ELECTRONIC SUPPORTING INFORMATION

(ESI)

Second-Harmonic-Generation of $[(Se,Te)Cl_3]^+[GaCl_4]^-$ with Aligned Ionic Tetrahedra

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Content

1. Analytical Techniques

X-ray powder diffraction (XRD). X-ray powder diffraction analysis (XRD) of **1** and **2** was performed on a Stoe Stadi-P diffractometer (Stoe, Germany) using Cu–$K_{\alpha 1}$ radiation ($\lambda = 154.06$ pm) with a Ge-monochromator. Rietveld refinements were performed with the program TOPAS-Academic (Version 5), using *hkl*-data approach to confirm the phase purity of the title compounds.

Fourier-transform infrared (FT-IR) spectra of **1** and **2** were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker, Germany). The samples were measured in transmission as pellets in KBr. Thus, 300 mg of dried KBr and 0.5-1.0 mg of **1** or **2** were carefully pestled and pressed to a thin pellet.

Thermogravimetry (TG) of **1** or **2** was carried out on a Netzsch STA 449 F3 Jupiter device (Netzsch, Germany), using α-Al_2O_3 as a crucible material and reference. Buoyancy effects were corrected by baseline subtraction based on a blank measurement. The samples were measured under dried nitrogen up to 600 °C with a heating rate of 5 K/min. The Netzsch software PROTEUS Thermal Analysis (Version 5.2.1) was used for graphical illustration.

2. Material Characterization

Formation and purity of the title compounds were evaluated by X-ray powder diffraction (XRD) with a Rietveld analysis (*see main paper: Figure 2*). A comparison of an experimental powder diffractogram with the refined diffractogram (using the data from single-crystal structure analysis as model for Rietveld refinement) shows good agreement for both compounds. Only for **1**, the nature of a single, low-intensity Bragg reflection remains unclear (marked by *).

The purity of the title compounds was further confirmed by Fourier-transform infrared (FT-IR) spectroscopy (Figure S1). The observed vibrations are in good agreement with $SeCl_4$, $TeCl_4$, and $GaCl_3$ as references. Even more important, the absence of any ν(O–H) (3500-3000 cm^{-1}) or ν(C–H) (3000-2800 cm^{-1}) vibrations point to the absence of water, moisture, as well as of organic compounds as impurities. An assignment of the broad, less specific absorption bands is not reasonable and, therefore, performed for Raman spectra exhibiting much narrower absorptions (*see main paper: Figure 4 and Figure 8*).

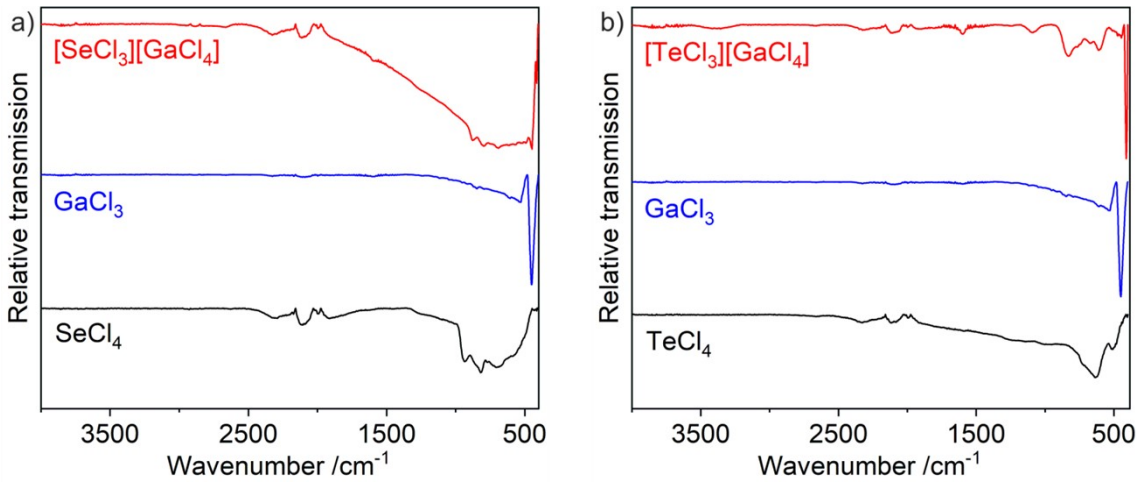

Figure S1. FT-IR spectra of (a) $[SeCl_3][GaCl_4]$ and (b) $[TeCl_3][GaCl_4]$ with $SeCl_4$, $TeCl_4$, and $GaCl_3$ as references.

