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New Aluminate with a Tetrahedral Structure Closely Related to the C_{84} Fullerene

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A new aluminate $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$, having an $F\bar{4}3m$ cubic structure ($a = 25.090$ Å, $Z = 4$) and forming a close packed face centered cubic array of "Al_{84}" fullerene geometry, has been discovered. This original structure consists of corner-sharing AlO_4 tetrahedra forming "$Al_{84}O_{106}$" cubic units whose assemblage delimits five types of cages, three of them being empty, one being occupied by strontium, and the fifth one forming the huge spheric fullerene-type cavity. In the latter, strontium, oxygen, and bismuth ions form concentric spheres, with an onion-skin-like configuration. The latter ions are disposed into a compact "$Bi_{16}O_{52-n}\square_n$" anion whose the exceptional geometry is characterized by a strong stereoactivity of the $6s^2$ lone pair of Bi^{3+}.

Aluminum, owing to its great ability to adopt the tetrahedral coordination, is often associated with silicon to form tridimensional tetrahedral frameworks characterized by large cages and tunnels such as zeolites and ultramarines,[1−4] which have been extensively studied for their ion exchange properties, their application as molecular sieves, and their catalytic properties. Pure aluminates forming such 3D-frameworks with large cages have also been synthesized but are much less numerous. It is the case of the sodalite family of generic formulation $A_8Al_{12}O_{24}(MO_n)$ with A = Ca, Sr, Ln and M = Cr, Mo, W, Pb.[5−13] The introduction of bismuth cations in an "Al−O" framework is also possible, as shown for instance by the bismuth−strontium aluminate $Sr_6Bi_2O_3(AlO_2)_{12}$[14] whose tetrahedral $[AlO_2]_\infty$ host lattice forms large cavities where strontium cations and Bi_2O_3 clusters are located. The latter results suggest that the association of bismuth−oxygen clusters to large cations such as strontium may be a very fruitful direction of research for the discovery of new aluminates involving large cages or tunnels. We have revisited the system Sr−Bi−Al−O, using solid-state techniques and working in a sealed tube. We describe here the synthesis, crystal growth, and structure of a new bismuth aluminate, $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$, with $\delta = 0.25$, whose tetrahedral "Al−O" framework consists of huge spherical cages "$Al_{84}O_{210}$" derived from the D_{2d} isomer of C_{84} fullerenes,[15] forming a closed packed face centered cubic array. We also show that, inside the "Al_{84}" spheres, the oxygen, strontium, and bismuth atoms form concentric spheres, leading to an onion-skin-like subnanostructure.

Experimental Section

Synthesis and Crystal Growth. The $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$ crystals were grown by classical solid-state techniques, grinding intimately a mixture of 0.5824 g of Bi_2O_3, 0.6578 g of SrO_2, and 0.3313 g of Al_2O_3. The mixture was pressed into pellets, introduced in a gold tube, and sealed in an evacuated silica ampule. The sample was heated at 1200 °C for 48 h, slowly cooled to 1000 °C for 100 h, kept at this temperature for 48 h, slowly cooled to 600 °C for 100 h, kept at this temperature for 24 h, and slowly cooled to RT

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Table 1. Crystallographic Data for $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$

chemical formula = $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$ ($\delta \approx 0.25$)	fw = 11517.6 g
$a = 25.090(6)$ Å	space group = $F\bar{4}3m$ (No. 216)
$b = 25.090(6)$ Å	$T = 20$°C
$c = 25.090(6)$ Å	$\lambda(\mathrm{Mo}\ K\alpha) = 0.71073$ Å
$\alpha = 90°$	$D_{calc} = 4.84\ g.cm^{-3}$
$\beta = 90°$	$\mu = 38.34\ mm^{-1}$
$\gamma = 90°$	$R(F_o) = 0.0400^a$
$V = 15794(7)$ Å^3	$R_w(F_o^2) = 0.0818^b$
$Z = 4$	

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Atomic Parameters of $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$

