Ba_4FeCuS_6: a new mixed metal sulfide with a pseudo-zero-dimensional structure containing rare CuS_3 units

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Electronic Supplementary Information (ESI)

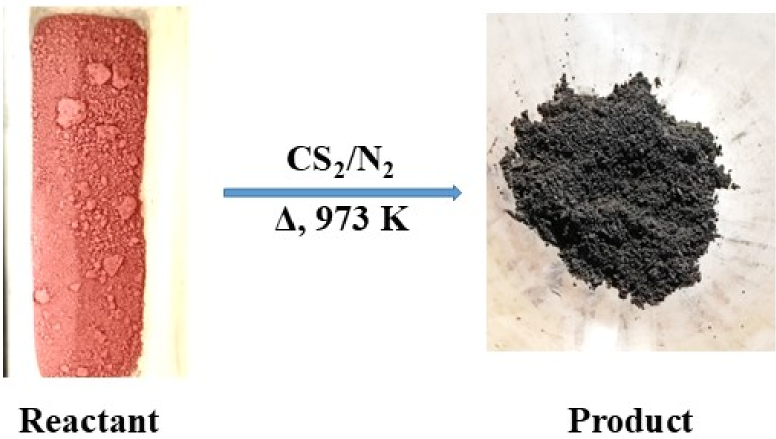

Fig. SI1: The polycrystalline Ba_4FeCuS_6 sample before and after reaction by the CS_2 method.

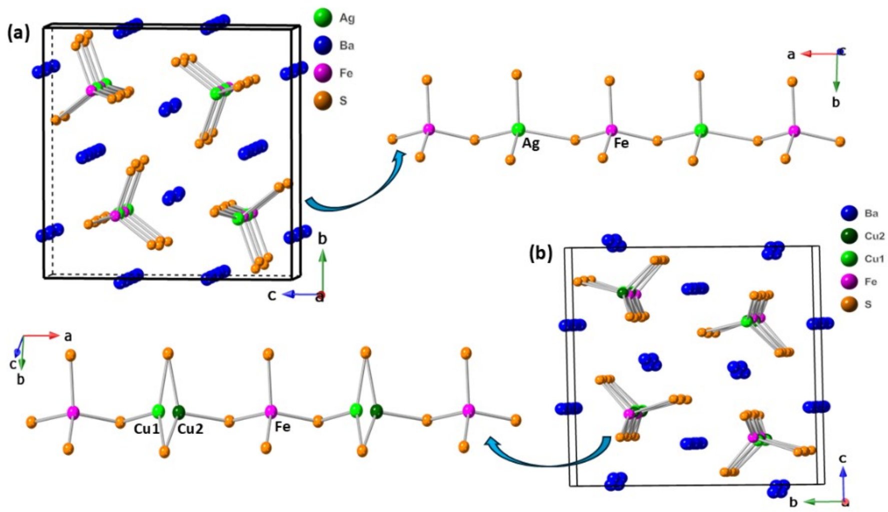

Fig. SI2: The structure comparison of **(a)** Ba_4FeAgS_6 (Ag site was fully occupied)[1] and **(b)** Ba_4FeCuS_6 (Cu site was split into two sites; Cu1 and Cu2).

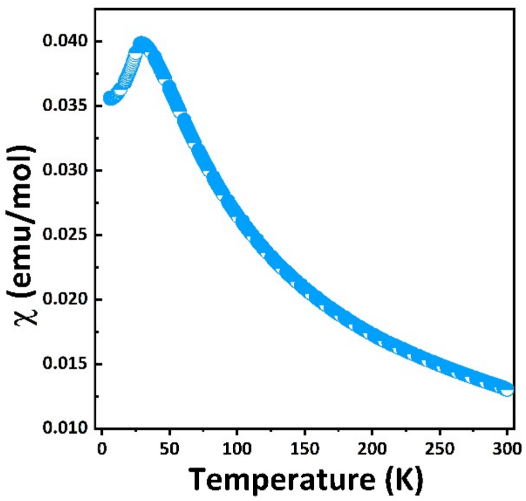

Fig. SI3: The temperature dependence (FW) of the molar magnetic susceptibility (χ_{mol}) of the polycrystalline Ba_4FeCuS_6 sample under an applied magnetic field of 1000 Oe (0.1 T).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0175(3)	0.0076(3)	0.0133(3)	-0.0003(3)	0.0043(3)	0.0002(2)
Ba2	0.0178(3)	0.0076(3)	0.0128(3)	0.0000(3)	0.0045(3)	-0.0003(2)
Ba3	0.0203(4)	0.0103(4)	0.0191(30	-0.0003(3)	0.0076(3)	0.0008(3)
Ba4	0.0175(4)	0.0115(4)	0.0173(3)	-0.0007(3)	0.0050(3)	-0.0022(3)
Fe1	0.0167(8)	0.0059(8)	0.0117(7)	0.0005(6)	0.0020(6)	-0.0006(6)
Cu1	0.0440(15)	0.0123(9)	0.0186(8)	-0.0035(9)	0.0126(9)	-0.0015(7)
Cu2	0.0440(15)	0.0123(9)	0.0186(8)	-0.0035(9)	0.0126(9)	-0.0015(7)
S1	0.0205(15)	0.0099(13)	0.0104(12)	-0.0009(11)	0.0038(11)	-0.0028(10)
S2	0.0198(15)	0.0087(13)	0.0157(13)	-0.0003(11)	0.0054(11)	-0.0004(11)
S3	0.0188(14)	0.0101(13)	0.0126(12)	0.0012(11)	0.0039(11)	0.0007(10)
S4	0.0195(15)	0.0098(13)	0.0134(13)	0.0007(11)	0.0045(11)	-0.0001(10)
S5	0.0204(14)	0.0068(13)	0.0133(13)	0.0000(11)	0.0028(11)	-0.0004(10)
S6	0.0294(17)	0.0097(14)	0.0180(14)	0.0025(13)	0.0093(13)	0.0019(11)

