

The same and not the same: The photovoltaic model system $\text{Zn}_{1+x}\text{Ge}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ and its two independent modes of cation disorder revealed by Neutron diffraction.

Joachim Breternitz¹, Zhenyu Wang^{1,2}, Stanislav Savvin³, Susan Schorr^{1,2}

¹Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Joachim.breternitz@helmholtz-berlin.de, Germany, ²Department Geosciences, Freie Universität Berlin, Germany, ³Institut Laue-Langevin, Grenoble, France

While the efficiencies of alternative solar cell materials like halide perovskites keep on reaching ever higher values, their use is flawed by the use of elements that are toxic (e.g. Pb in halide perovskites, Cd in CdTe) or scarce (e.g. In in (In,Ga)N and Cu(In,Ga)(S,Se)₂). A consideration of this would, however, be indispensable to facilitate the wider use of solar cells based on such technologies. One of the potential alternatives taking such sustainability arguments into account are ternary nitride materials formally based on the wurtzite-type III-V nitrides, where the trivalent cation is replaced with equimolar amounts of divalent and tetravalent ions.[1] When those cations are ordered in the ground state, a subgroup of the wurtzite-type (s.g. $P6_3mc$) is adopted (figure 1).[2]

Herein, we look at the model system $\text{Zn}_{1+x}\text{Ge}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ in detail, which can be conveniently synthesized through an ammonolysis reaction.[3] While the bandgap of these materials is in the range of 2.7-3.4 eV, which makes it unsuitable as a solar absorber itself, they can be understood as a model system for the heavier homologue $\text{Zn}_{1+x}\text{Sn}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ with bandgap energies in the range of 1.5 eV. The advantage of $\text{Zn}_{1+x}\text{Ge}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ is not only a well understood reaction mechanism,[4] but also the possibility to access large amounts of materials – a prerequisite for Neutron diffraction, which allows the distinction between the isoelectronic ions Zn^{2+} and Ge^{4+} as well as N^{3-} and O^{2-} .

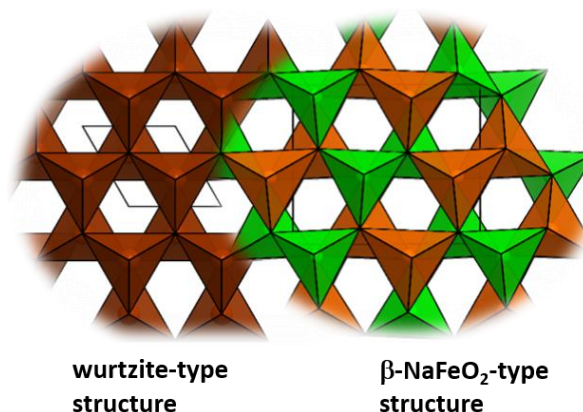


Figure 1 Disordered wurtzite-type structure vs. ordered β -NaFeO₂-type structure.

While $\text{Zn}_{1+x}\text{Ge}_{1-x}(\text{O}_x\text{N}_{1-x})_2$ with high oxygen content crystallizes in the wurtzite-type with only one distinct crystallographic site, a lower oxygen content appears to correlate with cation ordering in the β -NaFeO₂-type (s.g. $Pna2_1$) at first glance. In addition to this extrinsic cation disorder, theoretical calculations have suggested an intrinsic cation disorder through antisite defects, which affects the optical bandgap. Correlating Neutron diffraction data with optical bandgap measurements and chemical composition, we show that both disorder effects are independent of each other, but influence the optical bandgap of the resulting material in a similar way.

[1] Greenaway AL, Melamed CL, Tellekamp MB, Woods-Robinson R, Toberer ES, Neilson JR, et al. Ternary Nitride Materials: Fundamentals and Emerging Device Applications. *Ann. Rev. Mater. Res.*, 51, 591–618 (2021)

[2] Breternitz J, Schorr S. Symmetry relations in wurtzite nitrides and oxide nitrides and the curious case of $Pmc2_1$. *Acta Cryst A.*, 77, 208–216 (2021).

[3] Breternitz J, Wang Z, Glibo A, Franz A, Tovar M, Berendts S, et al. On the Nitridation of Zn_2GeO_4 . *Phys Status Solidi A.* 216, 1800885, 2019.

[4] Wang Z, Fritsch D, Berendts S, Lerch M, Breternitz J, Schorr S. Elucidation of the reaction mechanism for the synthesis of ZnGeN_2 through Zn_2GeO_4 ammonolysis. *Chem Sci.* 12, 8493–8500, 2021.

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