atom	Wyckoff position	x	y	z	$U_{eq}{}^a/U_{iso}$	occ
Bi(1)	16e	0.85005(4)	0.85005(4)	0.85005(4)	0.0156(4)^a	
Bi(2)	48h	0.29987(3)	0.29987(3)	0.59320(3)	0.0198(3)^a	
Bi(3)	48h	0.94475(4)	0.94475(4)	0.74886(6)	0.0238(5)^a	0.688(2)
Sr(1)	4c	0.75	0.25	0.75	0.007(1)^a	
Sr(2)	48h	0.82763(6)	0.82763(6)	0.46345(9)	0.0132(5)^a	
Sr(3)	48h	0.17534(7)	0.17534(7)	0.99084(9)	0.0218(6)^a	
Sr(4)	16e	0.92946(8)	0.92946(8)	0.92946(8)	0.0153(9)^a	
Sr(5)	16e	0.5870(1)	0.5870(1)	0.5870(1)	0.026(1)^a	
Al(1)	48h	0.0468(2)	0.0468(2)	0.1345(3)	0.011(2)	
Al(2)	48h	0.0895(2)	0.0895(2)	0.2444(3)	0.009(1)	
Al(3)	48h	0.7942(2)	0.7942(2)	0.1177(3)	0.007(1)	
Al(4)	48h	0.4545(2)	0.4545(2)	0.3661(3)	0.011(1)	
O(1)	24f	0.	0.	0.1121(9)	0.015(5)	
O(2)	48h	0.0259(6)	0.1083(4)	0.1083(4)	0.015(3)	
O(3)	96i	0.0421(7)	0.0585(7)	0.2042(6)	0.010(5)	0.5
O(4)	96i	0.1577(4)	0.0775(4)	0.2356(4)	0.015(2)	
O(5)	48h	0.0772(4)	0.0772(4)	0.3120(6)	0.012(3)	
O(6)	24g	0.75	0.75	0.1476(8)	0.011(5)	
O(7)	16e	0.8269(6)	0.8269(6)	0.1731(6)	0.011(6)	
O(8)	48h	0.5100(7)	0.4900(7)	0.345(1)	0.014(7)	0.5
O(9)	48h	0.4047(4)	0.4853(6)	0.4047(4)	0.018(4)	
O(10)	48h	0.796(1)	0.890(2)	0.796(1)	0.07(2)	0.61(9)
O(11)	96i	0.900(1)	0.826(1)	0.9206(9)	0.039(8)	0.5
O(12)	96i	0.2730(7)	0.3597(6)	0.5388(6)	0.055(4)	
O(13)	48h	0.331(2)	0.372(2)	0.628(2)	0.06(2)	0.333333

[a] $U_{eq} = {}^1/_3\sum U_{ij}$.

(room temperature) for 82 h. Four resulting products were obtained, yellow-orange crystals of $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$ and white, green, and black tiny crystals of unidentified compounds.

The quantitative synthesis in the form of polycrystalline powder was carried out also by solid-state reaction but from a stoichiometric mixture of oxides Bi_2O_3, SrO_2, and Al_2O_3 and of Al in order to obtain the final composition $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$. The mixture was inserted in a gold tube placed in an evacuated silica ampule, heated at 850 °C for 48 h, and cooled to room temperature for 16 h. By this method, a monophasic polycrystalline material was obtained.

The synthesis has been performed in a silica ampule in order to avoid the carbonatation of SrO_2 and the oxidation of Al in air. In order to avoid contact with silica, a gold tube was used rather than an alumina tube, which can react with the sample.

X-ray Single Crystal Study. A yellow platelet of $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$ with dimensions 0.111 × 0.060 × 0.050 mm^3 was chosen for the crystal diffraction study. The data were collected on a Bruker-Nonius Kappa CCD four circles diffractometer equipped with a bidimensional CCD detector. Pertinent parameters for the data collection are reported Table 1. The cubic cell parameters were refined using the whole data set. The data were corrected for Lorentz and polarization effects. The extinction conditions, $h + k = 2n + 1$, $k + l = 2n + 1$, and $h + l = 2n + 1$, are consistent with the following space groups: $Fm3m$ (No. 225), $F\bar{4}3m$ (No. 216), $F432$ (No. 209), $Fm3$ (No. 202), and $F23$ (No. 196). The heavy atom method was used for the structure determination. The calculations were performed using the SHELX 97 programs package.[16] Whereas no solutions were found using the $Fm3m$ space group, a structural model was obtained using the $F\bar{4}3m$ one. The refinement, using the data set corrected from the absorption by Gaussian integration method, leads to the agreement factors $R(F_o) = 0.04$ and $R_w(F_o^2) = 0.0818$ with the atomic parameters reported Table 2. In this model, several disorders exist. First, the Bi(3) site is partially occupied (at 69%); such occupation has been introduced because the electronic density observed on this site is low and because the Bi(3) environment is characteristic of a bismuth site (see Bi(3) environment in the description part). Second, several oxygen atoms have been split on sites located close to symmetry elements, because when they were placed on the symmetry elements they exhibit high thermal factors (being about four times higher than for the other oxygen atoms) and electronic residues are observed nearby on the difference Fourier maps. Thus, the O(3) and O(11) atoms have been split each on two sites located close to an m mirror: the O(8) atom has been split on 2 sites located in an m mirror but close to the intersection of two m mirrors, and the O(13) atom has been split on three sites close to a 3-fold axis. Third, the O(10) site is partially occupied, because if a full occupancy is introduced, the thermal factor is high and no electronic residues can be observed nearby on the difference Fourier map. Moreover, to ensure the charge balance in the chemical formula, partial occupancies have to be introduced on the oxygen sites. In order to propose a model with less disorder, we checked whether the crystal structure could be better described in a cubic and less symmetric space group. The model found with the $F\bar{4}3m$ space group indicates that no 4-fold axes and no inversion centers exist in this structure; consequently, the $F432$ and the $Fm3$ space groups have been discarded. On the opposite, the suppression of the m mirrors and the replacement of the $\bar{4}$ axes by 2-fold axes allow us to describe the structure with $F23$. The refinement in this space group leads to a structural model very close to the $F\bar{4}3m$ one with $R(F_o) = 0.0442$ and $R_w(F_o^2) = 0.0883$, 1886 independent reflections with $I > 3\sigma(I)$, and 126 parameters. In this model, the atoms corresponding to Bi(3) and O(10) sit on general positions, and they exhibit partial occupancies and thermal factors equal to those calculated for the previous model. The atoms corresponding to O(8) and O(13), located close to 2-fold and 3-fold axes, respectively, exhibit thermal factors equal to those calculated for the previous model. The atoms corresponding to O(3) and O(11) sit in general positions, and their isotropic thermal factors (equal to 0.039(5) and 0.09(2) Å^2, respectively) are much higher than those in the $F\bar{4}3m$ model. The $F23$ model does not improve the structural description (it even offers a worse model for O(3) and O(11)); consequently, we decide to keep the $F\bar{4}3m$ description. Note that, to clarify the representation of the structure, the O(3), O(8), O(11), and O(13) atoms were not split on the drawings.

