

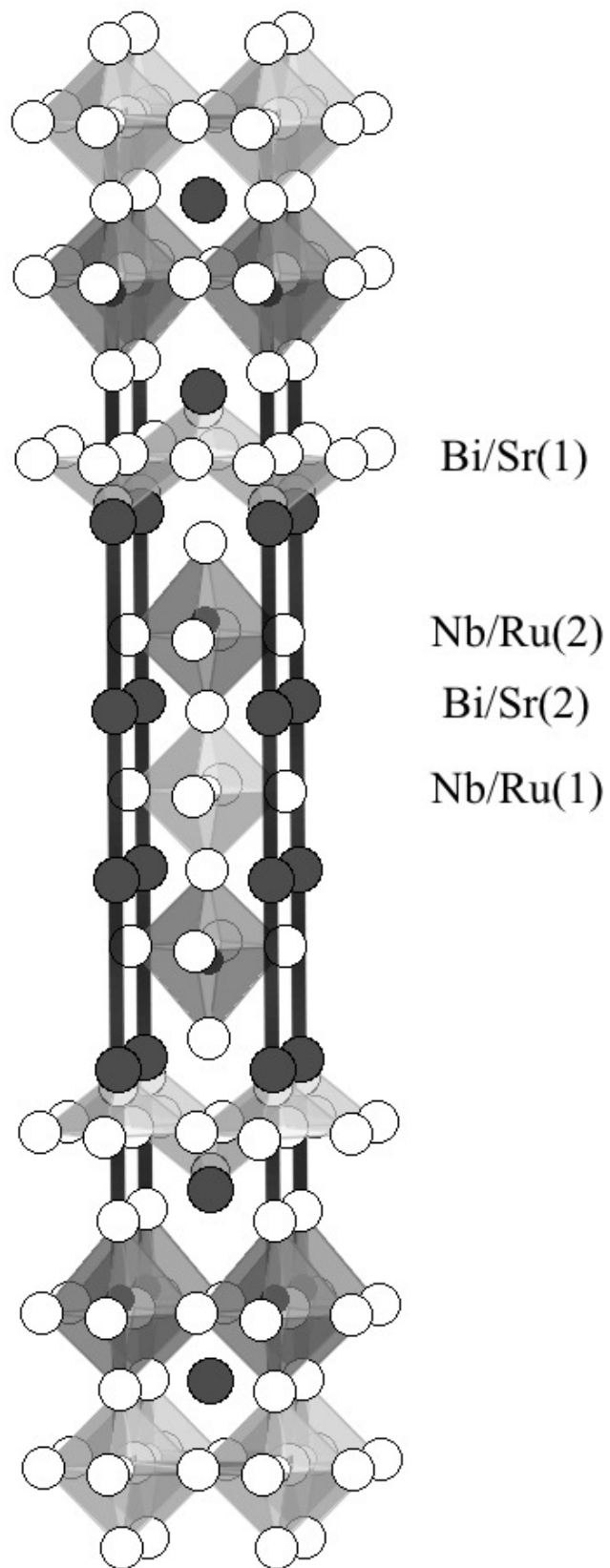
Layering of magnetic and non-magnetic cations in three-layer Aurivillius phases: crystallographic templates for multiferroicity

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Aurivillius phases $[\text{Bi}_2\text{O}_2]\cdot[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ are layered oxides composed of α -PbO-type layers $[\text{Bi}_2\text{O}_2]^{2+}$ alternating with n perovskite-type layers [1, 2]. They are strongly ferroelectric [3, 4] due to the rotation of BO_6 octahedra, lowering the symmetry from tetragonal to orthorhombic or monoclinic, and allowing the perovskite A- and B-site cations to be displaced relative to the oxygen anion array. Substituting magnetic transition metal cations into the central octahedral layer of the perovskite-type block, while maintaining ferroelectric displacements in the outer octahedral layers, therefore presents a possible route to multiferroic (magnetoelectric) materials. Three-layer ($n = 3$) Aurivillius phases present the greatest contrast between the coordination environments of the B-site cations in the central and outer octahedral layers of the perovskite-type block, maximizing the potential for layered B-site ordering. In this paper we will report the synthesis, structural and physical property characterization of a new series of phases $\text{Bi}_{2-x}\text{Sr}_{2+x}(\text{Nb},\text{Ta})_{2+x}(\text{Ru},\text{Ir},\text{Mn})_{1-x}\text{O}_{12}$, which represent the first incorporation of the magnetic transition metal cations Mn^{4+} , Ru^{4+} and Ir^{4+} into Aurivillius phases. The key appears to be the partial substitution of Sr^{2+} for Bi^{3+} in the α -PbO-type layer of the Aurivillius phase, leading to a concomitant decrease in the M^{4+} content. These compounds only exist over a narrow range of x , between an apparent minimum ($x \approx 0.4$) Sr^{2+} content in the α -PbO-type $[\text{Bi}_2\text{O}_2]$ layer required for Aurivillius phases to form with magnetic M^{4+} cations, and an apparent maximum ($x \approx 0.6$) Sr^{2+} substitution in this $[\text{Bi}_2\text{O}_2]$ layer. Rietveld-refinement of neutron powder diffraction and synchrotron X-ray powder diffraction data using of anomalous dispersion at the Nb and Ru K edges show that the overwhelming majority of the incorporated M cations occupy the central of the three MO_6 octahedral layers in the perovskite-type block.



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