

# Supporting Information for "Exploring the heteroanionic 2D materials RhSeCl and RhTeCl as promising semiconductor materials"

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## Scanning electron microscopy / Crystal morphologies

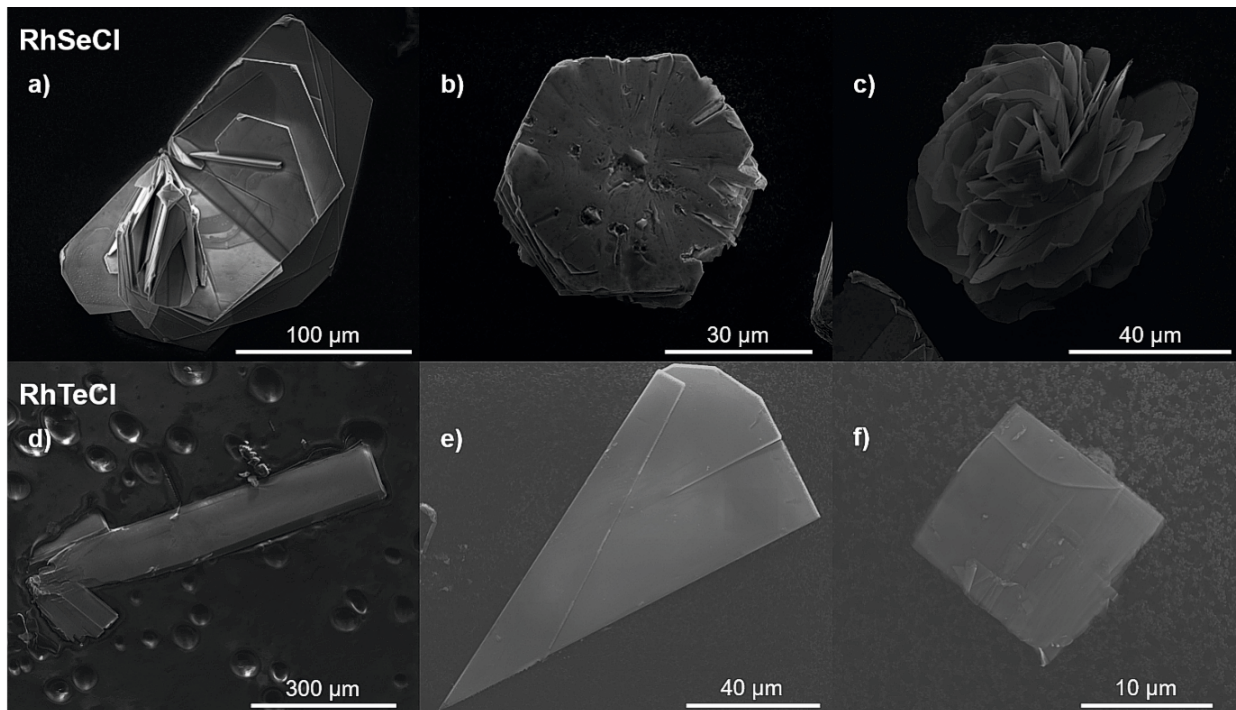


Figure S1: Different crystal morphologies of RhSeCl (a-c) and RhTeCl (d-f) bulk crystals under the electron microscope.

## Energy dispersive X-ray spectroscopy

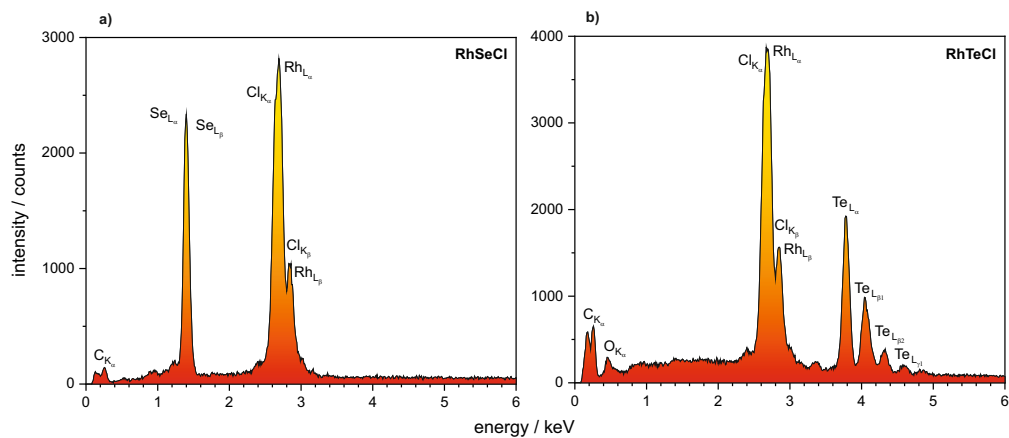


Figure S2: EDX-spectra of a RhSeCl (a) and RhTeCl (b) crystal are showing a strong overlap between the  $Cl_{K_{\alpha}}$  and the  $Rh_{L_{\alpha}}$  energy line.