Description of the Structure and Discussion

The crystal structure of this new aluminate consists of a 3D-framework of corner-sharing AlO_4 tetrahedra, $[Al_{48}O_{94}]_\infty$ (Figure 1) containing strontium cations and bismuth−oxygen clusters. The $[Al_{48}O_{94}]_\infty$ framework can be described as the assemblage of "$Al_{48}O_{106}$" cubic units through the corners of their tetrahedra, displayed at the nodes of a face centered

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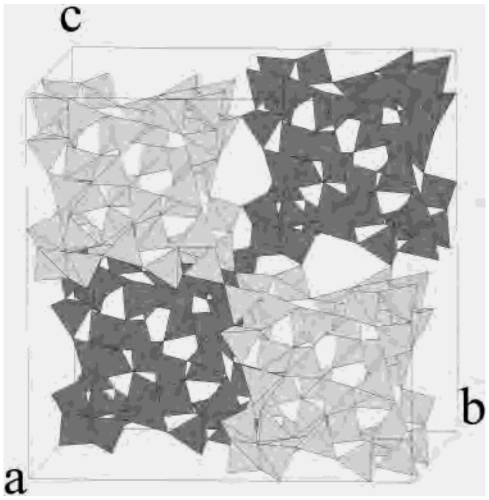

Figure 1. Representation of the $[Al_{48}O_{94}]_\infty$ aluminate framework of $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$ showing the face centered cubic arrangement of four $Al_{48}O_{106}$ cubic units within a unit cell. (For clarity, the cubic units located at $0 < x < 0.5$ and $0.5 < x < 1$ are drawn in dark and light gray, respectively.)

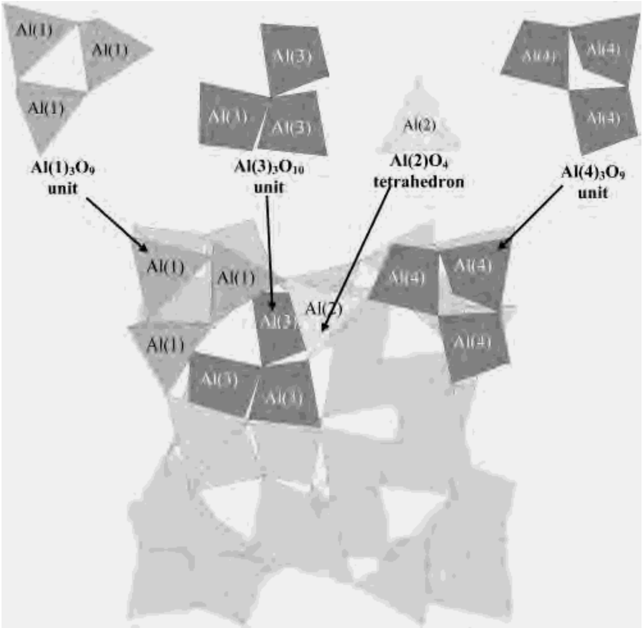

Figure 2. "$Al_{48}O_{106}$" unit formed by $Al(1)_3O_9$, $Al(4)_3O_9$, and $Al(3)_3O_{10}$ units and $Al(2)O_4$ tetrahedra.

cubic lattice, as shown in Figure 1. Each "$Al_{48}O_{106}$" unit contains four types of crystallographic aluminum sites, labeled Al(1), Al(2), Al(3), and Al(4), respectively. As shown in Figure 2, the Al(1) and Al(4) tetrahedra form separately triangular Al_3O_9 units, whereas the Al(3) tetrahedra form Al_3O_{10} units where three Al(3) tetrahedra share the same apex. Finally, the Al(2) tetrahedra are isolated from each other, each tetrahedron sharing its apices with two Al(3) tetrahedra, one Al(1) tetrahedron and, one Al(4) tetrahedron. The Al−O interatomic distances (Table 3) show that the Al(1), Al(2), and Al(4) tetrahedra are almost regular ranging from 1.74(1) to 1.78(2) Å. In contrast, the Al(3) tetrahedron is more distorted, with Al−O distances ranging from 1.74(1) to 1.811(17) Å. The longest distance is observed for the O(7) atom which is linked to three Al atoms.

