

PHYSICAL METHODS
OF INVESTIGATION

Study of Cationic Substitution in Bi_2WO_6 and Derived Structures in the Framework of the Modular Approach

D. O. Charkin^{a,b}, S. M. Kazakov^a, and D. N. Lebedev^b

^a Chemistry Department, Moscow State University, Moscow, 119992 Russia

^b Materials Science Department, Moscow State University, Moscow, 119992 Russia

Received October 8, 2009

Abstract—The possibilities of substitution of lead, alkaline and rare earth, antimony, and tellurium cations for bismuth ions in the structure of the Bi_2WO_6 ferroelectric and compounds with more complicated derived structures have been studied. The trends in the formation of solid solutions are well described in the framework of the modular approach in which layers are treated as building units of crystal structures. The underlying existence criteria (electroneutrality, geometric and chemical compatibility of layers) formulated for simple (two-layer) structures can be easily extended to more complicated (multilayer) structures. On the basis of the results obtained, the existence of new series of layered bismuth oxohalides was predicted.

DOI: 10.1134/S0036023610080164

Compounds with layered structures have been actively studied in the context of the unique features of their structural and applied chemistry. In particular, layered perovskites are widely represented by superconductors [1], ferroelectrics [2], ionic conductors [3], water photolysis catalysts [4], and others. Layered fluorites are known as scavengers for toxic and radioactive ions [5], catalysts of selective hydrocarbon oxidation [6], etc. The structures of these compounds stabilize ion combinations that are otherwise prone to redox processes, atypical coordination polyhedra, and metastable or even unknown polymorphs of 3D structures in a layered form. The need for targeted synthesis of new representatives of this promising class of compounds makes it essential to determine criteria for a priori evaluation of the possibility of their existence and their properties.

The modular approach is increasingly used in this field. Its underlying idea consists in regarding layers as building blocks (modules) of crystal structures (for details, see [7]). The successful use of this rather potent tool is currently hindered by the lack of systematic data on structurally and chemically related classes of compounds: the available data are fragmentary and unsuitable for required generalizations. To solve this problem, systematic studies of the most numerous and promising families of compounds under consideration are required.

Layered bismuth oxides and oxohalides have some advantages that make them a convenient object for such studies. First, this family is widely represented by both simple structures and complicated structures containing no less than three layers. Second, these compounds have exclusively rich chemistry, while the principles of construction of their structures are

straightforward and predictable. Within a series of structurally related structures, there are clearly pronounced relationships between the composition, structure, and properties. Third, many members of this family exhibit important applied properties (such as ferroelectricity, superionic oxide conductivity, and photocatalytic activity). Finally, the modular approach has been successfully used for predicting and synthesizing new members of this family [7].

For study, we chose bismuth tungstate $\gamma\text{-Bi}_2\text{WO}_6$ (**1**) and compounds with two more complicated structures **2** and **3**, derived from **1**, which contain halide and metal halide layers, respectively (Fig. 1). As is known, Bi_2WO_6 is a ferroelectric with rather high Curie temperature; however, this property is hard to control because of the very weak propensity of bismuth tungstate to form solid solutions. Structures like **2** and **3** offer wider possibilities for substitution in the perovskite *B* position [8–10], which is attributed to a relatively low substitution level required for formation of these structures [7]. The substitution variants studied so far are also shown in Fig. 1, which demonstrates that systematic analysis of these data is impracticable.

This study deals with the substitution in the cationic positions of fluorite layers in structures **1**–**3**. For all structures, we studied the possibility of substitution of Bi^{3+} by Te^{IV} , Cd^{2+} , and alkaline earth cations (hereinafter, Ae^{2+}). Such possibilities have been described for some structurally related layered bismuth oxides [11] and oxohalides [7, 12]. In addition, for structures **1** and **3**, the substitution of Pb^{2+} for Bi^{3+} was studied by analogy with structure **2** [10], and for structures **2** and **3**, the substitution of Sb^{3+} for Bi^{3+} was studied by analogy with **1** [13]. The substitution of Ln^{3+} for Bi^{3+} , partially studied for structure **3** [14], was considered in

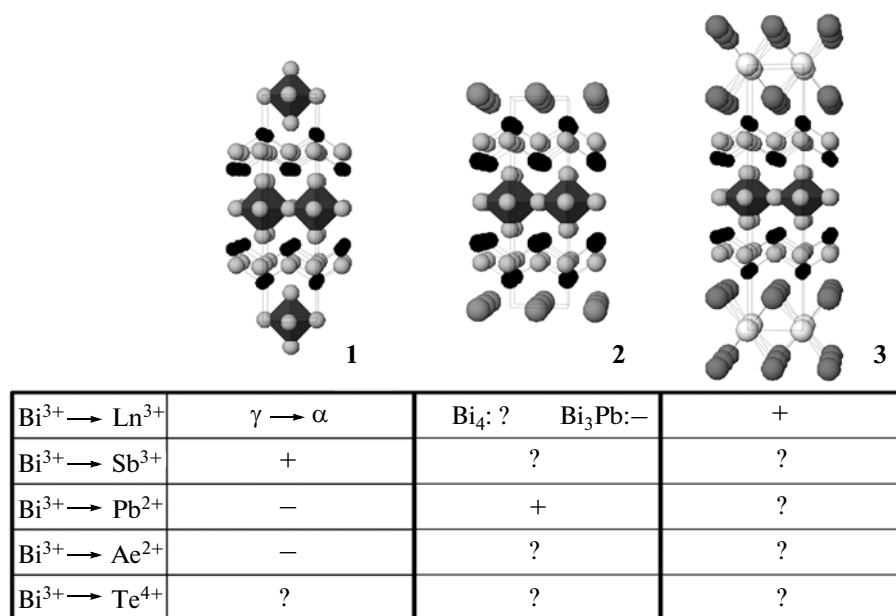


Fig. 1. Structures of Bi_2WO_6 (1) and its more complicated derivatives (2, 3) and the studied variants of Bi^{3+} substitution.

more detail. Finally, for structure 2, it turned out possible to study the simultaneous substitution of Pb^{2+} and Ln^{3+} for Bi^{3+} .

