

Synthesis and Structure of the Disordered Modification of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$

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We recently discovered a new compound with composition $\text{Ba}_7\text{F}_{12}\text{Cl}_2$. It was possible to show that the variation of the synthesis conditions makes it possible to obtain a disordered and an ordered modification with different lattice parameters and space groups ($P6_3/m$ [176] and $P\bar{6}$ [174]). For $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ an ordered modification is reported in the literature. In this paper we present the synthesis and structural characterization from X-ray diffraction data of the *disordered* modification of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$. Single crystals were grown from a flux and the structure was refined in the hexagonal space group $P6_3/m$ to $R(R_w) = 0.043(0.038)$ for 284 reflections and 26 parameters. Lattice parameters are $a = b = 1021.90(8)$ pm and $c = 361.93(6)$ pm with $Z = 1$. Propeller-type arrangements with chlorine as axis and fluorines as blades are observed. The ordered modification of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ was prepared by a new hydrothermal synthesis. Differences between both modifications are found in the lattice constants and atomic occupation parameters for the atom type Pb2 and the connected fluorine ions. © 2000 Academic Press

Key Words: lead halides; X-ray single crystal diffraction; disordered structure.

INTRODUCTION

Solid solutions of alkaline earth fluorohalides with the PbFCl structure doped with Sm(II) are at present the best crystalline systems for room temperature photochemical hole burning (1–3). In the course of our research on crystals for hole burning experiments, we discovered new barium fluoro-chlorides with the composition $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$ (4) and $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (5). For the latter compound, two distinct modifications, an ordered and a disordered modification, were found and characterized (5).

Recently, we studied mixed compounds of the type $M_{2x}\text{Pb}_{12-x}\text{F}_{18}\text{Cl}_6$ with $M = \text{K}^+$ and Na^+ (6, 7). During our attempts to vary the Na^+ concentration, we obtained

crystals corresponding to the stoichiometry of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$. Crystals with this composition were previously characterized by Aurivillius (8) and recently the structure of a natural variant, the mineral Laurelite, was described in literature (9).

Our structural characterization of the crystals synthesized at relatively low temperature revealed the presence of a new, disordered form of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$.

EXPERIMENTAL

Synthesis and Analysis

Crystalline needles of the *disordered* form of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ were prepared under oxygen-free atmosphere using a graphite crucible.

The reaction mixture consisted of PbF_2 (Alfa) and NaCl (Merck) with a molar ratio of 1:0.35, corresponding to a chloride mole fraction in the mixture of 1/7 with respect to fluoride.

The mixture was heated for 45 min to nominally 790°C, and subsequently cooled for 3 h to 500°C before switching off the furnace. The needle-shaped crystals were separated mechanically from the mass.

Quantitative analysis from powder diffraction data of the mixture after reaction revealed the formation of the title compound (~75 mol%) and a sodium containing phase. Experiments using higher chloride content in the mixture (e.g., chloride mole fraction of 0.25) yielded only crystals of this phase with the composition $\text{Pb}_{12-x}\text{Na}_{2x}\text{F}_{18}\text{Cl}_6$ (7).

High-quality crystalline needles of the *ordered* form of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ were prepared by hydrothermal synthesis methods in a Teflon crucible placed in a steel reactor. Stoichiometric amounts of PbF_2 and NaCl to form $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ (~1 g in 10 ml H_2O) in water are used for this synthesis. The reaction was completed after 1 week at 250°C. Powder diffraction refinement gave a composition of 95% of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ with lattice parameters of $a = 1026.7(1)$, $c =$

398.23(5) pm, and $V = 363.5(1) \cdot 10^6 \text{ pm}^3$. Five percent of orthorhombic PbF_2 was also found.

All samples were first inspected under a polarizing light microscope. $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ cannot easily be distinguished from the sodium containing hexagonal phases described by Aurivillius (6). In both cases, needle-shaped crystals are present. Powder diffraction analysis makes it possible to adjust the synthesis conditions and to obtain mainly the title compound.

RESULTS AND DISCUSSION

Crystal Description

The c_{hex} axis of the crystals points along the needle axis. Inspection in polarized light showed no birefringence along this direction. Together with the crystal shape it could be concluded that the crystal system is either hexagonal or rhombohedral.

X-Ray Diffraction of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$

The lattice constants of selected crystals were determined on an Stoe diffractometer. The refined values are given in Table 1. In Fig. 1 they are compared to those of the previous structural studies on $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ (8,9) and $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (5). The parameters suggest immediately a structural relationship to the hexagonal *disordered* variant of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$. The space group $P6_3/m$ was retained. Details of the data collection and refinement conditions are given in Table 1. The standardized (10) atomic positional and vibrational parameters are given in Table 2.

