction. [3,4] This does, however, afford the use of neutron diffraction for structural investigations, since  $\text{Zn}^{2+}$  and  $\text{Ge}^{4+}$  are isoelectronic and hence virtually indistinguishable by standard powder X-ray diffraction. [5]



**Figure 1.** Schematic of the influences of reaction conditions on the structural transition from completely disordered wurtzite-type crystal structures to ordered  $\beta\text{-NaFeO}_2$ -type crystal structures in the system  $\text{Zn}_{1+x}\text{Ge}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ . [4]

Using chemical analysis, we established a simple model for the reaction mechanism and thereby reducing the complexity of the system to the general chemical formula  $\text{Zn}_{1+x}\text{Ge}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ . This allows us to refine the neutron powder diffraction data with a highly reliable model and to extract accurate information on the cation disorder. We find that intrinsic cation disorder and cation disorder stemming from oxygen inclusion exist at the same time and we disentangle their effects on the optical bandgap of these materials.

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