

Synthesis and Crystal Structure of γ -BaZrF₆

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γ -BaZrF₆ is obtained from hydrothermal synthesis in HF solution. It crystallizes in the monoclinic system, with space group *C2/c*; $a = 13.193(2)$, $b = 7.499(1)$, and $c = 19.839(3)$ Å; $\beta = 91.69(1)^\circ$; and $Z = 16$. The structure is determined from X-ray single crystal data, $R = 0.016$ for 3390 unique observed reflections. Barium atoms are inserted between isolated $[\text{ZrF}_6]_n^{2n-}$ chains, built up from ZrF₈ bicapped trigonal prisms, linked alternately by faces and opposite vertices. A site has been found partly occupied by probably a water molecule, leading to the estimated BaZrF₆(H₂O)_{0.04} formula for the studied crystal © 1992 Academic Press, Inc.

Introduction

Before this study, crystalline BaZrF₆ was known to exist in low- and high-temperature modifications (α and β forms, respectively) (1). The structure of β -BaZrF₆ (2) belongs to the RbPaF₆ type (3), also adopted by α -PbSrF₆, α -SrZrF₆, and EuZrF₆ (1, 4); it is composed of ZrF₈ dodecahedra connected by edges forming infinite chains linked by Ba²⁺ cations. The structure of α -BaZrF₆ (5) is built up from $[\text{Zr}_2\text{F}_{12}]^{4-}$ complex anions resulting from the association of two monocapped trigonal prisms sharing an edge, linked by Ba²⁺ cations.

On the other hand, the BaF₂-ZrF₄ system is characterized by the coexistence of a large vitreous domain with numerous crystalline phases. For modeling the glass structures, advantage is generally taken of the knowledge of crystalline structures. Concerning the fluorozirconate glasses, the structure approaches were focused mainly on two nominal compositions: BaZr₂F₁₀ and precisely

BaZrF₆ [for a review see Ref. (6)]. In the latter case, the glass local structure was believed to be strongly related to those of α - and β -BaZrF₆ (7, 8).

Investigation of the BaF₂-ZrF₄-HF_{aq} system by hydrothermal synthesis led to a new BaZrF₆ form that we called γ . This compound could be of some importance at least for the structure modeling of glasses, so its structure determination was undertaken.

Experimental

Transparent prismatic crystals of γ -BaZrF₆ were grown by hydrothermal synthesis. A fluoride glass (1.5 g) with nominal composition BaZr₃F₁₄ (the same result was obtained from a mixture of the separated components BaF₂ and ZrF₄), together with 5 cm³ of a HF 5 M solution, was introduced into a 15-cm³ hermetic Teflon bucket, placed in a metallic container (Parr bomb). The bomb was heated at 200°C for 3 days and

then naturally cooled down; the maximal pressure was near 15 MPa (150 atm).

The thermal behavior was followed by DTA (Q1500D-MOM), DSC, and TG experiments (Perkin–Elmer DSC4 and TGS2, Ar gas stream), with a heating rate of $5^{\circ}\text{C} \cdot \text{min}^{-1}$. No thermal event could be detected on the DSC curve up to 500°C ; the X-ray powder pattern of the sample back at room temperature was unchanged. The DTA curve exhibited a weak endothermic event near 545°C . The quenched product was undoubtedly α -BaZrF₆ from its X-ray powder pattern, and this $\gamma \rightarrow \alpha$ transition is irreversible. At higher temperature, the reversible transition $\alpha \rightarrow \beta$ (565°C) and fusion ($T_m = 570^{\circ}\text{C}$) determined by Kawamoto and Sakaguchi (6) were confirmed. No mass loss was detected on the TG curve up to 450°C .

