Ba_4FeAgS_6: a new antiferromagnetic and semiconducting quaternary sulfide

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Electronic Supplementary Information (ESI)

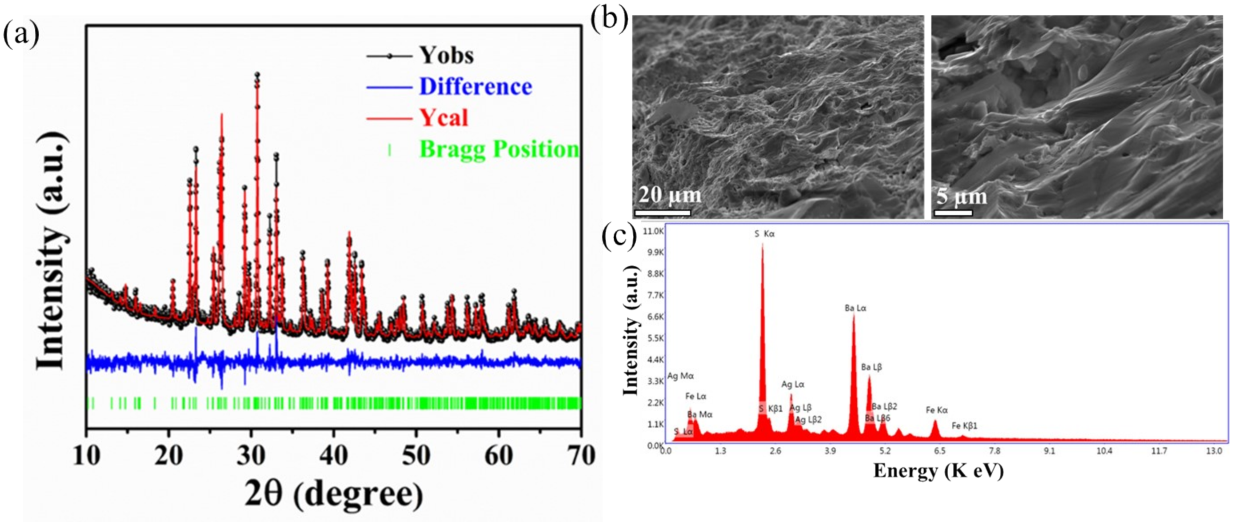

Fig. SI1: (a) The Le Bail refinement of the experimental PXRD data of the polycrystalline Ba_4FeAgS_6. The experimental X-ray pattern, Bragg positions of reflections, calculated pattern, and the difference plot are depicted as solid black dots, green ticks, solid red line, and solid blue line, respectively, **(b)** The SEM images of fracture pellet at different magnification, and **(c)** the EDX area analysis (15 μm × 15 μm) of the pellet shows an average composition of $Ba_{35.4(3)}Fe_{7.8(6)}Ag_{9.2(2)}S_{47.6(5)}$ which is close to the loaded Ba_4FeAgS_6 composition.

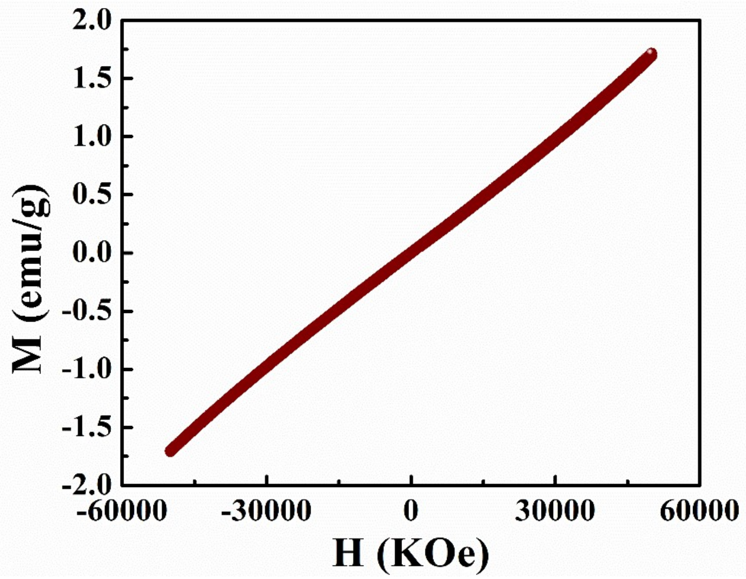

Fig. SI2: The M-H plot of the polycrystalline Ba_4FeAgS_6.

