Synthesis, crystal structure, magnetic and electronic properties of the caesium-based transition metal halide Cs$_3$Fe$_2$Br$_9$†

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The diversity of halide materials related to important solar energy systems such as CsPb$_3$X$_3$ (X = Cl, Br, I) is explored by introducing the transition metal element Fe. In particular a new compound, Cs$_3$Fe$_2$Br$_9$ (space group P6$_3$/mmc with a = 7.5427(8) and c = 18.5849(13) Å), has been synthesized and found to contain 0D face-sharing Fe$_2$Br$_9$ octahedral dimers. Unlike its isomorph, Cs$_3$Bi$_2$Br$_9$, it is black in color, has a low optical bandgap of 1.65 eV and exhibits antiferromagnetic behavior below $T_N = 13$ K. Density functional theory calculations shed further light on these properties and also predict that the material should have anisotropic transport characteristics.

1. Introduction

In the past few years, lead halide perovskites such as APb$_3$I$_3$ (A = methylammonium, MA, and cesium) have attracted much attention as photovoltaic materials because of their remarkable photo-conversion efficiency in solar cell devices.$^{1,2}$ Due to the toxicity of lead and the intrinsic moisture sensitivity of the lead(II) compounds, a search for environmentally friendly alternatives has been undertaken.$^3$ Several perovskite-related families have been proposed, such as double perovskites where Pb$_2+$ is replaced by iso electronic Bi/In/Sb$^{3+}$ and a monovalent cation, e.g. (MA)$_2$KBrI$_6$, (MA)$_2$TlBiBr$_6$, (MA)$_2$AgBiBr$_6$ and the inorganic phases Cs$_2$AgBX$_6$ (X = Cl, Br and B = Bi, In).$^4$–$^{11}$ Another popular candidate family is A$_3$M$_2$I$_9$, where A = K$^+$,Rb$^+$, Cs$^+$, etc., M = Bi$^{3+}$ and Sb$^{3+}$, consisting of either corner- and edge-sharing MI$_6$ octahedral layers or face-sharing MI$_6$ dimers.$^{12}$–$^{16}$ All of the above systems exhibit very interesting optoelectronic properties.

Transition metals have attracted our attention as a method of tuning the optoelectronic properties. For example, using Fe$^{3+}$ to replace Bi$^{3+}$ can reduce the bandgap: Cs$_2$NaFeCl$_6$ which adopts a double perovskite architecture (Fig. S1, ESI†) is red, while its Cl analogues with other trivalent cations show much lighter colours. For instance, Cs$_2$NaBiCl$_6$ is yellow$^{17}$ while the Cs$_2$NaLnCl$_6$ (Ln = Lanthanide) phases are mostly white.$^{18}$ A much darker color is expected for the hypothetical Cs$_2$NaFeBr$_6$, but our attempts to synthesize this compound yielded black octahedral crystals of composition Cs$_2$FeBr$_5$O octahedral monomers in which the oxygen is part of a water molecule, as in the known Cs$_2$FeCl$_5$H$_2$O.$^{19}$ The dimensionality indicates the degree of connectivity of the octahedra. In this case the octahedra are discrete. Incorporating Fe into the A$_3$Bi$_2$X$_9$ (X = Cl, Br and I) family turns out to have a long history. Cs$_3$Fe$_2$Cl$_9$, which is dark red in color, was reported to form two polymorphs: a 2D layered system with P$3$m1 symmetry and 0D dimeric system in space group P6$_3$/mmc.$^{20,21}$ In the latter, both intradimer and interdimer magnetic interactions are present, and the two competing interactions lead to very interesting magnetic properties. In the present work, we report a new compound, Cs$_3$Fe$_2$Br$_9$ (CCDC 1575068), which is isostructural with Cs$_3$Bi$_2$J$_9$ (red)$^{13}$ and (MA)$_2$Bi$_2$J$_9$ (red)$^{14}$ yet is black in color. Its variable temperature behavior, thermal stability, optical and magnetic properties are investigated in combination with density functional theory (DFT) calculations.

