

## Crystal Structure of BaNaZr<sub>2</sub>F<sub>11</sub>: A Phase Recrystallizing from Fluorozirconate Glasses

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BaNaZr<sub>2</sub>F<sub>11</sub>, prepared by recrystallization of the fluoride glass of the same composition, was obtained as very small single crystals. It crystallizes with tetragonal symmetry, the *I*4<sub>1</sub>/*a* space group, and the parameters *a* = 8.223(5) Å; *c* = 23.610 Å (*Z* = 8). Its crystal structure was determined (*R* = 0.055) on the basis of data recorded on a four-circle diffractometer. This structure results from the stacking, on the one hand, of [ZrF<sub>5,5</sub>]<sub>n</sub> sheets composed of edge- and corner-shared [ZrF<sub>8</sub>]<sup>4-</sup> square antiprisms and, on the other hand, of 4<sup>4</sup> sheets containing alternate rows of Ba<sup>2+</sup> and Na<sup>+</sup>. BaNaZr<sub>2</sub>F<sub>11</sub>, by the presence of 3<sup>2</sup>.4.3.4. Zr plane nets, can be compared to several fluoro-zirconates like α- and βLnZr<sub>3</sub>F<sub>15</sub>, PrZr<sub>3</sub>F<sub>11</sub>, and LiTiZr<sub>5</sub>F<sub>22</sub>. However, it is better related, by a simple mechanism of rotation of [Na<sub>2</sub>Zr<sub>4</sub>F<sub>28-4</sub>]<sup>14-</sup> units, to KY<sub>3</sub>F<sub>10</sub>. Therefore, it can be linked to the well-known structural family of "anion-excess fluorite-related superstructures." © 1992 Academic Press, Inc.

### Introduction

In the recent years, several crystal structures of fluoro-zirconates of composition close to that of corresponding glasses, or directly recrystallizing from them, were determined: SmZrF<sub>7</sub> (1), α- and β-BaZrF<sub>6</sub> (2, 3), β-BaZr<sub>2</sub>F<sub>10</sub>, (4), α- and β-LnZr<sub>3</sub>F<sub>15</sub> (5–7), and PrZr<sub>2</sub>F<sub>11</sub> (8). After recrystallization of glasses prepared from ternary mixtures, ZrF<sub>4</sub>–BaF<sub>2</sub>–NaF, a new crystalline phase, formulated BaNaZr<sub>2</sub>F<sub>11</sub>, was identified by Parker *et al.* (9). Owing to the need for structural information concerning fluoride glasses and related phases, the existence of this phase was verified by direct synthesis in a Pt sealed tube and its structure

solved from single crystal data obtained on a X-ray four-circle diffractometer.

### Experimental

BaNaZr<sub>2</sub>F<sub>11</sub> was prepared in the best way by a slow cooling from 500 to 450°C and a 3-day annealing at this last temperature of the corresponding melted mixture of binary fluorides (melting point = 490°C). Very small size single crystals were grown under these conditions and a small platelet was selected for X-ray study. The integrated intensities of the diffraction pattern were measured on a AED2-SIEMENS four-circle diffractometer. Table I reports structural information about BaNaZr<sub>2</sub>F<sub>11</sub> and recording conditions.

The structure of BaNaZr<sub>2</sub>F<sub>11</sub> was solved

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TABLE I  
DATA COLLECTION PARAMETERS

Symmetry: tetragonal
Space group: $I4_1/a$ (No. 88); $Z = 8$
Cell parameters: $a = 8.223(5)$ Å, $c = 23.610(14)$ Å
Crystal dimensions: $0.04 \times 0.07 \times 0.02$ mm diameter
Radiation: MoK $\alpha$
Recording range: $2^\circ < 2\theta < 70^\circ$ ; $0 \leq h \leq 13$ , $0 \leq k \leq 13$ , $0 \leq l \leq 38$
Number of observed reflections: 2081
Number of weak reflections: 838
Number of observed reflections with $I/\sigma(I) > 3$ : 468
Number of refined variables: 42
Weighting scheme: $1/(\sigma^2(F) + 0.011096F^2)$
$R = 0.055$ ; $R_w = 0.057$ .

with the program SHELX76 (10). Atomic scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-Ray Crystallography" (11). Starting coordinates for cations were deduced from a Patterson function calculation. After alternate series of refinement cycles and Fourier-difference calculations, the respective distributions of Zr, Ba, and Na on three cationic sites and of F on six anionic ones were determined and refined to  $R =$

5.5%. Anisotropic thermal factors were used only for cations in order to decrease the number of refined variables, owing to the limited number of experimental reflections resulting from the low size of the crystal. The corresponding parameters are listed in Table II. All calculated interatomic distances correspond to the ones generally observed in related structures and are gathered in Table III.