Structure Determination

Single crystal X-ray data were collected on a Siemens AED-2 four-circle diffractometer from a translucent prismatic crystal. Lattice constants of the monoclinic cell were based on 30 reflections at $2\theta \approx 30^{\circ}$. Conditions limiting possible reflections were consistent with the space groups $C2/c$ and Cc . The structure was solved using direct methods from the *EEES* option of the *SHELX76* program (9). A starting solution was obtained, with two Ba and two Zr atoms in general positions. Refinements of their atomic coordinates and isotropic thermal motion led to $R = 0.156$. Ionic scattering factors for Ba^{2+} , Zr^{4+} , and F^{-} and anomalous dispersion terms were taken from the “*International Tables for X-Ray Crystallography*” (10). Twelve fluorine atoms in general position were located from a Fourier difference synthesis. Further refinement of their atomic coordinates and isotropic thermal motion led to $R = 0.039$. The residual decreased to $R = 0.017$ when anisotropic thermal parameters were refined. At this stage, a Fourier difference synthesis evi-

denced a new site, the peak height being $2.7 \text{ e} \cdot \text{\AA}^3$ (the next most intense one being smaller than $1.2 \text{ e} \cdot \text{\AA}^3$). This peak was still there when using scattering factors for neutral instead of ionized atoms. As justified in the discussion, a water molecule was allowed to occupy partly the corresponding $0, y, \frac{1}{4} 4e$ site; simultaneous refinement of the y coordinate, an isotropic thermal parameter, and the occupancy factor (in spite of 75% correlation with the latter) was found to be possible and led to the final residuals listed in Table I, which gives the conditions for X-ray data measurements and refinements. No significative improvement of these results was observed when using the noncentrosymmetrical Cc space group. Final atomic coordinates and temperature factors are listed in Table II. Selected bond lengths and angles are gathered in Table III. A listed of observed and calculated structure factors may be obtained on request to the authors.

Description of the Structure and Discussion

The structure of γ -BaZrF₆ consists of infinite isolated $[\text{ZrF}_6]_n^{2n-}$ chains built up from ZrF₈ distorted bicapped trigonal prisms linked alternately by faces and opposite vertices. These chains are stacked at four well-defined levels along the c axis. The z coordinates of the Zr(1) and Zr(2) zirconium atoms, which alternate along the chains, are near $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, and $\frac{7}{8}$ for both of them. At each level, a chain is parallel to the neighboring one. It appears (Fig. 1) that the $[\text{ZrF}_6]_n^{2n-}$ chains may point toward two directions: they are parallel to the [110] direction at levels $\frac{1}{8}$ and $\frac{7}{8}$, whereas they are parallel to the $[1\bar{1}0]$ direction at levels $\frac{3}{8}$ and $\frac{5}{8}$.

The environment of the two independent Zr atom sites is remarkably similar. The two ZrF₈ bicapped trigonal prisms are quasi-related by a mirror in the plane defined by the face-sharing fluorine atoms (Fig. 2). The

TABLE I
 CRYSTALLOGRAPHIC DATA FOR γ -BaZrF₆

Formula weight	342.54
Space group	<i>C2/c</i>
<i>Z</i>	16
Calculated density	4.64
Radiation	MoK α
Monochromator	Graphite
μ (mm ⁻¹), MoK α	10.12
Crystal size (mm)	0.21 \times 0.14 \times 0.10
Lattice constants	
<i>a</i> (Å)	13.193(2)
<i>b</i> (Å)	7.499(1)
<i>c</i> (Å)	19.839(3)
β (°)	91.69(1)
<i>V</i> (Å ³)	1961.9(6)
Scan type	ω -2 θ
<i>T</i>	20°C
Angular range (2 θ_{\max})	70°
Standard reflections	2,4,4; -4,0,14; 2, -4,4
Min and max <i>hkl</i>	-21,0,0; 21,12,31
Data examined	4566
Absorption correction	Gauss method
Min and max transmission factors	0.27 0.43
Unique reflections, <i>R</i> _{int}	4250, 0.024
Data retained [<i>I</i> > 3 σ (<i>I</i>)]	3390
Extinction correction, SHELX76	2.5(1) \times 10 ⁻⁷
Weighting scheme	$w = 1.00/[\sigma^2(F_0) + 0.00040 F_0^2]$
Discrepancy factors	<i>R</i> = 0.016 <i>R</i> _w = 0.018
Parameters refined	149
Max shift/e.s.d.	0.002
Max and min electron density in final Fourier difference map (e.Å ⁻³)	1.16, -1.09

distances between the F(1), F(9), and F(10) fluorine atom sites, involved in the face-sharing, are unusually short: they range from 2.388(2) to 2.421(2) Å; all other F-F distances are larger than 2.51 Å. A clear difference between terminal (t) and bridging (b) fluorine atoms is observed in γ -BaZrF₆: the Zr-F_t distances range from 2.035(1) to 2.094(2) Å, whereas the Zr-F_b ones range from 2.124(1) to 2.246(1) Å.

