# $Ba_3Zr_2Cu_4S_9$: the first quaternary phase of the Ba–Zr–Cu–S system

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**Electronic Supplementary Information (ESI)**

The complex dielectric function $\varepsilon(\omega)$ and absorption coefficient $\alpha(\omega)$ are computed in the independent-particle approximation. The imaginary part of the dielectric function $\varepsilon''(\omega)$ is obtained from the joint density of states (JDOS) and the optical momentum matrix in the long wave length limit $\vec{q} = |\vec{k}' - \vec{k}| \to 0$. The expression for the $\varepsilon''(\omega)$ is given as[1]:

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

Here $V_c$ is the primitive cell volume; $w_{\vec{k}}$ is the weight of the k-points; $\hat{e}_i$ and $\hat{e}_j$ are the unit vectors for the three Cartesian directions; indices *c* and *v* refer to conduction band (CB) and valence band (VB) states respectively; $u_{c\vec{k}}$ is the cell periodic 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 real part of the dielectric function $\varepsilon'(\omega)$ is obtained from the Kramers-Kronig transformation as follows:

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

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

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

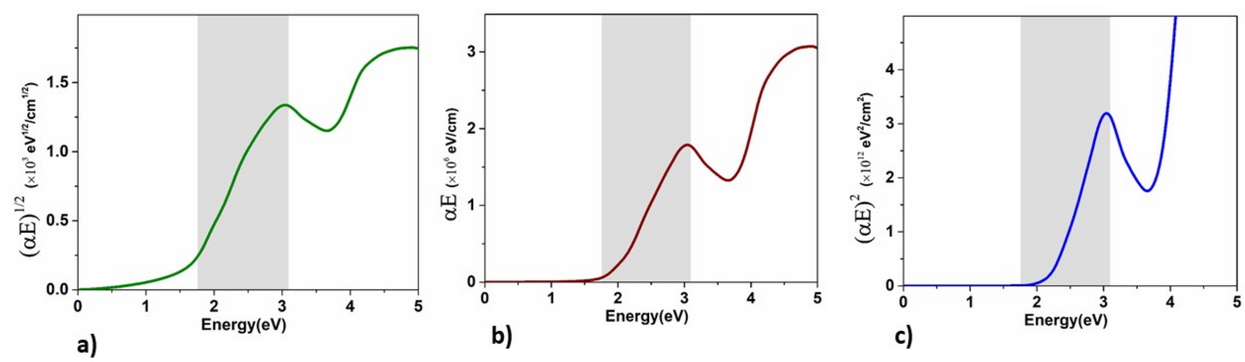


**Fig. S1: (a)** $(\alpha E)^{1/2}$, **(b)** $(\alpha E)$, and **(c)** $(\alpha E)^2$ as function of energy. $\alpha$ and $E$ are absorption and energy, respectively.

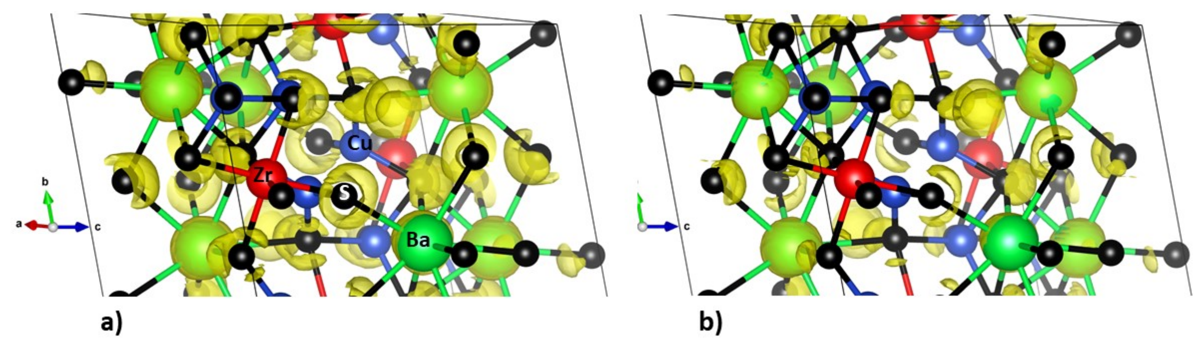


**Fig. S2:** 3D isosurfaces of the electron localization function (ELF) for $Ba_3Zr_2Cu_4S_9$ **(a)** $ELF = 0.85$ and **(b)** $ELF = 0.87$. The yellow cloud indicates the charge density due to charge transfer. Green, red, blue and black back ball indicate Ba, Zr, Cu and S atoms respectively.

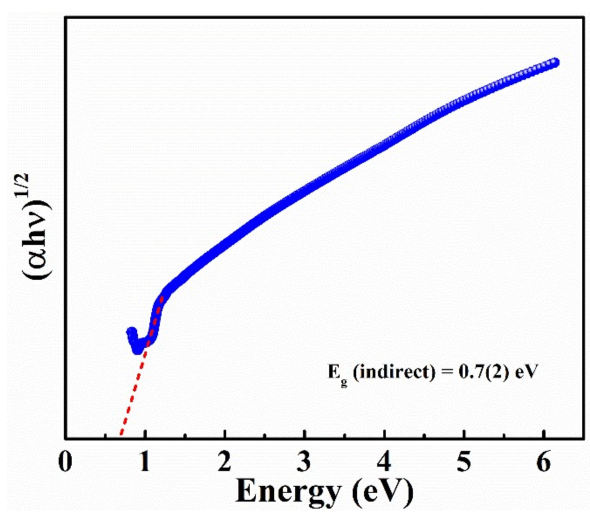


**Fig. S3:** The indirect bandgap Tauc plot of the $Ba_3Zr_2Cu_4S_9$ polycrystalline sample.

**Table S1:** The computed fractional atomic coordinates $(x, y, z)$ in $Ba_3Zr_2Cu_4S_9$ unit cell.

| | $x$ | | $y$ | | $z$ | |
|---|---|---|---|---|---|---|
| | **Cal.** | **Exp.** | **Cal.** | **Exp.** | **Cal.** | **Exp.** |
| **Ba(1)** | 0.01747 | 0.01802 | 0.27960 | 0.27871 | 0.51270 | 0.51290 |
| **Ba(2)** | 0.30659 | 0.30795 | 0.24541 | 0.24620 | 0.83308 | 0.83313 |
| **Ba(3)** | 0.65079 | 0.65117 | 0.23106 | 0.23065 | 0.15857 | 0.15715 |
| **Zr(1)** | 0.15555 | 0.15627 | 0.48505 | 0.48563 | 0.15889 | 0.15931 |
| **Zr(2)** | 0.33895 | 0.33931 | 0.01538 | 0.01462 | 0.34447 | 0.34427 |
| **Cu(1)** | 0.13244 | 0.13197 | 0.05723 | 0.05741 | 0.11966 | 0.12001 |
| **Cu(2)** | 0.14526 | 0.14696 | 0.75271 | 0.75455 | 0.08268 | 0.08244 |
| **Cu(3)** | 0.38731 | 0.38616 | 0.42916 | 0.42810 | 0.36928 | 0.36920 |
| **Cu(4)** | 0.53698 | 0.53636 | 0.25820 | 0.26012 | 0.60098 | 0.60063 |
| **S(1)** | 0.05490 | 0.05218 | 0.43269 | 0.43441 | 0.32647 | 0.32618 |
| **S(2)** | 0.14670 | 0.14581 | 0.74847 | 0.74816 | 0.27357 | 0.27349 |
| **S(3)** | 0.15722 | 0.15909 | 0.22901 | 0.22928 | 0.04666 | 0.04698 |
| **S(4)** | 0.30810 | 0.30684 | 0.05454 | 0.05320 | 0.56118 | 0.56037 |
| **S(5)** | 0.40068 | 0.40573 | 0.94857 | 0.95002 | 0.13206 | 0.13424 |
| **S(6)** | 0.54034 | 0.54174 | 0.26557 | 0.26485 | 0.41321 | 0.41189 |
| **S(7)** | 0.54183 | 0.54166 | 0.54198 | 0.54088 | 0.27358 | 0.27128 |
| **S(8)** | 0.76866 | 0.76900 | 0.44856 | 0.44921 | 0.02199 | 0.02232 |
| **S(9)** | 0.99470 | 0.99430 | 0.06239 | 0.06044 | 0.26597 | 0.26729 |

