

New phases in the $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5\text{-MO}_y$ systems : a goldmine for solid state physico-chemists

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In this lecture, we will investigate the possibility for rational design of new inorganic Bi-based phosphates by intergrowth of versatile building units (BU's). In the whole series of compounds predicted/prepared up today, the concerned BU's are infinite 2D-polycationic ribbons formed of oxygen centered $\text{O}(\text{Bi},\text{M})_4$ tetrahedra. The width of the ribbons is tunable, according to the number N of connected tetrahedra. The connection between them is achieved by isolated PO_4 groups, sometimes surrounding 1D-channels hosting M^{n+} cations. The versatility of these chemical systems arises from the possibility of partial occupancy of these tunnels, while edges of BU's can host M/Bi mixed positions. It is such that a number of new compounds with N ranging from 1 to ∞ are stable with respect to the electroneutrality.

From the crystal structure point of view, these systems present the possibility to design in a rational manner complex intergrowths according to “empirical rules”, priority deduced from known parent-members. In addition, we have shown that for great N values, several BU's are polar. Then, the prediction/formulation/preparation of non-centrosymmetric materials is possible. Examples of efficient second harmonic generators will be given.

From the experimental point of view, our finding for new materials is often helped by High Resolution Electron Microscopy in complementarity to diffraction techniques. Here, it is worth arguing that due to the strong contrast between Bi rich-BU's and their surrounding PO_4 , a particular image code is associated with each BU, helpful for the crystal structure determination from HREM images only. The figure 1 depicts the primary evidence (as defects) of intergrown $N=5$ BU's which are polar and arranged in a non-centrosymmetric manner. Its precise crystal structure has been deduced from powder XRD after formulation and synthesis. SHG is comparable to those KDP.

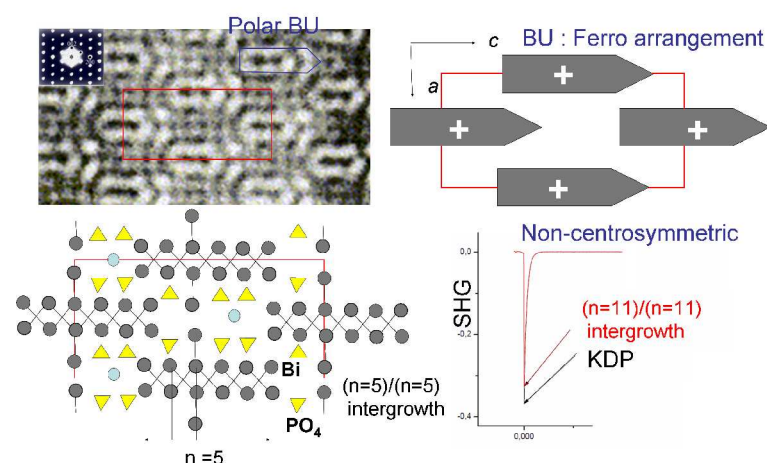


Figure 1 : From the HREM observation of defects with evidence of intergrown $N=5$ ribbons, to the certified non-centrosymmetric crystal structure. The $N=5$ ribbons are decorated by Bi-excesses responsible for their polar character. The afterward-prepared pure compound shows efficient SHG.

From the point of view of their electric and magnetic particularities, it is remarkable that some compounds assorted with small N -values show strong interaction between M^{n+} cations (both intra- and inter-BU's exchanges co-exist). Then, a number of different magnetic behaviour have been evidenced. We will develop recent cases, including the strongly frustrated $S=1/2$ ladders formed inside $N=2$ BU's in the spin-gapped BiCu_2PO_6 .

We will try to adapt most of the “solid-state chemistry” aspects to the interest of both the MICO and CRISTECH communities.