Modular Approach Applied to Tailoring of Bismuth-Containing Layered Perovskites

Dmitri O. Charkin[a], Igor V. Kul'bakin[a] , Dmitri N. Moskvin[b], [a]*Department of Materials Sciences.* [b]*Department of Chemistry, Moscow State University,* E-mail: charkin@inorg.chem.msu.ru

Layered bismuth-containing perovskites and related oxyhalides are promising superconductors, ferroelectrics, ion conductors oxidation catalysts, *etc*. Most properties are very sensitive to chemical composition, but doping of different sites is restricted. Only recently it was understood that the problem could be overcome via more complicated mixed-layer structures involving additional new non-stoichiometric structural moduli (2D building blocks). To keep the charge balance, perovskitic layers must change their composition.

The general algorithm is suggested which consists of i) finding, by *a priori* modeling or otherwise, new 2D blocks, ii) elucidating their compositional range, both in chemistry and non-stoichiometry; iii) estimating the most reliable compositions of target mixed-layer structures, and iv) exploring full compositional range of the formed complex structures and establishing the structure - property relationship. Step ii) resulted in discovery of new unexpected structures involving novel building blocks.

The approach has been applied to structural modification of Aurivillius-type ferroelectrics and resulted in synthesis of over200 new compounds contributing to more than 20 novel structure types. Complication of a simple structure of Bi_2WO_6 with non-stoichiometric metal-halide layers permitted to partially substitute W^{VI} by more than 20 cations, the resulting Curie points ranging from 700°C to below r.t.

Keywords: bismuth compounds, perovskite layered compounds, ferrolelectric and related materials