

The structural investigation of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$

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Abstract

The anion-excess ordered fluorite-related phase $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ has been synthesized by a solid state reaction of BaF_2 and BiF_3 at 873 K. The crystal structure of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ has been studied using electron diffraction and X-ray powder diffraction ($a=11.2300(2)\text{Å}$, $c=20.7766(5)\text{Å}$, S.G. $R\bar{3}$, $R_1=0.020$, $R_p=0.036$). Interstitial fluorine atoms in the $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ structure are considered to form isolated cuboctahedral 8:12:1 clusters. The structural relationship between $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ and similar rare-earth-based phases is discussed.

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1. Introduction

An association of anionic defects (so-called clustering) is frequently used in description of physico-chemical properties of solid solutions. However, almost every time these models serve only as logical explanations and remain without direct proofs. As a rule, only the exact determination of atomic positions in the crystal structure of ordered phases derived from the solid solutions allows to reveal these clusters.

Clustering in anion-excess fluorite-like phases was first proposed when studying optical properties of $\text{Ca}_{1-x}\text{Ln}_x\text{F}_{2+x}$ solid solutions [1] and was confirmed by structural investigations and a cluster modelling [2,3]. Cuboctahedral clusters (in this case 8:12:0 or 8:12:1; the different cluster notations are given in [4]), which are often used for description of the structure and properties of fluorite-derived phases were found for the first time for the rare-earth (RE)-containing compound in 1973 (KY_3F_{10} [5]). These cuboctahedral clusters may interact in different ways giving rise to several types of ordered phases [6] and can be present in disordered phases as well [7]. The progress in understanding of clustering is presented in [8].

Similar clustering models were proposed for fluorite-like Bi-containing phases because of the close size of Bi^{3+} and RE^{3+} cations ($\text{K}_{1-x}\text{Bi}_x\text{O}_z\text{F}_{2+2x-z}$ [7], $\text{Sr}_{1-x}\text{Bi}_x\text{F}_{2+x}$ [9], $\text{Ba}_{1-x}\text{Bi}_x\text{F}_{2+x}$ [10], $\text{Na}_{0.5-x}\text{Bi}_{0.5+x}(\text{O},\text{F})_{2+\delta}$ [11,12]); however, there are quite few structural studies of ordered compounds ($\text{BiZr}_3\text{F}_{15}$ [13], MBiF_4 ($M=\text{K}, \text{Rb}$) [14], CsBi_2F_7 [15], $\text{Bi}(\text{O},\text{F})_{2.43-2.50}$ [16]). Bi-containing phases are much less studied than RE-containing ones because of difficulties in their preparation. BiF_3 is not as thermally stable as LnF_3 and less stable to pyrohydrolysis compared to LnF_3 , more volatile and subjected to reduction to metallic Bi with a material of the reaction vessel.

The ordered phase $\text{Ba}_{1-x}\text{Bi}_x\text{F}_{2+x}$ ($0.45 < x < 0.50$) was previously found on the isothermal section (700°C) of the BaF_2 – BiF_3 system [17]. The compound with $\text{Ba}_{0.55}\text{Bi}_{0.45}\text{F}_{2.45}$ composition was described as hexagonal with cell parameters $a=11.22\text{Å}$ and $c=20.76\text{Å}$. The goal of the present work is to prepare this compound in pure form and to perform a structural investigation using X-ray powder diffraction and electron diffraction.

2. Experimental

The starting materials were high-purity (>99.9%) barium and bismuth fluorides. BaF_2 was treated with

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gaseous HF on heating (623 K, 3 h) to remove traces of water and degassed under dynamic vacuum (~ 10 Pa) at 473 K for 2 h. BiF_3 was prepared from $\text{Bi}(\text{OH})_3$ by a reaction with aqueous HF (40%) and the precipitate obtained was heated at 623 K for 3 h under flow of gaseous HF. Ready to use starting materials were kept in a desiccator. The mixed powders of BaF_2 and BiF_3 were pressed to pellets and introduced into copper tubes. Primary investigations showed absence of interactions of copper with studied fluorides and oxyfluorides at temperatures lower than 923 K when neither water vapor nor oxygen is present in the reaction atmosphere. After degassing in dynamic vacuum at 473 K for 2 h and filling with dry argon, the tubes were sealed, heated at 873 ± 10 K for 24 h and quenched in icy water. The best (almost monophase) sample was obtained when BiF_3 was taken with the ratio $\text{BaF}_2:\text{BiF}_3 = 0.55:0.45$.

