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The Crystal Structure of CsBeF₃*

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CsBeF₃ crystallizes in space group *Pnma* with $a_0 = 4.828$, $b_0 = 6.004$, $c_0 = 12.794$ Å. The X-ray density is 3.55 g.cm⁻³ and $Z = 4$. Nine positional parameters and 16 anisotropic temperature factors were determined from reflections measured on a Norelco PAILRED automatic crystal data collector and a General Electric single-crystal orienter. The parameters were refined by least squares to an R of 0.067 for 267 reflections $> \sigma$. Each Cs⁺ ion is surrounded by 8 F⁻ nearest neighbors with bond distances of 2.96 to 3.40 Å. The Be²⁺ ions have four nearest neighbor F⁻ ions at the corners of a tetrahedron. The Be²⁺-F⁻ distances are 1.50 to 1.62 Å. The structure of this compound is similar to that of the high temperature form of BaGeO₃. The repulsion of the doubly charged Be²⁺ ions increases the Be-F distances where the F⁻ ions are shared between two tetrahedra. This accounts for the unusually long (1.62 Å) Be²⁺-F⁻ distances.

Introduction

Liebau (1960) among others has shown that in the case of silicates of the formula MSiO₃ (M = cations of small or medium size) the type of structure depends upon the size of M. The same statement applies to corresponding silicates with large cations (Ba, Sr) as well as to alkali germanates MGeO₃, fluoroberyllates MBeF₃, phosphates MPO₃, arsenates MAsO₃, arsenatophosphates M(P, As)O₃ and vanadates MVO₃. Liebau points out that there are two modifications of BaSiO₃ and BaGeO₃ and that the low temperature forms appear to have the same structure as pseudowollastonite (the high temperature form of CaSiO₃) while the high temperature phases together with KBeF₃ and NH₄BeF₃ form a group with a new structure type. The structure of BaGeO₃ (high temperature) [BaGeO₃(h), Liebau (1960)] has since been determined by Hilmer (1962).

The intermediate compound CsBeF₃ was included by Liebau in the group with BaGeO₃(h). However, there are three structural modifications of CsBeF₃ (Breusov, Novoselova & Simanov, 1958); α -CsBeF₃ $> 360^\circ\text{C}$ $> \beta$ -CsBeF₃ $> 140^\circ\text{C}$ $> \gamma$ -CsBeF₃. Mil'kova & Porai-Koshits (1962) made a preliminary X-ray study of CsBeF₃ (phase unknown) as well as RbBeF₃ and NH₄BeF₃ prepared from aqueous solution. They give the lattice parameters for CsBeF₃ as $a_0 = 6.09$, $b_0 = 4.81$, $c_0 = 12.88$ Å, and the diffraction symmetry consistent with space groups *Bmmb*, *Bm2b* or *B2mb*. The space group determined from our data is none of these, but is *Pnma*. The space group for RbBeF₃ was unambiguously $P2_12_12_1$; the space group for NH₄BeF₃ was $P2_1/n$, and they conclude that the three compounds are not isostructural. Mil'kova & Porai-Koshits present structures for RbBeF₃ and NH₄BeF₃ and suggest that 'in particular, it appears certain that the fluoroberyllate chain in the Cs salt must also be oriented along the short 4.81 Å c axis'. The germanium oxide chain in BaGeO₃ (Hilmer, 1962) is oriented along the short a

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axis. Our results show the same orientation for the fluoroberyllate chain.

Thus, there is a clear need for detailed structural information about the three phases of CsBeF₃.

Experimental

A single crystal of CsBeF₃ was selected from an anhydrous mixture of CsF-BeF₃ 50-50 mole% which was quenched (Friedman, Hebert & Thoma, 1962) after being heated in the range 317-392°C for 18 days. The CsF-BeF₃ mixture was pretreated with NH₄HF and heated to 700°C in a dry helium atmosphere to remove moisture. The crystal is thought to be the β form because of the temperature at which it formed, but there is no convincing evidence that it is not γ -CsBeF₃. There is a pronounced thermal break at 140°C, and most of the CsBeF₃ quenched from above this temperature has been polycrystalline. The crystals have very low birefringence, with an average index of refraction of 1.380.

The first single crystal was a rectangular parallelepiped (optically positive with positive elongation) with dimensions 0.075 × 0.110 × 0.225 mm which were parallel to the *c*, *b*, and *a* axes respectively. The second single crystal was similar to the first with dimensions 0.108 × 0.162 × 0.63 mm. The crystals were mounted parallel to the long axis (*a* axis) and Weissenberg and precession X-ray diffraction photographs were consistent with the diffraction symbol *mmmPn*-*a*. The single crystals are hygroscopic and soft. They bend very easily and as a result the diffraction maxima are broad and diffuse, which probably accounts for the rather poor statistics. The attempted solution of the structure in the centrosymmetric and acentric space groups showed that *Pnma* was probably correct. The parameters for the unit cell were refined by a least-squares fitting of 17 reflections obtained on PAILRED with copper *K* α radiation, ($\lambda = 1.54180$ Å) and the parameters are $a = 4.828 \pm 0.002$, $b = 6.004 \pm 0.002$, $c = 12.794 \pm 0.003$ Å. The calculated density for four formula weights in the unit cell is 3.55 g.cm⁻³.

