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Matlockite-type PbFI

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Lead fluoride iodide adopts the matlockite (PbFCl) structure type and is isotypic with other fluoride halides *MFX* (*M* = Ca, Sr, Ba, Sm, Eu, Pb; *X* = Cl, Br, I). The Pb and I atoms are situated on positions with site symmetry 4*mm* and the F atom on a position with site symmetry $\bar{4}m2$. The Pb atom is surrounded by four F atoms and four I atoms at the vertices of a square antiprism with distances of *d*(Pb—F) = 2.5631 (5) Å and *d*(Pb—I) = 3.3613 (7) Å.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Pb–F) = 0.001 Å
R factor = 0.041
wR factor = 0.098
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Compounds of the matlockite (PbFCl) structure type are technologically interesting materials. For example, Sm^{2+}- or Eu^{2+}-doped BaF*X* (*X* = Cl, Br, I) crystals are well established optical luminophores (Takahashi *et al.*, 1985) or can be used as X-ray phosphors in imaging plate systems (Tanaka *et al.*, 1990; Sato *et al.*, 1992). Many isotypic representatives *MFX* of divalent lead, the larger alkaline earth ions (*M* = Ca, Sr, Ba) and of stable divalent rare earth elements (*M* = Sm, Eu) have been synthesized in the past and their structures determined from single-crystal or powder data.

Focusing on the system PbF*X*, the structures of PbFCl (Nieuwenkamp & Bijvoet, 1932*a*) and PbFBr (Nieuwenkamp & Bijvoet, 1932*b*) were the first to be characterized by X-ray diffraction techniques within this structure family. Synthesis

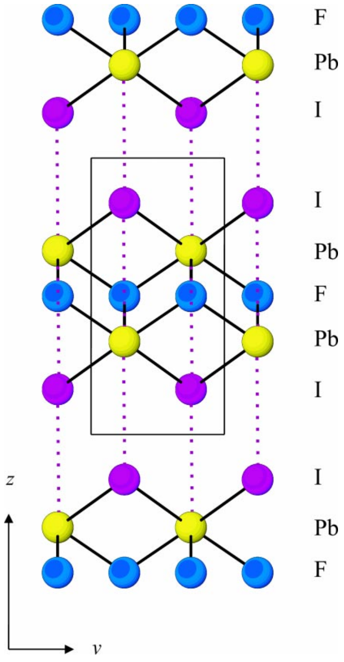

Figure 1
Projection of the structure along [100]. The stacking sequence of coplanar layers along [001] is shown. Weaker interactions between Pb and I atoms of neighbouring layers are denoted with dashed lines.

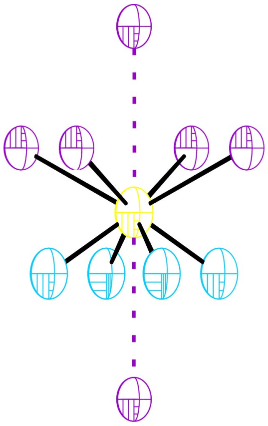

Figure 2
Coordination around the Pb atom (yellow) with anisotropic displacement ellipsoids drawn at the 99% probability level. F atoms are blue and I atoms are purple.

and lattice parameters of microcrystalline PbFI have already been described by Rulmont (1973) and Aurivillius (1976), but no structural parameters of this compound have been published up to now, although high quality powder refinements have been previously performed (Haberkorn, 1988).

The crystal structure of PbFI consists of a lattice of alternating coplanar layers with a sequence I—Pb—F—Pb—I—(I—Pb—F—Pb—I)- extending along [001] (Fig. 1). The coordination polyhedron around the Pb atom is a square antiprism with four short Pb—F bonds and four longer Pb—I bonds (Fig. 2). In contrast to the other lead halide fluorides, PbFCl and PbFBr, where an appreciable interaction between the metal atom and the neighbouring halide layers was observed (and which results in a [4+4+1] coordination with a monocapped square antiprism as corresponding coordination figure), only very weak interactions between the Pb atom and the more distant iodine layers [*d*(Pb—I) *ca* 4.4 Å] can be found. Between two adjacent iodine layers [distance layer–layer = 2.8681 Å, *d*(I—I) within a layer = 4.2374 (3) Å, *d*(I—I) between two I atoms of different layers = 4.1478 (17) Å] only van der Waals interactions stabilize the structure. This is consistent with the very easy cleavage of the crystals along [001].

The single-crystal results presented here are in good agreement with the results obtained from powder data (Haberkorn, 1988).

Experimental

Single crystals of PbFI were synthesized under hydrothermal conditions, starting from stoichiometric amounts of PbI_2 (Riedel-de Haën, pure) and PbF_2 (Aldrich, 99+%). The materials were homogenized by grinding and placed in a 5 ml teflon-lined tube which was two-thirds filled with demineralized water. The tube then was closed, placed in a steel autoclave and heated in a laboratory furnace. The heating rate was 298 → 523 K [2 h], 523 K [10 d], 523 → 298 K [10 h]. Very thin crystals of the title compound were obtained, with plate-like habit and light yellow colour. Microcrystalline samples of PbFI were prepared by reaction of PbI_2 and PbF_2 in sealed and evacuated silica ampoules at 653 K for one week.

Crystal data

PbFI
$M_r = 353.09$
Tetragonal, $P4/nmm$
$a = 4.2374$ (3) Å
$c = 8.800$ (2) Å
$V = 158.00$ (4) Å^3
$Z = 2$
$D_x = 7.422$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 21 reflections
$\theta = 6.8$–$21.8°$
$\mu = 62.89$ mm^{-1}
$T = 293$ (2) K
Plate, light yellow
0.17 × 0.15 × 0.01 mm

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical (*SHELXTL*; Siemens, 1995)
$T_{\min} = 0.023$, $T_{\max} = 0.611$
1724 measured reflections
162 independent reflections
143 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.107$
$\theta_{\max} = 29.5°$
$h = -5 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.098$
$S = 1.13$
162 reflections
10 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 5.98$ e Å^{-3}
$\Delta\rho_{\min} = -2.37$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.008 (3)

Table 1
Selected bond lengths (Å).

Pb—F$^{\rm i}$	2.5631 (5)	Pb—I	4.3915 (18)
Pb—I$^{\rm ii}$	3.3613 (7)	Pb—I$^{\rm iii}$	4.4082 (18)

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

Data collection, cell refinement and data reduction: *PW*1100 *Operation Software* (Philips, 1980); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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