EXPERIMENTAL

Synthesis. The initial reagents were bismuth, antimony, tellurium, tungsten, niobium, and lanthanide oxides (lanthanide oxides were preliminarily calcined at 1100°C for 24–48 h); ammonium perrhenate NH_4ReO_4 ; cesium halides CsCl and CsBr (preliminarily dehydrated at $500\text{--}600^\circ\text{C}$ for 1–2 h); and bismuth and lanthanide oxohalides MOX obtained as described in [15]. Weighed samples (0.7–0.8 g) were thoroughly ground, compacted into pellets under a pressure of 5–10 ton/cm², and annealed two or three times in evacuated (to a residual pressure of $(2\text{--}3) \times 10^{-2}$ Torr) quartz ampoules for 48–60 h at $725\text{--}800^\circ\text{C}$. Synthesis conditions were chosen by analogy with the literature data for related compounds.

It is worth noting that optimal synthesis conditions and a set of initial compounds considerably depend on the composition of the samples under consideration. Several tendencies are here traced. First, it is desirable to introduce transition metal oxides (Nb_2O_5 , WO_3 , etc.) into the reaction mixture in the chemically bound form (PbWO_4 , BiNbO_4 , LnNbO_4 , Bi_2WO_6 , Bi_3ReO_8). LnOX ($X = \text{Cl}, \text{Br}$) can be used as the source of Ln^{3+} only for synthesizing compounds of structure 3 with the highest content of halide ions. Second, the synthesis of samples with relatively low contents of Ln^{3+} should be carried out with gradually increasing temperature at each next stage of annealing. Third, when samples contain elements forming rather vola-

tile halides or oxohalides (Pb, Sb), special precautions should be taken to reduce the temperature gradient in the ampoule. To do this, ampoules were horizontally placed in a thick-walled metal cylinder filled with calcined alumina.

X-ray powder diffraction (XRD) analysis was carried out using a Guinier camera (Enraf-Nonius FR-552). Germanium of semiconductor purity grade was used as the internal reference. The compositions of the samples studied, synthesis conditions, and XRD data are summarized in Table 1.

The crystal structure of $\text{Pb}_{0.4}\text{Bi}_{3.1}\text{La}_{0.5}\text{Nb}_{0.6}\text{W}_{0.4}\text{O}_8\text{Cl}$ was refined using X-ray powder diffraction data collected on a Rigaku D/MAX 2500 diffractometer (CuK_α radiation; 2θ range, $10^\circ\text{--}120^\circ$; step, 0.02°) by the Rietveld full-profile method with the TOPAS3 program [22]. The refinement results, atomic coordinates, and selected interatomic distances are presented in Tables 2, 3, and 4, respectively. The X-ray powder diffraction pattern of the sample shows the peaks of the $\text{La}_2\text{W}_3\text{O}_{12}$ impurity phase (about 2%), which was included in the refinement. The theoretical, experimental, and difference profiles are shown in Fig. 2.

RESULTS AND DISCUSSION

Substitution for Bi^{3+} in Structures 1–3

Aliovalent substitution. Substitution $\text{Bi}^{3+} \rightarrow \text{Te}^{\text{IV}}$, rather typical of “thick” fluorite layers $[\text{Bi}_{3-n}\text{Te}_n\text{O}_{4+n/2}]^+$ in Sillen structures [12], is almost not observed in Aurivillius structures containing $[\text{Bi}_{2-x}\text{M}_x\text{O}_2]$ ($M = \text{Pb}, \text{Ln}$) layers. The preparation of

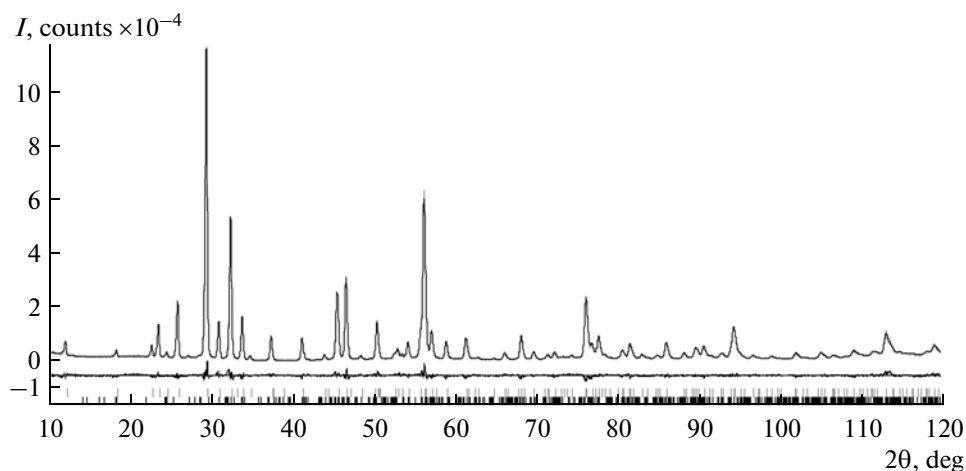


Fig. 2. Theoretical, experimental and difference curves for $\text{Pb}_{0.4}\text{Bi}_{3.1}\text{La}_{0.5}\text{Nb}_{0.6}\text{W}_{0.4}\text{O}_8\text{Cl}$. Positions of the reflections of (top) the major phase and (bottom) $\text{La}_2\text{W}_3\text{O}_{12}$ are shown.

a solid solution based on another Aurivillius phase $\text{Bi}_{2-x}\text{Te}_x\text{SrNb}_{2-x}\text{Hf}_x\text{O}_9$ ($x \leq 0.5$) has been reported [11]; the authors used a large TeO_2 excess, and the chemical composition of the resulting samples was not determined; therefore, the question about their exact composition is still open. In our case, the Te^{IV} solubility was almost lacking. The only evidence of the formation of the substitutional solid solution with Te^{IV} substituted for Bi^{3+} in structure **3** is a small change in the X-ray diffraction pattern (coalescence of characteristic doublets leading to a metrically tetragonal unit cell, which is analogous to the data in [11] for the solid solution with an Aurivillius structure). It is worth noting that high coordination numbers (four, as in the structures under consideration, or higher) are mainly typical of Te^{IV} compounds stable at relatively low temperatures. This can be exemplified by the related family of tellurium lanthanide oxohalides: compounds with high tellurium CNs were obtained at 700°C or lower temperatures [12], whereas in the structures of most compounds obtained at temperatures above 750°C tellurium has $\text{CN} = 3$ [16].

