$K_2Hg_2Te_3$ – Straightforward, Large-Scale, Mercury-Flux Synthesis of a Small Band Gap Photoconducting Material

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Supporting Information

Contents

1. Synthesis details

WARNING: Mercury compounds are harmful if consumed. They need to be treated with due care and must not be swallowed or inhaled. Skin and eyes must be effectively protected throughout work.

$K_2Hg_2Te_3$ (**1**) is obtained by solid-state reaction of thoroughly mixed HgTe and K_2Te in a 2:1 ratio in a sealed silica glass ampoule with an excess of elemental Hg (1 mL Hg per 20 mL ampoule volume). The ampoule is heated for 3 days to 350°C, the reaction product is pestled and subsequently filtrated to remove remaining excess of Hg. Through application of high vacuum ($p < 10^{-6}$ mbar) and heating to 100 °c for at least 3 days, all remaining surface bound Hg is evaporated. **1** is obtained in quantitative yields as black, highly air and moisture sensitive powder. The synthesis can be scaled from 5 to 150 g (only limited by the size of the ampoule).

2. X-Ray diffraction and refinement details for $K_2Hg_2Te_3$

Experimental

Single crystals of $Hg_2K_2Te_3$ (**1**) were obtained from the flux method described above. Large black single crystals of improved quality but with an overall smaller yield can be obtained from solvothermal treatment of 2 g of **1** in 2 mL en at 150 °C for two days. A suitable crystal was selected and mounted in Paratone® oil on a STOE IPDS II diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using intrinsic phasing and refined with the ShelXL[3] refinement package using least squares minimization.

Crystal data

$Hg_2K_2Te_3$ (M = 862.18 g/mol): tetragonal, space group $P4_2/ncm$ (no. 138), a = 16.0211(4) Å, c = 7.4882(3) Å, V = 1922.04(12) Å^3, Z = 8, T = 100(2) K, $\mu(MoK_\alpha)$ = 41.614 mm^{-1}, D_{calc} = 5.959 g/cm^3, 2483 reflections measured ($5.086° \leq 2\Theta \leq 58.364°$), 1347 unique ($R_{int}$ = 0.0493, R_{sigma} = 0.0522) which were used in all calculations. The final R_1 was 0.0397 ($I > 2\sigma(I)$) and wR_2 was 0.0850 (all data). Full lists of measurement and refinement details are given in tables S1 to S4. Detailed views of the structure are provided in Figure S1.

Table S1: Crystal data and structure refinement for Compound **1**.

Identification code	**1**
Empirical formula	$Hg_8K_8Te_{12}$
Formula weight	3448.72
Temperature/K	100(2)
Crystal system	tetragonal
Space group	$P4_2/ncm$
a/Å	16.0211(4)
c/Å	7.4882(3)
Volume/Å^3	1922.04(12)
Z	2
ρ_{calc}g/cm^3	5.959
μ/mm^{-1}	41.614
F(000)	2832.0
Crystal size/mm^3	0.056 × 0.035 × 0.03
Radiation	MoK$_\alpha$ (λ = 0.71073)
2Θ range for data collection/°	5.086 to 58.364
Index ranges	-15 ≤ h ≤ 15, 0 ≤ k ≤ 21, 0 ≤ l ≤ 10
Reflections collected	2483
Independent reflections	1347 [R_{int} = 0.0493, R_σ = 0.0522]
Data/restraints/parameters	1347/0/38
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.0815
Final R indexes [all data]	R_1 = 0.0535, wR_2 = 0.0850
Largest diff. peak/hole / e Å^{-3}	2.80/-4.85

Table S2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U_{eq}
Hg1	6909.0(2)	131.8(2)	4018.1(5)	9.18(13)
Te2	6312.1(4)	-1312.1(4)	2430.4(12)	6.87(18)
Te3	5700.4(4)	1628.1(4)	2594.5(8)	5.76(15)
K1	7500	2500	5000	10.3(8)
K2	5000	0	0	8.4(8)
K3	6504.8(12)	-1504.8(12)	7442(4)	9.4(6)