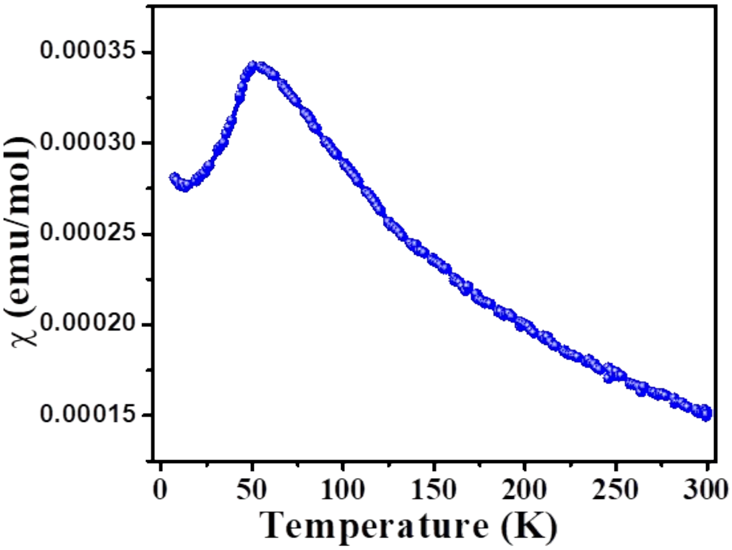

Fig. SI3 The temperature dependence of zero field cooled (ZFC) molar magnetic susceptibility (χ_{mol}) data of the polycrystalline Ba_4FeAgS_6 sample under an applied magnetic field of 10000 Oe.

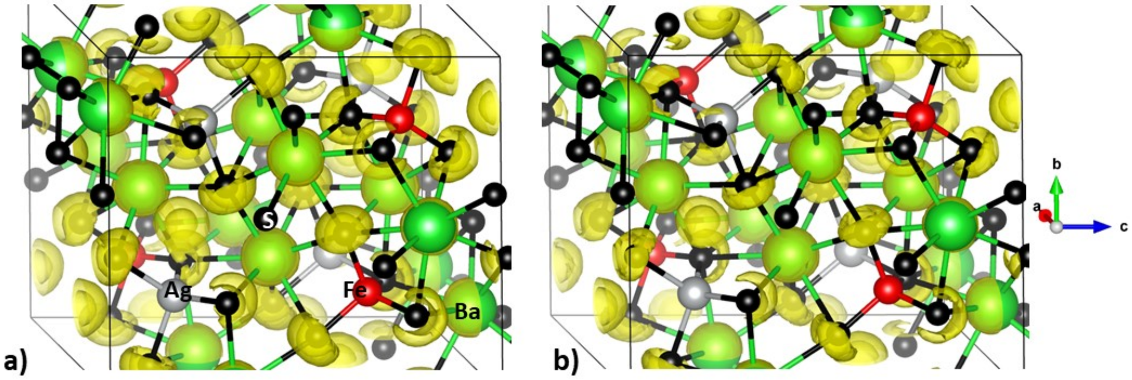

Fig. SI4: The 3D iso-surfaces of the electron localization function (ELF) for the Ba_4FeAgS_6 **(a)** $ELF = 0.70$ **(b)** $ELF = 0.72$. The yellow cloud indicates the density of the transferred charge. Green, grey, red, and black spheres indicate Ba, Ag, Fe, and S atoms, respectively.