The substitution of Pb^{2+} for Bi^{3+} is possible only in a type **2** structure. Although in other Aurivillius phases, for example, $\text{PbBi}_2\text{Nb}_2\text{O}_9$, some Pb^{2+} ions are involved in fluorite layers [17] and maximal percentage of substitution in oxohalide structures is 50% [7], under our conditions, the substitution of Pb^{2+} for Bi^{3+} in structures **1** and **3** is impossible. In the former case, the failure is presumably due to the impossibility of the substitution of Re^{VII} for W^{VI} (Re^{VII} seems to be too small to fill the octahedral cavity in this structure). It is likely that the $\text{Bi}_{2-x}\text{Pb}_x\text{WO}_{6-x}\text{F}_x$ solid solution will be more extended.

An attempt to substitute Pb^{2+} for Bi^{3+} in a type **3** structure leads to its decomposition into simpler fragments Bi_2WO_6 and $\text{Pb}_{0.6}\text{Bi}_{1.4}\text{Cs}_{0.6}\text{O}_2\text{Cl}_2$.

Substitution of Ca^{2+} and Sr^{2+} for Bi^{3+} turned out to be impossible in all cases under consideration. The annealed samples always contain tungstates AeWO_4 .

Isovalent substitution. $\text{Bi}^{3+} \rightarrow \text{Sb}^{3+}$. In contrast to the data [13] indicating the existence of the extended solid solution $\text{Bi}_{2-x}\text{Sb}_x\text{WO}_6$ with $x \leq 1.25$ at 450°C , in our experiments at $750\text{--}775^\circ\text{C}$, the extent of the solid solution does not exceed $x = 0.1$. Inasmuch as we found that PbBiO_2Cl at 600°C also dissolves noticeable Sb^{3+} amounts, the lack of extended solid solutions based on $\text{Bi}_4\text{NbO}_8\text{Cl}$ and especially $\text{PbBi}_3\text{WO}_8\text{Cl}$ can be explained only by the fact that large CNs are not typical of Sb^{3+} at high temperatures, as discussed above for Te^{IV} . At lower temperatures, the reaction between BiNbO_4 (PbWO_4) and $\text{Bi}_{3-x}\text{Sb}_x\text{O}_4\text{Cl}$ is incomplete, while the use of more reactive PbBiO_2Cl and $\text{Bi}_{2-x}\text{Sb}_x\text{WO}_6$ inevitably leads to the formation of the abundant sublimate of BiOCl , $\text{PbBi}_{2-x}\text{Sb}_x\text{O}_2\text{Cl}$, or, more often, $\text{PbBi}_3\text{O}_4\text{Cl}_3$.

Substitution of Ln^{3+} for Bi^{3+} . As follows from Table 1, this substitution is possible for structures **2** and **3** and follows the same trend as the substitution of cations without a lone pair (Ae^{2+} , Ln^{3+}) in the structures of other Aurivillius phases with thicker perovskite layers [18, 19]: the maximal degree of substitution and thermal stability decrease as the radius of the substituting cation decreases. For example, in the $\text{Bi}_2\text{AeNb}_2\text{O}_9$ and $\text{Bi}_2\text{AeTa}_2\text{O}_9$ structures, the composition of the $[\text{Bi}_{2-x}\text{Ae}_x\text{O}_2]$ layers is $x \approx 0.05$ for Ca^{2+} ($r = 1.12 \text{ \AA}$), $x \approx 0.15$ for Sr^{2+} ($r = 1.26 \text{ \AA}$), and $x \approx 0.44$ for Ba^{2+} ($r = 1.42 \text{ \AA}$) [19, 20]. According to neutron diffraction data on the $\text{Sr}_{2.2}\text{Bi}_{1.8}\text{Nb}_{2.2}\text{Ti}_{0.8}\text{O}_{12}$ structure [21], the Bi^{3+} ion, which has a lone electron pair, forms four short Bi–O bonds with oxygen atoms of the fluorite layer, whereas the distance to the apical oxygen atoms of the perovskite layer are long and correspond to weak interactions. Conversely, the Sr^{2+} ions, which have a large

Table 1. Compositions of the sample series, synthesis conditions, and X-ray powder diffraction data

