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FeBiS₂Cl – A new iron-containing member of the *MPnQ₂X* family

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Abstract: The new sulfochloride FeBiS₂Cl is obtained as a black powder following a mechanochemical synthesis procedure. The product crystallizes in the orthorhombic space group *Cmcm* (no. 63) with lattice parameters $a = 3.82142(7)$, $b = 12.2850(2)$ and $c = 9.2911(2)$ Å. While the iron atom has an octahedral coordination environment, the bismuth atom is coordinated in the form of a bicapped trigonal prism. Both cation polyhedra form alternating layers, for iron built up of corner sharing octahedra along the *c* axis and edge sharing ones along the *a* axis. The bismuth polyhedra are connected through shared faces along the *c* axis and common edges along the *a* axis. Because of the distribution of sulfur and chlorine on a mixed anion site, the bismuth atoms occupy split positions. Experimental observations are supported by theoretical calculations.

Keywords: bismuth; iron; mechanochemical synthesis; quantum-chemical calculations; Rietveld refinement; sulfochloride.

Dedicated to: Professor Robert Glaum on the occasion of his 60th birthday.

1 Introduction

There is a small variety of compounds of the general formula *MPnQ₂X* with *M* = transition metal, *Pn* = pnictide, *Q* = chalcogenide, and *X* = halide [1–7]. Looking at sulfur as the chalcogenide, different combinations of elements from the other groups have been synthesized, using manganese

or cadmium as the bivalent transition metal, antimony or bismuth as the pnictide, and chlorine or bromine as the halide. While the sulfochlorides MnBiS₂Cl [1], MnSbS₂Cl [2], CdBiS₂Cl [3], and CdSbS₂Cl [3] all crystallize in the orthorhombic space group *Pnma*, the corresponding sulfo-bromides [3–5] exhibit the monoclinic space group *C2/m*. However, with iron as the transition metal, only the sulfo-bromides [8] but not the sulfochlorides are known. In this work, we present the synthesis and the crystal structure of the first iron-containing sulfochloride of this family, FeBiS₂Cl.

2 Results and discussion

The sulfochloride FeBiS₂Cl has been synthesized by a two-step process with mechanochemical ball milling followed by annealing in nitrogen atmosphere. The product was obtained as a black powder that is air stable. Heating the powder to or above $T = 673$ K for a longer time results in the formation of byproducts, therefore the annealing process is discontinued after a few minutes at 673 K. Temperature dependent X-ray diffraction experiments show no phase transition, but the thermal decomposition of the product leads mainly to the binary sulfides. Contrary to other known sulfochlorides mentioned in the introduction, this compound does not crystallize in the space group *Pnma*. Comparing the X-ray diffraction pattern of the synthesized compound with data of MnBiS₂Cl, the diffraction patterns appear similar, but for FeBiS₂Cl some reflections are missing, indicating a space group of higher symmetry. Using JANA 2006 [9] and implemented programs, the orthorhombic space group *Cmcm* was identified as the most probable space group for FeBiS₂Cl, which is a supergroup of *Pnma*. Further investigations of the crystal structure show that it is closely related to two other bismuth-containing sulfochlorides, namely AgBiS₂Cl and CuBiS₂Cl, which also crystallize in space group *Cmcm* [10].

The X-ray diffraction pattern of FeBiS₂Cl is shown in Figure 1. Further details and the results of the Rietveld refinement [11] are depicted in Table 1. The experimental diffraction pattern is in good agreement with the calculated one, resulting in a residual value of $R_p = 0.0123$. Wyckoff positions, atomic coordinates and Debye-Waller factors are

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Figure 1: X-ray diffraction pattern of FeBiS₂Cl with the results of the Rietveld refinement; experimental data in red, calculated data in black, and difference plot in blue.

presented in Table 2. Isotropic displacement parameters were refined for all atoms.