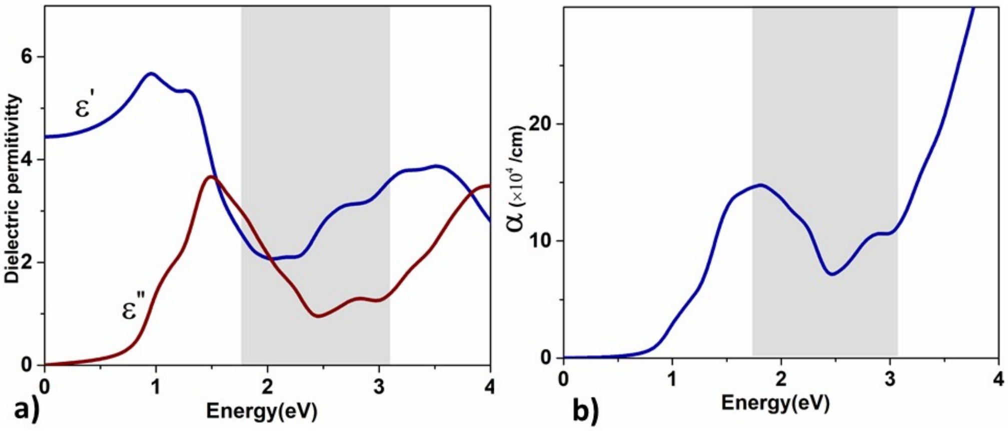

Fig. SI5: **(a)** The real $(\varepsilon^{'})$ and imaginary $(\varepsilon^{''})$ parts of the frequency-dependent dielectric function. **(b)** The variation of the theoretical absorption coefficient (α) as a function of photon energy for the Ba_4FeAgS_6.

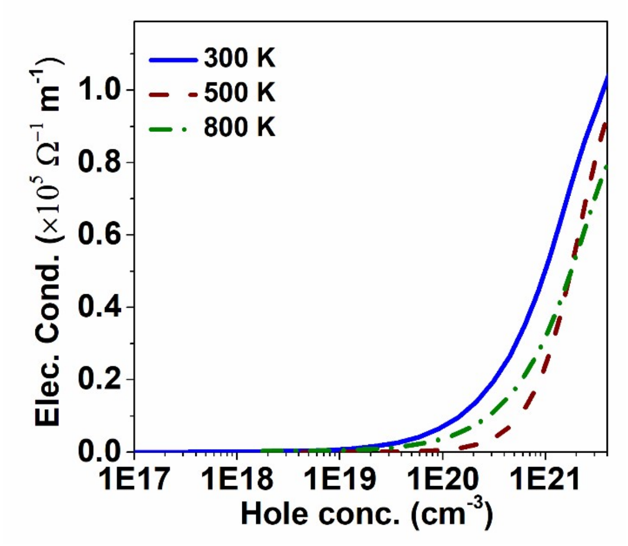

Fig. SI6 Electrical conductivity (σ) as function of hole concentration for hole doped Ba_4FeAgS_6.

Table SI1: The atomic displacement parameters (Å^2) for the Ba_4FeAgS_6 structure.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.01134(10)	0.00905(7)	0.01096(7)	0.00035(8)	0.00404(10)	0.00037(5)
Ba2	0.01194(10)	0.00930(7)	0.01165(8)	-0.00008(8)	0.00434(11)	-0.00082(5)
Ba3	0.01172(9)	0.01098(7)	0.01267(7)	0.00018(10)	0.00415(8)	0.00068(6)
Ba4	0.01027(9)	0.01335(8)	0.01143(7)	-0.00072(9)	0.00332(8)	-0.00172(6)
Ag1	0.02623(15)	0.01464(10)	0.01512(10)	-0.00124(14)	0.00696(14)	-0.00031(7)
Fe1	0.0101(2)	0.00869(16)	0.00874(16)	-0.0014(2)	0.0039(2)	-0.00025(12)
S1	0.0135(3)	0.0104(3)	0.0100(3)	-0.0002(3)	0.0038(4)	-0.0009(2)
S2	0.0127(3)	0.0102(3)	0.0124(3)	-0.0002(3)	0.0034(4)	0.0003(2)
S3	0.0136(3)	0.0096(3)	0.0123(3)	0.0010(3)	0.0042(4)	0.0008(2)
S4	0.0142(4)	0.0106(3)	0.0102(3)	-0.0009(4)	0.0036(4)	-0.0007(2)
S5	0.0109(4)	0.0120(3)	0.0121(3)	-0.0008(3)	0.0030(3)	-0.0011(2)
S6	0.0112(4)	0.0119(3)	0.0126(3)	-0.0007(3)	0.0040(3)	-0.0008(2)