x	Initial compounds	Synthesis conditions*	XRD data
$\text{Bi}_{2-x}\text{Pb}_x\text{W}_{1-x}\text{Re}_x\text{O}_6$ (1) 0.1–0.3	Bi_3ReO_8 , PbO , Bi_2O_3 , WO_3	800°C, two anneals	Bi_2WO_6 + unidentified impurities
$\text{Bi}_{2-x}\text{Te}_x\text{W}_{1-x}\text{Nb}_x\text{O}_6$ (1) 0.1–0.3	BiNbO_4 , TeO_2 , Bi_2O_3 , WO_3	750°C, two anneals	Bi_2WO_6 + BiNbO_4 + unidentified impurities
$\text{Bi}_{2-x}\text{Sb}_x\text{WO}_6$ (1) 0.1 0.2–0.4	Bi_2O_3 , Sb_2O_3 , WO_3	The same	Solid solution based on Bi_2WO_6 Solid solutions based on Bi_2WO_6 and Sb_2WO_6
$\text{Bi}_{4-x}\text{Sb}_x\text{NbO}_8\text{Cl}$ (2) 0.1–0.2 0.3–0.5	BiNbO_4 , Bi_2O_3 , Sb_2O_3 , BiOCl	750°C, 775°C	Solid solution based on $\text{Bi}_4\text{NbO}_8\text{Cl}$ Solid solution + BiNbO_4 + $\text{Bi}_{3-x}\text{Sb}_x\text{O}_4\text{Cl}$
$\text{PbBi}_{3-x}\text{Sb}_x\text{WO}_8\text{Cl}$ (2) 0.1 0.2–0.4	PbWO_4 , Bi_2O_3 , Sb_2O_3 , BiOCl	725°C, 750°C	Solid solution based on $\text{PbBi}_3\text{WO}_8\text{Cl}$ Solid solution + $\text{PbBi}_{1-x}\text{Sb}_x\text{O}_2\text{Cl}$ + Bi_2WO_6
$\text{Bi}_{4-x}\text{La}_x\text{NbO}_8\text{Cl}$ (2) 0.1–0.4 0.5–0.8 0.9	BiNbO_4 , LaNbO_4 , Bi_2O_3 , BiOCl	800°C, two anneals	Solid solution based on $\text{Bi}_4\text{NbO}_8\text{Cl}$ orthorhombic Solid solution tetragonal The same + unidentified impurities
$\text{Bi}_{4-x}\text{Gd}_x\text{NbO}_8\text{Cl}$ (2) 0.1–0.4 0.5	BiNbO_4 , GdNbO_4 , Bi_2O_3 , BiOCl	775°C, two anneals	Solid solution based on $\text{Bi}_4\text{NbO}_8\text{Cl}$ orthorhombic The same + unidentified impurities
$\text{Bi}_{4-x}\text{La}_x\text{NbO}_8\text{Br}$ (2) 0.1–0.4 0.5–0.7 0.8	BiNbO_4 , LaNbO_4 , Bi_2O_3 , BiOBr	800°C, two anneals	Solid solution based on $\text{Bi}_4\text{NbO}_8\text{Br}$ orthorhombic Solid solution tetragonal The same + unidentified impurities
$\text{Bi}_{4-x}\text{Ca}_x\text{Nb}_{1-x}\text{W}_x\text{O}_8\text{Cl}$ (2) 0.1, 0.2	CaBiO_2Cl , BiNbO_4 , Bi_2O_3 , WO_3 , BiOCl	750°C, two anneals	$\text{Bi}_4\text{NbO}_8\text{Cl}$ + CaWO_4 + $\delta\text{-Bi}_2\text{O}_3$ + $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$
$\text{Pb}_x\text{Bi}_{4-x}\text{Nb}_{1-x}\text{W}_x\text{O}_8\text{Cl}$ (2) 0.1–0.9	PbWO_4 , BiNbO_4 , Bi_2O_3 , BiOCl	800°C, two anneals	Complete mutual solubility
$\text{Pb}_{0.4}\text{Bi}_{3.6-x}\text{La}_x\text{Nb}_{0.6}\text{W}_{0.4}\text{O}_8\text{Cl}$ (2) 0.1, 0.2 0.3–0.5 0.6	PbWO_4 , BiNbO_4 , LaNbO_4 , Bi_2O_3 , BiOCl	775°C, 800°C 800°C, two anneals	Solid solution orthorhombic Solid solution tetragonal The same + PbBiO_2Cl + $\alpha\text{-Bi}_{1-x}\text{La}_x\text{WO}_6$

Table 1. (Contd.)

x	Initial compounds	Synthesis conditions*	XRD data
$Pb_{0.4}Bi_{3.6-x}La_xNb_{0.6}W_{0.4}O_8Br$ (2) 0.1, 0.2 0.3, 0.4 0.5	$PbWO_4$, $BiNbO_4$, $LaNbO_4$, Bi_2O_3 , $BiOBr$	775°C, 800°C 800°C, two anneals	Solid solution orthorhombic Solid solution tetragonal The same + $PbBiO_2Br + \alpha-Bi_{2-x}La_xWO_6$
$Pb_xBi_{3.5-x}La_{0.5}Nb_{1-x}W_xO_8Cl$ (2) 0.1–0.5 0.6	$PbWO_4$, $BiNbO_4$, $LaNbO_4$, Bi_2O_3 , $BiOCl$	800°C, two anneals	Solid solution tetragonal The same + $PbBiO_2Cl + \alpha-Bi_{2-x}La_xWO_6$
$Pb_xBi_{3.5-x}La_{0.5}Nb_{1-x}W_xO_8Br$ (2) 0.1, 0.2 0.3, 0.4 0.5	$PbWO_4$, $BiNbO_4$, $LaNbO_4$, Bi_2O_3 , $BiOBr$	800°C, two anneals	$PbBiO_2Br + Bi_2WO_6 +$ solid solution $Pb_xBi_{3.5-x}La_{0.5}Nb_{1-x}W_xO_8Br$ ($x > 0.2$) Solid solution tetragonal The same + $PbBiO_2Br + \alpha-Bi_{2-x}La_xWO_6$
$PbBi_{3-x}La_xWO_8Cl$ (2) 0.1, 0.2	$PbWO_4$, $BiNbO_4$, $LaNbO_4$, Bi_2O_3 , $BiOCl$	800°C, two anneals	$PbBi_3WO_8Cl + PbBiO_2Cl + \alpha-Bi_{2-x}La_xWO_6$
$Bi_{4-x}Te_xNb_{0.6+x}W_{0.4-x}Cs_{0.6}O_8Cl_2$ (3) 0.1 0.2, 0.3	Bi_2O_3 , TeO_2 , $BiNbO_4$, WO_3 , $BiOCl$, $CsCl$	750°C, two anneals	Solid solution pseudotetragonal The same + Bi_3NbO_7 (?)
$Bi_{4-x}Sb_xNb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2$ (3) 0.1, 0.2	Bi_2O_3 , Sb_2O_3 , $BiNbO_4$, WO_3 , $BiOCl$, $CsCl$	725°C, two anneals	$Bi_4Nb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2 +$ unidentified impurities
$Bi_{4-x}Pb_xNb_{0.6-x}W_{0.4+x}Cs_{0.6}O_8Cl_2$ (3) 0.1–0.2 0.3–0.7 0.8	$PbWO_4$, $BiNbO_4$, Bi_2O_3 , WO_3 , $BiOCl$, $CsCl$	750°C, two anneals	$Bi_4Nb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2 + Pb_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2 + Bi_2WO_6$
$Bi_{4-x}La_xNb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2$ (3) 0.1–0.2 0.3–0.7 0.8	$BiNbO_4$, Bi_2O_3 , WO_3 , $BiOCl$, $LaOCl$, $CsCl$	750°C, 775°C 800°C, two anneals	Solid solution tetragonal The same + unidentified impurities
$Bi_{4-x}Nd_xNb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2$ (3) 0.1–0.2 0.3–0.6 0.7	$BiNbO_4$, Bi_2O_3 , WO_3 , $BiOCl$, $NdOCl$, $CsCl$	750°C, 775°C 800°C, two anneals	Solid solution tetragonal The same + unidentified impurities
$Bi_{4-x}Gd_xNb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2$ (3) 0.1–0.4 0.5	$BiNbO_4$, Bi_2O_3 , WO_3 , $BiOCl$, $GdOCl$, $CsCl$	750°C, 775°C	Solid solution tetragonal The same + unidentified impurities
$Bi_{4-x}Y_xNb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2$ (3) 0.1–0.4 0.5	$BiNbO_4$, Bi_2O_3 , WO_3 , $BiOCl$, $YOCl$, $CsCl$	750°C, 775°C	Solid solution orthorhombic The same + unidentified impurities
$Bi_{4-x}Ca_xNb_{0.6+x}W_{0.4-x}Cs_{0.6}O_8Cl_2$ (3) 0.1, 0.2	$CaBiO_2Cl$, $BiNbO_4$, Bi_2O_3 , WO_3 , $BiOCl$, $CsCl$	750°C, two anneals	$Bi_4Nb_{0.6}W_{0.4}Cs_{0.6}O_8Cl_2 + CaWO_4 + Bi_{24}O_{31}Cl_{10}$

