

Low Temperature Crystal Growth and Structure of Ordered Ba₇F₁₂Cl₂

F. Kubel^a, H. Bill^b, H. Hagemann^b

^a Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9, Wien

^b Dépt. de Chimie Physique, Univ. de Genève, 30, quai Ernest-Ansermet, CH 1211 Geneva 4, Switzerland

Z. Naturforsch. **54b**, 515–518 (1999); received November 30, 1998

Bariumfluorochloride, Hexagonal Crystal Structure, Crystal Growth, Low Temperature Gel Method

Crystals of composition Ba₇F₁₂Cl₂ were obtained by a reaction at room temperature between Ba²⁺/Cl⁻/F⁻ in a gel of agar-agar/water. The hexagonal crystals have space group P6̄, *a*=1064.69(8), *c*=417.89(5)pm, *V*=410.24(8) 10⁶ pm³ and *Z*=1. The anions form a propeller type network located in tunnels parallel to the *c*_{hex} axis; the chloride ions are located at the center on the propeller axes. The Ba²⁺ ions are coordinated by a (distorted) tricapped trigonal environment of fluoride and chloride anions. Disorder is present for one particular Ba²⁺ site. The average structure is isotypic with the structure of Pb₇F₁₂Cl₂.

1. Introduction

Recently new compounds in the Ba-Cl-F phase diagram were obtained by high temperature solid state reaction and flux growth methods. One of them has the composition Ba₁₂F₁₉Cl₅ and is of space group P6̄2m [1], whereas the other two are both of the composition Ba₇F₁₂Cl₂ but have mutually different structures, depending on the high temperature synthesis conditions. One is a disordered variant with space group P6₃/m [2] whereas the other one is an ordered structure with space group P6 [2]. These structures are all hexagonal, thus different from the (tetragonal) matlockite structure BaFCl observed in the same phase diagram. A characteristic propeller type arrangement of anions with three- respectively two- different barium sites of coordination number (C. N.) nine is observed. These new compounds show promising optical properties when doped with Rare Earth ions.

This paper reports the synthesis at room temperature of the ordered Ba₇F₁₂Cl₂(o) variant. The compound was obtained by slow diffusion in a gel of Ba²⁺/Cl⁻ from one interface and of F⁻ from the other one. In addition to the crystals of Ba₇F₁₂Cl₂(o), crystalline BaFCl and BaF₂ in a spherical arrangement were obtained.

2. Experimental

It is known that BaFCl is only slightly soluble in water, and reaction mixtures of BaCl₂ and NaF were observed to form solid BaFCl and BaF₂ [3]. Powder X-ray diffraction diagrams of the precipitated solids indeed showed the sole presence of BaFCl and BaF₂. However compounds with other ratios of Ba²⁺, Cl⁻ and F⁻ are possible too. Fessen-

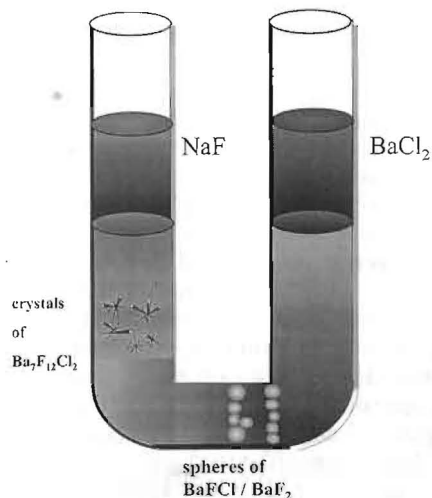


Fig. 1. Schematic layout of the room temperature gel type crystal growth equipment. The gel of agar-agar/water separates the solutions NaF/H₂O and BaCl₂/H₂O. Further are indicated the growth regions of the Ba₇F₁₂Cl₂ crystal aggregates below the NaF agar-agar interface (lower Cl⁻ concentration) and, at the bottom, of the spherically shaped BaFCl/BaF₂ hybrids.