Table SI1: Atomic displacement parameter ($Å^2$) for monoclinic Ba_4FeCuS_6

Table SI2: Geometric parameters (Å, °) for monoclinic Ba_4FeCuS_6

Ba1−S4^{i}	3.107(3)	Ba3−S1	3.310(3)
Ba1−S1^{ii}	3.172(3)	Ba3−S4^{vi}	3.323(3)
Ba1−S4	3.174(3)	Ba3−Cu2^{ix}	3.602(18)
Ba1−S6	3.186(3)	Ba3−Fe1	3.6553(18)
Ba1−S5^{ii}	3.200(3)	Ba3−Cu1^{ix}	3.712(2)
Ba1−S3^{iii}	3.201(3)	Ba3−Cu2	3.81(2)
Ba1−S2	3.311(3)	Ba4−Cu2^{vi}	3.035(19)
Ba1−Cu2^{iv}	3.64(2)	Ba4−S3	3.138(3)
Ba1−Cu1^{ii}	3.651(2)	Ba4−S4	3.175(3)
Ba1−Fe1^{ii}	3.8467(18)	Ba4−S6	3.204(3)

$Ba1-Ba2^{iv}$	4.2791(11)	$Ba4-S2^{x}$	3.209(3)
$Ba1-Ba2^{v}$	4.4089(11)	$Ba4-S5^{v}$	3.254(3)
$Ba2-S3^{vi}$	3.121(3)	$Ba4-S1^{xi}$	3.311(3)
$Ba2-S4^{iii}$	3.129(3)	$Ba4-S2^{vii}$	3.345(3)
$Ba2-S6$	3.150(3)	$Ba4-Cu1^{vi}$	3.550(2)
$Ba2-S1^{v}$	3.197(3)	$Ba4-Fe1^{xi}$	3.5521(18)
$Ba2-S2^{vii}$	3.236(3)	$Ba4-Fe1^{v}$	3.7794(18)
$Ba2-S1^{viii}$	3.236(3)	$Fe1-S1$	2.272(3)
$Ba2-S5$	3.236(3)	$Fe1-S6^{vii}$	2.282(4)
$Ba2-Cu1$	3.650(2)	$Fe1-S2^{vii}$	2.287(3)
$Ba2-Cu2^{iv}$	3.67(2)	$Fe1-S5$	2.296(3)
$Ba2-Fe1$	3.8767(18)	$Cu1-Cu2$	0.88(3)
$Ba2-Fe1^{v}$	3.8858(18)	$Cu1-S4^{vi}$	2.280(3)
$Ba3-S3$	3.087(3)	$Cu1-S3^{vi}$	2.290(4)
$Ba3-Cu1$	3.236(2)	$Cu1-S5$	2.332(4)
$Ba3-S2^{vii}$	3.247(3)	$Cu2-S3^{vi}$	2.311(19)
$Ba3-S6^{vi}$	3.294(3)	$Cu2-S4^{vi}$	2.315(19)
$Ba3-S3^{vi}$	3.303(3)	$Cu2-S6^{xii}$	2.45(3)
$Ba3-S5^{ix}$	3.303(3)		
$S4^{i}-Ba1-S1^{ii}$	85.92(8)	$Cu1^{vi}-Ba4-Fe1^{xi}$	87.85(5)
$S4^{i}-Ba1-S4$	80.98(9)	$Cu2^{vi}-Ba4-Fe1^{v}$	136.6(4)
$S1^{ii}-Ba1-S4$	79.43(8)	$S3-Ba4-Fe1^{v}$	133.74(6)
$S4^{i}-Ba1-S6$	133.11(8)	$S4-Ba4-Fe1^{v}$	93.80(6)
$S1^{ii}-Ba1-S6$	123.23(9)	$S6-Ba4-Fe1^{v}$	37.00(6)
$S4-Ba1-S6$	71.15(8)	$S2^{x}-Ba4-Fe1^{v}$	127.42(6)
$S4^{i}-Ba1-S5^{ii}$	77.10(8)	$S5^{v}-Ba4-Fe1^{v}$	37.16(6)
$S1^{ii}-Ba1-S5^{ii}$	71.30(8)	$S1^{xi}-Ba4-Fe1^{v}$	91.81(6)
$S4-Ba1-S5^{ii}$	144.32(8)	$S2^{vii}-Ba4-Fe1^{v}$	74.71(6)
$S6-Ba1-S5^{ii}$	142.88(8)	$Cu1^{vi}-Ba4-Fe1^{v}$	127.54(5)
$S4^{i}-Ba1-S3^{iii}$	88.04(8)	$Fe1^{xi}-Ba4-Fe1^{v}$	127.73(5)
$S1^{ii}-Ba1-S3^{iii}$	153.35(8)	$Cu2^{vi}-Ba4-Ba3^{vi}$	60.9(5)
$S4-Ba1-S3^{iii}$	125.13(8)	$S3-Ba4-Ba3^{vi}$	50.78(6)
$S6-Ba1-S3^{iii}$	78.82(8)	$S4-Ba4-Ba3^{vi}$	51.05(6)
$S5^{ii}-Ba1-S3^{iii}$	82.05(8)	$S6-Ba4-Ba3^{vi}$	50.43(6)
$S4^{i}-Ba1-S2$	155.46(8)	$S2^{x}-Ba4-Ba3^{vi}$	140.03(6)
$S1^{ii}-Ba1-S2$	88.29(8)	$S5^{v}-Ba4-Ba3^{vi}$	124.52(6)
$S4-Ba1-S2$	121.30(8)	$S1^{xi}-Ba4-Ba3^{vi}$	136.42(6)
$S6-Ba1-S2$	68.94(8)	$S2^{vii}-Ba4-Ba3^{vi}$	87.04(6)
$S5^{ii}-Ba1-S2$	78.46(8)	$Cu1^{vi}-Ba4-Ba3^{vi}$	48.28(4)
$S3^{iii}-Ba1-S2$	86.52(8)	$Fe1^{xi}-Ba4-Ba3^{vi}$	136.11(3)
$S4^{i}-Ba1-Cu2^{iv}$	107.9(4)	$Fe1^{v}-Ba4-Ba3^{vi}$	87.43(3)
$S1^{ii}-Ba1-Cu2^{iv}$	164.2(4)	$S1-Fe1-S6^{vii}$	106.19(13)
$S4-Ba1-Cu2^{iv}$	94.9(3)	$S1-Fe1-S2^{vii}$	108.59(12)
$S6-Ba1-Cu2^{iv}$	41.3(4)	$S6^{vii}-Fe1-S2^{vii}$	107.25(13)
$S5^{ii}-Ba1-Cu2^{iv}$	118.5(3)	$S1-Fe1-S5$	108.78(12)
$S3^{iii}-Ba1-Cu2^{iv}$	38.8(3)	$S6^{vii}-Fe1-S5$	116.45(13)
$S2-Ba1-Cu2^{iv}$	82.1(3)	$S2^{vii}-Fe1-S5$	109.32(13)
$S4^{i}-Ba1-Cu1^{ii}$	38.37(6)	$S1-Fe1-Ba4^{xi}$	65.03(9)

