Solving incommensurately modulated structures using precession electron diffraction: the case of Bi$_5$Nb$_3$O$_{15}$

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The structures of bismuth layered oxides from the Aurivillius family of general formula Bi$_{2m}$A$_n$-mB$_n$O$_3$$_{3(n+m)}$ are usually described as resulting from the regular stacking of [Bi$_2$O$_2$]$^{2+}$ slabs and perovskite-like [A$_{p-1}$B$_p$O$_{3p+1}$]$^{2-}$ blocks. The best characterized cases correspond to "simple" members having a unique size for all the perovskite-like blocks (m=1) but "mixed-layer" members (m=2) also exist, where perovskite blocks of size p and p+1 separated by the [Bi$_2$O$_2$] slabs regularly alternate along the stacking direction. Known for decades, the phase Bi$_5$Nb$_3$O$_{15}$ has been first considered as such a "mixed-layer" compound and described as the intergrowth of n=1 and n=2 members [1]. Later, Bi$_5$Nb$_3$O$_{15}$ has been clearly identified as having an incommensurately modulated structure and an approximate structural model incorporating a step-like dislocation has been proposed based on Transmission Electron Microscopy investigations [2-5]. Nonetheless, all the crystallographic investigations using either X-ray or Neutron diffraction [6] eluded this specificity and no structural model taking into account the incommensurate nature of this compound has been proposed and refined.

In the present work, the structure of Bi$_5$Nb$_3$O$_{15}$ is solved using two precession electron diffraction datasets (total of 165 patterns) collected sequentially in angular steps (1°) with a precession semi-angle of 1.2°. Both datasets were acquired on the same crystallite, one in selected area mode (SA-PED) and the other in nanobeam mode (NB-PED). They are complementary in terms of reciprocal space coverage (Fig. 1). The cell parameters and extinction conditions in the superspace were first estimated from examination of sections of the reciprocal space and tested against data using JANA2006 [7]. The superspace group Xma2000 with X=(½,½,½,½), a=5.47Å , b=5.47Å, c=41.9Å, and q=0.176b* was finally retained for the structure determination in the superspace using the charge-flipping algorithm [8] and assuming kinematical diffraction intensities. After data extraction and reduction (see [9] for details), a total of 7747 independent reflections (2862 obs. with I>3σ) were obtained with a data coverage of 96%, a redundancy of 3 and a Rint(all) of 15.8%.

The interpretation of the structure from the ab-initio reconstructed electron density map allows finding all cationic and some oxygen positions. The assignment of the chemical types to the cationic positions (6 Bi and 4 Nb) has been made directly from the intensity of the peaks in the electron density map including cases where discontinuities in the modulation functions where present (Fig. 2b). The center and length of the crenel function used to describe these discontinuities affecting 2 Bi and 2 Nb positions where obtained directly from the electron density map. This partial 4D structure solution refined against the electron diffraction data was found to be stable and allowed completing the structure and finding missing oxygen positions. At the final stage, 16 oxygen’s positions were successfully added in the structure with 3 of them defined by crenel functions. We have imposed soft O-O distance constraints that tend to consider the O$_6$ octahedra as rigid-body units. The refinement converged to a solution with R$_{obs}$ of 29.9% and give an incommensurate structure (Fig. 2) that can be described as a sequence of |p=2|p=1|p=1|p=2| perovskite blocks along the stacking direction c with a periodic "shear" leading to a step-like structure that agrees with the previously suggested unrefined 3D model constructed in an approximant six-fold supercell [5]. This model was then refined against X-ray powder diffraction (XRPD) data using JANA2006 and yield to fairly good reliability factors (GoF=2.6%, R$_{p}$=8.2% and Rp=8.4%) with only small changes from the structure obtained by PED. The XRPD data were sufficient for a successful refinement, but it must be emphasized once more that the ab-initio structure solution of such a complex phase would not have been possible from XRPD only.
References


Figure 1. a) [100] ZAP obtained by SA-PED vs. 0kl reciprocal space sections reconstructed from electron diffraction tomography experiments obtained by b) SA-PED and c) NB-PED on the same crystal.

Figure 2. a) structure of the n=1+2 intergrowth Bi$_5$Ti$_{1-2}$W$_{1-5}$O$_{15}$ [10], b) average structure of Bi$_5$Nb$_2$O$_{15}$ and c) supercell along the modulated direction b revealing an unconventional stacking sequence |2|1|1|2| along c and the periodic “shear” both characteristic of this phase.