* Reprint requests to Prof. H. Bill.

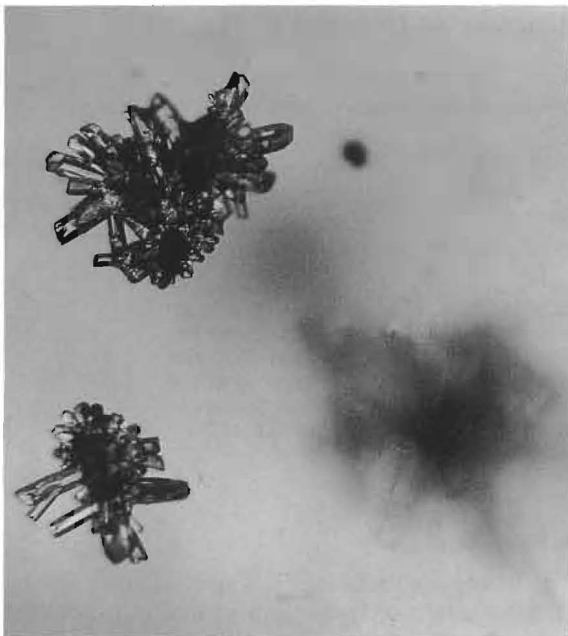


Fig. 2. Star-shaped crystalline units of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ in the gel of agar-agar/water. Several high quality single crystals are visible. Magnification: 10x.

den and Levin [3] suggested the formation of a compound with the stoichiometry $\text{Ba}_2\text{F}_3\text{Cl}$, but our experiments to obtain this phase were unsuccessful until now. Crystal growth in gels suggested itself as a method to obtain crystalline units of these compounds. Gels were prepared from commercial agar-agar which was dissolved in hot water. On cooling, the polymerization was completed in U-shaped glass tubes with diameter of 25 mm. Several tubes with different reactant concentrations and compositions were prepared. The compound reported was grown in a U-tube containing a dilute solution of approximately 30 ml 0.1 mol $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$ placed on the gel surface of one side of the tube (see Fig. 1). On the surface of the other side, 30 ml of a 0.1 molar solution of NaF was added. To avoid rapid evaporation of water and drying out of the gel, the U-tube was then covered with plastic foils. The tubes were shelved in the laboratory under anti-shock conditions. After one month, spherical crystalline units up to 2 mm \varnothing formed at the center of the tube (see Fig. 1). They are composed of BaFCl and BaF_2 . Close to the NaF solution growth of hexagonal crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ mutually intertwined into star-shaped arrangements was observed (Fig. 2). The individual crystals increased in size from a

center to all directions during the growth. After two months the crystallization was completed.

3. Results and Discussion

Optical examination: The crystals were analyzed by means of optical microscopy in polarized light. They form regular hexagonal polyhedra which appear to be individual single crystals, with well developed faces. Their top part was found to be hollow. Probably, the crystals contain small amounts of gel, as was observed for the crystals of $\alpha\text{-KCoPO}_4$ [4].

Optical inspection of the spherical objects in the center of the U-tube showed that the spheres consist of crystalline units. The center is birefringent in polarized light, whereas the outer shell is cubic (no birefringence). X-ray diffraction of a powdered sphere showed that the center consists of BaFCl and the surface of BaF_2 .