Table SI2: The computed fractional atomic coordinates (x, y, z) in the Ba_4FeAgS_6 unit cell.

	x		**y**		**z**	
	Cal.	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**
Ba1	0.46907	0.46975	-0.00818	0.00885	0.67657	0.67634
Ba2	0.54181	0.54267	0.49127	0.49081	0.82487	0.82543

Ba3	0.62314	0.62357	0.67606	0.67609	0.51483	0.51649
Ba4	0.86197	0.86114	0.32474	0.32579	0.49291	0.49440
Ag1	0.72257	0.71944	0.25508	0.25465	0.70844	0.70744
Fe1	0.22812	0.22879	0.25382	0.25368	0.70266	0.70314
S1	0.15713	0.15731	0.13926	0.13792	0.56007	0.55980
S2	0.19947	0.20009	0.43115	0.43266	0.64141	0.64118
S3	0.69067	0.69018	0.45344	0.45416	0.63879	0.63944
S4	0.65036	0.64955	0.12834	0.12773	0.54710	0.54678
S5	0.49603	0.49805	0.22540	0.22383	0.79880	0.80192
S6	0.04613	0.04650	0.22516	0.22439	0.79102	0.79224

SI1: Optical Properties:

The optical parameters are obtained from the complex dielectric function $\varepsilon(\omega) = \varepsilon'(\omega) + \varepsilon''(\omega)$ which is computed in the independent-particle approximation. The imaginary part of the dielectric function $\varepsilon''(\omega)$ can be expressed as:

$$\varepsilon''_{ij}(\omega) = \frac{4\pi^2 e^2}{V_c}\lim_{q\to 0}\sum_{c,v,\vec{k}} 2w_{\vec{k}}\delta\left(\varepsilon_{c\vec{k}} - \varepsilon_{v\vec{k}} - \omega\right) \times \left\langle u_{c\vec{k}+\hat{e}_i q} \middle| u_{v\vec{k}}\right\rangle \left\langle u_{c\vec{k}+\hat{e}_j q} \middle| u_{v\vec{k}}\right\rangle^* \tag{S1-1}$$

where V_c is the primitive cell volume; indices *c* and *v* refer to the conduction band (CB) and valence band (VB) states, respectively; $w_{\vec{k}}$ is the weight of the k-points; $\hat{e}_i$ and $\hat{e}_j$ are the unit vectors for the three Cartesian directions; $u_{c\vec{k}}$ is the periodic cell part of the orbitals at the *k*-point $\vec{k}$; $\varepsilon_{c\vec{k}}$ and $\varepsilon_{v\vec{k}}$ are CB and VB single-electron energy at wave vector $\vec{k}$. The Kramers-Kronig transformation is used to obtain the real part of the dielectric function. The expression for $\varepsilon'(\omega)$ is given as:

$$\varepsilon'_{ij}(\omega) = 1 + \frac{2}{\pi}P\int_0^\infty \frac{\varepsilon''_{ij}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta}d\omega' \tag{S1-2}$$

where P is the principal value and η is a small complex shift. The absorption coefficient $\alpha(\omega)$ is obtained from the dielectric function using the expression:

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c}\left[\sqrt{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2} - \varepsilon'(\omega)\right]^{1/2} \tag{S1-3}$$

