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Structure-composition relationships in layered perovskite-related materials

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Layered perovskite-related materials have garnered significant attention in recent years owing to their fascinating physical properties such as ferroelectricity, piezoelectricity, antiferroelectricity[1-4] and technological applications.[5] Dion-Jacobson (DJ) phases, a type of layered perovskite-related material, have emerged as an intriguing class of materials with crystal structure comprising of perovskite layers separated by an intrusive alkali metal (e.g., Rb^+, Cs^+) layer (Fig. 1a).[6, 7] Our preliminary neutron powder diffraction (NPD) data together with the density functional theory (DFT) calculations for $A'A_2B_3O_{10}$ (A'=Rb,Cs; A=Ca, Sr, Ba; and B=Nb,Ta) suggest that tolerance factor plays an important role in explaining the structure and stability of these materials.

Aurivillius phases (AP) are a type of layered perovskite-related material where the perovskite like layers are separated by fluorite like $[Bi_2O_2]^{2+}$ layers.[7] We have synthesised several series of n = 2 APs ($Bi_2A_{0.5}La_{0.5}B_2O_9$ (A = Na, K and B = Nb, Ta)) to investigate the relative energies of polar and non-polar states and whether this can be tuned by composition. This work is motivated by the observation of a non-polar ground state of *Pbcn* symmetry (Fig. 1b) for the A-site deficient Aurivillius phase $Bi_2W_2O_9$, an A-site deficient Aurivillius phase, and the prediction of a metastable polar phase (of $A2_1am$ symmetry).[8] This suggests it might be possible to tune between polar and non-polar ground states in this family, raising the possibility of antiferroelectric behaviour in Aurivillius and related phases.[8]

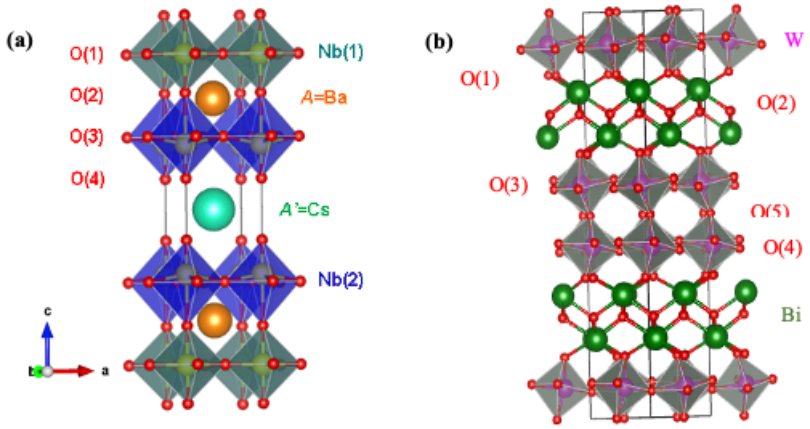

Figure 1. Crystal structure of (a) n=3 DJ Phase showing high symmetry *P*4/*mmm* model (b) n=2 AP showing distorted orthorhombic *Pbcn* model. Cs, Ba, Bi, W, Nb and O sites are shown in cyan, orange, green, pink, yellow, and red, NbO_6 octahedra are shown in blue, and WO_6 octahedra in grey, respectively.

The aim of our project is to understand the geometric and electronic factors that stabilise polar vs antipolar phases in layered perovskite-related materials, and whether their relative energies can be tuned by composition. Insights from this work will be useful for designing new ferroelectric and antiferroelectric materials.

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