Table S3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg1	11.79(19)	10.97(19)	4.78(18)	-1.40(14)	2.10(14)	-2.30(13)
Te2	7.9(2)	7.9(2)	4.7(4)	-0.7(2)	0.7(2)	-0.1(3)
Te3	8.0(3)	7.2(3)	2.1(3)	-0.2(2)	-0.3(2)	0.6(2)
K1	12.2(11)	12.2(11)	6.4(19)	0	0	-3.2(16)
K2	9.9(11)	9.9(11)	5.5(18)	0.3(10)	-0.3(10)	1.0(14)
K3	8.7(8)	8.7(8)	10.8(14)	-0.5(8)	0.5(8)	0.3(10)

Table S4: Bond Lengths for Compound **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Hg1	Te2	2.7712(6)	Te2	K3[3]	3.511(2)
Hg1	Te3[1]	2.7894(7)	Te3	K1[6]	3.7468(6)
Hg1	Te3	3.2608(7)	Te3	K1	3.6754(6)
Hg1	Te3[2]	2.7325(7)	Te3	K2	3.4406(6)
Hg1	K1	3.9790(4)	Te3	K3[7]	3.5386(19)
Hg1	K3[3]	3.8373(11)	K1	K1[8]	3.74410(15)
Hg1	K3	3.724(3)	K1	K1[6]	3.74410(15)
Te2	K2	3.4857(9)	K2	K3[7]	3.911(3)
Te2	K3	3.778(3)	K2	K3[4]	3.911(3)
Te2	K3[4]	3.760(3)	K3	K3[9]	4.510(6)
Te2	K3[5]	3.511(2)			

[1]1-Y,-1/2+X,1/2-Z; [2]1/2+Y,-1/2+X,1-Z; [3]1+Y,1/2-X,-1/2+Z; [4]+X,+Y,-1+Z; [5]1/2-Y,-1+X,-1/2+Z; [6]1/2+Y,1-X,1/2-Z; [7]1-X,-Y,1-Z; [8]1/2+Y,1-X,3/2-Z; [9]3/2-X,-1/2-Y,+Z