Three-dimensional data to $\sin \theta/\lambda = 0.704$ were collected with a Phillips automatic single crystal diffractometer, PAILRED, using monochromatized Mo *K* α radiation. After the data had been collected and the structure determined ($R = 0.15$), we discovered that the scintillometer crystal had become unsealed, had adsorbed moisture and had disintegrated during the data collection. The first crystal was accidentally lost in transfer and the second crystal was mounted on a General Electric single-crystal orienter to obtain 279 additional three-dimensional data. The 279 reflections represent the low angle reflections plus their '*n*' orders to 75° 2 θ (Mo *K* α -Zr filter). The final parameters and statistics are based upon the reflections from the second crystal.

The reflection data were corrected for the Lorentz polarization factors and for absorption and were re-

Table 1. Atomic parameters for CsBeF₃

Atom	$x \pm \sigma \times 10^3$	$y \pm \sigma \times 10^3$	$z \pm \sigma \times 10^3$	$*\beta_{11} \pm \sigma \times 10^3$	$\beta_{22} \pm \sigma \times 10^3$	$\beta_{33} \pm \sigma \times 10^3$	$\beta_{12} \pm \sigma \times 10^3$	$\beta_{13} \pm \sigma \times 10^3$	$\beta_{23} \pm \sigma \times 10^3$
Cs	0.2641 (0.3)	0.250	0.1063 (0.2)	0.0216 (0.8)	0.0163 (0.5)	0.0058 (0.2)	0.0	0.0002 (0.2)	0.0
F(1)	0.240 (2)	0.039 (3)	0.879 (1)	0.036 (7)	0.017 (5)	0.014 (1)	0.008 (3)	-0.001 (2)	0.005 (1)
F(2)	0.884 (4)	0.250	0.782 (1)	0.040 (8)	0.030 (5)	0.008 (1)	0.0	0.005 (3)	0.0
Be	0.686 (7)	0.250	0.680 (3)	0.022 (16)	0.015 (10)	0.005 (2)	0.0	0.008 (5)	0.0

* Coefficients in the temperature factor expression: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

duced to structure factors, F_o . For the absorption correction the crystal shape was described by six faces appropriate for a rectangular parallelepiped of the dimensions given above (Wehe, Busing & Levy, 1962). The empirical equation

$$\sigma^2(F) = \frac{F^2}{4(T-B)^2} [T + B + 0.0009(T-B)^2]$$

was used to estimate the variance for each structure factor where T = total count, B = background count, and the additive term involving $T-B$ is to allow for errors proportional to the net count, such as variation in the beam intensity and absorption errors.

Structure determination

Three-dimensional Patterson sections gave the positions of the cesium and the two crystallographically independent fluoride ions [Cs and F(2) at sites 4(c) and F(1) at 8(d)], and these positions were used to calculate a set of phases from which the three-dimensional electron density map was computed. The Fourier map showed that the structure was correct, but the beryllium atoms could not be located from it. Cs⁺ and two

F⁻ ions were used in a least-squares refinement and the resultant signs used to calculate a three-dimensional difference map which clearly showed the beryllium ions. All of the atomic positions located from electron density maps and anisotropic temperature factors for each ion were refined by a three-dimensional full-matrix least-squares refinement using the program XFLS, a modification of ORFLS (Busing, Martin & Levy, 1962). A dispersion corrected scattering factor for Cs⁺ and the scattering factors for F⁻ and Be²⁺ were taken from Cromer & Waber (1964). The structure factors were weighted as $1/\sigma^2$ and the quantity $\sum w(F_o - F_c)^2$ was minimized with the summation taken over all the independent reflections. The refinement was based on F_o , the discrepancy index R is 0.07 for all 279 reflections and is 0.067 for 267 reflections greater than σ . The standard deviation of an observation of unit weight

$$[\sum w(F_o - F_c)^2 / (n_o - n_v)]^{1/2}$$

is 5.90 where n_o is the number of reflections and n_v the number of variables. The atomic parameters and anisotropic temperature factors for CsBeF₃ are listed in Table 1, the interatomic distances and angles with their standard deviations in Table 2, and the observed and calculated structure factors are shown in Table 3.