## Structure Description

### 1. Anionic Polyhedra

Three different kinds of anionic polyhedra are present in the structure:

— A  $[\text{ZrF}_8]^{4-}$  square antiprism (S.A.), drawn in Fig. 1a; it is composed of two opposite square faces whose distance to  $\text{Zr}^{4+}$  is rather dissymmetrical: the  $\text{F}_1\text{--F}_2\text{--F}_4\text{--F}_6$  face is much closer to Zr ( $d_{\text{Zr--F}} = 2.01\text{--}2.10$  Å) than the  $\text{F}_3\text{--F}_5\text{--F}_{31}\text{--F}_{51}$  one ( $d_{\text{Zr--F}} = 2.15\text{--}2.23$  Å). Like in many S.A., F–F distances are shorter in square faces ( $2.37\text{--}2.56$  Å) than between opposite ones ( $2.61\text{--}2.77$  Å). The average  $\langle \text{Zr--F} \rangle$  value,  $2.12$  Å, matches the generally observed ones for

TABLE II  
ATOMIC PARAMETERS AND ISOTROPIC AND ANISOTROPIC TEMPERATURE FACTORS FOR BaNaZr<sub>2</sub>F<sub>11</sub>

Atom	Site	x	y	z	$B$ or $B_{\text{eq}}$ (Å <sup>2</sup> )	
Zr	16f	0.1391(2)	0.0354(2)	0.8747(1)	0.52(6)	
Ba	8e	0.	0.25	0.5359(1)	0.74(8)	
Na	8e	0.	0.25	0.0093(6)	1.7(7)	
F1	8e	0.	0.25	0.3771(8)	1.4(3)	
F2	16f	0.1880(19)	0.1383(20)	0.7962(6)	0.9(2)	
F3	16f	0.0713(21)	0.0397(21)	0.1773(7)	1.2(3)	
F4	16f	0.1164(15)	0.4429(15)	0.6251(7)	0.8(2)	
F5	16f	0.2038(18)	0.3167(19)	0.1732(6)	0.7(3)	
F6	16f	0.1810(21)	0.6343(21)	0.0489(7)	1.3(3)	
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Zr	0.0038(8)	0.0039(8)	0.0120(8)	-0.0015(10)	0.0016(10)	0.0010(6)
Ba	0.0073(12)	0.0077(12)	0.0130(8)	0.	0.	0.0008(10)
Na	0.016(9)	0.029(10)	0.018(6)	+0.	0.	0.017(8)

TABLE III  
MAIN INTERATOMIC DISTANCES IN BaNaZr<sub>2</sub>F<sub>11</sub>

Intercationic distances		Cation-anion distances
Zr-Zr (edge-sharing)	: 3.692(4) Å *2	About Zr (Fig. 1a)
(corner-sharing)	: 4.206(4)	F <sub>1</sub> : 2.103(7) Å
Zr-Na (edge-sharing)	: 3.784(5)	F <sub>2</sub> : 2.077(16)
(edge-sharing)	: 3.774(5)	F <sub>3</sub> : 2.210(17)
(edge-sharing)	: 3.811(5)	F <sub>31</sub> : 2.233(17)
Zr-Ba	: 4.039(2)	F <sub>4</sub> : 2.018(14)
	: 4.047(2)	F <sub>5</sub> : 2.151(15)
	: 4.336(2)	F <sub>51</sub> : 2.190(15)
		F <sub>6</sub> : 2.008(17)
		+(F <sub>4</sub> : 3.052(14))
		<Zr-F = 2.124 Å>
		About Na (Fig. 1b)
		F <sub>3</sub> : 2.361(18) Å *2
		F <sub>5</sub> : 2.377(16) *2
		F <sub>6</sub> : 2.238(18) *2
		<Na-F = 2.325 Å>
		About Ba (Fig. 1c)
		F <sub>2</sub> : 2.736(15) Å *2
		F <sub>31</sub> : 2.644(15) *2
		F <sub>3</sub> : 3.549(17) *2
		F <sub>4</sub> : 2.801(14) *2
		F <sub>41</sub> : 2.805(14) *2
		F <sub>6</sub> : 2.807(17) *2
		<Ba-F = 2.890 Å>

eightfold coordinated Zr (2.09 <Zr-F < 2.13 Å) (12).