The barium atoms environment may be defined by considering Ba-F distances smaller than 3.06 Å, the next ones being larger than 3.30 Å. In this way, a [Ba(2)F₁₀] pentagonal prism and a distorted [Ba(1)

F₁₁O_w] hexagonal cubooctahedron are recognized in Fig. 3. The main distortion of the hexagonal cubooctahedron is due to one of the F(11) atoms being quite out of the cubooctahedron hexagonal section (near O_w). The subnetwork built up from [Ba(1)F₁₁O_w] and [Ba(2)F₁₀] polyhedra is tridimensional according to a complex corner-, edge- and face-sharing linkage which may be seen in Figs. 4, 5, and 6.

As the synthesis conditions could have led to some F-OH substitutions and to the inclusion of water or even HF₂ molecules, a valence bond analysis was performed. Results are given in Table IV; they are consis-

TABLE II
 ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS, AND ANISOTROPIC
 THERMAL PARAMETERS $U_{ij} \times 10^4$ WITH e.s.d.'s IN PARENTHESES

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$		
Ba(1)	0.32238(1)	0.04532(2)	0.20900(1)	0.92(1)		
Ba(2)	0.59026(1)	0.23555(2)	0.05596(1)	0.90(1)		
Zr(1)	0.15283(1)	0.02202(2)	0.37282(1)	0.63(1)		
Zr(2)	0.43164(1)	0.25112(2)	0.87041(1)	0.63(1)		
F(1)	0.4803(1)	0.4359(2)	0.56097(6)	1.00(4)		
F(2)	0.2349(1)	0.3143(2)	0.66426(7)	1.12(4)		
F(3)	0.5487(1)	0.1202(2)	0.54013(7)	1.36(4)		
F(4)	0.6381(1)	0.2594(2)	0.72242(7)	1.20(4)		
F(5)	0.2882(1)	0.3921(2)	0.53683(6)	1.29(4)		
F(6)	0.3251(1)	0.5970(2)	0.71877(6)	1.07(4)		
F(7)	0.3991(1)	0.7278(2)	0.60613(7)	1.25(4)		
F(8)	0.6647(1)	0.4595(2)	0.61204(8)	1.32(5)		
F(9)	0.4889(1)	0.4546(2)	0.68117(7)	1.38(5)		
F(10)	0.4041(1)	0.2038(2)	0.62730(8)	1.39(5)		
F(11)	0.0415(1)	0.5020(2)	0.16988(8)	1.50(5)		
F(12)	0.7097(1)	0.1269(2)	0.61173(7)	1.31(4)		
O _w ^a	0.0	0.252(2)	$\frac{1}{4}$	1.6(3)		
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	130(1)	95(1)	126(1)	12(1)	25(1)	16(1)
Ba(2)	106(1)	102(1)	134(1)	6(1)	1(1)	-8(1)
Zr(1)	68(1)	75(1)	97(1)	-6(1)	10(1)	8(1)
Zr(2)	72(1)	68(1)	97(1)	3(1)	-5(1)	-13(1)
F(1)	134(5)	133(5)	116(5)	8(4)	17(4)	13(4)
F(2)	127(5)	144(5)	157(5)	6(4)	32(4)	-26(4)
F(3)	205(6)	154(5)	156(6)	-63(5)	-44(4)	54(5)
F(4)	173(6)	151(5)	132(5)	-16(4)	-28(4)	36(4)
F(5)	135(5)	223(6)	132(5)	-54(5)	-5(4)	11(5)
F(6)	152(5)	121(5)	136(5)	-13(4)	29(4)	22(4)
F(7)	159(5)	102(5)	218(6)	15(4)	50(5)	-10(4)
F(8)	142(5)	137(6)	223(6)	46(5)	-15(5)	-27(4)
F(9)	154(5)	240(7)	130(5)	-67(5)	-24(4)	71(5)
F(10)	130(5)	102(5)	300(7)	46(5)	37(5)	14(4)
F(11)	175(6)	118(6)	274(7)	-53(5)	-15(5)	8(4)
F(12)	119(5)	198(6)	182(6)	-6(5)	12(4)	82(4)

