Antiperovskite Chalco-Halides
Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, and Ba$_3$(FeSe$_4$)Br with Spin Super-Super Exchange

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Perovskite-related materials have received increasing attention for their broad applications in photovoltaic solar cells and information technology due to their unique electrical and magnetic properties. Here we report three new antiperovskite chalco-halides: Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, and Ba$_3$(FeSe$_4$)Br. All of them were found to be good solar light absorbers. Remarkably, although the shortest Fe-Fe distance exceeds 6 Å, an unexpected anti-ferromagnetic phase transition near 100 K was observed in their magnetic susceptibility measurement. The corresponding complex magnetic structures were resolved by neutron diffraction experiments as well as investigated by first-principles electronic structure calculations. The spin-spin coupling between two neighboring Fe atoms along the b axis, which is realized by the Fe-S···S-Fe super-super exchange mechanism, was found to be responsible for this magnetic phase transition.

Perovskite oxides of the general formula of $\text{ABO}_3$ ($\text{A}$ = alkali metal ions, alkaline metal ions, rare earth ions etc; $\text{B}$ = transition metal ions; $\text{O}$ = oxygen), are a large material family with abundant physical properties. Important physical effects of perovskite oxides include ferroelectrics (PbTiO$_3$)$_{1-3}$, colossal magnetoresistance (CMR, La$_{1-x}$Ca$_x$MnO$_3$)$_{4-6}$, dynamic random access memory (D-RAM, BaTi$_{1-x}$Zr$_x$O$_3$)$_{7,8}$, high temperature superconductivity (cuprate perovskites and derivatives)$_{9-13}$, and so on. Surprisingly, perovskite halides $\text{ABX}_3$ ($\text{A}$ = Cs or methylamine; $\text{B}$ = Sn, Pb; $\text{X}$ = Cl, Br, I)$_{14-22}$ have become popular in less than five years due to their very high solar conversion efficiency of up to $>20\%$$_{23}$. New perovskite materials have been infused with various undiscovered new physical functions.

Antiperovskites have similar structure to that of the perovskites, where the positions of the cation and anion constituents are reversed$^{24,25}$. Different from the perovskite materials common in nature, the number of antiperovskites is much smaller. Most naturally occurring antiperovskite minerals were formed due to geological activities$^{24}$. There are only several structure types of artificial antiperovskites so far. The metallic antiperovskites $\text{M}_3\text{AB}$ ($\text{M}$ = Mn, Ni, Fe; $\text{A}$ = Ga, Cu, Sn, Zn; $\text{B}$ = N, C, B)$_{25}$ with strong correlations among lattice, spin, and charge possess to cause such unusual physical properties as superconductivity (MgCNi$_3$)$_{26}$, negative/zero thermal expansion$^{27}$, magnetostriction$^{28,30}$, piezomagnetic$^{29,30}$, and novel

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magneto electronic effects. Recently, lithium rich antiperovskites (Li$_3$O$_X$, $X$ = Cl, Br) are recognized as a new type of antiperovskites, which have demonstrated superionic conductivity of lithium ions in solid state batteries. As mentioned above, the perovskite halides MA$_3$Pb$_X$$_3$ (MA = methylamine) have successfully been used in solar cells. It is interesting to investigate what properties will appear in the antiperovskite halides for $B=X$ ($X$ = Cl, Br, I). Similar to MA$^+$ in MA$_3$Pb$X$$_3$, an anisotropic atomic group containing a transition metal at the A site may result in certain new novel chemical/physical properties, e.g., band gap tuning or spin polarization. In this work, three new antiperovskite chalco-halides $M$$_3$AB (Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, and Ba$_3$(FeSe$_4$)Br), are synthesized. All these chalco-halides showed semiconducting behavior in UV-vis absorption and electrical transport measurements. Meanwhile, an unexpected anti-ferromagnetic phase transition around 100 K was observed during the magnetic susceptibility measurements. The transition is attributed to the anti-ferromagnetic super-super exchange of Fe$^{3+}$ spins which have the shortest distance of more than 6.267 Å.