X-ray powder diffraction analysis for all samples was performed with a focusing Guinier camera FR-552 ($\text{CuK}\alpha_1$ radiation) using germanium as an internal standard. X-ray powder diffraction data for structure refinement were collected on a STADI-P diffractometer ($\text{CuK}\alpha_1$ -radiation, curved Ge monochromator, transmission mode, linear PSD). The WINCSD program package was used for the structure determination from X-ray powder data [18]. The final refinement was performed with RIETAN-2000 program [19].

Samples for electron microscopy were made by crushing the crystals in ethanol and depositing fragments on a holey carbon grid. Electron diffraction (ED) and EDX analysis were carried out using a Philips CM20 microscope with a LINK-2000 attachment.

3. Results and discussion

The X-ray diffraction pattern of the $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ sample was indexed on a hexagonal lattice with the unit cell parameters $a = 11.224(1) \text{ \AA}$, $c = 20.782(4) \text{ \AA}$, which are in good agreement with those reported previously [17]. The parameters of the hexagonal unit cell can be related to the parameters of fluorite subcell as $a = a_f \sqrt{7/2}$, $c = a_f 2\sqrt{3}$ (a_f —the parameter of fluorite subcell). The reflections $-h + k + l \neq 3n$ were systematically absent which indicates a *R*-centered unit cell. Apart from this extinction condition, no other conditions were observed.

Electron diffraction patterns (Fig. 1) reveal a clear relationship between the basic fluorite structure and the structure of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$. The brighter spots on the ED patterns can be indexed on a face-centered cubic lattice with cell parameter $a \approx 6.0 \text{ \AA}$; these spots belong to the fluorite sublattice. Weaker spots are superstructure reflections, they were successfully indexed in a hexagonal unit cell with $a \approx 11.2 \text{ \AA}$ and $c \approx 20.8 \text{ \AA}$, in good

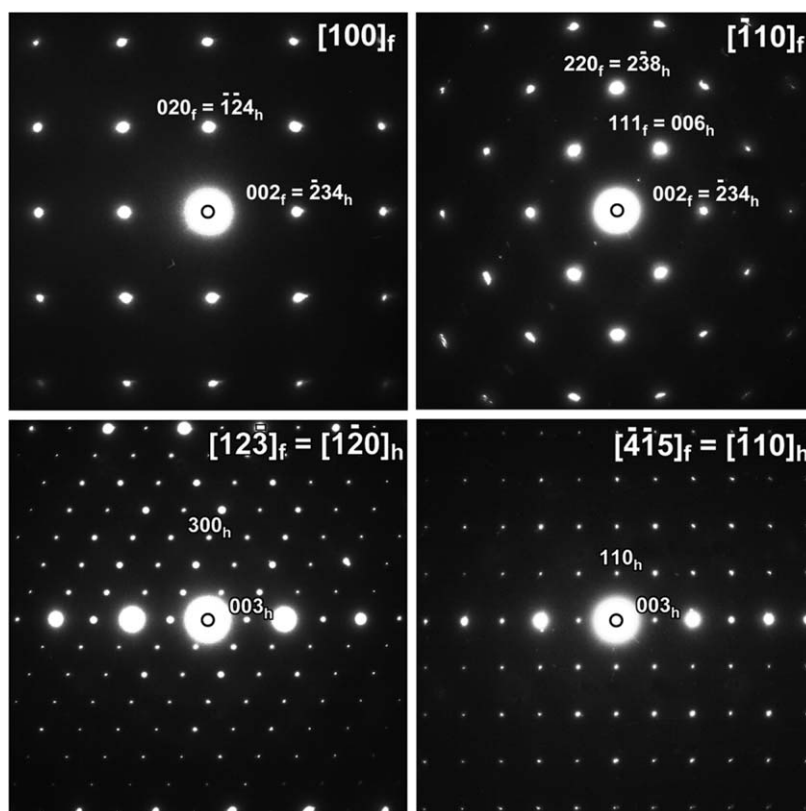


Fig. 1. Electron diffraction patterns of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$. Indexes belonging to the fluorite subcell and the hexagonal supercell are marked with the subscripts f and h, respectively.

