

# Synthesis and Structure of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>

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**Abstract.** Crystals of ordered and disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> were prepared by flux growth and solid state reactions. These new structures were characterized by single crystal and powder X-ray diffraction. The disordered variant which shows disorder on one of the cation sites was obtained from a BaF<sub>2</sub> + BaCl<sub>2</sub> + NaCl/NaF flux. It has hexagonal space group P6<sub>3</sub>/m (176) with one formula unit per unit cell. The lattice constants are  $a = b = 1059.55(5)$  pm and  $c = 420.10(4)$  pm (at 21 °C). The structure was refined to  $R(R_w) = 0.026(0.030)$  for 346 independent reflections and 26 parameters.

Slow cooling of a mixture of BaF<sub>2</sub> and LiCl yields the ordered variant. This one crystallizes in the hexagonal space group P6̄ (174) with one formula per unit cell. Lattice constants at 21 °C are  $a = b = 1063.46(2)$  pm and  $c = 417.52(1)$  pm. The structure was refined to  $R(R_w) = 0.017(0.017)$  for 638 independent reflections and 45 parameters.

The structural arrangement and the interatomic distances of the two variants are mutually similar. The barium atoms have coordination number nine. Propeller-type arrangements with a chloride ion on the axis and the fluoride ions as blades are observed. These latter ones are interconnected into 'channels' of tricapped fluoride prisms. Occupation disorder of the barium sites in the channels of the disordered variant makes the main difference between the two. An unexpectedly high X-ray density obtained for both variants of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> can be correlated to the density of other barium fluorohalides having a coordination number of nine for the barium ion.

**Keywords:** Barium; fluoro-halides; disordered structure, X-ray single crystal and powder diffraction, flux and solid state synthesis, ferroelectric monodomains

## Synthese und Struktur von Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>

**Inhaltsübersicht.** Kristalle von geordnetem und fehlgeordnetem Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> wurden aus der Schmelze sowie durch Feststoffreaktion erhalten und durch Einkristallstrukturanalyse und Pulverdiffraktogramm charakterisiert. Die fehlgeordnete Variante, mit Fehlordnung auf einer Kationlage, wurde aus einer Schmelze von BaF<sub>2</sub> + BaCl<sub>2</sub> + NaCl/NaF erhalten (Raumgruppe P6<sub>3</sub>/m (176) mit  $Z = 1$ ,  $a = b = 1059,55(5)$  und  $c = 420,10(4)$  pm bei 21 °C). Die Struktur wurde bis zu  $R(R_w) = 0,026$  (0,030) verfeinert (346 unabhängige Reflexe, 26 Parameter).

Langsames Abkühlen eines Gemenges von BaF<sub>2</sub> und LiCl ergibt die geordnete Variante, die in der hexagonalen Raumgruppe P6̄ (174) mit  $Z = 1$  kristallisiert. Die Gitterkonstanten bei 21 °C sind  $a = b = 1063,46(2)$  und  $c =$

417,52(1) pm. Die Struktur wurde bis zu  $R(R_w) = 0,017$  (0,017) verfeinert (638 unabhängige Reflexe, 45 Parameter).

Der strukturelle Aufbau und die atomaren Abstände beider Varianten sind annähernd gleich. Die Bariumatome haben die Koordinationszahl neun. Es werden propellerartige Anordnungen mit einem Chloridion in der Achse und den Fluoridionen als Flügel beobachtet. Die letzteren sind durch Kanäle von dreifach bekappten Fluoridprismen verbunden. Die Besetzung der fehlgeordneten Bariumlagen in den Kanälen der Fehlordnungsvariante ist der wesentliche Unterschied zwischen beiden Varianten. Die unerwartet hohe Röntgendichte für beide Formen von Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> entspricht der Dichte anderer Bariumfluoridhalogenide mit der Koordinationszahl 9 für das Bariumatom.

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## Introduction

Layered fluorohalides having the PbFCl structure doped with samarium impurities are at present among the most promising candidates when high density data storage application of optical spectral hole burning (OSHB) at room temperature [1, 2, 3, 4] is envisioned. Material research is a necessary part of the ongoing activity on this issue. Indeed, the electronic and vibrational properties of the photoactive impurity involved in OSHB depend in an important manner on the nature and structure of the host – as do the mechanisms of OSHB. This important interaction needs

to be explored much more to increase our understanding and to find even better systems.

We recently discovered a new barium fluoride-chloride compound with the composition  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  [5]. In view of the information published in 1955 [6] on the solid state synthesis of  $\text{Ba}_2\text{F}_3\text{Cl}$  (at a temperature of 900 °C) we subsequently performed a series of synthesis experiments at temperatures below 900 °C by varying the ratios of the alkaline earth halides. A hitherto unpublished substance with composition  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ , was thereby found and shown to form two different structural variants, depending on the conditions of synthesis. One variant (called disordered (d) in the following) presents structural disorder on one barium site together with disorder of the connected fluoride ions. An ordered variant (denoted by (o) in the following) of this compound with a structure similar to the one reported for  $\text{Pb}_7\text{F}_{12}\text{Cl}_2$  [7] was further obtained. The use of LiCl as a flux or heating crystals of the disordered structure to above ca 860 °C enabled to obtain this variant. Its structural parameters are clearly distinct from those of disordered  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ . A detailed X-ray diffraction study and synthesis experiments were performed on both  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  variants and the results we obtained are presented in this paper.