According to thermal analysis including thermogravimetry (TG) and differential thermal analysis (DTA), $[SeCl_3][GaCl_4]$ and $[TeCl_3][GaCl_4]$ are thermally stable up to 200 °C (**1**) and 300 °C (**2**). They show dissociative sublimation at higher temperature via $SeCl_4$/$TeCl_4$ and $GaCl_3$ (Figure S2a). **1** and **2** re-crystallize from the gas phase as indicated by X-ray powder diffraction, showing diffractograms similar to the as-prepared compounds (*see main paper: Figure 2*). TG also confirms the purity of **1** and **2**. Accordingly, complete thermal evaporation of $SeCl_4$, $TeCl_4$, and $GaCl_3$ was observed with a single step, which occurs above 200 °C (**1**) and above 300 °C (**2**) with a mass loss of 98%. DTA, first of all, shows endothermal peaks at 280 °C (**1**) and 380 °C (**2**), which relate to the dissociative sublimation (Figure S2b). An additional endothermal peak is observed for **2** at 140 °C, which indicates the melting point of $[TeCl_3][GaCl_4]$. The more ionic $[SeCl_3][GaCl_4]$ remains solid until the temperature of sublimation is reached.

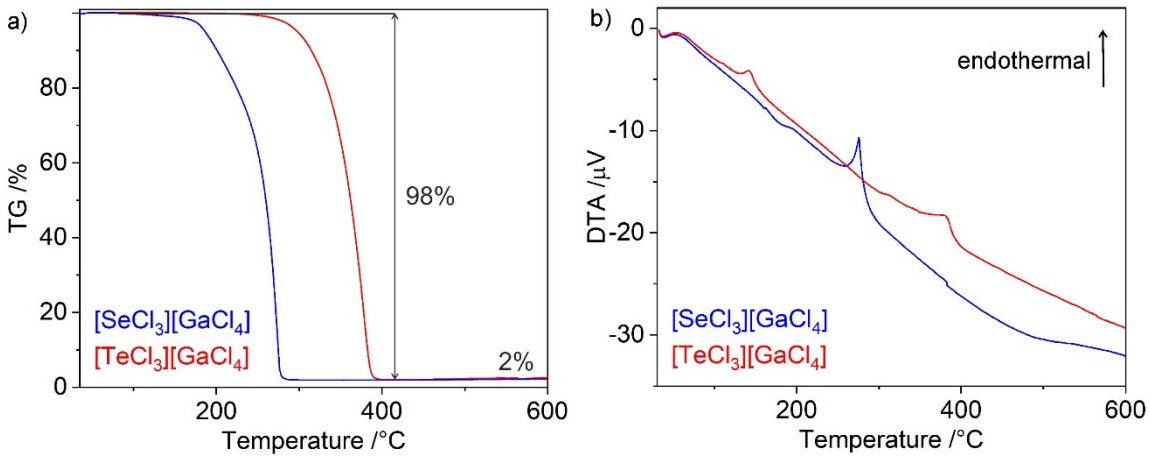

Figure S2. Thermal analysis of $[SeCl_3][GaCl_4]$ and $[TeCl_3][GaCl_4]$: (a) thermogravimetry (TG), (b) differential thermal analysis (DTA).

Crystallographic data and refinement details of both title compounds are listed in Table 1 of the main paper and can be also obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the CCDC numbers 2216148 and 2216149.

The unit cells of **1** and **2** are shown in Figure S3. Beside single-crystal structure analysis, the purity and crystal structures of **1** and **2** were as well evidenced by X-ray powder diffraction (XRD) with a Rietveld analysis (*see main paper: Figure 2*).

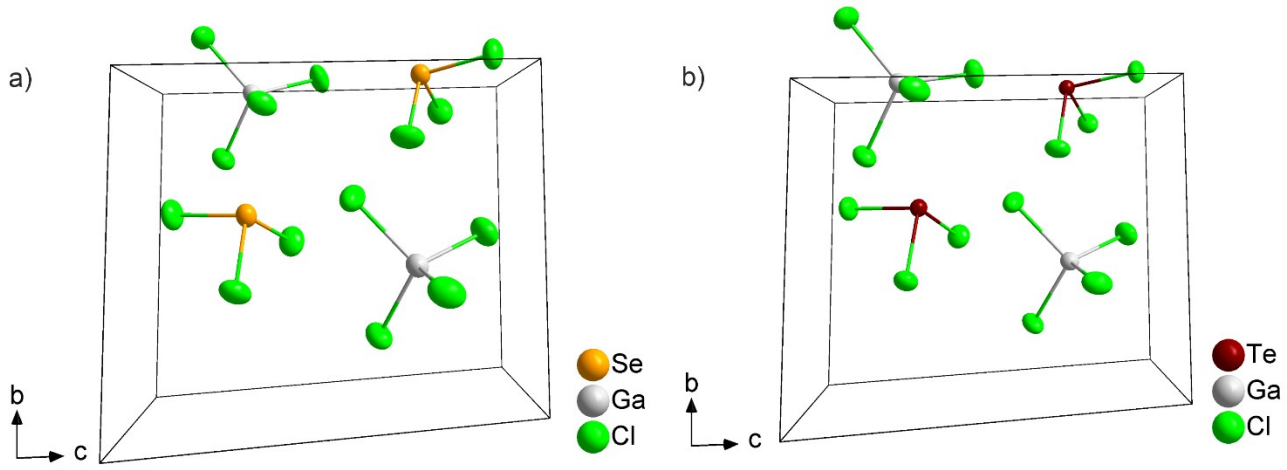

Figure S3. Unit cells of (a) **1** and (b) **2**.