Note. Vibrational U_{ij} coefficients relate to the expression

$$T = \exp[-2\pi^2(h^2a^*U_{11} + k^2b^*U_{22} + l^2c^*U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})].$$

^a 4e position with refined occupancy 0.15(1).

tent with the proposed formula and particularly with the hypothesis of the water molecule O_w partly occupying a $0, y, \frac{1}{4}$ site. The F(11) valence shows a slight deficiency which could be compensated by hydrogen bonding with O_w. The nearest neighbors of

O_w are two F(11) atoms at 2.51 Å (the next neighbors are at 2.62 Å) and the F(11)-O_w-F(11) angle is 85.2(6)°. The formula of the particular crystal studied here is estimated to be BaZrF₆(H₂O)_{0.04}. It seems that γ -BaZrF₆ free of the water molecule

TABLE III
 SELECTED BOND LENGTHS (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

		Zr(1) polyhedron ($\langle \text{Zr-F} \rangle = 2.115$)						
	F(5)	F(7)	F(6)	F(2)	F(9)	F(12)	F(10)	F(1)
F(5)	2.037(1)	3.202(1)	3.940(1)	2.708(1)	3.871(1)	2.544(2)	2.719(2)	2.586(1)
F(7)	103.4(1)	2.042(1)	2.653(2)	3.973(1)	2.777(2)	2.616(1)	3.952(2)	2.607(2)
F(6)	148.8(1)	80.8(1)	2.053(1)	2.647(2)	2.542(2)	2.586(1)	3.631(1)	3.979(1)
F(2)	82.3(1)	149.6(1)	79.7(1)	2.075(1)	3.519(1)	2.583(2)	2.511(2)	3.988(1)
F(9)	136.2(1)	83.3(1)	74.7(1)	113.4(1)	2.134(1)	4.103(1)	2.421(2)	2.388(2)
F(12)	74.9(1)	77.3(1)	76.0(1)	75.5(1)	147.1(1)	2.144(1)	4.086(2)	4.003(1)
F(10)	80.0(1)	138.1(1)	117.7(1)	72.1(1)	68.1(1)	141.1(1)	2.189(1)	2.419(2)
F(1)	74.1(1)	74.7(1)	135.4(1)	134.7(1)	66.0(1)	131.5(1)	66.1(1)	2.246(1)
		Zr(2) polyhedron, ($\langle \text{Zr-F} \rangle = 2.114$)						
	F(4)	F(3)	F(8)	F(11)	F(12)	F(9)	F(10)	F(1)
F(4)	2.035(1)	3.912(1)	2.686(2)	2.545(2)	2.612(2)	2.567(2)	3.595(1)	3.994(1)
F(3)	147.7(1)	2.038(1)	3.275(1)	2.737(2)	2.521(1)	3.856(0)	2.687(2)	2.571(2)
F(8)	82.2(1)	106.4(1)	2.051(1)	4.006(1)	2.564(2)	2.729(1)	3.956(1)	2.614(1)
F(11)	76.1(1)	82.9(1)	150.3(1)	2.094(2)	2.709(2)	3.502(2)	2.508(2)	4.000(1)
F(12)	77.8(1)	74.5(1)	75.8(1)	79.9(1)	2.124(1)	4.082(1)	4.093(1)	3.920(1)
F(9)	76.1(1)	135.4(1)	81.5(1)	112.0(1)	147.3(1)	2.130(1)	2.421(2)	2.388(2)
F(10)	116.3(1)	78.7(1)	137.4(1)	71.5(1)	142.8(1)	68.1(1)	2.195(1)	2.419(2)
F(1)	138.0(1)	73.7(1)	74.8(1)	134.5(1)	127.7(1)	66.1(1)	66.0(1)	2.243(1)
Ba(1) polyhedron			Ba(2) polyhedron					
Ba(1)-F(6)	2.673(1)		Ba(2)-F(8)	2.714(1)				
Ba(1)-F(6)	2.689(1)		Ba(2)-F(3)	2.740(1)				
Ba(1)-F(4)	2.702(1)		Ba(2)-F(5)	2.741(1)				
Ba(1)-F(10)	2.717(1)		Ba(2)-F(3)	2.745(1)				
Ba(1)-F(8)	2.791(1)		Ba(2)-F(7)	2.752(1)				
Ba(1)-F(2)	2.848(1)		Ba(2)-F(5)	2.817(1)				
Ba(1)-F(4)	2.857(1)		Ba(2)-F(2)	2.856(1)				
Ba(1)-F(7)	2.865(1)		Ba(2)-F(1)	2.862(1)				
Ba(1)-Ow	2.890(8)		Ba(2)-F(1)	2.894(1)				
Ba(1)-F(11)	2.975(2)		Ba(2)-F(11)	2.945(2)				
Ba(1)-F(11)	3.033(1)							
Ba(1)-F(2)	3.055(1)							
Zirconium linkage								
By face								
Zr(1)-Zr(2)	3.377(1)		Zr(1)-F(1)-Zr(2)	97.6(1)				
			Zr(1)-F(9)-Zr(2)	104.7(1)				
			Zr(1)-F(10)-Zr(2)	100.8(1)				
By corner								
Zr(1)-Zr(2)	4.212(1)		Zr(1)-F(12)-Zr(2)	161.4(1)				