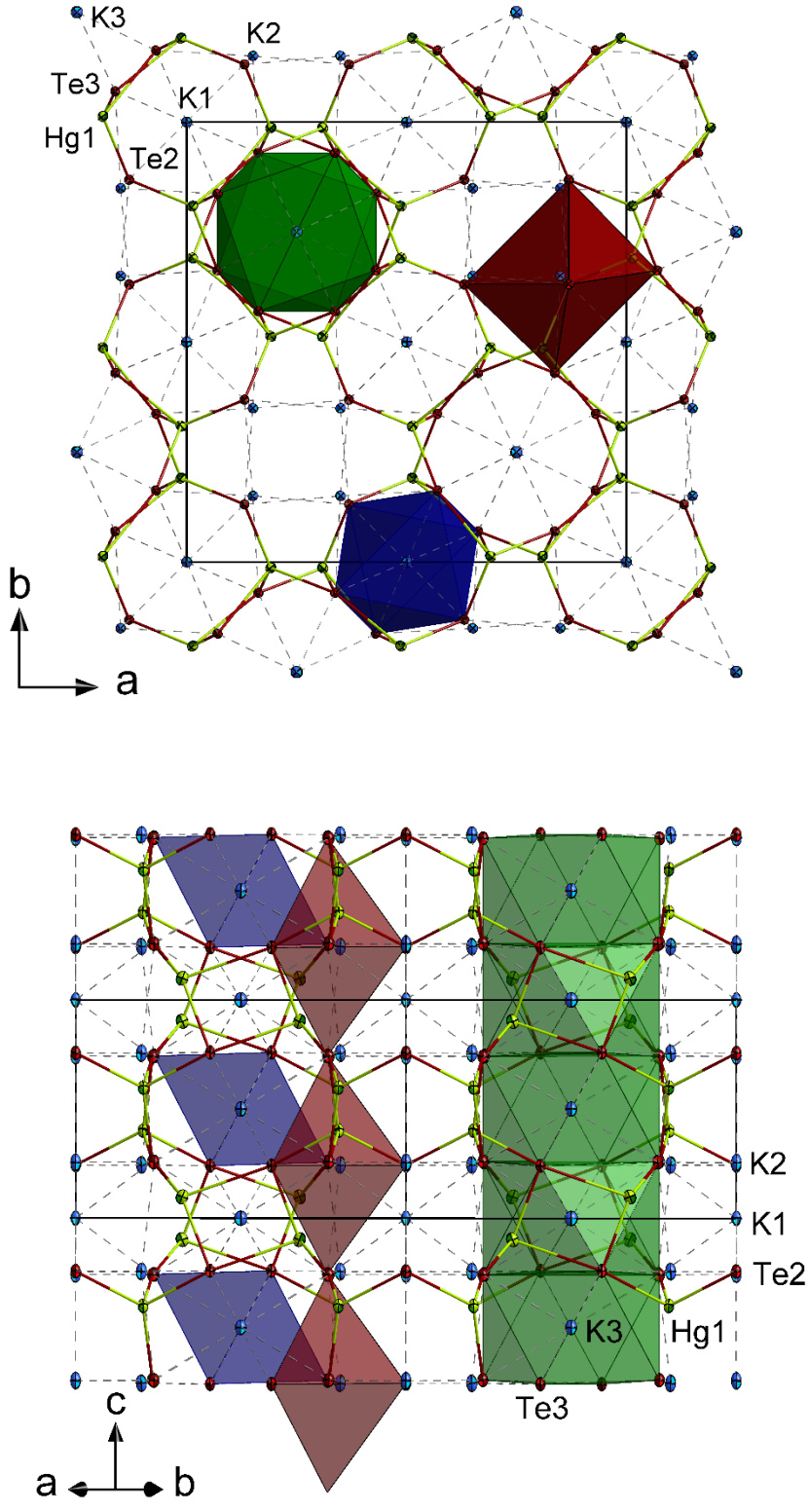

Figure S1: Detailed views of the crystal structure in **1**.

3. Thermal analyses

Thermogravimetric analysis (TGA) were performed on a NETZSCH STA 409 CD device under Ar atmosphere with the following settings: temperature range 20-700°C, scanning rate of 10 K/min (Figure S2).

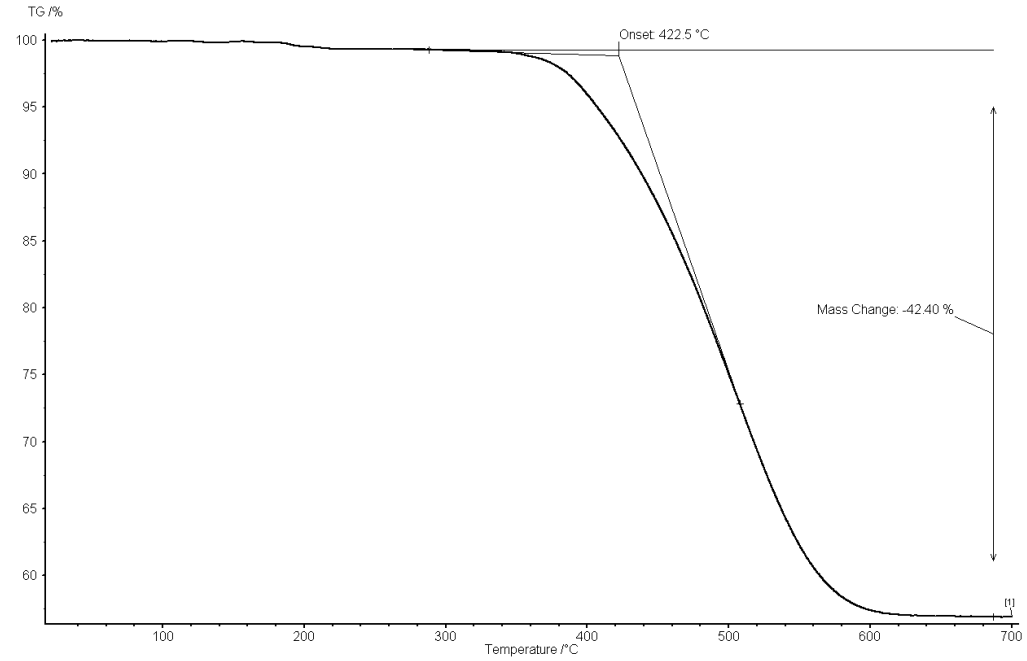

Figure S2: Thermogravimetric results for **1**.