SI2: Thermoelectric properties

The *ab-initio* thermoelectric parameters such as the figure of merit (zT), Seebeck coefficient (S), electrical conductivity (σ), electronic thermal conductivity (k_{elec}) are obtained from the electronic band structure and semi-classical Boltzmann transport theory within the rigid band approach. The *p*-type or *n*-type doping and, thus, the carrier concentration in the compound is simulated by shifting the chemical potential. In this approach, the electrical conductivity (σ_{ij}) as a function of temperature (T) and chemical potential (μ) are given by:

$$\sigma_{ij}(T;\mu) = \frac{1}{V}\int \sigma_{ij}(\epsilon)\left[-\frac{\partial f_\mu(T;\mu)}{\partial \epsilon}\right]d\epsilon \tag{S2-1}$$

where V is the volume, $f_\mu(T;\mu)$ is the Fermi function and ϵ is the energy. σ_{ij} as a function of energy (ϵ) can be expressed as:

$$\sigma_{ij}(\epsilon) = \frac{1}{N}\sum_{n,\vec{k}} \sigma_{ij}(n,\vec{k})\ \delta\left(\epsilon - \epsilon_{n,\vec{k}}\right) \tag{S2-2}$$

where $\epsilon_{n,\vec{k}}$ are the band energies and N is the number of $\vec{k}$ points in the Brillouin zone. $\sigma_{ij}(n,\vec{k})$ is given in terms of relaxation time $\tau_{n,\vec{k}}$ and group velocity $\vec{v}(n,\vec{k})$ as:

$$\sigma_{ij}(n,\vec{k}) = e^2\tau_{n,\vec{k}}v_i(n,\vec{k})v_j(n,\vec{k}) \tag{S2-3}$$

The Seebeck coefficient tensors (S_{ij}) as a function of temperature (T) and chemical potential (μ) can be expressed as:

$$S_{ij}(T;\mu) = \frac{1}{eTV\sigma_{ij}(T;\mu)}\int \sigma_{ij}(\epsilon)(\epsilon - \mu)\left[-\frac{\partial f_\mu(T;\mu)}{\partial \epsilon}\right]d\epsilon \tag{S2-4}$$

The total thermal conductivity (k_{tot}) is given as $k_{tot} = k_{elec} + k_{latt}$ where k_{elec} is the electronic component and k_{latt} is the lattice (phonon) component of k_{tot}. The electronic part of thermal conductivity (k_{elec}) is related to electrical conductivity (σ) as $k_{elec} = L_0\sigma T$ (Wiedemann-Franz relation), where $L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = (156\ \mu V/K)^2$ is the Lorentz number. The quantities σ and k_{elec} are computed with respect to the relaxation time (τ) which is given as $\tau = \left(T_0 \times n_0^{1/3}\right)/\left(Tn^{1/3}\right) \times 10^{-14}s$ and where $T_0 = 300\ K$ and n_0 is carrier concentration at T_0. The figure of merit (zT) is calculated using the standard expression given by

$$zT = \frac{S^2 \sigma T}{(k_e + k_l)} \qquad \text{(S2-5)}$$

SI3: The details of the orthorhombic model of the structure.

The orthorhombic structural model has several problems. The space group is non-centrosymmetric, but the PLATON's ADDSYM detected a local/non-crystallographic center of inversion. The orthorhombic model has six Ba, one Fe, one Ag, one mixed Ag2/Fe2, and nine sulfur sites. We had tried mixing Fe at the Ag1 site, but the fractional occupancy of Fe turned out negative. Similarly, the inclusion of Ag at the Fe1 position showed negative occupancy for Ag atoms. The following are the additional indicators showing that the orthorhombic structural model is incorrect:

1. The anisotropic thermal parameters of the S4 site are non-positive definite (NPD)
2. Ninety-four systematic absence violations [I>3sig(I)]
3. The S8 and S9 atoms have cigar-shaped (elongated) thermal parameters (see Table SI6)
6. Refined composition of $Ag_{2.22}Ba_8Fe_{1.57}S_{12}$ does not charge balance.
7. Flack parameter is almost 0.5, indicative of centrosymmetric structure.
8. High value of the 2nd weight (44.59) parameter and the first weight term is zero.