Table **S1**: Atomic distribution of the elements in the measured areas according to the EDX spectra of RhTeCl.

	Rh/At-%	Cl/At-%	Te/At-%
<b>1</b>	34.4	32.8	32.8
<b>2</b>	34.1	33.8	32.1
<b>3</b>	34.3	31.6	34.1
<b>4</b>	36.3	30.4	33.3
<b>5</b>	34.9	30.4	34.7
<b>6</b>	36.3	30.5	33.2
<b>7</b>	36.0	30.0	34.0
<b>8</b>	35.1	30.3	34.6
<b>9</b>	35.7	29.9	34.4
<b>10</b>	35.7	29.7	34.6
<b>Average</b>	<b>35.3</b>	<b>30.9</b>	<b>33.8</b>

## Long-term stability

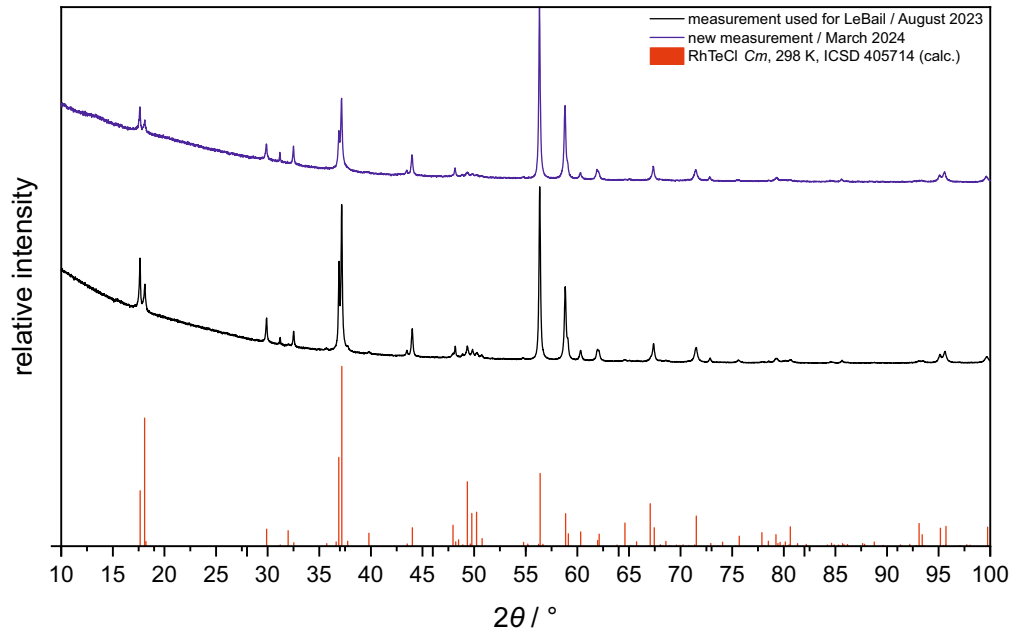


Figure **S3**: Powder X-ray diffraction of the same RhTeCl sample after half a year show no additional reflexes. The measurement was carried out using a Cobalt  $K_{\alpha}$  X-ray source ( $\lambda = 1.78896 \text{ \AA}$ ).<sup>1</sup>