Results and Discussion

Three isostructural compounds (Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, Ba$_3$(FeSe$_4$)Br) are crystallized in the orthorhombic space group Pnma, and their crystal structure is shown in Fig. 1a. The structure of Ba$_3$(FeS$_4$)Br contains two independent Ba sites, one independent Fe site, three independent S sites, and one independent Br site. The structure ($M$$_3$AB) can be considered as an antiperovskite-like structure, which consists of a 3D octahedral framework of [Ba$_3$$X$] filled by A$=FeS_4$ tetrahedra (Fig. 1b). The Br atom at the B site is coordinated to six Ba atoms ($M$ sites), as shown in Fig. 1c, with an average Br-Ba distance of 3.41 Å, comparable to the Br-Ba distance of 3.42 Å in BaBr$_2$. There are two zigzag arrangements for the FeS$_4$ tetrahedra: one along the $a$ axis (Supplementary Fig. S1a) separated by three Ba atoms with the nearest Fe···Fe distance of 6.267(2) Å and S···S distance of 4.069(3) Å; the other along the $b$ axis (Supplementary Fig. S1b) only separated by two Ba atoms with the nearest Fe···Fe and S···S distances of 6.324(1) Å and 3.817(2) Å, respectively. The FeS$_4$ tetrahedra (A sites) have an average Fe··S distance of 2.246(2) Å.

Tolerance factors ($\tau$) of the new antiperovskites were calculated as 0.882, 0.843, and 0.872 for Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, and Ba$_3$(FeSe$_4$)Br, respectively. The oxidation states of these antiperovskites Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, and Ba$_3$(FeSe$_4$)Br can be assigned as Ba$^{2+}$, FeO$^{2-}$, S$^{2-}$, and Se$^{2-}$. Surprisingly, the charge of the A-site group (FeO$^{2-}$) is −5, compared with those in perovskites (+1 for alkali metal or MA group, +2 for alkaline-earth metal, +3 for rare earth metal, +4 for Th) and those in antiperovskites (−2 in Li$_2$OCl, −3 in Mg$_5$SbN, −4 of SiO$_4$ in naturally formed antiperovskite materials Ca$_3$(SiO$_4$)O). The atomic groups at the A site in AB$_X$$_3$ or $M$$_3$AB have been found to be MA$^+$ in MAPbX$_3$, and SiO$_4$ in Ca$_3$(SiO$_4$)O. Compared with one single atom at the A site, these atomic groups are more anisotropic to cause charge polarization, e.g., dipole moment as that occurring in MAPbX$_3$. The three compounds Ba$_3$(FeS$_4$)Cl, Ba$_3$(FeS$_4$)Br, and Ba$_3$(FeSe$_4$)Br can be called as a chalco-halides. Note that, five other reported compounds Ba$_3$MQ$_X$ ($M=Ga, In; Q=S, Se; X=Cl, Br$) can also be included in this chalco-halide family, although they have not been noticed to be antiperovskites. Furthermore, if the Ba atoms in these chalco-halides are replaced

Figure 1. (a) Schematic diagram of the crystal structure of Ba$_3$(FeS$_4$)Br viewing down the a axis. (b) Coordination environments of (b) Fe and (c) Br atoms.
by Pb, the carrier mobility can greatly be enhanced in the perovskite-like framework of PbX filled by the A-site tetrahedral groups, which may be another promising photovoltaic material after MAPbX₃ for the next generation solar cells.

The phase purity of the given powder was indexed on PXRD patterns (Supplementary Fig. S2a for Ba₃(FeS₄)Cl and Fig. 2a for Ba₃(FeS₄)Br). No extra peaks were observed. Optical properties of the pure Ba₃(FeS₄)Cl (Supplementary Fig. S2b) and Ba₃(FeS₄)Br (Fig. 2b) samples were investigated by UV-visible diffuse reflectance spectroscopy (UV-Vis). The compounds show sharp absorption edges, indicating semiconductive nature with a rather high absorption coefficient. Consistent with the dark red color of the fine powders, the final band gap energies obtained using the extrapolation method are 1.65 and 1.71 eV from the main absorption edges of Ba₃(FeS₄)Cl and Ba₃(FeS₄)Br, respectively. The band gaps, which are close to the optimized band gap (1.0−1.8 eV) for solar cells (MAPbI₃, 1.55 eV), are even smaller than that of MAPbBr₃ (2.3 eV)36.

