inorganic compounds

A hexagonal $2a,c$ superstructure of $Ba_7F_{12}Cl_2$

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Hydrothermal synthesis yielded crystals of heptabarium dodecafluoride dichloride, $Ba_7F_{12}Cl_2$, displaying a new $2a,c$ hexagonal superstructure with $P\bar{6}$ symmetry. The superstructure results from the disorder of Ba^{2+} cations over two adjacent tricapped trigonal prismatic sites located in channels parallel to the c axis.

Comment

Barium fluorochlorides and -bromides with the composition $Ba_7F_{12}X_2$ (X = Cl or Br) can be synthesized by high-temperature flux growth, room-temperature gel-growth (Kubel *et al.*, 1999*a*,*b*; Kubel, 2005) and hydrothermal methods. For $Ba_7F_{12}Cl_2$, two distinct modifications have been characterized to date, including an ordered and a disordered modification grown from an LiF and an NaCl flux, respectively (Kubel *et al.*, 1999*a*). Crystals obtained from gel growth showed further disorder (Kubel *et al.*, 1999*b*).

In this study, selected crystals of $Ba_7F_{12}Cl_2$ grown by hydrothermal synthesis have been investigated. A superstructure modification, which can be described as an ordered (position) and disordered (occupancy) variant, has been discovered. The hydrothermal synthesis was carried out under the same conditions as described for $Pb_7F_{12}Cl_2$ (Kubel *et al.*, 2000).

The basic crystal structure of $Ba_7F_{12}Cl_2$ is built up of a matrix of matlockite-like units where one type of Ba^{2+} cation has a coordination number of 9 (2Cl+7F). Fig. 1 shows the propeller-type arrangements, with Cl^- ions as the axes and F^- ions as the blades of the propellers. Within this framework, tricapped trigonal channels filled with the second type of Ba^{2+} ions complete the structure. Two hypothetical positions separated by a distance of $c/2$ can be occupied within the channels (Kubel *et al.*, 1999*a*). An average 50% occupancy of both sites or a full occupancy of one site defines the disordered and ordered modifications, respectively. The lattice parameters are slightly different in each case. Crystals grown by gel-growth methods show small but significant deviations from the ideal ordered structure and a small increase in unit-cell volume (V).

For the new hexagonal superstructure, the c parameter is close to that of the disordered variant and the normalized a axis is close to that of the ordered modification. As seen in Fig. 2, the c/a ratio is different for all types of order and disorder. A small increase of disorder as found in the gel-grown crystals shows a higher V but a similar c/a ratio. This tendency is strongly increased for the new superstructure, for which a, c and V are significantly increased. Lattice parameters of several crystals were measured. The refinements showed only small deviations from the structure described here with, for example, slightly different populations of the Ba sites responsible for the superstructure. The superstructure was also confirmed from powder diffraction refinements showing superstructure reflections at low diffraction angle.

The formation of the $2a,c$ superstructure is related to the different occupancies of the Ba3 and Ba6 sites in the channels, which vary slightly with the growth conditions in the hydrothermal system. Fig. 1 can be compared with the drawing in Kubel *et al.* (2000). In the present superstructure, a new arrangement of three propellers connected to the fluoride channel is formed, which is not observed in the ordered or
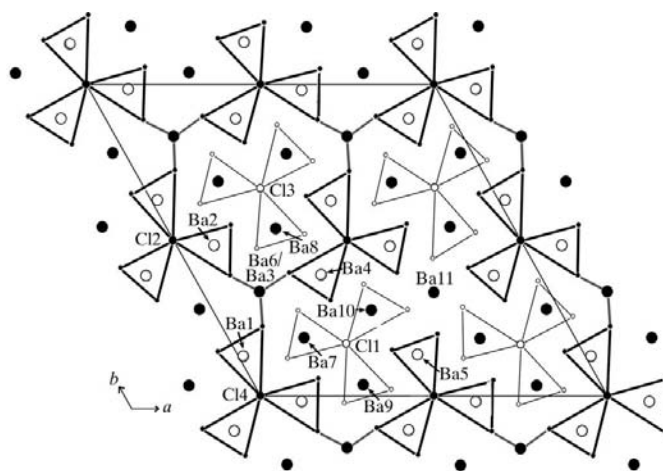

