Compressing secondary arsenic···halogen bonds: high-pressure X-ray diffraction study of As_2O_3 intercalation compounds

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Arsenic atoms form in arsenic(III) oxycompounds three strong primary bonds and, in addition to that, up to three weaker secondary bonds which are localized *trans* with respect to primary bonds [1]. It has recently been demonstrated that arsenic···halogen (hereafter denoted As···Hal, where Hal stands for Cl, Br and I) secondary bonds exist in arsenic(III) oxide intercalates, and their nature is analogous to that of secondary As···O bonds [2]. Herein, we will present the results of high-pressure structural studies of three As_2O_3 intercalates, which have been carried out to investigate the influence of pressure on As···Hal secondary bonds and to compare it to the pressure variation of As···O secondary bonds.

Crystal structures of arsenic(III)-oxide intercalation compounds with ammonium chloride ($NH_4Cl{\cdot}As_2O_3{\cdot}{}^1/_2H_2O$), ammonium bromide ($NH_4Br{\cdot}2As_2O_3$), and ammonium iodide ($NH_4I{\cdot}2As_2O_3$) have been determined under high pressure up to 15, 11 and 15 GPa, respectively. The compression of As···Hal secondary bonds, expressed as penetration indices of the bonds [3], has been shown to be a linear function of unit cell volume ratio V/V_0, where V_0 is the unit cell volume at ambient pressure, with similar slopes as the compression of As···O secondary bonds (see Fig. 1). The behavior of arsenic first-order valence entropy coordination number at high pressures and the stereoactivity of arsenic lone electron pairs in the studied intercalates is the same as in arsenic(III) oxide polymorphs – the former decreases linearly with V/V_0, while the latter remains unchanged [4]. The high-pressure study lends further support to the fact that the nature of As···Hal and As···O secondary bonds is the same

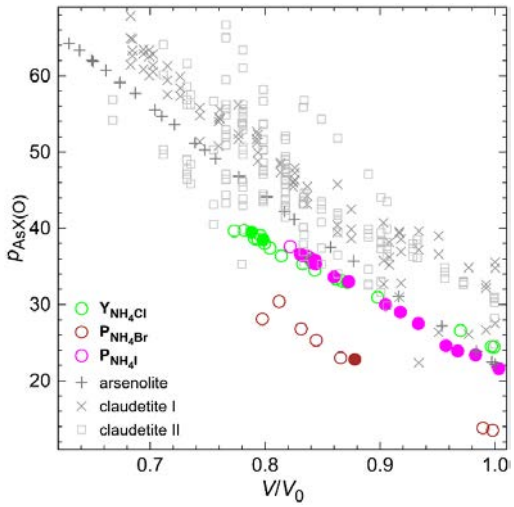

Figure 1. Penetration indices of As···X and As···O secondary bonds in the studied intercalates and As_2O_3 polymorphs plotted as a function of V/V_0 unit cell volume ratio.

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