* Annealing time is 60 h at 725–750°C and 48 h at 775–800°C.

Table 2. Crystallographic data and experimental detail

Formula	Pb _{0.4} Bi _{3.1} La _{0.5} Nb _{0.6} W _{0.4} O ₈ Cl
Color	Yellow
FW	1092.9
Symmetry	Tetragonal
Space group	<i>P4/mmm</i> (no. 123)
Unit cell parameters	
<i>a</i> , Å	3.8774(1)
<i>c</i> , Å	14.3429(3)
<i>V</i> , Å ³	215.63(1)
<i>Z</i>	1
ρ_{calcd} , g/cm ³	8.42(1)
Diffractometer	Rigaku
Radiation	CuK($\alpha_1 + \alpha_2$)
Software	TOPAS3 [22]
2 θ range and step, deg	10–120, 0.02
Weight fraction of the phase, %	98(1)
Number of processed reflections	140
Number of measurements	5500
Total number of variables	50
Number of structural variables	14
<i>R</i> values:	
<i>R</i> _B	0.027
<i>R</i> _p	0.057
<i>R</i> _{wp}	0.076
<i>R</i> _c	0.049
χ^2	1.55

ionic radius and tend to have an isotropic environment, are shifted toward the apical oxygen atoms of perovskite layers; therefore, all eight Sr–O distances are almost equal. We assume that, in other structures of bismuth oxohalides, including our structures, the Ae²⁺ and Ln³⁺ ions in fluorite layers have similar arrangement. It is evident that, as the radius of a lan-

thanide or alkaline earth cation decreases, it fits less and less into an antiprismatic cavity formed by eight oxygen atoms (four atoms from the fluorite and four atoms from the perovskite layer), which is reflected in a decrease in both the maximal degree of substitution (in our case, the solid solution extent) and the thermal stability (high CNs for cations, including Ln³⁺, are also observed at lower temperatures). It is evident that the Ln³⁺ cations fit even worse into antiprismatic cavities O₄X₄ (X is a halogen), which accounts for the tendency of Ln³⁺ ions to be substituted for Bi³⁺ only in positions with an oxygen environment (i.e., inside the Aurivillius part of the structure). To confirm this hypothesis, we attempted to substitute La³⁺ for Bi³⁺ in PbBiO₂Cl and Pb_{0.6}Bi_{1.4}Cs_{0.6}O₂Cl₂, which are fragments of structures **1** and **2**, all Bi³⁺ ions being in O₄Cl₄ antiprisms. As expected, we failed to obtain such solid solutions.

It seems evident that an increase in the size of the O₈ antiprism should be accompanied by a decrease in the maximal Ln³⁺ concentration in fluorite layers. In particular, the extent of the Bi_{4-x}La_xNbO₈Cl (**2**) and Bi_{4-x}La_xNb_{0.6}W_{0.4}Cs_{0.6}O₈Cl₂ (**3**) solid solutions is almost the same ($x \leq 0.7$). A slight difference in the behavior of these solid solutions is that rhombic distortion in **2** becomes unnoticeable at $x > 0.4$, whereas rhombic distortion in **3** is imperceptible even at $x = 0.1$. However, when the bulkier Pb²⁺ ion is substituted for some of the Bi³⁺ ions, the extent of the Pb_{0.4}Bi_{3.6-x}La_xNb_{0.6}W_{0.4}O₈Cl (**2**) solid solutions decreases to $x \leq 0.5$. In much the same way, the substitutional solid solutions in which Gd³⁺ is substituted for Bi³⁺ are stable to $x \leq 0.4$ (Bi_{4-x}Gd_x) and $x \leq 0.2$ (Pb_{0.4}Bi_{3.6-x}Gd_x). The replacement of Cl⁻ by bulkier Br⁻ also decreases the La³⁺ solubility by about $\Delta x = 0.1$. Thus, the composition of the perovskite layer has little effect on the Ln³⁺ solubility (${}^{\text{VI}}r(\text{Nb}^{\text{V}}) \approx {}^{\text{VI}}r(\text{W}^{\text{VI}})$ [20], the nature of the halide layer has a somewhat stronger effect, and the composition of fluorite layers involving Ln³⁺ ions has the strongest effect. The lack of Ln³⁺ solubility in the compound of limiting composition PbBi₃WO₈Cl is comprehensively considered later.

