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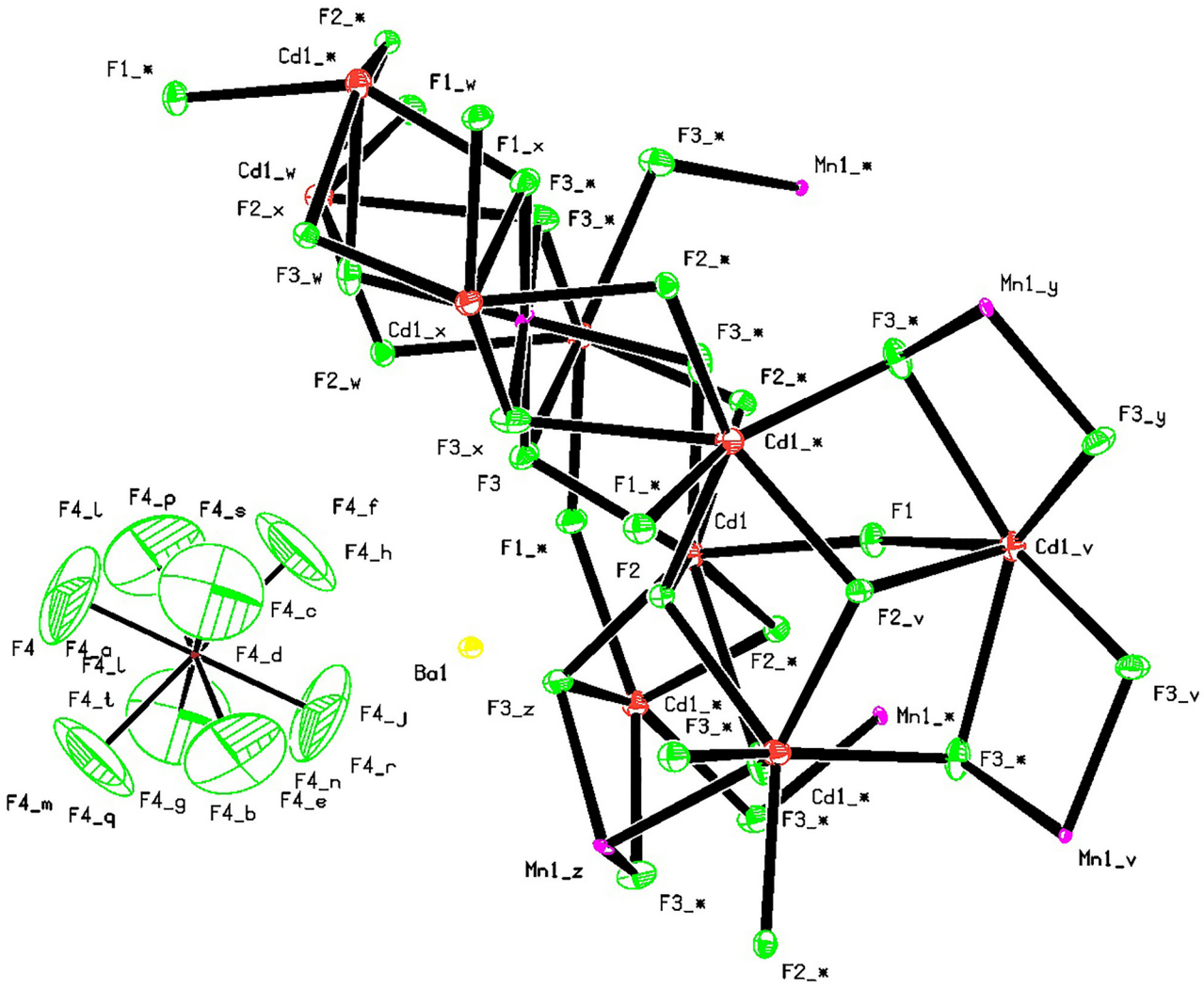
Crystal structure of $Ba_6Cd_{12}Mn_4SiF_{48}$



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Abstract

$Ba_6Cd_{12}Mn_4SiF_{48}$, cubic, $Im\bar{3}$ (no. 204), a = 12.57060(10) Å, V = 1986.41(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0286, $wR_{ref}(F^2)$ = 0.0784, T = 296(2) K.

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Table 1: Data collection and handling.