Figure 1
The superstructure of $Ba_7F_{12}Cl_2$, projected along the c axis, showing the propeller-type arrangement. Large, medium and small circles represent Ba, Cl and F atoms, respectively. Bold lines and filled circles correspond to $z = 0$ and thin lines and open circles to $z = \frac{1}{2}$.
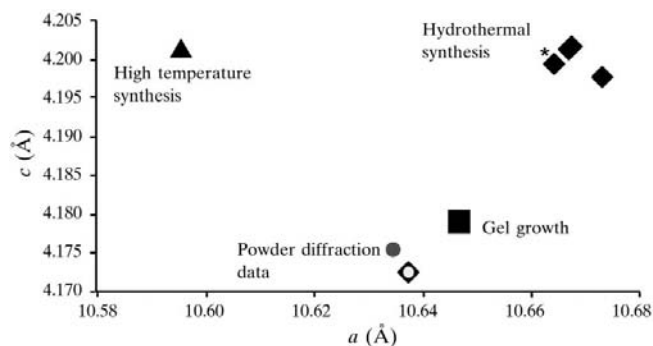

Figure 2
Lattice parameters of $Ba_7F_{12}Cl_2$ for different synthesis procedures (s.u. values are typically about 0.001 Å). High-temperature and gel-growth data are taken from Kubel *et al.* (1999*a*,*b*), hydrothermal data from Kubel (2005), and powder diffraction data from Es-Sakhi *et al.* (1998) and Kubel (2005). The asterisk represents the present data.

disordered modifications. The Ba—X distances are not changed significantly but consist of two sets of distances similar to each modification. The environments of Ba1, Ba3, Ba4 and Ba6 are similar to the ordered variant, whereas those of Ba2, Ba5, B7 and Ba8 are similar to the disordered modification.

Experimental

Crystalline needles of $Ba_7F_{12}Cl_2$ up to 5 mm in length were formed by hydrothermal synthesis from the corresponding aqueous fluorides and chlorides placed in Teflon-lined steel containers at 523 K for 40 d. Detailed synthesis conditions have been described previously in the case of $Pb_7F_{12}Cl_2$ (Kubel & Voellenkle, 2000). Hexagonal and optically uniaxial crystals were broken from the needles and selected under polarized light (Leitz Orthoplan Wild M3 microscope). X-ray fluorescence analysis showed only Ba, F and Cl signals. The lattice constants and unit-cell volumes of several individual crystals were determined on a Bruker SMART diffractometer with a graphite monochromator and a SMART APEX detector. Selected powdered crystals were analyzed with powder X-ray diffraction [Philips Xpert diffractometer and *TOPAS* refinement package (Bruker, 2000)].

Crystal data

$Ba_{4.67}Cl_{1.33}F_8$	$D_x = 5.06$ Mg m^{-3}
$M_r = 840.14$	Mo $K\alpha$ radiation
Hexagonal, $P\bar{6}$	$\mu = 16.81$ mm^{-1}
$a = 21.3281$ (7) Å	$T = 293$ K
$c = 4.1993$ (3) Å	Needle, colourless
$V = 1654.29$ (16) Å^3	$0.24 \times 0.08 \times 0.04$ mm
$Z = 6$	

Data collection

Bruker SMART CCD area-detector diffractometer	19682 measured reflections
ω scans	1970 independent reflections
Absorption correction: analytical (*SADABS*; Sheldrick, 1996)	1405 reflections with $I_{net} > 3\sigma(I_{net})$
$T_{min} = 0.217$, $T_{max} = 0.510$	$R_{int} = 0.056$
	$\theta_{max} = 31.0°$

Refinement

Refinement on I_{net}	$\Delta\rho_{max} = 1.95$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{min} = -5.63$ e Å^{-3}
$wR(F^2) = 0.031$	Extinction correction: Zachariasen (1968)
$S = 2.38$	Extinction coefficient: 1.05 (5) $\times 10^2$
1768 reflections	Absolute structure: Flack (1983)
124 parameters	Flack parameter: 0.01 (7)
$w = 1/\sigma^2$	
$(\Delta/\sigma)_{max} < 0.001$	