**Table S2:** The atomic displacement parameters (Å$^2$) for $Ba_3Zr_2Cu_4S_9$ structure.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ba(1) | 0.01604(11) | 0.01584(11) | 0.00967(10) | 0.00746(8) | 0.00387(9) | 0.00429(9) |
| Ba(2) | 0.01126(11) | 0.01336(10) | 0.01206(11) | 0.00422(8) | 0.00428(9) | 0.00623(9) |
| Ba(3) | 0.01455(11) | 0.01335(10) | 0.01217(11) | -0.00128(8) | 0.00156(9) | 0.00537(9) |
| Zr(1) | 0.00921(17) | 0.00930(15) | 0.00891(16) | 0.00198(12) | 0.00291(13) | 0.00377(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Zr(2) | 0.00941(17) | 0.00924(15) | 0.00847(16) | 0.00265(12) | 0.00276(13) | 0.00364(13) |
| Cu(1) | 0.0247(3) | 0.0472(4) | 0.0295(3) | 0.0209(3) | 0.0164(2) | 0.0287(3) |
| Cu(2) | 0.0156(2) | 0.0132(2) | 0.0176(3) | 0.00174(18) | 0.0069(2) | 0.0039(2) |
| Cu(3) | 0.0179(3) | 0.0452(4) | 0.0337(3) | 0.0143(3) | 0.0115(2) | 0.0299(3) |
| Cu(4) | 0.0147(2) | 0.0161(2) | 0.0170(3) | 0.00248(18) | 0.0054(2) | 0.0040(2) |
| S(1) | 0.0111(4) | 0.0112(4) | 0.0110(4) | 0.0020(3) | 0.0044(3) | 0.0043(3) |
| S(2) | 0.0106(4) | 0.0080(4) | 0.0091(4) | 0.0019(3) | 0.0027(3) | 0.0031(3) |
| S(3) | 0.0156(4) | 0.0108(4) | 0.0116(5) | 0.0043(3) | 0.0042(4) | 0.0047(4) |
| S(4) | 0.0099(4) | 0.0122(4) | 0.0092(4) | 0.0034(3) | 0.0033(3) | 0.0050(3) |
| S(5) | 0.0114(4) | 0.0094(4) | 0.0105(4) | 0.0025(3) | 0.0045(3) | 0.0037(3) |
| S(6) | 0.0131(4) | 0.0113(4) | 0.0108(5) | -0.0001(3) | 0.0011(4) | 0.0052(3) |
| S(7) | 0.0096(4) | 0.0104(4) | 0.0121(4) | 0.0025(3) | 0.0034(3) | 0.0042(3) |
| S(8) | 0.0098(4) | 0.0106(4) | 0.0098(4) | 0.0030(3) | 0.0035(3) | 0.0045(3) |
| S(9) | 0.0105(4) | 0.0117(4) | 0.0104(4) | 0.0034(3) | 0.0033(3) | 0.0039(3) |

**Table S3:** The geometric parameters of $Ba_3Zr_2Cu_4S_9$ structure.

| | | | |
|---|---|---|---|
| Ba1—S9$^{i}$ | 3.0504(10) | Zr1—S7 | 2.5524(10) |
| Ba1—S1$^{ii}$ | 3.1485(10) | Zr1—S3 | 2.5611(10) |
| Ba1—S6$^{i}$ | 3.1685(10) | Zr1—S2 | 2.6355(9) |
| Ba1—S2$^{ii}$ | 3.1873(10) | Zr1—S8$^{i}$ | 2.6679(10) |
| Ba1—S1 | 3.2492(10) | Zr1—S8$^{ix}$ | 2.6817(10) |
| Ba1—S7$^{iii}$ | 3.3015(10) | Zr1—Cu3 | 2.9334(7) |
| Ba1—S4 | 3.3504(9) | Zr1—Cu2$^{x}$ | 3.1565(6) |
| Ba1—Cu4 | 3.5116(6) | Zr1—Cu4$^{iii}$ | 3.2169(6) |
| Ba1—S4$^{iv}$ | 3.5749(9) | Zr1—Cu2 | 3.2340(6) |

| | | | |
|---|---|---|---|
| Ba1—Cu4$^{i}$ | 3.7599(5) | Zr2—S9$^{i}$ | 2.4904(10) |
| Ba1—Cu3 | 3.8999(6) | Zr2—S6 | 2.5483(10) |
| Ba1—Ba2 | 4.0550(4) | Zr2—S5$^{viii}$ | 2.6093(10) |
| Ba2—S5$^{iii}$ | 3.0530(10) | Zr2—S4 | 2.6138(10) |
| Ba2—S2$^{ii}$ | 3.0837(10) | Zr2—S2$^{viii}$ | 2.6673(9) |
| Ba2—S3$^{v}$ | 3.1007(10) | Zr2—S4$^{vi}$ | 2.7043(10) |
| Ba2—S7$^{iii}$ | 3.1054(10) | Zr2—Cu1 | 2.9499(7) |
| Ba2—S9$^{vi}$ | 3.2382(10) | Zr2—Cu4 | 3.1308(6) |
| Ba2—S8$^{iii}$ | 3.2514(9) | Zr2—Cu2$^{viii}$ | 3.2364(6) |
| Ba2—S4 | 3.2675(10) | Zr2—Cu4$^{vi}$ | 3.3018(6) |
| Ba2—S8$^{v}$ | 3.3558(10) | Cu1—S9$^{i}$ | 2.2412(11) |
| Ba2—Cu2$^{ii}$ | 3.5581(5) | Cu1—S3 | 2.2575(11) |
| Ba2—Cu4 | 3.6311(6) | Cu1—S5$^{viii}$ | 2.3057(11) |
| Ba2—Cu2$^{iii}$ | 3.6407(6) | Cu1—Cu1$^{xi}$ | 2.7801(13) |
| Ba3—S1$^{vii}$ | 3.0225(10) | Cu1—Cu2$^{viii}$ | 3.0418(8) |
| Ba3—S5$^{viii}$ | 3.0800(10) | Cu2—S8$^{ix}$ | 2.3082(10) |
| Ba3—S3 | 3.3132(10) | Cu2—S5 | 2.3263(11) |
| Ba3—S6 | 3.3134(11) | Cu2—S3$^{x}$ | 2.3513(12) |
| Ba3—S5$^{ix}$ | 3.3194(10) | Cu2—S2 | 2.3637(12) |
| Ba3—S7 | 3.3211(10) | Cu3—S6 | 2.2443(11) |
| Ba3—S8 | 3.3630(9) | Cu3—S1 | 2.2449(11) |
| Ba3—S9 | 3.3898(10) | Cu3—S7 | 2.2974(11) |
| Ba3—Cu2$^{ix}$ | 3.6005(6) | Cu3—Cu3$^{iii}$ | 2.9289(13) |
| Ba3—Cu1 | 3.6610(7) | Cu4—S4 | 2.3356(10) |

