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On the melting of boron chalcogenides B₆S and B₆Se under pressure

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Melting of new of boron-rich chalcogenides, orthorhombic B₆S and B₆Se, has been studied at pressures up to 8 GPa using *in situ* electrical resistivity measurements. It was found that above 2.5 GPa both chalcogenides melt congruently, and the melting curves have a negative slope (-61(5) K/GPa for B₆S and -80(2) K/GPa for B₆Se), indicating a higher density of the melts compared to the solid phases. The melting points at ambient pressure were estimated to be 2190(30) K for B₆S and 2347(12) K for B₆Se.

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

Two novel boron-rich chalcogenides, B₆S and B₆Se, have recently been synthesized by chemical interaction of elemental boron with sulfur and selenium melts at high pressures and high temperatures [1]. Both phases have orthorhombic symmetry and belong to the same space group *Pmna*, which is unusual for boron-rich compounds of light elements. Both chalcogenides are low-compressible phases [1,2] characterized by high Vickers hardness [1] and relatively high oxidation resistance [3]. In the present study, the melting of new boron chalcogenides was investigated at pressures up to 8 GPa.

Single-phase polycrystalline orthorhombic B₆S and B₆Se were synthesized by reaction of amorphous boron (Grade I ABCR) with sulfur and selenium (both Alfa Aesar, 99.5%) at 6.1 GPa and 2700 K in a toroid-type high-pressure apparatus according to the method described previously [1]. Melting of both boron chalcogenides in the pressure range of 2.5–8 GPa was studied *in situ* by electrical resistivity measurements [4] in a specially designed high-temperature cell [5] 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 interaction between the samples and graphite electrical inputs was observed over the entire pressure-temperature range studied. The samples recovered from high-pressure experiments were characterized by powder X-ray diffraction (Equinox 1000 Inel diffractometer; Cu K α radiation).

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The experimental data are shown in the Figure. The melting curves of B₆S and B₆Se (dashed lines obtained by the least-squares method) have negative slopes of $-61(5)$ K/GPa and $-80(2)$ K/GPa, respectively, indicating the higher density of the melts of both boron chalcogenides compared to the solid phases in the pressure range studied. A similar melting behavior has been previously observed for the orthorhombic boron silicide B₆Si (the melting slope is $-31(2)$ K/GPa) [6]. Conversely, in the case of rhombohedral boron-rich compounds of light elements (B₆O, B₁₃N₂, B₁₂P₂), the melting slopes are positive [7-9] and vary from $23(6)$ K/GPa for B₁₂P₂ [9] to ~ 60 K/GPa for B₆O [7]. Such a significant difference in the melting behavior of boron-rich solids with orthorhombic and rhombohedral crystal structures is apparently due to the difference in the structure (and hence the density) of their melts.

Extrapolation of the melting lines to the low-pressure region allows the estimation of the melting points at ambient pressure of $2190(30)$ K for B₆S and $2347(12)$ K for B₆Se, which is close to the melting temperature of rhombohedral boron β -B₁₀₆ (~ 2360 K [10]).

The lattice parameters of the samples quenched from different pressures immediately after melting (overheating relative to the melting curve did not exceed 100 K) are exactly the same as those of the pristine B₆S and B₆Se, and no lines of other phases are present in the diffraction patterns, indicating the congruent type of melting of both boron chalcogenides above 2.5 GPa.

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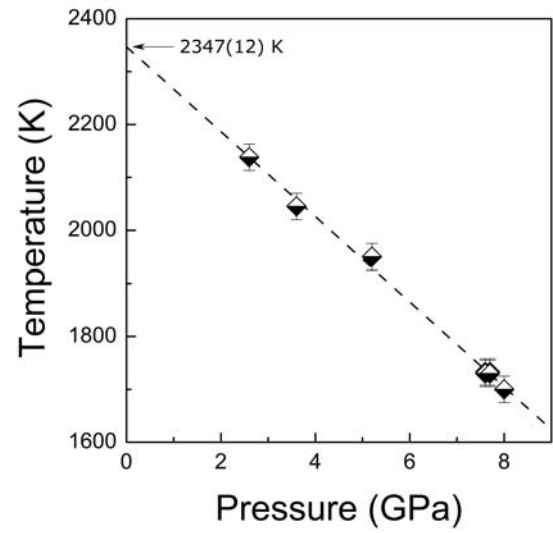
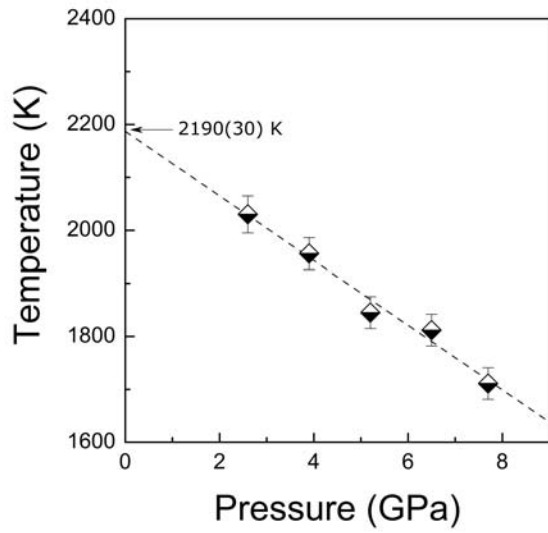


Figure Melting temperatures of orthorhombic B_6S (left) and B_6Se (right) versus pressure. Half-filled diamonds show the onset of melting as determined *in situ* by electrical resistivity measurements. Dashed lines are the linear approximations of the melting curves.