Control of A-site cation order and concentration in Prussian blue analogues

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Prussian blue analogues (PBAs) are a structurally diverse family of materials, considered as cyanide-based versions of double perovskites with the general formula $A_xM[M'(CN)_6]_y$. Here, A is denoting an alkali metal cation, M/M' are transition metal ions, x = A-site cation concentration and y = defects/vacancies [1–2]. Such variability in structure and stoichiometry enables several different applications, for example, in batteries, sensors or catalysis [3–6].

The ordering of A-site cations can enable or enhance piezoelectric and ferroelectric behaviour. Typically, PBAs adapt cubic symmetry in a centrosymmetric space group, which precludes piezoelectricity. However, the alternating order of A-site cations results in a symmetry lowering, and a breaking of inversion symmetry occurs, as required for piezo- and ferroelectricity.

Hence, it is important to develop methods to control the A-site cation order, which can be synthetically difficult. The choice of synthetic method can affect reproducibility, and hydration of the A-site cation in the typical water-based synthesis is believed to affect the final structure. In this work, we synthesise PBAs solvent-free *via* a mechanochemical method at varying milling frequencies (f) and milling times (t). The studied system has the general composition: $A_xMn[Co(CN)_6]_y$, where A = Cs, Rb, or K. Preliminary results indicate a correlation between A-site cation concentration, A-site cation ordering, and milling frequency. This study presents the road to the control of A-site cation ordering and occupancy through mechanochemical synthesis by ball milling using powder X-ray diffraction as primary analytical technique [Fig. 1].

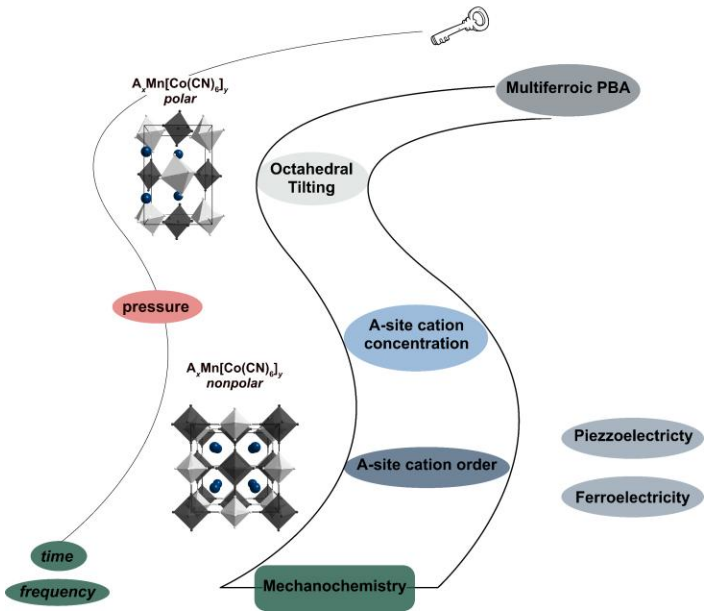


Figure 1. *Schematic overview of the synthetic road to a multiferroic PBA using mechanochemistry.*

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