## Experimental

The starting compounds  $\text{BaF}_2$ ,  $\text{BaCl}_2$ , NaF, NaCl, LiCl (all Suprapur, E. Merck, Darmstadt) were carefully dried under high vacuum with gradual increase of the temperature to 150 °C, to avoid contamination with oxygen, water.

**Flux synthesis experiments:** Small needle shaped crystals of the disordered variety of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  were obtained in a high vacuum tight Kyropoulos crystal furnace. For instance a 6:1 molar mixture of  $\text{BaF}_2$  and  $\text{BaCl}_2$  with 20% of NaCl or NaF was filled into a carbon crucible (Vitreous Carbon, Le Carbone, France) in a Mecaplex® glove box (partial pressure of oxygen < 8 ppm), degassed and molten in this furnace under ultrapure (Ar 57) argon. The melt was then slowly cooled from about 840 °C (at rates ranging from 0.1 to 0.5 °C/min) to 720 °C. According to the phase diagram of the  $\text{Na}_2\text{Cl}_2$ – $\text{BaF}_2$  system [8], the content of  $\text{Na}_2\text{Cl}_2$  should not exceed ca 30%; above this value the solid in equilibrium with the melt is reported to be  $\text{BaFCl}$  [8]. The crystals are stable to air and water. They were inspected and selected in polarized light under a microscope.

The ordered variant of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  was obtained by flux growth or solid state reactions in the Kyropoulos apparatus as well as with the conventional equipment. Experiments were performed by using the lower melting LiCl (mp = 605 °C) instead of NaCl (mp = 801 °C). Experiments with different LiCl– $\text{BaF}_2$  ratios were realized. The  $\text{Li}_2\text{Cl}_2$ – $\text{BaF}_2$  mixture (15mole% and 85mole%) was one of the successful compositions. It was typically heated above its melting point and slowly cooled to room temperature (at rates ranging from 0.1 to 0.5 °C/min). Needle shaped hexagonal crystals were obtained and isolated by washing the flux with warm water.  $\text{LiBaF}_3$  and  $\text{BaF}_2$  were further present in the flux but they were easily identified with optical means.

## Results and Discussion

**Crystal description:** The crystals of both variants of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  grow as needles with hexagonal habit. Crystals with a size of up to several mm in length can be grown by slowly cooling the flux. The needle axis is  $c_{\text{hex}}$  in accordance with the absence of birefringence when inspected along this direction. The crystals can be cleaved easily along and perpendicular to the needle axis and plates can be obtained by cleavage. In general {110} faces are developed. The respective growth habits of the two modifications of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  show mutual differences. In particular, the ordered phase presents a typical non-centrosymmetric – close to triangular growth section.

### X-ray diffraction

**Disordered  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ :** The lattice constants of a single crystal were determined on an Stoe diffractometer and correspond to a hexagonal crystal system (see Table 1). No superstructure reflections were found in any of the crystals. The structure was solved by direct methods in space group  $\text{P6}_3/\text{m}$  (see discussion below). Details of the data collection and refinement conditions are summarized in Table 1. A full sphere in the reciprocal space was measured. Table 2 gives the standardized [9] atomic positions and vibrational parameters.

Choice of the space group: the compound crystallizes in the  $\text{Fe}_{12}\text{Zr}_2\text{P}_7$  structure type (space group:  $\text{P6}_3/\text{m}$  or  $\text{P6}$ ) [10] and can be related to the structure of  $\text{Pb}_7\text{F}_{12}\text{Cl}_2$  [7]. Note

**Table 1** Crystal data (e. s. d. s in brackets) and conditions of data collection and refinement for  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$

	disordered	ordered
Formula mass	1260.22	1260.22
Crystal system/ space group	hexagonal, $\text{P6}_3/\text{m}$ (No. 176)	hexagonal, $\text{P6}$ (No. 174)
$a = b$ (pm)	1059.55(5)	1063.46(2)
$c$ (pm)	420.10(4)	417.52(1)
$V$ ( $10^6 \text{ pm}^3$ )	408.44(5)	408.93(2)
$Z$	1	1
Density (in $\text{g/cm}^3$ )	5.123	5.117
Crystal size in $\text{mm}^3$	0.100 × 0.106 × 0.250	0.370 × 0.152 × 0.114
Diffractometer type	STOE	STOE
Wavelength, radiation	$\text{MoK}\alpha$ , 71.073 pm	$\text{MoK}\alpha$ , 71.073 pm
Method	$\omega/\theta$ -scan	$\omega/\theta$ -scan
Temperature	300 K	300 K
$\theta$ range	2.2–27.3	2.2–35.0
No. of reflections measured	3871	5649
No. of independent refl.	357	647
$R_{\text{int}}$	0.036	0.023
No. of refl. with $I > 3\sigma(I)$	346	636
Program used	XTAL 3.2 [14]	XTAL 3.2 [14]
Absorption coefficient	17.02	17.00
Abs. corr. anal. $T_{\text{min}}/T_{\text{max}}$ I,	0.192/0.309	0.071/0.106
$R$ ( $R_w$ )	0.026 (0.030)	0.017 (0.017)
Number of parameters	26	45
Extinction (Zachariasen)		0.59(2)
Goodness of fit	2.90	2.16
$e_{\text{min}}/\text{max}$ density values ( $\text{pm}^{-3}$ )	−0.93/2.27 · $10^{-6}$	−1.7/2.0 · $10^{-6}$