agreement with the cell parameters determined from powder X-ray diffraction data. Indexes belonging to the fluorite subcell and the hexagonal supercell are marked with the subscript letters f and h, respectively. The reciprocal lattice vectors of the fluorite subcell and the hexagonal supercell are related by the matrix:

$$\begin{pmatrix} 3/2 & -1/2 & -1 \\ -1/2 & -1 & 3/2 \\ 2 & 2 & 2 \end{pmatrix}$$

Only $-h + k + l = 3n$ reflections were observed, which corresponds to possible $R\bar{3}m$, $R3m$, $R\bar{3}$ and $R3$ space groups. The sample was found to be very sensitive to the intense electron beam. Under beam irradiation the superstructure reflections gradually become weaker and finally disappear, then the sample decomposes. To avoid decomposition, ED patterns were taken with widely spread weak electron beam. However, high-resolution electron microscopy investigation of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ was not possible since the sample decomposes under a focused electron beam.

The Ba:Bi ratio was determined by EDX analysis performed with BaL and BiM lines at 12 points on four different crystallites. The determined Ba:Bi = 4.02(5):2.98(5) ratio confirms the proposed $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ composition. Thus, the almost monophasic stoichiometric sample of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ was obtained when starting BiF_3 was taken with a small excess in relation to this composition. Probably the excessive BiF_3 was removed from the reaction due to its volatility and possible reduction.

The crystal structure of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ was refined from X-ray powder diffraction data. Careful analysis of the raw X-ray powder profile revealed the presence of three reflections of admixture phases with intensities of 0.4–1.2%. The admixture phases were identified as BaF_2 ($d = 3.57 \text{ \AA}$, $I/I_0 = 0.8\%$) and metallic Bi ($d = 3.279 \text{ \AA}$, $I/I_0 = 1.2\%$; $d = 2.273 \text{ \AA}$, $I/I_0 = 0.4\%$). Their appearance can be explained by a partial reduction of BiF_3 to metallic Bi, which often leads to a difference between the initial bulk composition and the final stoichiometry. Since the admixture reflections have very low intensities and do not overlap with the reflections of the main phase, their impact to the diffraction profile was subtracted using profile decomposition prior to the refinement.

The cation and anion positions for the initial structure model were taken from the $\text{Ba}_4\text{Ln}_3\text{F}_{17}$ ($\text{Ln} = \text{Y}, \text{Yb}$) [20] structure, which has similar cell parameters: $\text{Ba}_4\text{Y}_3\text{F}_{17}$ — $a = 11.075(1) \text{ \AA}$, $c = 20.372(2) \text{ \AA}$; $\text{Ba}_4\text{Yb}_3\text{F}_{17}$ — $a = 11.000(1) \text{ \AA}$, $c = 20.262(1) \text{ \AA}$. The $R\bar{3}$ space group was chosen by analogy with the $\text{Ba}_4\text{Ln}_3\text{F}_{17}$ compounds. At a first step the F8 atom was placed at $(0,0,1/2)$ position ($3b$) with full occupancy, but this resulted in an abnormally high atomic displacement parameter

(ADP) ($\sim 19 \text{ \AA}^2$). The refinement of the occupancy factor of this position gave the value of 0.71(3). However, in the $\text{Ba}_4\text{Ln}_3\text{F}_{17}$ structure the F8 atom is shifted from the ideal $(0,0,1/2)$ position into a general $18f$ position with an occupancy factor of 1/6. The refinement of the F8 atoms in $18f$ position resulted in even slightly negative ADP. Some fluorine atoms also had negative ADPs since the correct refinement of the atomic displacement parameters of such light scatterers as fluorine is hampered by the presence of Ba and Bi in the structure and by strong correlations between the ADPs of the anion positions, which were symmetrically dependent in the fluorite subcell. This circumstance was overcome by the refinement of all fluorine atoms with the common ADP. ADPs for Ba and Bi cations were refined independently in an isotropic approximation. The final refinement led to good values of reliability factors $R_1 = 0.020$ and $R_p = 0.036$. The crystallographic parameters, reliability factors, atomic coordinates and the most relevant interatomic distances for $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ are listed in Tables 1–3. The experimental, calculated and difference X-ray patterns are shown in Fig. 2. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (49) 7247-808-666; E-mail: crysdata@fiz.karlsruhe.de), on quoting the depository number CSD-391210, the names of the authors and the chemical formula.