—A [NaF<sub>6</sub>]<sup>5-</sup> very irregular trigonal prism (Fig. 1b): Na<sup>+</sup> is coordinated on one

side by four anions forming a square F<sub>3</sub>-F<sub>5</sub>-F<sub>31</sub>-F<sub>51</sub> face ( $d_{\text{Na-F}} = 2.36$  and 2.38 Å) parallel to the *xOy* plane and on the other side by two F<sub>6</sub> anions, closer to Na<sup>+</sup> (2.24

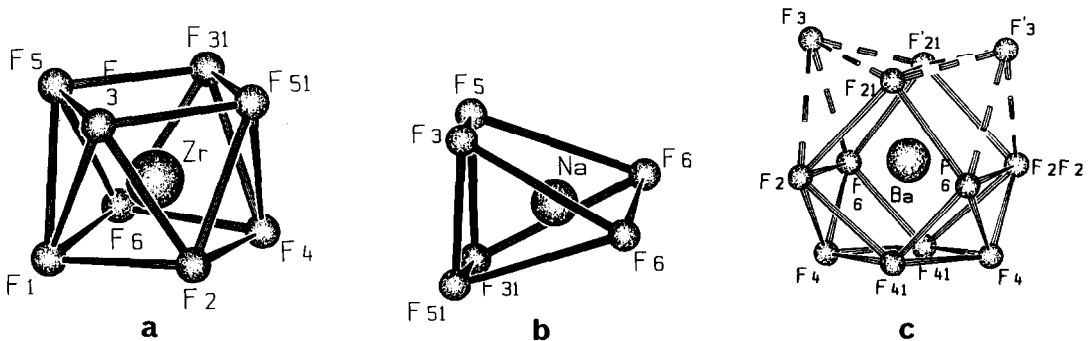


FIG. 1. Perspective drawing of (a) a [ZrF<sub>8</sub>]<sup>4-</sup> square antiprism (S.A.), (b) a [NaF<sub>6</sub>]<sup>5-</sup> irregular trigonal prism, (c) a [BaF<sub>12</sub>]<sup>10-</sup> distorted cuboctahedron.

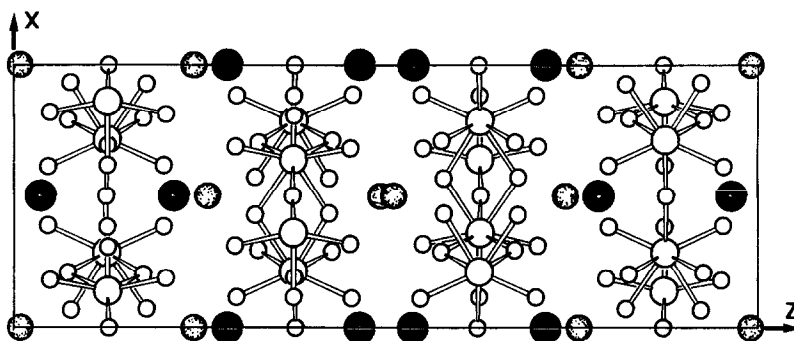


FIG. 2. (010) projection of the unit cell content of BaNaZr<sub>2</sub>F<sub>11</sub>, with representation of Zr-F bonds, in order to emphasize layer stacking along the [001] axis.

Å) but rather distant from each other ( $F_6-F_6 = 3.53$  Å) and also from  $F_3$  and  $F_5$  of the square face (respectively, 3.27 and 3.20 Å).

—A  $[\text{BaF}_{12}]^{10-}$  distorted cuboctahedron (Fig. 1c): 10 of the 12 Ba-F bonds are distributed between 2.64 and 2.81 Å and two  $F_3$  anions are much more distant (3.55 Å). The true coordination of  $\text{Ba}^{2+}$  is then [10 + 2] rather than [12].