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the deposition numbers CSD-410678, CSD-410679, the name of the authors and citation of the paper.

**Table 2** Standardized atomic positional parameters, population and atomic displacement factors ( $\times 100$ ), Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>, with e. s. d.'s in parenthesesDisordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>

Ion	Wyk	x	y	z	U <sub>iso</sub>	pop
F(1)	6 (h)	0.1183(8)	0.2167(10)	1/4	1.9(3)	0.5
F(11)	6 (h)	0.1542(8)	0.2780(9)	1/4	1.9(3)	0.5
Ba(1)	6 (h)	0.40447(4)	0.29356(4)	1/4	1.39(2)	
F(3)	6 (h)	0.4332(4)	0.0560(4)	1/4	2.0(1)	
Cl	2 (c)	1/3	2/3	1/4	1.97(7)	
Ba(2)	2 (a)	0	0	1/4	2.86(5)	0.5

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>
Ba(1)	1.58(3)	1.49(3)	1.28(3)	0.90(2)
Ba(2)	2 U <sub>12</sub>	2 U <sub>12</sub>	4.9(1)	0.92(2)
Cl	2 U <sub>12</sub>	2 U <sub>12</sub>	1.8(1)	1.02(4)
F(1)/(11)	0.8(4)	1.7(3)	2.8(3)	0.3(4)
F(3)	2.3(2)	1.7(2)	1.8(2)	0.9(1)

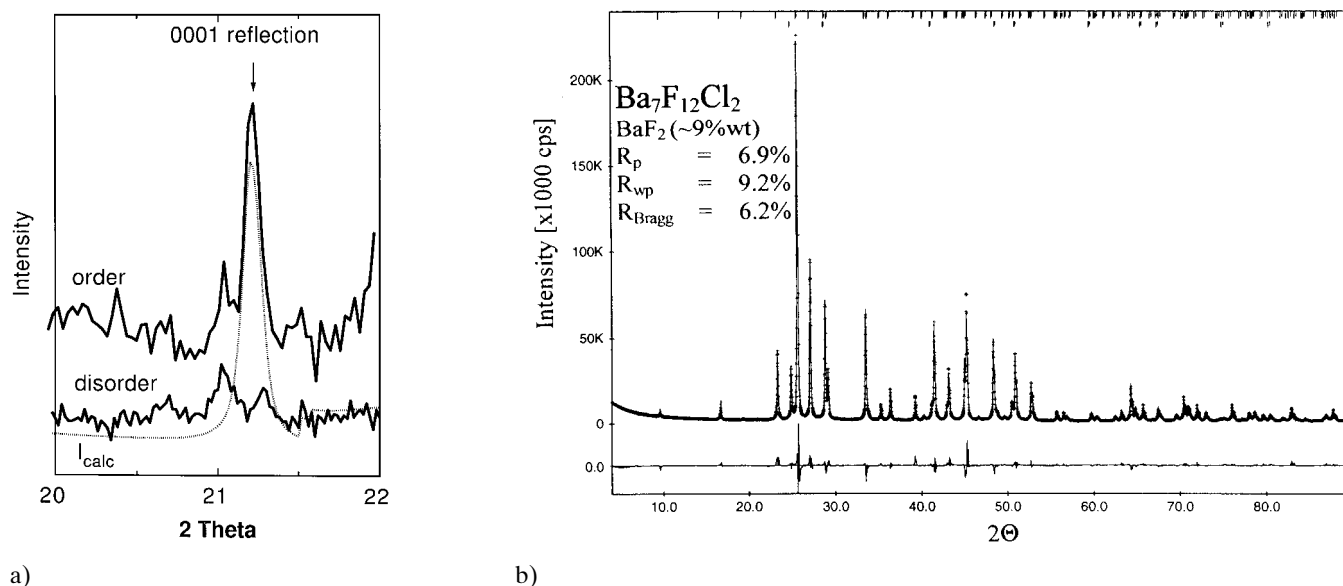
[The anisotropic displacement factor in the structure factor expression is:  $U_{ij} = \exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*)$ . Note that  $U_{13} = 0$  and  $U_{23} = 0$ .]

Ordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>

Ion	Wyk	x	y	z	U <sub>iso</sub>
F(1)	3 (k)	0.0498(4)	0.4367(4)	1/2	1.6(1)
F(2)	3 (k)	0.2166(5)	0.1178(4)	1/2	2.4(1)
Ba(1)	3 (k)	0.28799(3)	0.40138(3)	1/2	1.16(1)
F(3)	3 (j)	0.1213(4)	0.2763(4)	0	1.8(1)
Ba(2)	3 (j)	0.4103(3)	0.10948(3)	0	1.22(1)
F(4)	3 (j)	0.4304(4)	0.3679(4)	0	1.8(1)
Cl(1)	1 (f)	2/3	1/3	1/2	1.71(5)
Cl(2)	1 (e)	1/3	2/3	0	1.80(5)
Ba(3)	1 (a)	0	0	0	1.81(1)

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>
F(1)	1.8(1)	1.4(1)	1.6(2)	0.8(1)
F(2)	2.9(2)	2.0(1)	2.6(2)	1.5(1)
Ba(1)	1.21(1)	1.24(1)	1.08(1)	0.67(1)
F(3)	1.5(1)	2.0(1)	1.7(2)	0.8(1)
Ba(2)	1.09(1)	1.18(1)	1.34(2)	0.546(9)
F(4)	2.0(1)	1.7(1)	2.0(2)	1.1(1)
Cl(1)	2 U <sub>12</sub>	2 U <sub>12</sub>	1.6(1)	0.88(3)
Cl(2)	2 U <sub>12</sub>	2 U <sub>12</sub>	1.7(1)	0.93(3)
Ba(3)	2 U <sub>12</sub>	2 U <sub>12</sub>	2.89(3)	0.634(7)

[See above for the definition of the anisotropic displacement factors]



**Fig. 1** a) (left) The 0001 reflection of ordered and disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (X-ray powder diffraction). The calculated [15] intensity for the ordered structure ( $P\bar{6}$ ) is presented as a broken line. b) (right) Powder diffraction diagram of disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (CuK $\alpha$  radiation). Observed, calculated and difference intensities are given. No reflection indicating a superstructure is found.

that the space group of this type of compounds is still open to question. The highest symmetry group  $P6_3/m$  (176) is possible; but also  $P6$  (168),  $P\bar{6}$  (174) may be discussed if reflections of the type 0001 with  $l \neq 2n$  would be observed. In fact, the powder diffraction data of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (d) showed absence of any line at the  $2\theta$  position of the 0001 reflection (see Fig. 1 a and discussion below).

Within the single crystal studies refinement in space group  $P\bar{6}$  was at first attempted. Strong correlation renders, however, the refinement of positions and atomic displacement factors rather unstable. Further, disorder on the Ba(2) site cannot be avoided in this lower space group; therefore no similarity with the compound Pb<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (where the metal

is ordered [7]) was found. Refinement in  $P\bar{6}$  allows to simulate the reflections 0001 and for this space group a reflection 0003 was calculated to give intensity ( $F_c \sim 8.5$ ). No intensity for this latter reflection was, however, found experimentally (see Fig. 1 a). For comparison a reflection at a similar angle and with similar intensity ( $hkl = 421$ ,  $2\theta = 28.4^\circ$ ,  $F_{\text{obs}} = 9.1(9)$ ) was clearly identified experimentally. In the noncentrosymmetric space group  $P\bar{6}$  the calculated absolute structure factor [11] did not deviate from 0.5 for all refinements. For all these reasons we chose the highest symmetry space group,  $P6_3/m$ , for the disordered variant of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>.

A powder X-ray diffraction analysis of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>(d) was performed, with the intention to confirm the structure and

**Table 3** Conditions of powder data recording (20 °C) and refinement of disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (and BaF<sub>2</sub>)

Diffractometer type	Philips					
Space group	P6 <sub>3</sub> /m					
$\theta$ range	4–90°					
Step scan	0.02°					
Time/step (sec)	50					
Number of reflections	316					
Number of parameters	32					
Program used	DBWS-9411 [15]					
Radiation CuK $\alpha$ <sub>1/2</sub>	154.06/154.43 pm					
Background steps	29					
Zero point	–0.0162(12)					
Asymmetry parameter	0.842(8)					
Pseudo Voigt profile parameters	0.229(3) –0.129(4) 0.0404(3)					
Reliability factors						
R <sub>p</sub>	6.9%					
R <sub>wp</sub>	9.2%					
R <sub>Bragg</sub>	6.2%					
R <sub>exp</sub>	1.4%					
S	6.6%					
Phase Ba <sub>7</sub> F <sub>12</sub> Cl <sub>2</sub>	→ %Mass = 91.25(1) %Molar = 85.30(1)					
Phase BaF <sub>2</sub>	→ %Mass = 8.75(1) %Molar = 14.70(1)					
cell						
$a = b = 1060.83(6)$ pm	$c = 419.28(1)$ pm $V = 408.23(4)$ 10 <sup>6</sup> pm <sup>3</sup>					
Atom	Wyk	x	y	z	B <sub>iso</sub>	pop
F(1)	6 (h)	0.129(2)	0.223(2)	1/4	1.3(3)	0.5
F(11)	6 (h)	0.159(2)	0.285(2)	1/4	1.3(3)	0.5
Ba(1)	6 (h)	0.4049(1)	0.2932(1)	1/4	3.18(5)	
F(3)	6 (h)	0.438(1)	0.055(1)	1/4	4.1(2)	
Cl	2 (c)	1/3	2/3	1/4	2.9(2)	
Ba(2)	2 (a)	0	0	1/4	2.35(17)	0.5