2. Experimental and computational methods and results

2.1 Synthesis

A two-step synthesis method was used, involving both hydrothermal and room temperature crystallization. 2 mmol CsBr (99.9%, Sigma Aldrich), 1 mmol FeCl$_3$·6H$_2$O (> 99%, Sigma Aldrich) together with 1.5 ml HBr acid (47 wt%) were placed in...
Fe₂Br₉ octahedral dimers with Cs serving as bridging atoms. Cs₃Fe₂Br₉ crystallizes in the hexagonal space group P6₃/mmc (a = 7.5427(8) and c = 18.5849(13) Å). It consists of face-sharing Fe₂Br₉ octahedral dimers with Cs serving as bridging atoms between the dimers (Fig. 1a and b). The octahedra are slightly distorted, with two sets of Fe–Br bonds (2.427(1) Å and 2.701(2) Å) and distorted Br–Fe–Br angles (80.76(6)°, 90.55(3)° and 97.01(7)°), compared to the nominal octahedral angle of 90°. Due to the Coulombic repulsive force between the cations within the dimer (Fe–Fe distance = 3.585(3) Å), the Fe³⁺ ions are displaced outwards with respect to the shared face. Therefore, the smallest octahedral angles and longer Fe–Br bonds are found with the shared Br⁻ ions (Fig. 1) and the largest angles and shorter Fe–Br distances are from the unshared ones. According to the interatomic distances, the bond strengths between Fe³⁺ and unshared Br⁻ are stronger than those with shared Br⁻ ions. Moreover, the angular distortion of the Brshared–Fe–Brunshared angle is minor (90.55°). The shortest distance between Cs and Br is 3.762(1) Å.

During the hydrothermal process, reaction (1) dominates and almost no black Cs₃Fe₂Br₉ is formed. Even using exact stoichiometric ratios of the starting reagents does not result in the target material. However, black octahedral crystals of Cs₃Fe₂Br₉, ~0.5 mm in size, can be collected after standing at room temperature for 3 weeks. The sample is soluble in most polar solvents, including water, ethanol and acetone.

### 2.2 Crystallographic studies

Cs₃Fe₂Br₉ crystallizes in the hexagonal space group P6₃/mmc (a = 7.5427(8) and c = 18.5849(13) Å). It consists of face-sharing Fe₂Br₉ octahedral dimers with Cs serving as bridging atoms between the dimers (Fig. 1a and b). The octahedra are slightly distorted, with two sets of Fe–Br bonds (2.427(1) Å and 2.701(2) Å) and distorted Br–Fe–Br angles (80.76(6)°, 90.55(3)° and 97.01(7)°).

[Fig. 1](#) (a) Crystal structure of Cs₃Fe₂Br₉ viewed along the c-axis, (b) view along the b-axis showing of the Fe₂Br₉ dimers. The angles and bond lengths illustrate the distortion of the octahedra. The subscripts s and u indicate shared and unshared Br anions respectively and the arrows indicate the direction of Coulombic repulsion between cations, (c) cell volume and (d) lattice parameters as a function of temperature measured using single crystal X-ray diffraction.

### 2.3 Thermal analysis

Thermal stability was investigated using an SDT (simultaneous differential scanning calorimetry (DSC) – thermogravimetric analysis (TGA) Q600 instrument. Powder samples were heated from room temperature to 1123 K at 10 K min⁻¹ under an air flow of 100 ml min⁻¹. Cs₃Fe₂Br₉ is stable until 537.5 K and then experiences a two-step decomposition process (Fig. 2). When the sample is heated, moisture and residual HBr at the particle surfaces start to evaporate, resulting in a small weight loss (~3.6%) at the beginning of the curve. For comparison, the thermal stability of its bismuth analogues Cs₃Bi₂I₉ and MA₃Bi₂I₉ were also measured; the former decomposed at 636.4 K, while the latter was stable until 529.3 K (Fig. S5 and S6, ESI†).

