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Bulk moduli and high-pressure crystal structures of minium, Pb_3O_4, determined by X-ray powder diffraction

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ABSTRACT

We report the pressure dependence of the crystal structure of lead tetroxide ($p \leq 41.05$ GPa, $T = 298$ K) using high-resolution angle-dispersive X-ray powder diffraction. Pb_3O_4 shows two reversible phase transitions in the measured pressure range. The crystal structures of the modifications identified have in common frameworks of $Pb^{+4}O_6$ octahedra and irregular $Pb^{+2}O_{4+1}$ respectively $Pb^{2+}O_{6+1}$ polyhedra. At ambient conditions, Pb_3O_4 crystallizes in space group $P4_2/mbc$ (phase I). Between 0.11 and 0.3 GPa it exhibits a displacive second order phase transition to a structure with space group *Pbam* (phase II). A second displacive phase transition occurs between 5.54 and 6.6 GPa to another structure with space group *Pbam* (phase III) but halved *c* dimension. A non-linear compression behavior over the entire pressure range is observed, which can be described by two Vinet relations in the ranges from 0.28 to 5.54 GPa and from 6.6 to 41.05 GPa. The extrapolated bulk moduli of the high-pressure phases were determined to be $K_0 = 21(2)$ GPa for phase II and $K_0 = 91(3)$ GPa for phase III. The crystal structures of all phases were refined from X-ray diffraction powder data collected at several pressures between 0.06 and 41.05 GPa. Except for their cell dimensions, phases I and II were found to be isostructural to the corresponding phases at low temperatures, whereas phase III can be derived from the Sr_2PbO_4 aristotype. With increasing pressure, the lone pair which is localized at Pb^{2+} adopts increasingly pure *s*-character, which is reflected by the similar coordination polyhedra of Pb^{2+} in Pb_3O_4 (phase III) and of Sr^{2+} in Sr_2PbO_4.