**Table 4** Selected interatomic distances in pm for Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>

	(ordered)		(disordered)	
	Ba(1)–		Ba(1)–	
x2	–F(3)	262.9(5)	265.2(5)	–F(11)
	–F(1)	265.6(4)	265.3(3)	–F(3)
x2	–F(4)	270.5(5)	266.7(3)	–F(3)
	–F(2)	271.7(7)	271.9(18)	–F(1)
	–F(1)	274.0(5)	268.2(8)	–F(3)
x2	–Cl	334.50(2)	333.67(4)	–Cl
	Ba(2)–		Ba(1)–	
	–F(3)	259.5(3)	257.3(20)	–F(11)
x2	–F(1)	262.1(2)	266.7(3)	–F(3)
	–F(4)	264.5(6)	265.3(3)	–F(3)
	–F(4)	264.9(4)	268.2(8)	–F(3)
x2	–F(2)	296.5(5)	292.1(4)	–F(1)
x2	–Cl	331.18(2)	333.67(4)	–Cl
			∅–	
x3			199.1(7)	–F(11)
	Ba(3)–		Ba(2)–	
x3	–F(3)	255.2(5)	255.6(8)	–F(11)
x6	–F(2)	289.0(3)	289.4(5)	–F(1)
Empty triangle within the channels				
x3	F(4)–F(4)	346.1(6)	344.9(12)	F(1)–F(1)
Filled triangle within the channel				
x3	F(3)–F(3)	442.0(9)	442.8(14)	F(11)–F(11)

the choice of the space group. The powder sample with main composition Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> was prepared by grinding crystals isolated from the flux by washing. A short (30 sec/step;  $\Delta = 0.03^\circ$ , transmission) and a long (50 sec/step;  $\Delta = 0.02^\circ$ , reflection) intensity accumulation was performed on two different powder diffractometers (Guinier geometry and a Philips diffractometer) from 8 to 90° in  $2\theta$  (CuK $\alpha$ ). Details of the enhanced powder data collection and refinement conditions are given in Table 3. About 4 to 9 mass% of insoluble BaF<sub>2</sub> are still present in the samples depending on the synthesis conditions and was used as an internal calibration standard. The refined heavy halogen composition, the lattice parameters and the atomic positional parameters do not differ significantly ( $< 3\sigma$ ) from those determined from single crystal data. Fig. 1 b shows the observed, the calculated and the difference diagram for Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>(d).

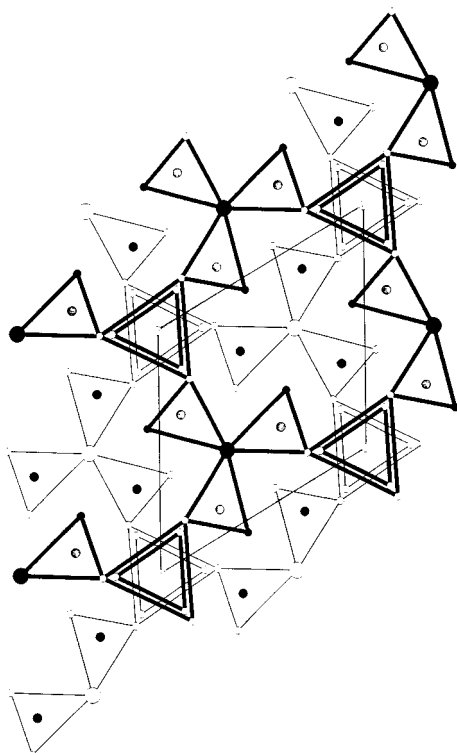
*Ordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>*: The lattice constants were determined on the Stoe diffractometer. No doubt was possible about the space group P $\bar{6}$  (174) for the ordered compound. The observation of reflections of the type 0001 with  $l \neq 2n$  allowed indeed to exclude the higher space group P6<sub>3</sub>/m established for the disordered crystal structure (see Fig. 1 a). A full sphere in the reciprocal space was measured and the refinement was performed with the aid of the already known structure of Pb<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (space group P $\bar{6}$  (174)) [7] as a starting model. Some interatomic lead fluoride distances were found to be irrationally short within the published Pb<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> model, visibly due to a misprint in the paper [7]. Only the positions of the heavy Ba and Cl ions could be detected with the aid of this model whereas the fluoride ions were determined from difference Fourier analysis. Details of the data collection and of the refinement conditions are summarized in Table 1. Table 2 gives the lattice parameters, the standardized [9] atomic positions and the vibrational parameters. The absolute structure factor converged to 1.0(2) within the polar space group. Thus the selected crystal was a ferroelectric (polar) single domain. Note that for the disordered structure the assumption of the polar group had led to a structure factor of  $\sim 0.5$ . Selected interatomic distances are given in Table 4 together with the corresponding quantities of the disordered structure.

