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$Bi(F, O)_{2.45}$: An Anion-Excess Fluorite Defect Structure Deriving from Rhombohedral *Ln*FO Type

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During a reinvestigation of the Bi_2O_3–BiF_3 system, a nonstoichiometric oxidefluoride, of composition range $Bi(F, O)_{2.50}$–$Bi(F, O)_{2.43}$ at 500°C, was characterized by annealing at temperatures higher than 300°C.

Its crystal structure was solved by X-ray diffraction on a single crystal of composition $Bi(F, O)_{2.45}$, in the *R*-3*m* space group with cell parameters: $a = 4.1378(9)$ Å and $c = 20.321(3)$ Å (Shelxl program: $wR_2 = 7.2\%$, $R_1 = 3.5\%$).

The structure of $BiF_{1.90}O_{0.55}$ derives from the well-known rhombohedral *Ln*FO type by formation of 1 : 0 : 3 (or 1 : 0 : 2) clusters orientated along the [001] axis of the hexagonal associated cell in a partly ordered way. This orientation of the clusters preserves the O/F long range order characteristic of the *Ln*FO type, despite a statistical replacement of almost half the O anions by F ones. As in the tetragonal anion-excess $LaF_{1+2x}O_{1-x}$ and the orthorhombic $SmF_{1+2x}O_{1-x}$ fluorite-related phases, the clustering mainly affects the F site: F anionic vacancies are associated to F_i interstitial anions and to F_r anions relaxed from the normal F site. In the clusters, Bi cations are in 9-fold or 10-fold coordination and the higher limit of anionic insertion (Bi_2F_4O composition) corresponds to a complete juxtaposition of 1 : 0 : 3 clusters. Near this limit, the excess anions tend to form quasi-continuous irregular 3^6 sheets perpendicular to the [001] axis of the hexagonal cell. © 1999 Academic Press

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INTRODUCTION

A reinvestigation of the Bi_2O_3–BiF_3 system, in the $BiFO$–BiF_3 part, showed (1–3) the presence of phases either stoichiometric or almost stoichiometric as, e.g., $Bi_7F_5O_{11}$ of which a crystal structure was recently described (4) or presenting a composition range. All these phases derive from fluorite type and are characterized by an extensive ordering of O and F anions. The present paper describes the structural features of a nonstoichiometric rhombohedral phase of composition range $Bi(F, O)_{2.43\text{–}2.50}$, stable above 300°C.

EXPERIMENTAL

For temperatures higher than 300°C, a nonstoichiometric domain $BiF_{1+2x}O_{1-x}$ has been isolated. It is delimited by a Bi_2F_4O ($Bi(F, O)_{2.50}$) composition on one side and by a limit varying with temperature on the other side ($Bi(F, O)_{2.43}$ at 500°C). The samples were prepared at 500°C for 12 h, in gold sealed tubes, and then water-quenched. This phase has been indexed on a single crystal in the rhombohedral system (*R*-3*m*, *R*3*m* or related space group) with the hexagonal cell parameters: $a = 4.1378(9)$ Å and $c = 20.321(3)$ Å for the composition $Bi(F, O)_{2.45}$. The X-ray powder pattern shows the presence of a strong distorted fcc sublattice of average cell parameter a_F, from which a superlattice derives by the relationship: $a = a_F\sqrt{2}$ and $c = 2c_F\sqrt{3}$. Thus, this Bi oxidefluoride could be related, in spite of its chemical formula, to the well-known rhombohedral rare earth oxidefluorides, characterized by a similar unit cell (e.g., LaFO: $a = 4.051$ Å, $c = 20.212$ Å; *R*-3*m* space group). This last structure derives from the fluorite type of a O/F ordering along a [111] axis of the fluorite cell. Single crystals suitable for a structure determination have been prepared by a slow cooling down to 500°C and a one-day-annealing at this last temperature of a mixture of $Bi(F, O)_{2.45}$ composition, previously heated at 800°C for one day in a gold sealed tube.

Thus, considering the interest to determine the structural features of this new kind of defect structure deriving from the fluorite type, a single crystal of good quality has been

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TABLE 1
Crystal Data and Structure Refinement for $BiO_{0.55}F_{1.90}$

Empirical formula	$BiF_{1.90}O_{0.55}$ ($z = 6$)
Formula weight	2669.76
Wavelength	0.71073 Å
Crystal system	rhombohedral
Space group	*R*-3*m*
Cell parameters (hex.)	$a = 4.1378(9)$ Å, $c = 20.321(3)$ Å $V = 301.31(12)$ Å^3
Density	$d_{th} = 8.40$, $d_{exp} = 8.47$
Absorption coefficient	174.57 mm^{-1}
F(000)	1074
Crystal size	$0.1 \times 0.1 \times 0.1$ mm
Angular range for data collection (2θ)	6.02 to 76.42°.
Index range	$-5 \leq h \leq 5$, $-5 \leq k \leq 1$, $-25 \leq l \leq 25$
Collected reflections	648
Independent reflections	113 [*R*(int) = 0.0818]
Refinement method	full matrix least-squares on F^2
Data/restraints/parameters	113/1/ 18
R [$I > 2\sigma$(I)]	$R_1 = 0.0351$, $wR_2 = 0.0721$
R (all data)	$R_1 = 0.0392$, $wR_2 = 0.0763$
Extinction coefficient	0.00000(9)
Largest diff. peak and hole	4.77 and -3.20 e. Å^{-3}

chosen and measured on a Siemens P4 diffractometer under the conditions presented in Table 1.

