MS42 Solving Structures Through Combination of Reciprocal and Direct Space Methods

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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 Be*Pn*$_2$ – not only because of the high toxicity of beryllium, but mainly because of complications concerning structure analyses. We have now elucidated the structures of BeP_2, $BeAs_2$ and $BeSb_2$ 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.

$BeSb_2$ 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.

$BeAs_2$ and isotypic BeP_2 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 $BeAs_2$ that adopts the $BeSb_2$ structure type could also be characterized.

References

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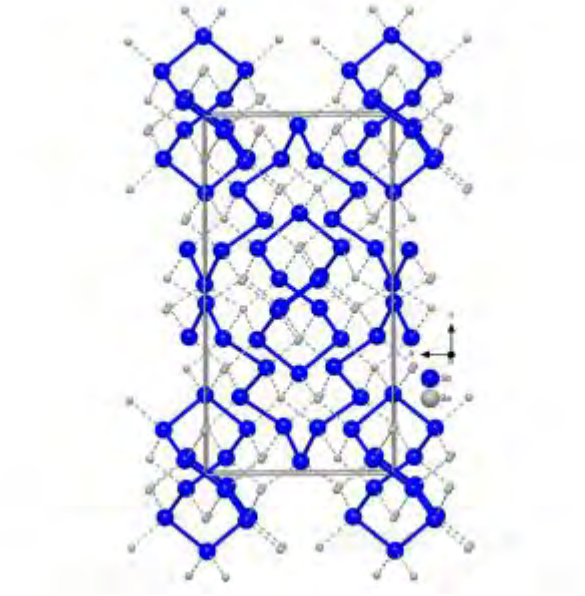
Chain-like structure of beryllium antimonide.



Ring-like structure of beryllium arsenide.