### Structure Description and Discussion

*Disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>*: A projection of its structure along the  $c_{\text{hex}}$ -axis is shown in Fig. 2. Ions of one layer are drawn in bold. One recognizes there a propeller type arrangement of Ba(1), Cl, F(3) and F(1)/F(11), respectively. The chloride ions are situated on the threefold axis. Disorder was found for the Ba(2) atoms in position 2 a (50% occupation to achieve neutrality) and a corresponding splitting of the position of one fluoride ion into two (F(1)/F(11)). Indeed, the fluoride ions on these positions before splitting showed in a first refinement strong anisotropic atomic displacements and unrealistically short Ba–F distances. Splitting increased the quality of the refinement markedly and also gave reasonable interatomic distances and displacement factors for the structure (see Table 4). The two positions F(1) and F(11) are equally occupied and are separated by  $\sim 56.5(1.1)$  pm.

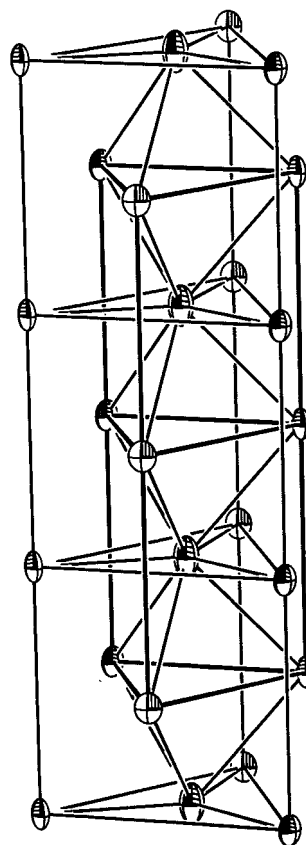
Together with the ordered halogens they are part of the propeller-type arrangement. These propellers are linked together by channels of tricapped trigonal prisms of F(1)/F(11) and are deformed as a function of their linking fluoride ions. The Ba(2) ions with 50% occupancy are located in the center of these channels in order to assure stoichiometry. This results in alternate stacking of small empty fluoride triangles (without Ba) and filled ones (with Ba) (see Fig. 3). To avoid too short Ba–Ba distances a regular stacking (...Ba  $\emptyset$  Ba  $\emptyset$  Ba  $\emptyset$ ...) was assumed. These stacked columns seem to be statistically distributed within the crystal as no superstructure was found. Fig. 4 shows the local environment around Ba(1) which gives a distorted monocapped square antiprism. Selected interatomic distances are given in Table 4.

The chemical environment and coordination around Ba(1) is very similar to that of Ba(2) in  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  [5]. However the shortest Ba–F distance of 251 pm found in this latter compound is increased to 257 pm in disordered  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ . The Ba–Cl distances are slightly shorter, 334 pm vs 335 pm, and the other Ba(1)–F distances follow this trend (average 266 pm vs 262 pm). The tricapped trigonal prisms coordinat-

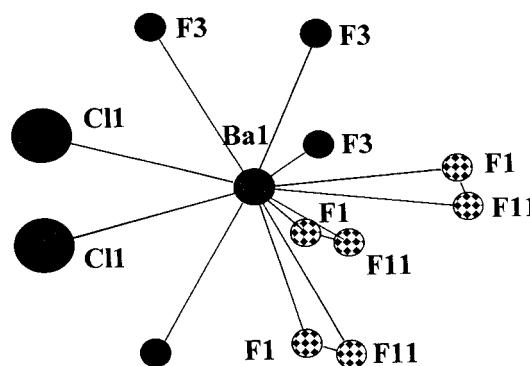


**Fig. 2** Projection of the disordered  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  structure along the  $c_{hex}$ -axis. Large spheres are chloride ions, connected small spheres are fluoride ions, isolated spheres are barium ions. Ions and their interconnection within one layer are presented in bold. In any layer, a statistical distribution of small and large fluoride triangles may be assumed, illustrated here as double triangles.

ing Ba(2) involve rather short interatomic distances too (256 pm towards the capping fluoride ions compared to 289 pm towards the corners of the trigonal prism). The relatively high  $U_{33}$  value of Ba(2) indicates largest thermal vibration along the  $c$  direction.



**Fig. 3** The connected fluoride triangles (open spheres) along  $c_{hex}$  are shown for  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  (d). The large ellipsoids represent the Ba(2) ions. Each one is surrounded by nine fluoride ions forming a tricapped trigonal prism.



