

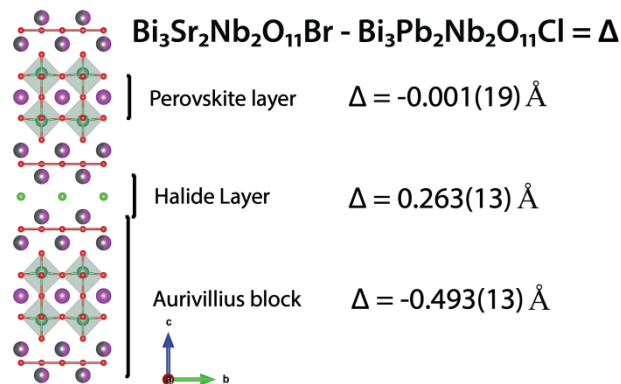
## Designing new $n = 2$ Sillen-Aurivillius phases by lattice-matched substitutions in the halide and $[\text{Bi}_2\text{O}_2]^{2+}$ layer

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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. Ferroelectric and ferromagnetic properties have been particularly important drivers of research into layered perovskite phases. Sillen-Aurivillius phases are related to Aurivillius phases by the insertion of an additional halide layer between every second  $[\text{Bi}_2\text{O}_2]^{2+}$  layers [1].

Sillen-Aurivillius phases exist in various  $A_nX_m$  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  $\text{Pb}^{2+}$  with  $\text{Sr}^{2+}$  and  $\text{Cl}^-$  with  $\text{Br}^-$ . Rietveld refinements against X-ray and neutron powder diffraction data revealed a significant relative compression in the stacking axis ( $c$  axis) of 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.



**Fig. 1.** The structure of the  $A_2X_1$  Sillen-Aurivillius phase where  $\Delta$  denotes differences between key distances in  $\text{Bi}_3\text{Sr}_2\text{Nb}_2\text{O}_{11}\text{Br}$  and  $\text{Bi}_3\text{Pb}_2\text{Nb}_2\text{O}_{11}\text{Cl}$ .

In our new compound,  $\text{Sr}^{2+}$  doping reduces the impact of the stereochemically active  $6s^2$  lone pair found on  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$ , resulting in a contraction of the  $c$  axis by 1.22 % and an expansion of the  $a$ - $b$  plane by

0.25 %. This improves the inter-layer compatibility with the larger halide  $\text{Br}^-$ . The  $\text{NbO}_6$  octahedra themselves in the  $n = 2$  perovskite layer are less distorted the parent compound and other  $n = 2$  Aurivillius phases ( $\text{Bi}_2\text{PbNb}_2\text{O}_9$  and  $\text{Bi}_2\text{SrNb}_2\text{O}_9$ ).

Analysis of X-ray absorption near-edge spectroscopy data show 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* (Accepted July 8, 2013)

[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.