The $[Al_{48}O_{94}]_\infty$ framework delimits five types of cages. Four of them are located either inside the $Al_{48}O_{106}$ units (labeled A, B, C) or at the junction between four units (labeled D). Three cages (A, B, and D) are empty, and the fourth one, C, is occupied by strontium. The A cage (Figure 3a) is delimited by nine AlO_4 tetrahedra (3Al(3), 3Al(2), 3Al(1)) and exhibits three pentagonal windows. The B cage (Figure 3b) is formed by 12 AlO_4 tetrahedra (3Al(4), 3Al(2), and 6Al(3)), and it exhibits four hexagonal windows. The C cage (Figure 3c) is located at the center of the $Al_{48}O_{106}$ cubic unit and is built up from the assemblage of 12 AlO_4 tetrahedra Al(3). This cage, which has a pseudotetrahedral configuration, exhibits four large six-sided windows. The strontium cation Sr(1) sits at the center of this cage and is surrounded by 6 oxygen neighbors, forming an octahedral coordination with Sr−O distances equal to 2.57(2) Å (Table 4). The D cage (Figure 3d) sits at the center of the cubic cell, at the junction of four "$Al_{48}O_{106}$" cubic units. It is delimited by 12 Al(4) tetrahedra forming four six-sided windows. The fifth cage is large and cannot easily be seen from Figure 1, since it is surrounded by six "$Al_{48}O_{106}$" cubic units. Due to the fact that the faces of the cubic $Al_{48}O_{106}$ units are not planar, but are concave, the so-formed huge cavity is spheric. This cage is formed by the assemblage of 84 AlO_4 tetrahedra and can be formulated as an "$Al_{84}O_{210}$" sphere (Figure 4). It is in these large spheres that sit the majority of strontium cations and bismuth oxygen clusters.

In fact, the whole structure of this aluminate can be better described from the "$Al_{84}O_{210}$" spheres or more exactly from the corresponding networks of aluminum atoms. The aluminum atoms form indeed huge "Al_{84}" spheres (Figure 5) whose geometry is identical to that observed for the D_{2d} isomer of C_{84} fullerenes.[15] Thus, each "Al_{84}" sphere is built up of Al_5 pentagons and Al_6 hexagons similarly to this fullerene, the only difference being the size of the "Al_{84}" sphere whose diameter, close to 18.5 Å, is about twice as large as that for the C_{84} fullerene. This larger size of "Al_{84}" compared to C_{84} is due to the presence of oxygen, located halfway between two adjacent Al atoms, forming −Al−O−Al− bonds around all the surface of the sphere. But the main difference with the fullerenes deals with the fact that the "Al_{84}" spheres are not isolated. Each sphere shares indeed an hexagonal "Al_6" face with 12 other identical spheres, forming a face centered cubic array of spheres as shown from the projection of the $[Al]_\infty$ lattice along a direction close to [100] (Figure 6). The assemblage of the "$Al_{84}O_{210}$" spheres leads to the $[Al_{48}O_{94}]_\infty$ framework. Considering one "$Al_{84}O_{210}$" sphere, one observes that 84 oxygen atoms are located outside the sphere, 72 of them are shared with the adjacent spheres (6 × 12), and the other 12 oxygen atoms ensure Al−O−Al bonds between two neighboring spheres. The remaining 126 oxygen atoms plaster the internal wall of the "Al_{84}" sphere, forming an "O_{126}" sphere (Figure 7). The latter is built up of corner-sharing "O_3" triangles forming hexagonal "O_6" and pentagonal "O_5" windows similar to the "Al_{84}" sphere but sharing corners instead of edges.

The strontium cations (Sr(1) excepted) and the "$Bi_{16}O_{52-n}\square_n$" anion ($n \approx 4.625$) are then inserted in the "Al_{84}"

Table 3. Distances (Å) and Angles (deg) in Polyhedra of $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$

Al(1)	O(1)	O(2)	O(2^{i})	O(3)/O(3^{ii})
O(1)	**1.75(1)**	105.5(7)	105.5(7)	112(1)/112(1)
O(2)	2.80(1)	**1.757(8)**	112(1)	101.8(8)/118.4(7)
O(2^{i})	2.80(1)	2.92(3)	**1.757(8)**	118.4(7)/101.8(8)
O(3)/O(3^{ii})	2.94(2)/2.94(2)	2.74(2)/3.04(2)	3.04(2)/2.74(2)	**1.78(2)/1.78(2)**

Al(2)	O(3)/O(3^{ii})	O(4)	O(4^{ii})	O(5)
O(3)/O(3^{ii})	**1.74(2)/1.74(2)**	121.2(7)/104.3(7)	104.3(7)/121.2(7)	111.2(8)/111.2(8)
O(4)	3.04(2)/2.76(2)	**1.75(1)**	108.7(8)	105.3(5)
O(4^{ii})	2.76(2)/3.04(2)	2.85(2)	**1.75(1)**	105.3(5)
O(5)	2.88(2)/2.88(2)	2.78(2)	2.78(2)	**1.75(2)**

Al(3)	O(6)	O(4^{iii})	O(4^{iv})	O(7)
O(6)	**1.74(1)**	114.7(5)	114.7(5)	104(1)
O(4^{iii})	2.93(2)	**1.74(1)**	105.2(7)	109.0(6)
O(4^{iv})	2.93(2)	2.77(2)	**1.74(1)**	109.0(6)
O(7)	2.80(2)	2.89(1)	2.89(1)	**1.811(7)**