The Rietveld refinement from X-ray powder diffraction data does not allow one to differentiate between two possible alternatives of arrangement of the F8 atoms in the structure: either these atoms are located at $3b$ position with an occupancy of 0.71 or at $18f$ position with an occupancy of 1/6. The former results in an overall amount of anions in the structure less than 17 and requires a partial replacement of fluorine by oxygen to keep the electroneutrality. Oxygen may appear in the substance because of partial pyrohydrolysis that cannot be totally excluded. The resulting composition of the phase then corresponds to $\text{Ba}_4\text{Bi}_3\text{F}_{16.72}\text{O}_{0.14}$. The latter was proved by means of monocrystals $\text{Ba}_4\text{Ln}_3\text{F}_{17}$ ($\text{Ln} = \text{Y}, \text{Yb}$) studies [20].

Table 1
Selected parameters from Rietveld refinement of X-ray powder data for $\text{Ba}_4\text{Bi}_3\text{F}_{17}$

Space group	$R\bar{3}$
a (\AA)	11.2300(2)
c (\AA)	20.7766(5)
Z	6
Cell volume (\AA^3)	2269.16(8)
Calculated density (g/cm^3)	6.583
2θ range, step (deg)	$9 \leq 2\theta \leq 102$; 0.01
Number of reflections	281
Refinable parameters	31
R_1, R_p, R_{wp}	0.020; 0.036; 0.047

Table 2
Positional and thermal parameters for Ba₄Bi₃F₁₇

Atom	Position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} (Å ²)
Ba1	6 <i>c</i>	0	0	0.2629(2)	0.58(9)
Ba2	18 <i>f</i>	0.2252(2)	0.0275(2)	0.0851(1)	0.91(5)
Bi	18 <i>f</i>	0.0850(2)	0.6202(1)	0.08171(9)	1.06(2)
F1	18 <i>f</i>	0.483(1)	0.090(2)	0.0372(9)	0.23(9)
F2	18 <i>f</i>	0.238(2)	0.061(1)	0.2171(9)	0.23(9)
F3	18 <i>f</i>	0.145(1)	0.181(1)	0.6118(7)	0.23(9)
F4	18 <i>f</i>	0.582(1)	0.017(1)	0.8372(8)	0.23(9)
F5	18 <i>f</i>	0.451(1)	0.083(1)	0.2913(8)	0.23(9)
F6	6 <i>c</i>	0	0	0.853(1)	0.23(9)
F7	3 <i>a</i>	0	0	0	0.23(9)
F8 ^a	18 <i>f</i>	0.962(20)	0.925(5)	0.491(6)	0.23(9)

^aOccupancy factor *g* = 1/6.

Table 3
Selected interatomic distances for Ba₄Bi₃F₁₇ (Å)

Ba1–F1 2.562(15) × 3	Ba2–F1 2.80(2)	Bi–F1 2.48(2)
Ba1–F2 2.586(15) × 3	Ba2–F2 2.630(13)	Bi–F1 2.49(2)
Ba1–F3 3.202(14) × 3	Ba2–F2 2.76(2)	Bi–F2 2.58(2)
Ba1–F6 2.41(2)	Ba2–F3 2.981(13)	Bi–F3 2.344(11)
	Ba2–F4 2.936(14)	Bi–F3 2.386(12)
	Ba2–F4 3.224(12)	Bi–F4 2.309(15)
	Ba2–F5 2.644(11)	Bi–F4 2.482(14)
	Ba2–F5 2.65(2)	Bi–F5 2.322(12)
	Ba2–F5 2.710(12)	Bi–F8 2.60(16)
	Ba2–F6 2.714(10)	Bi–F8 2.72(11)
	Ba2–F7 2.973(2)	Bi–F8 2.99(20)

The structure of the Ba₄Bi₃F₁₇ phase can be described as a derivative from the fluorite structure. All cation positions deviate slightly from the ideal positions in the fluorite sublattice. The cation sublattice is shown in Fig. 3 where the hexagonal supercell (solid line) and the cubic fluorite subcell (dotted line) are outlined. The cation sublattice has six close-packed layers, twice more in comparison with the parent fluorite structure. The doubling occurs due to ordering of the Bi and Ba cations. The coordination polyhedra for the cations are presented in Fig. 4. The Ba1 atoms are situated in a 10-fold polyhedron (Fig. 4a), which can be described as a cube with one apex substituted by a triangular face formed by the F3 atoms (shaded). The Ba2 atoms have CN = 11 and their polyhedron (Fig. 4b) is also a cube with a triangle of one F3 and two F4 atoms instead of one apex (shaded) and with a cap above one of the square faces (F7 atom, shaded dark). The polyhedron around Bi is a one-capped square antiprism (Fig. 4c, CN = 8 + 1), the cap is the F8 atom (shaded dark).