S1^{ii}−Ba1−Cu1^{ii}	79.64(7)	S6^{vii}−Fe1−Ba4^{xi}	79.04(10)
S4−Ba1−Cu1^{ii}	116.55(6)	S2^{vii}−Fe1−Ba4^{xi}	62.30(9)
S6−Ba1−Cu1^{ii}	157.10(8)	S5−Fe1−Ba4^{xi}	164.48(10)
S5^{ii}−Ba1−Cu1^{ii}	39.10(6)	S1−Fe1−Ba3	62.90(9)
S3^{iii}−Ba1−Cu1^{ii}	79.55(7)	S6^{vii}−Fe1−Ba3	156.14(11)
S2−Ba1−Cu1^{ii}	117.10(6)	S2^{vii}−Fe1−Ba3	61.23(8)
Cu2^{iv}−Ba1−Cu1^{ii}	115.9(4)	S5−Fe1−Ba3	87.41(9)
S4^{i}−Ba1−Fe1^{ii}	87.35(6)	Ba4^{xi}−Fe1−Ba3	77.10(4)
S1^{ii}−Ba1−Fe1^{ii}	36.18(6)	S1−Fe1−Ba4^{vii}	127.63(10)
S4−Ba1−Fe1^{ii}	115.31(6)	S6^{vii}−Fe1−Ba4^{vii}	57.66(9)
S6−Ba1−Fe1^{ii}	138.48(7)	S2^{vii}−Fe1−Ba4^{vii}	123.68(9)
S5^{ii}−Ba1−Fe1^{ii}	36.59(6)	S5−Fe1−Ba4^{vii}	58.88(8)
S3^{iii}−Ba1−Fe1^{ii}	117.65(6)	Ba4^{xi}−Fe1−Ba4^{vii}	136.49(5)
S2−Ba1−Fe1^{ii}	74.16(6)	Ba3−Fe1−Ba4^{vii}	146.14(5)
Cu2^{iv}−Ba1−Fe1^{ii}	148.3(3)	S1−Fe1−Ba1^{xiii}	55.51(8)
Cu1^{ii}−Ba1−Fe1^{ii}	60.30(5)	S6^{vii}−Fe1−Ba1^{xiii}	113.15(10)
S4^{i}−Ba1−Ba2^{iv}	46.89(6)	S2^{vii}−Fe1−Ba1^{xiii}	139.29(10)
S1^{ii}−Ba1−Ba2^{iv}	132.79(6)	S5−Fe1−Ba1^{xiii}	56.18(8)
S4−Ba1−Ba2^{iv}	92.08(6)	Ba4^{xi}−Fe1−Ba1^{xiii}	120.45(5)
S6−Ba1−Ba2^{iv}	96.38(6)	Ba3−Fe1−Ba1^{xiii}	79.27(4)
S5^{ii}−Ba1−Ba2^{iv}	93.08(6)	Ba4^{vii}−Fe1−Ba1^{xiii}	83.79(4)
S3^{iii}−Ba1−Ba2^{iv}	46.62(5)	S1−Fe1−Ba2	141.00(10)
S2−Ba1−Ba2^{iv}	133.13(6)	S6^{vii}−Fe1−Ba2	112.63(10)
Cu2^{iv}−Ba1−Ba2^{iv}	61.6(4)	S2^{vii}−Fe1−Ba2	56.49(9)
Cu1^{ii}−Ba1−Ba2^{iv}	62.87(4)	S5−Fe1−Ba2	56.49(8)
Fe1^{ii}−Ba1−Ba2^{iv}	123.09(3)	Ba4^{xi}−Fe1−Ba2	118.46(5)
S4^{i}−Ba1−Ba2^{v}	132.35(6)	Ba3−Fe1−Ba2	79.58(4)
S1^{ii}−Ba1−Ba2^{v}	46.43(6)	Ba4^{vii}−Fe1−Ba2	78.83(3)
S4−Ba1−Ba2^{v}	88.72(6)	Ba1^{xiii}−Fe1−Ba2	109.58(4)
S6−Ba1−Ba2^{v}	84.80(6)	S1−Fe1−Ba2^{vii}	55.35(8)
S5^{ii}−Ba1−Ba2^{v}	85.70(6)	S6^{vii}−Fe1−Ba2^{vii}	54.16(9)
S3^{iii}−Ba1−Ba2^{v}	133.41(6)	S2^{vii}−Fe1−Ba2^{vii}	136.87(10)
S2−Ba1−Ba2^{v}	46.94(5)	S5−Fe1−Ba2^{vii}	113.77(9)
Cu2^{iv}−Ba1−Ba2^{v}	119.3(4)	Ba4^{xi}−Fe1−Ba2^{vii}	75.30(4)
Cu1^{ii}−Ba1−Ba2^{v}	115.88(4)	Ba3−Fe1−Ba2^{vii}	118.18(4)
Fe1^{ii}−Ba1−Ba2^{v}	55.66(3)	Ba4^{vii}−Fe1−Ba2^{vii}	81.99(4)
Ba2^{iv}−Ba1−Ba2^{v}	178.74(3)	Ba1^{xiii}−Fe1−Ba2^{vii}	69.52(3)
S3^{vi}−Ba2−S4^{iii}	89.09(8)	Ba2−Fe1−Ba2^{vii}	160.75(5)
S3^{vi}−Ba2−S6	84.75(8)	Cu2−Cu1−S4^{vi}	81.2(12)
S4^{iii}−Ba2−S6	78.75(9)	Cu2−Cu1−S3^{vi}	80.2(12)
S3^{vi}−Ba2−S1^{v}	154.64(8)	S4^{vi}−Cu1−S3^{vi}	116.08(13)
S4^{iii}−Ba2−S1^{v}	88.34(8)	Cu2−Cu1−S5	137.3(12)
S6−Ba2−S1^{v}	70.01(8)	S4^{vi}−Cu1−S5	116.96(14)
S3^{vi}−Ba2−S2^{vii}	83.37(8)	S3^{vi}−Cu1−S5	117.87(14)
S4^{iii}−Ba2−S2^{vii}	156.79(8)	Cu2−Cu1−Ba3	125.2(12)
S6−Ba2−S2^{vii}	78.72(8)	S4^{vi}−Cu1−Ba3	71.73(9)
S1^{v}−Ba2−S2^{vii}	89.19(8)	S3^{vi}−Cu1−Ba3	71.08(9)
S3^{vi}−Ba2−S1^{viii}	121.96(8)	S5−Cu1−Ba3	97.48(11)