The Bi position has been determined by direct methods with the SHELXS86 program and refined with SHELXL93 (5), in the *R*-3*m* space group, on a 6*c* site (0, 0, *z*; $z = 0.2471$). Then, five anionic positions were detected by Fourier-difference calculations. The first two (O and F_1) correspond to quite the same anionic sites as in the rh-*Ln*FO mother structure. The three other sites (for which Fourier-difference maps are shown on Fig. 1) are interstitial sites. Owing to the nonstoichiometric character of this defect structure, the occupation rate of these five anionic sites has been refined in successive steps, alternating with refinement of atomic coordinates and of isotropic thermal vibration factors. However, as in many crystal structures involving a statistical distribution of atoms on close sites, some correlations between structural parameters of the closest sites occur and a need to apply some constraints arises. Therefore, the thermal parameters of the closest F sites (F_2 and F_4 on one side, F_1 and F_3 on the other side) have been constrained to be the same and the sum of occupancies has been fixed to the experimental number of anions O and F resulting from a chemical analysis. Under these conditions, a good convergence of the refinement has been effective in the *R*-3*m* space group. Attempts in the *R*-3 space group do not improve the results. After introduction of an anisotropic thermal vibration coefficient for Bi, of extinction, and of a weighting scheme, the final *R* values converge to $wR_2 = 7.2\%$ and $R_1 = 3.5\%$. The refined parameters are presented in Table 2 and the main interatomic distances in Table 3.

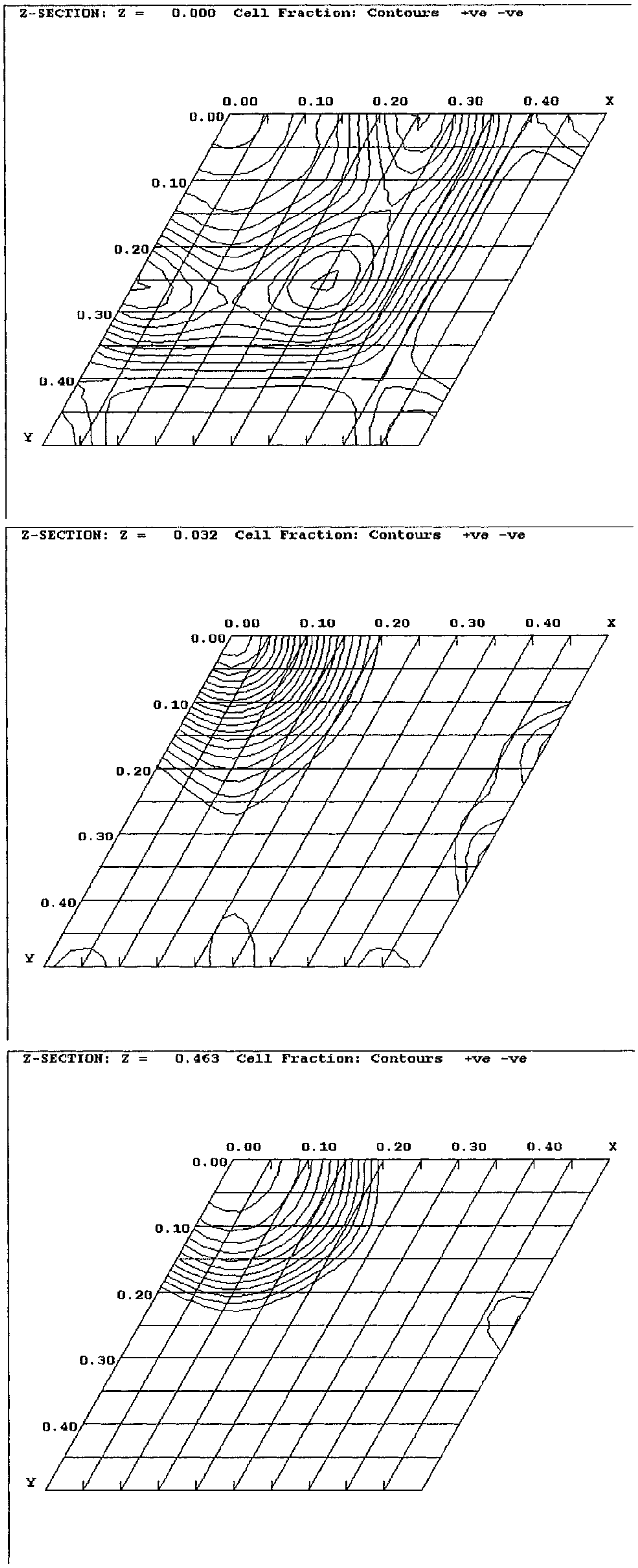

FIG. 1. Fourier-difference maps at three *z* levels (0, 0.032, and 0.463), showing, respectively, the F_2, F_4, and F_3 interstitial sites.

TABLE 2
Atomic Coordinates, Anisotropic and Equivalent Isotropic Displacement Parameters (Å^2)

Atom	x	y	z	U_{eq} (Å^2)	τ^a
Bi	0	0	0.2471(1)	0.057(1)	1
O	0	0	0.130(1)	0.061(8)	0.90(6)
F(1)	0	0	0.378(2)	0.097(1)	0.66(5)
F(2)	0.237(23)	0	0	0.067(2)	0.40(8)
F(3)	0	0	0.463(4)	0.097(1)	0.29(6)
F(4)	0	0	0.031(4)	0.067(2)	0.20(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi	0.059(1)	0.059(1)	0.054(1)	0	0	0.029(1)

Note. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[a] Site occupancy by reference to 1 for Bi site (6*c*).

