Structure of intermediate high pressure phase of PbX compounds

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The lead chalcogenides PbX (X=Te, Se, S) are narrow-gap semiconductors (group IV-VI), which crystallise at ambient conditions in the cubic NaCl (B1) structure. It has been known for 20 years that they transform at 6, 4.5 and 2.2 GPa, respectively, to an intermediate phase, and at higher pressures (between 13 and 22 GPa) to the 8-fold coordinated CsCl (B2) structure. The intermediate phase has been referred to as being of the "GeS" type (B16, space group Pbnm) rather than of the "TlI" type as suggested for PbS and PbSe (B33, space group Cmcm), but there is evidence that this is incorrect [1,2]. This is also in contrast to computational results which affirm that all three systems PbTe, PbS and PbSe indeed adopt the TlI structure [3].

In this presentation, we report recent X-ray powder diffraction obtained at synchrotron sources on PbX compounds under pressure, that allowed us to solve the structure of the intermediate phase of PbTe, from simulated annealing techniques and Rietveld refinement : the phase transition at 6 GPa is not to the GeS (B16) or TlI (B33) type structures as previously reported, but to an orthorhombic Pnma structure, with cell parameters a=8.157(1), b=4.492(1), c=6.294(1) Ǻ at 6.7 GPa. This structure corresponds to a distortion of the low pressure NaCl structure with a coordination intermediate between the six-fold B1 and the eightfold B2 structure. These new results may modify the admitted paths of phase transitions between the B1 (NaCl) and B2 (CsCl) structures. We will also reconsider the intermediate high pressure phases of PbS and PbSe.

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