Table 2. *Interatomic distances and bond angles in CsBeF₃*

	d	$\sigma(d)$	Unbonded contacts		
Cs-F(1)	2.96 Å	0.01 Å	F(1)-F(2)	2.47 Å	0.02 Å
Cs-F(1)	2.96	0.01	F(1)-F(1)	2.54	0.03
Cs-F(1)	2.99	0.01	F(1)-F(2)	2.52	0.02
Cs-F(1)	2.99	0.01	F(2)-F(2)	2.55	0.01
Cs-F(1)	3.17	0.02			
Cs-F(1)	3.17	0.02			
Cs-F(2)	3.400	0.007			
Cs-F(2)	3.400	0.007			
Be-F(1)	1.50	0.03	Bonds	Angle	σ
Be-F(1)	1.50	0.03	F(1)-Be-F(1)	115°	3°
Be-F(2)	1.54	0.04	F(1)-Be-F(2)	109	1
Be-F(2)	1.54	0.04	F(1)-Be-F(2)	108	1
Be-F(2)	1.62	0.04	F(2)-Be-F(2)	108	3

Table 3. F_o and F_c for CsBeF₃

																				PAGE	
L	FBS	FCAL	L	FBS	FCAL	L	FBS	FCAL	L	FBS	FCAL	L	FBS	FCAL	L	FBS	FCAL	L	FBS	FCAL	
4	160	-187	12	10	-7	1	152	-154	0	207	-111	8	37	34	16	4	-2	6	10	-9	
6	89	-95	16	5	-4	2	28	27	1	4	12	0	-1	2	5	-4	12	8	8	4	
8	70	75	0	5	L	3	76	73	2	33	-36	14	29	-28	4	22	22	15	15	15	
10	73	77	5	9	8	4	10	-10	3	40	45	16	7	-5	6	12	12	18	1	0	
12	12	-14	15	7	8	5	147	152	4	141	157	18	9	10	8	11	-9	3	6	L	
14	34	-35	0	6	L	6	4	6	5	16	-17	20	4	4	10	11	-11	3	11	4	
16	6	-6	0	72	-71	7	7	-7	6	67	72	2	3	L	3	0	L	6	31	30	
18	13	13	2	12	-9	8	16	-15	7	12	-13	0	32	-31	1	16	17	9	9	-7	
0	1	L	6	32	34	9	72	-72	8	58	-62	1	82	-82	2	70	74	12	15	-15	
1	84	-68	10	32	-31	10	5	6	9	0	-2	14	5	3	3	-15	4	2	0	34	
3	175	-176	12	5	3	1	2	L	10	63	-58	3	113	-111	4	49	54	3	9	L	
5	35	34	14	17	17	1	13	9	12	9	8	4	11	8	5	31	-30	3	3	9	
7	110	111	0	7	L	2	203	198	14	34	33	5	23	23	6	57	-57	7	4	0	
9	18	18	7	40	-38	3	12	5	16	6	5	6	19	16	7	3	5	0	98	97	
0	2	L	0	8	L	4	62	59	18	13	-10	2	4	L	9	13	13	1	27	-28	
0	187	-154	0	31	35	5	25	-26	20	5	-4	0	117	-108	12	37	38	2	28	29	
2	11	-6	4	23	-24	6	102	-100	0	2	1	L	1	15	7	15	4	-3	4	84	
4	88	75	8	10	11	7	13	11	0	44	47	2	19	-18	18	6	-4	6	38	-40	
6	75	75	12	4	-1	8	82	-80	1	79	83	3	22	23	3	1	L	8	37	37	
8	36	-34	0	9	L	9	4	2	2	13	-11	4	88	85	1	96	99	10	37	35	
10	65	-65	3	17	-18	1	3	L	3	114	116	6	41	42	2	38	-35	12	5	-3	
14	32	32	9	0	5	1	93	82	4	0	-6	8	37	-36	3	54	-56	14	75	-21	
18	14	-11	0	10	L	2	18	-17	5	17	-16	10	39	-37	4	4	-2	16	1	-3	
0	3	L	0	15	-18	3	43	-36	6	20	-19	12	7	5	5	83	-86	18	0	7	
1	93	81	1	0	L	4	10	7	7	89	-91	14	23	22	6	10	11	4	7	L	
3	166	156	1	4	-3	5	96	-90	8	2	2	L	18	7	-7	1	22	-23	2	24	
5	37	-34	2	107	-117	6	9	-2	2	2	L	18	7	-7	1	22	-23	2	24	-24	
7	112	-103	3	9	-10	7	2	0	0	110	99	2	6	L	2	111	-115	4	58	56	
9	13	-12	4	55	-59	8	11	11	1	6	5	2	12	13	3	10	7	6	34	35	
15	16	-13	5	25	28	1	4	L	2	27	28	4	25	-63	4	49	-50	8	23	-23	
0	4	L	6	53	56	1	10	-2	3	31	-28	6	28	-28	5	34	34	10	32	-30	
0	155	150	7	9	-11	2	95	-82	4	83	-77	8	20	19	3	3	L	12	2	1	
2	11	9	8	81	86	3	13	-3	5	13	12	10	26	26	1	66	-61	14	21	19	
4	103	-94	9	0	1	4	47	-42	6	57	-58	12	5	-1	2	28	28	14	1	4	
6	50	-50	10	26	-27	5	14	13	7	9	8	14	14	-14	3	36	34	4	4	L	