$S4^{iii}$–Ba2–$S1^{viii}$	79.13(8)	Cu2–Cu1–$Ba4^{vi}$	48.4(12)
S6–Ba2–$S1^{viii}$	144.72(8)	$S4^{vi}$–Cu1–$Ba4^{vi}$	61.52(9)
$S1^{v}$–Ba2–$S1^{viii}$	82.22(8)	$S3^{vi}$–Cu1–$Ba4^{vi}$	60.54(9)
$S2^{vii}$–Ba2–$S1^{viii}$	123.33(8)	S5–Cu1–$Ba4^{vi}$	174.25(12)
$S3^{vi}$–Ba2–S5	77.02(8)	Ba3–Cu1–$Ba4^{vi}$	76.77(4)
$S4^{iii}$–Ba2–S5	128.96(8)	Cu2–Cu1–Ba2	114.3(12)
S6–Ba2–S5	145.69(8)	$S4^{vi}$–Cu1–Ba2	160.11(12)
$S1^{v}$–Ba2–S5	123.11(8)	$S3^{vi}$–Cu1–Ba2	58.12(8)
$S2^{vii}$–Ba2–S5	70.57(8)	S5–Cu1–Ba2	60.86(9)
$S1^{viii}$–Ba2–S5	68.39(7)	Ba3–Cu1–Ba2	88.70(6)
$S3^{vi}$–Ba2–Cu1	38.55(6)	$Ba4^{vi}$–Cu1–Ba2	118.42(5)
$S4^{iii}$–Ba2–Cu1	108.85(7)	Cu2–Cu1–$Ba1^{xiii}$	116.4(12)
S6–Ba2–Cu1	120.42(7)	$S4^{vi}$–Cu1–$Ba1^{xiii}$	57.80(9)
$S1^{v}$–Ba2–Cu1	160.91(7)	$S3^{vi}$–Cu1–$Ba1^{xiii}$	158.62(12)
$S2^{vii}$–Ba2–Cu1	78.23(7)	S5–Cu1–$Ba1^{xiii}$	59.94(9)
$S1^{viii}$–Ba2–Cu1	92.68(6)	Ba3–Cu1–$Ba1^{xiii}$	87.86(5)
S5–Ba2–Cu1	39.00(6)	$Ba4^{vi}$–Cu1–$Ba1^{xiii}$	119.21(5)
$S3^{vi}$–Ba2–$Cu2^{iv}$	78.8(3)	Ba2–Cu1–$Ba1^{xiii}$	119.59(6)
$S4^{iii}$–Ba2–$Cu2^{iv}$	38.8(3)	Cu2–Cu1–$Ba3^{viii}$	76.0(12)
S6–Ba2–$Cu2^{iv}$	41.1(4)	$S4^{vi}$–Cu1–$Ba3^{viii}$	116.61(10)
$S1^{v}$–Ba2–$Cu2^{iv}$	83.5(3)	$S3^{vi}$–Cu1–$Ba3^{viii}$	116.88(10)
$S2^{vii}$–Ba2–$Cu2^{iv}$	118.1(3)	S5–Cu1–$Ba3^{viii}$	61.33(8)
$S1^{viii}$–Ba2–$Cu2^{iv}$	116.4(3)	Ba3–Cu1–$Ba3^{viii}$	158.80(8)
S5–Ba2–$Cu2^{iv}$	153.1(4)	$Ba4^{vi}$–Cu1–$Ba3^{viii}$	124.42(7)
Cu1–Ba2–$Cu2^{iv}$	115.0(3)	Ba2–Cu1–$Ba3^{viii}$	80.62(4)
$S3^{vi}$–Ba2–Fe1	86.56(6)	$Ba1^{xiii}$–Cu1–$Ba3^{viii}$	81.70(4)
$S4^{iii}$–Ba2–Fe1	165.23(7)	Cu1–Cu2–$S3^{vi}$	77.6(13)
S6–Ba2–Fe1	114.82(7)	Cu1–Cu2–$S4^{vi}$	76.7(13)
$S1^{v}$–Ba2–Fe1	101.54(6)	$S3^{vi}$–Cu2–$S4^{vi}$	113.9(8)
$S2^{vii}$–Ba2–Fe1	36.11(6)	Cu1–Cu2–$S6^{xii}$	152.7(15)
$S1^{viii}$–Ba2–Fe1	91.23(6)	$S3^{vi}$–Cu2–$S6^{xii}$	116.9(9)
S5–Ba2–Fe1	36.27(6)	$S4^{vi}$–Cu2–$S6^{xii}$	113.5(9)
Cu1–Ba2–Fe1	60.02(5)	Cu1–Cu2–$Ba4^{vi}$	119.0(14)
$Cu2^{iv}$–Ba2–Fe1	152.4(3)	$S3^{vi}$–Cu2–$Ba4^{vi}$	70.4(5)
$S3^{vi}$–Ba2–$Fe1^{v}$	119.06(6)	$S4^{vi}$–Cu2–$Ba4^{vi}$	71.4(5)
$S4^{iii}$–Ba2–$Fe1^{v}$	90.43(6)	$S6^{xii}$–Cu2–$Ba4^{vi}$	88.2(7)
S6–Ba2–$Fe1^{v}$	35.96(6)	Cu1–Cu2–$Ba3^{viii}$	90.2(12)
$S1^{v}$–Ba2–$Fe1^{v}$	35.77(6)	$S3^{vi}$–Cu2–$Ba3^{viii}$	120.3(6)
$S2^{vii}$–Ba2–$Fe1^{v}$	74.40(6)	$S4^{vi}$–Cu2–$Ba3^{viii}$	119.5(7)
$S1^{viii}$–Ba2–$Fe1^{v}$	117.65(6)	$S6^{xii}$–Cu2–$Ba3^{viii}$	62.6(4)
S5–Ba2–$Fe1^{v}$	139.22(6)	$Ba4^{vi}$–Cu2–$Ba3^{viii}$	150.8(9)
Cu1–Ba2–$Fe1^{v}$	147.03(4)	Cu1–Cu2–$Ba1^{xii}$	121.1(14)
$Cu2^{iv}$–Ba2–$Fe1^{v}$	64.6(4)	$S3^{vi}$–Cu2–$Ba1^{xii}$	60.2(4)
Fe1–Ba2–$Fe1^{v}$	104.017(18)	$S4^{vi}$–Cu2–$Ba1^{xii}$	155.7(9)
$S3^{vi}$–Ba2–$Ba1^{xii}$	48.19(6)	$S6^{xii}$–Cu2–$Ba1^{xii}$	59.3(5)
$S4^{iii}$–Ba2–$Ba1^{xii}$	46.46(6)	$Ba4^{vi}$–Cu2–$Ba1^{xii}$	84.9(5)
S6–Ba2–$Ba1^{xii}$	96.29(7)	$Ba3^{viii}$–Cu2–$Ba1^{xii}$	79.3(4)
$S1^{v}$–Ba2–$Ba1^{xii}$	134.80(6)	Cu1–Cu2–$Ba2^{xii}$	118.6(14)

