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Melting temperatures of (super)hard cubic boron pnictides

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Based on the analysis of the established empirical relationship between the elastic constants and the melting temperatures for cubic pnictides of group IIIa elements, the melting temperatures of hypothetical cubic BSb and BBi have been predicted. A critical analysis of the melting data for the (super)hard cubic boron pnictides BX ($X = \text{N, P, As, Sb, Bi}$) has been performed, and it has been shown that their melting temperatures at ambient pressure, as well as their Vickers hardness, are a linear functions of the pnictogen Mendeleev number.

Keywords: boron pnictides, melting temperatures, elastic constants, hardness

Cubic ($F-43m$) boron pnictides, BX ($X = \text{N, P, As}$), are refractory and low-compressible phases characterized by an interesting combination of physical and chemical properties, making them materials of choice for a wide range of engineering applications [1-6]. Although boron pnictides are a well-established and fairly well-studied group of compounds, some of their fundamental properties are still poorly understood, in particular the melting temperatures. At ambient pressure, all of these compounds begin to decompose at temperatures below their melting points, so it is not possible to determine their melting temperatures experimentally.

It is expected that the decomposition temperatures of boron pnictides will increase under pressure, so the study of their melting at high pressures seems to be the only way for the experimental construction of their melting curves, whose extrapolation to the low-pressure region would allow a correct estimation of the melting temperatures at ambient pressure (T_m). In this way, the melting points of cubic BP and BAs at ambient pressure have been determined to be 2840(40) [7] and 2410(30) [8], respectively. To estimate the melting temperature of cubic BN at ambient pressure, the melting curve of this phase in the equilibrium p-T phase diagram of boron nitride [9] was extrapolated to zero pressure, yielding a value of $T_m = 3250(50)$ K.

As for cubic BSb and BBi, they have not yet been synthesized and have only been studied by theoretical methods (see recent work [10] and references therein). The phase diagrams of the B-Sb [11] and B-Bi [12] systems at ambient pressure have the same topology, characterized by the absence of binary compounds and the presence of invariant reactions of decomposition of the liquid phase into β -rhombohedral boron and a vapor phase. Therefore, cubic BSb and BBi, which have been claimed to be the ground-state phases, are hypothetical. However, their formation at

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high pressures and high temperatures is highly likely.

To estimate the melting temperatures of these hypothetical phases at ambient pressure, we used the approach previously considered for the case of cubic metals, where an empirical linear relationship between melting temperature and elastic constants (in particular C_{11}) was established and used for predictive purposes [13]. In our case, we have considered the T_m vs. C_{11} relationship for cubic pnictides of group IIIa elements. The room-temperature C_{11} data were obtained from the compilation of single crystal elastic constants published by Simmons and Wang [14] and more recent original publications [10,15-17]. The melting point data were taken from Refs. 7,8,18,19. The correlation for 8 compounds (Fig. 1, blue spheres) is quite good over a rather wide range of melting temperatures (from 1215 K for InAs to 3020 K for AlN). A least-squares best fit straight line was obtained as $T_m(\text{K}) = 732.0 + 6.422 \times C_{11}(\text{GPa})$. This equation is represented by the dashed line in Fig. 1. Thus, C_{11} is a highly reliable T_m predictor for cubic III-V semiconductor compounds and can be used to estimate the melting temperatures of previously reported hypothetical cubic BSb and BBi [10]. Using C_{11} values of 182 GPa for BSb and 124 GPa for BBi (both taken from Ref. 10), the melting temperatures are estimated to be 1890 K and 1525 K, respectively (Fig. 1, red spheres).

Table 1 summarizes data on melting temperatures, C_{11} elastic constants, and Vickers hardness (H_V) of all cubic boron pnictides, as well as pnictogen Mendeleev numbers (MN) according to the nonempirical universal sequence of elements (USE) [20]. Fig. 2 shows the melting temperatures of cubic boron pnictides as a function of the pnictogen Mendeleev number. The linearity of this relationship is obvious. The relationship between Vickers hardness and the Mendeleev number of the pnictogen is also nearly linear for all cubic boron pnictides (Fig. 3). Finally, the observed relationship between melting temperatures and Vickers hardness of cubic boron pnictides (Fig. 4) is fully consistent with the thermodynamic model of hardness [24,25].

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Table 1 C_{11} elastic constants, melting temperatures (T_m), and Vickers hardness (H_V) of cubic boron pnictides, and pnictogen Mendeleev numbers (MN) according to USE. Uncertainties of the values (when available) are given in parentheses next to the values.