| | | | |
|---|---|---|---|
| Ba3—Cu3 | 3.7574(7) | Cu4—S6 | 2.3372(12) |
| Ba3—Zr1$^{vii}$ | 4.1140(4) | Cu4—S7$^{iii}$ | 2.3583(11) |
| Zr1—S1 | 2.5254(10) | Cu4—S2$^{iii}$ | 2.3617(13) |
| S9$^{i}$—Ba1—S1$^{ii}$ | 152.01(3) | S5$^{viii}$—Zr2—Cu2$^{viii}$ | 45.34(2) |
| S9$^{i}$—Ba1—S6$^{i}$ | 90.13(3) | S4—Zr2—Cu2$^{viii}$ | 132.58(2) |
| S1$^{ii}$—Ba1—S6$^{i}$ | 73.99(2) | S2$^{viii}$—Zr2—Cu2$^{viii}$ | 45.96(3) |
| S9$^{i}$—Ba1—S2$^{ii}$ | 131.41(3) | S4$^{vi}$—Zr2—Cu2$^{viii}$ | 100.99(2) |
| S1$^{ii}$—Ba1—S2$^{ii}$ | 68.07(2) | Cu1—Zr2—Cu2$^{viii}$ | 58.686(18) |
| S6$^{i}$—Ba1—S2$^{ii}$ | 76.82(2) | Cu4—Zr2—Cu2$^{viii}$ | 177.962(18) |
| S9$^{i}$—Ba1—S1 | 70.90(3) | S9$^{i}$—Zr2—Cu4$^{vi}$ | 129.90(3) |
| S1$^{ii}$—Ba1—S1 | 84.33(3) | S6—Zr2—Cu4$^{vi}$ | 132.41(3) |
| S6$^{i}$—Ba1—S1 | 83.75(3) | S5$^{viii}$—Zr2—Cu4$^{vi}$ | 96.70(2) |
| S2$^{ii}$—Ba1—S1 | 149.62(2) | S4—Zr2—Cu4$^{vi}$ | 75.17(2) |
| S9$^{i}$—Ba1—S7$^{iii}$ | 122.75(3) | S2$^{viii}$—Zr2—Cu4$^{vi}$ | 45.07(3) |
| S1$^{ii}$—Ba1—S7$^{iii}$ | 71.80(2) | S4$^{vi}$—Zr2—Cu4$^{vi}$ | 44.40(2) |
| S6$^{i}$—Ba1—S7$^{iii}$ | 145.54(2) | Cu1—Zr2—Cu4$^{vi}$ | 133.73(2) |
| S2$^{ii}$—Ba1—S7$^{iii}$ | 86.73(3) | Cu4—Zr2—Cu4$^{vi}$ | 102.928(15) |
| S1—Ba1—S7$^{iii}$ | 96.79(2) | Cu2$^{viii}$—Zr2—Cu4$^{vi}$ | 75.180(15) |
| S9$^{i}$—Ba1—S4 | 70.54(3) | S9$^{i}$—Zr2—Ba1 | 47.92(2) |
| S1$^{ii}$—Ba1—S4 | 136.36(3) | S6—Zr2—Ba1 | 72.54(2) |
| S6$^{i}$—Ba1—S4 | 135.99(2) | S5$^{viii}$—Zr2—Ba1 | 133.92(2) |
| S2$^{ii}$—Ba1—S4 | 86.93(2) | S4—Zr2—Ba1 | 54.67(2) |
| S1—Ba1—S4 | 122.87(2) | S2$^{viii}$—Zr2—Ba1 | 110.24(2) |
| S7$^{iii}$—Ba1—S4 | 71.58(2) | S4$^{vi}$—Zr2—Ba1 | 130.31(2) |

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|---|---|---|---|
| S9$^{i}$—Ba1—Cu4 | 84.32(2) | Cu1—Zr2—Ba1 | 86.626(15) |
| S1$^{ii}$—Ba1—Cu4 | 111.92(2) | Cu4—Zr2—Ba1 | 56.254(12) |
| S6$^{i}$—Ba1—Cu4 | 174.09(2) | Cu2$^{viii}$—Zr2—Ba1 | 125.459(14) |
| S2$^{ii}$—Ba1—Cu4 | 105.37(2) | Cu4$^{vi}$—Zr2—Ba1 | 126.781(14) |
| S1—Ba1—Cu4 | 96.33(2) | S9$^{i}$—Cu1—S3 | 125.11(4) |
| S7$^{iii}$—Ba1—Cu4 | 40.356(19) | S9$^{i}$—Cu1—S5$^{viii}$ | 110.78(4) |
| S4—Ba1—Cu4 | 39.712(17) | S3—Cu1—S5$^{viii}$ | 114.66(4) |
| S9$^{i}$—Ba1—S4$^{iv}$ | 66.98(2) | S9$^{i}$—Cu1—Cu1$^{xi}$ | 117.19(4) |
| S1$^{ii}$—Ba1—S4$^{iv}$ | 123.11(2) | S3—Cu1—Cu1$^{xi}$ | 74.44(4) |
| S6$^{i}$—Ba1—S4$^{iv}$ | 65.73(2) | S5$^{viii}$—Cu1—Cu1$^{xi}$ | 109.14(4) |
| S2$^{ii}$—Ba1—S4$^{iv}$ | 64.97(2) | S9$^{i}$—Cu1—Zr2 | 55.32(3) |
| S1—Ba1—S4$^{iv}$ | 126.82(2) | S3—Cu1—Zr2 | 136.66(4) |
| S7$^{iii}$—Ba1—S4$^{iv}$ | 133.06(2) | S5$^{viii}$—Cu1—Zr2 | 58.00(3) |
| S4—Ba1—S4$^{iv}$ | 70.31(2) | Cu1$^{xi}$—Cu1—Zr2 | 148.35(4) |
| Cu4—Ba1—S4$^{iv}$ | 109.970(18) | S9$^{i}$—Cu1—Cu2$^{viii}$ | 87.02(3) |
| S9$^{i}$—Ba1—Cu4$^{i}$ | 116.36(2) | S3—Cu1—Cu2$^{viii}$ | 146.95(4) |
| S1$^{ii}$—Ba1—Cu4$^{i}$ | 63.789(19) | S5$^{viii}$—Cu1—Cu2$^{viii}$ | 49.25(3) |
| S6$^{i}$—Ba1—Cu4$^{i}$ | 38.24(2) | Cu1$^{xi}$—Cu1—Cu2$^{viii}$ | 84.33(3) |
| S2$^{ii}$—Ba1—Cu4$^{i}$ | 38.65(2) | Zr2—Cu1—Cu2$^{viii}$ | 65.367(17) |
| S1—Ba1—Cu4$^{i}$ | 117.76(2) | S9$^{i}$—Cu1—Ba3 | 127.70(4) |
| S7$^{iii}$—Ba1—Cu4$^{i}$ | 118.46(2) | S3—Cu1—Ba3 | 62.93(3) |
| S4—Ba1—Cu4$^{i}$ | 116.553(18) | S5$^{viii}$—Cu1—Ba3 | 56.85(3) |
| Cu4—Ba1—Cu4$^{i}$ | 143.95(2) | Cu1$^{xi}$—Cu1—Ba3 | 114.49(3) |
| S4$^{iv}$—Ba1—Cu4$^{i}$ | 59.604(16) | Zr2—Cu1—Ba3 | 83.872(17) |