Anion positions in Ba₄Bi₃F₁₇ can be divided into three groups. The F1, F2, F5 and F6 positions, which correspond to the tetrahedral hollows in the close packing, are “regular” referred to the parent fluorite structure (where all tetrahedral sites are occupied and all octahedral ones stay vacant). Anions in the F3 and F4

positions are situated in octahedrally coordinated sites and thus are “interstitial” in the parent fluorite structure (F' type [2]). These atoms in Ba₄Bi₃F₁₇ form cuboctahedral entities and the F8 position is situated in the center of the cuboctahedra. The F8 anions are also situated in octahedral hollows of the cationic sublattice and are of F'' type [2]. The centered cuboctahedron of fluorine atoms, which is characteristic for the structure of Ba₄Bi₃F₁₇, is equivalent to a cuboctahedral cluster (8:12:1) reported in a number of anion-excess fluorite-type solid solutions [8, 10, 21, 22] and ordered phases [6]. The F7 position is situated in the center of a cube formed by the F5 and F6 atoms and is also an “interstitial” one of F'' type.

The entire anionic sublattice is presented in Fig. 5. It can also be described as an alternation of six layers of “building parts”—centered cubes and cuboctahedra. Cubes formed of the F5 and F6 atoms (shaded dark) are centered by the F7 anions, cuboctahedra of the F3 and F4 atoms (shaded) are centered by the F8 ones. The F1 and F2 atoms are not involved in formation of these “blocks” and are shown as separate circles.

The crystal structure of the Ba₄Bi₃F₁₇ phase contains centered cuboctahedral clusters in the anion sublattice (Fig. 6). An insertion of excess fluorine atoms (compared to the initial fluorite structure) and a decrease of the volume of the fluorite subcell because of partial substitution of barium by bismuth (for Ba₄Bi₃F₁₇ *a*_{sub} = 6.000(1) Å, for BaF₂ *a* = 6.200(2) Å) do not lead to abnormally short F–F distances and even the shortest F–F distance in these cuboctahedra (2.821 Å) exceeds the doubled ionic radius of an F[−] anion (1.29 Å). Probably, the association of several defects: eight anionic vacancies V_F[•] in tetrahedral positions and 13 interstitial fluorine atoms F_i' and their interaction with six Bi_{Ba}[•] atoms in the face centers (Fig. 6), provides stability to the cuboctahedral cluster. Perhaps this is the reason why cuboctahedral clusters in such compounds are present over a large temperature and composition range.

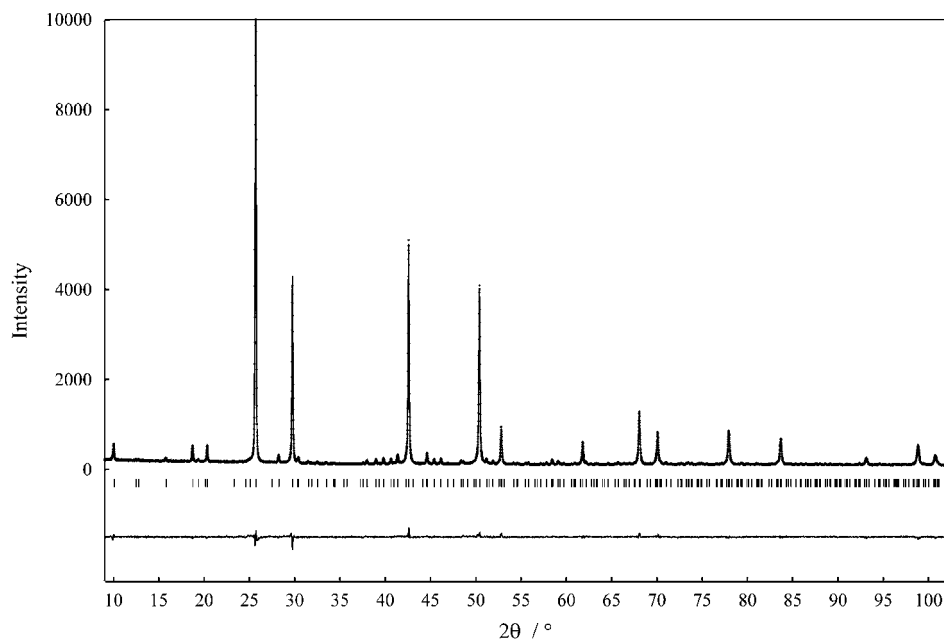


Fig. 2. Experimental, calculated and difference X-ray diffraction profiles for $\text{Ba}_4\text{Bi}_3\text{F}_{17}$.

