Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information "Uncovering cation disorder in ternary $Zn_{1+x}Ge_{1-x}(N_{1-x}O_x)_2$ and its implications on the optoelectronic properties."

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Table S1: Sample list for samples measured with neutron diffraction

reaction temperature /°C	**dwelling time /h**	**x in $Zn_{1+x}Ge_{1x}(O_xN_{1-x})_2$ from XRF**	**a [Å]**	**b [Å]**	**c [Å]**	**Ge_{Zn}**	**Zn_{Ge}**	**distortion factor α** $\frac{(\frac{b}{2}-\frac{a}{\sqrt{3}})}{\sqrt[3]{\frac{abc}{4}}}$	**E_g [eV]**	**neutron instrument used**
850	21.33	0.089(9)	5.500(1)	6.417(1)	5.192(1)	0.15(2)	0.24(2)	0.0092(9)	2.99(5)	D2B
850	23.33	0.065(9)	5.491(1)	6.420(1)	5.191(1)	0.14(2)	0.21(2)	0.0111(9)	3.11(5)	D2B
850	25.33	0.068(9)	5.480(1)	6.428(1)	5.190(1)	0.07(2)	0.14(2)	0.0140(9)	3.20(5)	D2B
865	12.00	0.137(9)	5.513(1)	6.419(1)	5.195(1)	0.28(8)	0.41(8)	0.0074(9)	2.84(5)	E9
865	14.20	0.074(9)	5.500(1)	6.415(1)	5.191(1)	0.15(2)	0.22(2)	0.0090(9)	2.98(5)	D2B
865	16.20	0.046(9)	5.479(1)	6.429(1)	5.190(1)	0.09(2)	0.13(2)	0.0143(9)	3.24(5)	D2B
865	18.20	0.035(9)	5.464(1)	6.443(1)	5.188(1)	0.01(2)	0.05(2)	0.0187(9)	3.43(5)	D2B
895	1.00	0.34(1)	5.558(1)	6.428(1)	5.197(1)	0.26 (5)	0.60 (5)	0.0014(9)	2.70(5)	D2B
895	2.00	0.33(1)	5.556(1)	6.426(1)	5.197(1)	0.23 (5)	0.57 (5)	0.0015(9)	2.73(5)	D2B
895	6.17	0.104(9)	5.506(1)	6.416(1)	5.192(1)	0.16(2)	0.27(2)	0.0081(9)	2.92(5)	D2B
895	6.67	0.107(9)	5.495(1)	6.419(1)	5.192(1)	0.13(2)	0.24(2)	0.0103(9)	3.03(5)	D2B
895	7.67	0.044(9)	5.476(1)	6.434(1)	5.190(1)	0.08(2)	0.12(2)	0.0155(9)	3.16(5)	D2B
895	8.00	0.019(9)	5.461(1)	6.447(1)	5.190(1)	0.10(8)	0.12(8)	0.0198(9)	3.40(5)	E9
910	4.33	0.115(9)	5.495(1)	6.420(1)	5.192(1)	0.11(2)	0.23(2)	0.0105(9)	3.00(5)	D2B
910	4.67	0.036(9)	5.487(1)	6.425(1)	5.191(1)	0.12(2)	0.16(2)	0.0125(9)	3.06(5)	D2B
910	5.33	0.032(9)	5.469(1)	6.439(1)	5.189(1)	0.03(2)	0.06(2)	0.0173(9)	3.36(5)	D2B
910	6.00	0.027(9)	5.461(1)	6.448(1)	5.191(1)	0.11(8)	0.14(8)	0.0198(9)	3.36(5)	E9

Table S2: Sample list for the samples measured with anomalous diffraction at KMC2.