STRUCTURE DESCRIPTION

Projections of the content of the unit cell of Bi(F, O)$_{2.45}$ onto *xy* and *yz* planes are represented in Fig. 2. Bi cations constitute, as in the rhombohedral *Ln*FO type, a slightly distorted fcc network, with a [111] direction colinear with the [001] axis of the hexagonal supercell. Bi–Bi shorter distances range from 4.05 to 4.24 Å. O and F$_1$ sites, respectively, correspond to O and F anionic sites of the *Ln*FO structure and therefore to normal anionic sites of the fluorite subcell. Figure 3 shows the “BiFO” (rh-*Ln*FO-type) part of the structure and the F$_2$, F$_3$, and F$_4$ additional sites. If the O site is almost filled ($\tau = 0.90(6)/1$), the F$_1$ site contains about 1/3 vacancies and the three new anionic sites are only partly occupied: F$_2$ (x, 0, 0; $x = 0.237$), F$_3$ (0, 0, z; $z = 0.463$), and F$_4$ (0, 0, z; $z = 0.031$). The O/F long range order characteristic of the rhombohedral *Ln*FO phases is maintained in Bi oxidefluoride, as attested by a bond valence calculation of the anionic sites (Table 4) (6). Although the accuracy of such a calculation in a partly statistical structure is rather poor, it shows that the F$_1$ normal site and the three other ones are undoubtedly occupied by fluoride anions. Conversely, the value of the bond valence of the O site (1.35), intermediate between 2 (O^{2-}) and 1 (F$^-$), and the almost complete occupancy of this site strongly suggest that nearly half of the O^{2-} anions are statistically replaced by F$^-$ anions of the site, in agreement with the chemical formula.

TABLE 3
Main Interatomic Distances in BiF$_{1.90}$O$_{0.55}$

Bond length	Å	Bond length	Å
Bi–Bi	4.138(1)	F(1)–F(2)	1.85(4)
	4.242(2)	F(1)–F(2)	2.75(5)
	4.049(2)	F(1)–F(3)	1.72(8)
Bi–O	2.39(2)	F(1)–F(4)	2.41(2)
Bi–O	2.546(8)	F(1)–F(4)	2.84(7)
Bi-F(2)	2.38(4)	F(2)–F(2)	2.2(2)
Bi-F(1)	2.533(12)	F(2)-F(2)	2.8(4)
Bi-F(3)	2.54(3)	F(2)-F(2)	1.2(1)
Bi-F(4)	2.64(4)	F(2)-F(2)	1.0(1)
O–O	2.82(2)	F(2)–F(2)	1.7(2)
		F(2)–F(2)	2.0(1)
O–F(1)	2.95(2)	F(2)–F(4)	1.17(8)
O–F(2)	2.81(3)		
O–F(3)	2.32(9)	F(3)–F(3)	1.50(2)
O–F(3)	2.82(5)		
O–F(4)	2.00(12)	F(4)–F(4)	1.3(2)

This anionic distribution characterizes a defect structure based on anionic clusters as previously described in all anion-excess fluorite-related solid solutions already studied. These clusters are generally based on the association of anionic vacancies and of one or another of two kinds of interstitial anions respectively called X' (1/2, y, y) and X'' (x, x, x). These sites can be considered in a F*m*-3*m* fluorite structure as shifted from the cubic ideal interstitial site (1/2, 1/2, 1/2) respectively toward [110] and [111] directions.

The clusters described till now belong to two main families:

— M_6X_{37} cuboctahedral clusters (also called 8 : 12 : 1 clusters in Willis notation (7)). These clusters, fully ordered in superstructures of fluorite type like KY$_3$F$_{10}$ (8), β-U$_4$O$_9$ (9), Ca$_{14}$Y$_5$F$_{43}$ (10), and Na$_7$Zr$_6$F$_{31}$ (11), are likely to be present in a disordered way in cubic *Fm*-3*m* solid solutions like, e.g., Na$_{0.5-x}$Y$_{0.5+x}$F$_{2+2x}$ (12), Sr$_{0.84}$Lu$_{0.16}$F$_{2.16}$ (13), and Ca$_{1-x}$$Ln_xF_{2+x}$ with the smallest Ln^{3+} cations (Ho–Lu) (14, 15). They associate about a cuboctahedral cavity, six MX_8 square antiprisms sharing corners or (considering an isolated defect in a fluorite *Fm*-3*m* solid solution) eight anionic vacancies, 12 X' (1/2, y, y; $y \approx 0.37$), and 1 X'' (x, x, x; $x \approx 0.41$) interstitial anions.

— 1 : 0 : n ($n = 2$, 3) small clusters (Fig. 4), associating one anionic vacancy and two or three X'' interstitial anions (x, x, x; $x \approx 0.41$). Proposed for the first time to explain the structural features of Ca$_{1-x}$U$_x$F$_{2+2x}$ and Ca$_{1-x}$Th$_x$F$_{2+2x}$ solid solutions (16, 17), 1 : 0 : 3 clusters were successively found in ThF$_{2x}$O$_{2-x}$ (18), Ca$_{1-x}$$Ln_xF_{2+x}$ (*Ln* = La–Tb) (14, 19), *Ln*$_3$NF$_6$ (*Ln* = Ce, Pr) (20), and rare-earth oxidefluorides. In this last series, 1 : 0 : 3 clusters, present in a tetragonal LaF$_{1.70}$O$_{0.65}$ phase (21), are likely replaced by 1 : 0 : 2 clusters in an orthorhombic SmF$_{1.60}$O$_{0.70}$ homologous phase (22). 1 : 0 : 3 and 1 : 0 : 2 clusters are well adapted to dopant cations of high size, able to form anionic polyhedra with 9-fold or 10-fold coordination. They also accept much more easily than cuboctahedral clusters a mixed anionic