### 2.4 Optical characterization

The optical bandgap was measured on a PerkinElmer Lambda 750 UV-Visible spectrometer in the absorption mode with a...
The presence of Fe in the material suggests that it could exhibit magnetic ordering due to unpaired 3d electrons. To examine this possibility, spin-polarized calculations were performed on the optimized structure in the ferromagnetic (FM) state and three possible antiferromagnetic (AFM) states. It was found that one of the AFM states in which neighboring Fe atoms have opposite spin orientation is significantly lower in energy than either the FM or non-magnetic states, by 80 meV F.U.\(^{-1}\) and 335 meV F.U.\(^{-1}\) respectively (see Table S2 (ESI\(^{†}\)) for details). The calculations therefore predict that at very low temperatures Cs\(_3\)Fe\(_2\)Br\(_9\) prefers to be antiferromagnetic. The calculated magnetic moment on each Fe atom is 3.38 \(\mu_B\). This value is lower than the value of 5.79 \(\mu_B\) obtained from analysis of the magnetic susceptibility data in the higher temperature paramagnetic region (see below). There are several reasons for this, including the well-known reduction in spin in magnetically ordered structures due to covalency. For example, neutron scattering measurements on FeCl\(_3\) show that the spin is reduced to 4.7(3) \(\mu_B\) in the antiferromagnetic phase.\(^{26}\) Fig. 3 shows charge density isosurfaces corresponding to the HOCO and LUCO for the lowest energy AFM state.

In order to determine an improved band structure for Cs\(_3\)Fe\(_2\)Br\(_9\), the HSE06 hybrid exchange–correlation functional was used,\(^{27}\) although it is acknowledged that GW would normally be the preferred method. The calculation was performed on the non-magnetic state to contain the cost of the calculation and because previous work has indicated that, while HSE06 provides a reasonable band structure, it may not be adequate for magnetic properties.\(^{28}\) The material is found to have a 2.254 eV direct band gap which occurs at the \(\Gamma\) point with a relatively flat band structure (Fig. 3). At the band edge it is possible to calculate the effective masses in the parabolic approximation (Table 1). The values indicate a high anisotropy with reduced transport along the \(c\)-direction (\(\Gamma \rightarrow A\)). The Fe atoms have been described with \(3p^5 3d^7 4s^2\) valence electrons, while other core states have been substituted by the pseudo-potential. The valence band maximum (VBM) contains Fe 3d and Br 4p states, whereas the conduction band minimum (CBM) contains mostly Fe 3d, Fe 4s and Br 4p states.

### 2.5 Density functional calculations

The DFT calculations were performed using the projector augmented wave (PAW) method as implemented in VASP.\(^{24}\) The experimental structure obtained at room temperature was fully optimized using the PBEsol exchange–correlation functional\(^{25}\) which reduced the atomic forces below 1 meV Å\(^{-1}\) at effectively zero Kelvin (see ESI\(^{†}\) for further computational details). The resulting atomic positions are given in Table S1 (ESI\(^{†}\)). The presence of Fe in the material suggests that it could exhibit magnetic ordering due to unpaired 3d electrons. To examine this possibility, spin-polarized calculations were performed on the optimized structure in the ferromagnetic (FM) state and three possible antiferromagnetic (AFM) states. It was found that one of the AFM states in which neighboring Fe atoms have opposite spin orientation is significantly lower in energy than either the FM or non-magnetic states, by 80 meV F.U.\(^{-1}\) and 335 meV F.U.\(^{-1}\) respectively (see Table S2 (ESI\(^{†}\)) for details). The calculations therefore predict that at very low temperatures Cs\(_3\)Fe\(_2\)Br\(_9\) prefers to be antiferromagnetic. The calculated magnetic moment on each Fe atom is 3.38 \(\mu_B\). This value is lower than the value of 5.79 \(\mu_B\) obtained from analysis of the magnetic susceptibility data in the higher temperature paramagnetic region (see below).

