The crystal chemistry of binary beryllium dipnictides – new binary structure types between Zintl polyanions and Grimm Sommerfeld compounds

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Abstract

Compounds with an average valence electron concentration of four often form colouring variants of diamond-like frameworks according to the Grimm Sommerfeld concept. Although the crystal structure of sphalerite was determined already in the 1920s,[1] there are still binary main group compounds with diamond-like frameworks lacking investigation. This is the case for binary beryllium pnictides BePn2 – not only because of the high toxicity of beryllium, but mainly because of complications concerning structure analyses. We have now elucidated the structures of BeP2, BeAs2 and BeSb2 by combining single-crystal diffraction using microfocused synchrotron radiation with HRTEM imaging as well as electron crystallography for very precise data sets of crystallites on the sub-micron scale.[2] Phase-pure samples [3,4] were obtained by solid-state reactions or in salt flux, but the syntheses result in microcrystalline powders that do not allow data collection on laboratory diffractometers.

BeSb2 features a diamond-like framework consisting of spiral-like antimony chains with ten atoms per translation period, which are interconnected by beryllium atoms. The antimony substructure represents a new homonuclear Zintl ion. Ab initio DFT calculations for this new structure type reveal semiconducting properties and confirm the considerations based on the Zintl and Grimm Sommerfeld concept, respectively: Valence electron density is almost fully located on the antimony substructure to form the corresponding chains and diamond-like framework. Bader charges nearly correspond to the expected formal oxidation states, while Electron Localized Function suggests the presence of homonuclear Sb–Sb bonds within the polyanions.

BeAs2 and isotypic BeP2 exhibit stacking disorder in a typical OD structure. This results from different possibilities of stacking layers built up from arsenic eight-rings and beryllium atoms. The cyclic Zintl polyanions were first revealed by electron crystallography. A disorder model was derived from the diamond-like average structure taking into account twinning as well as diffuse streaks in diffraction patterns. A second polymorph of BeAs2 that adopts the BeSb2 structure type could also be characterized.

References

Chain-like structure of beryllium antimonide.

Ring-like structure of beryllium arsenide.