Crystal:	Pink block
Size:	0.21 × 0.20 × 0.19 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	13.6 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.2°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18,964, 472, 0.093
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 472
$N(param)_{refined}$:	38
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4]

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Ba1	0.500000	0.500000	0.20122 (6)	0.0066 (3)
Cd1	0.14763 (6)	0.500000	0.17432 (6)	0.0100 (3)
Mn1	0.250000	0.750000	0.250000	0.0036 (4)
Si1	0.500000	0.500000	0.500000	0.0008 (14)
F1	0.1083 (7)	0.500000	0.000000	0.0121 (16)
F2	0.3119 (4)	0.500000	0.1070 (4)	0.0089 (11)
F3	0.1896 (4)	0.6070 (3)	0.3111 (3)	0.0142 (9)
F4[a]	0.5765 (8)	0.5765 (8)	0.5765 (8)	0.109 (9)

[a]Occupancy: 0.75.

1 Source of materials

BaF_2 (Alfa Asear, 99 %), CdF_2 (Alfa Asear, 99.9 %), MnF_3 (Alfa Asear, 98 %), SiO_2 (Alfa Asear, 99.0 %) and CF_3COOH (Alfa Aesar, 99 %) were used without any further purification. Crystals of $Ba_6Cd_{12}Mn_4SiF_{48}$ were obtained by hydrothermal method using a diluted CF_3COOH aqueous solution. 0.100 g of BaF_2 (0.570 mmol), 0.0860 g of CdF_2 (0.570 mmol), 0.1276 g of MnF_3 (1.14 mmol), 0.0180 g of SiO_2 (0.300 mmol), 3 ml of CF_3COOH (39 mmol) and 5 ml of H_2O were combined in a 23-ml Teflon-lined stainless autoclave. The autoclave was subsequently closed, gradually heated to 230 °C, held for 24 h, and cooled slowly to room temperature at a rate of 6 °C/h. The mother liquor was decanted from the products, and products were recovered by filtration and washed with distilled water and ethanol. Pink colored block shaped crystals of $Ba_6Cd_{12}Mn_4SiF_{48}$ were isolated by hand sorting. Energy-dispersive X-ray spectroscopy (EDX) analysis of the crystal indicated a chemical composition of $Ba_{6.12}Cd_{11.8}Mn_{3.94}Si_{1.01}F_{47.78}$.

2 Experimental details

The structure was solved by Direct Methods with SHELXS and further refined with the SHELXL program [5]. The crystal structure of $Ba_6Cd_{12}Mn_4SiF_{48}$ was refined as merohedral twin.

3 Comment

Mixed metal fluoride materials have been investigated thoroughly attributable to their diverse crystal structures and significant magnetic, electric, multiferroic, optical, and luminescent properties [6, 7]. A search for barium cadmium manganese silicon fluorides in the Inorganic Structure Database (ICSD, web version 5.1.0) [8] yielded no relevant results. In fact, only six crystal structures could be found in barium manganese fluorides, cadmium manganese fluorides and barium silicon fluorides, for example, $BaMnF_4$ [9], $BaMnF_5$ [10], $BaMnF_5(H_2O)$ [11], $Ba_5Mn_3F_{19}$ [12], $CdMnF_5$ [13], and $BaSiF_6$ [14].

The crystal structure of $Ba_6Cd_{12}Mn_4SiF_{48}$ belongs to the cubic $Im\bar{3}$ (no. 204) space group with lattice parameter $a = b = c = 12.5706(1)$ Å. This structure manifests a complex three-dimensional arrangement comprising distinct sites for Ba, Cd, Mn, and Si. In moiety formula, the structure can be expressed as $[(Cd_{12}^{2+}Mn_4^{2+}F_{42})^{10-}(Si^{4+}F_6)^{2-}]$, with charge balance maintained by six Ba^{2+} cations. The Mn atom coordinates with six fluorine atoms in an octahedral geometry, with Mn–F bond distances of 2.098(4) Å. The Cd atom exhibits coordination with eight fluorine atoms in a distorted square antiprismatic geometry, and the cadmium-fluorine bond distances range from 2.231(6) to 2.582(5) Å. The Ba atom resides in 12-fold coordination environments, with Ba–F distances ranging from 2.645(6) to 3.108(3) Å. The Si atom demonstrates coordination with eight fluorine atoms, each partially occupied at 0.75, arranged in a cubic geometry. Bond valence sum (BVS) calculations [15] resulted in values of 2.15, 2.03, and 2.04 for Ba, Cd, and Mn, respectively.

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