MS17-2-4 Ordered and disordered structural variety in supposedly simple beryllium arsenide and beryllium phosphide
#MS17-2-4

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Abstract
A broad range of AB_2-type crystal structures containing main-group element anions in combination with divalent cations has been characterized for more than 100 years. Thus, one would expect that the crystal structure of $BeAs_2$ is well known.[1] However, pronounced stacking disorder, polymorphism and microcrystallinity have impeded structure elucidation for decades. Microfocused synchrotron radiation in combination with electron microscopy now allowed us to understand the structural variety of $BeAs_2$ including diffraction phenomena such as twinning and diffuse scattering.
The structural variety of $BeAs_2$ can be described and understood recognizing its relation to the diamond structure, considering group-subgroup relations. All polymorphs derive from an average structure model in space group $I4_1/amd$. Different possibilities of atomic ordering lead to two hettotypes. In comparison with the diamond structure, structures with significantly higher complexity are expected due to partially ionic interactions between beryllium and arsenic next to covalent As–As bonding. In $BeAs_2$, every beryllium atom is coordinated by four arsenic atoms whilst the coordination sphere of the arsenic atoms comprises two beryllium and two arsenic atoms, creating a diamond-like framework. The formation of arsenic rings or chains is in accordance with the 8–N rule and the Zintl concept. Two completely different polymorphs were found in the product of the same synthesis.
The structural motif of the first polymorph is an As_8 ring. These rings are arranged in long-range ordered layers while showing characteristic stacking disorder. This can be described in a classical way based on *OD* theory. Hypothetical long-range order, i.e. a *MDO* polytype, which is observed only in domains, corresponds to an ordered structure model in space group $C2/c$. The layers with As_8 rings feature a higher layer symmetry in comparison with the whole structure. Thus, there are energetically equivalent stacking variants that lead to disorder based on varying interconnection of the As_8 rings by Be atoms. A complex disorder model was developed to simulate sections through reciprocal space with diffuse streaks that can be compared to experimental data.[2] Crystallites exhibit different degrees of disorder which can be approximately quantified. In addition to this disorder, which leads to twin boundaries and various hypothetical polytypes, further twinning effects need to be considered in “single” crystals. These correspond to the symmetry reduction from the cubic diamond type to the tetragonal average structure. The average degree of disorder in a specific sample has been evaluated from powder diffraction data by comparing them to simulated ones. The domain structure as well as the local structure of e.g. twin boundaries have been investigated by HRTEM, which confirms that the results of X-ray diffraction can deliver valuable information for simulations. The structural features of this first polymorph are also present in BeP_2, which has been investigated in the same way.[3]
The second polymorph of $BeAs_2$ has a completely ordered crystal structure governed by chain-like As polyanions. They form a complex ordered arrangement in space group $I4_1/a$ containing twisted As chains that are separated by beryllium atoms to form a colouring variant of the diamond structure.

References
[1] R. Gerardin, J. Aubry, *J. Solid State Chem.* **1976**, *17*, 239.
[2] M. M. J. Treacy, J. M. Newsam, M. W. Deem, *Proc. Roy. Soc. Lond. A* **1991**, *433*, 499.
[3] J. F. Brice, R. Gérardin, M. Zanne, *Mater. Res. Bull.* **1975**, *10*, 1237.