Chemical doping in Sillen-Aurivillius phases: Perovskites in low dimensional multi-layer structure types

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This study introduces two examples of structure property relationships within the multilayered Sillen-Aurivillius family (shown in Figure) and investigates the effect of chemical doping and lattice matching. The first example involves doping 1/3 of the \(n = 3\) ferroelectric perovskite layers with magnetic transition metal cations in Bi\(_5\)PbTi\(_3\)O\(_{14}\)Cl \[1\] with charge balancing by removing Pb\(^{2+}\) for Bi\(^{3+}\). Magnetic doping was confirmed by Rietveld analysis against X-ray diffraction data. Neutron diffraction data revealed a statistical 1:2 distribution of M\(^{3+}\) and Ti\(^{4+}\) across all three perovskite layers for Bi\(_6\)Ti\(_2\)M\(_{O14}\)Cl, \(M = Cr^{3+}, Mn^{3+}, Fe^{3+}\)[2]. These highly strained structures have higher Curie temperatures compared to Bi\(_5\)PbTi\(_3\)O\(_{14}\)Cl and pronounced spin-glass behaviour below \(T_{\text{irr}}(0) = 4.46\) K. Ferroelectric properties were also measured on Bi\(_6\)Ti\(_2\)FeO\(_{14}\)Cl using piezoresponse force microscopy showing hysteretic behavior.

The second example is a new \(n = 2\) Sillen-Aurivillius compound Bi\(_3\)Sr\(_2\)Nb\(_2\)O\(_{11}\)Br \[3\] based on Bi\(_3\)Pb\(_2\)Nb\(_2\)O\(_{11}\)Cl \[4\] by simultaneously replacing Pb\(^{2+}\) with Sr\(^{2+}\) and Cl\(^-\) with Br\(^-\). Inter-layer mismatch prevented the formation of Bi\(_3\)Sr\(_2\)Nb\(_2\)O\(_{11}\)Cl and Bi\(_3\)Pb\(_2\)Nb\(_2\)O\(_{11}\)Br. Sr\(^{2+}\) doping reduces the impact of the stereochemically active 6\(\sigma^2\) lone pair found on Pb\(^{2+}\) and Bi\(^{3+}\), resulting in a stacking contraction in the lattice parameters by 1.22 \% and an expansion of the \(a\)-\(b\) plane by 0.25 \%, improving inter-layer compatibility with Br\(^-\). X-ray Absorption Near Edge Structure analysis shows that the ferroelectric distortion of the B-site cation is less apparent in Bi\(_3\)Sr\(_2\)Nb\(_2\)O\(_{11}\)Br compared to Bi\(_3\)Pb\(_2\)Nb\(_2\)O\(_{11}\)Cl. Variable-temperature neutron diffraction data show no evidence for a ferroelectric distortion.