TABLE 1
Conditions of Structure Analysis for $\text{Pb}_7\text{F}_{12}\text{Cl}_2$

Space group	$P6_3/m$ [176]
Z	1
a (pm)	1021.90(8)
c (pm)	400.20(3)
V (10^6 pm^3)	361.93(6)
X-ray density (g cm^{-3})	8.025
Crystal size (mm^3)	$0.046 \times 0.050 \times 0.132$
Absorption coefficient (cm^{-1})	15.94
R_{int}	3.5%
Diffractometer/radiation	STOE, $\text{CuK}\alpha$ 154.18 pm
Scan method	$\omega/2\theta$
Refinement program	Xtal 3.2 [13]
measured intensities	2941
independent intensities	289
Used reflections	284
No. of refined parameters	26
$R(R_w)$ on F	0.043 (0.038)
max.shift/esd	0.003
Residual e^- density ($e/10^6 \text{ pm}^3$)	4.7 (−4.5)

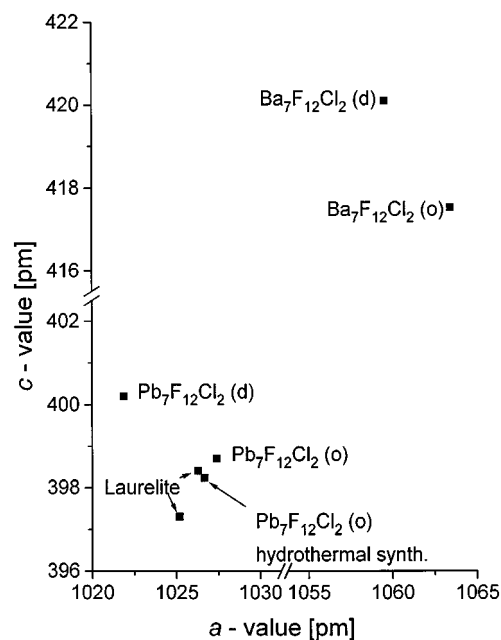


FIG. 1. Lattice parameters of the different modifications of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ and $\text{Ba}_7\text{F}_{12}\text{Cl}_2$.

Structure Description and Discussion

The lead atoms in the structure have a coordination number of nine with one Pb^{2+} surrounded by two chlorines and seven fluorines and one Pb^{2+} by nine fluorines.

TABLE 2
Standardized Atom Positions with ESDs in Parentheses and Atomic Displacement Parameters ($\times 100$) with ESDs in Parentheses (U_{13} and $U_{23} = 0$)

Atom	Wykoff	x/a	y/b	z/c	$U_{\text{iso}} \times 100$	Pop
F1	6(h)	0.132(2)	0.212(2)	1/4	2.3(5)	0.5 ^a
F2	6(h)	0.157(2)	0.275(2)	1/4	2.3(5)	0.5 ^a
Pb1	6(h)	0.40587(4)	0.29523(4)	1/4	2.01(4)	
F3	6(h)	0.4283(6)	0.0420(7)	1/4	2.30(3)	
C1	2(c)	1/3	2/3	1/4	2.0(1)	
Pb2	2(a)	0	0	1/4	5.5(1)	0.5 ^a
		U_{11}	U_{22}	U_{33}	U_{12}	
Pb1		2.41	2.13	1.97	1.49	
Pb2		$2U_{12}$	$2U_{12}$	11.61	1.25	
C1		$2U_{12}$	$2U_{12}$	2.24	0.97	
F3		1.17	2.11	2.93	0.29	
F1		1.58	2.10	4.00	1.49	
F2		1.58	2.10	4.00	1.49	

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

Propeller-type arrangements with chlorine as axes and fluorines as blades are observed; they are connected to “channels” of tricapped fluorine prisms. In contrast to the ordered variant of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ a disorder of occupation on the lead sites within in these “channels” was found. Disorder was found for the atom types Pb2 (50% occupation to achieve neutrality) along the c_{hex} axis and a corresponding splitting of the position of one fluorine ion into two positions (F1/F2) was found.

Figure 2 shows the atomic displacements of the atoms in one channel. As a consequence of a compactation in the a, b plane due to smaller lattice parameters, a rotation of the empty triangular prisms against the filled ones is observed (see inset to Fig. 2). In the ordered variant, the projection of the Pb–F bond is almost perpendicular to the F–F bond of the empty triangles.

Structural characteristics are similar to those found for the barium analog compound and are discussed in Ref. (5). Selected interatomic distances are given in Table 3.