## 2. Structure Organization

The projection of the unit cell onto the  $xOz$  plane is represented in Fig. 2. BaNaZr<sub>2</sub>F<sub>11</sub> is a layer structure, based on the stacking perpendicular to the [001] axis of quasi-planar sheets of  $[\text{ZrF}_8]^{4-}$  S.A. and of rippled sheets containing alternating  $\text{Ba}^{2+}$  and  $\text{Na}^+$  rows lined up along [010] or [100] axes. Figures 3 and 4 give a polyhedral representation of such sheets, showing, respectively, edge-sharing  $[\text{NaF}_6]^{5-}$  and  $[\text{BaF}_{12}]^{10-}$  polyhedra on the one hand and corner and edge-sharing  $[\text{ZrF}_8]^{4-}$  S.A. on the other hand. In a Zr sheet, four  $[\text{ZrF}_8]^{4-}$  S.A. are connected by edge-sharing about a cubic empty cavity, forming a  $[\text{Zr}_4\text{F}_{24}]^{8-}$  structural unit. Neighboring units share  $F_1$  corners to give complete  $[\text{ZrF}_{5.5}]_n$  sheets. Two Na cations, located exactly up and down each cubic empty hole (e.g., in  $z = 0.01$  and 0.24) are linked to four Zr cations (in  $z = 0.12$  and 0.13) of the same unit by  $F_5-F_3$  edges. These six polyhedra form in this way three-dimensional  $[\text{Na}_2\text{Zr}_4\text{F}_{28}]^{10-}$  units, reminiscent of the  $[\text{Y}_6\text{F}_{32}]^{14-}$  groups of six  $[\text{YF}_8]^{5-}$  S.A. about a cubic empty hole described in KY<sub>3</sub>F<sub>10</sub> (13), an anion-excess fluoride-related superstructure (see next paragraph). Each Ba cation (e.g., in  $z = 0.21$ ) is also located above or under an anionic

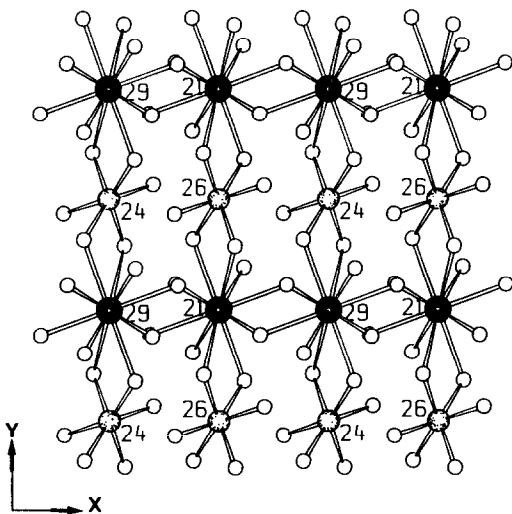


FIG. 3. Representation of a sheet, perpendicular to the [001] axis, associating parallel rows of  $[\text{NaF}_6]^{5-}$  and  $[\text{BaF}_{12}]^{10-}$  polyhedra. Ba: large black spheres, Na: large stippled spheres, F: small white spheres.

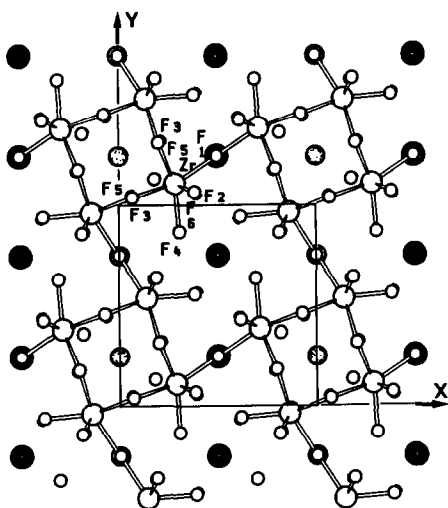


FIG. 4.  $[\text{ZrF}_{5.5}]_n$  sheet, perpendicular to the  $[001]$  axis ( $z = 0.12\text{--}0.13$  for  $\text{Zr}^{4+}$ ). Some of the Ba and Na cations of the adjacent sheets are also represented except Ba in  $z = 0.29$  and Na in  $z = 0.26$  hiding F anions (refer to Fig. 3). The  $z$  values for all cations are reported in Fig. 6. Zr: large white spheres. Other symbols are the same as those in Fig. 3.