Because it is not possible to distinguish sulfur from chlorine with X-ray diffraction methods, theoretical calculations were used to determine the anion distribution on the two possible anion positions 4c and 8f. For these calculations, the space group and the lattice parameters of FeBiS₂Cl were taken from the present experiments (Table 1) and fixed. All possible S/Cl occupancies within the primitive unit cell containing two formula units (Fe₂Bi₂S₄Cl₂) were considered. For each configuration, the atom

positions were optimized within the respective symmetry restrictions. The results show an unexpected anion distribution: In the most stable configuration, the 4c anion Wyckoff site is completely occupied by sulfur, while the 8f position is a mixed anion position occupied equally by sulfur and chlorine. The optimized fractional coordinates are shown in Table 3. Compared to the configuration presented in Table 3, the other 2S/2Cl configurations where site 4c is fully occupied by sulfur are less stable by 10 kJ mol⁻¹ and 24 kJ mol⁻¹ per formula unit, respectively. Configurations with a mixed S/Cl occupation of site 4c are less stable by 36 kJ mol⁻¹ and 53 kJ mol⁻¹ per formula unit, respectively. The configuration where both chlorine atoms occupy site 4c is 102 kJ mol⁻¹ per formula unit less stable.

Considering this for further Rietveld refinements, sulfur completely occupies the 4c position, and the occupation of this position was set to its ideal value. The position 8f was split to be occupied equally with sulfur and chlorine. The sum of the occupancies was kept at the ideal value and the coordinates as well as the isotropic displacement parameters were kept identical. Refinement with these settings did not lead to acceptable *R* values. A significant drop in the *R* values could be observed after applying the refinement of anisotropic displacement parameters for the bismuth atom on Wyckoff position 4c, which led to a deformed ellipsoid with a strong elongation along the *c* axis. Therefore, the displacement parameters were set back to isotropic, and the *z* coordinate of the bismuth atom was allowed to be refined, leading to a split position of the bismuth atom with two possible positions stacked along the *c* axis and bismuth now occupying the Wyckoff position 8f instead of 4c. The occupancies of the bismuth atom on position 8f and of the iron atom on position 4a were set to their ideal value. Unlocking them to be refined led to no significant improvement of the *R* values. In the final refinement cycle, all parameters causing correlations greater than 0.9 were fixed.

Similar to related compounds, the bivalent cation, in this case iron, is surrounded octahedrally. It is coordinated by two sulfur atoms on Wyckoff position 4c and four anions on the Wyckoff position 8f, forming a layer of octahedra corner sharing along the *c* axis and edge sharing along the *a* axis (Figure 2).

Between this layer of octahedrally coordinated iron atoms another layer of bismuth atoms coordinated by bicapped trigonal prisms is built. These are face sharing along the *a* axis and edge sharing along the *c* axis, in the same way as in AgBiS₂Cl₂ and CuBiS₂Cl₂ [10]. But different from these compounds, the bismuth atom occupies a split position. As already mentioned above, instead of a 4c position, bismuth occupies half of an 8f position with two

Table 1: Results of the Rietveld refinement for FeBiS₂Cl.

Empirical formula	FeBiS ₂ Cl
<i>M_r</i>	364.4
Space group	<i>Cmcm</i> (no. 63)
Crystal system	Orthorhombic
<i>Z</i>	4
<i>a</i> /Å	3.82140(7)
<i>b</i> /Å	12.2850(2)
<i>c</i> /Å	9.2911(2)
<i>V</i> /Å ³	436.177(15)
$\rho_{\text{calc}}/\text{g cm}^{-3}$	5.55
Refined parameters	50
Constraints	3
<i>R_p</i> ; <i>wR_p</i> ^b	0.0123; 0.0166
<i>R_{exp}</i> ; <i>S</i> (all)	0.0088; 1.88
<i>R_F</i> (obs ^a ; all)	0.0297; 0.0305
<i>wR_F</i> ^b (obs ^a ; all)	0.0348; 0.0349
<i>R_B</i> (obs ^a)	0.0467
$\Delta\rho^b$ (min; max)/fm Å ⁻³	-1.17; 1.05

^a*I* > 3 $\sigma(I)$. ^b*w* = 1/[$\sigma^2(I)$ + (0.01)²].