reaction temperature /°C	**dwelling time /h**	**x in $Zn_{1+x}Ge_{1x}(O_xN_{1-x})_2$ from XRF**	**a [Å]**	**b [Å]**	**c [Å]**	**Ge_{Zn}**	**Zn_{Ge}**	**distortion factor α** $\frac{(\frac{b}{2}-\frac{a}{\sqrt{3}})}{\sqrt[3]{\frac{abc}{4}}}$	**E_g [eV]**
850	17	0.19(1)	5.5296(1)	6.41566(9)	5.19638(3)	0.239(12)	0.429(12)	0.0043(9)	2.80(5)
850	27.1	0.03(1)	5.46889(5)	6.44090(5)	5.19071(4)	0.043(8)	0.071(8)	0.0176(9)	3.38(5)
865	6	0.27(1)	5.5410(1)	6.42503(5)	5.19610(2)	0.36(2)	0.63(2)	0.0037(9)	2.78(5)
865	8	0.27(1)	5.5381(2)	6.42557(8)	5.19795(2)	0.32(2)	0.59(2)	0.0043(9)	2.79(5)
895	3	0.26(1)	5.5391(1)	6.42622(4)	5.19765(2)	0.34(3)	0.60(3)	0.0042(9)	2.83(5)
895	4	0.21(1)	5.5348(2)	6.41841(8)	5.19727(3)	0.33(3)	0.53(3)	0.0038(9)	2.80(5)
910	2	0.31(1)	5.5489(1)	6.42659(4)	5.19856(2)	0.33(3)	0.63(3)	0.0027(9)	2.73(5)
910	3	0.19(1)	5.5326(1)	6.41792(6)	5.19703(2)	0.28(2)	0.48(2)	0.0041(9)	2.81(5)
910	4	0.14(1)	5.51449(6)	6.41966(5)	5.19552(4)	0.27(2)	0.41(2)	0.0073(9)	2.77(5)

Refinement details for Anomalous diffraction

A non-standard approach was followed for the refinement of the anomalous data: All three powder diffraction data sets collected at different energies were refined jointly with identical structural parameters; to correct for minor deviations the wavelengths for the two higher energies were refined.

Additional corrections had to be applied for a number of samples. These showed significant *hkl*-dependent asymmetry of the peaks in agreement with the presence of a distribution of fractions with different unit cells or a significant amount of anisotropic strain. This was modelled by refining two or three phases with slightly different lattice parameter *a*, but otherwise identical structural parameters. In these cases, the lattice parameters used are the average ones, weighted with the refined fraction of the model phases.

Furthermore, several samples had to be mounted on aluminum samples holders due to constraints of the experimental setup. Diffractograms of these samples showed some aluminum peaks, especially the one measured at 9659 eV, where absorption by the sample was lowest. These reflections were excluded from the refinement.

Atomic positions were refined, as were groupwise isotropic displacement parameters for cations and anions each. All atomic positions were assumed to the fully occupied. The distribution of Zn and Ge over the two sites was refined, while keeping the overall composition fixed to the results of the chemical analysis. The distribution of N and O over their two sites was modelled as random.

The energy-dependent factors f' and f'' of the scattering factors were interpolated from tabulated data[S1] according to the theoretical approximation developed by Cromer and Liberman.[S2,S3]

The atomic form factors of the cations Zn^{2+} and Ge^{4+} were taken from International Tables of Crystallography C, Table 6.1.1.4;[S4] these are the widely used default values.

For the anions N^{3-} and O^{2-}, no form factors are given in the International Tables. The use of values for the neutral atoms of O resulted in unsatisfactory site occupation factors and displacement parameters. For these reasons, published values for these anions were taken from the literature: For N^{3-}, three models for the free anion and two different diameters of the Watson sphere were taken from Schmidt (1979)[S5], and another five models with different diameters of the Watson sphere were taken from Schmidt (1980).[S6] The 9-parameter expansion used in the International Tables (and also by Fullprof) was fitted to the tabulated $\sin\theta/\lambda$ -depended data.

A highly ordered sample with Zn/Ge distribution predetermined from neutron diffraction and with low oxygen content, was used to select the best nitrogen model, based on overall fit quality χ^2, refined thermal displacement parameter, overall site occupation factors, refined Zn/Ge- and O/N-ratio and Zn/Ge distribution for otherwise identical refinements. The best results were found for the calculation of Schmidt (1979)[S5] using the small Watson sphere of 1.24 Å, fitted with parameters A1 = 5.45670, B1 = 25.04595, A2 = 2.66752, B2 = 9.84859, A3 = 1.56590, B3 = 0.45126, A4 = 0.04754, B4 = 912.05902, C=0.26263.

The oxygen anion form factor was determined from a sample with a known comparatively high oxygen content. The three O^{2-} calculations of Schmidt (1979)[S5] were compared with the one of Hovestreydt (1983)[S7] and the two calculations of Azavant (1993).[S8] The results were less conclusive, but the calculation of Schmidt (1979) using the small Watson sphere of 1.32 Å was among the best and was selected. Fitted parameters are A1 = 4.24527, B1 = 16.54067, A2 = 2.61926, B2 = 6.40260, A3 = 1.54742, B3 = 0.33739, A4 = 1.32078, B4 = 39.28574, C = 0.26619.

References

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