Al(4)	O(8)/O(8^{ii})	O(9)	O(9^{v})	O(5^{vi})
O(8)/O(8^{ii})	**1.74(1)/1.74(1)**	120.9(9)/100.5(1.0)	100.5(1.0)/120.9(9)	110.9(9)/110.9(9)
O(9)	3.04(2)/2.69(2)	**1.761(8)**	108.7(9)	107.5(6)
O(9^{v})	2.69(2)/3.04(2)	2.86(3)	**1.761(8)**	107.5(6)
O(5^{vi})	2.88(2)/2.88(2)	2.84(2)	2.84(2)	**1.76(2)**

Bi(1)	O(10)	O(10^{i})	O(10^{v})	O(11)/O(11^{vii})	O(11^{i})/O(11^{viii})	O(11^{ii})/O(11^{v})
O(10)	**2.17(4)**	101(1)	101(1)	165(1)/165(1)	93(1)/79(1)	93(1)/79(1)
O(10^{i})	3.35(7)	**2.17(4)**	101(1)	79(1)/93(1)	165(1)/165(1)	79(1)/93(1)
O(10^{v})	3.35(7)	3.35(7)	**2.17(4)**	93(1)/93(1)	79(1)/93(1)	165(1)/165(1)
O(11)/ O(11^{vii})	4.38(5)/ 4.38(5)	2.82(5)/ 3.22(4)	3.22(4)/ 3.36(5)	**2.26(2)/** **2.26(2)**	85.7(9)/96(1)/ 72(1)/85.7(9)	72(1)/85.7(9)/ 85.7(9)/96(1)
O(11^{i})/ O(11^{viii})	3.22(4)/ 2.82(5)	4.38(5)/ 4.38(5)	2.82(5)/ 3.22(4)	3.07(4)/2.64(5)/ 3.36(5)/3.07(4)	**2.26(2)/** **2.26(2)**	96(1)/85.7(9)/ 85.7(9)/72(1)
O(11^{ii})/ O(11^{v})	3.22(4)/ 2.82(5)	2.82(5)/ 3.22(4)	4.38(5)/ 4.38(5)	2.64(5)/3.07(4)/ 3.07(4)/3.36(5)	3.36(5)/3.07(4)/ 3.07(4)/2.64(5)	**2.26(2)/** **2.26(2)**

Bi(2)	O(12)	O(12^{ii})	O(13)/O(13^{ii})	O(10^{ix})	O(10^{x})
O(12)	**2.14(2)**	92.0(9)	77(2)/106(2)	80(1)	142(1)
O(12^{ii})	3.08(3)	**2.14(2)**	106(2)/77(2)	142(1)	80(1)
O(13)/O(13^{ii})	2.68(5)/3.42(2)	3.42(2)/2.68(5)	**2.16(3)/2.16(3)**	109(2)/141(2)	141(2)/109(2)
O(10^{ix})	2.95(3)	4.33(4)	3.74(6)/4.34(5)	**2.45(3)**	84(2)
O(10^{x})	4.33(4)	2.95(3)	4.34(5)/3.74(6)	3.27(9)	**2.45(3)**

Bi(3)	O(12^{xi})	O(12^{xii})	O(11^{i})/O(11^{viii})
O(12^{xi})	**2.24(2)**	107.0(8)	78.0(7)/92.5(7)
O(12^{xii})	3.60(3)	**2.24(2)**	92.5(7)/78.0(7)
O(11i)/O(11^{viii})	2.87(3)/3.29(3)	3.29(3)/2.87(3)	**2.31(2)/2.31(2)**

sphere in the form of concentric spheres, showing an onion-skin-like subnanostructure. Inside the "O_{126}" sphere, the remaining strontium cations (Sr(2), Sr(3), Sr(4), Sr(5)) and a part of the bismuth cations (labeled Bi(3)) form a third smaller concentric pseudosphere $Sr_{32}(Bi_{8+\delta}\square_{4-\delta})$ (with $\delta \approx 0.25$) (Figure 8). The latter can be described as an interpenetration of two sorts of pseudospheric arrays, the "Sr_{32}" array and the lacunar array "$Bi_{8+\delta}\square_{4-\delta}$" where $^{1}/_{3}$ of the bismuth sites (Bi(3)) are statistically unoccupied. The "Sr_{32}" array is built up of edge-sharing four-sided and six-sided rings. The Sr(2), Sr(4), and Sr(5) cations sit in front of the hexagonal windows of the "O_{126}" sphere, whereas the Sr(3) cations sit in front of the pentagonal windows of the same sphere. The partially occupied pseudospheric array of bismuth " $Bi_{8+\delta}\square_{4-\delta}$" consists of "$Bi_4$" squares and "$Bi_3$" triangles. These bismuth cations (labeled Bi(3)) sit in front of some hexagonal windows formed by the "O_{126}" sphere. The pseudosphere "$Sr_{32}Bi_{8+\delta}\square_{4-\delta}$" is in fact sandwiched between the "O_{126}" sphere and a fourth sphere containing only oxygen, formulated "O_{40}" (Figure 9). In this sphere, the oxygen array forms O_3 triangles and O_4 squares. The coordination of the strontium cations is variable (see drawings of the Sr environments in Supporting Information). The Sr(2) cation exhibits a monocapped prismatic coordination with 6 Sr−O distances ranging from 2.47(2) to 2.626(6) Å and one distance equal to 2.79(2) Å. The Sr(3) cation is surrounded by 8 oxygen atoms and exhibits a complex coordination polyhedron having a pentagonal face (with Sr−O distances ranging from 2.69(1) to 2.71(4) Å) opposite to a triangular face (with Sr−O distances ranging from 2.54(1) to 2.59(3) Å). The Sr(4) cation exhibits a tricapped prismatic coordination with 6 Sr−O distances ranging from 2.711(9) to 2.71(2) Å and 3 longer distances equal to 2.77(2) Å. The Sr(5) cations exhibit tetrahedral coordination with short Sr−O distances ranging from 2.52(6) to 2.57(2) Å. The coordination of Bi(3) emphasizes the stereoactivity of its $6s^2$ lone pair. Each partially occupied Bi(3) site is surrounded by three oxygen atoms (one O(11) and two O(12)) with rather short Bi−O distances ranging from 2.24(2) to 2.31(2) Å. The disposition of the oxygen atoms with respect to Bi(3))