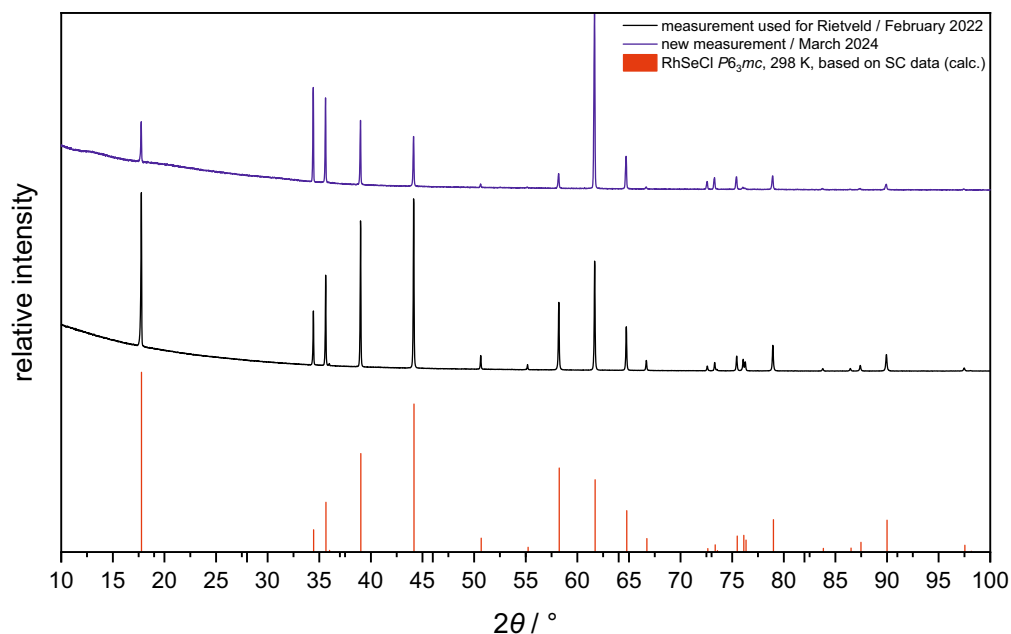


Figure S4: Powder X-ray diffraction of the same RhSeCl sample after two years show no additional reflexes. The measurement was carried out using a Cobalt  $K_{\alpha}$  X-ray source ( $\lambda = 1.78896 \text{ \AA}$ ).<sup>2</sup>

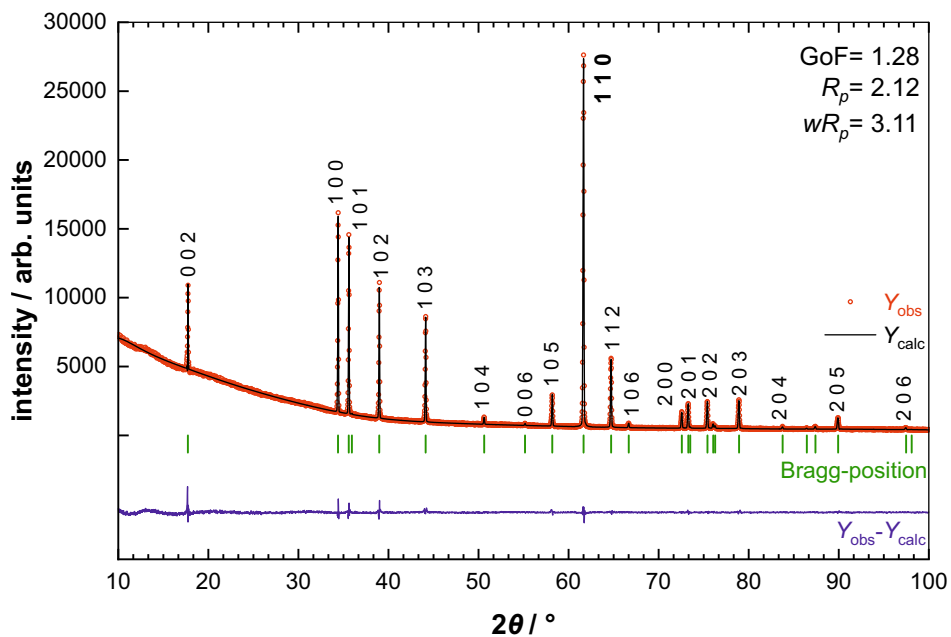


Figure S5: Powder X-ray diffraction data of a two-year-old RhSeCl sample with superimposed LeBail refinement simulations and their corresponding differences. The measurements indicates there are no further phases in the sample present and the differences in the intensities hail from a preferred orientation in the  $[110]$  direction. The measurement was carried out using a Cobalt  $K_{\alpha}$  X-ray source ( $\lambda = 1.78896 \text{ \AA}$ ).<sup>3</sup>