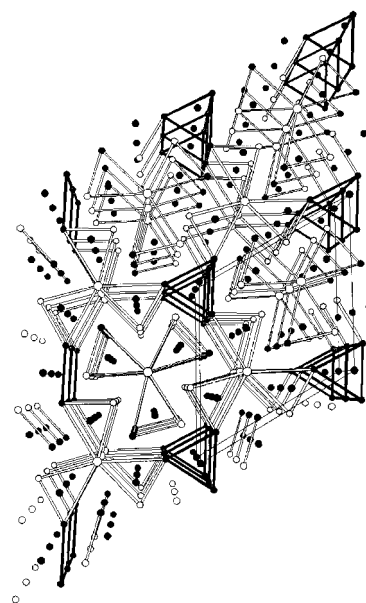
**Fig. 4** The local environment around Ba(1) in  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  (d), a monocapped square antiprism formed by 2 chloride and 7 fluoride ions. The disordered pairs (black-white) are shown connected.

The fluoride to fluoride distances vary as a function of the occupation of the channels and range from 345 pm to 443 pm.

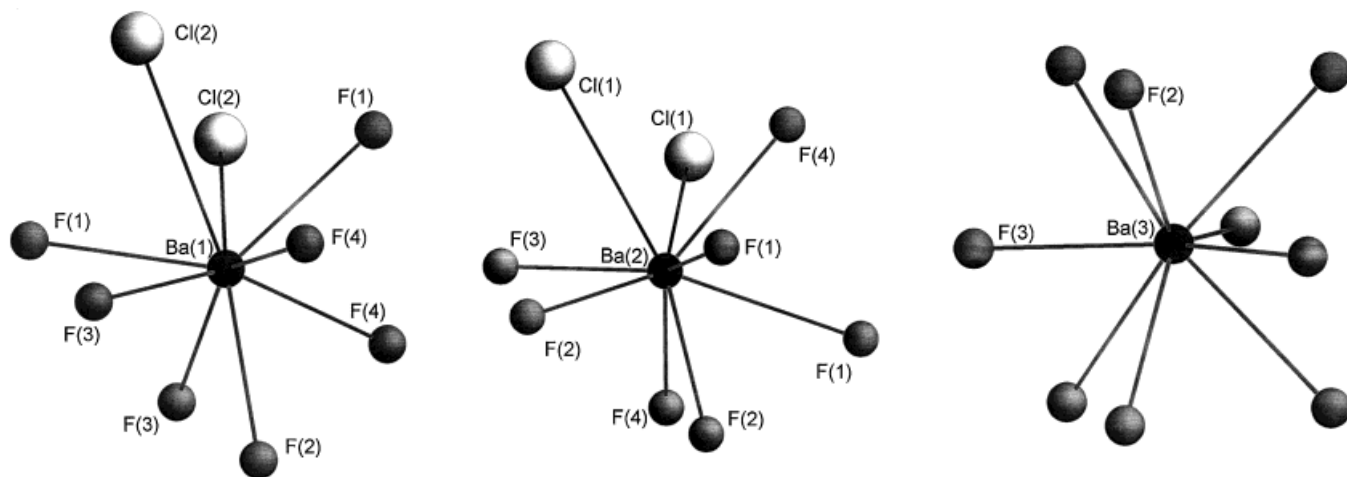
**Ordered  $Ba_7F_{12}Cl_2$ :** The Fig. 5 shows a three-dimensional view of  $Ba_7F_{12}Cl_2(o)$  along the  $c_{hex}$ -axis. One recognizes the characteristic propeller type arrangement of Ba(1), Ba(2), Cl and F(1)–F(4) similar to  $Ba_7F_{12}Cl_2(d)$  and  $Pb_7F_{12}Cl_2$ . No disorder was found for Ba(3) along the  $c_{hex}$  axis. Fig. 6 shows the local environment around Ba(1), Ba(2) and Ba(3). The former two consist of a monocapped antiprism similar to the arrangement found in  $Ba_{12}F_{19}Cl_5$  (see Fig. 1 in ref. [5]). Interatomic distances are significantly different for all three barium surroundings. The shortest Ba(2)–F distance is 260 pm and the longest one is 297 pm whereas the corresponding values are 263 pm and 274 pm for Ba(1)–F (see Table 4). Corresponding distances of the disordered compound are 265 pm and 292 pm. Similar significant differences are seen for Ba–Cl distances as can be seen from Table 4. The disorder does not seem to affect the environment of the barium Ba(3) coordinated to nine fluoride ions, where for the ordered (*disordered*) compound distances of  $3 \times$  (= capping) 255.2(5) pm (255.8(6) pm) and  $6 \times$  289.0(3) pm (289.4(5) pm) were obtained.

Our structural data for the ordered form of  $Ba_7F_{12}Cl_2$  allows to show that the disordered form is genuine and not a twin of the ordered one. Firstly, the respective lattice parameters are significantly different for both compounds. Then, 0001 reflections with  $l=1,3$  are clearly observed for the ordered form, while they are absent for the disordered one (see Fig. 1 a, b). In addition, the respective powder diffraction diagrams are different. Finally, we constructed a hypothetical disordered state as an intergrowth of polar blocks of ordered  $Ba_7F_{12}Cl_2(o)$  by applying the

symmetry operation  $x,y,z \rightarrow \bar{x},\bar{y},\bar{z} + 1/2$  on this structure. Comparison between the calculated structure results of this model and the structure data of the disordered compound shows that the model comes close to, *but is not identical with* the real disordered  $Ba_7F_{12}Cl_2(d)$  crystal structure. In the theoretical twin, the interatomic distances between “split atoms” are 17.8(5) pm for equivalent fluoride ions and 0.0 pm and 12.11(10) pm for Ba(1) and Ba(2). Chloride ions and Ba(3) do not split in this model. At the same time these interatomic distances clearly reflect the polar character of the noncentrosymmetric structure. Thus,



**Fig. 5** A 3-dimensional view, along a chloride axis in the direction of the  $c_{hex}$  axis, of the ordered  $Ba_7F_{12}Cl_2$  structure.