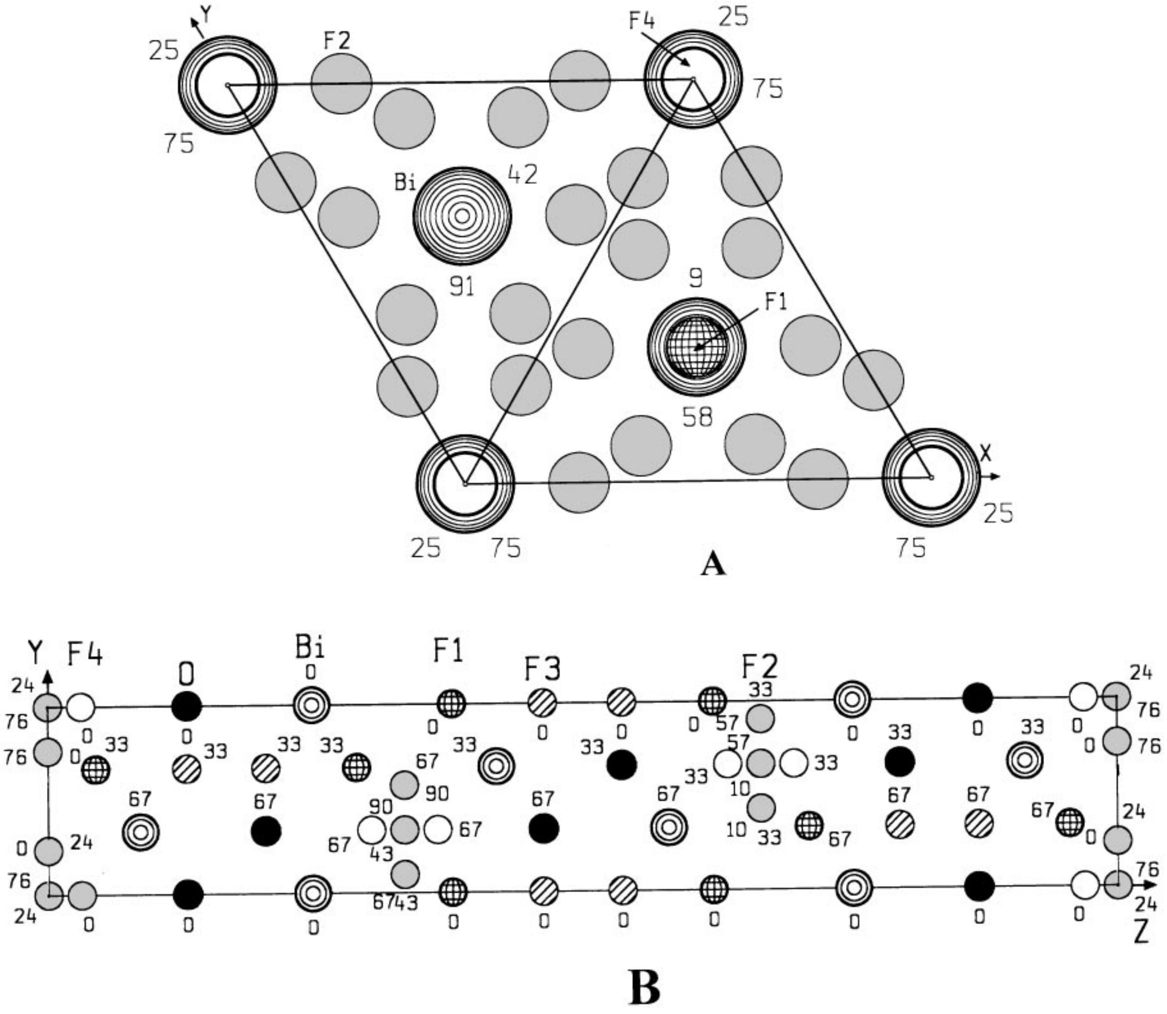

FIG. 2. Projection of the $BiF_{1.90}O_{0.55}$ structure onto the (A) xy plane and (B) yz plane. The same symbols for atoms are used in all the figures.

network, e.g., O + F or N + F, and even a long range anionic ordering as in the tetragonal La oxidefluoride which contains alternate sheets of O^{2-} and F^- anions, perpendicular to a [001] axis of the fluorite cell. In this last phase, 1 : 0 : 3 clusters are only located about F vacancies and the O sheets are completely filled.

Thus, the 1 : 0 : n clusters seem good candidates to explain the defect structure of $Bi(F, O)_{2.45}$. Moreover, the upper limit of anionic densification for the solid solutions involving 1 : 0 : 3 clusters, without interpenetration of these clusters, is more extended ($MX_{2.50}$) than with cuboctahedral clusters ($\sim MX_{2.42}$).

CLUSTERING INSIDE THE F SHEETS

In the R-3m structure of $BiF_{1.90}O_{0.55}$, the ideal cubic interstitial site (1/2, 1/2, 1/2 in Fm-3m cubic fluorite) is split in two sites of coordinates (0, 0, 0) and (0, 0, 1/2). F_2 (0.24, 0, 0) and F_4 (0, 0, 0.03) sites are close to the (0, 0, 0) cubic site and F_3 (0, 0, 0.46) to its homologous (0, 0, 1/2) site. No occupancy of a site close to F_3 and homologous to F_2 about (0, 0, 1/2) site can be detected. The F_3 and F_4 sites correspond to X''-type interstitial sites and the F_2 site is close to a X'-type one. The analysis of interatomic distances between these interstitial anions and the normal O and F_1 sites shows that all interstitial anions are compatible ($d > 2.4$ Å) with the O site except the F_4 site (O–F_4 = 2.00 Å). On the contrary, the F_1 site cannot be simultaneously occupied with F_3 and F_2 close neighbors (F_1–F_3 = 1.72 Å, F_1–F_2 = 1.85 Å). Therefore, a clustering of anionic vacancies and interstitials is compulsory, mainly about F_1. Moreover, the F_2 interstitial site is statistically occupied by anions very close one to another (see Table 3) and only some anionic distributions allow a reasonable short range order between vacancies and interstitials.