## Crystal structure

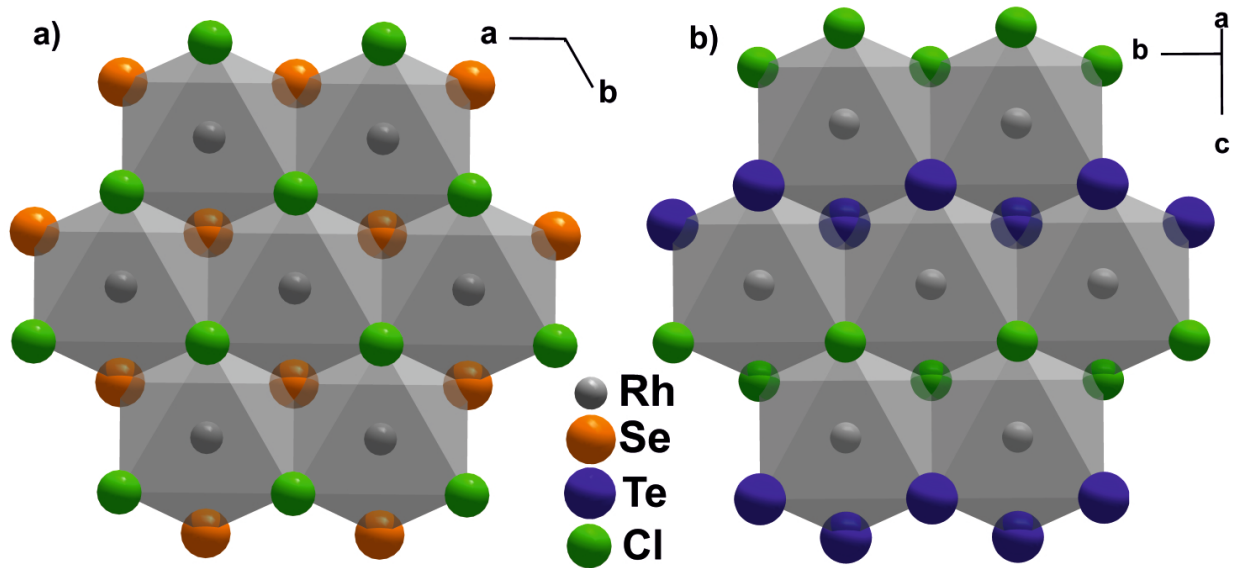


Figure S6: View along the longest axis of one layer of RhSeCl (a) and RhTeCl (b).<sup>4</sup>

## DFT simulations of the loss function

In the framework of DFT theory, we have studied the loss functions in these materials. The FPLO package was used for the calculations (see the main text). The loss function results are presented in Fig. S7. The calculated loss functions indicate the presence of optical gaps in RhSeCl and RhTeCl, with values of 1.48 eV and 0.78 eV, respectively. The low energy region of the loss functions  $Im\varepsilon_{xx,yy}^{-1}(\omega)$  are characterized by an almost featureless increase and a peak at 6 eV and 8 eV in RhSeCl and RhTeCl, respectively. This behavior is in full agreement with the experimental observations (see the main text).

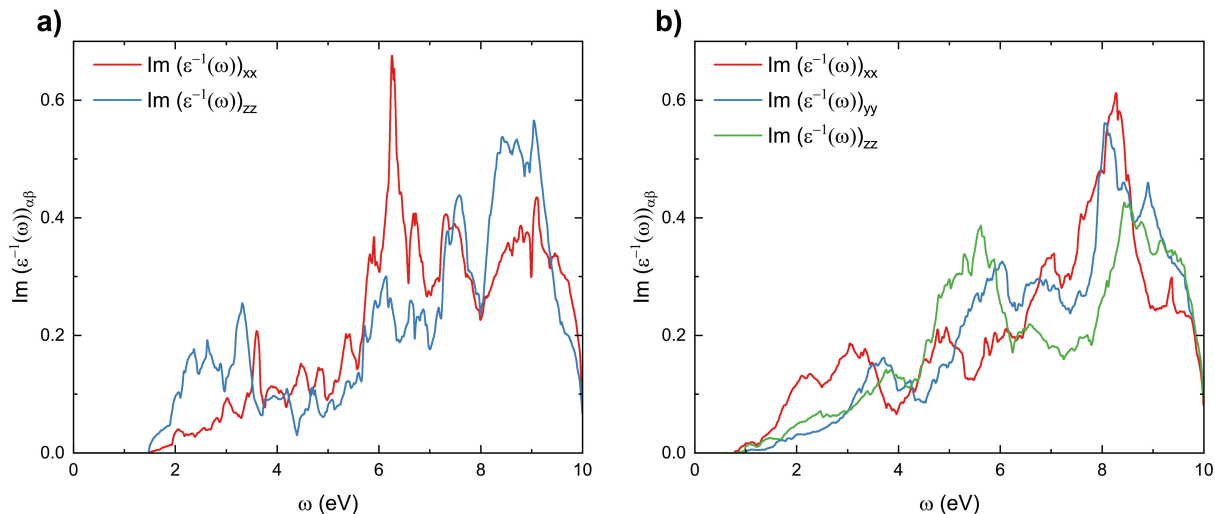


Figure S7: Loss function: a) RhSeCl, b) RhTeCl calculated by PBE functional. The low energy region of the loss function  $\text{Im}\epsilon_{xx,yy}^{-1}(\omega)$  is characterized by an almost featureless increase and a peak at 6 eV and 8 eV in RhSeCl and RhTeCl, respectively.