could exist and we can remember that no mass loss could be detected during the TG experiment. Further IR measurements were not decisive about the presence of water,

representing less than 1% of the anions in the crystal studied. Nevertheless, the site partly occupied really exists in the structure. Thus, it may be that BaZrF₆(H₂O)_{0.25}

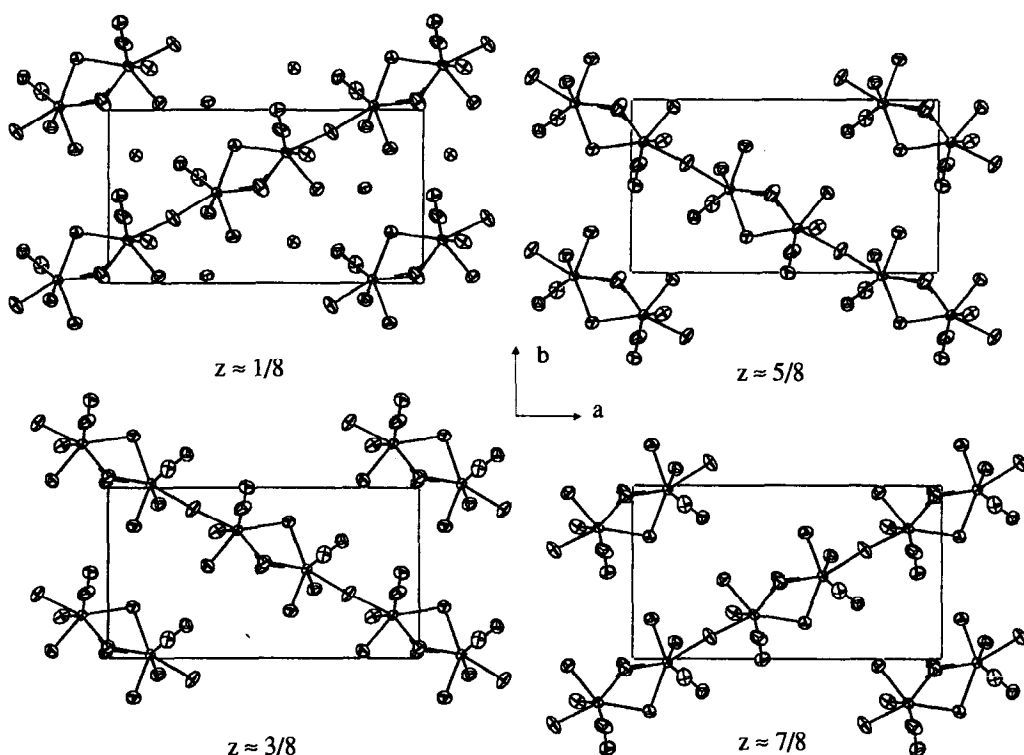


FIG. 1. Stacking of the $[\text{ZrF}_6]_n^{2-}$ infinite chains at four levels along the c axis in $\gamma\text{-BaZrF}_6$. 90% probability ellipsoids—ORTEP drawing (11).

also could exist, with a full O_w site occupancy. To verify these hypotheses would require structure refinements applied on data from several crystals. Synthesis from more or less diluted HF solutions could have

some influence also on the exact formulation in such a case. Such results are not forthcoming; thus this study represents the best information currently available on this new phase.