Refinement of the structure of $\text{Ba}_7\text{F}_{12}\text{Cl}_2(\text{gel})$: the hexagonal crystals show the same features as does the recently investigated $\text{Ba}_7\text{F}_{12}\text{Cl}_2(\text{o})$ [2]. Individual single crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_2(\text{gel})$ (size 0.10x0.10x0.25 mm) were selected from a star-shaped cluster for crystal structure determination. The cell parameters were refined from 25 reflections, the parameters were $a=1064.69(8)$, $c=417.89(8)\text{pm}$, $a/c=2.548$. In all, three crystals were studied in detail by single crystal diffraction refinement. No significant differences in unit cell parameters, atom positions and composition were found. One of the sets of results is presented in detail. The intensities of 8269 reflections were measured on a CAD4 automatic diffractometer (radiation $\text{MoK}\alpha$, $\lambda=71,073\text{ pm}$ at 300 K). Among these reflections 936 were independent; 917 were considered as observed according to the criterion $I>3\sigma(I)$. Absorption correction was applied based on the morphology of the crystal. Graphical representation of the diffracted intensities showed the presence of all $000l$ reflections confirming space group P6. The positions of the heavy atoms were taken from reference [2]. Calculations of the difference electron density (program XTAL 3.2 [5]) allowed to locate the light halogen ions. Arguments in favor of the group P6, *i.e.* the ordered structure of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ are: Lattice parameters are similar to those of the ordered variant [2] and $000l$ reflections with $l = 1,3,5$ reflections are observed.

They agree within 3σ with the calculated values. The numbers are: $F_{\text{obs}}(\sigma)[F_{\text{calc}}]=20.2(2)[20.0]$, $11.67(7)[12.7]$, $5(12)[6.4]$, $3.2(17)[2.3]$. We note that a similar discussion was made with respect to $U_2Ni_{12}P_7$ [6].

The standardized [7] atomic position are given in Table I. The structure is polar but ferroelectric twinning with an amount of 50% volume for both units was found in all three species ($x_{\text{abs}}=0.54(6)$, $0.48(8)$ and $0.52(7)$ [7]).

Description of the average and fine structure: The average structure of Ba₇F₁₂Cl₂ is isotopic to Fe₁₂Zr₂P₇ [8] and Pb₇F₁₂Cl₂ ($a=1027.4$, $c=398.7$ pm, $a/c=2.577$ [9]). Fig. 3 shows a projection of the structure along the c_{hex} axis. Basically, a network

of connected propeller type halogen units (ClF₆) with chlorides on the axis is formed. This network is presented in Fig. 3 by thick lines. In the tunnel parallel to the axis a further column (presented by thin lines between the halides) is located. The alkaline earth atoms are either below (or above) the blades and located in a tricapped trigonal prismatic environment. They have coordination number C. N.=9, Ba(1/2) are surrounded by seven fluorides and two chlorides, Ba(3) by nine fluorides [2]. Almost linear variation of the unit cell volume between BaCl₂, BaFCl, Ba₁₂F₁₉Cl₅, Ba₇F₁₂Cl₂ and BaF₂ (high pressure modification) with CN=9 can be observed. Interatomic barium halide distances are given in Table II.

Table I. Standardized positional and isotropic displacement parameters ($/100 \text{ pm}^2$).

Atom	x/a	y/b	z/c	U_{iso}	Pop
F(1)	0.2717(7)	0.120(6)	1/2	1.9(2)	
Ba(1)	0.11095(5)	0.40796(5)	1/2	1.10(1)	
F(2)	0.3719(6)	0.4305(6)	1/2	1.5(2)	
F(3)	0.4370(6)	0.0537	0	1.7(2)	
F(4)	0.1175(7)	0.2165(7)	0	2.2(2)	0.780(3)
F(5)	0.151(3)	0.275(3)	0	2.2(2)	0.220(3)
Ba(2)	0.40365(5)	0.29104(4)	0	1.07(1)	
Ba(3)	0	0	0.25	1.52(2)	0.043(1)
Cl(1)	1/3	2/3	0	1.70(9)	
Cl(2)	2/3	1/3	1/2	1.56(8)	
Ba(4)	0	0	1/2	1.52(2)	0.627(4)
Ba(5)	0	0	0	1.52(2)	0.220(3)

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the deposition number CSD- 410680, the name of the authors and citation of the paper.

Table II. Selected metal-halogen bond distances and angles (*split positions are in italic*).