Typical exponential temperature dependence was observed in the resistivity of the sample disk, indicating semiconducting behavior (Fig. 2c). There are two well-known models that have been used to describe the semiconducting transport: the small polaron hopping (SPH) model and the variable range hopping (VRH) model. In the SPH model, $\rho(T)$ is expressed as $\rho(T) \propto T^{x} \exp(E_p/k_B T)$, where the $E_p$ is the activation energy37; while in the VRH model, $\rho(T)$ is expressed as $\rho(T) \propto T^{x} \exp(T/T_0)^{1/4}$, where the $T_0$ is the characteristic temperature38. Apparently, the resistivity $\rho(T)$ of Ba₃(FeS₄)Br can be fitted by the VRH model (Fig. 2c inset) instead of the SPH model (Supplementary Fig. S3).

Temperature dependent DC magnetic susceptibility of Ba₃(FeS₄)Br single crystals is shown in Fig. 2d. It exhibits a broad maximum peak around 100 K and a sharp decrease at 84 K, indicating the presence of antiferromagnetic phase transition below 84 K. Similar transitions, with higher transition temperature of 95 K, are also found in the Ba₃(FeS₄)Cl single crystals (Supplementary Fig. S2c). Note that the antiferromagnetic phase transition temperature is much higher than that of Ba₃BiFeS₅ ($T_N = 35$ K)39, Ba₃SbFeS₅ ($T_N = 13$ K)39, and Ba₃FeS₄ (paramagnetic)40,41. The inverse magnetic susceptibility of Ba₃(FeS₄)Br (Fig. 2d inset) shows a typical Curie-Weiss behavior at high temperature. The effective magnetic moment per Fe atom in Ba₃(FeS₄)Br is derived to be 2.92 $\mu_B$, indicative of the high spin state of the Fe atoms. Linear-dependency of the $M$ vs $H$ curves at 50 K, 100 K and 300 K of Ba₃(FeS₄)Cl (Supplementary Fig. S2d) and Ba₃(FeS₄)Br (Supplementary Fig. S4) also reveals the antiferromagnetic character. It is obvious that the further the magnetic ions separate, the weaker that the spin-spin coupling will be. However, from the crystal structure the nearest Fe-Fe distance in Ba₃(FeS₄)Br is 6.267(2) Å, which is too far for.
the direct spin-spin interaction between Fe atoms. Therefore, it will be of great interest to investigate the origin of the antiferromagnetic order at 84 K.

First, neutron powder diffractions (NPD) experiments were conducted at different temperatures to determine the magnetic structure of Ba₃(FeS₄)Br. The refined structural parameters for Ba₃(FeS₄)Br at different temperatures are summarized in Supplementary Table S1–S4. At high temperature (130 K and 300 K), all the diffraction peaks of Ba₃(FeS₄)Br can be accounted for the orthorhombic crystal structure with Pnma space group (Supplementary Fig. S5, S6 and Supplementary Table S1, S2). The NPD pattern measured at 4 K (Fig. 3a) shows clear extra magnetic reflections (difference profile in Fig. 3a inset), which can be indexed in the Pn'm'a' Shubnikov group. Temperature dependent intensities of the (010) magnetic reflection (Fig. 3b) imply a magnetic phase transition at ~88 K, which is consistent with the anti-ferromagnetic ordering at 84 K observed in the magnetic susceptibility measurements. The final magnetic structure, with Fe moment of 3.85(3) μB along the a-axis, is shown in Fig. 3c. Therefore, from the magnetic structure it seems that the low temperature anti-ferromagnetic order originates from the high spin Fe atoms. Next, it is necessary to reveal the spin-spin coupling type in these new antiperovskite chalcogenides.

We then performed the spin-polarized first-principles electronic structure calculations on Ba₃(FeS₄)Br to understand the electronic and magnetic structures of these new compounds (for computational details, refer to Methods). We considered six possible magnetic orders in a primitive cell with four Fe atoms (spin patterns shown in Supplementary Fig. S7). Their respective energies in the fully relaxed crystal structures with respect to the nonmagnetic state are listed in Supplementary Table S5, which indicate that the AFM1 (Fig. 4a) and AFM2 (Fig. 4b) orders are the ground states with degenerate energy. The common feature of these two magnetic orders is that they both contain antiferromagnetic Fe chains along the b axis. Particularly, the spin pattern of the AFM1 order is consistent with the one resolved from the NPD experiment (Fig. 3c).