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|---|---|---|---|
| S9$^{i}$—Ba1—Cu3 | 69.23(2) | Cu2$^{viii}$—Cu1—Ba3 | 105.665(18) |
| S1$^{ii}$—Ba1—Cu3 | 97.91(2) | S8$^{ix}$—Cu2—S5 | 111.17(4) |
| S6$^{i}$—Ba1—Cu3 | 118.61(2) | S8$^{ix}$—Cu2—S3$^{x}$ | 107.28(4) |
| S2$^{ii}$—Ba1—Cu3 | 156.54(2) | S5—Cu2—S3$^{x}$ | 109.74(4) |
| S1—Ba1—Cu3 | 35.129(19) | S8$^{ix}$—Cu2—S2 | 106.97(4) |
| S7$^{iii}$—Ba1—Cu3 | 70.68(2) | S5—Cu2—S2 | 103.82(4) |
| S4—Ba1—Cu3 | 91.667(18) | S3$^{x}$—Cu2—S2 | 117.82(4) |
| Cu4—Ba1—Cu3 | 61.204(13) | S8$^{ix}$—Cu2—Cu1$^{xii}$ | 148.41(3) |
| S4$^{iv}$—Ba1—Cu3 | 136.025(19) | S5—Cu2—Cu1$^{xii}$ | 48.66(3) |
| Cu4$^{i}$—Ba1—Cu3 | 151.696(14) | S3$^{x}$—Cu2—Cu1$^{xii}$ | 68.16(3) |
| S9$^{i}$—Ba1—Ba2 | 121.406(19) | S2—Cu2—Cu1$^{xii}$ | 102.16(3) |
| S1$^{ii}$—Ba1—Ba2 | 86.409(18) | S8$^{ix}$—Cu2—Zr1$^{x}$ | 55.88(3) |
| S6$^{i}$—Ba1—Ba2 | 125.35(2) | S5—Cu2—Zr1$^{x}$ | 137.26(3) |
| S2$^{ii}$—Ba1—Ba2 | 48.60(2) | S3$^{x}$—Cu2—Zr1$^{x}$ | 53.00(3) |
| S1—Ba1—Ba2 | 145.283(19) | S2—Cu2—Zr1$^{x}$ | 118.85(3) |
| S7$^{iii}$—Ba1—Ba2 | 48.621(17) | Cu1$^{xii}$—Cu2—Zr1$^{x}$ | 118.44(2) |
| S4—Ba1—Ba2 | 51.293(17) | S8$^{ix}$—Cu2—Zr1 | 54.85(3) |
| Cu4—Ba1—Ba2 | 56.812(11) | S5—Cu2—Zr1 | 130.42(3) |
| S4$^{iv}$—Ba1—Ba2 | 85.818(17) | S3$^{x}$—Cu2—Zr1 | 119.84(3) |
| Cu4$^{i}$—Ba1—Ba2 | 87.253(12) | S2—Cu2—Zr1 | 53.47(2) |
| Cu3—Ba1—Ba2 | 114.267(12) | Cu1$^{xii}$—Cu2—Zr1 | 155.63(2) |
| S5$^{iii}$—Ba2—S2$^{ii}$ | 143.02(2) | Zr1$^{x}$—Cu2—Zr1 | 78.935(15) |
| S5$^{iii}$—Ba2—S3$^{v}$ | 91.70(3) | S8$^{ix}$—Cu2—Zr2$^{xii}$ | 137.67(3) |
| S2$^{ii}$—Ba2—S3$^{v}$ | 81.52(2) | S5—Cu2—Zr2$^{xii}$ | 52.93(3) |

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|---|---|---|---|
| S5$^{iii}$—Ba2—S7$^{iii}$ | 113.89(3) | S3$^{x}$—Cu2—Zr2$^{xii}$ | 115.01(3) |
| S2$^{ii}$—Ba2—S7$^{iii}$ | 92.11(3) | S2—Cu2—Zr2$^{xii}$ | 54.21(2) |
| S3$^{v}$—Ba2—S7$^{iii}$ | 141.90(3) | Cu1$^{xii}$—Cu2—Zr2$^{xii}$ | 55.948(16) |
| S5$^{iii}$—Ba2—S9$^{vi}$ | 75.08(2) | Zr1$^{x}$—Cu2—Zr2$^{xii}$ | 164.051(19) |
| S2$^{ii}$—Ba2—S9$^{vi}$ | 68.12(2) | Zr1—Cu2—Zr2$^{xii}$ | 102.476(19) |
| S3$^{v}$—Ba2—S9$^{vi}$ | 73.38(3) | S8$^{ix}$—Cu2—Ba2$^{ii}$ | 122.46(3) |
| S7$^{iii}$—Ba2—S9$^{vi}$ | 138.40(3) | S5—Cu2—Ba2$^{ii}$ | 126.23(3) |
| S5$^{iii}$—Ba2—S8$^{iii}$ | 141.25(3) | S3$^{x}$—Cu2—Ba2$^{ii}$ | 59.17(3) |
| S2$^{ii}$—Ba2—S8$^{iii}$ | 70.54(2) | S2—Cu2—Ba2$^{ii}$ | 58.70(3) |
| S3$^{v}$—Ba2—S8$^{iii}$ | 71.65(2) | Cu1$^{xii}$—Cu2—Ba2$^{ii}$ | 83.260(16) |
| S7$^{iii}$—Ba2—S8$^{iii}$ | 70.83(2) | Zr1$^{x}$—Cu2—Ba2$^{ii}$ | 81.739(14) |
| S9$^{vi}$—Ba2—S8$^{iii}$ | 128.67(2) | Zr1—Cu2—Ba2$^{ii}$ | 82.649(13) |
| S5$^{iii}$—Ba2—S4 | 72.95(2) | Zr2$^{xii}$—Cu2—Ba2$^{ii}$ | 82.693(13) |
| S2$^{ii}$—Ba2—S4 | 90.16(3) | S8$^{ix}$—Cu2—Ba3$^{ix}$ | 65.16(3) |
| S3$^{v}$—Ba2—S4 | 141.78(2) | S5—Cu2—Ba3$^{ix}$ | 63.95(3) |
| S7$^{iii}$—Ba2—S4 | 75.20(2) | S3$^{x}$—Cu2—Ba3$^{ix}$ | 83.68(3) |
| S9$^{vi}$—Ba2—S4 | 68.93(2) | S2—Cu2—Ba3$^{ix}$ | 158.40(3) |
| S8$^{iii}$—Ba2—S4 | 139.79(3) | Cu1$^{xii}$—Cu2—Ba3$^{ix}$ | 83.265(17) |
| S5$^{iii}$—Ba2—S8$^{v}$ | 73.08(2) | Zr1$^{x}$—Cu2—Ba3$^{ix}$ | 74.690(14) |
| S2$^{ii}$—Ba2—S8$^{v}$ | 143.17(2) | Zr1—Cu2—Ba3$^{ix}$ | 119.412(16) |
| S3$^{v}$—Ba2—S8$^{v}$ | 92.92(3) | Zr2$^{xii}$—Cu2—Ba3$^{ix}$ | 116.872(16) |
| S7$^{iii}$—Ba2—S8$^{v}$ | 70.10(2) | Ba2$^{ii}$—Cu2—Ba3$^{ix}$ | 142.848(19) |
| S9$^{vi}$—Ba2—S8$^{v}$ | 144.82(2) | S8$^{ix}$—Cu2—Ba2$^{iii}$ | 64.18(3) |
| S8$^{iii}$—Ba2—S8$^{v}$ | 73.15(3) | S5—Cu2—Ba2$^{iii}$ | 56.51(3) |

