MS15-O2 From simple O(Bi,M)4 entities to the large family of bismuth based oxyphosphate compounds: use of High Resolution Electron Microscopy Imaging to the deduction of new structure types. Marie Colmont, Diana Endara, Almaz Aliev, Marielle Huve and Olivier Mentre, *Université Lille Nord de France. UCCS,CNRS UMR 8181, ENSCL-USTL, Villeneuve d'Ascq, France.*
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The resolution of crystal structures is almost exclusively the result of diffraction techniques, even if sometimes supported by complementary *ab-initio* calculations and/or spectroscopic analyses such as solid-state NMR. This latter can give reliable information on site multiplicities and atomic coordination through relative intensities and chemical shift. However, it is clear that in several cases, such as inhomogeneous samples, disordered or defected materials the possibility to deduce the crystal structure from the observation of single nano-domains would drive new insights in this field. This utopia became reality concerning the HREM analysis of complex intergrowths materials of the Bi_2O_3-MO-P_2O_5. The investigation of this system pointed out a large number of related compounds. Oxocentered OM_x polyhedra revealed as a power tool for the description and prediction of novel structural types, in our case: $O(Bi,M)_4$ tetrahedra[1] predominate. These subunits are connected together into modulable polycationic ribbons of variable width, from n= 1 tetrahedra wide to infinite planes[2, 3], at the origin of an extended series of compounds, concerned here.

All homologous members consist of framework based on these BUs surrounded by PO_4 groups and interstitial cationic channels. The sizes of BUs and their association are variable and differ from one compound to the other one with respect to unified empirical rules. Due to the existence of strong HREM contrasts between Bi/M/O-based BUs and the inner space a high resolution image code has been established for most of the BUs met so far. Here, the combined use of the unified structural rules and the decoding of experimental contrasts lead to the vision of the crystal structure from nano-domains HREM contrasts. It is striking that the contrasts of long BUs can be deduced from shortest ones using a *copy/paste* principle adapted to new experimental contrasts. The figure 1 gives the decoding of experimental contrasts of a new compound with n=9 and n=10 tetrahedra-long BUs from the slicing/rebuilding of known contrasts of shorter BUs. The next stage concerns the formulation of the phases, leading to the synthesis of single-phased materials necessary for the structural certification and physical characterisation[4, 5]. The new structure evidenced so far opens the door to the easy prediction of new materials with new specificities.

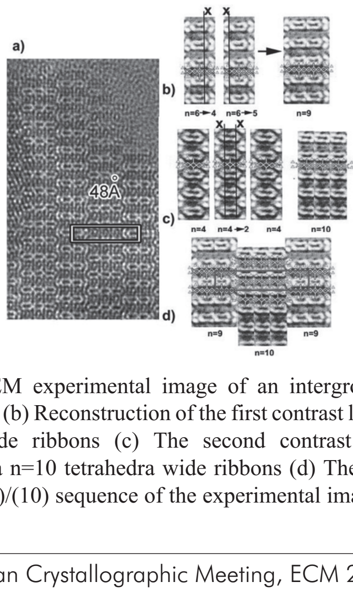

Figure1: HREM experimental image of an intergrowth of novel column-types. (b) Reconstruction of the first contrast leading to n = 9 tetrahedra wide ribbons (c) The second contrast leads to the formation of a n=10 tetrahedra wide ribbons (d) Their intergrowth leads to the (9)/(10) sequence of the experimental image

Especially, it is rather interesting to anticipate all possible (n)/(n') intergrowths, opening the door to an infinite number of original materials.

[1] Cornei; N., Tancret; N., Abraham; F., Mentré; O., (2006) *Inorg. Chem*. **45** 4886
[2] Colmont; M., Huvé, M., Abraham, F., Mentré, O.,(2004) *Solid State Chem*. **177** 4149
[3] Colmont; M., Huvé, M., Ketatni, E.M., Mentré, O.,(2008) *Solid State Sci*. **10** 53
[4] M. Huvé; M. Colmont; O. Mentré; *Inorg. Chem*. **45** (2006) 6604
[5] Huvé, M. Colmont, M., Lejay, J., Aschehoug, P. Mentré, O., (2009) *Chem. Mater*. **21** 4019

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