The diversity of halide materials related to important solar energy systems such as CsPbX₃ (X = Cl, Br, I) is explored by introducing the transition metal element Fe. In particular a new compound, Cs₃Fe₂Br₉ (space group P6₃/mmc with a = 7.5427 Å and c = 18.5849(13) Å), has been synthesized and found to contain 0D face-sharing Fe₂Br₉ octahedral dimers. Unlike its isomorph, Cs₂Bi₂I₉, it is black in color, has a low optical bandgap of 1.65 eV and exhibits antiferromagnetic behavior below Tₘ = 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 APbI₃ (A = methylammonium, MA, and cesium) have attracted much attention as photovoltaic materials because of their remarkable photo-conversion efficiency in solar cell devices. 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. Several perovskite-related families have been proposed, such as double perovskites where Pb²⁺ is replaced by isoelectronic Bi/In/Sb³⁺ and a monovalent cation, e.g. (MA)₃Bi₂I₉, (MA)₂TlBiBr₆, (MA)₂AgBiBr₆ and the inorganic phases Cs₃AgBX₆ (X = Cl, Br and B = Bi, In). Another popular candidate family is A₃M₂I₉, where A = K⁺, Rb⁺, NH₄⁺, MA⁺, Cs⁺ etc., M = Bi³⁺ and Sb³⁺, consisting of either corner- and edge-sharing MI₆ octahedral layers or face-sharing MI₆ dimers. All of the above systems exhibit very interesting optoelectronic properties.

Transition metal halide Cs₃Fe₂Br₉ has a double perovskite architecture (Fig. S1, ESI†) is red, while its Cl analogues with other trivalent cations show much lighter colours. For instance, Cs₂NaBiCl₆ is yellow while the Cs₂NaLnCl₆ (Ln = Lanthanide) phases are mostly white. A much darker color is expected for the hypothetical Cs₂NaFeCl₆, but our attempts to synthesize this compound yielded black octahedral crystals of composition Cs₂FeBr₅ (Fig. S2, ESI†), crystallizing in space group Pnma. This material consists of 0D FeBr₅ octahedral monomers in which the oxygen is part of a water molecule, as in the known Cs₂FeCl₃·H₂O. The dimensionality indicates the degree of connectivity of the octahedra. In this case the octahedra are discrete.

Incorporating Fe into the A₃Bi₂X₉ (X = Cl, Br and I) family turns out to have a long history. Cs₃Fe₂Cl₉, which is dark red in color, was reported to form two polymorphs: a 2D layered system with P3m1 symmetry and 0D dimeric system in space group P6₃/mmc. 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, Cs₃Fe₂Br₉ (CCDC 1575068), which is isostructural with Cs₂Bi₂I₉ (red) and (MA)₂Bi₂I₉ (red), 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 FeCl₃·6H₂O (≥ 99%, Sigma Aldrich) together with 1.5 ml HBr acid (47 wt%) were placed in...
a 23 ml stainless steel Parr autoclave and heated at 160 °C for 3 days. Intermediate products of brown needle shaped crystals of CsFeBr₃ (Fig. S3, ESI†) were formed. The Teflon autoclave was then left in the fume hood at room temperature (> 15 °C) and black crystals formed after one week. The following chemical reactions take place during the synthesis:

\[
\text{CsBr + FeCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{HBr} \rightarrow \text{CsFeBr}_4 + 3\text{HCl} + 6\text{H}_2\text{O} \quad (1)
\]

\[
\text{CsBr + 2CsFeBr}_4 \rightarrow \text{Cs}_3\text{Fe}_2\text{Br}_9 \quad (2)
\]

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 \((a = 7.5427(8) \text{ Å}, c = 18.5849(13) \text{ Å})\). It consists of face-sharing FeBr₉ 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.

Variable temperature single crystal X-ray diffraction suggests no phase transition down to 120 K. The thermal expansion coefficients are approximately linear with \(x_a = 45.3 \text{ MK}^{-1}, \ x_c = 39.6 \text{ MK}^{-1}\), giving \(x_v = 131.2 \text{ MK}^{-1}\). The repulsion between the Fe³⁺ ions in the dimeric unit decreases upon cooling, as shown by the less distorted octahedral dimer and reduced interatomic Fe···Fe distances (Fig. S4, ESI†). As a result, negative expansion occurs for the shorter bonds and positive thermal expansion is found for the longer bonds. A similar phenomenon is observed for the octahedral angles: on cooling, the smaller angles tend to increase, while the larger angles decrease.

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 MA₃Bi₂I₆ 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
presence of Fe in the material suggests that it could exhibit zero Kelvin (see 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. 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, 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. 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$^6$3d$^7$4s$^1$ as 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.

### 2.6 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 $\mu_0 H = 0.01$ T over the temperature range $2 \leq T \leq 300$ K. Cs$_3$Fe$_2$Br$_9$ shows antiferromagnetic behavior with a Neél 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. The results are in good agreement with the DFT calculations.
3. Conclusions

We have synthesized black crystals of Cs$_2$Fe$_2$Br$_9$ and determined its crystal structure. Cs$_2$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 form octahedral dimers. The Fe–Br bond strengths differ between the shared and unshared faces, and the distorted octahedra tend to form octahedral dimers. The Fe–Br bond strengths differ between the shared and unshared faces, and the distorted octahedra tend to form octahedral dimers. The Fe–Br bond strengths differ between the shared and unshared faces, and the distorted octahedra tend to form octahedral dimers. The Fe–Br bond strengths differ between the shared and unshared faces, and the distorted octahedra tend to form octahedral dimers. The Fe–Br bond strengths differ between the shared and unshared faces, and the distorted octahedra tend to form octahedral dimers.

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Conflicts of interest

There are no conflicts to declare.

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Notes and references