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Pb₁₂O₁₉ –ML-DFT-PDF crystal structure analysis from combined neutron and synchrotron total scattering data.

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Mixed valence lead oxide phases obtained at ambient pressure are reported by Byström [1] belonging to either black [2] or red minium [1, 3]. For red minium the composition of Pb₃O₄ is described without any variance in the number of oxygen atoms [1, 3]. The formula could therefore be written as Pb(II)₂Pb(IV)O₄, expressing the different oxidation states of lead. For the black minium Byström [1] proposed two structures, namely, α-PbO_x and β-PbO_x. Pure α-PbO_x exits for 1.628 (~ Pb₁₂O_{19.5}) > x ≥ 1.475 (~ Pb₁₂O_{17.7}). For lower x, β-PbO_x and red minium coexist in the range of x = 1.475 –1.352 (~ Pb₁₂O_{16.2}). We synthesized phase pure Pb₁₂O₁₉ by decomposing PbO_{1.96(2)} at 600 K for 1390 h, showing a dark brown color. Neutron time-of-flight (TOF) total scattering data (nPDF) were collected on the powder diffractometer POWGEN@SNS (Oak Ridge National Lab, USA) within the Proposal IPTS-20531 and respective synchrotron radiation data (xPDF) on the P02.1@Petra III (DESY, Germany) powder diffractometer at E = 59.78(3) keV (λ = 20.74(4) pm). The combined machine-learning (ML) –density function theory (DFT) –pair distribution function (PDF) approach [4] was used to refine the structure of Pb₁₂O₁₉ starting with an unbiased set of structural models using both neutron and X-ray PDF data sets at the same time. Based on the ML-DFT-xPDF-nPDF refinements a structure model with a 2x2x1 bigger unit cell compared to those reported by Byström [1] was found. Instead of the CaF₂-type [1] derived arachno-cube like coordination of the lead atoms, which could hardly be described as strongly distorted octahedra, different coordination numbers were found, giving rise for differently pronounced stereochemical activities of the Pb 6s² lone pairs and void channels in the structure which might be described with a triangular shape. The new crystal structure enables to additionally describe the non-explained weak reflections of the earlier findings [1].

1] A. Byström, Arkiv Kemi Mineral. Geol. 20(4) (1945) 1-31.
[2] M. Le Blanc, E. Eberius, Z. für Phys. Chem. 160A(1) (1932) 69-100.
[3] S.T. Gross, J. Am. Chem. Soc. 65(6) (1943) 1107-1110.
[4] M. Klove, S. Sommer, B.B. Iversen, B. Hammer, W. Dononelli, Adv Mater (2023) e2208220.

Figure: PDF-Plots of the refinement of the Pb₁₂O₁₉ structure to the synchrotron (a) and neutron data (b).

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Sitzung Einordnung: Session 2: Condensed Matter (Chairs: Werner Paulus, Holger Kohlmann & Simon Steinberg)

Track Klassifizierung: Condensed Matter