

## Supporting Information

**Three-dimensional frameworks of cubic  
(NH<sub>4</sub>)<sub>5</sub>Ga<sub>4</sub>SbS<sub>10</sub>, (NH<sub>4</sub>)<sub>4</sub>Ga<sub>4</sub>SbS<sub>9</sub>(OH)•H<sub>2</sub>O, and  
(NH<sub>4</sub>)<sub>3</sub>Ga<sub>4</sub>SbS<sub>9</sub>(OH<sub>2</sub>)•2H<sub>2</sub>O.**

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**Energy Dispersive Spectroscopy (EDS) analyses.** The analyses were performed using Hitachi S-3500 scanning electron microscope (SEM) equipped with a PGT energy dispersive X-ray analyzer. Data acquisition was performed with an accelerating voltage of 25 kV and 60 s accumulation time.

**Solid state reflectance UV-Vis-Near IR spectroscopy.** UV/vis/near-IR diffuse reflectance spectra were obtained at room temperature on a Shimadzu UV-3010 PC double beam, double monochromator spectrophotometer in the wavelength range of 200-2500 nm. BaSO<sub>4</sub> powder was used as a reference (100% reflectance) and base material on which the powder sample was coated. The reflectance data were converted to absorption using the Kubelka-Munk function, and the band edge for each sample was estimated from the intercept of the line extrapolated from the high-energy end of the absorption to the baseline (Wendlandt, W.W.; Hecht, H.G. in *Reflectance Spectroscopy*, Wiley Interscience, New York, 1966).

**Solid State Absorption Spectra.** Solid-state absorption spectra were measured with single crystal samples using a U-6000 microscopic FT spectrophotometer.

**Infrared spectroscopy.** Infrared spectra (IR) in the mid-IR region [4000-400 cm<sup>-1</sup>, diffuse reflectance infrared Fourier transform (DRIFT) method] were recorded on a Nicolet 6700 series spectrometer with 2 cm<sup>-1</sup> resolution. Single crystal spectra were recorded on a CRAIC QDI 2010 spectrometer

**Thermal Analysis.** Thermogravimetric analysis (TGA) was carried out with a Shimadzu TGA 50. Samples (10±0.5 mg) were placed in quartz crucible. Samples were heated from ambient temperature to 500 °C in a 20 ml/min flow of N<sub>2</sub> or air. Heating rate of 10 °C/min was used and continuous records of sample temperature, sample weight and its first derivative (DTG) were taken.

**Single Crystal X-ray Crystallography.** A STOE imaging plate diffraction system (IPDS-2, IPDS-2T) operating at 100 K and using graphite-monochromatized Mo K $\alpha$  radiation, was used for data collection of **1**. Cell refinement, data reduction and numerical absorption correction were carried out using X-area suite program. A Bruker APEX2 CCD diffractometer was used with a synchrotron radiation of 0.41328 Å operating at 100K was used for the data collection of **2**. Cell refinement, data reduction and numerical absorption correction were carried out using Bruker AXS suite program. The intensities were extracted by the program XPREP (Sheldrick, G. M. In *SHELXTL*; 5.1 ed.; Bruker-AXS: Madison, WI, 1998). The structures were solved with direct methods using SHELXS and least square refinement were done against  $F_{obs}^2$  using routines from SHELXTL software (Sheldrick, G. M. In *SHELXTL*; 5.1 ed.; Bruker-AXS: Madison, WI, 1998). Refinements of the structures omitted hydrogens as they could not be located in the Fourier difference map. Ammonium ions and water ions for **2** are indecipherable from one another as the scattering factors for N and O are too similar and were chosen based on charge balancing arguments.

## Second Harmonic Generation Measurements

We use the frequency-tripled output of a passive-active mode-locked Nd:YAG laser with a pulse width of about 30 ps and a repetition rate of 10 Hz to pump an optical parametric amplifier (OPA). The OPA generates vertically polarized pulses in the range of 400 ~ 3156 nm. In order to check the second harmonic generation (SHG) efficiency as a function of the fundamental wavelength  $\omega$ , we tune  $\omega$  from 1240 ~ 1700 nm and record the corresponding SHG response at  $2\omega$ . The incident laser pulse of 20 mJ was focused onto a spot of 1 mm in diameter using a 3 cm focal-length lens. The corresponding incident photon flux per pulse is about  $85 \text{ MW/cm}^2$ . The SHG signal is collected in a reflection geometry from the excitation surface and focused onto a fiber optic bundle. The output of the fiber optic bundle is coupled to the entrance slit of a Spex Spec-One 500 M spectrometer and detected using a nitrogen-cooled CCD camera. The data collection time is 60 s.

### Pore-Cavity Calculations:

After solving the crystal data, all cations in the framework were removed. The Cavity-Plot program in PLATON was then used to calculate the void space within the structure. The calculation uses model atoms and the van der Waal's radii of the framework to calculate the cavity spacing.

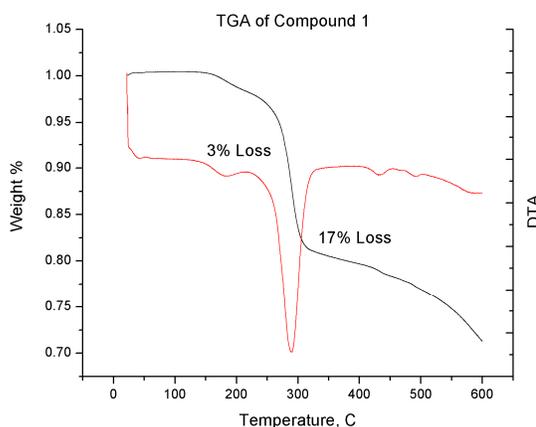


Figure S11. The thermogravimetric analysis of **1**. The TGA of **1** shows a 3% weight loss from 130 °C to 217 °C and it is attributed to loss of water within the crystal. A weight loss of 17% from 220 °C to 333 °C is consistent with the losses of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  described in eq. (1) and (2). Further weight losses from 333 °C to 600 °C are attributed to the complete decomposition of the structure.