	C_{11} (GPa)	T_m (K)	H_V (GPa)	MN [20]
BN	820 [15]	3250(50) ^{<i>pw</i>}	49 [21,22]	94
BP	336 [17]	2840(40) [7]	34(2) [23]	81
BAs	268 [10]	2410(30) [8]	22(3) [6]	71
BSb	182 [10]	1890 ^{<i>pw</i>}	18 [10]	56
BBi	124 [10]	1525 ^{<i>pw</i>}	14 [10]	51

pw – present work

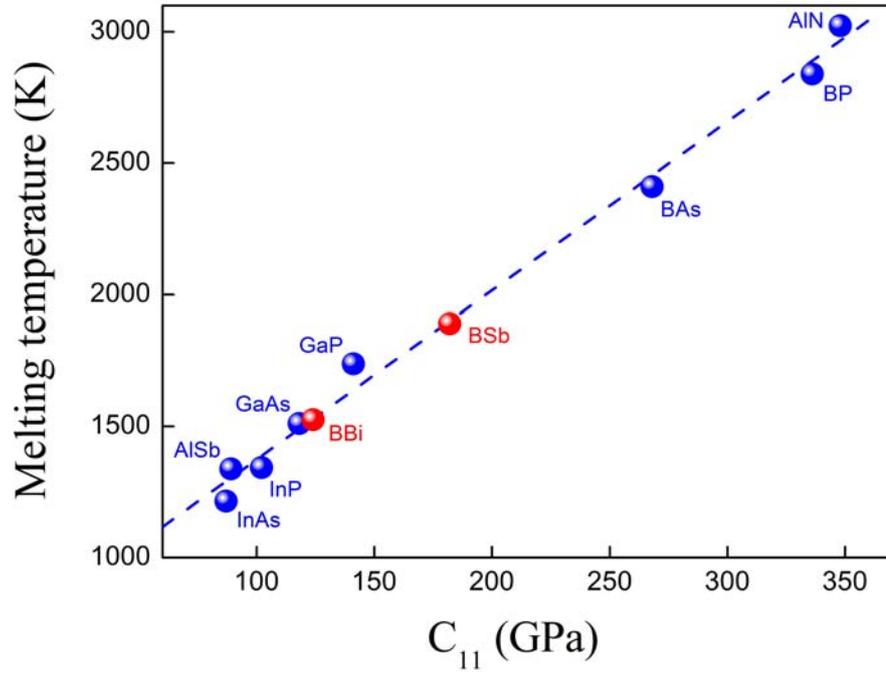


Figure 1 Relationship between melting temperatures and C_{11} elastic constants for cubic pnictides of group IIIa elements. The dashed line is a least squares fit to the data.

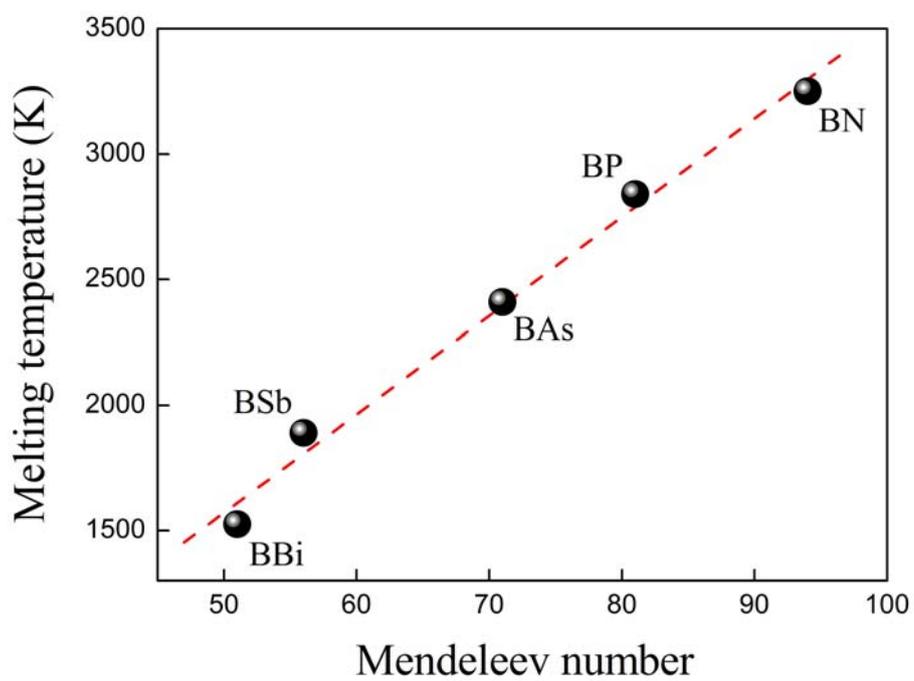


Figure 2 Relationship between melting temperatures of cubic boron pnictides and pnictogen Mendeleev numbers. The dashed line is a least squares fit.

