Supporting Information for:

Lone-pair self-containment in pyritohedron-shaped closed cavities: Optimized hydrothermal synthesis, structure, magnetism and lattice thermal conductivity of $Co_{15}F_2(TeO_3)_{14}$

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Tables

Table S1. BVS of the atoms in $Co_{15}F_2(TeO_3)_{14}$

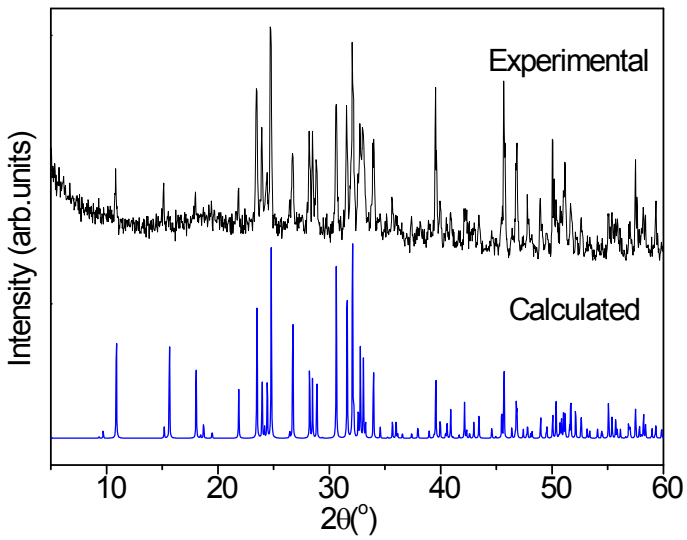
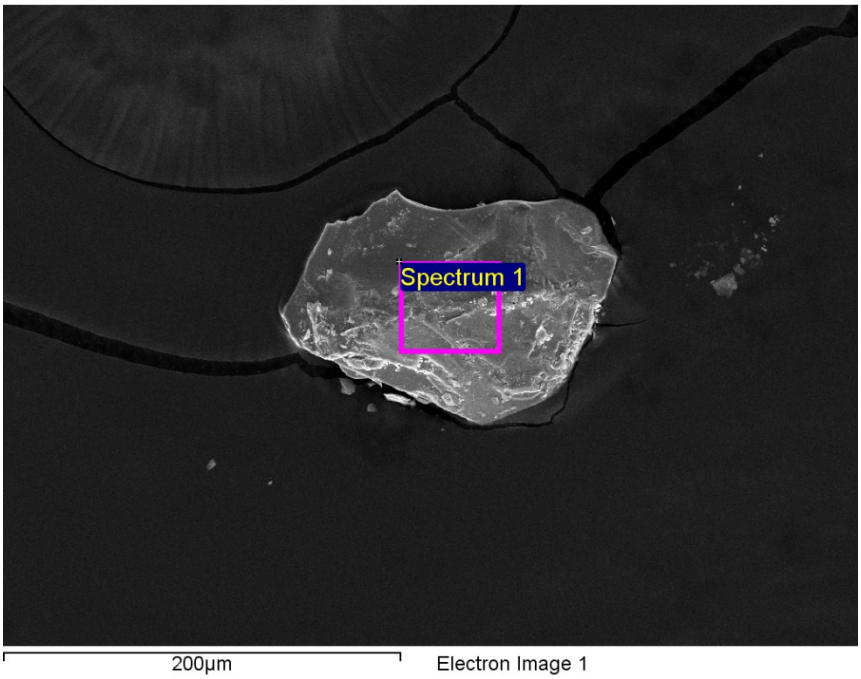


Figure S1**.** Calculated and observed powder X-ray diffraction patterns for $Co_{15}F_2(TeO_3)_{14}$