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| S4—Ba2—S8$^{v}$ | 114.44(2) | S3$^{x}$—Cu2—Ba2$^{iii}$ | 152.97(3) |
| S5$^{iii}$—Ba2—Cu2$^{ii}$ | 123.90(2) | S2—Cu2—Ba2$^{iii}$ | 89.02(3) |
| S2$^{ii}$—Ba2—Cu2$^{ii}$ | 40.92(2) | Cu1$^{xii}$—Cu2—Ba2$^{iii}$ | 104.941(18) |
| S3$^{v}$—Ba2—Cu2$^{ii}$ | 40.63(2) | Zr1$^{x}$—Cu2—Ba2$^{iii}$ | 118.584(16) |
| S7$^{iii}$—Ba2—Cu2$^{ii}$ | 122.16(2) | Zr1—Cu2—Ba2$^{iii}$ | 77.697(13) |
| S9$^{vi}$—Ba2—Cu2$^{ii}$ | 65.435(19) | Zr2$^{xii}$—Cu2—Ba2$^{iii}$ | 76.943(14) |
| S8$^{iii}$—Ba2—Cu2$^{ii}$ | 63.478(17) | Ba2$^{ii}$—Cu2—Ba2$^{iii}$ | 147.717(19) |
| S4—Ba2—Cu2$^{ii}$ | 122.315(19) | Ba3$^{ix}$—Cu2—Ba2$^{iii}$ | 69.405(10) |
| S8$^{v}$—Ba2—Cu2$^{ii}$ | 123.229(19) | S6—Cu3—S1 | 129.29(4) |
| S5$^{iii}$—Ba2—Cu4 | 82.79(2) | S6—Cu3—S7 | 113.83(4) |
| S2$^{ii}$—Ba2—Cu4 | 104.82(2) | S1—Cu3—S7 | 110.49(4) |
| S3$^{v}$—Ba2—Cu4 | 173.62(2) | S6—Cu3—Cu3$^{iii}$ | 77.69(3) |
| S7$^{iii}$—Ba2—Cu4 | 40.036(19) | S1—Cu3—Cu3$^{iii}$ | 112.23(4) |
| S9$^{vi}$—Ba2—Cu4 | 108.07(2) | S7—Cu3—Cu3$^{iii}$ | 106.11(4) |
| S8$^{iii}$—Ba2—Cu4 | 110.859(19) | S6—Cu3—Zr1 | 140.55(4) |
| S4—Ba2—Cu4 | 39.133(17) | S1—Cu3—Zr1 | 56.51(3) |
| S8$^{v}$—Ba2—Cu4 | 82.422(19) | S7—Cu3—Zr1 | 56.86(3) |
| Cu2$^{ii}$—Ba2—Cu4 | 145.726(17) | Cu3$^{iii}$—Cu3—Zr1 | 140.62(4) |
| S5$^{iii}$—Ba2—Cu2$^{iii}$ | 39.46(2) | S6—Cu3—Ba3 | 61.00(3) |
| S2$^{ii}$—Ba2—Cu2$^{iii}$ | 171.33(2) | S1—Cu3—Ba3 | 128.00(4) |
| S3$^{v}$—Ba2—Cu2$^{iii}$ | 107.14(2) | S7—Cu3—Ba3 | 61.01(3) |
| S7$^{iii}$—Ba2—Cu2$^{iii}$ | 80.82(2) | Cu3$^{iii}$—Cu3—Ba3 | 119.43(3) |
| S9$^{vi}$—Ba2—Cu2$^{iii}$ | 114.198(19) | Zr1—Cu3—Ba3 | 85.192(17) |
| S8$^{iii}$—Ba2—Cu2$^{iii}$ | 111.307(19) | S6—Cu3—Ba1 | 79.34(3) |

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| S4—Ba2—Cu2$^{iii}$ | 83.227(19) | S1—Cu3—Ba1 | 56.39(3) |
| S8$^{v}$—Ba2—Cu2$^{iii}$ | 38.254(17) | S7—Cu3—Ba1 | 166.53(3) |
| Cu2$^{ii}$—Ba2—Cu2$^{iii}$ | 147.72(2) | Cu3$^{iii}$—Cu3—Ba1 | 78.71(2) |
| Cu4—Ba2—Cu2$^{iii}$ | 66.530(12) | Zr1—Cu3—Ba1 | 111.396(18) |
| S5$^{iii}$—Ba2—Ba1 | 125.944(19) | Ba3—Cu3—Ba1 | 128.082(19) |
| S2$^{ii}$—Ba2—Ba1 | 50.84(2) | S4—Cu4—S6 | 107.17(4) |
| S3$^{v}$—Ba2—Ba1 | 132.33(2) | S4—Cu4—S7$^{iii}$ | 111.96(4) |
| S7$^{iii}$—Ba2—Ba1 | 52.914(18) | S6—Cu4—S7$^{iii}$ | 114.87(4) |
| S9$^{vi}$—Ba2—Ba1 | 88.060(18) | S4—Cu4—S2$^{iii}$ | 105.84(4) |
| S8$^{iii}$—Ba2—Ba1 | 88.703(19) | S6—Cu4—S2$^{iii}$ | 114.36(4) |
| S4—Ba2—Ba1 | 53.144(18) | S7$^{iii}$—Cu4—S2$^{iii}$ | 102.37(4) |
| S8$^{v}$—Ba2—Ba1 | 122.990(18) | S4—Cu4—Zr2 | 54.83(3) |
| Cu2$^{ii}$—Ba2—Ba1 | 91.701(12) | S6—Cu4—Zr2 | 53.18(3) |
| Cu4—Ba2—Ba1 | 54.029(10) | S7$^{iii}$—Cu4—Zr2 | 140.11(3) |
| Cu2$^{iii}$—Ba2—Ba1 | 120.497(11) | S2$^{iii}$—Cu4—Zr2 | 117.29(3) |
| S1$^{vii}$—Ba3—S5$^{viii}$ | 136.36(3) | S4—Cu4—Zr1$^{iii}$ | 136.19(3) |
| S1$^{vii}$—Ba3—S3 | 139.54(3) | S6—Cu4—Zr1$^{iii}$ | 116.55(3) |
| S5$^{viii}$—Ba3—S3 | 73.76(2) | S7$^{iii}$—Cu4—Zr1$^{iii}$ | 51.74(3) |
| S1$^{vii}$—Ba3—S6 | 84.96(3) | S2$^{iii}$—Cu4—Zr1$^{iii}$ | 53.77(2) |
| S5$^{viii}$—Ba3—S6 | 69.46(2) | Zr2—Cu4—Zr1$^{iii}$ | 164.875(19) |
| S3—Ba3—S6 | 83.81(2) | S4—Cu4—Zr2$^{vi}$ | 54.10(3) |
| S1$^{vii}$—Ba3—S5$^{ix}$ | 120.63(3) | S6—Cu4—Zr2$^{vi}$ | 115.82(3) |
| S5$^{viii}$—Ba3—S5$^{ix}$ | 82.33(3) | S7$^{iii}$—Cu4—Zr2$^{vi}$ | 129.23(3) |
| S3—Ba3—S5$^{ix}$ | 83.48(2) | S2$^{iii}$—Cu4—Zr2$^{vi}$ | 53.09(2) |