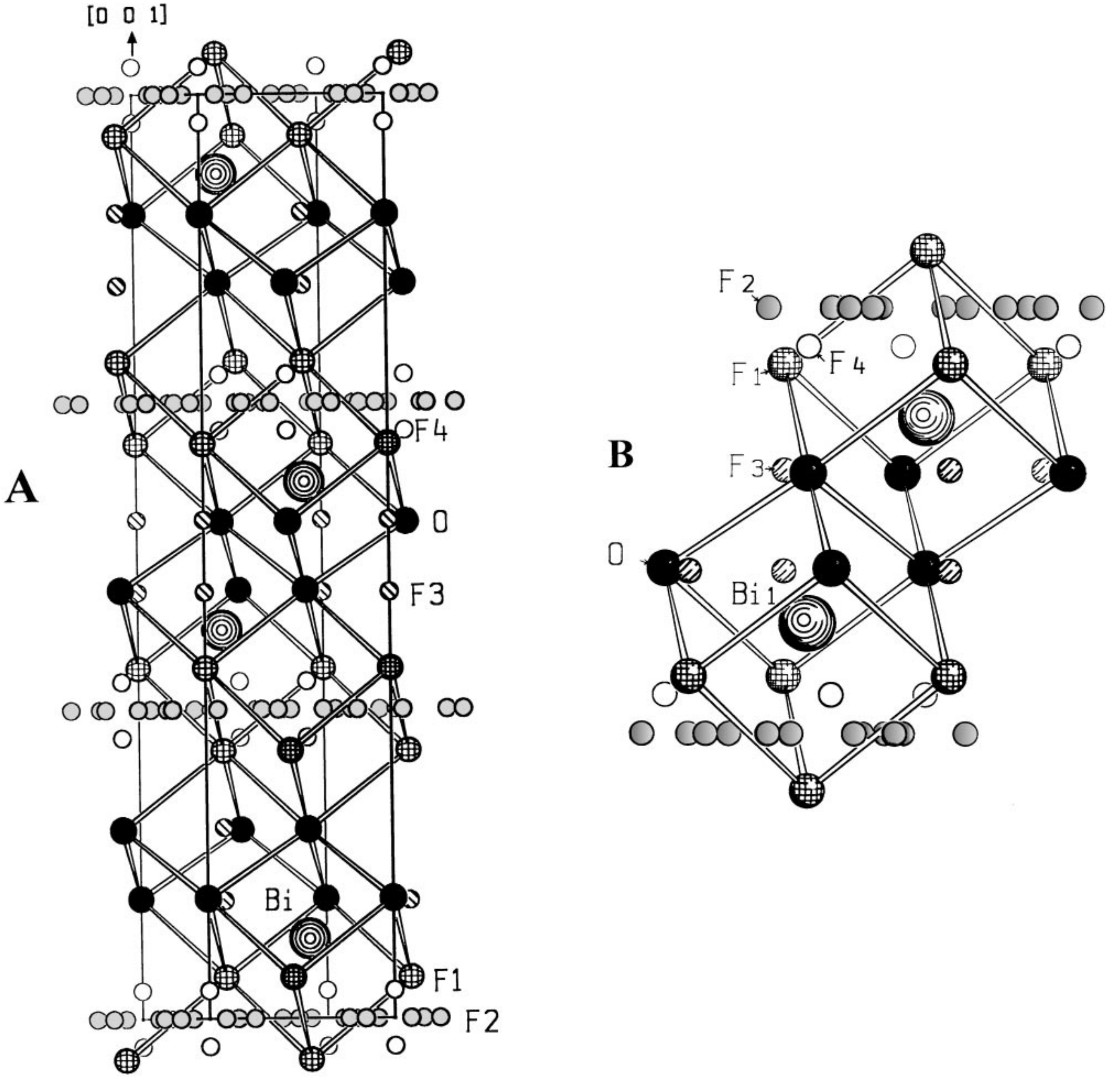

FIG. 3. (A) Visualisation of the anionic stacking (–O–O–F_1–F_1–) along the [001] axis. The anionic cubes of the rh-*Ln*FO type are represented. The interstitial anions in F_2, F_3, and F_4 sites are shown as smaller circles. (B) Detailed view of two BiF_4O_4 cubes (rh-*Ln*FO type) and of all the interstitial sites.

An example of such a defect model is represented in Fig. 5. It corresponds to the formation of an isolated 1 : 0 : 2 cluster inside a sheet of fluoride anions at $z = 0.29$ and $z = 0.38$. The complete cluster involves four anionic polyhedra about one Bi cation at $z = 0.25$ and three Bi cations at $z = 0.42$. In this simple model, a F_1 anion at $z = 0.38$ is replaced by two F_2 anions at $z = 0.33$ forming a F_2–F_2 edge about the F_1 vacancy. To avoid F_2–F_1 distances that are too short, some of the F_1 anions at $z = 0.29$ are strongly relaxed to the F_3 site at $z = 0.21$, which is the same z level as three O anions of the normal fluorite cube. In this way, BiX_9 and BiX_8 polyhedra are formed, as e.g., the BiF_5O_4 one represented in Fig. 6A. Some analogies with Bi polyhedra isolated in other Bi phases can be noted, e.g., with a BiF_6O_2 polyhedron (Fig. 6B), described in $Bi_7F_{11}O_5$ (4), a fully ordered phase deriving from fluorite type by a different structural mechanism. This analogy confirms the realism of the proposed cluster model and the respective role of F_2 and F_3 anions:

TABLE 4
Bond Valences for Anions in $BiF_{1.90}O_{0.55}$

Site	Coordination	Bond valence *V*
O	4	1.35
F(1)	4	0.95
F(2)	2 + 2	0.88
F(3)	3 + 3	0.82
F(4)	3 + 3	0.66

F_2 are true interstitials whereas the F_3 site corresponds to highly relaxed F anions. Moreover, the similarity of the shape of these polyhedra, despite their different coordination, and their "open" character suggest that in $Bi(F, O)_{2.45}$ as in $Bi_7F_{11}O_5$, the lone pair of Bi^{+3} is stereochemically active. E.g., the BiF_5O_4 polyhedron, represented in Fig 6A, can be described as a tricapped trigonal prism of lateral edges: F_2–F_2, O–O, and F_3–F_3, in which two square faces are capped by one F_1 and one O anion. The last O anion is pushed out of the third square face by the influence of the lone pair of Bi^{+3}.