$S2^{vii}$−Ba2−$Ba1^{xii}$	131.51(6)	$S3^{vi}$−Cu2−$Ba2^{xii}$	155.1(8)
$S1^{viii}$−Ba2−$Ba1^{xii}$	87.95(6)	$S4^{vi}$−Cu2−$Ba2^{xii}$	57.8(4)
S5−Ba2−$Ba1^{xii}$	92.88(6)	$S6^{xii}$−Cu2−$Ba2^{xii}$	57.9(4)
Cu1−Ba2−$Ba1^{xii}$	62.87(4)	$Ba4^{vi}$−Cu2−$Ba2^{xii}$	84.8(5)
$Cu2^{iv}$−Ba2−$Ba1^{xii}$	61.9(4)	$Ba3^{viii}$−Cu2−$Ba2^{xii}$	80.5(4)
Fe1−Ba2−$Ba1^{xii}$	122.77(3)	$Ba1^{xii}$−Cu2−$Ba2^{xii}$	116.4(7)
$Fe1^{v}$−Ba2−$Ba1^{xii}$	126.43(3)	Cu1−Cu2−Ba3	43.9(10)
S3−Ba3−Cu1	126.29(7)	$S3^{vi}$−Cu2−Ba3	59.4(5)
S3−Ba3−$S2^{vii}$	85.62(8)	$S4^{vi}$−Cu2−Ba3	59.9(5)
Cu1−Ba3−$S2^{vii}$	84.43(7)	$S6^{xii}$−Cu2−Ba3	163.2(8)
S3−Ba3−$S6^{vi}$	82.89(8)	$Ba4^{vi}$−Cu2−Ba3	75.1(4)
Cu1−Ba3−$S6^{vi}$	98.42(7)	$Ba3^{viii}$−Cu2−Ba3	134.1(7)
$S2^{vii}$−Ba3−$S6^{vi}$	167.50(8)	$Ba1^{xii}$−Cu2−Ba3	119.6(5)
S3−Ba3−$S3^{vi}$	85.31(8)	$Ba2^{xii}$−Cu2−Ba3	117.6(5)
Cu1−Ba3−$S3^{vi}$	40.99(6)	Fe1−S1−$Ba1^{xiii}$	88.31(10)
$S2^{vii}$−Ba3−$S3^{vi}$	80.40(8)	Fe1−S1−$Ba2^{vii}$	88.88(10)
$S6^{vi}$−Ba3−$S3^{vi}$	93.72(8)	$Ba1^{xiii}$−S1−$Ba2^{vii}$	87.61(8)
S3−Ba3−$S5^{ix}$	82.13(8)	Fe1−S1−$Ba2^{ix}$	169.85(13)
Cu1−Ba3−$S5^{ix}$	150.26(7)	$Ba1^{xiii}$−S1−$Ba2^{ix}$	99.57(8)
$S2^{vii}$−Ba3−$S5^{ix}$	90.01(8)	$Ba2^{vii}$−S1−$Ba2^{ix}$	97.78(8)
$S6^{vi}$−Ba3−$S5^{ix}$	93.29(8)	Fe1−S1−Ba3	79.44(10)
$S3^{vi}$−Ba3−$S5^{ix}$	164.74(8)	$Ba1^{xiii}$−S1−Ba3	95.20(8)
S3−Ba3−S1	138.75(8)	$Ba2^{vii}$−S1−Ba3	167.87(10)
Cu1−Ba3−S1	84.10(7)	$Ba2^{ix}$−S1−Ba3	93.39(7)
$S2^{vii}$−Ba3−S1	68.74(7)	Fe1−S1−$Ba4^{xi}$	76.51(9)
$S6^{vi}$−Ba3−S1	123.57(8)	$Ba1^{xiii}$−S1−$Ba4^{xi}$	164.45(10)
$S3^{vi}$−Ba3−S1	119.51(7)	$Ba2^{vii}$−S1−$Ba4^{xi}$	88.71(8)
$S5^{ix}$−Ba3−S1	66.73(7)	$Ba2^{ix}$−S1−$Ba4^{xi}$	95.90(8)
S3−Ba3−$S4^{vi}$	140.84(8)	Ba3−S1−$Ba4^{xi}$	85.45(7)
Cu1−Ba3−$S4^{vi}$	40.64(6)	$Fe1^{v}$−S2−$Ba4^{iii}$	78.57(9)
$S2^{vii}$−Ba3−$S4^{vi}$	119.63(7)	$Fe1^{v}$−S2−$Ba2^{v}$	87.40(10)
$S6^{vi}$−Ba3−$S4^{vi}$	68.00(8)	$Ba4^{iii}$−S2−$Ba2^{v}$	164.47(11)
$S3^{vi}$−Ba3−$S4^{vi}$	71.62(8)	$Fe1^{v}$−S2−$Ba3^{v}$	80.65(10)
$S5^{ix}$−Ba3−$S4^{vi}$	123.62(8)	$Ba4^{iii}$−S2−$Ba3^{v}$	88.19(8)
S1−Ba3−$S4^{vi}$	80.36(8)	$Ba2^{v}$−S2−$Ba3^{v}$	96.14(8)
S3−Ba3−$Cu2^{ix}$	80.4(3)	$Fe1^{v}$−S2−Ba1	87.33(10)
Cu1−Ba3−$Cu2^{ix}$	132.8(4)	$Ba4^{iii}$−S2−Ba1	88.03(8)
$S2^{vii}$−Ba3−$Cu2^{ix}$	140.8(4)	$Ba2^{v}$−S2−Ba1	84.66(7)
$S6^{vi}$−Ba3−$Cu2^{ix}$	41.3(4)	$Ba3^{v}$−S2−Ba1	167.89(11)
$S3^{vi}$−Ba3−$Cu2^{ix}$	133.9(4)	$Fe1^{v}$−S2−$Ba4^{v}$	170.33(13)
$S5^{ix}$−Ba3−$Cu2^{ix}$	52.1(4)	$Ba4^{iii}$−S2−$Ba4^{v}$	95.08(8)
S1−Ba3−$Cu2^{ix}$	99.2(4)	$Ba2^{v}$−S2−$Ba4^{v}$	99.65(8)
$S4^{vi}$−Ba3−$Cu2^{ix}$	93.1(4)	$Ba3^{v}$−S2−$Ba4^{v}$	91.95(8)
S3−Ba3−Fe1	123.61(6)	Ba1−S2−$Ba4^{v}$	99.84(8)
Cu1−Ba3−Fe1	66.00(5)	$Cu1^{vi}$−S3−$Cu2^{vi}$	22.2(6)
$S2^{vii}$−Ba3−Fe1	38.12(6)	$Cu1^{vi}$−S3−Ba3	162.59(14)
$S6^{vi}$−Ba3−Fe1	153.46(6)	$Cu2^{vi}$−S3−Ba3	164.9(5)
$S3^{vi}$−Ba3−Fe1	87.73(6)	$Cu1^{vi}$−S3−$Ba2^{vi}$	83.33(10)