As can be gathered from the curves given in Figure S2, $K_2Hg_2Te_3$ is thermally stable up to approx. 350 °C. Above that temperature, an overall mass loss of 42.40 % is observed that corresponds to the weight-% of mercury in **1** (46.53 %). In combination with the boiling point of elemental mercury (357°C) the following equation can be assumed for the thermal decomposition above 350 °C:

$$K_2Hg_2Te_3 \rightarrow 2\ Hg + K_2Te_3$$

4. Micro X-ray fluorescence analysis (μ-RFA)

Elemental analyses were performed using an M4-Tornado of Bruker with a rhodium target X-ray tube on a single crystal of **1**. Data acquisition was performed with 100 s accumulation time. The radiation emitted by the atoms was analyzed: Hg-L, Te-L, K-K (Figure S3, Table S5). K values are typically overestimated due to decomposition during the measurement setup leading to a migration of K^+ ions to the surface and the formation of potassium oxides-hydroxides. The integral difference to 100% is caused by detection of the sources' K and L lines (rhodium).

Table S5. Quantification results of μ-RFA-measurement of $K_2Hg_2Te_3$ (**1**). (ImpD.: 71,89 kcps)

Element	**OZ**	**Series**	**Found [w.%]**	**Calculated [w.%]**	**Calculated [At.%]**
K	19	K-Serie	9,07	9,07	28,33
Te	52	K-Serie	39,53	46,85	44,84
Hg	80	L-Serie	37,19	44,08	26,83
Sum			**85,80**	**100,00**	**100,00**

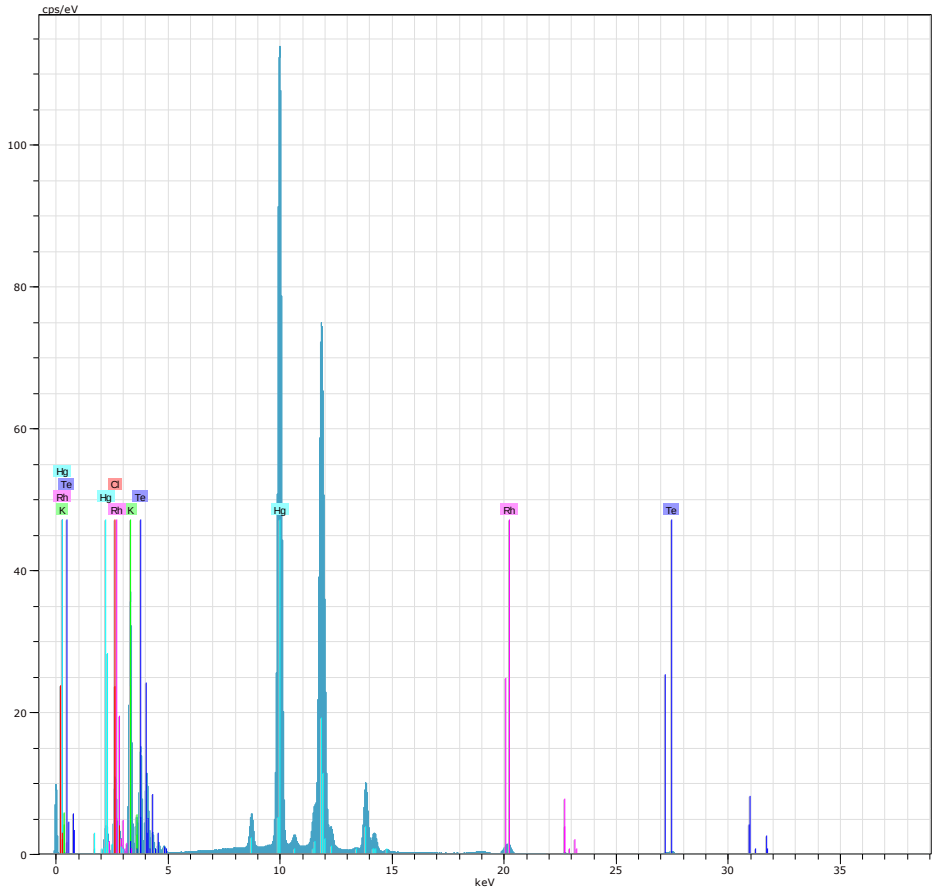

Figure S3: μ-RFA spectrum of $K_2Hg_2Te_3$ (**1**). Additional Rh signals are caused by the X-ray tube.

