The search for new materials with targeted properties has always been a hot research field in solid state chemistry due to promising properties in many fields. For example, new inorganic compounds, at the basis of novel properties are studies for their application in energy, electronics, nuclear etc... In this context, an original predictive approach to elaborate novel inorganic compounds was established. Concretely, the design of new compounds with 1D, 2D and 3D structures is based on original building units consisting in oxo-centered OM₄ tetrahedrons assembled into a structuring framework. The empty spaces are filled by anionic groups of various natures (XO₄ groups X= V, P , As... or halogens...). This global approach can be fully rationalized. In that sense, this method is placed in the frame of the renewal of inorganic chemistry since the majority of structures predicted so far were mainly obtained through variable stacking of 2D building blocks. In the case of Bi-based oxo-centered units, the possibility to design new structures with various dimensionalities (1D to 3D) was proved. The preliminary meticulous study of numerous new compounds in the Bi₂O₃-X₂O₅-MₓOᵧ (M= P, V, As..., X= Li, Na, Cu, Co, Ni, Mg, Cd...) chemical system already enriched our experience in this field and opened large perspectives. From a structural point of view, all the phases are deduced from one another by topological relationship linked to the existence of secondary building units based on O(Bi,M)₄ tetrahedrons. A particular dependence between the nature of the units and the inter-layers space was evidenced, leading to empirical rules at the basis of the real prediction of new complex structures. Changing the building units sizes, topologies and chemical systems enlarged the self-assembly possibilities. This necessarily involved a systematic rationalization of the preexisting phases to evidence structural relationships and the pertinent chemical parameters controlling the final structure. The possibility to tackle a large variety of crystal architectures is strongly related to the asymmetric coordination of Bi³⁺ cation linked to its 6s2 stereoactive lone pair and its ability to form OBiₙ units (n= 3, 4 and 5) stacked into 0D, 1D, 2D and 3D frameworks. Recently, the combination, in the same compound, of 2D layers and 1D channels was reported, yielding unique structural types (figure). Several cations are able to go into the mentioned oxo-centered units. Their reactivity was recently reviewed. For example, the substitution of bismuth by lanthanum led to other crystal structures, OLa₄ units been less flexible. In addition, the difficulties encountered to solve the crystal structures of La-based oxy-salts imposed the use of innovative methods such as precession electron crystallography. Topological relationships between bismuth and lanthanum oxy-salts will be detailed as well as their synthesis routes and crystal structures. In addition, the predictive approach will be largely developed for both systems.


Keywords: anion-centered tetrahedra, bismuth and lanthanum oxides, modular chemistry