$S5^{ix}$−Ba3−Fe1	92.02(6)	$Cu2^{vi}$−S3−$Ba2^{vi}$	96.7(5)
S1−Ba3−Fe1	37.66(5)	Ba3−S3−$Ba2^{vi}$	98.45(9)
$S4^{vi}$−Ba3−Fe1	87.50(6)	$Cu1^{vi}$−S3−Ba4	80.00(10)
$Cu2^{ix}$−Ba3−Fe1	136.1(4)	$Cu2^{vi}$−S3−Ba4	65.7(5)
S3−Ba3−$Cu1^{ix}$	80.02(6)	Ba3−S3−Ba4	99.19(8)
Cu1−Ba3−$Cu1^{ix}$	142.76(5)	$Ba2^{vi}$−S3−Ba4	162.35(11)
$S2^{vii}$−Ba3−$Cu1^{ix}$	127.51(7)	$Cu1^{vi}$−S3−$Ba1^{x}$	97.43(11)
$S6^{vi}$−Ba3−$Cu1^{ix}$	55.04(7)	$Cu2^{vi}$−S3−$Ba1^{x}$	81.0(6)
$S3^{vi}$−Ba3−$Cu1^{ix}$	146.70(7)	Ba3−S3−$Ba1^{x}$	99.97(9)
$S5^{ix}$−Ba3−$Cu1^{ix}$	38.26(6)	$Ba2^{vi}$−S3−$Ba1^{x}$	85.19(7)
S1−Ba3−$Cu1^{ix}$	90.38(6)	Ba4−S3−$Ba1^{x}$	91.23(8)
$S4^{vi}$−Ba3−$Cu1^{ix}$	102.12(6)	$Cu1^{vi}$−S3−$Ba3^{vi}$	67.94(9)
$Cu2^{ix}$−Ba3−$Cu1^{ix}$	13.8(4)	$Cu2^{vi}$−S3−$Ba3^{vi}$	83.6(6)
Fe1−Ba3−$Cu1^{ix}$	125.21(5)	Ba3−S3−$Ba3^{vi}$	94.68(8)
S3−Ba3−Cu2	120.9(3)	$Ba2^{vi}$−S3−$Ba3^{vi}$	97.27(8)
Cu1−Ba3−Cu2	10.9(3)	Ba4−S3−$Ba3^{vi}$	81.83(7)
$S2^{vii}$−Ba3−Cu2	93.3(3)	$Ba1^{x}$−S3−$Ba3^{vi}$	164.63(11)
$S6^{vi}$−Ba3−Cu2	88.4(3)	$Cu1^{vi}$−S4−$Cu2^{vi}$	22.2(6)
$S3^{vi}$−Ba3−Cu2	37.0(3)	$Cu1^{vi}$−S4−$Ba1^{i}$	83.83(10)
$S5^{ix}$−Ba3−Cu2	156.9(3)	$Cu2^{vi}$−S4−$Ba1^{i}$	97.9(5)
S1−Ba3−Cu2	93.2(3)	$Cu1^{vi}$−S4−$Ba2^{x}$	99.71(11)
$S4^{vi}$−Ba3−Cu2	37.0(3)	$Cu2^{vi}$−S4−$Ba2^{x}$	83.5(6)
$Cu2^{ix}$−Ba3−Cu2	125.2(6)	$Ba1^{i}$−S4−$Ba2^{x}$	86.65(8)
Fe1−Ba3−Cu2	76.9(3)	$Cu1^{vi}$−S4−Ba1	158.38(14)
$Cu1^{ix}$−Ba3−Cu2	137.0(3)	$Cu2^{vi}$−S4−Ba1	162.6(5)
$Cu2^{vi}$−Ba4−S3	43.9(4)	$Ba1^{i}$−S4−Ba1	99.02(9)
$Cu2^{vi}$−Ba4−S4	43.7(4)	$Ba2^{x}$−S4−Ba1	101.85(9)
S3−Ba4−S4	75.78(8)	$Cu1^{vi}$−S4−Ba4	79.34(10)
$Cu2^{vi}$−Ba4−S6	105.6(5)	$Cu2^{vi}$−S4−Ba4	64.9(5)
S3−Ba4−S6	98.76(8)	$Ba1^{i}$−S4−Ba4	162.75(11)
S4−Ba4−S6	70.92(8)	$Ba2^{x}$−S4−Ba4	92.42(8)
$Cu2^{vi}$−Ba4−$S2^{x}$	94.1(4)	Ba1−S4−Ba4	98.03(8)
S3−Ba4−$S2^{x}$	89.36(8)	$Cu1^{vi}$−S4−$Ba3^{vi}$	67.62(9)
S4−Ba4−$S2^{x}$	130.58(8)	$Cu2^{vi}$−S4−$Ba3^{vi}$	83.1(6)
S6−Ba4−$S2^{x}$	158.47(8)	$Ba1^{i}$−S4−$Ba3^{vi}$	96.18(8)
$Cu2^{vi}$−Ba4−$S5^{v}$	155.4(4)	$Ba2^{x}$−S4−$Ba3^{vi}$	166.52(11)
S3−Ba4−$S5^{v}$	160.21(8)	Ba1−S4−$Ba3^{vi}$	90.76(8)
S4−Ba4−$S5^{v}$	117.53(8)	Ba4−S4−$Ba3^{vi}$	80.97(7)
S6−Ba4−$S5^{v}$	74.12(8)	Fe1−S5−Cu1	109.10(13)
$S2^{x}$−Ba4−$S5^{v}$	91.58(8)	Fe1−S5−$Ba1^{xiii}$	87.22(10)
$Cu2^{vi}$−Ba4−$S1^{xi}$	92.5(4)	Cu1−S5−$Ba1^{xiii}$	80.96(9)
S3−Ba4−$S1^{xi}$	130.93(8)	Fe1−S5−Ba2	87.24(10)
S4−Ba4−$S1^{xi}$	85.61(8)	Cu1−S5−Ba2	80.14(10)
S6−Ba4−$S1^{xi}$	117.48(8)	$Ba1^{xiii}$−S5−Ba2	157.34(10)
$S2^{x}$−Ba4−$S1^{xi}$	69.17(8)	Fe1−S5−$Ba4^{vii}$	83.95(10)
$S5^{v}$−Ba4−$S1^{xi}$	67.28(7)	Cu1−S5−$Ba4^{vii}$	166.36(13)
$Cu2^{vi}$−Ba4−$S2^{vii}$	127.1(4)	$Ba1^{xiii}$−S5−$Ba4^{vii}$	104.21(9)
S3−Ba4−$S2^{vii}$	83.18(8)	Ba2−S5−$Ba4^{vii}$	97.03(8)