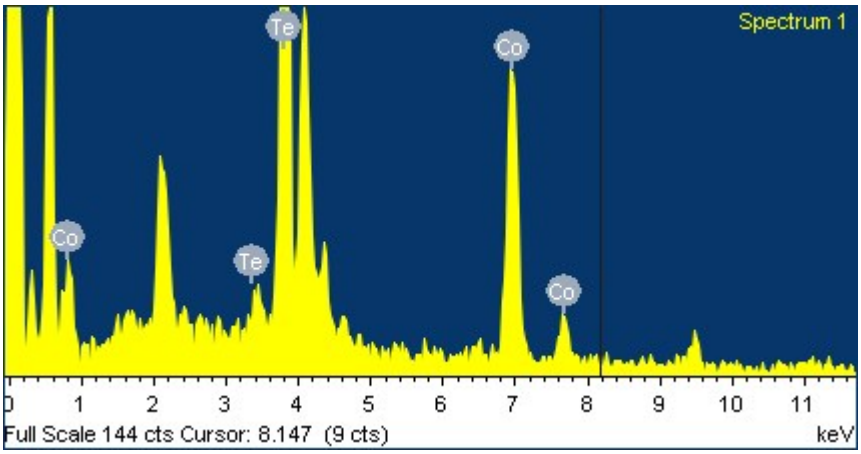


Figure S2**.**The corresponding EDXRD spectra (I) for $Co_{15}F_2(TeO_3)_{14}$

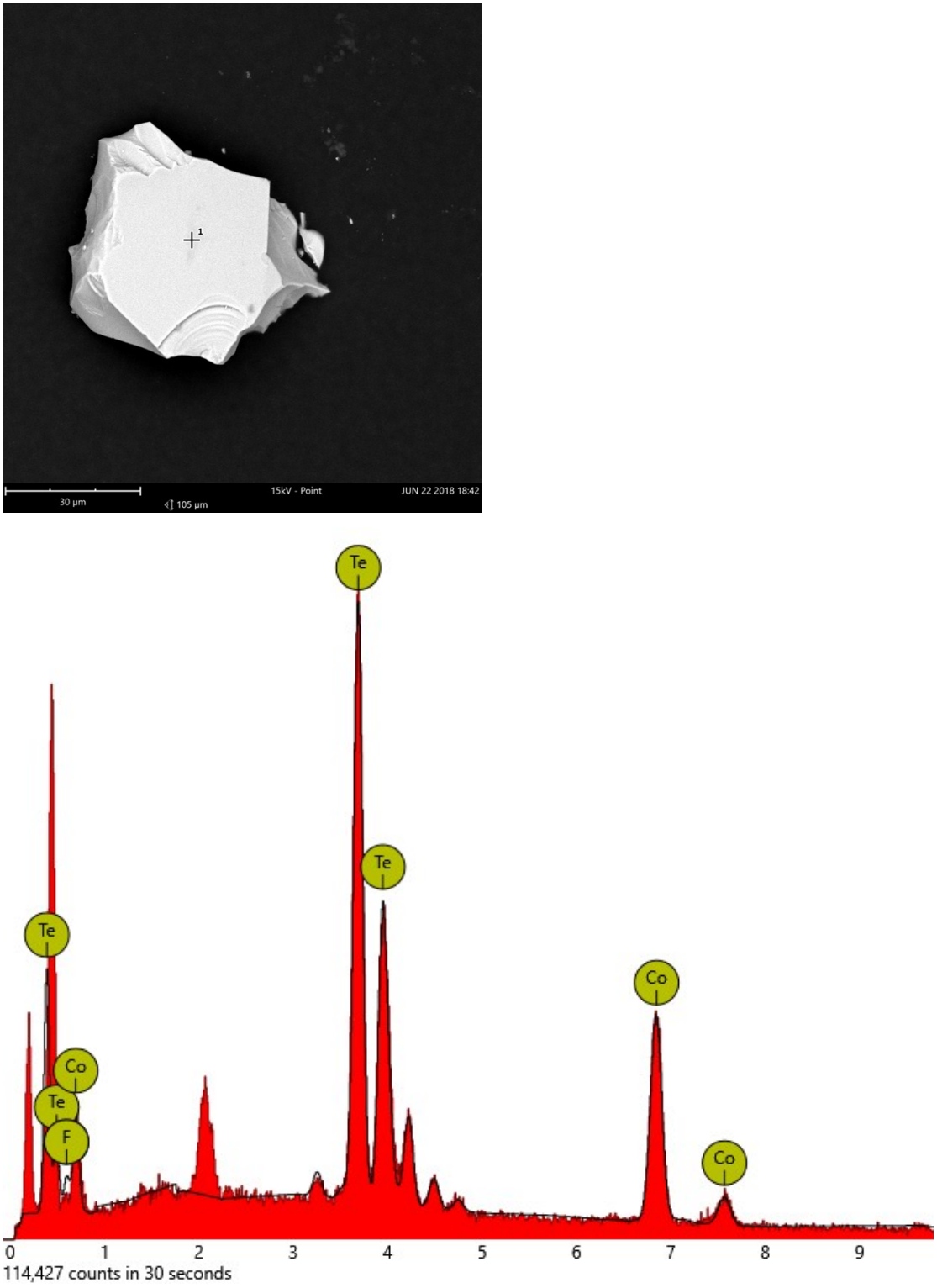


Figure S3**.**The corresponding EDXRD spectra (II) for $Co_{15}F_2(TeO_3)_{14}$

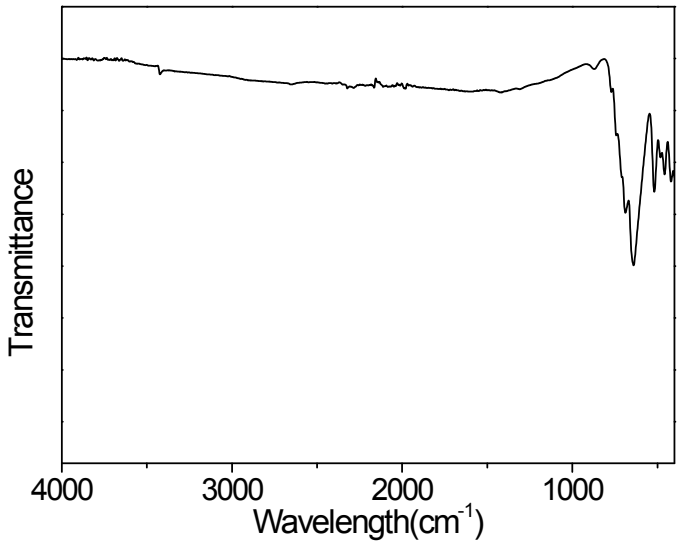


