

*On the stability boundaries of the LaOAgS structure type*Igor Plokhikh¹, Dmitry Charkin², Alexey Kuznetsov²¹Chemistry Department, Lomonosov Moscow State University, Moscow, Russian Federation, ²Lomonosov MSU, Moscow, Russian Federation

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Among layered inorganic structure types, that of LaOAgS, numbering over 200 representatives, has been studied extensively due to their promising physical properties (magnetic, thermoelectric, ion conducting, semiconducting, or superconducting). The relative simplicity of this structure type formed by anti-isostructural litharge and mackinawite-derived slabs suggests even larger number of representatives. However, out of over 500 possible candidates suggested from structure modeling, less than 50% could be realized synthetically. In order to gain deeper insight into the "crystal chemical stability boundaries", we employed a complex approach based on synthesis, geometry analysis, and computational estimates of relative structural stability.

Two groups of representatives were studied: i) LaOAgCh (Ch = S, Se, Te) chalcogenides, where stability was estimated (by calculating DFT ground-state energies) against La₂O₂Ch and Ag₂Ch, and ii) AFTPn (A = Ca, Sr, Ba, Eu; T = Zn, Mn, Cd; Pn = P, As, Sb, Bi) pnictides and AeFAITt (Ae = Sr, Ba; Tt = Si, Ge, Sn) tetrelides where stability was studied against binary alkaline-earth fluorides and ternary AT₂X₂ compounds (X = Group 14, 15, or 16 element).

For the group i), we found that these three compounds were energetically more preferable. Indeed, our attempts to prepare both known S and Se representatives and yet unknown telluride were successful, although the latter has not yet been obtained phase-pure. For the case ii), the calculated pattern agrees well with the experimental results and predictions from geometrical considerations. No Ca compounds were found to exist, and neither do the proposed SrFCdPn. The most interesting case is the AFZnP group (A = Eu, Sr), where, apparently, just a subtle difference in the radii of Sr²⁺ and Eu²⁺ allows only the Sr compound to exist. The same pattern is also observed for AFAgS with A = Sr and Eu. Quite interesting findings are the first fluoride tetrelides BaFAITt (Tt = Si, Ge) which are, in addition, first examples that are free from transition metals; the latter is also true for an elusive BaFMgAs pnictide.

Despite the complexity of the considered systems, our approach permitted us to successfully predict and prepare over 20 new LaOAgS-type compounds. Moreover, we can likely extend it to other related groups, e.g. iron pnictides, which can probably serve as parent compounds for iron-based superconductors. These results together will be presented in the report.

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