

Designing new $n = 2$ Sillen-Aurivillius phases by lattice-matched substitutions in the halide and $[\text{Bi}_2\text{O}_2]^{2+}$ layer

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The chemical and structural flexibility of the perovskite structure, which makes it so ubiquitous in nature and useful in a range of technological applications, extends to layered variants such as Ruddlesden-Popper, Dion-Jacobson and Aurivillius phases. Multi-layered variants such as the Sillen-Aurivillius phases are related to Aurivillius phases by the insertion of an additional halide layer between every second $[\text{Bi}_2\text{O}_2]^{2+}$ layer [1].

Sillen-Aurivillius phases exist in various $AnXm$ combinations, where n is the number of perovskite layers A and m the number of halide layers X . We have synthesised a new $n = 2$ Sillen-Aurivillius compound $\text{Bi}_3\text{Sr}_2\text{Nb}_2\text{O}_{11}\text{Br}$ [2] based on $\text{Bi}_3\text{Pb}_2\text{Nb}_2\text{O}_{11}\text{Cl}$ [3] by simultaneously replacing Pb^{2+} with Sr^{2+} and Cl^- with Br^- . Rietveld refinements against X-ray and neutron powder diffraction data revealed a significant relative compression in the stacking axis (c axis) in contrary to the belief of inserting a significantly larger halide layer in the new compound. We could not stabilise other combinations such as $\text{Bi}_3\text{Sr}_2\text{Nb}_2\text{O}_{11}\text{Cl}$ and $\text{Bi}_3\text{Pb}_2\text{Nb}_2\text{O}_{11}\text{Br}$ due to inter-layer mismatch.

Sr^{2+} doping reduces the impact of the stereochemically active $6s^2$ lone pair found on Pb^{2+} and Bi^{3+} , resulting in a contraction of the c axis by 1.22 % and an expansion of the a - b plane by 0.25 %, improving inter-layer compatibility with Br^- . XANES analysis shows that the ferroelectric distortion of the B-site cation is less apparent in $\text{Bi}_3\text{Sr}_2\text{Nb}_2\text{O}_{11}\text{Br}$ compared to $\text{Bi}_3\text{Pb}_2\text{Nb}_2\text{O}_{11}\text{Cl}$. Variable-temperature neutron diffraction data show no evidence for a ferroelectric distortion.

[1] B. Aurivillius, *Chemica Scripta* 23 (1984) 143-156.

[2] S. Liu, P. E. R. Blanchard, M. Avdeev, B. J. Kennedy, C. D. Ling, *Journal of Solid State Chemistry* 205 (2013) 165-170.

[3] A. M. Kusainova, P. Lightfoot, W. Z. Zhou, S. Y. Stefanovich, A. V. Mosunov, V. A. Dolgikh, *Chemistry of Materials* 13 (2001) 4731-4737.