5. Thermoelectric measurements

Thermal diffusivity measurements were performed with a Linseis LFA1000 under static He atmosphere with an InSb detector and through-plane sample irradiation with 2 ms pulses of a Nd-YAG laser (532 nm). The data were analyzed using Dusza's model for simultaneous heat loss and finite pulse corrections.[4] The thermal conductivity κ was calculated as a product of the thermal diffusivity D, the density δ (4.12 g/cm^3; calculated from the experimentally determined mass and volume of the pellet) and the Dulong-Petit heat capacity C_p = 0.2025 J/gK. Values were averaged from 5 measurement points and linearly interpolated. Measurements of the electrical conductivity and the Seebeck coefficient were done on a Linseis LSR-3 under static He atmosphere with NiCr/Ni and Ni contacts). The samples were pressed to discs of 6 mm diameter and about 1 mm thickness, sintered at 300 °C and polished in a glove box. During mounting the samples in the devices, a N_2 dome was used to minimize exposure to moisture.

For comparison, the thermal conductivity of $K_2Hg_2Se_3$ is depicted in Figure S4.

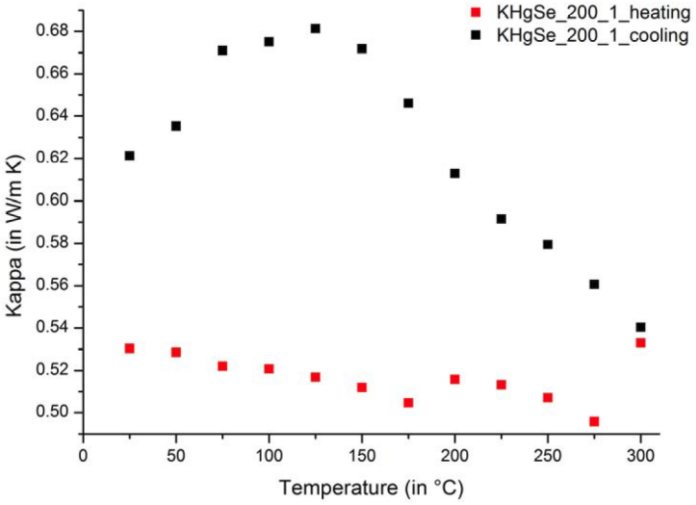

Figure S4: Thermal conductivity of $K_2Hg_2Se_3$.

6. Photoelectric measurements

The sample is electrically contacted by two tungsten needles with a tip diameter of 5 µm and a distance between the needles of 100µm. The sample was illuminated by light from a tungsten lamp after filtering by a monochromator (SPEX 1680). The focused excitation spot covered an area of hundreds of µm. An external voltage of +/- 10 V is applied to the sample.

The setup is placed in a nitrogen filled box. The detection limit of the setup is 100 fA. The photocurrent was recorded with a maximum wavelength resolution of 3 nm. The current was detected with a lock-in amplifier (Stanford research SR 850) after amplification with a current amplifier (Femto DLCPA-100).

The current-voltage characteristics were measured with the same setup. For detection a Keithley 617 Programmable Electrometer was used. The maximum applied voltage was +/- 10 V with voltage steps of 0.5 V. I-V-curves were recorded in dark environment and under white light exposure.

Absorption measurements were measured using a tungsten lamp. The white light transmitted through the sample was detected with an optical spectrum analyzer (ANDO AQ-6315A). The samples were measured as suspensions in Nujol oil between two quartz plates.

7. Powder X-ray diffraction (PXRD)

The phase purity of $K_2Hg_2Te_3$ was determined by X-ray powder diffraction, measured on a Panalytical X'Pert Pro PW3040/60. Co-K_α radiation (λ = 1.78901 Å) was used. As the high absorption coefficient of the compound (see Table S1) hampered a measurement in transmission mode using capillaries, the measurements were carried out in reflection mode, using Scotch© tape (Scotch Magic™ dull-transparent) for protection of the sample from reaction with air. The measurement time was restricted to 2 h as **1** reacts with Si sample holders over time. Furthermore, the use of Scotch tape typically affects the reflection intensities to a large extend, and covers the low 2Θ region, such that we show the raw diagram along with the simulation (Figure S5) and the manually baseline-corrected diagram (Figure S6). An additional reflection at 32° arises from the oxidation during the measurement proven by repetitive measurements over time and an increase in the respective intensity.

