Elements belonging to the group 15 are usually associated to the toxic properties of arsenic. These hazardous elements are chemical wastes of refining metals and contribute to the environmental pollution. The exploitation of these elements in functional materials will partially solve this problem. Thus, the aim of this work will be to study the different polymorphs of sesquioxides formed by group 15 elements (As, Sb and Bi) applying high pressure in order to better understand the intrinsic properties of these materials.

Among all the possible polymorphs, $\alpha$-As$_2$O$_3$ crystallizes in a cubic structure with strong molecular character being one of the most compressible solid inorganic compounds. In turn, isostructural $\alpha$-Sb$_2$O$_3$ shows two 2nd-order phase transitions driven by dynamical instabilities below 10 GPa. The completely different behavior of both compounds with the same structure points out that the lone electron pair effect could play an important role in the presence of slight changes of compressibility. Intermediate symmetric structures such as orthorhombic $\eta$-Sb$_2$O$_3$ and tetragonal $\beta$-Bi$_2$O$_3$ seem to be more prone to undergo anomalous compressibility. Finally, $\alpha$-Bi$_2$O$_3$ crystallizes in a monoclinic structure with the smaller cationic lone electron pair effect.

In summary, this work will show some guidelines in the stability of sesquioxide polymorphs and how the stereochemically active lone electron pair distribution affects the stability of the different structures, paying special attention on the intermediate symmetric structures where the most striking results have been observed.