Table SI3: Crystallographic Data and Structure Refinement Details for the orthorhombic $Ba_8Fe_{1.57}Ag_{2.22}S_{12}$ Structure[a]

Chemical formula	**$Ba_8Fe_{1.57}Ag_{2.22}S_{12}$**
Space group	*Cmc*2_1
a (Å)	8.6374(5)
b (Å)	25.0597(13)
c (Å)	12.0310(6)

V (Å^3)	2604.1(2)
Z	4
ρ (g cm^{-3})	4.617
μ (mm^{-1})	15.30
$R(F)^b$	0.028
$R_w(F_o^2)^c$	0.059

$^a\lambda = 0.71073$ Å, $T = 298(2)$ K.

$^bR(F) = \Sigma \,||F_o|-|F_c|| \,/\, \Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

$^cR_w(F_o^2) = \{\Sigma\, [w(F_o^2 - F_c^2)^2] \,/\, \Sigma wF_o^4\}^{1/2}$. For $F_o^2 < 0$, $w = 1/[\sigma^2(F_o^2) + 44.5934P]$
where $P = (F_o^2 + 2F_c^2)/3$

Table SI4: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for the $Ba_8Fe_{1.57}Ag_{2.22}S_{12}$.

	Wyckoff position	***Site symmetry***	**SOF**	***x***	***y***	***z***	U_{iso}*/U_{eq}
Ba01	8*b*	1		1.24203(6)	0.53704(3)	0.84345(6)	0.01112(17)
Ba02	4*a*	*m*..		1.000000	0.61565(4)	0.15683(8)	0.01254(19)
Ba03	4*a*	*m*..		0.500000	0.37717(4)	0.65947(8)	0.0144(2)
Ba04	8*b*	1		1.23639(7)	0.63021(3)	0.50845(6)	0.01200(16)
Ba05	4*a*	*m*..		0.000000	0.21182(4)	0.82525(7)	0.01110(19)
Ba06	4*a*	*m*..		1.000000	0.71312(4)	0.82563(7)	0.01135(19)
Fe01	4*a*	*m*..	0.779(8)	0.500000	0.52387(11)	0.5811(3)	0.0049(6)
Fe02	8*b*	1	0.390(9)	0.24128(11)	0.27233(6)	0.58861(17)	0.0178(4)
Ag01	4*a*	*m*..		1.000000	0.52081(5)	0.57960(14)	0.0185(3)
Ag02	8*b*	1	0.610(9)	0.24128(11)	0.27233(6)	0.58861(17)	0.0178(4)
S001	4*a*	*m*..		0.500000	0.59377(15)	0.6938(4)	0.0115(7)
S002	4*a*	*m*..		1.000000	0.60263(16)	0.7085(4)	0.0129(8)
S003	4*a*	*m*..		1.000000	0.55583(16)	0.3766(4)	0.0120(7)
S004	8*b*	1		0.7188(3)	0.47661(10)	0.6097(2)	0.0074(4)
S005	4*a*	*m*..		0.500000	0.55409(16)	0.4056(3)	0.0106(7)
S006	8*b*	1		0.2439(3)	0.30476(14)	0.7780(3)	0.0138(7)
S007	8*b*	1		0.2490(2)	0.34855(15)	0.4667(3)	0.0123(7)

S008	4*a*	*m*..		0.500000	0.22943(16)	0.5584(4)	0.0261(10)
S009	4*a*	*m*..		0.000000	0.22301(16)	0.5568(4)	0.0327(13)

$^{a}U_{\mathrm{iso}}/U_{\mathrm{eq}}$ is the one-third value of the trace of orthogonalized U_{ij} tensor.

Table SI5: The atomic displacement parameters (Å^2) for the $Ba_8Fe_{1.57}Ag_{2.22}S_{12}$ structure.