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| S6—Ba3—S5$^{ix}$ | 151.33(2) | Zr2—Cu4—Zr2$^{vi}$ | 77.071(15) |
| S1$^{vii}$—Ba3—S7 | 73.07(2) | Zr1$^{iii}$—Cu4—Zr2$^{vi}$ | 101.417(19) |
| S5$^{viii}$—Ba3—S7 | 125.12(3) | S4—Cu4—Ba1 | 66.42(3) |
| S3—Ba3—S7 | 66.55(2) | S6—Cu4—Ba1 | 87.26(3) |
| S6—Ba3—S7 | 70.00(2) | S7$^{iii}$—Cu4—Ba1 | 65.03(3) |
| S5$^{ix}$—Ba3—S7 | 126.74(2) | S2$^{iii}$—Cu4—Ba1 | 158.35(3) |
| S1$^{vii}$—Ba3—S8 | 72.54(2) | Zr2—Cu4—Ba1 | 75.900(14) |
| S5$^{viii}$—Ba3—S8 | 148.85(3) | Zr1$^{iii}$—Cu4—Ba1 | 116.765(16) |
| S3—Ba3—S8 | 89.10(2) | Zr2$^{vi}$—Cu4—Ba1 | 119.930(16) |
| S6—Ba3—S8 | 135.50(2) | S4—Cu4—Ba2 | 62.00(3) |
| S5$^{ix}$—Ba3—S8 | 69.80(2) | S6—Cu4—Ba2 | 156.30(3) |
| S7—Ba3—S8 | 66.92(2) | S7$^{iii}$—Cu4—Ba2 | 57.89(3) |
| S1$^{vii}$—Ba3—S9 | 69.28(2) | S2$^{iii}$—Cu4—Ba2 | 89.28(3) |
| S5$^{viii}$—Ba3—S9 | 72.55(2) | Zr2—Cu4—Ba2 | 115.644(16) |
| S3—Ba3—S9 | 146.21(2) | Zr1$^{iii}$—Cu4—Ba2 | 78.048(14) |
| S6—Ba3—S9 | 82.12(2) | Zr2$^{vi}$—Cu4—Ba2 | 76.293(13) |
| S5$^{ix}$—Ba3—S9 | 94.56(2) | Ba1—Cu4—Ba2 | 69.159(10) |
| S7—Ba3—S9 | 134.57(2) | S4—Cu4—Ba1$^{vii}$ | 125.05(3) |
| S8—Ba3—S9 | 121.97(2) | S6—Cu4—Ba1$^{vii}$ | 57.04(3) |
| S1$^{vii}$—Ba3—Cu2$^{ix}$ | 84.39(2) | S7$^{iii}$—Cu4—Ba1$^{vii}$ | 122.46(3) |
| S5$^{viii}$—Ba3—Cu2$^{ix}$ | 119.86(2) | S2$^{iii}$—Cu4—Ba1$^{vii}$ | 57.45(3) |
| S3—Ba3—Cu2$^{ix}$ | 103.53(2) | Zr2—Cu4—Ba1$^{vii}$ | 85.071(14) |
| S6—Ba3—Cu2$^{ix}$ | 169.26(2) | Zr1$^{iii}$—Cu4—Ba1$^{vii}$ | 79.806(13) |
| S5$^{ix}$—Ba3—Cu2$^{ix}$ | 39.022(18) | Zr2$^{vi}$—Cu4—Ba1$^{vii}$ | 84.072(13) |

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| $S7—Ba3—Cu2^{ix}$ | 105.428(19) | $Ba1—Cu4—Ba1^{vii}$ | 143.95(2) |
| $S8—Ba3—Cu2^{ix}$ | 38.527(17) | $Ba2—Cu4—Ba1^{vii}$ | 146.653(19) |
| $S9—Ba3—Cu2^{ix}$ | 95.367(19) | Cu3—S1—Zr1 | 75.64(3) |
| $S1^{vii}—Ba3—Cu1$ | 147.94(2) | $Cu3—S1—Ba3^{i}$ | 135.52(4) |
| $S5^{viii}—Ba3—Cu1$ | 38.81(2) | $Zr1—S1—Ba3^{i}$ | 95.31(3) |
| S3—Ba3—Cu1 | 37.352(19) | $Cu3—S1—Ba1^{ii}$ | 112.46(4) |
| S6—Ba3—Cu1 | 63.51(2) | $Zr1—S1—Ba1^{ii}$ | 104.25(3) |
| $S5^{ix}—Ba3—Cu1$ | 91.38(2) | $Ba3^{i}—S1—Ba1^{ii}$ | 111.97(3) |
| S7—Ba3—Cu1 | 89.79(2) | Cu3—S1—Ba1 | 88.48(3) |
| S8—Ba3—Cu1 | 125.89(2) | Zr1—S1—Ba1 | 158.09(4) |
| S9—Ba3—Cu1 | 109.34(2) | $Ba3^{i}—S1—Ba1$ | 85.43(2) |
| $Cu2^{ix}—Ba3—Cu1$ | 126.905(15) | $Ba1^{ii}—S1—Ba1$ | 95.67(3) |
| $S1^{vii}—Ba3—Cu3$ | 88.63(2) | $Cu4^{iii}—S2—Cu2$ | 115.15(4) |
| $S5^{viii}—Ba3—Cu3$ | 90.39(2) | $Cu4^{iii}—S2—Zr1$ | 79.94(3) |
| S3—Ba3—Cu3 | 60.52(2) | Cu2—S2—Zr1 | 80.42(3) |
| S6—Ba3—Cu3 | 36.329 (19) | $Cu4^{iii}—S2—Zr2^{xii}$ | 81.83(3) |
| $S5^{ix}—Ba3—Cu3$ | 143.81(2) | $Cu2—S2—Zr2^{xii}$ | 79.83(3) |
| S7—Ba3—Cu3 | 37.235(19) | $Zr1—S2—Zr2^{xii}$ | 144.15(4) |
| S8—Ba3—Cu3 | 103.765(18) | $Cu4^{iii}—S2—Ba2^{ii}$ | 164.46(4) |
| S9—Ba3—Cu3 | 117.03(2) | $Cu2—S2—Ba2^{ii}$ | 80.38(4) |
| $Cu2^{ix}—Ba3—Cu3$ | 141.819(14) | $Zr1—S2—Ba2^{ii}$ | 103.23(3) |
| Cu1—Ba3—Cu3 | 62.843(15) | $Zr2^{xii}—S2—Ba2^{ii}$ | 102.58(3) |
| $S1^{vii}—Ba3—Zr1^{vii}$ | 37.676(19) | $Cu4^{iii}—S2—Ba1^{ii}$ | 83.90(4) |
| $S5^{viii}—Ba3—Zr1^{vii}$ | 153.84(2) | $Cu2—S2—Ba1^{ii}$ | 160.62(4) |