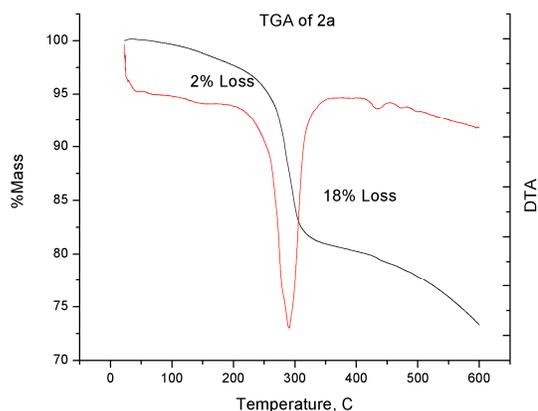


Figure SI2. The thermogravimetric analysis of **2a**. The analysis shows a near immediate loss of ~ 2 % again caused by the loss of disordered water within the system. From 195 °C to 364 °C a weight loss of 18% is also consistent with the theoretical losses described in (3) and (4). The compound then undergoes a continuous weight loss until 600 °C.

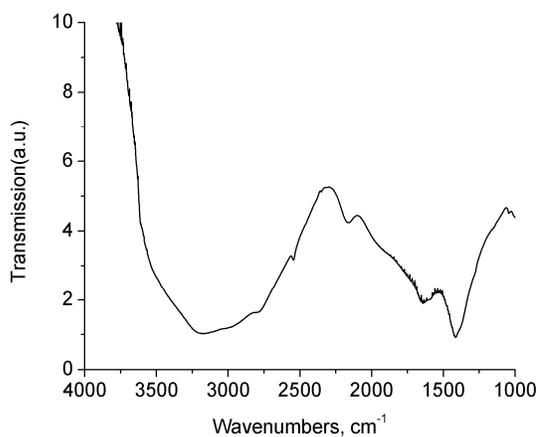


Figure SI3. Mid-IR of **1**. This shows the N-H and O-H stretching peaks clearly. Lack of peak at 2500 cm<sup>-1</sup> indicates no S-H stretching.

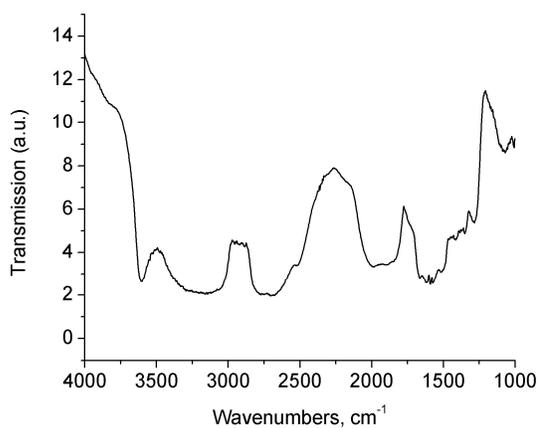


Figure SI4. Mid-IR of **2a**. This shows the N-H and O-H stretching peaks clearly. Lack of peak at  $2500\text{ cm}^{-1}$  indicates no S-H stretching.

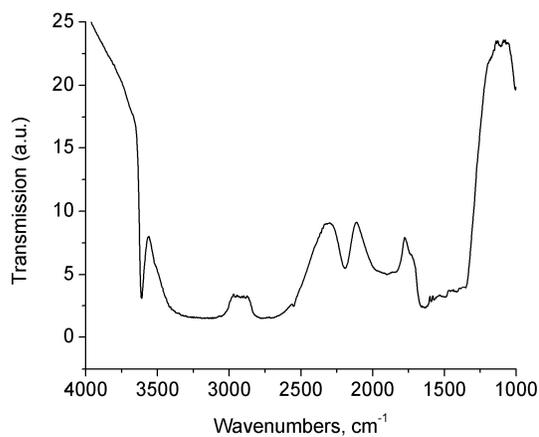


Figure SI5. Mid-IR of **2b**. This shows the N-H and O-H stretching peaks clearly. Lack of peak at  $2500\text{ cm}^{-1}$  indicates no S-H stretching.

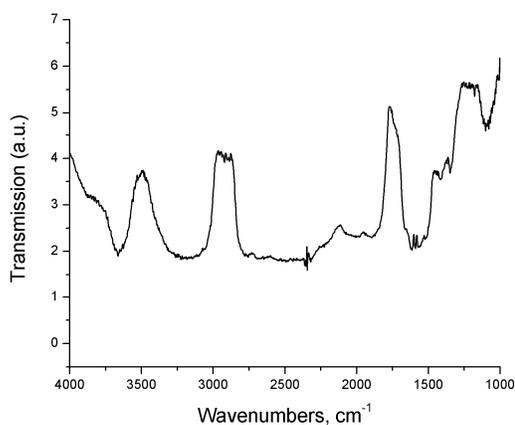


Figure SI6. Mid-IR of **2b**. This crystal was dipped in acid and turned more yellow as a result. The IR shows small changes from **2a**, but does not contain any S-H peaks at  $2500\text{ cm}^{-1}$ .