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On melting of boron arsenide under pressure

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Melting of cubic boron arsenide, BAs, has been studied at pressures up to 8 GPa using *in situ* electrical resistivity measurements. It was found that above 2.5 GPa BAs melts congruently, and the melting curve has a negative slope (-53 ± 5 K/GPa), indicating a higher density of the melt as compared to the solid phase. The melting point of BAs at ambient pressure has been estimated to be 2410(30) K.

Keywords: boron arsenide, melting, high pressure, high temperature

Cubic (*F*-43*m*) boron arsenide, BAs, is a semiconductor with an indirect band gap of ~ 1.5 eV [1] and a Vickers hardness of 22 GPa [2], characterized by an interesting combination of mechanical [2], thermal and electrical properties [3], and an ultra-high thermal conductivity (second only to diamond) [4], making it a material of choice for a wide range of engineering applications. Moreover, BAs is of particular interest because it is the most covalent III-V compound with a Phillips ionicity $f_i = 0.002$ [5].

At ambient pressure, the decomposition of boron arsenide is observed already at 1400 K [6], so the melting point of BAs has not been established. One would expect the decomposition temperature of BAs to be higher under pressure, but so far the high-pressure behavior of boron arsenide has only been studied at room temperature [7]. In the present work, the melting of boron arsenide at pressures up to 8 GPa has been studied for the first time.

Single-phase polycrystalline cubic BAs was synthesized by reaction of amorphous boron (Grade I ABCR) and arsenic (Sigma-Aldrich, 99.997%) at 4 GPa and 1600 K according to the method described elsewhere [8]. The lattice parameter of the sample was $a = 4.777(1)$ Å, which is in good agreement with the literature value ($4.7776(2)$ Å [9]).

Melting of boron arsenide in the pressure range 2.5–7.7 GPa was studied *in situ* by electrical resistivity measurements [10] in a specially designed high-temperature cell [11] of a toroid-type high-pressure apparatus. The cell was pressure-calibrated at room temperature using phase transitions in Bi (2.55 and 7.7 GPa), PbSe (4.2 GPa), and PbTe (5.2 GPa). Temperature calibration under pressure was performed using well-established reference points: melting of Si, NaCl, CsCl, Pt, Rh, Al₂O₃, Mo and Ni–Mn–C ternary eutectics. No evidence of chemical

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interaction between BAs and graphite electrical inputs was observed over the entire pressure-temperature range studied. The experimental data are shown in Figure 1.

The BAs melting curve (dashed line obtained by the least-squares method) has a negative slope of $-53(5)$ K/GPa, indicating the higher density of BAs melt as compared to the solid phase in the pressure range studied. A similar melting behaviour has been previously observed for cubic boron phosphide, BP [12]. Extrapolation of the BAs melting line to the low-pressure region allows us to estimate the melting point of boron arsenide at ambient pressure to be $2410(30)$ K, which is ~ 400 K lower than the melting temperature of boron phosphide [12]. The lattice parameters of the samples quenched from different pressures immediately after melting (overheating not exceeding 100 K) are very close to the literature value, and no lines of other phases ($B_{12}As_2$, arsenic, boron, etc.) are present in the diffraction patterns, indicating the congruent type of BAs melting at pressures above 2.5 GPa.

At significant (> 300 K) overheating relative to the melting line, the BAs melt appears to be unstable and undergoes disproportionation into arsenic and boron subarsenide $B_{12}As_2$, whose diffraction lines are present in the X-ray diffraction patterns of the quenched samples.

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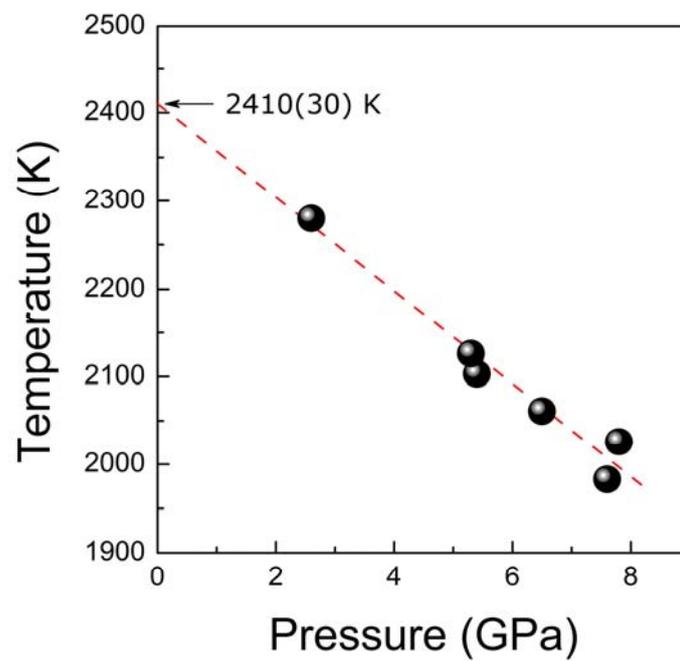


Figure 1 Pressure dependence of BAs melting temperature. Dashed line is the linear approximation of the melting curve defined by the least-squares method.