Heterovalent doping of a 1D hybrid pseudo-perovskite: B site vacancy and short-range order

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Hybrid halide perovskites are currently at the forefront of energy materials research for their appealing optical and electronic features, but applications in working devices are still hindered by chemical/structural stability. To enhance their properties, new hybrid compounds with a wide range of different organic cations have been proposed in the last years. The choice of bulky organic cations can reduce the dimensionality of the inorganic scaffold from 2D to 0D. These lower-dimensional perovskites, best defined as pseudoperovskites, feature useful structural flexibility that can be further exploited to enhance the materials properties. We present here monodimensional hybrid iodide pseudo-perovskites, with Pb^{2+} and Bi^{3+} as B site cations, and $(CH_3)_3SO^+$ (TMSO) in the A site. The Pb or Bi end members are isomorphic, and crystallize in the *Pnma* space group with wires of $[BX_6]$ octahedra along the **a** direction. As shown in the figure, the chains are continuous for the Pb sample, or interrupted, for the Bi sample, with a B-site vacancy every third site to maintain charge balance. We prepared doped samples with general formula $((TMSO)_3Pb_{3x}Bi_{2(1-x)}I_9$ with complete miscibility between ($0 \leq x \leq 1$) [1]. In the **a** direction, the structure is especially sensitive to Bi and cation vacancy (whose stoichiometry is (1-x) in the formula above) content. Interestingly, the XRD patterns of the samples with high Bi content (e.g. $x = 0.33$) feature a peculiar broadening of *hkl* peaks having non-zero *h*, while *0kl* peaks remain sharp (Figure 1). This broadening points out to a short-range order in the sequence of Pb-Bi-vacancy of the doped structure chains that can be successfully modeled using a stochastic matrix approach to model the Pb/Bi/V probability sequences and reconstruct the experimental XRD traces. The influence of bismuth doping on the optical properties is also significant: even a few % loading of bismuth lowers the band gap by about 0.5 eV. Further characterization using X-ray spectroscopies (X-ray Raman scattering, XANES) to correlate the local electronic states to Bi content is underway. This work is a first insight into the effect of inorganic cation doping on short-range order and electronic properties of a 1D hybrid pseudo perovskite structure.

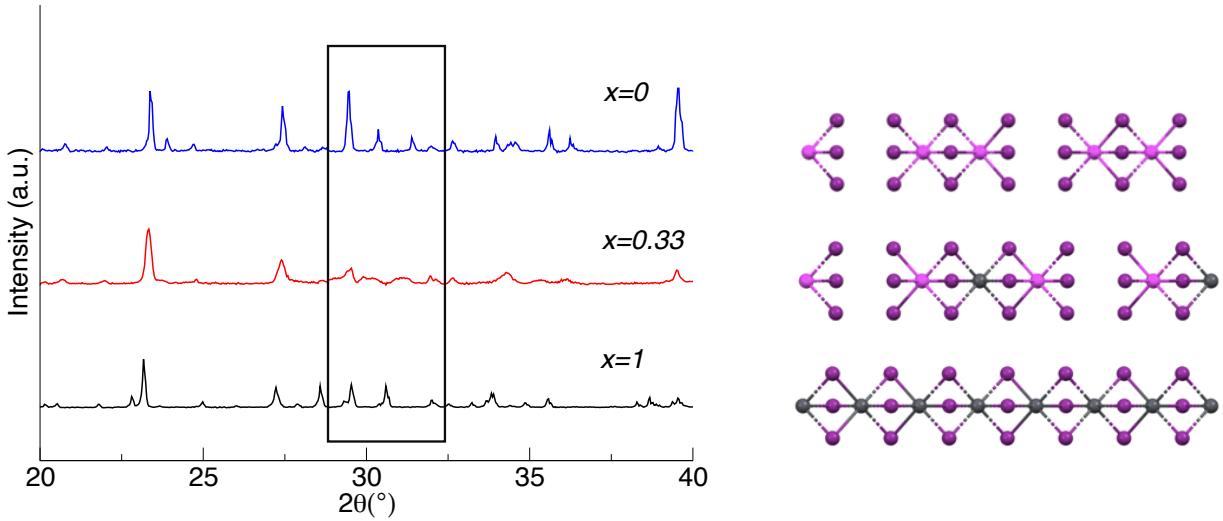

Figure 1 Magnification of XRD patterns of $((TMSO)_3Pb_{3x}Bi_{2(1-x)}I_9$ (x= *1, 0.33* and *0*) and chains connectivity.

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