In view of the aforesaid, it is of interest to compare the structure of Pb_{0.4}Bi_{3.1}La_{0.5}Nb_{0.6}W_{0.4}O₈Cl (**2**), obtained in this work, and Bi_{3.5}La_{0.5}Nb_{0.6}W_{0.4}Cs_{0.6}O₈Cl₂

Table 3. Atomic coordinates and site occupancies in the structure of Pb_{0.4}Bi_{3.1}La_{0.5}Nb_{0.6}W_{0.4}O₈Cl

Atom	Position	<i>z</i>	<i>F</i>	<i>B</i> , Å ²
Bi1	2 <i>g</i> (00 <i>z</i>)	0.1346(1)	0.20 Pb + 0.80 Bi	0.65(3)
Bi2	2 <i>h</i> (½½ <i>z</i>)	0.3108(1)	0.25 La + 0.75 Bi	2.12(3)
Nb	1 <i>b</i> (00½)	–	0.60 Nb + 0.40 W	0.14(4)
Cl	2 <i>d</i> (½½0)	–	1.00	2.1(2)
O1	4 <i>i</i> (0½ <i>z</i>)	0.2111(6)	1.00	1.0(3)
O2	2 <i>g</i> (00 <i>z</i>)	0.365(1)	1.00	1.0(7)
O3	2 <i>e</i> (½0½)	–	1.00	1.0(5)

Table 4. Bond lengths (Å) in the structures of $\text{Pb}_{0.4}\text{Bi}_{3.1}\text{La}_{0.5}\text{Nb}_{0.6}\text{W}_{0.4}\text{O}_8\text{Cl}$ (2) and $\text{Bi}_{3.5}\text{La}_{0.5}\text{Nb}_{0.6}\text{W}_{0.4}\text{Cs}_{0.6}\text{O}_8\text{Cl}_2$ (3)

Bond	2	3 [14]
Bi1–O1 × 4	2.228(4)	2.322(8)
Bi1–Cl × 4	3.351(4)	3.175(4)
Bi2–O1 × 4	2.409(5)	2.295(4)
Bi2–O2 × 4	2.851(4)	2.91(3)
Nb–O2 × 2	1.93(1)	1.69(3)
Nb–O3 × 4	1.939(1)	1.926(1)

(3), which we studied earlier [14], with the same composition of the perovskite layer and the same content of the introduced La^{3+} (Table 3). As is seen, structure 3 is characterized by almost regular (Nb,W)O₆ octahedra and the distances between the apical oxygen atoms and Nb(W) and Bi(Pb) are within common ranges. It is precisely these atoms in the parent orthorhombic structures that most strongly deviate from the “ideal” positions; therefore, in refinement of the oxohalide structures in the framework of the tetragonal symmetry, the positions of these atoms are determined with a minimal accuracy. Structure 2 is noticeably closer to ideal than 3 [14]. It is pertinent to draw an analogy with the related structure of $\text{Pb}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{Cl}$, in which the fluorite layers also contain noticeable amounts of Pb^{2+} [23]: despite the existence of noticeable second harmonic generation of laser radiation and the manifestation of the orthorhombic structures in electron diffraction patterns, it has been possible to solve the structure (according to neutron diffraction data) only for a centrosymmetric tetragonal subcell. It is likely that, in the structures of Aurivillius phases and their more complicated derivatives, the activity of the Pb^{2+} lone pair is rather poorly pronounced.

Compatibility Criteria in Multilayer Structures

As emphasized in reviews [7, 24] dealing with the application of the modular approach to design of layered structures, the probability of the existence of new compounds is estimated on the basis of four criteria: electroneutrality and geometric and chemical compatibility of layers; separate factors, which cannot be generalized, constitute the fourth “specific” criterion. Our studies show that, after some modification, these criteria deduced for the simplest two-layer structures are quite applicable to more complicated multilayer structures.

A specific feature of complicated layered structures of the $[\mathcal{A}][\mathcal{B}][\mathcal{A}][\mathcal{C}]$ type (in our case, $[\mathcal{A}]$ is the fluorite layer, $[\mathcal{B}]$ is the perovskite layer, and $[\mathcal{C}]$ is the halide or metal halide layer) is that, for some variants of chemical composition, the complicated structure can decompose into electroneutral fragments $[\mathcal{A}][\mathcal{B}]$

and $[\mathcal{A}][\mathcal{C}]$, for example, $\text{PbBi}_3\text{WO}_8\text{Cl} \rightleftharpoons \text{PbBiO}_2\text{Cl} + \text{Bi}_2\text{WO}_6$. In this case, the latter act as complex modules capable of forming structures of higher hierarchy. When complex structures can decompose into simpler ones, the criterion of the geometric compatibility of layers (first-order modules) and/or their combinations (second-order modules [7]) becomes very strict. For example, PbBiO_2Cl (unit cell parameter $a = 3.956$ Å) reacts with Bi_2WO_6 (the tetragonal subcell parameter $a_0 = 3.863$ Å) to form $\text{PbBi}_3\text{WO}_8\text{Cl}$ ($a_0 = 3.894$ Å), but the reaction of PbBiO_2Br ($a = 3.988$ Å) with Bi_2WO_6 proceeds with very low yield. As expected, the reaction of PbBiO_2I ($a = 4.053$ Å) with Bi_2WO_6 does not occur at all in the temperature range studied (750–800°C).

Conversely, if the chemical composition is such that the decomposition into neutral fragments is impossible and any $[\mathcal{A}][\mathcal{B}]$ or $[\mathcal{A}][\mathcal{C}]$ sequence bears an electrostatic charge (for example, in $\text{Bi}_4\text{Nb}_8\text{Br}[\text{Bi}_2\text{O}_2]^{2+}[\text{NbO}_4]^{3-}[\text{Bi}_2\text{O}_2]^{2+}[\text{Br}]^-$), the structure is stable even at significant distortions of one or several layers. For example, in the $\text{Bi}_4\text{Nb}_{0.6}\text{W}_{0.4}\text{Cs}_{0.6}\text{O}_8\text{Cl}_2$ structure in layers of the CsCl type, the CsCl₈ eight-vertex polyhedra are elongated from regular cubes with an edge of 4.115 Å (as in CsCl per se) to square prisms with the base length $a_0 = 3.876$ Å. The introduction of Pb^{2+} into this structure makes possible its decomposition into electroneutral fragments Bi_2WO_6 and $\text{Pb}_{0.6}\text{Bi}_{1.4}\text{Cs}_{0.6}\text{O}_2\text{Cl}_2$, the distortion of CsCl type layers in the latter being somewhat smaller ($a = 3.909$ Å, Fig. 3).