$\text{F}_4\text{--F}_4\text{--F}_4\text{--F}_4$  square face of a Zr sheet (e.g., in  $z = 0.12, 0.13$ ). It is also connected to the same Zr sheet by two  $\text{F}_2$  and two  $\text{F}_6$  anions at the same level ( $z = 0.20$ ) and to four anions of the adjacent Zr sheet (two close  $\text{F}_2$  and two distant  $\text{F}_3$  ones at, respectively,  $z = 0.30$  and  $0.32$ ) forming a distorted square face.

Stacked  $[\text{ZrF}_{5.5}]_n$  sheets along the  $[001]$  axis are successively shifted from  $x/2$ ,  $y/2$ ,  $-x/2$ , and  $-y/2$  and so the unit cell is composed of four Zr sheets (Fig. 2). On the contrary, Ba and Na cations are perfectly lined up along the  $Oz$  axis with sequences  $[\text{Na--Na--Ba--Ba}]$ .

### 3. Comparison with Other Structure Types

*a. Fluorite and  $\text{KY}_3\text{F}_{10}$ .* The presence in the  $\text{BaNaZr}_2\text{F}_{11}$  structure of  $[\text{Na}_2\text{Zr}_4\text{F}_{28}]^{10-}$  groups, analogous to  $[\text{Y}_6\text{F}_{32}]^{14-}$  ones described in the fluorite-related  $\text{KY}_3\text{F}_{10}$  superstructure (13), strongly suggests a close rela-

tionship between both phases.  $\text{KY}_3\text{F}_{10}$  is one of the most important members of a family of compounds deriving from the fluorite type by ordered insertion of anionic excess ( $\text{MF}_2 \rightarrow \text{MF}_{2.50}$ ) into so-called "cuboctahedral clusters." These clusters are created via a cooperative mechanism of  $45^\circ$  rotation of the six faces of empty anionic cubes of fluorite about the fourfold axis, which transforms these cubes into cuboctahedra and the six  $\text{MX}_8$  filled cubes capping each empty cube into  $\text{MX}_8$  square antiprisms. This operation creates four excess anionic sites for each cluster ( $\text{M}_6\text{X}_{32} \rightarrow \text{M}_6\text{X}_{36}$ ) without any high distortion of the fluorite structure.  $\text{KY}_3\text{F}_{10}$  (Fig. 5c) is constituted by the regular formation of such edge-sharing  $[\text{Y}_6\text{F}_{36}]^{18-}$  clusters along the three main axes of the fluorite subcell. From a purely descriptive point of view, it is strictly equivalent to describe the  $\text{KY}_3\text{F}_{10}$  structure as an ordered distribution of corner-sharing  $[\text{Y}_6\text{F}_{32}]^{14-}$  units corresponding to six S.A. capping an empty anionic cube and deriving from  $\text{M}_6\text{X}_{32}$  fluorite units by  $45^\circ$  rotation of the *outer* faces of the six  $\text{MX}_8$  filled cubes.

These last units are very similar to the  $[\text{Na}_2\text{Zr}_4\text{F}_{28}]^{10-}$  ones described above and all the more so because two  $\text{F}_5$  anions at  $3.22 \text{ \AA}$  about each Na cation form with two  $\text{F}_6$  anions at  $2.24 \text{ \AA}$  a very distorted square face which transforms the  $[\text{NaF}_6]^{5-}$  trigonal prisms to  $[\text{NaF}_{6+2}]^{7-}$  S.A. and therefore  $[\text{Na}_2\text{Zr}_4\text{F}_{28}]^{10-}$  units to  $[\text{Na}_2\text{Zr}_4\text{F}_{32}]^{14-}$  ones (Fig. 5a).

Figures 5b and 5c show how  $\text{BaNaZr}_2\text{F}_{11}$  and  $\text{KY}_3\text{F}_{10}$  are derived from each other by a  $\approx 20^\circ$  rotation of the  $[\text{M}_6\text{X}_{32}]^{14-}$  units about axes getting over the center of these units and parallel to the  $[001]$  direction.