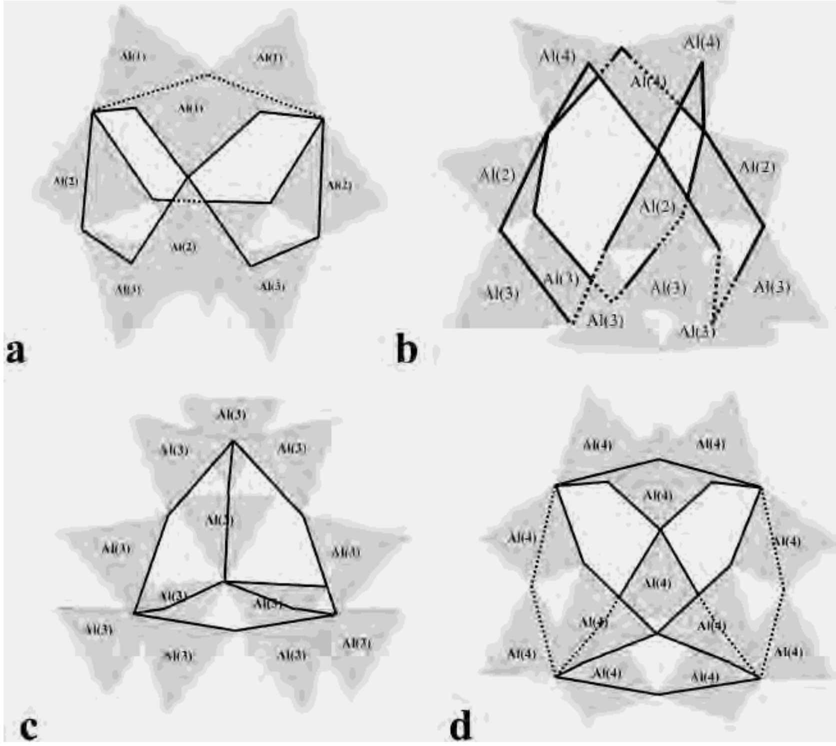

Figure 3. A, B, and C cages located inside the "$Al_{48}O_{106}$" units (a, b, c) and D cage located at the junction between four units (d). The borders of their windows are represented in bold.

Table 4. Distances (Å) in $Sr_{33}Bi_{24+\delta}Al_{48}O_{141+3\delta/2}$

O(3)−O(3^{ii})	0.58(4)
O(8)−O(8^{ii})	0.71(5)
O(11)−O(11^{vii})	0.73(5)
O(13)−O(13^{ii})	1.5(1)
O(13)−O(13^{xiii})	1.5(1)
Sr(1)−O(6)	2.57(2) × 6
Sr(2)−O(12)	2.47(2) × 2
Sr(2)−O(4)	2.55(1) × 2
Sr(2)−O(5)	2.626(6) × 2
Sr(2)−O(9)	2.79(2)
Sr(3)−O(2)	2.54(1)
Sr(3)−O(11)	2.59(3) × 2
Sr(3)−O(4)	2.69(1) × 2
Sr(3)−O(12)	2.71(2) × 2
Sr(3)−O(10)	2.71(4) × 0.61
Sr(4)−O(1)	2.711(9) × 3
Sr(4)−O(11)	2.71(2) × 3
Sr(4)−O(2)	2.77(2) × 3
Sr(5)−O(13)	2.52(6)
Sr(5)−O(9)	2.57(2) × 3
i	z, x, y
ii	y, x, z
iii	$-x + 1, -z + 1, y$
iv	$-z + 1, -x + 1, y$
v	y, z, x
vi	$-x + {}^1/_2, -y + {}^1/_2, z$
vii	z, y, x
viii	x, z, y
ix	$-z + 1, x - {}^1/_2, -y + {}^3/_2$
x	$z - {}^1/_2, -x + 1, -y + {}^3/_2$
xi	$-z + {}^3/_2, y + {}^1/_2, -x + 1$
xii	$y + {}^1/_2, -z + {}^3/_2, -x + 1$
xiii	$y, -z + 1, -x + 1$

shows that bismuth adopts a tetrahedral coordination forming a BiO_3L tetrahedron, whose fourth apex corresponds to its $6s^2$ electronic lone pair L.