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| S3—Ba3—Zr1$^{vii}$ | 128.239(19) | Zr1—S2—Ba1$^{ii}$ | 100.63(3) |
| S6—Ba3—Zr1$^{vii}$ | 121.540(18) | Zr2$^{xii}$—S2—Ba1$^{ii}$ | 107.82(3) |
| S5$^{ix}$—Ba3—Zr1$^{vii}$ | 86.257(18) | Ba2$^{ii}$—S2—Ba1$^{ii}$ | 80.56(2) |
| S7—Ba3—Zr1$^{vii}$ | 80.329(18) | Cu1—S3—Cu2$^{x}$ | 116.19(4) |
| S8—Ba3—Zr1$^{vii}$ | 40.257(17) | Cu1—S3—Zr1 | 125.63(5) |
| S9—Ba3—Zr1$^{vii}$ | 85.043(18) | Cu2$^{x}$—S3—Zr1 | 79.84(3) |
| Cu2$^{ix}$—Ba3—Zr1$^{vii}$ | 47.732(10) | Cu1—S3—Ba2$^{xiii}$ | 131.17(4) |
| Cu1—Ba3—Zr1$^{vii}$ | 165.577(12) | Cu2$^{x}$—S3—Ba2$^{xiii}$ | 80.20(3) |
| Cu3—Ba3—Zr1$^{vii}$ | 112.214(13) | Zr1—S3—Ba2$^{xiii}$ | 101.71(3) |
| S1—Zr1—S7 | 94.61(3) | Cu1—S3—Ba3 | 79.72(3) |
| S1—Zr1—S3 | 92.91(3) | Cu2$^{x}$—S3—Ba3 | 159.89(4) |
| S7—Zr1—S3 | 90.77(3) | Zr1—S3—Ba3 | 101.35(3) |
| S1—Zr1—S2 | 86.79(3) | Ba2$^{xiii}$—S3—Ba3 | 79.92(2) |
| S7—Zr1—S2 | 90.27(3) | Cu4—S4—Zr2 | 78.25(3) |
| S3—Zr1—S2 | 178.93(3) | Cu4—S4—Zr2$^{vi}$ | 81.50(3) |
| S1—Zr1—S8$^{i}$ | 93.62(3) | Zr2—S4—Zr2$^{vi}$ | 97.86(3) |
| S7—Zr1—S8$^{i}$ | 171.28(3) | Cu4—S4—Ba2 | 78.87(3) |
| S3—Zr1—S8$^{i}$ | 91.70(3) | Zr2—S4—Ba2 | 153.73(3) |
| S2—Zr1—S8$^{i}$ | 87.30(3) | Zr2$^{vi}$—S4—Ba2 | 91.35(3) |
| S1—Zr1—S8$^{ix}$ | 173.94(3) | Cu4—S4—Ba1 | 73.86(3) |
| S7—Zr1—S8$^{ix}$ | 90.44(3) | Zr2—S4—Ba1 | 85.80(3) |
| S3—Zr1—S8$^{ix}$ | 90.36(3) | Zr2$^{vi}$—S4—Ba1 | 153.84(3) |
| S2—Zr1—S8$^{ix}$ | 89.85(3) | Ba2—S4—Ba1 | 75.563(19) |
| S8$^{i}$—Zr1—S8$^{ix}$ | 81.18(3) | Cu4—S4—Ba1$^{iv}$ | 175.35(4) |

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| S1—Zr1—Cu3 | 47.85(3) | Zr2—S4—Ba1$^{iv}$ | 98.81(3) |
| S7—Zr1—Cu3 | 48.91(2) | Zr2$^{vi}$—S4—Ba1$^{iv}$ | 95.41(3) |
| S3—Zr1—Cu3 | 81.11(3) | Ba2—S4—Ba1$^{iv}$ | 104.77(2) |
| S2—Zr1—Cu3 | 99.42(3) | Ba1—S4—Ba1$^{iv}$ | 109.69(2) |
| S8$^{i}$—Zr1—Cu3 | 139.79(3) | Cu1$^{xii}$—S5—Cu2 | 82.09(4) |
| S8$^{ix}$—Zr1—Cu3 | 137.89(3) | Cu1$^{xii}$—S5—Zr2$^{xii}$ | 73.47(3) |
| S1—Zr1—Cu2$^{x}$ | 103.17(3) | Cu2—S5—Zr2$^{xii}$ | 81.73(3) |
| S7—Zr1—Cu2$^{x}$ | 134.29(3) | Cu1$^{xii}$—S5—Ba2$^{iii}$ | 164.71(4) |
| S3—Zr1—Cu2$^{x}$ | 47.16(3) | Cu2—S5—Ba2$^{iii}$ | 84.03(3) |
| S2—Zr1—Cu2$^{x}$ | 131.93(3) | Zr2$^{xii}$—S5—Ba2$^{iii}$ | 98.21(3) |
| S8$^{i}$—Zr1—Cu2$^{x}$ | 45.75(2) | Cu1$^{xii}$—S5—Ba3$^{xii}$ | 84.34(3) |
| S8$^{ix}$—Zr1—Cu2$^{x}$ | 75.44(2) | Cu2—S5—Ba3$^{xii}$ | 163.94(4) |
| Cu3—Zr1—Cu2$^{x}$ | 122.24(2) | Zr2$^{xii}$—S5—Ba3$^{xii}$ | 102.59(3) |
| S1—Zr1—Cu4$^{iii}$ | 78.88(3) | Ba2$^{iii}$—S5—Ba3$^{xii}$ | 110.29(3) |
| S7—Zr1—Cu4$^{iii}$ | 46.51(2) | Cu1$^{xii}$—S5—Ba3$^{ix}$ | 102.50(3) |
| S3—Zr1—Cu4$^{iii}$ | 134.64(3) | Cu2—S5—Ba3$^{ix}$ | 77.03(3) |
| S2—Zr1—Cu4$^{iii}$ | 46.29(3) | Zr2$^{xii}$—S5—Ba3$^{ix}$ | 158.74(4) |
| S8$^{i}$—Zr1—Cu4$^{iii}$ | 132.96(2) | Ba2$^{iii}$—S5—Ba3$^{ix}$ | 80.51(2) |
| S8$^{ix}$—Zr1—Cu4$^{iii}$ | 102.36(2) | Ba3$^{xii}$—S5—Ba3$^{ix}$ | 97.67(3) |
| Cu3—Zr1—Cu4$^{iii}$ | 60.275(18) | Cu3—S6—Cu4 | 111.52(4) |
| Cu2$^{x}$—Zr1—Cu4$^{iii}$ | 177.437(18) | Cu3—S6—Zr2 | 120.78(4) |
| S1—Zr1—Cu2 | 130.87(3) | Cu4—S6—Zr2 | 79.58(3) |
| S7—Zr1—Cu2 | 98.06(3) | Cu3—S6—Ba1$^{vii}$ | 128.93(4) |
| S3—Zr1—Cu2 | 133.89(3) | Cu4—S6—Ba1$^{vii}$ | 84.72(3) |