Figure S4. Infrared spectra of $Co_{15}F_2(TeO_3)_{14}$

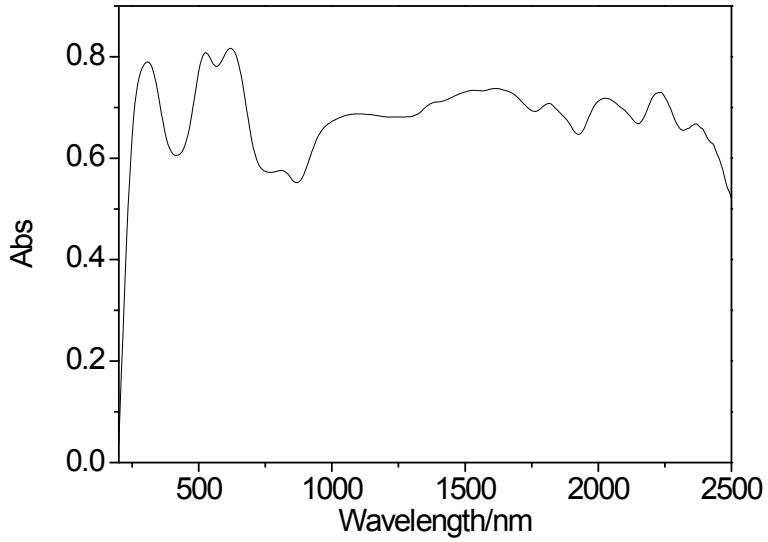


Figure S5. UV/Vis/NIR absorption spectrum of $Co_{15}F_2(TeO_3)_{14}$

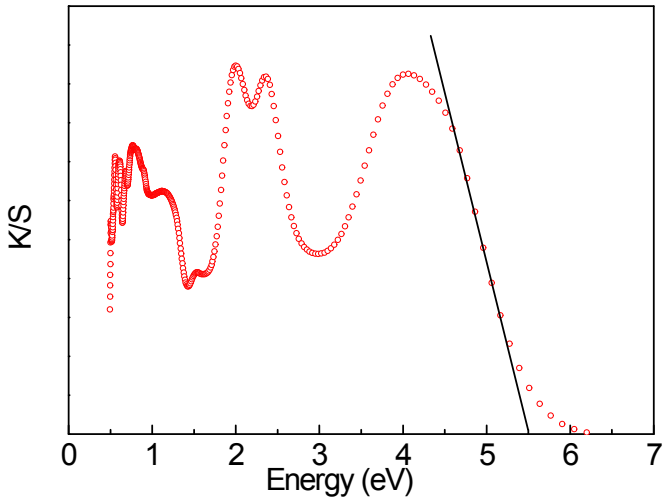


Figure S6. UV-vis diffuse reflectance spectra of $Co_{15}F_2(TeO_3)_{14}$.