S4−Ba4−S2^{vii}	137.41(8)	Fe1−S5−Ba3^{viii}	170.43(13)
S6−Ba4−S2^{vii}	76.38(8)	Cu1−S5−Ba3^{viii}	80.41(10)
S2^{x}−Ba4−S2^{vii}	84.92(8)	Ba1^{xiii}−S5−Ba3^{viii}	95.57(8)
S5^{v}−Ba4−S2^{vii}	77.22(7)	Ba2−S5−Ba3^{viii}	93.51(8)
S1^{xi}−Ba4−S2^{vii}	134.55(8)	Ba4^{vii}−S5−Ba3^{viii}	86.49(7)
Cu2^{vi}−Ba4−Cu1^{vi}	12.6(5)	Fe1^{v}−S6−Cu2^{iv}	117.5(5)
S3−Ba4−Cu1^{vi}	39.45(6)	Fe1^{v}−S6−Ba2	89.87(11)
S4−Ba4−Cu1^{vi}	39.13(6)	Cu2^{iv}−S6−Ba2	81.0(4)
S6−Ba4−Cu1^{vi}	93.99(7)	Fe1^{v}−S6−Ba1	90.50(11)
S2^{x}−Ba4−Cu1^{vi}	104.71(7)	Cu2^{iv}−S6−Ba1	79.4(4)
S5^{v}−Ba4−Cu1^{vi}	156.59(7)	Ba2−S6−Ba1	158.12(12)
S1^{xi}−Ba4−Cu1^{vi}	102.57(6)	Fe1^{v}−S6−Ba4	85.34(11)
S2^{vii}−Ba4−Cu1^{vi}	120.24(6)	Cu2^{iv}−S6−Ba4	156.8(5)
Cu2^{vi}−Ba4−Fe1^{xi}	75.3(5)	Ba2−S6−Ba4	104.64(9)
S3−Ba4−Fe1^{xi}	98.38(6)	Ba1−S6−Ba4	97.20(9)
S4−Ba4−Fe1^{xi}	96.05(6)	Fe1^{v}−S6−Ba3^{vi}	166.35(15)
S6−Ba4−Fe1^{xi}	155.06(7)	Cu2^{iv}−S6−Ba3^{vi}	76.1(5)
S2^{x}−Ba4−Fe1^{xi}	39.13(6)	Ba2−S6−Ba3^{vi}	93.67(8)
S5^{v}−Ba4−Fe1^{xi}	94.76(6)	Ba1−S6−Ba3^{vi}	91.09(8)
S1^{xi}−Ba4−Fe1^{xi}	38.46(6)	Ba4−S6−Ba3^{vi}	81.00(7)
S2^{vii}−Ba4−Fe1^{xi}	123.69(6)		