Figure 3. (a) Experimental (crosses), calculated (line), and difference (noisy line below observed and calculated patterns) NPD profiles for Ba₃(FeS₄)Br at 4 K. Vertical bars indicate the calculated positions of Bragg peaks from the nuclear phase and from the magnetic phase (from the top). λ = 1.5398 Å. Rwp = 0.0450, Rp = 0.0558, χ² = 1.742. Inset: Refinement with nuclear phase only. Some extra peaks from unknown impurities were excluded. (b) Temperature dependent intensities of the (010) magnetic reflection. (c) Magnetic structure of Ba₃(FeS₄)Br view down b axis (left) and c axis (right). Ba and Br atoms were omitted for clarity.
We further checked the detailed electronic structures of Ba₃(FeS₄)Br. The partial density of states (PDOS, Supplementary Fig. S8) reveals that both Fe and S atoms are spin polarized and there are intense hybridizations between the Fe d orbitals and the S p orbitals. Inspection of the local magnetic moments gives 3.41 μB on the Fe atom and 0.14~0.15 μB on the S atom, respectively. The spatial spin density distribution (Fig. 4c) indicates that the Fe and S atoms in the same FeS₅⁻ tetrahedra have the same spin polarization orientation. Thus a pair of the nearest Fe atoms can couple with each other via the S atoms in the neighboring FeS₅⁻ tetrahedra, albeit the significantly large nearest Fe-Fe distance (>6.2 Å).

The calculated (experimental) distances between the nearest S-S atoms in neighboring FeS₅⁻ tetrahedra are 4.139 (4.069) Å along the a axis and 3.843 (3.817) Å along the b axis, respectively. The shorter S-S separation along the b axis makes the interaction along this direction stronger than that along the a axis, as evidenced by the different charge density intensities between the two neighboring FeS₅⁻ tetrahedra depicted in Fig. 4d and Supplementary Fig. S9, respectively. Moreover, along the b axis, the four nearest S atoms in the neighboring FeS₅⁻ tetrahedra form an approximate rectangle (Fig. 4d and Supplementary Fig. S1b), with two same-spin S atoms in one FeS₅⁻ tetrahedron and two same-spin S atoms in the other. Their interactions via the Ba 6s orbitals (Supplementary Fig. S1b) prefer an antiferromagnetic coupling, rendering an exchange J₂~29 meV/S² with S = 3.41 μB. In contrast, along the a axis, three same-spin S atoms in one FeS₅⁻ tetrahedron interact with one S atom in the neighboring FeS₅⁻ tetrahedron, thus the four S atoms between two neighboring FeS₅⁻ tetrahedra also form an S₂ tetrahedron (Supplementary Fig. S1a). The geometrical frustration as well as the larger S-S distance along the a axis do not favor static magnetic order (J₁~0). This is also the reason that we get the AFM1 and AFM2 orders with degenerate energy (Fig. 4 and Supplementary Table S5). Therefore, the spin-spin coupling between the two nearest Fe atoms is realized by the Fe-S···S-Fe antiferromagnetic super-super exchange along the b axis.

In summary, we have synthesized three new chalco-halides Ba₃(FeS₄)X (X = Cl, Br) and Ba₃(FeSe₄)Br, all of which all belong to a new type of antiperovskites. The band gap estimations revealed that these antiperovskites are good solar light absorbers. Meanwhile, antiferromagnetic transitions near 100 K were observed in Ba₃(FeS₄)X (X = Cl, Br). The corresponding magnetic structures were resolved by neutron diffractions as well as studied by the first-principles electronic structure calculations. The calculations further showed that the antiferromagnetic ground states feature the opposite spin orientations in Fe−Fe zigzag chains along the b axis, and the spin-spin coupling between a pair of the nearest Fe atoms is realized by the Fe−S−S−Fe antiferromagnetic super-super exchange along the b axis. These antiperovskite chalco-halides may provide us new ways to searching new promising photovoltaic materials after MAPbX₃ for the next generation solar cells and new physical functions.