The structural role of the F_4 site is less clear. Located in a 0, 0, *z* site homologous to the F_3 site, it should play the same role of highly relaxed anion position from the O normal site as F_3 from the F_1 normal site. However, the number of O vacancies is close to zero which rules out this hypothesis. Associations of two F_2 and one F_4 interstitials forming 1 : 0 : 3 clusters should give convincing BiF_6O_4 polyhedra as the one in Fig. 6C, but with O–F_4 distance of 2.0(1) Å which

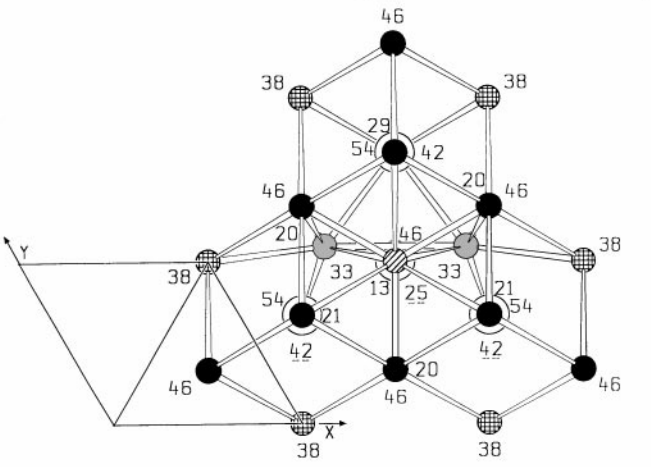

FIG. 5. A complete 1 : 0 : 2 cluster, orientated perpendicularly to the *z* axis, involving four Bi^{3+} cations at level $z = 0.25$ and 0.42 in the $BiF_{1.90}O_{0.55}$ defect structure.

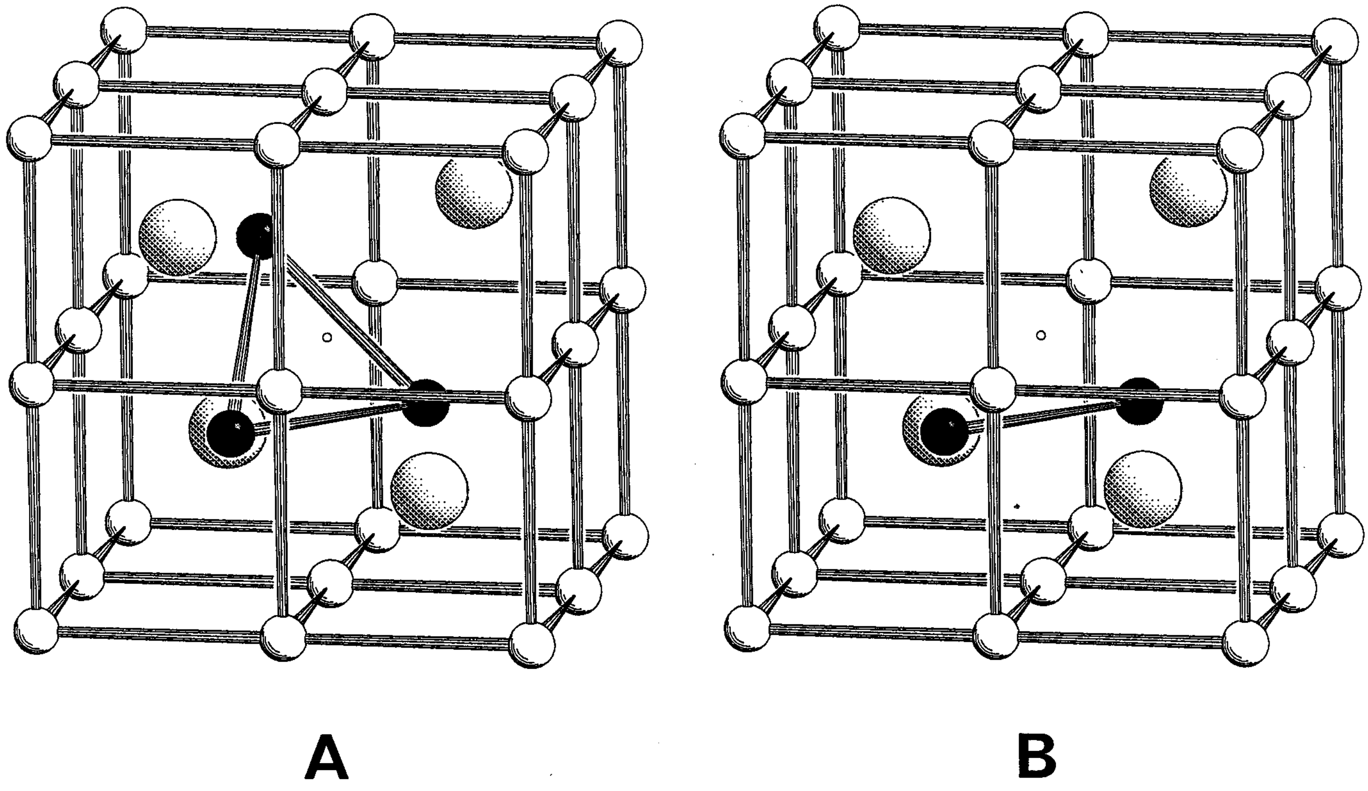

FIG. 4. Models of 1 : 0 : 3 (A) and 1 : 0 : 2 (B) clusters in the fluorite structure. The anionic vacancies are represented by very small circles.