The lack of solubility of Ln^{3+} in the $\text{PbBi}_3\text{WO}_8\text{Cl}$ structure cannot be explained by size mismatch between Ln^{3+} ions and O₈ antiprisms. In our opinion, the reason is that the introduction of Ln^{3+} entails the change in the Aurivillius part of the structure, as in Bi_2WO_6 , but the high-temperature α -(Bi,Ln)₂WO₆ form stabilized by lanthanide ions is incompatible with PbBiO_2Cl in the lattice parameters (Fig. 4). At the same time, the $\text{Pb}_{0.4}\text{Bi}_{3.6-x}\text{La}_x\text{Nb}_{0.6}\text{W}_{0.4}\text{O}_8\text{Cl}$ solid solution is quite stable since its decomposition into electroneutral fragments is hindered. In addition, it is likely that the presence of Nb^V suppresses the formation of α -(Bi,Ln)₂WO₆. This is indirectly confirmed by negative results of pilot experiments to search for (Bi,Ln)_{2-x}Th_xW_{1-x}Nb_xO₆ solid solutions. In this case, we are more likely dealing with the manifestation of the chemical compatibility criterion.

In our experiments, the chemical compatibility criterion is most clearly traced in all structures in the absence of Ae²⁺ cations, especially Sr²⁺, which is close in radius to Pb^{2+} and La^{3+} . It is likely that, in systems containing W (and, evidently, Mo), formation of alkaline earth tungstates is thermodynamically most favorable. An attempt to obtain $\text{CaBi}_3\text{WO}_8\text{Cl}$ from second-order modules CaBiO_2Cl and Bi_2WO_6 led to the formation of a mixture of CaWO_4 , $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$, and δ - Bi_2O_3 stabilized with W^{VI} (and presumably Ca²⁺). At the same time, in the systems that do not contain Mo and W, formation of phases with structure 2 in which

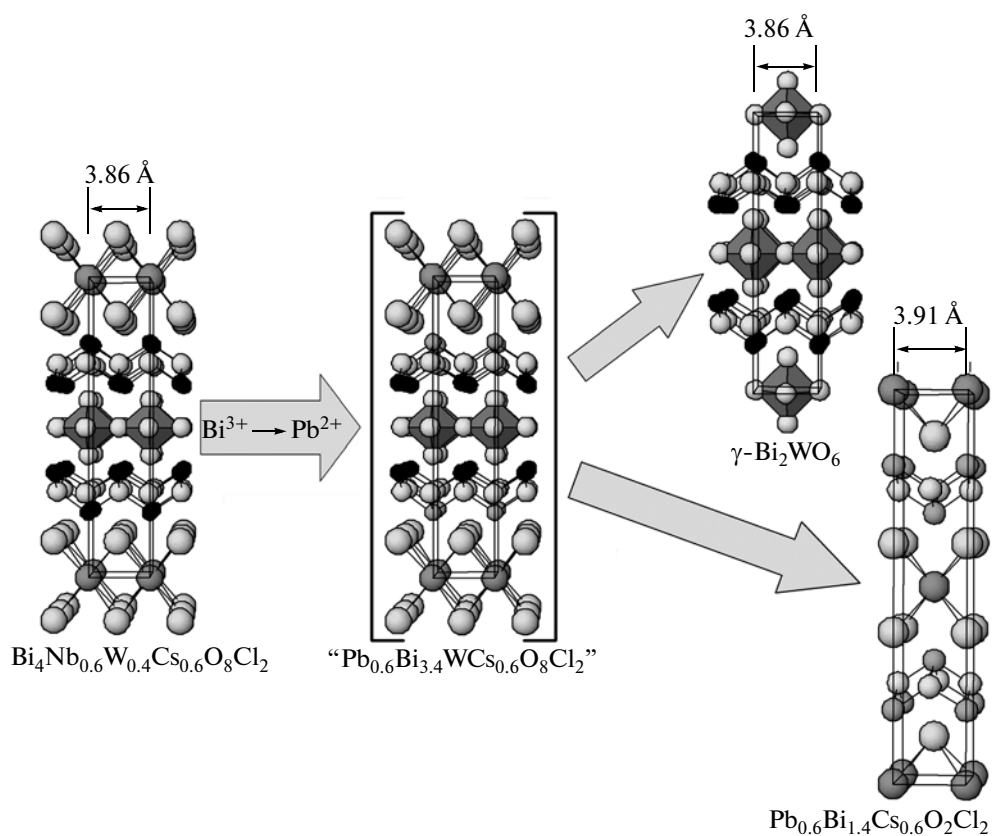


Fig. 3. Scheme of the decomposition of the solid solution $\text{Bi}_{4-x}\text{Pb}_x\text{Nb}_{0.6-x}\text{W}_{0.4+x}\text{Cs}_{0.6}\text{O}_8\text{Cl}_2$ (3).