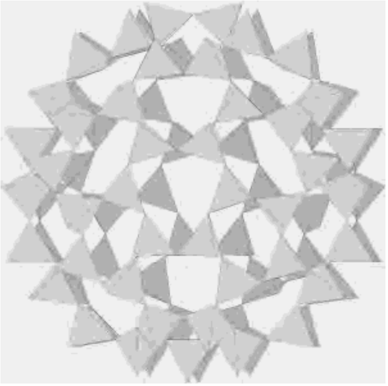

Figure 4. "$Al_{84}O_{210}$" cage projected along a direction close to [110]. The polyhedra located at the back are drawn in medium gray.

A fifth sphere is formed by the cluster "Bi_{16}" located at the center of the "O_{40}" sphere (Figure 10). The latter forms edge-sharing "Bi_3" triangles characterized by Bi−Bi distances ranging from 3.539(2) to 4.214(2) Å (bismuth atoms labeled Bi(1) and Bi(2)). This bismuth sphere contains an "$O_{12-n}\square_n$" truncated tetrahedron ($n \approx 4.625$) (Figure 11) whose sites are only occupied at 61% (oxygen labeled O(10)). The Bi(1) and Bi(2) cations of the "Bi_{16}" sphere, the oxygen O(10) atoms of the "$O_{12-n}\square_n$" truncated tetrahedron, and the oxygen atoms O(11), O(12), and O(13) of the "O_{40}" sphere form a complex anion "$Bi_{16}O_{52-n}\square_n$" with $n \approx 4.625$, whose geometry is exceptional and observed for the first time. Admitting in a first approach that the O(10) sites are fully occupied and that the O(11) and O(13) oxygens are not split, the "$Bi_{16}O_{52}$" pseudospheric anion (Figure 12) can be described by the association of six bipyramids "Bi_2O_8" (light gray colored) and four BiO_6 octahedra (medium gray

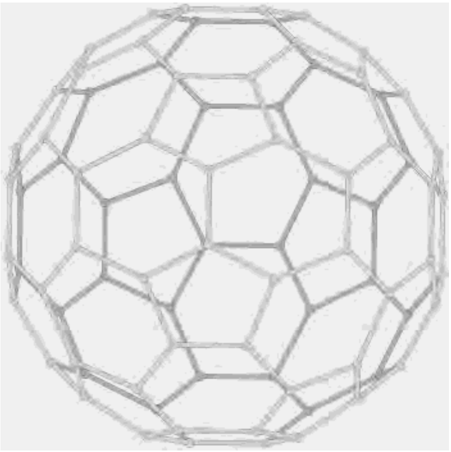

Figure 5. “Al_{84}” sphere. Al atoms located at the back are represented in medium gray.

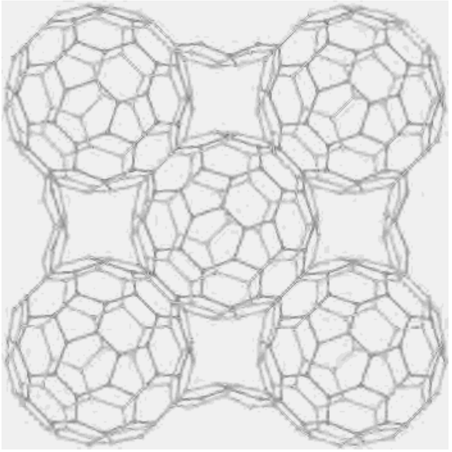

Figure 6. Face centered cubic arrangement of the “Al_{84}” spheres forming the $[Al_{84}O_{94}]_\infty$ framework. For clarity, only the spheres centered on one (100) plane of the fcc arrangement are drawn, and the Al atoms located in the back are represented in medium gray.

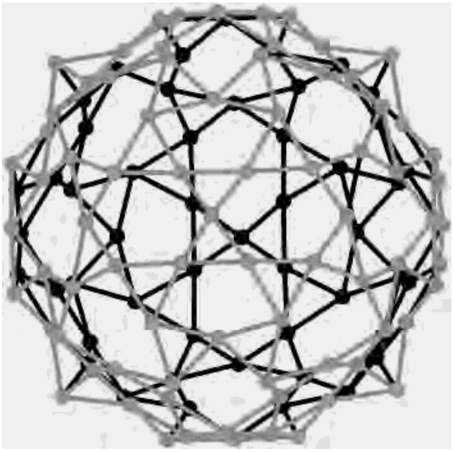

Figure 7. “O_{126}” sphere. The O atoms located in the back are drawn in black.

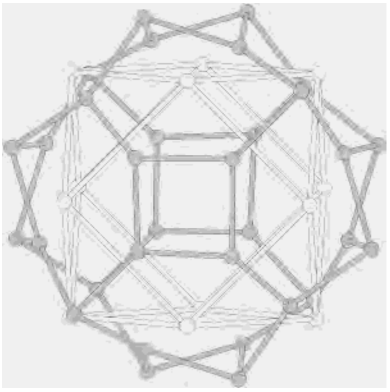

Figure 8. “$Sr_{32}Bi_{8+\delta}\square_{4-\delta}$” sphere. The “$Sr_{32}$” and the “$Bi_{8+\delta}\square_{4-\delta}$” arrays are drawn in light gray and white, respectively.