## XPS

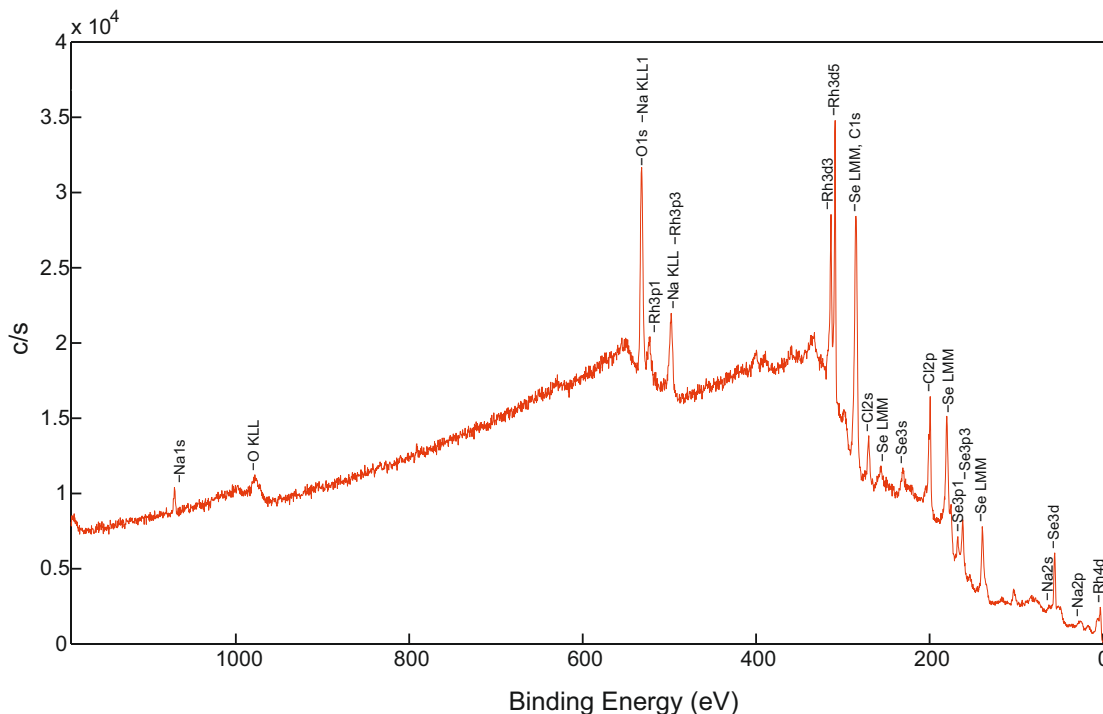


Figure S8: Full XP spectra of a RhSeCl crystal, showing contaminations of sodium and oxygen. The surface contamination of the crystal with sodium may have come from the crystal growth on the ampoule wall. Before the reaction, the ampoules were rinsed with tap water and heated in a furnace at 100 °C.

