



## Synthesis and XPS studies of uranium-bearing Aurivillius-derived layered perovskites



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### ABSTRACT

A series of new uranium-bearing layered perovskites with the Aurivillius-derived structures has been studied by X-ray diffraction and photoelectron spectroscopy. The results of both methods are in very good agreement and confirm the structural motifs suggested for these compounds. A new oxyfluoride  $\text{Ba}_2\text{F}_2\text{UO}_4$  has been prepared and characterized.

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## 1. Introduction

The Aurivillius family of layered perovskites, discovered over 70 years ago, hosts now many important materials exhibiting ferroelectricity [1], ionic conductivity [2], and catalytic activity in photodegradation of organic waste [3,4]. The overwhelming majority of these compounds belong to the family of oxides and sometimes oxide fluorides of bismuth (reviewed sometime ago in Ref. [5]) and obey the general formula  $[\text{Bi}_2\text{O}_2][\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$  wherein the former layers are sliced from the structure of fluorite, and the latter (with the "thickness",  $n$ , varying from 1 to 6), are carved out of the perovskite  $\text{ABO}_3$ . The  $n \geq 2$  compounds exhibit a relatively wide range of chemical compositions which is however limited by a series of empirical restrictions. The  $A$  positions in the perovskitic slabs can be fully occupied by  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ , alkaline earth, and early rare-earth (La–Gd) cations, some others (late  $\text{Ln}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ )

can occupy them only partially. The restrictions on the  $B$  position are more severe, and full occupation is permitted only for  $d^0$  transition metal cations with  $r^{\text{VI}} \approx 0.6 \text{ \AA}$  ( $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ , or  $\text{W}^{6+}$ ;  $r^{\text{N}}$  stands for the radius for the coordination number  $N$ ). Partial occupation (below 30%) is possible for several other cations like  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ru}^{4+}$  and  $\text{Ir}^{4+}$  [6–8]. All these significantly limit the possible compositions, thus the ranges of exhibited properties, which demands for new approaches for extending this interesting family of compounds.

The  $n = 1$  case is peculiar in several respects. In the Bi oxides, it consists of two separate families: ferroelectric bismuth tungstate and its solid solutions ( $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ , stable at low temperatures [9], and  $\text{Bi}_2\text{W}_{1-x}\text{U}_x\text{O}_6$ , stable at high temperatures [10]), and ion conducting bismuth vanadate  $\text{Bi}_2\text{V}_{1-x}\text{M}_x\text{O}_{5.5 \pm y}$  which forms substitutional solid solutions with dozens of  $M$  cations (see the most recent report [11] and references therein). Moreover, this structure motif is easily reproduced among quite different compositions, of which most common are fluorides and oxide fluorides of barium,  $[\text{Ba}_2\text{F}_2][\text{MX}_4]$  ( $M = \text{Mn–Zn}$ ,  $X = \text{F}$  [12,13];  $M = \text{Zr}$ ,  $\text{Sn}$ ,  $X = \text{O}$ ,  $\text{F}$  and  $\text{H}_2\text{O}$  [14,15]); even more exotic compounds, e.g. hydrides, have been reported [16]. The very restricted set of chemical compositions for

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the bismuth oxide ferroelectrics stimulated extensive searches for compounds with derived structures which resulted in a new chemical family, named Bipox (bismuth perovskite oxyhalides [17]). Therein, for the  $n = 1$  case, the frames of chemical compositions, particularly of the perovskitic layer, had widened greatly. In the structure shown on Fig. 1, *b*, it proved possible to partially substitute  $W^{6+}$  by  $Mn^{3+}$ ,  $Fe^{3+}$ , and  $Cu^{2+}$  which is “forbidden” for the archetypic tungstate [18–22]. In line with these findings, we have demonstrated that when passing from  $Bi_2W_{1-x}U_xO_6$  Aurivillius phases to the derived  $PbBi_3W_{1-x}U_xO_8X$  Bipox compounds ( $X = Cl$  and  $Br$ ), the maximal substitution degree ( $x$ ) increases, and the lower limit of thermal stability decreases [23]. This may be explained by the slight release of tensile/compressive strain, caused by size mismatch of the  $[Bi_2O_2]^{2+}$  and  $[W_{1-x}U_xO_4]^{2-}$  slabs, upon partial substitution of  $Bi^{3+}$  ( $r_{VIII} = 1.17 \text{ \AA}$ ) by larger  $Pb^{2+}$  ( $r_{VIII} = 1.29 \text{ \AA}$ ) [24]. In fact, the largest value of the tetragonal  $a$  parameter for the bismuth compounds is  $4 \text{ \AA}$  while for most related structures featuring the same  $[UO_4]$  slabs, these values exceed  $4.2 \text{ \AA}$  [25–27]. Among bismuth oxides, full replacement of  $W^VI$  by  $U^VI$  was probably achieved in a high-temperature compound of an approximate composition  $Bi_{1.5}La_{0.5}UO_6$ ; it exhibits a lower (orthorhombic) symmetry most likely due to strain-induced distortion of the  $[UO_4]^{2-}$  slabs [23].