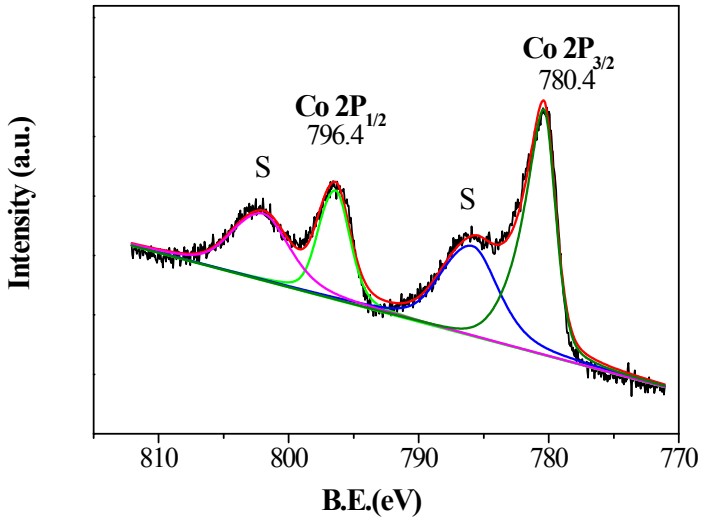


Figure S7. Co 2p doublet recorded for $Co_{15}F_2(TeO_3)_{14}$.

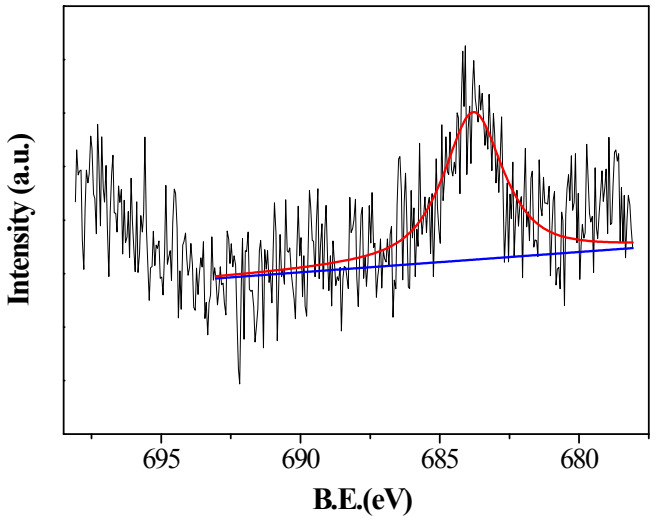


Figure S8. F 1s core level for $Co_{15}F_2(TeO_3)_{14}$.

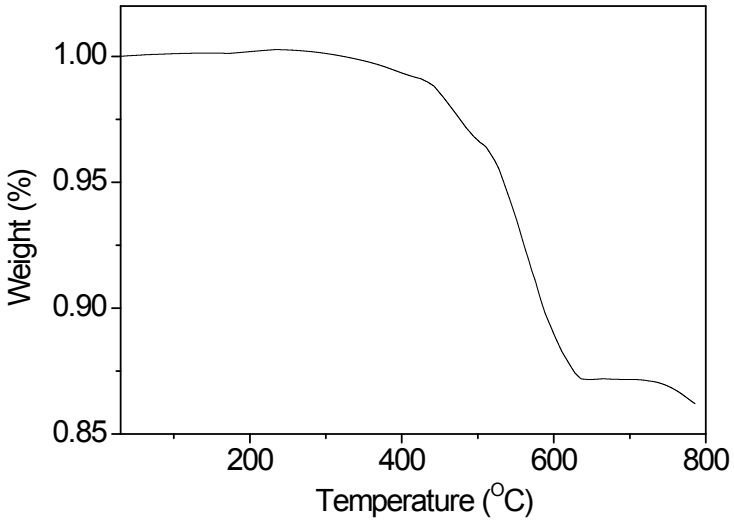


Figure S9. TGA diagram for $Co_{15}F_2(TeO_3)_{14}$.