The density of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ was calculated from our X-ray data to be 8.025 g cm^{-3} and can be compared with the density of other lead chloride fluorides (see Fig. 3). A linear

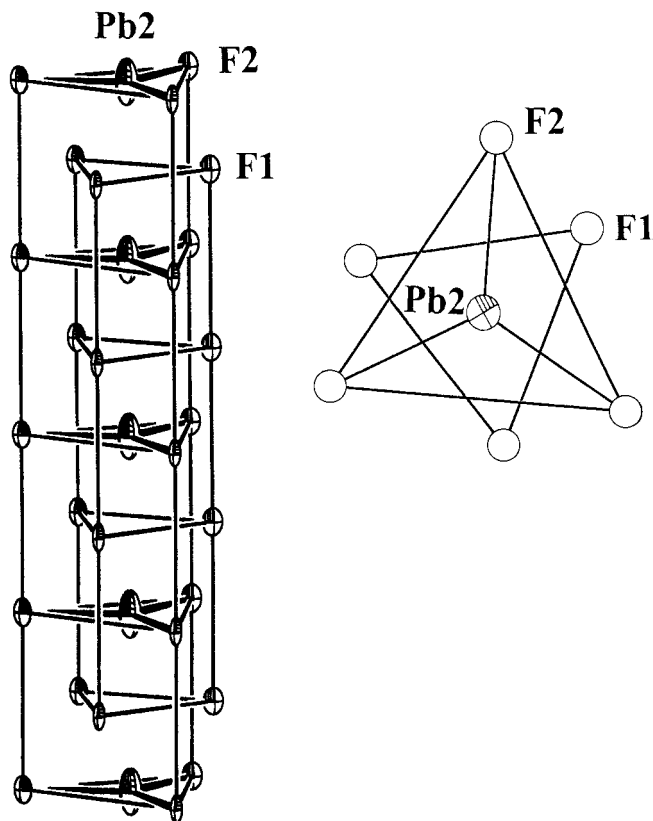


FIG. 2. Drawing of one individual fluorine channel of $\text{Pb}_7\text{F}_{12}\text{Cl}_2$ from the disordered modification parallel (left) and perpendicular (right) to c_{hex} .

TABLE 3

Selected Interatomic Distances in pm with ESDs in Parentheses

Pb1–F2		244.0(19)		[Pb2–F1 × 3 189.5(13)]
Pb1–F3	× 2	248.3(4)		[Pb2–Pb2 × 2 200.10(2)]
Pb1–F1		248.4(16)		Pb2–F2 × 3 243.9(14)
Pb1–F3		254.8(5)		Pb2–F1 275.6(9)
Pb1–F2	× 2	258.3(16)		Pb1–Pb2 × 6 371.37(4)
Pb1–F3		271.0(13)		
Pb1–Cl	× 2	319.70(4)		
[F1–F2		56(2)]		

Note. Values in squared brackets are artificially created by the disorder. F1–F1 distances of the empty triangles: 328.2(2) pm (326.6, ordered compound). F2–F2 distances of the filled triangles: 422.4(2) pm (428.9, ordered compound).

relationship is found between the density and the fluoride mole fraction. This value can be compared with the corresponding one for Laurelite, where a lower density of 7.65 g cm^{-3} was measured (9) and associated to the composition of $\text{Pb}_{0.97}[\text{F}_{1.68}\text{Cl}_{0.25}(\text{H}_2\text{O})_{0.07}]$ and $Z = 7$.

CONCLUSIONS

It is now clearly established that there are at least two different crystalline modifications for the compounds with composition $M_2\text{F}_{12}\text{Cl}_2$ ($M = \text{Ba}, \text{Pb}$). It is further possible that other crystal systems with the $\text{Fe}_{12}\text{Zr}_2\text{P}_7$ (12) crystal type present similar disordered modifications.

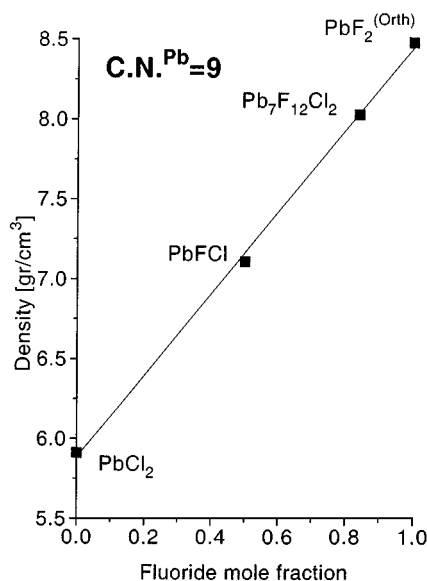


FIG. 3. Drawing of the density as a function of the fluoride mole fraction for different crystals in the PbCl_2 – PbF_2 system.

There are further chemical similarities between the barium and the lead compounds. For both cases it is necessary to use an alkali halide flux to obtain the disordered modification of $M_2\text{F}_{12}\text{Cl}_2$.

The ordered modification can be obtained either from the stoichiometric metal fluorochloride mixture or in presence of water either by gel growth for the barium compound (11) or by the hydrothermal preparation for the lead compound.

The structure determination of Laurelite, the natural form of ordered $\text{Pb}_7\text{F}_{12}\text{Cl}_2$, shows the occupation of the lead sites to be 95.5%. The missing 4.5% are on positions shifted by $\sim(x, y, z + 1/2)$ and suggests also a partial positional disorder. A similar behavior was found for ordered $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ grown at room temperature in a gel (11).

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