

Structural Chemistry of $M_{2/3}[\text{Bi}_{12}\text{O}_{14}](\text{MoO}_4)_5$ (M=Pb, Bi, Ln) and $\text{Bi}_{2n+4}\text{Mo}_n\text{O}_{6(n+1)}$ Phases: XRD, TEM, Spark Plasma Sintering, Anionic Conductivity.

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A number of new phases have been sintered and characterized in a system based on Bi_2O_3 and MoO_3 oxides: columnar ones $[\text{Pb}$ or $M_{2/3\ 1/3}][\text{Bi}_{12}\text{O}_{14}](\text{MoO}_4)_5$ with M= Bi or Ln at temperatures above 700°C and a homologous series of phases $\text{Bi}_{2n+4}\text{Mo}_n\text{O}_{6(n+1)}$, with $n = 3, 4, 5$ and 6 , below 600°C .

These phases have been characterized by single crystal and powder x-ray diffraction and transmission electron microscopy, mainly by selected area electron diffraction. Pellets of the phases have been obtained by the technique of spark plasma sintering (SPS) and their anionic conductivity measured by impedance spectroscopy. They are good conductors with values ranging from $3 \times 10^{-3} < \sigma < 19 \times 10^{-3} \text{ S.cm}^{-1}$.

The presentation will focus on:

- The close structural relationship between the phases and a common basic fluorite-type structure for the heavy atoms. The matrices relating their superstructures and the basic fluorite type unit cell are given, as well as a general one for the whole series. The impact of the heavy atom contributions on the powder patterns will be shown.
- The atomic structure/electric properties relationships of the columnar phases, where the role of the M vacancies and lone pair of Bi^{3+} cations will be emphasized together with thermal vibrations of MoO_4 tetrahedra.
- The reliability of SPS technique to obtain pellets allowing a reliable comparison of a series of ceramics.