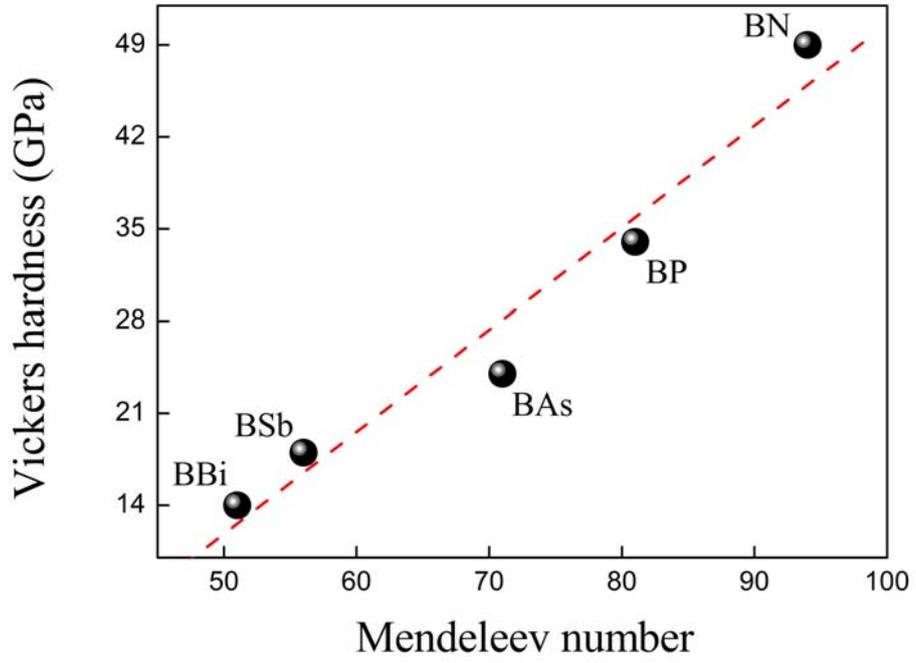


Figure 3 Relationship between Vickers hardness of cubic boron pnictides and pnictogen Mendeleev numbers. The dashed line is a least squares fit.

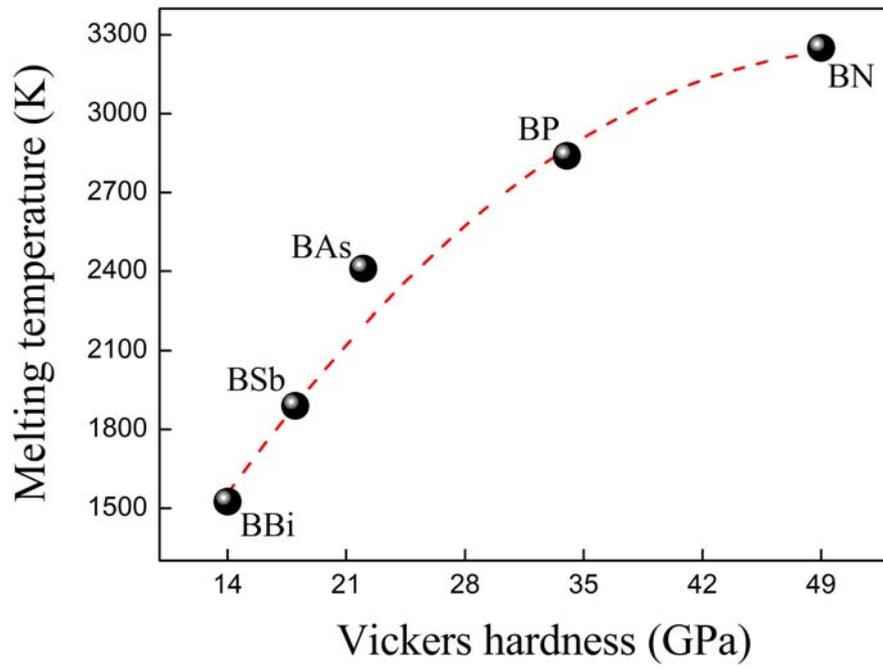


Figure 4 Relationship between melting temperatures and Vickers hardness of cubic boron pnictides. The dashed line is provided for illustrative purposes only.