**Methods**

**Synthesis of Ba₃(FeS₄)X (X = Cl, Br) and Ba₃(FeSe₄)Br Single Crystals.** All operations were carried out in an Ar-protected glove box. Single crystal samples were synthesized by traditional melting salt
method. A mixture of starting materials of Ba pieces (5.00 mmol), Ba₅Fe₂ (1.00 mmol), Fe powder (2.00 mmol), Q (S or Se) powder (8.00 mmol) and KI powder (50 mmol) was loaded in a carbon-coated fused silica tube. The tube was flame-sealed under vacuum (10⁻³ mbar) and heated slowly to 1073 K with a programmable furnace. The reaction was kept at this temperature for 2 days followed by cooling to 773 K at a rate of 2 K/h. Finally, the silica tube was quenched in air. The direct combination reaction at the presence of excess KI flux gave solidified melts. The melts were washed and sonicated by distilled water and dried with acetone. Then the black Ba₅(FeS₄)ₓCl, Br and Ba₅(FeSe₄)Br crystals were obtained. The presence of Ba, X, Fe and Q was confirmed by semi-quantitative energy dispersive X-ray analysis (Supplementary Fig. S10). A number of different crystals were chosen and their average atomic rates of Ba/X/Fe/Q are summarized in Supplementary Table S6.

**Single Crystal X-ray Crystallography.** A single crystal suitable for X-ray diffraction was chosen from the mixture growth via the melting salt method. Data collection was performed on a diffractometer equipped with mirror-monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares on F² using the SHELXTL program package. Multi-scan absorption corrections were performed. The crystal data and refinement details are summarized in Supplementary Table S7.

**Characterization.** X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer equipped with a monochromatized source of Cu Kα radiation (λ = 0.15406 nm) at 1.6 kW (40 kV, 40 mA). The patterns were recorded in a slow-scanning mode with 2θ from 10° to 80° with a scan-rate of 1°/min. Simulated patterns were generated using the CIF of the refined structure. Optical diffuse-reflectance measurements were carried out using a spectrophotometer operating from 1800 nm to 300 nm at room temperature. BaSO₄ powder was used as a 100% reflectance standard. Crystalline samples were ground and spread on a compacted base of BaSO₄ powder. The reflectance data were converted to absorbance data using the Kubelka-Munk equation to measure the band gap.

**Physical Properties Measurements.** Temperature variation of the resistance, R(T), was measured using the standard two-probe technique in the Resistivity model collected on a Physical Properties Measurement System (PPMS). For the electric properties measurements, single crystals were ground and pressed into disks, followed by calcination at 773 K for 5 h. Silver paste was applied which act as the contact electrode. Magnetic properties were studied using the PPMS. Temperature-dependent direct-current (DC) magnetic susceptibility (M−T) curve of the sample was measured from 400 to 2 K at 10000 Oe magnetic field under zero field cooling (ZFC) and field cooling (FC) conditions.

**Neutron Diffraction.** Neutron powder diffraction (NPD) data ranging from 4 K to 295 K were collected at the NIST Center for Neutron Research (NCNR) using the BT-1 high-resolution neutron powder diffractometer equipped with a Cu(311) monochromator at λ = 1.5398 Å. Rietveld structural refinements were performed using GSAS package.

**Electronic Structure Calculation.** First-principles calculations were carried out with the Vienna Ab initio Simulation Package (VASP), which makes use of the projector augmented wave method. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerh type for the exchange-correlation potential was adopted. The kinetic energy cutoff of the plane-wave basis was chosen to be 350 eV. A 4×4×6 k-point mesh for the Brillouin zone sampling and the Gaussian smearing technique with a width of 0.05 eV were used. In structure optimization, both cell parameters and internal atomic positions were allowed to relax until the forces were smaller than 0.01 eV/Å. Computational resources have been provided by the Physical Laboratory of High Performance Computing at Renmin University of China. The atomic structure and spin and charge densities were prepared with the XCRYSDEN program.

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X.Z. and K.L. contribute equally to this work. X.Z. performed sample synthesis and crystal structure, X-ray diffraction, UV-vis, magnetic susceptibility, and resistance measurements with assistant from J.H. K.L. did the spin-polarized electronic structure calculations. H.W. and Q.-Z.H. performed NPD experiment and did the Rietveld refinement. J.-H.L., Z.-Y.L. and F.-Q. H. are responsible for the infrastructure and project direction. All of the authors discussed the data and commented on the manuscript.

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