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| S2—Zr1—Cu2 | 46.11(3) | Zr2—S6—Ba1$^{vii}$ | 109.47(3) |
| S8$^{i}$—Zr1—Cu2 | 74.28(2) | Cu3—S6—Ba3 | 82.67(3) |
| S8$^{ix}$—Zr1—Cu2 | 44.73(2) | Cu4—S6—Ba3 | 164.90(4) |
| Cu3—Zr1—Cu2 | 136.42(2) | Zr2—S6—Ba3 | 97.92(3) |
| Cu2$^{x}$—Zr1—Cu2 | 101.065(15) | Ba1$^{vii}$—S6—Ba3 | 82.09(2) |
| Cu4$^{iii}$—Zr1—Cu2 | 76.386(15) | Cu3—S7—Cu4$^{iii}$ | 83.41(4) |
| S1—Zr1—Ba3$^{i}$ | 47.02(2) | Cu3—S7—Zr1 | 74.23(3) |
| S7—Zr1—Ba3$^{i}$ | 134.07(2) | Cu4$^{iii}$—S7—Zr1 | 81.75(3) |
| S3—Zr1—Ba3$^{i}$ | 71.01(2) | Cu3—S7—Ba2$^{iii}$ | 164.80(4) |
| S2—Zr1—Ba3$^{i}$ | 108.08(2) | Cu4$^{iii}$—S7—Ba2$^{iii}$ | 82.07(3) |
| S8$^{i}$—Zr1—Ba3$^{i}$ | 54.54(2) | Zr1—S7—Ba2$^{iii}$ | 99.21(3) |
| S8$^{ix}$—Zr1—Ba3$^{i}$ | 129.93(2) | Cu3—S7—Ba1$^{iii}$ | 101.93(4) |
| Cu3—Zr1—Ba3$^{i}$ | 86.028(15) | Cu4$^{iii}$—S7—Ba1$^{iii}$ | 74.62(3) |
| Cu2$^{x}$—Zr1—Ba3$^{i}$ | 57.576(12) | Zr1—S7—Ba1$^{iii}$ | 156.35(4) |
| Cu4$^{iii}$—Zr1—Ba3$^{i}$ | 124.078(14) | Ba2$^{iii}$—S7—Ba1$^{iii}$ | 78.46(2) |
| Cu2—Zr1—Ba3$^{i}$ | 125.243(14) | Cu3—S7—Ba3 | 81.75(3) |
| S9$^{i}$—Zr2—S6 | 96.15(3) | Cu4$^{iii}$—S7—Ba3 | 163.35(4) |
| S9$^{i}$—Zr2—S5$^{viii}$ | 94.40(3) | Zr1—S7—Ba3 | 101.33(3) |
| S6—Zr2—S5$^{viii}$ | 90.00(3) | Ba2$^{iii}$—S7—Ba3 | 113.22(3) |
| S9$^{i}$—Zr2—S4 | 93.02(3) | Ba1$^{iii}$—S7—Ba3 | 101.15(3) |
| S6—Zr2—S4 | 93.50(3) | Cu2$^{ix}$—S8—Zr1$^{vii}$ | 78.37(3) |
| S5$^{viii}$—Zr2—S4 | 171.41(3) | Cu2$^{ix}$—S8—Zr1$^{ix}$ | 80.42(3) |
| S9$^{i}$—Zr2—S2$^{viii}$ | 86.71(3) | Zr1$^{vii}$—S8—Zr1$^{ix}$ | 98.82(3) |
| S6—Zr2—S2$^{viii}$ | 176.98(3) | Cu2$^{ix}$—S8—Ba2$^{iii}$ | 174.04(4) |

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| S5$^{viii}$—Zr2—S2$^{viii}$ | 88.78(3) | Zr1$^{vii}$—S8—Ba2$^{iii}$ | 98.24(3) |
| S4—Zr2—S2$^{viii}$ | 87.33(3) | Zr1$^{ix}$—S8—Ba2$^{iii}$ | 95.37(3) |
| S9$^{i}$—Zr2—S4$^{vi}$ | 173.33(3) | Cu2$^{ix}$—S8—Ba2$^{xiii}$ | 77.57(3) |
| S6—Zr2—S4$^{vi}$ | 88.76(3) | Zr1$^{vii}$—S8—Ba2$^{xiii}$ | 152.17(3) |
| S5$^{viii}$—Zr2—S4$^{vi}$ | 90.11(3) | Zr1$^{ix}$—S8—Ba2$^{xiii}$ | 90.77(3) |
| S4—Zr2—S4$^{vi}$ | 82.14(3) | Ba2$^{iii}$—S8—Ba2$^{xiii}$ | 106.85(2) |
| S2$^{viii}$—Zr2—S4$^{vi}$ | 88.48(3) | Cu2$^{ix}$—S8—Ba3 | 76.31(3) |
| S9$^{i}$—Zr2—Cu1 | 47.74(3) | Zr1$^{vii}$—S8—Ba3 | 85.20(3) |
| S6—Zr2—Cu1 | 83.75(3) | Zr1$^{ix}$—S8—Ba3 | 155.08(3) |
| S5$^{viii}$—Zr2—Cu1 | 48.53(2) | Ba2$^{iii}$—S8—Ba3 | 108.46(3) |
| S4—Zr2—Cu1 | 139.68(3) | Ba2$^{xiii}$—S8—Ba3 | 75.700(19) |
| S2$^{viii}$—Zr2—Cu1 | 97.50(3) | Cu1$^{vii}$—S9—Zr2$^{vii}$ | 76.94(3) |
| S4$^{vi}$—Zr2—Cu1 | 137.74(3) | Cu1$^{vii}$—S9—Ba1$^{vii}$ | 135.35(4) |
| S9$^{i}$—Zr2—Cu4 | 103.02(3) | Zr2$^{vii}$—S9—Ba1$^{vii}$ | 94.79(3) |
| S6—Zr2—Cu4 | 47.24(3) | Cu1$^{vii}$—S9—Ba2$^{vi}$ | 105.43(4) |
| S5$^{viii}$—Zr2—Cu4 | 134.75(3) | Zr2$^{vii}$—S9—Ba2$^{vi}$ | 102.60(3) |
| S4—Zr2—Cu4 | 46.92(2) | Ba1$^{vii}$—S9—Ba2$^{vi}$ | 119.15(3) |
| S2$^{viii}$—Zr2—Cu4 | 133.07(3) | Cu1$^{vii}$—S9—Ba3 | 88.66(3) |
| S4$^{vi}$—Zr2—Cu4 | 77.03(2) | Zr2$^{vii}$—S9—Ba3 | 156.72(4) |
| Cu1—Zr2—Cu4 | 123.15(2) | Ba1$^{vii}$—S9—Ba3 | 82.59(2) |
| S9$^{i}$—Zr2—Cu2$^{viii}$ | 78.87(3) | Ba2$^{vi}$—S9—Ba3 | 98.79(3) |
| S6—Zr2—Cu2$^{viii}$ | 133.60 (3) | | |

Symmetry codes: (i) *x*-1, *y*, *z*; (ii) -*x*, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*+1, -*z*+1; (iv) -*x*, -*y*, -*z*+1; (v) *x*, *y*, *z*+1; (vi) -*x*+1, -*y*, -*z*+1; (vii) *x*+1, *y*, *z*; (viii) *x*, *y*-1, *z*; (ix) -*x*+1, -*y*+1, -*z*; (x) -*x*, -*y*+1, -*z*; (xi) -*x*, -

*y*, -*z*; (xii) *x*, *y*+1, *z*; (xiii) *x*, *y*, *z*-1.

**Reference:**

1 M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, and F. Bechstedt, *Phys. Rev. B* 2006, **73**, 045112.