Comparison of the crystallographic char-

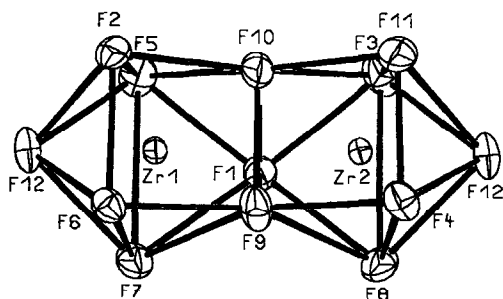


FIG. 2. Atomic numbering scheme of the two face-sharing ZrF_8 bicapped trigonal prisms in $\gamma\text{-BaZrF}_6$. 90% probability ellipsoids—ORTEP drawing (11).

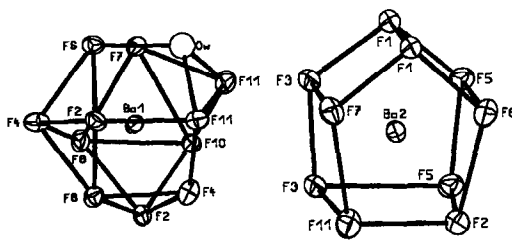


FIG. 3. Coordination of the two barium atom sites in $\gamma\text{-BaZrF}_6$. 90% probability ellipsoids—ORTEP drawing (11).

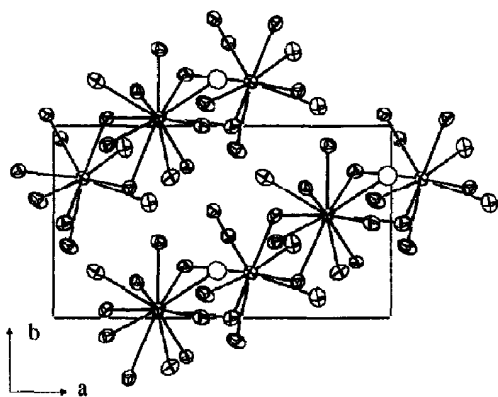


FIG. 4. Ba(1)–Ba(2) linkage in γ -BaZrF₆; Ow shown as open circles. 90% probability ellipsoids—ORTEP drawing (11).

acteristics of the three BaZrF₆ forms is made in Table V. The γ form is the less dense. In spite of the possible water presence, γ -BaZrF₆ cannot be excluded in modeling the BaZrF₆ glass structure since the volume per formula is 123.6 Å³ in the glass (8).

Face sharing is unusual in fluorozirconates; however, two cases were recently identified. Isolated Zr₂F₁₃²⁻ dimeric anions, formed by two ZrF₈²⁻ distorted bicapped trigonal prisms joined together through the

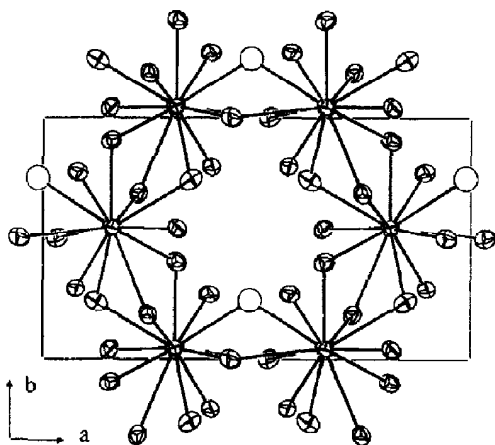


FIG. 5. Ba(1)–Ba(1) linkage in γ -BaZrF₆; Ow shown as open circles. 90% probability ellipsoids—ORTEP drawing (11).