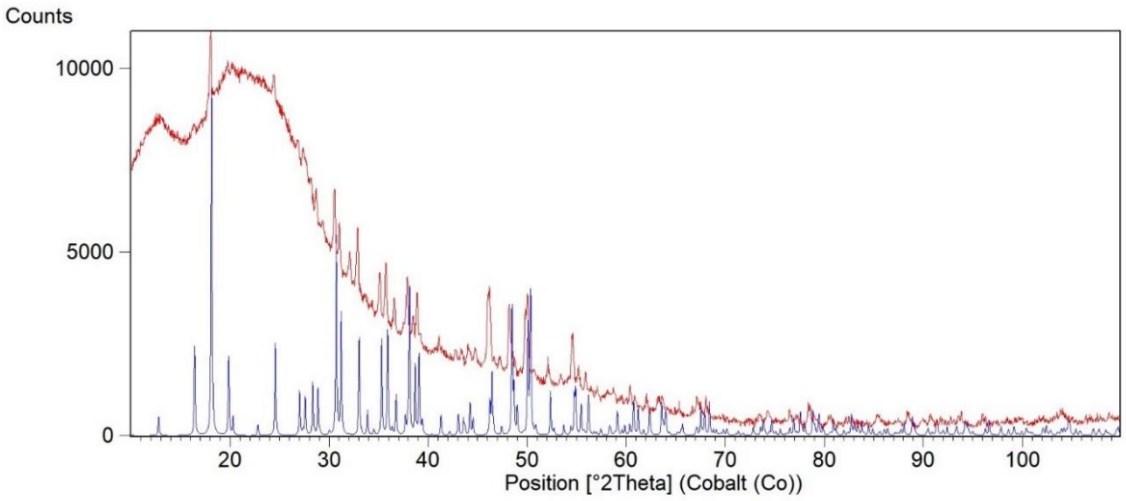

Figure S5: Raw PXRD diagram (red) and simulation (blue) of compound **1**.

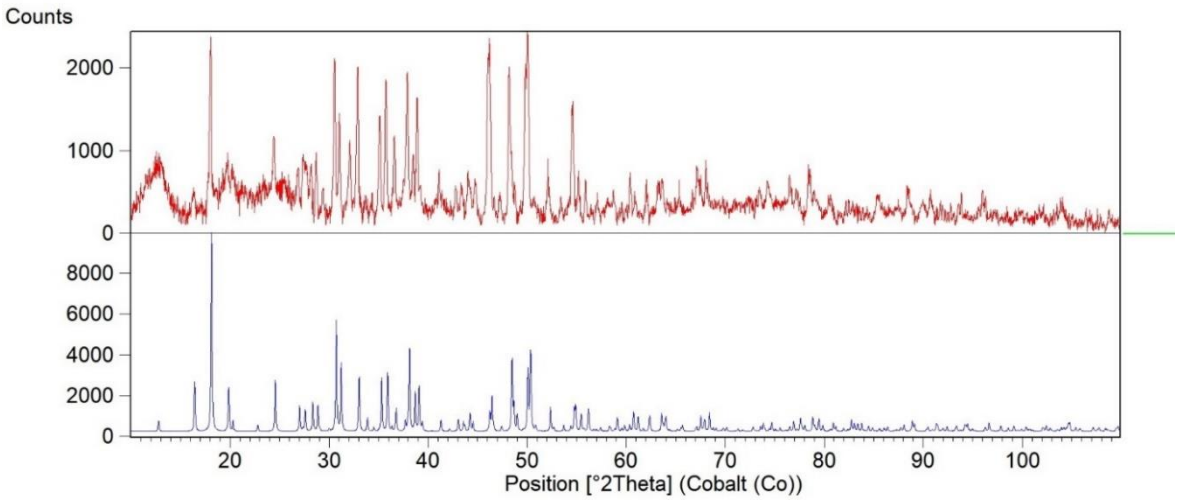

Figure S6: PXRD results with manual baseline correction (red) and simulation (black).

8. References

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2. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3-8.
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4. Dusza, L. Combined solution of the simultaneous heat loss and finite pulse corrections with the laser flash method. *High Temp. High Press.* **1995/1996,** *27/28*, 467-473.