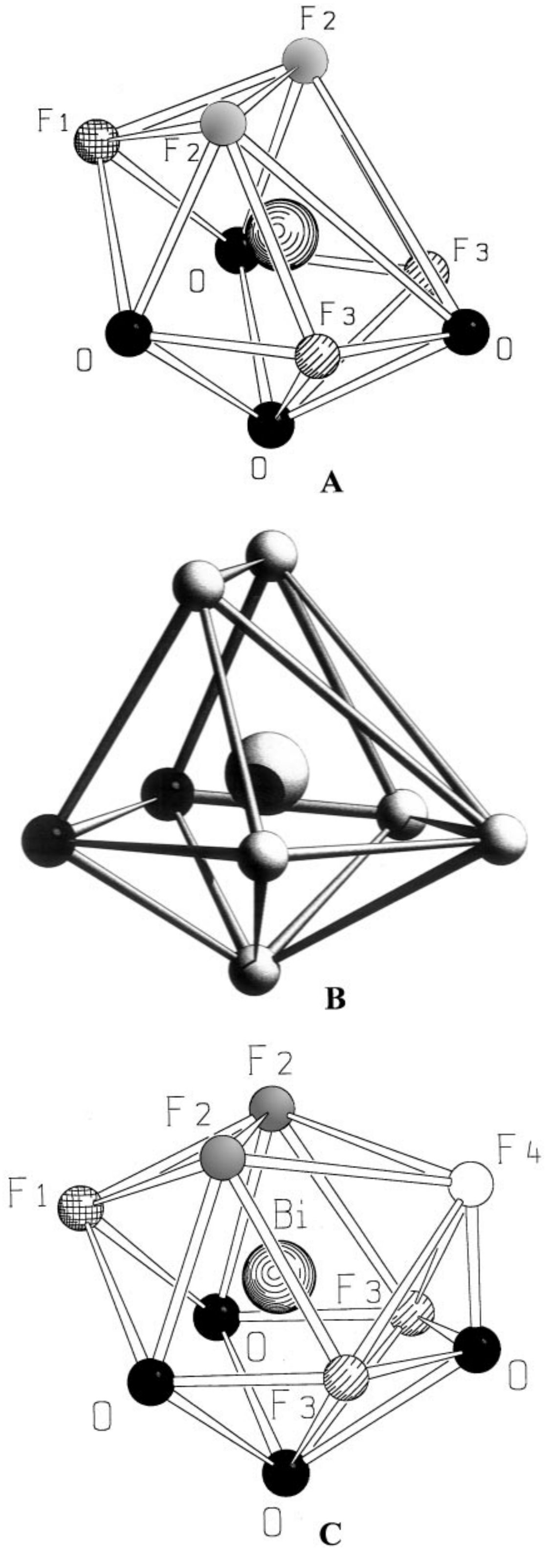

FIG. 6. Some examples of possible Bi polyhedra resulting from 1 : 0 : *n* clustering in the $BiF_{1.90}O_{0.55}$ defect structure: (A) BiF_5O_4 polyhedron model in a 1 : 0 : 2 cluster; (B) BiF_6O_2 polyhedron in the $Bi_7F_{11}O_5$ structure (4); (C) BiF_6O_4 polyhedron in a 1 : 0 : 3 cluster.

is too short (however much longer than the homologous unacceptable F_1–$F_3 = 1.72$ Å distance). This last difficulty can be overcome considering that:

— the high values of the cationic and anionic thermal vibration factors, characteristic of a strong positional disorder of all atoms in this defect structure, show that the bond distances are average values. Moreover, in order to limit the number of variables, the anions are refined with only isotropic thermal vibration factors, which, with such a disordered anionic network, can introduce small positional deviations. Besides, the final Fourier difference map shows small residues of electronic density mainly about the interstitial sites. Attempts to refine the anisotropy of thermal vibration for anions show that O and F_1 normal sites are nearly isotropic but that the F_4 site is clearly extended along the [001] axis ($U_{11} = U_{22} = 0.039$), $U_{33} = 0.116$, $U_{12} = 0.020$). That suggests that at a local scale, in some structural configurations, the true O–F_4 distance can be slightly longer than the calculated value and therefore that the coexistence of O and F_4 anions is possible.

— the O site is, in fact, occupied by almost half fluoride anions. As already proposed for tetragonal and orthorhombic *Ln* oxidefluorides, a O/F short range order inside O sheets is very likely. The fluoride anions of the O sheets are preferentially localized at the immediate neighboring of the clusters, so decreasing the electrostatic repulsions resulting from anionic close contacts. It can be noted that F–F contact distances are generally 2.4 Å (O–O = 2.6 Å) but are occasionnally as short as 2.25 Å.

Therefore, it is suggested that F_4 anions can be associated with F_2 interstitials to form 1 : 0 : 3 clusters, more suited than less dense 1 : 0 : 2 ones to explain the defect structure of this highly densified fluorite phase. Several kinds of polyhedra analogous to the ones already drawn on Fig. 6 can be described, depending on the number and the relative placing of the interstitials in the cluster and of the connection between close clusters.

