**Table S1.** Information on structural refinement for kenoargentotetrahedrite-(Zn).

|  |  |
| --- | --- |
| **Crystal data** | |
| General formula | Ag3.78Cu6.12Zn1.26Fe0.84Sb3.72As0.28S12.37 |
| Formula weight | 1796.36 |
| Crystal size/μm | 7×6×5 |
| Crystal system | cubic |
| Space group | *I*3m (#217) |
| Unit cell dimensions | *a* = 10.4624(4) Å |
| Volume | 1145.23(13) Å3 |
| *Z* | 2 |
| **Data collection and refinement** | |
| Instrument | Rigaku Synergy |
| Radiation, wavelength, temperature | Mo*K*α, 0.71073 Å, 293(2) K |
| *F*(000) | 1623.2 |
| 2θ range (°) | 5.50 to 56.48 |
| Total reflections | 1089 |
| Unique ref (all) | 294 |
| Unique ref [*I* > 4σ(*I*)] | 274 |
| *R*int | 0.0341 |
| *R*σ | 0.0328 |
| Range of *h*, *k*, *l* | -11 ≤ *h* ≤ 10; -10≤ *k* ≤ 3; -13 ≤ *l* ≤ 8 |
| *R*1, *wR*2\*[*I* > 4σ(*I*)] | *R*1 =0.0310, *wR*2 = 0.0587 |
| *R*1, *wR*2 [all data] | *R*1 =0.0351, *wR*2 = 0.0595 |
| Goodness-of-fit | 1.103 |
| No. of parameters, restraints | 18, 0 |
| Maximum and minimum residual peak (e Å−3) | 0.96 [0.90Å from *M*(2)]  -1.22[0.57 Å from *M*(2)] |
| Flack parameter† | -0.02(5) |

\* *w* = 1/[σ2()+(0.0135*P*)2+19.9691*P*], where *P*=(+2)/3

† Flack (1983)

**Table S2.** Site, Wyckoff position, site occupancy factors (s.o.f.), fractional atomic coordinates and equivalent isotropic displacement parameters (in Å2) for kenoargentotetrahedrite-(Zn).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Site | *Wyck.* | *s.o.f* | *x/a* | *y/b* | *z/c* | *U*eq |
| *M*(2) | 12*e* | Ag0.63Cu0.37 | 0.1953(2) | 0 | 0 | 0.0339(6) |
| *M*(1) | 12*d* | Cu0.65Zn0.21Fe0.14 | 1/4 | 1/2 | 0 | 0.0149(6) |
| *X*(3) | 8*c* | Sb0.93As0.07 | 0.26904(9) | 0.26904(9) | 0.26904(9) | 0.0138(4) |
| *S*(1) | 24*g* | S1.00 | 0.1180(3) | 0.1180(3) | 0.3629(4) | 0.0145(7) |
| *S*(2) | 2*a* | S0.37(5) | 0 | 0 | 0 | 0.017(10) |

**Table S3.** Anisotropic displacement parameters (in Å2) for kenoargentotetrahedrite-(Zn).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Site | *U*11 | *U*22 | *U*33 | *U*23 | *U*13 | *U*12 |
| *M*(2) | 0.0265(13) | 0.0376(8) | *U*22 | -0.0146(13) | 0 | 0 |
| *M*(1) | 0.0154(14) | 0.0147(7) | *U*22 | 0 | 0 | 0 |
| *X*(3) | 0.0138(4) | *U*11 | *U*11 | -0.0012(4) | *U*23 | *U*23 |
| *S*(1) | 0.0148(10) | *U*11 | 0.0140(19) | -0.0003(10) | *U*23 | -0.0002(13) |
| *S*(2) | 0.017(10) | *U*11 | *U*11 | 0 | 0 | 0 |

**Table S4.** Selected bond-lengths (Å) and polyhedral volumes (Å3) for kenoargentotetrahedrite-(Zn).

|  |  |  |  |
| --- | --- | --- | --- |
| *M*(2)—*S*(1)×2 | 2.475(4) | *M*(1)—*S*(1)×4 | 2.343(2) |
| —*S*(2)×1 | —\* | [*M*(1)*S*(1)4] Tel. vol. | 6.60 |
| [Ag6]4+ cluster Oct. vol. | 11.38 | *X*(3)—*S*(1)×3 | 2.441(4) |
|  |  | [*X*(3)*S*(1)3] Tri. Pyramid vol. | 2.38 |

*Notes*: \**M*(2). . .centroid distance for kenoargentotetrahedrite-(Zn) = 2.043(2)Å; Ag–Ag = 2.890(3)Å.

**Table S5.** Bond-valence (vu) analysis for kenoargentotetrahedrite-(Zn).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Site | *M*(2) | *M*(1) | *X*(3) | sum. | theor. |
| *S*(1) | 0.332×2↓ | 0.368×4↓×2→ | 0.996×3↓ | 2.063 | 2.000 |
| sum. | 0.664 | 1.471 | 2.987 |  |  |
| theor. | 0.667† | 1.333 | 3.000 |  |  |

*Notes*: Bond valence sums were calculated with the site-occupancy factors given in Table S2. Calculations were using the equation and constants of Brown (1977), *S* = exp[(*R*0–*d*0)/b]. Superscripts indicate the number of equivalent bonds involving cations and anions. The theoretical bond valence of *M*(2) and *M*(1) site is calculated on the basis of [Ag6]4+ and (2/3Me+ + 1/3Me2+), respectively.