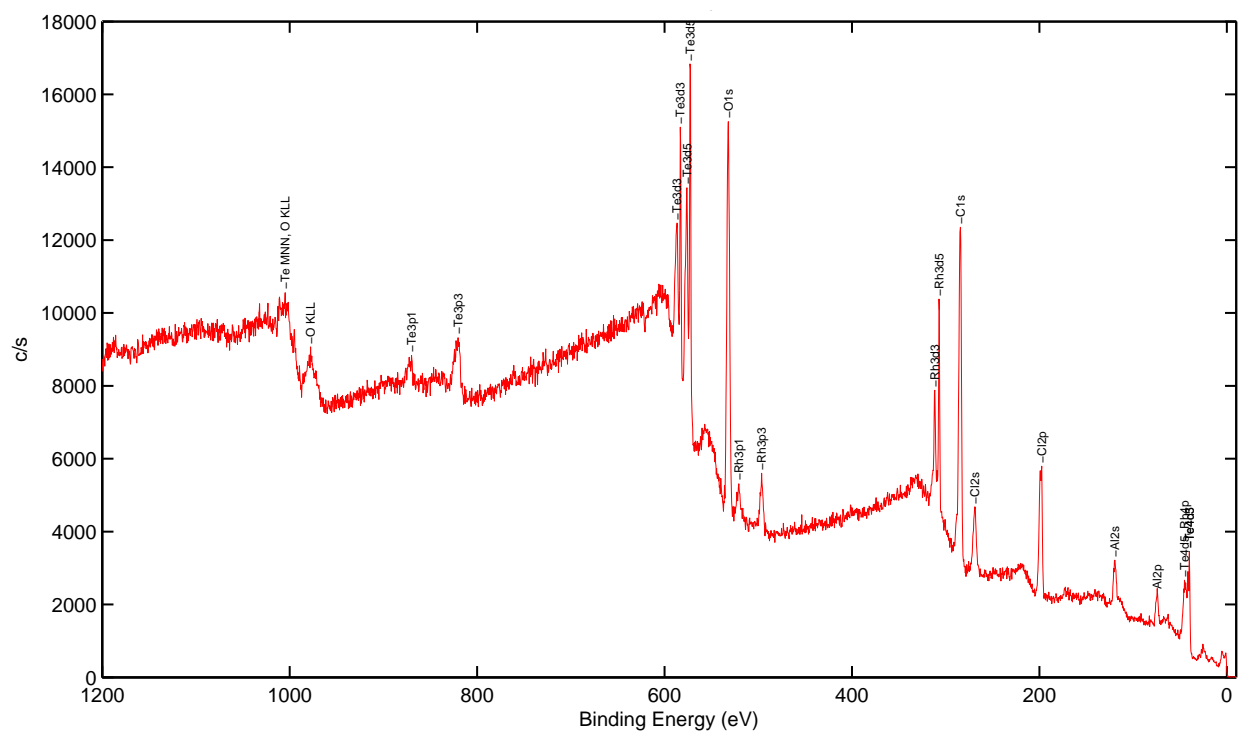


Figure S9: Full XP spectra of a RhTeCl crystal, showing contaminations of aluminum and oxygen. The surface contamination of the crystal with aluminum may have come from the transport agent  $\text{AlCl}_3$ .

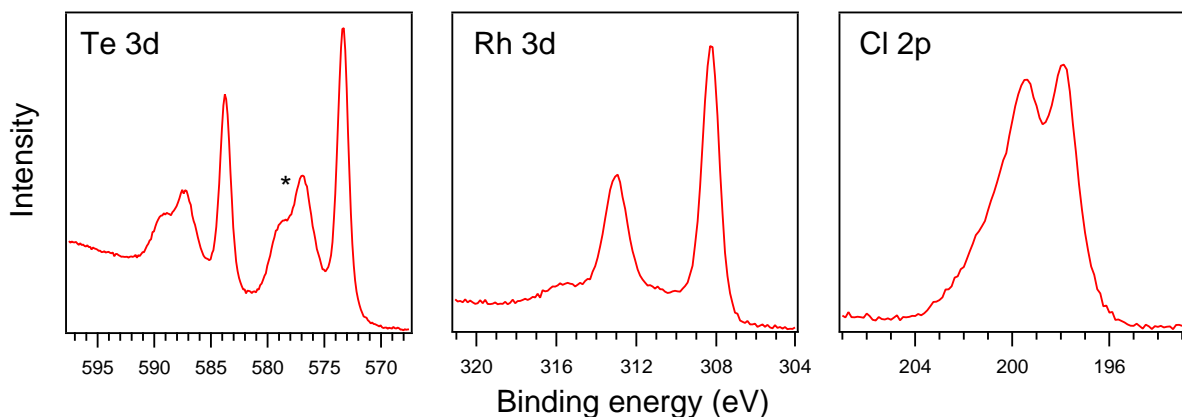


Figure S10: XP spectra of RhTeCl core levels. The Te 3d line shows a high energy component marked by (\*) indicative of oxide formation. The Rh 3d doublet appears to be of single component character whereas the Cl 2p line features a clear asymmetry on the high binding energy side. Energy scale has been calibrated to C 1s.

## Diffuse reflection measurement

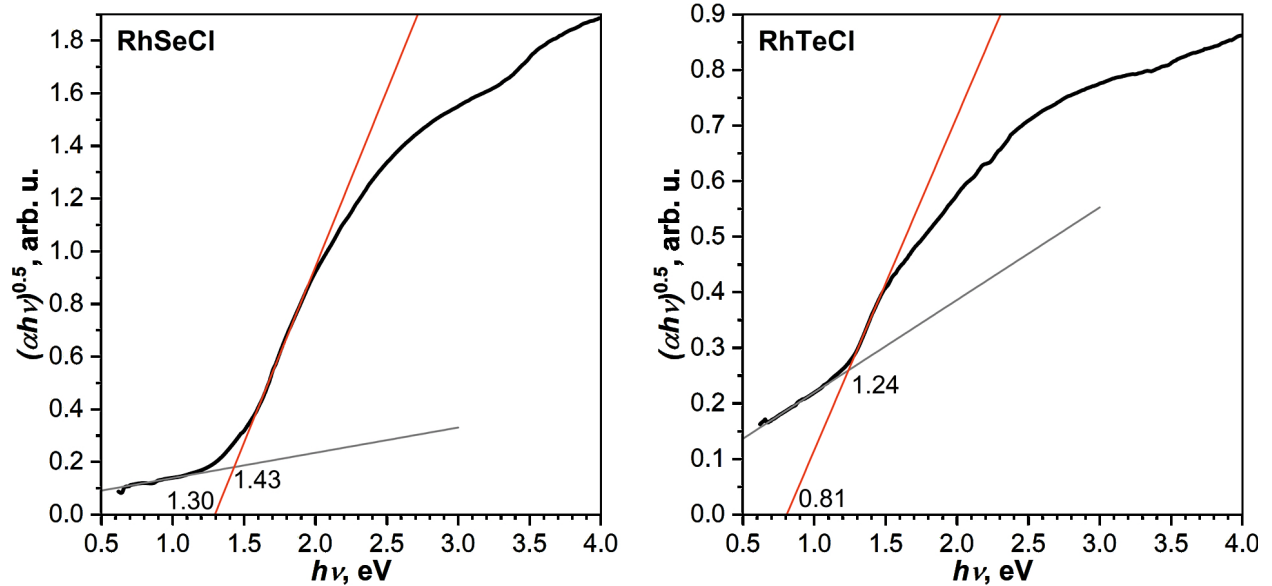


Figure S11: Tauc plots for polycrystalline RhSeCl and RhTeCl and band-gap values obtained for two approaches to a baseline.