Table 2: Refined atomic parameters for FeBiS₂Cl (standard deviation in parentheses).

Element	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	s.o.f.	<i>U</i> _{iso} (Å ²)
Fe	4 <i>a</i>	1/2	1/2	1/2	1	0.0121(7)
Bi	8 <i>f</i>	0	0.28430(4)	0.20583(9)	0.5	0.0192(4)
S	4 <i>c</i>	1/2	0.4327(2)	1/4	1	0.0155(11)
S/Cl	8 <i>f</i>	0	0.36788(15)	0.5563(2)	1	0.0151(8)

Table 3: Optimized atom positions of the most stable S/Cl configuration in FeBiS₂Cl calculated with PW1PW.

Element	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>
Fe	4 <i>a</i>	1/2	1/2	1/2
Bi	8 <i>f</i>	0	0.2870	0.2120
S	4 <i>c</i>	1/2	0.4377	0.2490
S	8 <i>f</i>	0	0.3756	0.5439
Cl	8 <i>f</i>	0	0.3773	0.5473

Figure 2: Crystal structure of FeBiS₂Cl with the layers of iron (petrol blue octahedra) and bismuth (grey polyhedra). Two unit cells are shown for more clarity. In every bismuth polyhedron, only one possible position is occupied.

possible positions stacked along the *c* axis. This may be derived from the particular anion distribution on the mixed anion position 8*f*. The bicapped trigonal prism is formed by two sulfur atoms on position 4*c* forming one edge of the trigonal prism and six anions on position 8*f*, with three anions being above the bismuth atom and three below following the *c* axis (Figure 3a).

The two possible bismuth positions have mirrored distances to the anions above and below with the mirror plane being perpendicular to the *c* axis incorporating the two sulfur atoms on position 4*c*. The most stable configuration derived from theoretical calculations is obtained if the shorter distances correspond to a coordination with sulfur and the longer distances to a coordination with

chlorine: Bismuth is coordinated by five sulfur atoms (bond distances 2.615 Å, 2.685 Å (×2), 3.174 Å (×2)) and three chlorine atoms (bond lengths 3.307 Å, 3.567 Å (×2)).

Therefore, the anions on one “side” of the bismuth atom are always of the same kind (Figure 3b,c). In addition, those calculations predict the formation of alternating waved chlorine and sulfur layers perpendicular to the *c* axis. This would cancel out the observed split position for the bismuth atom and require a subgroup of *Cmcm* to allow this distinct anion distribution on position 8*f*. All subgroups allowing such a distribution have been tested for refinement (*C2/m*, *Cmc2₁*, *Amm2*), but none of them led to acceptable *R* values without again establishing a split position for the bismuth atom. We assume that because of the quenching during the annealing process the proposed long-range order is not formed. Only the above-mentioned short-range order around every bismuth atom is established, with three anions on one side of the bismuth atom always being of one kind, but there is no formation of alternating anion layers along the whole structure, making a split position for the bismuth atom necessary.

This split position does not occur in the related compounds AgBiS₂Cl₂ and CuBiS₂Cl₂. Due to their anion ratio and distribution there is no mixed anion position. The 4*c* position is completely occupied by sulfur and the 8*f* position by chlorine [10]. Looking at the coordination prism of the bismuth atom, which is similar to the one depicted in Figure 3a, this means that there is no difference in the coordination above and below the bismuth atom and therefore no split position is observed.