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### 2.6 Magnetic measurements

Magnetic susceptibility measurements, \(\chi(T) = M(T)/H\), were conducted using a Quantum Design Magnetic Properties Measurement System (MPMS3) with a superconducting interference device (SQUID) magnetometer. Measurements were made after cooling in zero field (ZFC) and in a measuring field (FC) of \(\mu_B H = 0.01 T\) over the temperature range \(2 \leq T \leq 300 K\). Cs\(_3\)Fe\(_2\)Br\(_9\) shows antiferromagnetic behavior with a Néel temperature \(T_N = 13 K\) (Fig. 4), higher than that of analogous Cs\(_3\)Fe\(_2\)Cl\(_9\) which also exhibits an antiferromagnetic long range order at \(T_N = 5.3 K\).\(^{29}\) The results are in good agreement with the DFT calculations.

### Table 1 Calculated effective masses (relative to the rest mass \(m_0\))

| \(\Gamma\) → \(M\) | \(\Gamma\) → \(K\) | \(\Gamma\) → \(A\) |
|-----------------|-----------------|-----------------|
| \(m^*/m_0\)     | \(-0.11\)       | \(-0.06\)       | \(-1.02\)       |
| \(m^*/m_0\)     | \(0.25\)        | \(0.16\)        | \(13.87\)       |
Fig. 4  Magnetic susceptibility as a function of temperature, blue: experimental, red square: fitted curve using dimer model. The inset illustrates the definition of J, J_p, and J_c. Cs atoms are not included for clarity.

Applying the Curie–Weiss law in the paramagnetic region (from 50 K to 300 K), a negative Weiss constant of \(-36.10(3)\) K was obtained, as expected for an antiferromagnetic compound (Fig. S7, ESI†) and the calculated effective magnetic moment \(\mu_{\text{eff}}\) was 5.79(4) \(\mu_B\). In order to obtain a comprehensive \(J\) fitting from 2 K to 300 K, a weakly coupled dimer model was applied (see ESI† for fitting formula).30 This system contains Fe\(^{3+}\) ions as dimeric units Fe\(_2\)Br\(_9\), with three distinct Fe–Fe distances (3.585(3), 7.179(2) and 7.543(1) Å) corresponding to intradimer (J) and interdimer \((J_p + J_c)\) interactions, respectively. The dominant intradimer exchange yields \(J = -8.2\) K, while the weak interdimer interactions between the Fe\(^{3+}\) of neighbouring dimers are given as \(J_p + J_c = -3.4\) K. The intradimer interactions are weaker than those in the Cr counterpart, Cs\(_3\)Cr\(_2\)Br\(_9\), which was reported to have \(J_p + J_c = -1.1\) K due to the longer distances (7.420(1) and 7.507(1) Å).30 In the case of Cs\(_3\)Fe\(_2\)Cl\(_9\), both intra- and interdimer interactions are smaller \((J = -2.4)\) K and \(J_p + J_c = -1.2\) K for single crystals.29

3. Conclusions

We have synthesized black crystals of Cs\(_3\)Fe\(_2\)Br\(_9\) and determined its crystal structure. Cs\(_3\)Fe\(_2\)Br\(_9\) crystallizes in the hexagonal space group \(P6_3/mmc\) and the structure contains Fe\(_2\)Br\(_9\) face-sharing octahedral dimers. The Fe–Br bond strengths differ between the shared and unshared faces, and the distorted octahedra tend to become more symmetrical upon cooling due to the reduced cation–cation Coulombic repulsion. The compound is thermally stable up to 537.5 K, and has an optical bandgap of 1.65 eV. DFT calculations indicate that the band gap is direct and also predict reduced transport along the c-direction. Magnetic susceptibility measurements show antiferromagnetic behavior, with \(T_N = 13\) K, and can be fitted with a weakly coupled dimer model. The spin polarized DFT calculations agree with this behavior at low temperatures and predict which antiferromagnetic configuration is preferred.

Conflicts of interest

There are no conflicts to declare.

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