Possible cationic ordering in bismuth oxide phosphates.

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Inorganic compounds with structures containing XA₄ anion-centered tetrahedra (X = anion, A = metal cation, Bi³⁺ in our case) are very attractive for solid-state chemists¹, because of their interesting physical properties such as low dimensionality, ionic conductivity, luminescence, optical anisotropy, second harmonic generation, etc.

In particular, bismuth oxides and oxy-salts demonstrate a great structural diversity due to the often-found OBi₄ units able to organize into 0-dimensional (0D), 1D, 2D and 3D frameworks. Due to valence unit reasons, the OBi₄ tetrahedra are usually either strongly distorted, or admit the co-presence of a different cation M⁺ cation into O(Bi,M)₄ tetrahedra, whose M-O contribution is relaxing the central oxygen bond valence sum. The variety of aliovalent M cations that can be incorporated into the O(Bi,M)₄ tetrahedral bricks make this class of inorganic compounds a gold mine of inspiration for the findings of novel structural motifs and physical properties. Particularly, the Bi₂O₃-MO-P₂O₅ (M = divalent metals)²-⁵ ternary system displays an impressive number of distinct crystal structures based on the association of O(Bi)₄ and O(Bi,M)₄ sharing edges to form ribbons of variable width and differently connected and surrounded by phosphates. Sometimes, between four PO₄ groups takes place tunnels, hosting M²⁺ cations. These tunnels and the mixed Bi³⁺/M²⁺ at the edges of ribbons are responsible for strong disorder in the structure (around phosphorus). Most of the studied compounds show evidence of modulated structures either by electron diffraction⁶⁻⁷ but also sometimes on XRD single crystal patterns¹⁷ that denote a partial or complete ordering in large periodicities that could occur in small-sized domains but can also extend at a larger scale. Taking into account the number of concerned compounds this ambiguity between full, partial and complete disorder deserves attention. Here we present three new structural types that cover the full panorama in terms of order-disorder duality in this unique class of compounds using complementary methods such as NMR spectroscopy, electron microscopy and X-Ray diffraction. For example the [Bi10(Bi₀.₅Cd₀.₅)₈O₁₆ (PO₄)₈(Bi₀.₆Cd₀.₈)₂ new compound shows a modulation vector q ~ 0.4c* and the structure was solved using the 4D formalism. It led to the evidence of a partial cationic ordering in the 1D columns (figure 1 and 2).

Figure 1: a) Projection along c-axis of the crystal structure of [Bi10(Bi₀.₅Cd₀.₅)₈O₁₆ (PO₄)₈(Bi₀.₆Cd₀.₈)₂ b) the square based columns
Figure 2: a) Arrangement and disorder along c-axis of Cd and Bi atoms of tunnels b) ED image and c) precession (XRD on single crystal) of (h0l) layer with enhancement of surstructure spots (q =0.4 c*)


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