It has to be mentioned that the electronic band gap calculated with PW1PW ranges from 2.1 to 2.8 eV for all investigated configurations (the largest value was obtained for the most stable S/Cl configuration). This is not in agreement with the observed black color of the compound. It is therefore likely that the synthesized compound is partially disordered and/or contains impurities and defects, or the black color derives from a partial oxidation of bivalent iron to trivalent iron. Further research on the anion ordering with long-term annealing experiments to investigate whether sulfur and chlorine are distributed

Figure 3: (a) Polyhedron of the bismuth atom (grey) with sulfur atoms on position 4c (yellow) and the anion position 8f (green); (b) coordination and bond lengths of the “upper” bismuth atom (anions with shorter distances colored in pink); (c) coordination and bond lengths of the “lower” bismuth atom (anions with shorter distances in pink).

statistically or in distinct layers and a deeper insight into the oxidation state of iron is currently in progress.

3 Experimental section

3.1 Synthesis of FeBiS₂Cl

FeBiS₂Cl was synthesized using a high-energy planetary ball mill (Fritsch Pulverisette 7 *classic line*) followed by an annealing step at elevated temperatures to increase the crystallinity of the product. As starting materials FeCl₂ (99.5%, Alfa Aesar) and the binary sulfides Bi₂S₃ (99%, Sigma-Aldrich) and FeS (99%, abcr) were used in stoichiometric amounts and filled into a zirconia jar (45 mL) with six zirconia balls (1.5 cm in diameter). Milling was carried out under a nitrogen atmosphere at 400 rpm for a total of 4 h. After each hour the milling process was paused for 30 min to avoid overheating of the machine. The ground product was annealed in a tube furnace under a flowing nitrogen atmosphere (flow rate 5 L h⁻¹). The furnace was heated with a rate of 600 K h⁻¹ to reach 673 K after which the sample was quenched by opening the furnace to prevent the formation of byproducts. The product is obtained as a black powder.

3.2 Crystal structure determination of FeBiS₂Cl

X-ray powder diffractograms were measured using a PANalytical X'Pert PRO diffractometer in Bragg-Brentano geometry with nickel-filtered CuKα radiation. Data was collected at room temperature over an angular range of 10–120° with a step size of 0.026° and an exposure time of 60 s at each point. *In-situ* high-temperature X-ray powder diffractograms were measured using a Rigaku SmartLab 3 kW diffractometer with CuKα radiation in Bragg-Brentano geometry. Data was collected over an angular range of 10–70° with a step size of 0.015°. Diffractograms were measured

every 25 K in the range of 298–873 K. During the measurement the sample was kept under a flowing nitrogen atmosphere (flow rate of 200 mL min⁻¹).

For leBail fit, structure solution, and final Rietveld refinement, the program system JANA2006 [9] and its implemented programs were used. After the initial leBail fit the space group was determined to be *Cmcm* using the JANA2006 *Symmetry wizard* [9]. Following this, the structure was solved by using the program SUPERFLIP [12]. Finally, Rietveld refinement [11] was carried out applying a pseudo-Voigt function to fit the peak profiles. Displacement and transparency corrections were refined as well as reflection asymmetry correction according to Berar-Baldinozzi [13] and roughness correction according to Pitschke, Herrmann and Mattern [14].

For graphical representations the program DIAMOND was used [15].

Further details of the crystal structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: <https://www.ccdc.cam.ac.uk/structures/?> by quoting the deposition number CSD-2011933.

3.3 Theoretical calculations

The stability of all possible anion configurations within the primitive unit cell of FeBiS₂Cl was calculated at DFT level using the crystalline-orbital program package CRYSTAL17 (version 1.0.2) [16]. The calculations were performed with the hybrid functional PW1PW [17] that was successfully applied to the calculation of structural, energetic and electronic properties of chalcogenides before [18]. The revised version of triple-zeta valence plus polarization basis sets for solids (rev2-POB) [19] were used for Fe, S and Cl. A scalar-relativistic effective core potential (ECP60) was used to represent the core electrons of Bi. The valence electrons were described with a triple-zeta basis set derived by Heifets et al. [20].

Strict truncation thresholds (10⁻⁷, 10⁻⁷, 10⁻⁷, 10⁻⁷, 10⁻¹⁴) were set for the calculation of the Coulomb and Exchange

series. A $4 \times 4 \times 2$ Monkhorst-Pack grid was used for the integration in reciprocal space.

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