We measured diffuse-reflectance spectra of RhSeCl and RhTeCl powders, then performed a Kubelka-Munk transformation to obtain the absorption ( $\alpha$ ) from the reflectance data. Subsequently, we created Tauc plots suggesting an indirect bandgap, as shown in the figure below. However, it is important that the procedure cannot unambiguously determine the bandgap, because of the baseline ambiguity. Both spectra show a non-zero background absorption at low energy. One approach to estimate the bandgap is to extrapolate the linear part of the absorption band to zero  $\alpha$ , yielding values of 1.30 eV for RhSeCl and 0.81 eV for RhTeCl. Another approach is to approximate the background by a straight line and determine the bandgap as the intersection of this linear background with the linear part of the absorption curve. This method gives values of 1.43 eV for RhSeCl and 1.24 eV for RhTeCl. A relatively strong background was observed for RhTeCl, which may also indicate that it absorbs below 0.65 eV. This fact we can't confirm, because it is the limitation of our spectrometer.

# Full measurement range of the thermochemical characterization

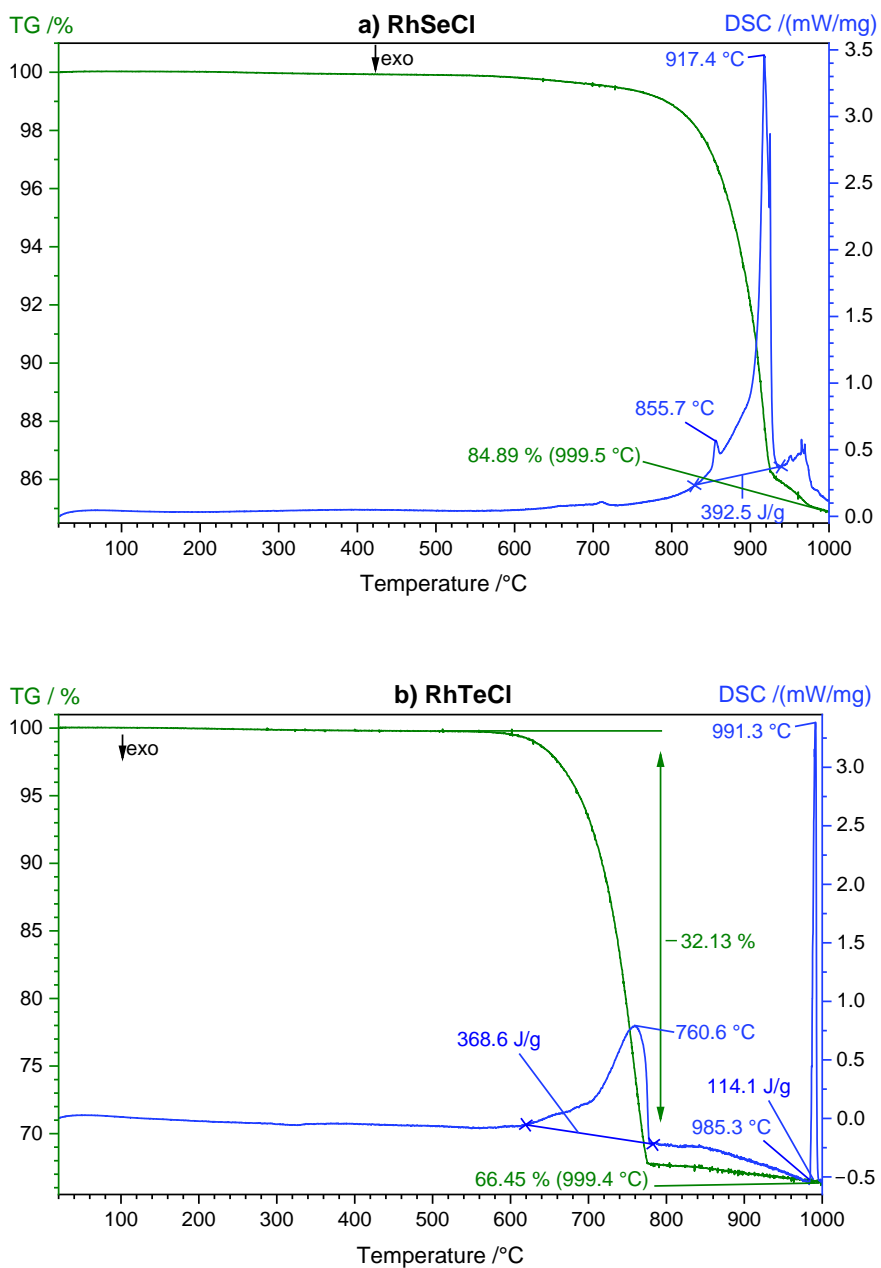