It is worth noting at the point that the radii of the cations substituting for tungsten in the Bipox compounds [18–20,23] and found in the Aurivillius-type barium fluorides and hydrated oxide fluorides [13–14], are very close to that of  $U^{6+}$  ( $Cu^{2+}$ :  $0.73 \text{ \AA}$ ,  $Zr^{4+}$ :  $0.72 \text{ \AA}$ ;  $Sn^{4+}$ :  $0.69 \text{ \AA}$ ;  $U^{6+}$ :  $0.73 \text{ \AA}$  [24]) which suggests that the size match between  $[Ba_2F_2]$  and  $[UO_4]$  may permit existence of new Aurivillius-like compounds, the  $[Sr_2F_2]$  and  $[Pb_2F_2]$  fluorite layers being the second best size-matching candidates. In addition, the

structures of  $PbUO_4$  [28] and  $BaUO_4$  [29] contain the same  $[UO_4]$  slabs (Fig. 2, *a*) which are corrugated since the cubic voids, observed in the ideal  $(TlAlF_4)$  [30] structure (Fig. 2, *b*) are too large to adapt  $Pb^{2+}$  or  $Ba^{2+}$  cations.

The crystal structures of the uranium-bearing Aurivillius and Bipox compounds had not been studied in detail since preparation of single crystals or large powder samples sufficient for conventional powder neutron diffraction is yet not feasible [23]; the powder X-ray methods, given the presence of heavy scatterers like U, Bi, Pb, and W, are often not enough powerful to determine the positions of the light atoms (O, Cl) with the desired precision. Hence, indirect methods, probing the various possible coordinations and oxidation states of the constituting elements, may appear helpful in getting a deeper insight into these peculiar compounds. In particular, synthesis protocols for these compounds (high-temperature annealing in silica tubes under low or no oxygen pressure) suggest possible silicon contamination and/or partial reduction of uranium. In the current paper, we report preparation of a new Aurivillius-like compound,  $Ba_2F_2UO_4$ , and the results of its investigations, along with the known  $Bi_2W_{1-x}U_xO_6$  and  $PbBi_3W_{1-x}U_xO_8Cl$  solid solutions, by means of X-ray photoelectron spectroscopy (XPS). Possible barium oxyfluoride analogs of  $PbBi_3W_{1-x}U_xO_8Cl$  were also addressed using the compositions  $[Ba_2F_2]_2[U_{1-x}M'_xO_4][I]$  by analogy with  $[Bi_2O_2]_2[W_{1-x}M'_xO_4][X]$  ( $X = Cl$  or  $Br$  [18–20];  $M' = Co$  ( $r_{VI}(Co^{2+}) = 0.65 \text{ \AA}$  [24],  $x = 0.25$ ) and  $In$  ( $r_{VI}(In^{3+}) = 0.80 \text{ \AA}$  [24],  $x = 0.33$ ) were chosen as possible substituents to  $U^{6+}$ .

Upon XPS studies of electronic structures, particularly of actinide compounds [31–35], the oxidation states, physico-chemical properties, and the nature of chemical bond may be acquired not only from the chemical shifts ( $\Delta E_b$ ) of their core electronic levels,

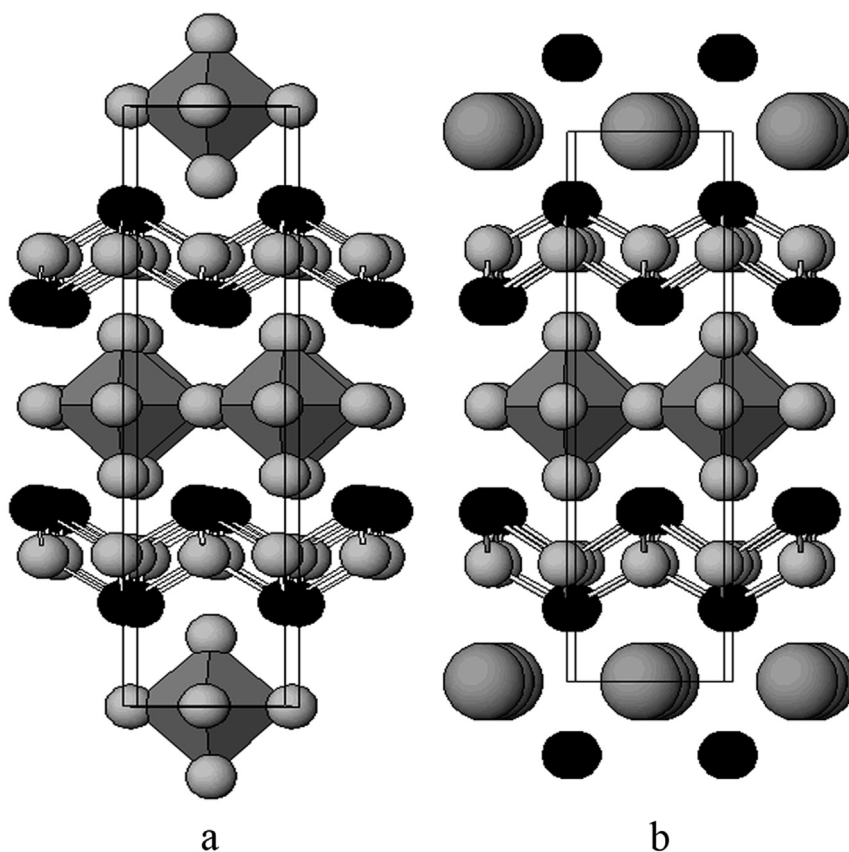


Fig. 1. The atomic arrangements of  $n = 1$  Aurivillius (*a*) and Bipox (*b*) structures. The archetypic tetragonal body-centered and primitive unit cells are shown, for clarity.

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