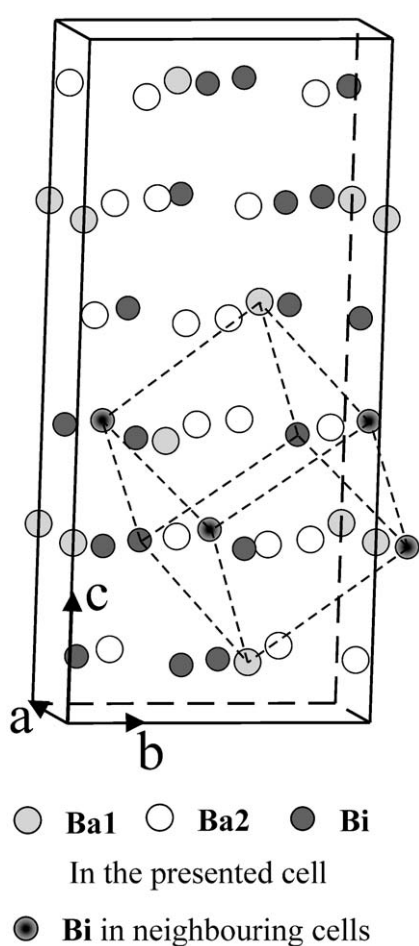


Fig. 3. Cationic sublattice of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$. The cubic fluorite subcell (dotted line) and hexagonal supercell (solid line) are shown.

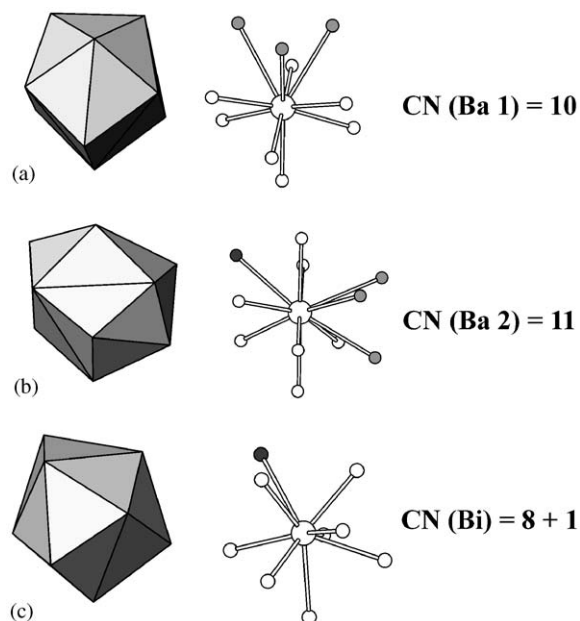


Fig. 4. Cation polyhedra in $\text{Ba}_4\text{Bi}_3\text{F}_{17}$: (a) Ba1 polyhedron—a cube with one apex substituted by a triangle (shaded); (b) Ba2 polyhedron—a cube with a triangle instead of one apex (shaded) and with a cap above one of the square faces (shaded dark); (c) Bi polyhedron—a one-capped square antiprism, the cap shaded dark.

The $\text{Ba}_4\text{Bi}_3\text{F}_{17}$, $\text{Ba}_4\text{Ln}_3\text{F}_{17}$ ($\text{Ln}=\text{Y}$, Yb [20], Er [23]) and $\text{Pb}_8\text{Y}_6\text{F}_{32}\text{O}$ [24] phases can be described with the same structural model. They are based on a cationic sublattice with a fixed 4:3 ratio of two- and three-charged cations, and “regular” anions in the F1–F6 positions. Variable occupation of cubic (F7) and