Figure S12: TG-DSC data of RhSeCl (a) and RhTeCl (b) crystals starting from room temperature up to 1000 °C, in green the TG and in blue the DSC measurement is plotted.

# XRD measurement after thermochemical investigation

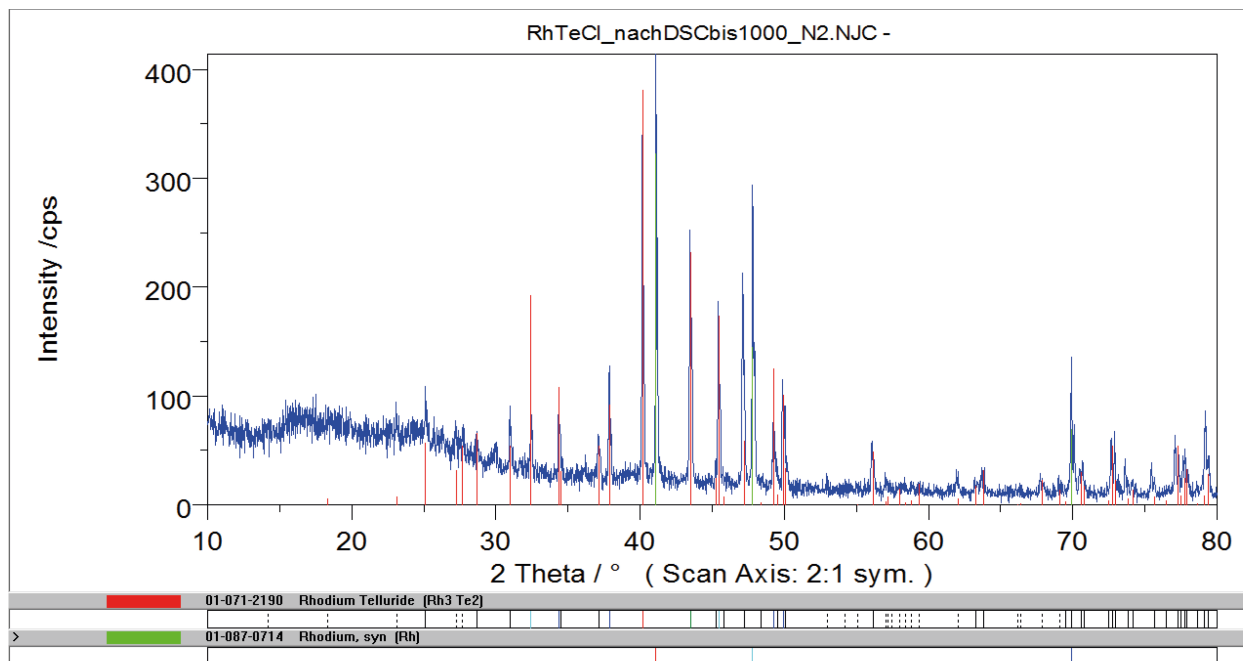


Figure S13: XRD pattern of the decomposition products from RhTeCl measured with a Cu source in reflection geometry. The observed reflexes correspond to the pattern of elemental Rhodium as well as Rh<sub>3</sub>Te<sub>2</sub>.

## References

- (1) Köhler, J.; Umland, W. RhTeCl – das erste Chalkogenidhalogenid eines Platinmetalls mit Schichtstruktur. *Zeitschrift für anorganische und allgemeine Chemie* **1997**, *623*, 583–586.
- (2) Nowak, D.; Valldor, M.; Rubrecht, B.; Froeschke, S.; Eltoukhy, S.; Büchner, B.; Hampel, S.; Gräßler, N. Crystal growth of the 2D Janus rhodium chalcogenide RhSeCl. *Inorganic Chemistry Frontiers* **2023**, *10*, 2911–2916.
- (3) Petříček, V.; Palatinus, L.; Plášil, J.; Dušek, M. Jana2020 – a new version of the crystallographic computing system Jana. *Zeitschrift für Kristallographie - Crystalline Materials* **2023**, *238*, 271–282.

(4) Dr. H. Putz & Dr. K. Brandenburg GbR Diamond - Crystal and Molecular Structure  
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