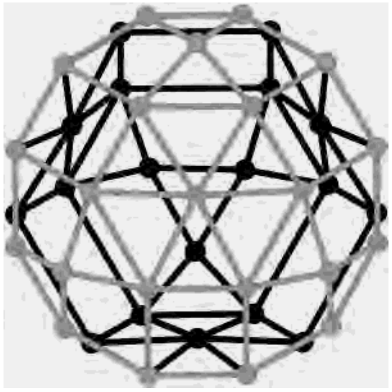

Figure 9. “O_{40}” sphere. The O atoms located in the back are drawn in black.

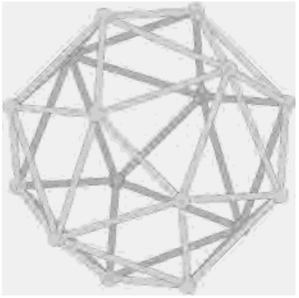

Figure 10. “Bi_{16}” sphere. The Bi atoms located in the back are drawn in medium gray.

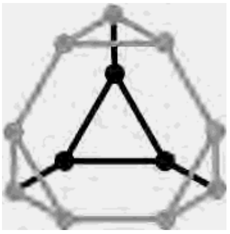

Figure 11. “$O_{12-n}\square_n$” truncated tetrahedron. The O atoms located in the back are drawn in black.

colored) sharing their apices. In this “ideal” anion, the bipyramidal units consist of two edge-sharing $Bi(2)O_5$ pyramids, and the apical apex (oxygen O(13)) of each Bi(2) pyramid is shared by three different Bi_2O_8 units. The 12 oxygen atoms of the common edges of the Bi_2O_8 units (labeled O(10)) are shared by four BiO_6 octahedra. They form the “$O_{12-n}\square_n$” truncated tetrahedra located inside the “Bi_{16}” spheres. The remaining oxygens of the Bi_2O_8 units and of the BiO_6 octahedra (O(12), O(13), and O(11), respectively) form the “O_{40}” sphere enveloping the “Bi_{16}” spheres.

In fact, the coordination of bismuth is more complex than that expressed herein, since the O(10) site is only $^2/_3$ occupied and the O(11) and O(13) sites are split into two and three sites, respectively. Such disorders allow the strains to be

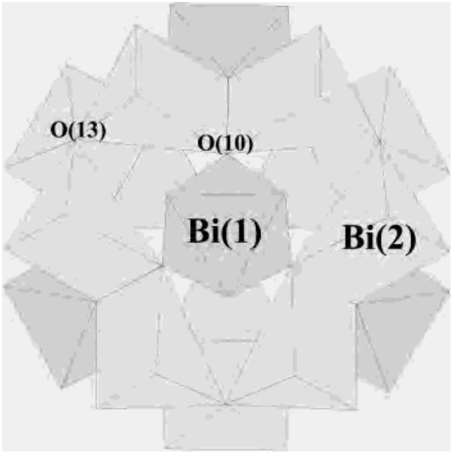

Figure 12. "$Bi_{16}O_{52}$" anion with $Bi(1)O_6$ octahedra in medium gray and $Bi(2)_2O_8$ units in light gray.

relaxed, demonstrating that such a compact anion can be stabilized. As a consequence, Bi(1) exhibits not only octahedral coordination but also pyramidal coordination due to the existence of $^1/_3$ vacancies on the O(10) sites. The latter can also be expressed as the result of a lone pair effect, forming BiO_5 L octahedra. It is worth noting that the Bi(1)−O distances, ranging from 2.17(4) to 2.26(2) Å (Table 3), are all very short, suggesting strong covalency. Similarly, the coordination of the Bi(2) cation should not be described as pyramidal only since $^1/_3$ of its two O(10) neighbors and $^2/_3$ of its O(13) neighbors are missing. Thus, Bi(2) can be also surrounded either by four oxygen atoms forming BiO_4L trigonal bipyramids or by three oxygen atoms forming BiO_3L tetrahedra. The relative disposition of the atoms and the observed Bi(2)−O interatomic distances (Table 3) are in agreement with this viewpoint. The absence of oxygen on the O(13) site may indeed lead to the square pyramid BiO_4L characterized by two short equatorial Bi−O bonds of 2.14(2) Å and two long equatorial ones equal to 2.45(3) Å, the lone pair being apical. Similarly, the absence of two oxygen atoms O(10) may lead to the BiO_3L tetrahedron characterized by three short Bi−O bonds (ranging from 2.14(2) to 2.16(3) Å).

In conclusion, a new aluminate with a tridimensionnal framework built up of AlO_4 tetrahedra, closely related to the fullerenes, has been synthesized. To our knowledge, this is the first example of a fullerenoid oxide. There is no doubt that the presence of bismuth−oxygen clusters plays a dominant role in the stabilization of the huge "Al_{84}" fullerene-type spheres of this very original structure. The $6s^2$ electronic lone pair of Bi^{3+} is certainly an important factor for the creation of pseudospheric anions, similar to its important role for the creation of layer structures such as Aurivillius phases. The close relationships of this structure with the fullerenes open the route to the research of other members, varying the size of the "Al_n" spheres and their mode of connection in the structure. The potential of these materials for various properties, using the possibility of numerous possible substitutions, should be investigated in the future.

Supporting Information Available: Crystallographic data in CIF format and drawings of the Sr and Bi environments. This material is available free of charge via the Internet at http://pubs.acs.org.

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