

Oral Contributions

[MS15-02] Aperiodic structures related to Aurivillius phases solved by precession electron diffraction.

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Oxides of the Aurivillius family $[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{p-1}\text{B}_p\text{O}_{3p+1}]^{2-}$ (A=Ca, Sr, Ba, Pb, ... and B= Ti, Nb, W,...) have attracted constant interest in the solid state chemistry community considering both their complex layered structure and their wide range of potential applications. A large number of Aurivillius phases exhibit ferroelectric properties at room temperature and present structural distortions leading to predictable structures and space groups [1].

The best characterized cases correspond to "simple" members having a unique size for all the perovskite-like blocks but "mixed-layer" members also exist, where perovskite blocks of size p and p+1 separated by the $[\text{Bi}_2\text{O}_2]$ slabs regularly alternate along the stacking direction. Known for decades, the phase $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ has been first considered as such a "mixed-layer" compound and described as the intergrowth of p=1 and p=2 members [2]. Later, $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ has been 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 [3-6]. Nonetheless, all the crystallographic investigations using either X-ray or Neutron diffraction [7] eluded this specificity. In the present work (see also [8]), the crystal structure of the 1D incommensurately modulated phase $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ [superspace group $X2mb(0b0)000$, $a = 5.46781(7) \text{ \AA}$, $b = 5.47381(8) \text{ \AA}$, $c = 41.9005(5) \text{ \AA}$, and $q = 0.17588(8)b^*$] is

solved by electron diffraction using a tomography technique combined with precession of the electron beam. The (3+1)D structure is further validated by a refinement against powder X-ray diffraction (PXRD). A coherent picture of the true nature of this compound is obtained, conciliating experimental observations made by different groups using transmission electron microscopy and PXRD.

$\text{Bi}_5\text{Nb}_3\text{O}_{15}$ does not have a mixed-layer Aurivillius-type structure but does contain structural elements, $[\text{Bi}_2\text{O}_2]^{2+}$ slabs, and perovskite-like blocks, characteristic of Aurivillius phases. The presence of aperiodic crystallographic shear planes (CSPs) along the modulated direction b leads to the formation of an original layered structure containing both continuous and discontinuous $[\text{Bi}_2\text{O}_2]^{2+}$ and perovskite-like octahedral layers.

Related to this preliminary work, we will show how complex incommensurately modulated structure can be investigated using precession electron diffraction tomography and ab-initio phasing by charge flipping.

This will be illustrated on a series of new layered materials closely related to the Aurivillius phases in the pseudo-binary system $\text{Bi}_5\text{Nb}_3\text{O}_{15}-\text{ABi}_2\text{Nb}_2\text{O}_9$ (A=Pb, Sr, Ca, Ba). The new materials possess a layered Aurivillius-type structure with periodic crystallographic shear planes (CSP) leading to the formation of "collapsed" structures with discontinuous $[\text{Bi}_2\text{O}_2]^{2+}$ slabs and perovskite blocks. Contrary to the trend observed in "conventional" Aurivillius phases, where the possibility of non-stoichiometry is mostly limited to a partial substitution of A cations for Bi in the $[\text{Bi}_2\text{O}_2]^{2+}$ slabs, the newly found compounds exhibit a wide compositional stability domain.

[1] Boullay, P., Trolliard, G., Mercurio, M., Perez-Mato, J.M. & Elcoro, L. (2002). *J. Solid State Chem.* **164**, 252.

[2] Gopalakrishnan J. et al, (1984). *J. Solid State Chem.* **55**, 101.

[3] Zhou, W., Jefferson, D.A., & Thomas, J.M. (1986). *Proc. R. Soc. London ser A* **406**, 173.

- [4] Zhou, W., Jefferson, D.A., & Thomas, J.M. (1989). *Geophys. Monograph.* **43**, 113.
- [5] Ling, C.D. et al (1998). *J. Solid State Chem.* **137**, 42.
- [6] Ling, C.D. (1999). *J. Solid State Chem.* **148**, 380.
- [7] Tahara S. et al (2007), *J. Solid State Chem.* **180**, 2517.
- [8] Boullay, P., Barrier, N., & Palatinus, L. (2013). *Inorg.Chem.* **52**, 6127.

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