TABLE IV

VALENCE-BOND ANALYSIS OF γ -BaZrF₆ USING THE ZACHARIASEN LAW FOR Ba–F^a AND Zr–F^b BONDS AND THE BROWN–SHANNON INVERSE POWER LAW FOR THE Ba–O^c BOND

<i>j/i</i>	Ba(1)	Ba(2)	Zr(1)	Zr(2)	$\sum_i s_{ij}$
F(1)		0.16	0.35	0.36	1.02
F(2)	0.16	0.15	0.54		0.96
F(3)	0.10	0.22		0.59	1.02
F(4)	0.24	0.21		0.60	1.00
F(5)	0.16	0.22	0.60		1.00
F(6)	0.26	0.18	0.57		1.08
F(7)	0.16	0.21	0.59		0.96
F(8)	0.19	0.23		0.58	1.00
F(9)		0.02	0.47	0.47	0.96
F(10)	0.23	0.02	0.41	0.40	1.06
F(11)	0.12	0.13		0.52	0.87
	0.10				
F(12)	0.04	0.05	0.46	0.48	1.03
O(w)	0.20 × 2				0.40
	× 0.15				
$\sum_j s_{ij}$	2.04	1.96	3.99	4.00	

$$^a s_{ij} = 0.25 \exp[(2.685 - d_{ij})/0.391] \quad (14).$$

$$^b s_{ij} = \exp[-(d_{ij} - 1.83)/0.4] \quad (15).$$

$$^c s_{ij} = (d_{ij}/d_0)^{-N}, \text{ with } d_0 = 2.297 \text{ and } N = 7 \quad (16).$$

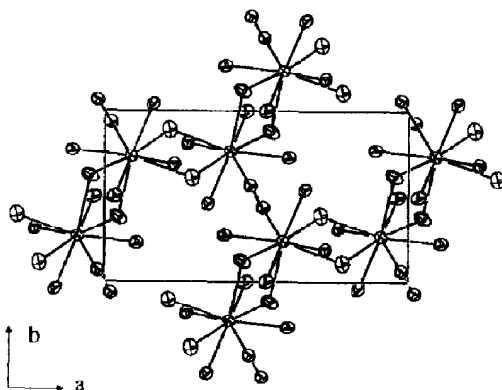


FIG. 6. Ba(2)–Ba(2) linkage in γ -BaZrF₆. 90% probability ellipsoids—ORTEP drawing (11).

TABLE V
 CRYSTALLOGRAPHIC CHARACTERISTICS OF BaZrF₆ PHASES

	Space group	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>Z</i>	<i>V/Z</i>	Ref.
α	<i>P2₁/c</i>	6.493(2)	9.530(3)	9.203(3)	127.09(7)	4	113.56	(6)
β	<i>Cmma</i>	7.632(4)	11.406(6)	5.470(3)		4	119.04	(3)
γ	<i>C2/c</i>	13.193(2)	7.499(1)	19.839(3)	91.69(1)	16	122.62	This work

common face of the cap, were evidenced in (N₂H₆)₃Zr₂F₁₃ · F (12). There is a great similitude between these Zr₂F₁₃⁵⁻ isolated dimeric anions and those connected in γ -BaZrF₆ from the point of view of distances, angles, and topology. Even the short Zr–Zr distance, through face sharing, is very similar: 3.374 Å in (N₂H₆)₃Zr₂F₁₃ · F and 3.377 Å in γ -BaZrF₆. Very different are the other known Zr₂F₁₃⁵⁻ dimeric anions in (NH₄)₂ZrF₆ (13). They are also built from bi-capped ZrF₈ trigonal prisms sharing a face and they are connected by opposite vertices to form infinite [ZrF₆]_{*n*}²ⁿ⁻ chains as in γ -BaZrF₆. However, the eight fluorine atoms quasi-related by a mirror passing through the common face in γ -BaZrF₆ (namely F(2), F(5), F(6), and F(7) related, respectively, to F(11), F(3), F(4), and F(8) in Fig. 2) form an antiprism in (NH₄)₂ZrF₆. Moreover, the short Zr–Zr distance (3.481 Å) through the common face is quite a bit longer in (NH₄)₂ZrF₆ than in γ -BaZrF₆.

A reconsideration of the current view of the BaZrF₆ glass structure could now be necessary. Until the recent publication of the (N₂H₆)₃Zr₂F₁₃ · F and (NH₄)₂ZrF₆ crystal structures (12, 13), face sharing was unknown, to our knowledge, in the fluorozirconate crystal chemistry. This linkage mode was never considered possible for the glasses. Moreover, face sharing does not seem to occur spontaneously in molecular dynamic simulation of the fluorozirconate glass structures [for a review see Ref. (17)]. Thus a question arises now about the possibility that ZrF₈ face-sharing polyhedra occur in fluorozirconate glasses.

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