Bal-	CN					
Ba1-	CN 9	F1	260.9(8)..			
		2x F3	265.5(8)..			
		2x F2	266.7(8)..			
		2x <i>F5(4)</i>	267.6(40)	{294.4(10)..}		
		2x Cl1	332.25(7).			
Ba2-	CN 9	<i>F5(4)</i>	261.0(40)	{273.8(7)..}		
		F3	263.8(6).			
		F1	266.2(3)..			
		F2	268.0(5)..			
		F3	272.2(7)..			
Ba3-	CN 6	Cl1	333.87(5).			
		2x <i>F5(4)</i>	274.3(30)	{225.5(6)..}		
		3x F1	272.0(6)..			
		Ba4-	CN 9	F1	251.1(7)..	
				6x <i>F5(4)</i>	328.6(25)	{289.2(4)..}
defects.						
Ba5-	CN 9	3x <i>F5</i>	253.6(32).			
		6x F1	326.7(5)			

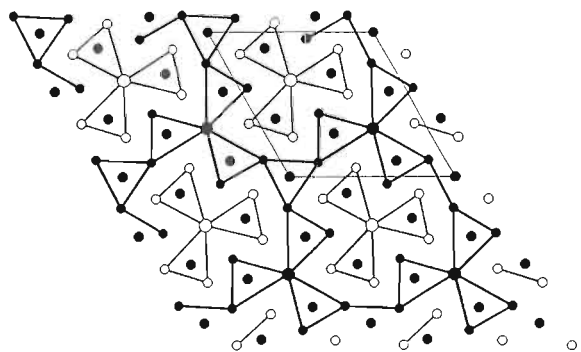


Fig. 3. Projection of the structure of Ba₇F₁₂Cl₂ along the c_{hex} axis.

The real structure seems to be more complex. It is found for all three crystals, that a *partial* disorder (or split position) is present for the barium ion at the Wyckoff position 1b. For this atom, three positions (0,0,1/2) (1b); (0,0,0) (1a) and (0,0,1/4) (2g) were refined with approximate populations for Ba(4): 0.627(4), Ba(5): 0.220(3) and Ba(3): 0.043(1) (see Table I); the populations were *not* constrained! The refinement confirms the given composition and a final composition of Ba_{6.93(3)}F₁₂Cl₂ is found. The final agreement factor is $R_w=1.8\%$. We note that the position (0,0,1/4) (2g) has coordination number 6 as the Ba ion is

halfway in between two empty fluoride triangles. The order/disorder behavior on this particular crystallographic site might be related to the formation of growth twins.

4. Conclusions

Single crystal of Ba₇F₁₂Cl₂ can be synthesized at room temperature in an organic gel. The com-

pound crystallizes in the polar space group $P\bar{6}$ but merohedral twinning was observed for all three tested crystals. The structures are similar to Pb₇F₁₂Cl₂ but a complex disorder appears on one cation site. In the same gel, spherical units of crystalline BaFCl and BaF₂ are also formed.

-
- [1] F. Kubel, H. Hagemann, H. Bill, *Z. Anorg. Allg. Chem.* **622**, 343 (1996).
[2] F. Kubel, H. Bill, H. Hagemann, *Z. Anorg. Allg. Chem.*, accepted for publication.
[3] E. Fessenden, S. Z. Lewin, *J. Am. Chem. Soc.* **77**, 4221 (1955).
[4] M. Lujan, F. Kubel, H. Schmid, *Z. Naturforsch.* **49b**, 1256 (1994).
[5] S. R. Hall, H. D. Flack, G. M. Stewart, Editors of *XTAL 3.2 Users Manual* (1992) Universities of Western Australia, Geneva and Maryland. Lamb: Perth.
[6] T. Ebel, J. H. Albering, W. Jeitschko, *J. Alloys. Comps.* **266**, 71 (1998).
[7] L. M. Gelato, E. Parthé, *J. Appl. Crystallogr.* **20**, 139 (1987).
[8] E. Ganglberger, *Monatsh. Chem.* **99**, 557 (1968).
[9] B. Aurivillius, *Chem. Scr.* **10**, 206 (1976).