	U^{11}	**U^{22}**	**U^{33}**	**U^{12}**	**U^{13}**	**U^{23}**
Ba01	0.0102 (3)	0.0128 (4)	0.0104 (4)	-0.00066 (16)	0.0011 (2)	0.0009 (3)
Ba02	0.0170 (4)	0.0088 (3)	0.0118 (4)	0.000	0.000	0.0005 (3)
Ba03	0.0189 (4)	0.0088 (3)	0.0155 (4)	0.000	0.000	0.0019 (4)
Ba04	0.0070 (2)	0.0169 (3)	0.0121 (3)	0.00019 (17)	-0.0003 (2)	-0.0004 (3)
Ba05	0.0133 (4)	0.0105 (4)	0.0095 (4)	0.000	0.000	0.0009 (3)
Ba06	0.0145 (4)	0.0105 (4)	0.0090 (4)	0.000	0.000	0.0001 (3)
Fe01	0.0017 (9)	0.0066 (12)	0.0062 (13)	0.000	0.000	-0.0011 (10)
Fe02	0.0215 (6)	0.0152 (6)	0.0167 (8)	0.0011 (3)	-0.0005 (4)	-0.0003 (6)
Ag01	0.0308 (6)	0.0129 (5)	0.0118 (6)	0.000	0.000	-0.0005 (5)
Ag02	0.0215 (6)	0.0152 (6)	0.0167 (8)	0.0011 (3)	-0.0005 (4)	-0.0003 (6)
S001	0.0191 (16)	0.0068 (13)	0.0085 (16)	0.000	0.000	-0.0036 (11)
S002	0.0196 (17)	0.0098 (14)	0.0092 (17)	0.000	0.000	-0.0023 (12)
S003	0.0177 (15)	0.0131 (14)	0.0051 (14)	0.000	0.000	0.0022 (11)
S004	-0.0009 (6)	0.0147 (10)	0.0083 (10)	0.0014 (6)	-0.0002 (6)	0.0001 (8)
S005	0.0152 (14)	0.0144 (14)	0.0021 (12)	0.000	0.000	0.0010 (10)
S006	0.0117 (11)	0.0118 (12)	0.0180 (15)	-0.0007 (7)	0.0013 (7)	-0.0004 (10)
S007	0.0098 (12)	0.0135 (12)	0.0135 (15)	0.0024 (7)	-0.0023 (6)	-0.0009 (10)
S008	0.051 (3)	0.0109 (15)	0.0165 (18)	0.000	0.000	0.0013 (12)
S009	0.070 (4)	0.0097 (15)	0.0181 (19)	0.000	0.000	0.0017 (13)

Table SI6: The geometric parameters (Å) for the $Ba_8Fe_{1.57}Ag_{2.22}S_{12}$ structure.

Ba01—S002	3.116 (3)	Ba04—S001$^{\mathrm{ii}}$	3.315 (3)
Ba01—S003$^{\mathrm{i}}$	3.154 (3)	Ba04—Ag01	3.5238 (14)
Ba01—S001$^{\mathrm{ii}}$	3.198 (3)	Ba04—Fe01$^{\mathrm{ii}}$	3.612 (2)
Ba01—S004$^{\mathrm{iii}}$	3.212 (3)	Ba04—Ag02$^{\mathrm{xiv}}$	3.6947 (17)
Ba01—S007$^{\mathrm{iv}}$	3.228 (4)	Ba04—Ba04$^{\mathrm{iii}}$	4.0836 (12)
Ba01—S004$^{\mathrm{i}}$	3.239 (3)	Ba04—Ba04$^{\mathrm{v}}$	4.5538 (12)
Ba01—S005$^{\mathrm{i}}$	3.277 (3)	Ba05—S007$^{\mathrm{xv}}$	3.144 (3)