Both structures mainly differ by the connections between adjacent  $[\text{M}_6\text{X}_{32}]^{14-}$  units, performed by two shared corners in  $\text{KY}_3\text{F}_{10}$  and only by one  $\text{F}_1$  corner in  $\text{BaNaZr}_2\text{F}_{11}$ . The sheet formula is  $[\text{YF}_5]_n$  in  $\text{KY}_3\text{F}_{10}$  and  $[\text{ZrF}_{5.5}]_n$  in  $\text{BaNaZr}_2\text{F}_{11}$ . The rotation of these S.A. groups is then a structural means

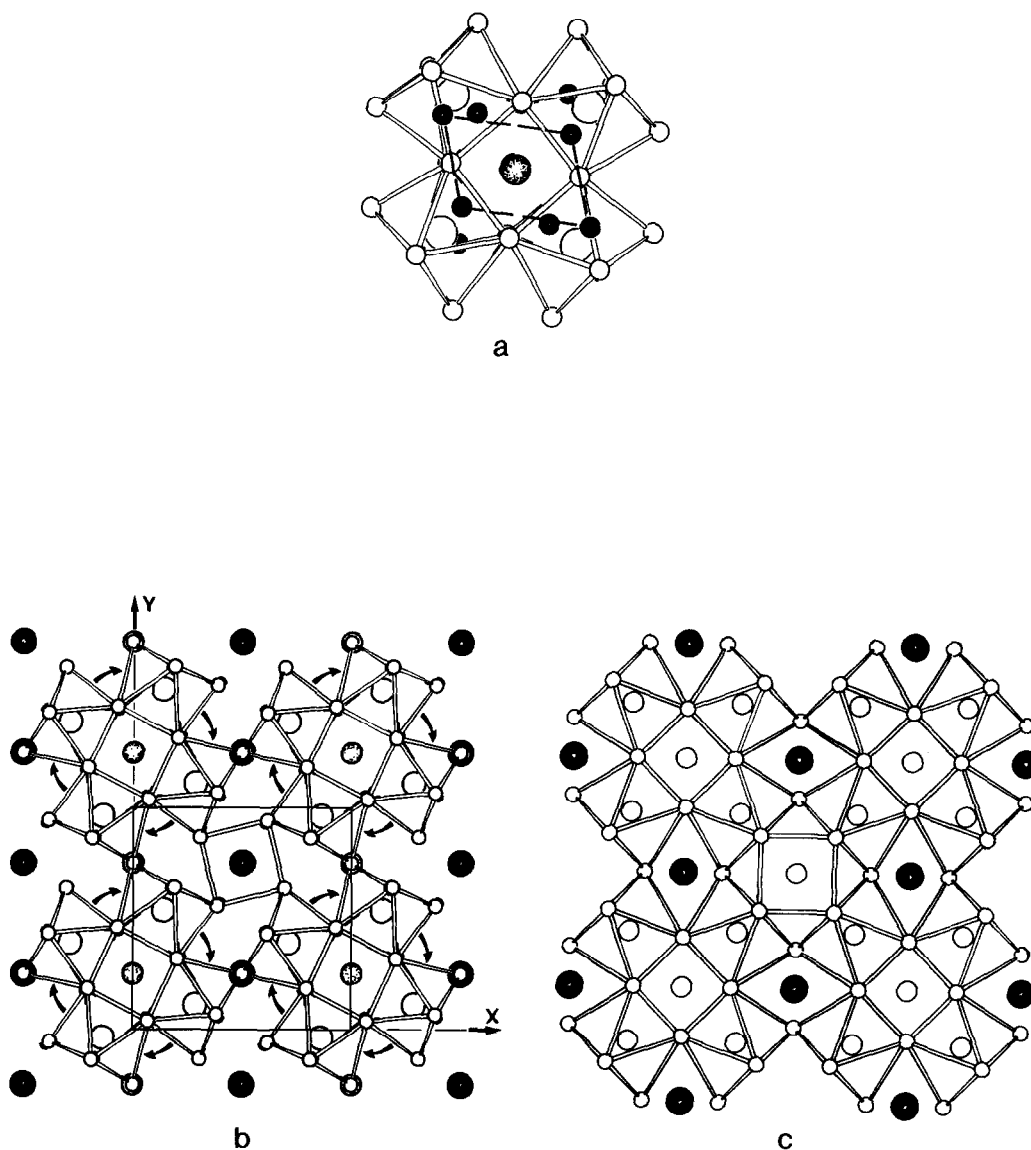


FIG. 5. (a) Representation of a  $[\text{Na}_2\text{Zr}_4\text{F}_{28+4}]^{14-}$  structural unit of  $\text{BaNaZr}_2\text{F}_{11}$ , homologous to the  $[\text{Y}_6\text{F}_{32}]^{14-}$  one in the anion-excess fluorite superstructure  $\text{KY}_3\text{F}_{10}$ . The anions of the outer distorted square faces of  $[\text{NaF}_{6+2}]^{7-}$  polyhedra are represented by small black spheres. The anions of the upper face are connected by dashed lines. (b) Representation of a  $[\text{ZrF}_{3.5}]_n$  sheet with  $[\text{ZrF}_8]^{4-}$  S.A. sharing edges to form  $[\text{Zr}_4\text{F}_{24}]^{18-}$  planar units which each associate with two  $[\text{NaF}_{6+2}]^{7-}$  polyhedra to give the structural units of Fig. 5a. These units share corners and their cooperative rotation from  $\approx 20^\circ$ , as shown by arrows, transforms the structure of  $\text{BaNaZr}_2\text{F}_{11}$  in structure type  $\text{KY}_3\text{F}_{10}$ , represented in Fig. 5c. (c) (001) projection of  $\text{KY}_3\text{F}_{10}$ : this structure can be described as a regular association of  $[\text{Y}_6\text{F}_{32}]^{14-}$  fluorite-related units and of  $[\text{Y}_6\text{F}_{36}]^{18-}$  anion-excess fluorite units called "cuboctahedral clusters."