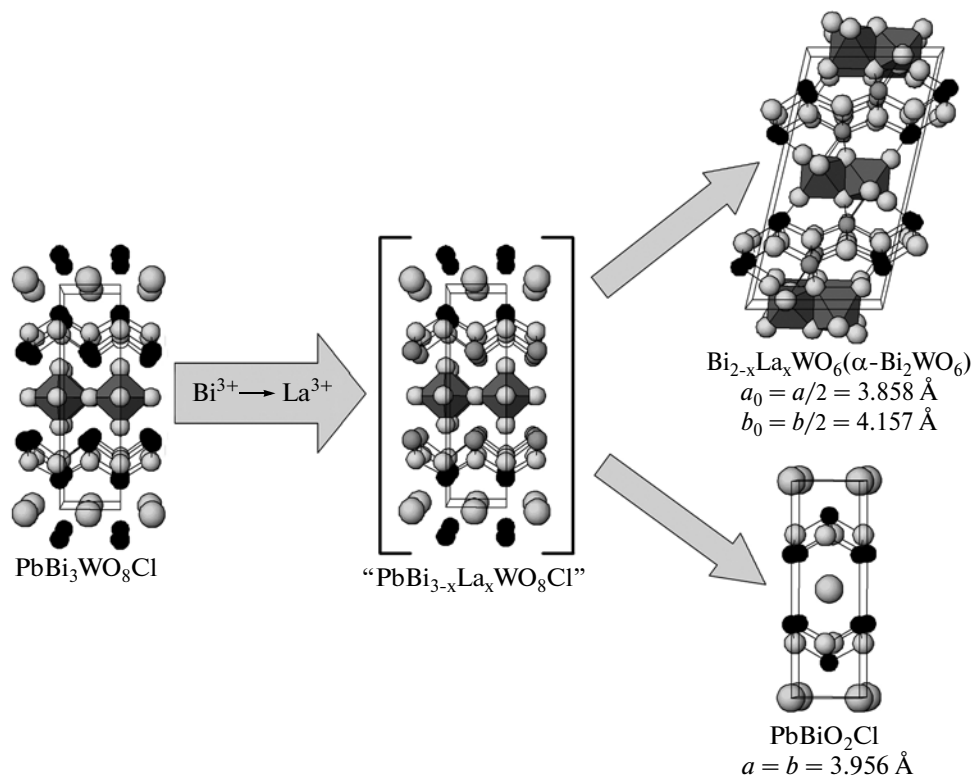


Fig. 4. Scheme of the decomposition of the solid solution $\text{PbBi}_{3-x}\text{La}_x\text{WO}_8\text{Cl}$ (2).

Sr²⁺ ions are substituted for some of the Bi³⁺ ions is quite possible. This is exemplified by SrBi₃NbO₇FCI [25].

To summarize, we can state that the modular approach developed for relatively simple structures can be easily and efficiently extended to more complicated structures and can be used not only for explaining the stability of compounds but also for predicting the existence of new compounds and structure types. In particular, we predict that details of substitution in structures similar to **3** but containing other metal halide layers, for example, [Cd_{1-x}Cl₃], [Cu_{1-x}Cl₂], etc. [7], will be very similar to those observed for structure **3**. Inasmuch as the nature of the perovskite layer has a relatively weak effect on the degree of substitution, the differences revealed will be most likely due to specific features of the chemical nature of metal halide layers. To check the generality and formulations of quantitative criteria, additional studies of considered and newly predicted structures are evidently required, which we intend to perform in the future.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 09-03-01064.

REFERENCES

1. S. N. Putilin, E. V. Antipov, O. Chmaissem, and M. Marezio, *Nature* **362**, 226 (1993).
2. V. A. Isupov, *Zh. Neorg. Khim.* **39**, 731 (1994).
3. J. C. Boivin and G. Mairesse, *Chem. Mater.* **10**, 2870 (1998).
4. H. Kodama and N. Kabay, *Solid State Ionics* **141–142**, 603 (2001).
5. M. Nachida, J.-I. Yabunaka, T. Kijima, et al., *Int. J. Inorg. Mater.* **3**, 545–550 (2001).
6. J. M. Thomas, W. Ueda, J. Williams, and K. D. M. Harris, *Faraday Discuss. Chem. Soc.* **87**, 33 (1989).
7. D. O. Charkin, *Russ. J. Inorg. Chem.* **53** (13), 1977 (2008).
8. D. Ávila-Brande, L. C. Otero-Díaz, Á. R. Landa-Cánovas, et al., *Eur. J. Inorg. Chem.*, 1853 (2006).
9. D. Ávila-Brande, A. Gomez-Herrero, A. R. Landa-Cánovas, and L. C. Otero-Díaz, *Solid State Sci.* **7**, 486 (2005).
10. J. F. Ackerman, *J. Solid State Chem.* **62**, 92 (1986).
11. A. R. Paschoal, E. N. Silva, A. P. Ayala, et al., *Ferroelectrics* **337**, 207 (2006).
12. L. N. Kholodkovskaya, V. A. Dolgikh, and B. A. Popovkin, *Zh. Neorg. Khim.* **36**, 2205 (1991).
13. A. Castro, P. Millan, and R. Enjalbert, *Mater. Res. Bull.* **30**, 871 (1995).
14. D. O. Charkin and D. N. Lebedev, *Al'tern. Energ. Ekol.*, No. 1 (2008).
15. *Handbuch der präparativen anorganischen Chemie*, Ed. by G. Brauer (Ferdinand Enke, Stuttgart, 1975–1981; Moscow, 1985).
16. S. F. Meier and T. Schleid, *Z. Anorg. Allg. Chem.* **628**, 526 (2002).
17. V. Srikanth, H. Idink, W. B. White, et al., *Acta Crystallogr., Sect. B: Struct. Sci.* **52**, 432 (1996).
18. I. G. Ismailzade, *Problems of Crystallography* (Mosk. Gos. Univ., Moscow, 1972), pp. 265–277 [in Russian].
19. R. Marquart, B. J. Kennedy, and Y. Shimakawa, *J. Solid State Chem.* **160**, 174 (2001).
20. R. D. Shannon, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **32**, 751 (1976).
21. C. H. Hervoches and P. Lightfoot, *J. Solid State Chem.* **153**, 66 (2000).
22. TOPAS, version 3, Bruker AXS, Karlsruhe, Germany, 2005.
23. A. M. Kusainova, P. Lightfoot, W.-Z. Zhou, et al., *Chem. Mater.* **13**, 4731 (2001).
24. A. M. Abakumov, E. V. Antipov, L. M. Kovba, et al., *Usp. Khim.* **64**, 769 (1995).
25. B. Aurivillius, *Chem. Scr.* **23**, 143 (1984).