MEDIUM RANGE ORDERING OF THE 1 : 0 : 3 CLUSTERS

Owing to the very high anionic densification presented by this phase ($BiX_{2.43–2.50}$), the 1 : 0 : 3 clusters described above cannot be considered as isolated one from another, as, e.g., in the classical $M_{1-x}M'_xF_{2+x}$; ($0 \leq x \leq 0.4$) fluorite solid solutions. Indeed, the limit of composition Bi_2F_4O ($MX_{2.50}$) corresponds to a complete juxtaposition of 1 : 0 : 3 clusters and the solid solution no longer exists for $MX_{<2.43}$. Thus, a description of the defect structure by creation of independent 1 : 0 : 3 clusters is not sufficient and interactions or interpenetration of clusters must be considered. Moreover, these interactions are strongly enhanced by the limited number of orientations of the clusters resulting from the lowering of symmetry ($Fm\text{-}3m \rightarrow R\text{-}3m$) by reference to a fully disordered solid solution. Indeed, in $Bi(F, O)_{2.45}$, the

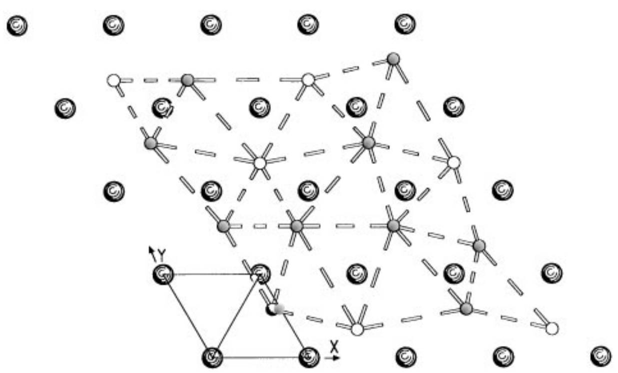

FIG. 7. Some possible associations of F_2 and F_4 interstitial anions in F_2–F_2 edges and F_2–F_2–F_4 triangular faces, forming a densified 3^6 sheet perpendicular to the [001] axis at $z = 0.30$–0.36.

F_2–F_2 edges and the triangular F_2–F_2–F_4 faces characteristic of the 1 : 0 : 2 and 1 : 0 : 3 clusters are all orientated perpendicularly to the [001] axis of the hexagonal supercell, and then steric constraints become severe in the densified (001) layers. For $x = 0.50$, the close neighboring of each ideal cubic interstitial site is occupied by the F_2 or one F_4 anion. That corresponds to the full occupancy of this ideal site ($\tau = 0.50$ at the reference scale = 3 anions per unit cell) and even for $x = 0.45$, the experimental value already reaches this maximum ($\tau_{exp.}$ $(F_2 + F_4) = 0.60(14)$) in the limit of uncertainties. These interstitial anions F_2 and F_4 tend to form, for high anionic densifications, a quasi-continuous irregular 3^6 sheet (in Schläffli notation (23)), as, e.g., at the level $z = 0.30$–0.36 (Fig. 7). Thus, the defect structure for such an anionic excess is better described as a more or less disordered distribution of the BiX_{10} and BiX_9 polyhedra with the excess anions forming irregular F_2–F_2–F_4 triangular faces, interconnected by F_4 anions located exactly between F_2 anions of two close polyhedra. Such a model preserves a partly disordered character to this metastable structure, takes into account the irregular shape of Bi^{3+} polyhedra resulting from the stereochemical activity of the lone pair of Bi^{3+} and explains the stability of O/F ordering in this phase.

The structural formula of $BiF_{1.90}O_{0.55}$ can be written:

	O site	F site + relaxed site	Interstitial sites
Bi_6	$(O_{3.3}F_{2.1})$	$F_{(1)4.0}F_{(3)1.7}$	$F_{(2)2.4}F_{(4)1.2}$
	5.4	5.7	3.6

the ideal formula for the upper limit of densification Bi_2F_4O being:

Bi_6	(O_3F_3)	$(F_{(1)}, F_{(3)})_6$	$(F_{(2)}, F_{(4)})_3$
	6	6	3

This last formula corresponds to the complete filling of all the available anionic sites for the composition $Bi(F, O)_{2.50}$ and thus to the upper structural limit of the anionic densification for this kind of defect structure.

CONCLUSION

Among the various ways of accommodating anion excess in fluorite type, the best known involve a three-dimensional distribution of discrete clusters, either cuboctahedral or 1 : 0 : *n*, in disordered solid solutions of F*m*-3*m* space group. The small 1 : 0 : 2 and 1 : 0 : 3 clusters can be inserted in the F sheets of tetragonal and orthorhombic solid solutions of rare-earth oxidefluorides, characterized by a long range O/F order, in a wide range of composition and without loss of this order. Until now, the rhombohedral *Ln*FO type was considered, contrary to the tetragonal *Ln*FO type, as unable to accept high anionic excess in solid solution. The present study shows that, at least in a narrow range of composition and for a very high anionic insertion rate ($MX_{2.43}$–$MX_{2.50}$), this rhombohedral type is able to accept the formation of 1 : 0 : *n* clusters, in a way preserving the O/F long range order responsible of the rhombohedral superstructure. These 1 : 0 : *n* clusters are not isolated but interconnected in such a way as to form quasi-continuous 3^6 sheets of F_2 and F_4 interstitials, perpendicular to the hexagonal [001] axis. The strong steric constraints resulting from the close contact of the clusters in this metastable high temperature phase and the stereochemical role of the lone pair of Bi^{3+} are probably the main factors influencing the complex ordering behaviour that Bi oxidefluorides present at lower temperature in the same domain of composition and which is currently under study.

The universal character of the small 1 : 0 : *n* clusters, in anion-excess fluorites with a mixed anionic network, is once more confirmed.

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