to add even more excess anions in the anion-excess fluorite-related  $KY_3F_{10}$  superstructure, from  $MX_{2.50}$  to  $MX_{2.75}$ . It does not modify Ba and Na cation plane nets which remain square ones. Emphasizing the similarity between  $BaNazr_2F_{11}$  and  $KY_3F_{10}$ , Ba and Na cations play a double structural role: half  $Ba^{2+}$  and  $Na^+$  are situated as  $Y^{3+}$  and the other half as  $K^+$  in  $KY_3F_{10}$ , justifying the structural formula  $(Ba_{0.5}Na_{0.5})(Ba_{0.5}Na_{0.5}Zr_2)F_{10+1}$ . This relationship explains why  $Ba^{2+}$  and  $Na^+$  environments are not fundamentally different (Fig. 3), with respect to the relative size of these cations.

*b. Anion-excess  $ReO_3$  type.* The rotation of  $\approx 20^\circ$  of  $[Na_2Zr_4F_{28+4}]^{14-}$  units in  $BaNazr_2F_{11}$ , compared to the homologous units in  $KY_3F_{10}$ , corresponds to the transformation of cationic  $Y^{3+}$  square nets to  $3^2.4.3.4$ . semiregular ones, intermediate between  $4^4$  square and  $3^6$  triangular nets. This transformation and analogous ones, thoroughly studied by O'Keeffe and Hyde (14), were recently considered (7) a consequence of F-bridging between two M cations situated at two opposite corners of a square face of a  $ReO_3$ -related network, shortening then the M-M distance and changing this square face into two triangular ones. In  $BaNazr_2F_{11}$ , the characterization of  $3^2.4.3.4$ . Zr plane nets, easier to describe in also considering anions directly connecting these cations as in Fig. 6, involves a ninth Zr-F weak bond ( $Zr-F_4 = 3.05 \text{ \AA}$ ), represented as dashed lines. Indeed, Zr-Zr distances about large-size Ba cations are stretched to such an extent that the  $3^2.4.3.4$ . plane nets are not regular and tend to break in partly isolated  $[Zr_4F_{22}]^{6-}$  units.