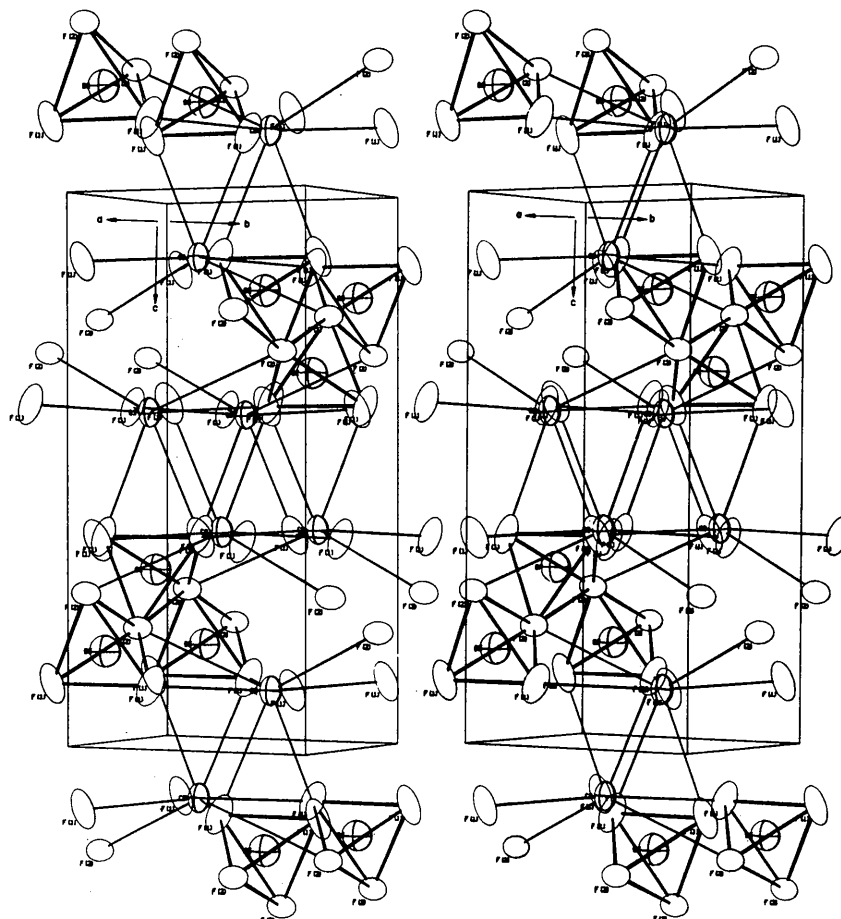


Fig. 1. A stereoscopic drawing of the structure of CsBeF₃ tilted 30° from $\gamma-z$ plane. One unit cell is outlined. The ellipses are representations of thermal ellipsoids.

Discussion

Fig. 1 is a stereoscopic drawing of the structure, which consists of BeF₄ tetrahedra linked through corners into chains parallel to the a axis. The fluoride tetrahedra are only slightly distorted with F⁻-F⁻ contacts nearly alike and equal to 2.5 Å on the average. The angles between beryllium and fluoride ions are nearly tetrahedral, but the Be-F distances differ considerably, with the distance to the ion which is common to two tetrahedra considerably longer than the distance to the fluoride ion which is unshared. The same observation was made by Hilmer (1962) in the BaGeO₃ structure, where the distance between the central atom and the O²⁻ ions shared by two tetrahedra is always greater than to the atoms which are not shared.

The cesium ion is surrounded by four nearest neighbors which form a square configuration around the cation at a distance approximately equal to the sum of the ionic radii. Two additional F⁻ ions are located at 3.17 Å, and these six fluoride ions can be considered to form a trigonal prism around the central cation. Two more fluoride ions at 3.40 Å could be considered as completing an eightfold coordination polyhedron around the cation.

The structure of CsBeF₃ is similar to BaGeO₃ and RbBeF₃ in that there are BeF₄ or GeO₄ tetrahedra linked at corners to form chains parallel to the shortest axis of the unit cell. The alkali cation in each case has eightfold coordination and seems to link the chains together. (If the nearest oxygen neighbor to Ba²⁺ at 3.26 Å in Hilmer's structure is included, the coordination of Ba in BaGeO₃ is eightfold.)

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