Tolerance Factors and Solid Solutions in Three-Layer Aurivillius Ceramics

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The Aurivillius phases are of interest in ferroelectric random access memory devices. We present first a range of solid solubility data for isovalent and aliovalent doping in the 3-layer Aurivillius phases that were prepared using solid state and polymerized complex methods. A range of approximately 100 compositions were investigated, and many were evaluated using electrical conductivity measurements to determine the total conductivity and type of charge carriers.

Early reports of tolerance factors, similar to those developed by Goldschmidt for perovskites, have been revisited by considering strain between the structural layers and the total oxygen concentration. Neutron diffraction results that include bond valence sum calculations show that the static disorder that is often observed in the Aurivillius phases in the form of site mixing between the large cation in the perovskite block and Bi in the $[Bi_2O_2]^{2+}$ layer. The interlayer strains evidenced from the calculations are supported by the experimental results. Finally, the model is used to show that the average oxidation state of cations that can take mixed valence, for example the transition metals, is a function of the strains imposed by the layered structure.

Keywords: Perovskite structures, structural stability, ferroelectrics