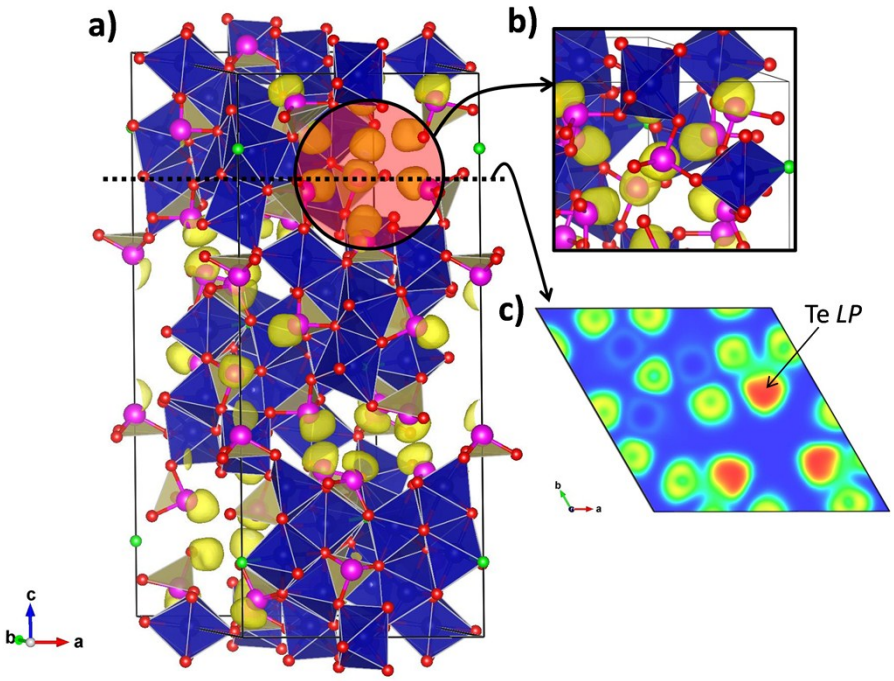


Figure S10**.** View of Calculated Tellurium atoms lone pairs.

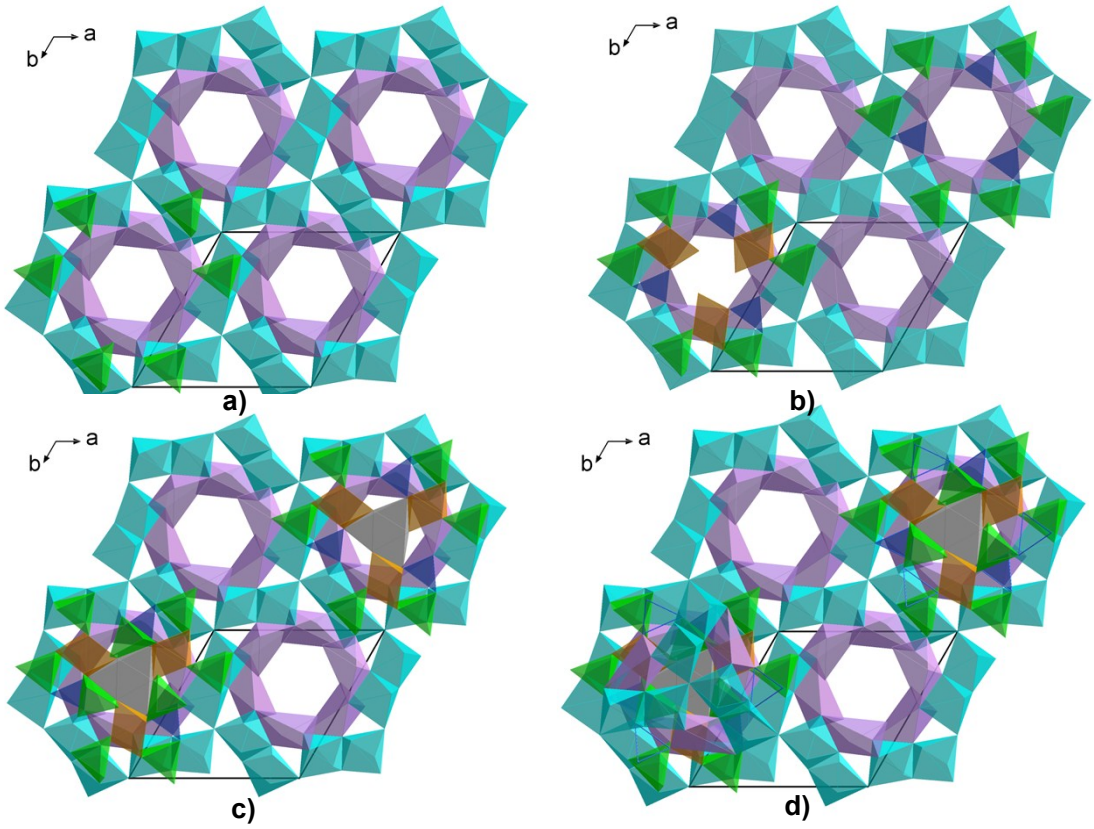


Figure S11: View down [001] of a slab of $Co_{15}F_2(TeO_3)_{14}$ showing the honeycomb layers, built up from Co and Te centered polyhedral. a-f:

a) The way the Co and Te centered polyhedral cap the top and bottom of each 12 ring of Co3 (turquoise) units and 6 rings of Te2 (lavender) groups (12-Co3+6-Te2 ring) result in closed pyritohedron-shaped cavities are shown sequentially: a) "empty" 12+6 ring hole (*top right*), 12-Co3+6-Te2 ring with capped hexads of Co2 (bright green) centered groups (6-Co2) on both sides (*bottom left*).

b) 12-Co3+6-Te2 ring+ 6-Co2 attached with trios of Te2 centered groups (3-Te2) (light blue) on both sides (*top right*), 12-Co3+6-Te2 ring + 6-Co2+3-Te2 attached with trios of Co1 (light orange)-centered groups (3-Co1) attached on both sides (*bottom left*).

c) 12-Co3+6-Te2 ring+6-Co2+3-Te2+3-Co1 attached with one of Te1 (gray) centered groups (1-Te1) on both sides (*top right*). *Another trio of Co2*-centered polyhedral capped the top of trios of Co1-centered octahedron (*bottom left*).

d) *Another trio of Te3*-centered polyhedral attached to the trios of Co1 and the abovementioned *trios of Co2*-centered groups (*top right*). *Another Co3/Te2*-centered polyhedral in the next *Co3/Te2* layer attached the abovementioned *trios of* the *Co2* layer (*bottom left*).

e) These honeycomb layers fused sequentially to form a continuous, three-dimensional structure, which encloses pyritohedron-shaped Te(IV) lone-pair self-contained cavities.

f) Note that rhombohedral crystal symmetry dictates that, with respect to the *z* direction, the adjacent basal Co3 sheets are laterally displaced from each other by $x = 1/3$ and $y = 2/3$. Thus, additional Co3 sheets capped afterwards face on the center of Co12 polyhedral units along the [001] direction in the next sheet, and there are no continuous channels of any significant size in this structure.

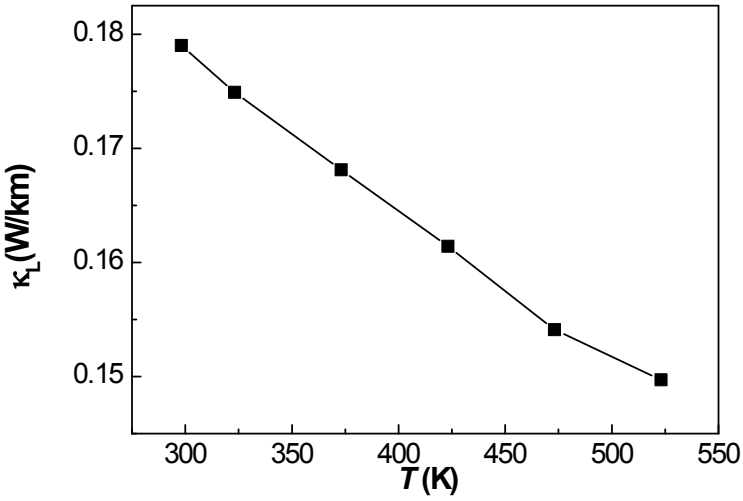


Figure S12. Lattice thermal conductivity as a function of temperature for $Co_{15}F_2(TeO_3)_{14}$ samples.

Table S1. BVS of the atoms in $Co_{15}F_2O_{42}Te_{14}$.

*Atom**	*BVS*
Te1	4.06(3)
Te2	4.28(3)
Te3	4.03(3)
Co1	1.965(10)
Co2	1.810(10)
Co3	1.983(9)
O1	–1.964(17)
O2	–2.197(14)
O3	–2.162(14)
O4	–1.93(2)
O5	–2.041(16)
O6	–1.898(16)
O7	–1.942(14)
F1	–0.964(2)

* (R, b) parameters: Te^{4+}–O (1.977, 0.37), Co^{2+}–O (1.692, 0.37), Co^{2+}–F (1.640, 0.37)