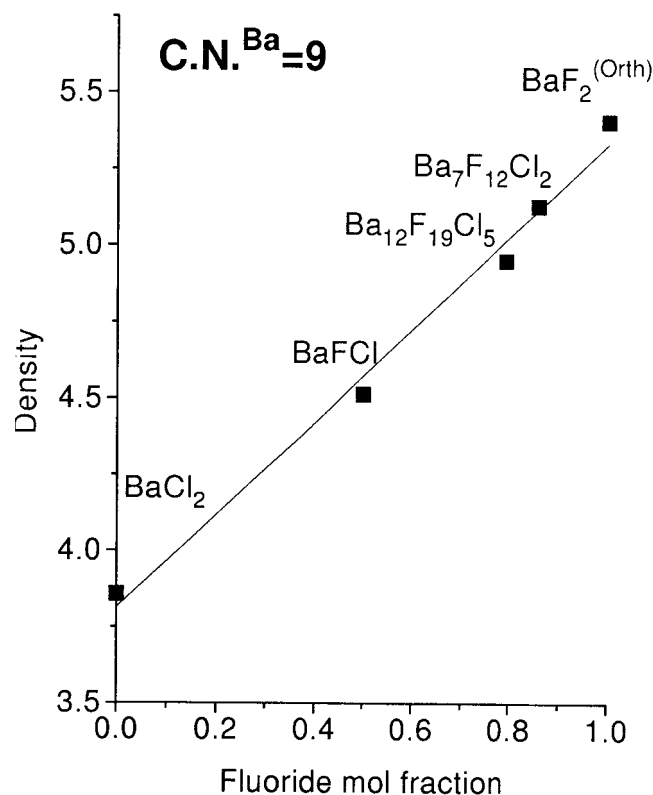


**Fig. 6** Local environment around Ba(1): (a), Ba(2): (b) and Ba(3): (c) in  $Ba_7F_{12}Cl_2(o)$ . A monocapped square antiprism formed by 2 chloride ions (large circles) and 7 fluoride ions (small circles) for the former two and a tricapped trigonal prism of fluoride ions coordinating Ba(3).

significant differences exist between both structural variants of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>.

**Physico-chemical properties:** The X-ray density of disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (5.123 g/cm<sup>3</sup>) corresponds to the *highest* density found for stable compounds in the Ba/F/Cl system. Only the metastable orthorhombic BaF<sub>2</sub> modification (stable above ca 2.3 GPa) shows at ambient pressure a higher value of 5.4 g/cm<sup>3</sup> (6.05 g/cm<sup>3</sup> at ca 10 GPa) [12]. In comparison to the disordered variety a slightly lower X-ray volume density (5.117 g/cm<sup>3</sup>) is obtained for Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>(o).

As illustrated in Fig. 7, where the density is presented as a function of fluoride mole fraction, a quasi linear behavior is found for compounds ranging from BaCl<sub>2</sub> to BaF<sub>2</sub><sup>orth</sup>. For all these compounds a local coordination of 9 of the Ba ion is observed. This latter fact enables comparison of interatomic distances between the two structures of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> and the high pressure orthorhombic structure of BaF<sub>2</sub> [12]. In the latter compound barium is surrounded by a tricapped prism of fluoride ions. Distances in the plane are 248, 260, 261 pm (average = 256 pm), similar to those



**Fig. 7** The fluoride mole fraction of compounds in the Ba/F/Cl system (with coordination number 9 for Ba<sup>2+</sup>) as a function of the density (in g/cm<sup>3</sup>).

found for Ba(2) in Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (d) (256 pm). Out of plane distances (2 × 255 pm, 269 pm, 291 pm, average 271 pm) are shorter (289 pm for Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> (d)). The density comparison and these considerations allow to conclude that Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> is similar to a high pressure modification of BaF<sub>2</sub>.

Other A<sub>7</sub>B<sub>12</sub>C<sub>2</sub> compounds reported in the literature [10] crystallize as the ordered form in the space group P6. Disordered Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> appears therefore to be truly a new structure type. It is interesting to note that the ordered variant is the thermodynamically favored species. It should also be stated that neither form of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub> has been reported previously in the literature – even in those publications which discuss the phase diagram of barium with fluoride and chloride in the presence of Na<sup>+</sup> [8] or Li<sup>+</sup> [13] which include in principle the compositions used for the synthesis of these new compounds.

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