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1; (ii) *x*, *y*+1, *z*; (iii) *x*+1/2, −*y*+3/2, *z*+1/2; (iv) −*x*+3/2, *y*+1/2, −*z*+3/2; (v) −*x*+1/2, *y*+1/2, −*z*+3/2; (vi) −*x*+1, −*y*+1, −*z*+1; (vii) −*x*+1/2, *y*−1/2, −*z*+3/2; (viii) *x*+1/2, −*y*+1/2, *z*+1/2; (ix) *x*−1/2, −*y*+1/2, *z*−1/2; (x) *x*−1/2, −*y*+3/2, *z*−1/2; (xi) −*x*, −*y*+1, −*z*+1; (xii) −*x*+3/2, *y*−1/2, −*z*+3/2; (xiii) *x*, *y*−1, *z*.

Table SI3: The fractional atomic coordinates and U_{iso}/U_{eq} values for the orthorhombic Ba_4FeCuS_6 (space group: *Pnma*) structure.[a]

Atoms	Wyckoff position	Site symmetry	SOF	*x*	*y*	*z*	U_{iso}/U_{eq}
Ba1	4*c*	.*m*.	1	0.48949(9)	0.250000	0.32485(9)	0.0160(3)
Ba2	4*c*	.*m*.	1	0.82477(11)	0.250000	0.51773(14)	0.0304(4)
Fe1	4*c*	.*m*.	0.5	0.7563(3)	0.750000	0.3061(3)	0.0677(18)
Cu1	4*c*	.*m*.	0.5	0.7563(3)	0.750000	0.3061(3)	0.0677(18)
S1	4*c*	.*m*.	1	0.6338(4)	0.750000	0.4451(4)	0.0176(10)
S2	4*c*	.*m*.	1	0.9384(4)	0.750000	0.3609(4)	0.0206(10)
S3	4*c*	.*m*.	1	0.7240(4)	0.250000	0.2068(4)	0.043(2)

[a]U_{iso}/U_{eq} is the one-third value of the trace of the orthogonalized U_{ij} tensor.

Table SI4: Atomic displacement parameter ($Å^2$) for Orthorhombic Ba_4FeCuS_6 (space group: *Pnma*)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0084(5)	0.0244(6)	0.0153(5)	0.000	−0.0001(4)	0.000
Ba2	0.0123(6)	0.0265(7)	0.0524(9)	0.000	0.0048(5)	0.000
Fe1	0.0125(14)	0.165(6)	0.0252(17)	0.000	0.0047(12)	0.000
Cu1	0.0125(14)	0.165(6)	0.0252(17)	0.000	0.0047(12)	0.000
S1	0.0115(19)	0.028(3)	0.0134(19)	0.000	0.0012(16)	0.000
S2	0.015(2)	0.029(3)	0.018(2)	0.000	−0.0025(17)	0.000
S3	0.008(2)	0.104(7)	0.019(2)	0.000	0.0022(18)	0.000

Reference

1 G. Panigrahi, S. Yadav, S. Jana, K. V. Ramanujachary, M. K. Niranjan and J. Prakash, *Dalton Trans.*, 2023, **52**, 621–634.