Aurivillius oxyfluorides: nuclear and magnetic order and the role of the anion sublattice

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The Aurivillius materials are well known for their ferroelectric properties [1] and associated structural distortions.[2] They form a class of layered perovskite-related phases with general formula $Bi_2A_{n-1}B_nX_{3n+3}$ (X is usually oxide, but halides are also known), with structures built up from alternating fluorite-like $[Bi_2O_2]^{2+}$ layers and $[A_{n-1}B_nX_{3n+1}]^{2-}$ perovskite-like layers. The search for magnetoelectrics, with coupled magnetic and ferroelectric order, has motivated investigations to introduce magnetic ions into the B cation sites. However, this has been challenging and the concentrations of magnetic B cations in Aurivillius oxides is typically low. [3-5] Redirecting research away from oxides and towards mixed-anion systems, including Aurivillius oxyfluorides, opens up a wider compositional range, as well as the possibility of tuning structure and properties by anion order.[6, 7]

This presentation describes work on $n = 1$ Aurivillius oxyfluorides including $Bi_2TiO_4F_2$ and $Bi_2CoO_2F_4$. Our symmetry analysis [8] of possible anion-ordered structures highlights the challenges of packing polar heteroanionic units to break inversion symmetry, as well as means by which this might be achieved for $Bi_2TiO_4F_2$. We also explore methods to determine anion ordering in materials with anions with similar scattering lengths.[9]

Increasing the fluoride content in these oxyfluorides gives access to phases with lower oxidation states for B cations, and the report of $Bi_2CoO_2F_4$, with long-range magnetic order of the Co^{2+} sublattice,[10] motivated our investigation using neutron powder diffraction. We've explored its nuclear structure and in particular, the anion sublattice and structural distortions, and determined its magnetic structure.[11] This gives insight into its physical properties and opens the door to designing and preparing new multiferroics.

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