Ba01—Ag01^{i}	3.8137 (17)	Ba05—S007^{xvi}	3.144 (3)
Ba01—Ag01	3.8226 (18)	Ba05—S008^{xv}	3.168 (5)
Ba01—Fe01^{ii}	3.877 (3)	Ba05—S006^{xvii}	3.191 (3)
Ba01—Ba01^{iii}	4.1811 (11)	Ba05—S006	3.191 (3)
Ba01—Ba01^{v}	4.4563 (11)	Ba05—S009	3.241 (5)
Ba02—S003	3.040 (4)	Ba05—S001^{xviii}	3.355 (4)
Ba02—S006^{vi}	3.247 (3)	Ba05—Ag02	3.840 (2)
Ba02—S006^{vii}	3.247 (3)	Ba05—Ag02^{xvii}	3.840 (2)
Ba02—S007^{vii}	3.265 (4)	Ba05—Ag02^{xv}	3.898 (2)
Ba02—S007^{vi}	3.265 (4)	Ba05—Ag02^{xvi}	3.898 (2)
Ba02—S004^{viii}	3.401 (3)	Ba06—S002	3.107 (4)
Ba02—S004^{ix}	3.401 (3)	Ba06—S007^{iv}	3.146 (3)
Ba02—Ag01^{ix}	3.5435 (16)	Ba06—S007^{xi}	3.146 (3)
Ba02—Ag02^{vi}	3.5914 (16)	Ba06—S009^{xi}	3.209 (5)
Ba02—Ag02^{vii}	3.5914 (16)	Ba06—S006^{xiv}	3.240 (3)
Ba02—Ba03^{ix}	4.3226 (2)	Ba06—S006^{xii}	3.240 (3)
Ba02—Ba03^{vii}	4.3226 (3)	Ba06—S008^{xii}	3.241 (5)
Ba03—S004^{x}	3.184 (3)	Ba06—Ag02^{iv}	3.806 (2)
Ba03—S004	3.184 (3)	Ba06—Ag02^{xi}	3.806 (2)
Ba03—S006	3.197 (3)	Ba06—Ag02^{xii}	3.915 (2)
Ba03—S006^{x}	3.197 (3)	Ba06—Ag02^{xiv}	3.915 (2)
Ba03—S007^{x}	3.255 (4)	Fe01—S001	2.215 (5)
Ba03—S007	3.255 (4)	Fe01—S005	2.244 (6)
Ba03—S005^{xi}	3.426 (4)	Fe01—S004^{x}	2.256 (3)
Ba03—Ag02	3.5528 (16)	Fe01—S004	2.256 (3)
Ba03—Ag02^{x}	3.5529 (16)	Ag01—S002	2.570 (4)
Ba03—Fe01	3.795 (3)	Ag01—S003	2.595 (5)
Ba04—S003	3.187 (3)	Ag01—S004	2.694 (2)
Ba04—S006^{vi}	3.216 (4)	Ag01—S004^{iii}	2.694 (2)
Ba04—S005^{ii}	3.218 (3)	Ag02—S007	2.409 (4)
Ba04—S002	3.231 (4)	Ag02—S006	2.420 (5)
Ba04—S008^{xii}	3.273 (3)	Ag02—S009	2.453 (2)
Ba04—S009^{xiii}	3.306 (3)	Ag02—S008	2.506 (2)

Symmetry codes: (i) -*x*+2, -*y*+1, *z*+1/2; (ii) *x*+1, *y*, *z*; (iii) -*x*+2, *y*, *z*; (iv) *x*+1, -*y*+1, *z*+1/2; (v) -*x*+3, *y*, *z*;

(vi) x+1, -y+1, z-1/2; (vii) -x+1, -y+1, z-1/2; (viii) x, -y+1, z-1/2; (ix) -x+2, -y+1, z-1/2; (x) -x+1, y, z; (xi) -x+1, -y+1, z+1/2; (xii) x+1/2, y+1/2, z; (xiii) x+3/2, y+1/2, z; (xiv) -x+3/2, y+1/2, z; (xv) -x+1/2, -y+1/2, z+1/2; (xvi) x-1/2, -y+1/2, z+1/2; (xvii) -x, y, z; (xviii) x-1/2, y-1/2, z; (xix) x-1, y, z; (xx) -x+3/2, y-1/2, z; (xxi) -x+1/2, -y+1/2, z-1/2; (xxii) x-1, -y+1, z-1/2; (xxiii) x-1, -y+1, z+1/2; (xxiv) x-3/2, y-1/2, z.