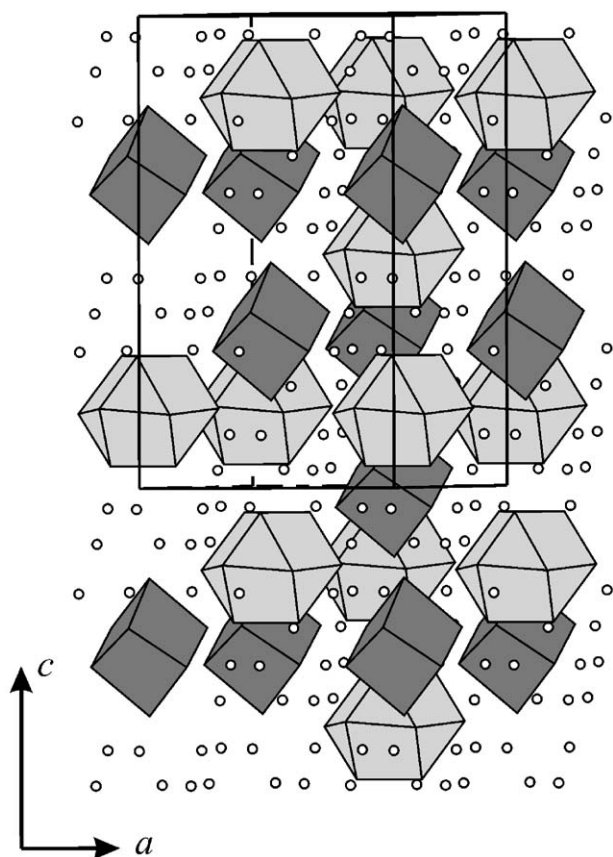


Fig. 5. Anionic sublattice of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$. Cuboctahedra of F3 and F4 (shaded) are centered by F8, cubes of F5 and F6 (shaded dark) are centered by F7, separate circles—F1 and F2.

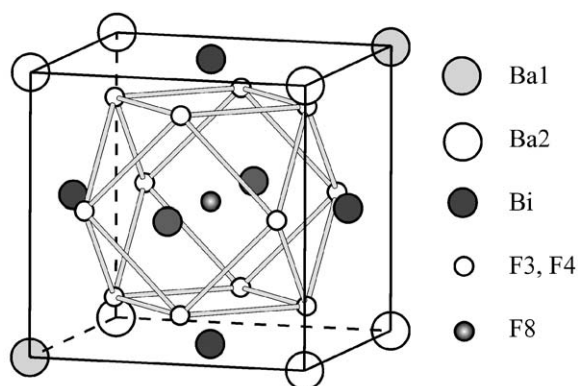


Fig. 6. The cuboctahedral cluster 8:12:1 in the structure of $\text{Ba}_4\text{Bi}_3\text{F}_{17}$.

cuboctahedral (F8) hollows formed in such structure influences the final anion composition. Varying occupancies with maintaining electroneutrality can be achieved through a partial substitution of F^- ions by O^{2-} . Then the anion homogeneity range of such phases would be limited by $\text{M}_4^{\text{II}}\text{M}_3^{\text{III}}\text{X}_{16}$, (i.e. $\text{M}_4^{\text{II}}\text{M}_3^{\text{III}}\text{F}_{15}\text{O}$) and $\text{M}_4^{\text{II}}\text{M}_3^{\text{III}}\text{X}_{17}$ (i.e. $\text{M}_4^{\text{II}}\text{M}_3^{\text{III}}\text{F}_{17}$) compositions. It means that if the pyrohydrolysis partially occurs then both the

oxyfluoride $\text{Pb}_8\text{Y}_6\text{F}_{32}\text{O}$ [24] and probably our phase are inside of the predicted homogeneity range of the solid solution based on the phase $\text{M}_4^{\text{II}}\text{M}_3^{\text{III}}\text{F}_{17}$.

4. Conclusions

In the present work the synthesis conditions of the ordered fluorite-related phase $\text{Ba}_4\text{Bi}_3\text{F}_{17}$ are described and a structural information is obtained, which proves the existence of the 8:12:1 anionic cuboctahedral clusters in this compound.

Similar rare-earth-based phases are stable at 800–1000 K; however, they can only be obtained through crystallization from the melt only for small RE cations (RE = Gd–Lu, Y). Compounds with large rare earths (Ce–Sm) are stable only at lower temperatures (673 K) [25]. For the largest La^{3+} cation the ordered $\text{Ba}_4\text{La}_3\text{F}_{17}$ compound is not observed. The Bi-containing phase perfectly gets in this row of isostructural phases according to its size factor because the crystallographic radius of Bi^{3+} (CN=8, $R(\text{Bi}^{3+})$ 1.25 Å [26]) is close to the larger RE radii (CN=8, $R(\text{Nd}^{3+})$ = 1.26 Å [26]).

