

MS15-2-9 Crystal structures of AB₂ pnictogen compounds related to the diamond structure type – an overview #MS15-2-9N. Langer¹, A. Feige¹, L. Bradaczek¹, O. Oeckler¹¹Institut für Mineralogie, Kristallographie und Materialwissenschaft - Leipzig (Germany)**Abstract**

Structures representing colouring variants of cubic or hexagonal diamond or containing cutouts of these follow the Grimm-Sommerfeld or Zintl concepts. Binary pnictides MPn_2 ($Pn = P, As, Sb$) related to diamond are formed by only few cations M such as Be, Zn, Cd, Si and Ge. Crystal structures of MPn_2 typically contain tetrahedral coordination spheres and pnictogen polyanions that are part of six-membered rings. Most MPn_2 compounds are semiconductors and theoretical calculations suggest favorable transport properties for thermoelectric or photovoltaic applications.^[1-4]

Structures of $BePn_2$ compounds can be derived from cubic diamond by group-subgroup relations. Literature on these compounds seems rather superficial, probably due to experimental and crystallographic complications. BeP_2 ,^[5] $BeAs_2$ and $BeSb_2$ adopt two different structure types. Neglecting stacking disorder, the atom sites of BeP_2 and $BeAs_2$ correspond to a distorted diamond structure with eight-membered pnictogen rings interconnected by Be atoms. The ordered diamond-like structure of $BeSb_2$, which has also been observed for a new polymorph of $BeAs_2$, contains twisted polyanionic chains. Be atoms complete this Sb substructure to produce six-membered rings with chair conformation.

Although for Zn and Cd, the VEC of MPn_2 is 4, these compounds do not form colouring variants of diamond but closely related structures. All atoms are fourfold coordinated with Pn forming polyanionic chains. Black ZnP_2 and β - $CdAs_2$ share the $ZnAs_2$ type,^[6-8] which contains As helices. These form parts of six- and five-membered rings. Zn atoms complete the rings and interconnect the As helices. One translation period of these helices comprises five atoms. The structure of red ZnP_2 (also adopted by β - CdP_2) is closely related,^[6,9] but its P-atom helices exhibit four atoms per translation period. Such helices are also present in orthorhombic α - CdP_2 as well as in α - $CdAs_2$ and the isotypic tetragonal α' - CdP_2 .^[10-12] Whereas α - CdP_2 is rather similar to β - CdP_2 , the tetrahedra in α - $CdAs_2$ are extremely distorted and do not form a dense network.

Whereas GeP_2 and polymorphs of SiP_2 and $SiAs_2$ crystallize in the pyrite type,^[13-15] the layered structure of $GeAs_2$ contains motifs of cubic diamond that comprise rows of pairs of chair-like six-membered rings.^[16] In these rows, As zigzag chains are integrated. One fragment is connected to two others by six-membered rings in distorted chair or boat conformation, giving rise to the formation of additional five-membered rings. Although the structure does not form a 3D network, all Si atoms are tetrahedrally coordinated by As. The As atoms of the zigzag chains are bound to one additional Ge atom, the other As atoms are coordinated by three Ge atoms. Whereas $SiAs_2$ and one polymorph of SiP_2 adopt the $GeAs_2$ type with space group $Pbam$,^[17] there is another closely related polymorph of SiP_2 with $Pnma$.^[18]

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Crystal structures of $M\text{Pn}_2$ compounds.[5-18]

$M\text{Pn}_2$	Be	Zn	Cd	Si	Ge
P	BeP ₂ <i>I</i> ₄₁ / <i>amd</i> (average structure)	black ZnP ₂ → ZnAs ₂ type	α -CdP ₂ <i>Pna</i> 2 ₁	SiP ₂ <i>Pnma</i>	GeP ₂ → pyrite type
		red ZnP ₂ <i>P</i> ₄₁ 2 ₁ 2	β -CdP ₂ → red ZnP ₂ type	SiP ₂ → GeAs ₂ -type	
			CdP ₂ → α -CdAs ₂ type	SiP ₂ → pyrite type	
As	BeAs ₂ → BeP ₂ type	ZnAs ₂ <i>F</i> ₂₁ / <i>c</i>	α -CdAs ₂ <i>I</i> ₄₁ /22	SiAs ₂ → GeAs ₂ type	GeAs ₂ <i>Pbam</i>
	BeAs ₂ → BeSb ₂ type		β -CdAs ₂ → ZnAs ₂ type	SiAs ₂ → pyrite type	
Sb	BeSb ₂ <i>I</i> ₄₁ / <i>a</i>	-	-	-	-