The refined parameters varied slightly from one sample to another and differed from those of the ordered and disordered $Ba_7F_{12}Cl_2$ phases. A doubling of the a and b axes was found for several crystals with a normalized V larger than expected from our former data. Substitution with larger bivalent ions can be excluded, so a new structural arrangement had to be taken into consideration. To improve the ratio of variables to intensities, the F atoms were refined isotropically. The quality of the refinement did not improve when anisotropic displacement parameters were used. The absorption correction was carried out using the crystal shape method and the corresponding absorption coefficient. All atomic positions were standardized using *STIDY* (Gelato & Parthe, 1987). Constraints were applied to the x and y coordinates and the occupancies of the Ba3 and Ba6 sites. The maximum residual electron density was found in position (0.6956, 0.3482, 0.0957) and the minimum residual density was found in position $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$.

Table 1
Selected bond lengths (Å).

Ba1—F1	2.590 (10)	Ba6—F9	2.089 (11)
Ba1—F3	2.659 (12)	Ba6—F10	2.080 (11)
Ba1—F3^i	2.668 (12)	Ba6—F13	2.076 (12)
Ba1—F10	2.927 (7)	Ba7—F3	2.669 (8)
Ba1—F12^i	2.668 (7)	Ba7—F5	2.670 (6)
Ba1—C14	3.3258 (10)	Ba7—F10	2.685 (11)
Ba2—F2	2.582 (13)	Ba7—F12	2.597 (11)
Ba2—F4	2.602 (10)	Ba7—F14	2.704 (12)
Ba2—F6^i	2.614 (13)	Ba7—Cl1	3.351 (5)
Ba2—F9	2.918 (8)	Ba8^{ii}—F2	2.746 (8)
Ba2—F11	2.628 (6)	Ba8—F4	2.670 (6)
Ba2—C12	3.294 (5)	Ba8^{ii}—F11	2.667 (11)
Ba3—F1	2.612 (10)	Ba8—F11	2.784 (10)
Ba3—F4	2.590 (10)	Ba8—F13	2.743 (12)
Ba3—F5	2.569 (10)	Ba8—Cl3	3.3411 (10)
Ba3—F9	2.962 (8)	Ba9^i—F1	2.654 (6)
Ba3—F10	2.955 (7)	Ba9—F6	2.713 (8)
Ba3—F13	2.953 (8)	Ba9^i—F9	2.719 (11)
Ba4^{ii}—F2	2.615 (13)	Ba9—F12	2.774 (11)
Ba4—F5	2.599 (10)	Ba9—F15	2.664 (10)
Ba4—F7	2.670 (11)	Ba9—Cl1	3.361 (4)
Ba4—F13	2.911 (8)	Ba10—F7	2.630 (7)
Ba4—F14	2.674 (7)	Ba10—F8	3.019 (8)
Ba4—C12^{iii}	3.327 (4)	Ba10—F14	2.606 (13)
Ba5—F6	2.713 (12)	Ba10—F15	2.687 (9)
Ba5^{iv}—F7	2.772 (12)	Ba10—F16^{iv}	2.641 (9)
Ba5—F8	2.709 (11)	Ba10—Cl1	3.293 (5)
Ba5—F15	2.677 (6)	Ba11—F8	2.869 (7)
Ba5—F16	2.670 (6)	Ba11—F16	2.540 (9)
Ba5—C12^v	3.385 (5)		

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, 1-x, z$; (iii) $1-y, 1+x-y, z$; (iv) $1-x+y, 1-x, z$; (v) $-x+y, -x, z$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *ADDREF* and *SORTRF* in *Xtal3.2* (Hall *et al.*, 1992); program(s) used to solve structure: *Xtal3.2*; program(s) used to refine structure: *Xtal3.2*; molecular graphics: *POWDER CELL* (Version 2.4; Kraus & Nolze, 1996); software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal3.2*.

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