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References

- [1] V.V. Osiko, Fizika Tverdogo Tela 7 (1965) 1294–1302.
- [2] A.K. Cheetham, B.E.F. Fender, M.J. Cooper, J. Phys. C 4 (1971) 3107–3121.
- [3] C.R.A. Catlow, J. Phys. C 6 (1973) L64–L67.
- [4] P.P. Fedorov, Bull. Soc. Cat. Cien. 12 (1991) 349–381.
- [5] J.W. Pierce, Y.Y.-P. Hong, Proceedings of the 10th Rare Earth Conference, USA, 1973, pp. 527–537.
- [6] A.M. Golubev, V.I. Simonov, Kristallografiya 31 (1986) 478–487.
- [7] J.L. Soubeyroux, P. Laborde, J.-M. Reau, P. Hagenmuller, J. Solid State Chem. 73 (1988) 217–223.
- [8] B.P. Sobolev, The Rare Earth Trifluorides, Parts 1, 2, Institut d'Estudis Catalans, Barcelona, 2000, 2001.
- [9] J.L. Soubeyroux, J.-M. Reau, M. Wahbi, J. Senegas, Suh Kyung Soo, Solid State Commun. 83 (1992) 259–267.
- [10] Suh Kyung Soo, J. Senegas, J.-M. Reau, M. Wahbi, P. Hagenmuller, J. Solid State Chem. 97 (1992) 212–223.
- [11] T.V. Serov, R.Ya. Zakirov, E.I. Ardashnikova, V.A. Dolgikh, M. El Omari, J. Senegas, J.-M. Reau, Solid State Ionics 138 (2001) 233–242.
- [12] El Omari Malika, El Omari Mohamed, A. Abaouz, A. Zahouane, T.V. Serov, E.N. Dombrovski, E.I. Ardashnikova, N.G. Chaban,

- V.A. Dolgikh, J. Senegas, *Mater. Lett.* 57, 26–27 (2003), 4115–4126.
- [13] E. Caignol, J. Metin, R. Chevalier, J.C. Cousseins, D. Avignant, *Eur. J. Solid State Inorg. Chem.* 25 (1988) 399.
- [14] S.F. Matar, J.-M. Reau, P. Laborde, A. Rhandour, *J. Phys. Chem. Solids* 49 (1988) 285.
- [15] R.K. Rastsvetaeva, A.V. Butashin, B.A. Maksimov, A.M. Golubev, A.A. Kaminskii, *Kristallografiya* 41 (1996) 444–449.
- [16] J.-P. Laval, J.C. Champarnaud-Mesjard, A. Britel, A. Mikou, *J. Solid State Chem.* 146 (1999) 51–59.
- [17] J.-M. Reau, Shun Bao Tian, A. Rhandour, S. Matar, P. Hagenmuller, *Solid State Ionics* 15 (1985) 217–223.
- [18] L.G. Akselrud, Yu.N. Grin, P.Yu. Zavalij, V.K. Pecharsky, V.S. Fundamentsky, *The report on 12th European Crystallography Meeting, Moscow, 1989*, p. 155.
- [19] F. Izumi, T. Ikeda, *Mater. Sci. Forum* 198 (2000) 321.
- [20] B.A. Maximov, H. Solans, A.P. Dudka, E.A. Genkina, M. Badria-Font, I.I. Buchinskaya, A.A. Loshmanov, A.M. Golubev, V.I. Simonov, M. Font-Altaba, B.P. Sobolev, *Crystallogr. Rep.* 41 (1996) 56.
- [21] L. Pontonnier, J. Patrat, S. Aleonard, J.J. Capponi, M. Brunel, F. De Bergevin, *Solid State Ionics* 9–10 (1983) 549.
- [22] J.-P. Laval, A. Abaouz, B. Frit, A. Le Bail, *J. Solid State Chem.* 85 (1990) 133–143.
- [23] A.K. Tyagi, J. Kohler, *Solid State Sci.* 3 (2001) 689–695.
- [24] A. Dib, S. Aleonard, *J. Solid State Chem.* 64 (1986) 148–161.
- [25] M. Kieser, O. Greis, *Z. Anorg. Allg. Chem.* 469 (1980) 164–171.
- [26] R.D. Shannon, C.T. Prewitt, *Acta Crystallogr. Sect. B* 25 (1969) 925–946.