

Order-Disorder Phenomena in Nitridosilicates and Nitridophosphates

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Among numerous (oxo-)nitridosilicates synthesized in the past years, some compounds exhibit interesting order-disorder phenomena. Whereas the ordered structure of $\text{Ho}_2[\text{Si}_4\text{N}_6\text{C}]$ [1] can be derived from the highly symmetrical framework nitridosilicate $\text{BaYb}[\text{Si}_4\text{N}_7]$ [2] by “chemical twinning”, the same $\text{N}^{[4]}(\text{SiN}_{3/2})_4$ ($\text{X} = \text{N}, \text{C}$) building blocks form microdomains with different interconnection in $\text{Sm}_2[\text{Si}_4\text{N}_6\text{C}]$, leading to pronounced diffuse scattering. A change of cations can impede long-range order in layered oxonitridosilicates as well. $\text{Ca}[\text{Si}_2\text{N}_2\text{O}_2]$ constitutes a well-ordered compound, the same anionic layers in $\text{Eu}[\text{Si}_2\text{N}_2\text{O}_2]$, however, exhibit severe stacking disorder with the tendency to form a superstructure.

The $[\text{PN}_2]^-$ frameworks of $\text{M}^{\text{II}}\text{P}_2\text{N}_4$ (and other) nitridophosphates are isoelectronic with SiO_2 and thus exhibit numerous structural analogies to SiO_2 . The highly symmetrical tetrahedral basic structures are always distorted due to the adaptation of voids to cation size and ordering as well as due to the tendency to avoid linear P–N–P bridges. However, only in some cases these distortions lead to long-range ordering by symmetry reduction or superstructure formation. Order-disorder effects, i. e. chemical and positional disorder, diffuse scattering and modulations will be discussed on the basis of X-ray powder data and electron diffraction.

[1] Huppertz H., Schnick W., *Angew. Chem.* 1996, **108**, 2115. [2] Höpfe H.A., Kotzyba G., Pöttgen R., Schnick W., *J. Mater. Chem.* 2001, **11**, 3300.

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