The presence of such  $3^2.4.3.4$ . plane nets establishes a link between  $BaNazr_2F_{11}$  and fluoride phases like  $\beta PrZr_3F_{15}$ ,  $YZr_3F_{15}$ ,  $PrZr_2F_{11}$ , and  $LiTiZr_5F_{22}$ (15), whose structure was previously discussed as a stacking of these (or of similar) plane nets, either directly connected to each other (e.g., in

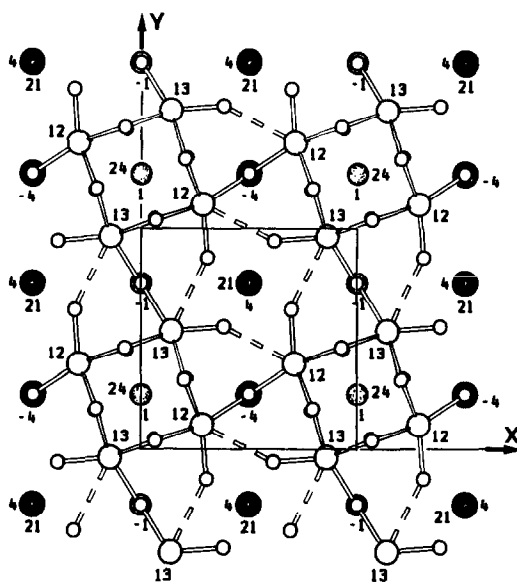


FIG. 6.  $3^2.4.3.4$ . Zr plane net (with F anions directly connecting  $Zr^{4+}$ ). The "broken" Zr-F<sub>4</sub> bonds ( $d = 3.05 \text{ \AA}$ ), represented as dashed lines, are correlated to a dilatation of the cationic Zr net about high size Ba cations.

$\beta PrZr_3F_{15}$ ) or separated by sheets of a different nature (e.g., Pr sheets in  $PrZr_2F_{11}$ , Li-Tl sheets in  $LiTiZr_5F_{22}$ ). Some analogies are to be noted between the respective situation of  $Tl^+ - Li^+$  sheets in  $LiTiZr_5F_{22}$  and  $Ba^{2+} - Na^+$  ones in  $BaNazr_2F_{11}$ , with respect to  $3^2.4.3.4$ . Zr plane nets but, on the one hand, the cationic order is not the same between  $Tl^+$  and  $Li^+$  as that between  $Ba^{2+}$  and  $Na^+$  and, on the other hand, layer stacking is rather different. A more detailed study of such relationships will be developed in a forthcoming work.

In fact,  $BaNazr_2F_{11}$ , although containing cationic Zr plane nets similar to those present in the above quoted phases, has specific structural characteristics resulting from its relationship with the  $KY_3F_{10}$  fluorite superstructure (distorted f.c.c. cationic network) and from the presence of large-size  $Ba^{2+}$

cations which tend to break the [ZrF<sub>5.5</sub>]<sub>n</sub> layers into smaller units. Therefore BaNaZr<sub>2</sub>F<sub>11</sub> seems to be intermediate between anion-excess fluorite-related superstructures like KY<sub>3</sub>F<sub>10</sub>, BaCaLu<sub>2</sub>F<sub>10</sub> (16), PbZr<sub>3</sub>F<sub>6</sub>O<sub>4</sub> (17) . . . and phases related more or less closely to the anion-excess ReO<sub>3</sub> type, like α- and βLnZr<sub>3</sub>F<sub>15</sub>, PrZr<sub>2</sub>F<sub>11</sub>, LiTiZr<sub>3</sub>F<sub>22</sub> . . .

### Conclusion

The structure of BaNaZr<sub>2</sub>F<sub>11</sub> is a new original layer structure based on the stacking along the Oz axis of [ZrF<sub>5.5</sub>]<sub>n</sub> sheets of edge- and corner-shared [ZrF<sub>8</sub>]<sup>14-</sup> S.A. alternating with other sheets containing rows of Ba<sup>2+</sup> and Na<sup>+</sup> cations parallel to the Oy or to the Ox axes and forming ordered 4<sup>4</sup> square planes. The presence of Ba<sup>2+</sup> rows leads to a weakening of [ZrF<sub>5.5</sub>]<sub>n</sub> layers, emphasizing the presence of stable [Na<sub>2</sub>Zr<sub>4</sub>F<sub>28+4</sub>]<sup>14-</sup> units which relate this phase to the well-known "anion-excess fluorite type," characterized by large-size anionic clusters.

BaNaZr<sub>2</sub>F<sub>11</sub> appears, like βBaZr<sub>2</sub>F<sub>10</sub>, PrZr<sub>2</sub>F<sub>11</sub>, and some other phases recrystallizing from fluorozirconate glasses, to be a key structure in helping to understand short- and medium-range order in these glasses. The amount of structural information already gathered concerning these last phases suggests the possibility of correlating the structural information available on both kinds of materials.

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