



Reversible sorption in the crystalline microporous semiconductor Rb-CTH-1

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ABSTRACT

The sorption capacity of the recently reported crystalline microporous semiconductor Rb-CTH-1 was investigated, revealing that the structure demonstrates heat-induced reversible sorption of 3 wt% water and hydrocarbons. The Rb-CTH-1 structure maintains its crystallinity and semiconducting properties when heated to 150 °C. The treatment causes desorption induced irreversible rearrangements of the remaining guest species with a response in the semiconductive properties of the material.

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1. Introduction

The class of crystalline microporous semiconducting materials has recently been expanded with the discovery of a novel antimony(III) oxide antimony telluride coined Rb-CTH-1 with the crystal chemical formula $\text{Rb}_{18}[\text{Sb}_{36}\text{O}_{54}][(\text{SbTe}_3)_2(\text{Te}_2)_6]$ [1]. The structure of Rb-CTH-1 contains a unique 18-ring $\{\text{Sb}_{18}\text{O}_{27}\}$ tubular unit that hosts rubidium cations and which itself is enclosed in an intricate arrangement of $\{\text{SbTe}_3\}^{3-}$ pyramidal anions and Te_2^{2-} dumbbells, as shown in Fig. 1a. Rb-CTH-1 was reported to possess semiconducting properties featuring a band-gap of approximately 0.85 eV at room temperature. The $\{\text{Sb}_{18}\text{O}_{27}\}$ tube in Rb-CTH-1 is wider than the similar 12-ring antimony(III) oxide tubular units in structurally related microporous antimony oxide chalcogenides such as the cetineites [2] and K-SBC-1 [3].

The usefulness of microporous semiconductors is directly related to their sorption properties and to their semiconductor response to sorption. It has been shown that the bandgap of cetineites is largely dependent on framework composition and counter ion [4]. And it was recently shown that the K;Se cetineite can be used to sense noble gases [5]. Single crystal X-ray diffraction of Rb-CTH-1 has shown that its channels are occupied by disordered guest species under ambient conditions [1]. The disorder complicates unambiguous identification of the nature of the guests. Most probably the channels of Rb-CTH-1 contain

disordered molecules of water and *n*-propylamine used in the synthesis of the material. The residual electron density within the pores of Rb-CTH-1 varies from crystal to crystal as exemplified in Fig. 1b. Here we report on sorption properties and their effect on electronic transitions of Rb-CTH-1 investigated by means of temperature-resolved DRIFT analysis, combined use of TGA and DSC techniques, and X-ray powder diffraction.

2. Materials and methods

FTIR spectroscopy analysis of Rb-CTH-1 was performed in diffuse reflectance (DR) geometry. A small amount of Rb-CTH-1 was grinded together with calcined KCl in an agate mortar in a ratio of about 1 to 6 in volume for measurements in mid-IR and 1 to 1 in volume for near-IR measurements. The measurements were performed on a Bruker IFS 66v/S FTIR instrument, using a Harrick diffuse reflection unit, model Praying Mantis. The signal in mid-IR ($660\text{--}7000\text{ cm}^{-1}$ or $80\text{--}870\text{ meV}$) was detected using a KBr beam-splitter and an MCT detector. Diffuse reflectance spectra in mid-IR were collected in the temperature range between -150 and 150 °C , increasing the temperature by 50 °C before each consecutive measurement. Additional spectra were collected upon cooling the sample to 100 , 50 °C , room temperature, whereafter the sample was left standing in air for 1 day and 1 week, respectively. The signal in NIR ($5700\text{--}10,000\text{ cm}^{-1}$ or $710\text{--}1240\text{ meV}$) was detected using a quartz beam-splitter and an InGaAs detector. Diffuse reflectance spectra in near-IR were collected at temperatures as follows: room temperature, -150 ,

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30, 150 and 30 °C finally. For each measurement a sample of pure calcined KCl was subjected to the same treatment and used as a reference.

The TGA/DSC data were collected using a NETZSCH STA 409 PC Luxx instrument under flowing nitrogen. Two Rb-CTH-1 samples were subjected to analysis. In the first case a sample of Rb-CTH-1 was grinded to powder, charged into an Al₂O₃ crucible and subsequently heated from ambient temperature to 150 °C at a rate of 5 °C/min. Thereafter the sample was subjected to a constant temperature of 150 °C for 15 min. In the second case a sample of Rb-CTH-1 was heated from ambient temperature to 300 °C at a rate of 5 °C/min, where it was kept at a constant temperature of 300 °C for 15 min, which was followed by a temperature decrease to ambient temperature at a rate of 5 °C/min.

Powder XRD analysis of a Rb-CTH-1 sample prior to and after the two TGA/DSC analyses was performed on a Siemens D5000 powder X-ray diffractometer (CuK α ₁, λ =1.54056 Å), using a sample holder specially designed for small sample amounts.

3. Results and discussion

The results of the TGA/DSC analysis upon heating a sample of Rb-CTH-1 to 300 °C in nitrogen are presented in Fig. 2. The mass reduction of the sample is mainly linked to the desorption of the loosely bound disordered guest species. The endothermic DSC signal between 35 and 90 °C suggests that desorption initiates in this temperature interval. At temperatures above 90 °C the sample continues to loose mass due to desorption, but the process becomes exothermic likely due to rearrangements of the remaining guest species revealed by the DRIFT analysis below. As the temperature reaches 150 °C the rate of mass decrease diminishes, which is accompanied by an increased rate of enthalpy change. These observations suggest that gradual decomposition of the material in nitrogen initiates at 150 °C, giving rise to structural defects. Sendor et al. [5] have recently reported that structural defects may hinder the desorption of guest water molecules from the 1-D channels of the K;Se cetineites. The mass loss of Rb-CTH-1 at 150 °C is approximately 3%, which corresponds to 18 water molecules per formula unit (1 water molecule per Rb⁺ cation).

The sample loses an additional approximate 1.5% in mass upon further heating to 300 °C, which would correspond to a total of 27 water molecules per formula unit (1.5 water molecule per Rb⁺ cation). It is worth noticing that both the cetineites [2] and K-SBC-1 [3] feature only one ordered water molecule per counter cation. However, mass reduction may to a certain extent be attributed to desorption of disordered molecules of the structure directing agent *n*-propylamine or other amines plausibly present within the channels of Rb-CTH-1, as described below. The desorption of guest species from the channels of Rb-CTH-1

possibly prevents the sample from preserving its original periodicity, where the structure either attains lower crystallographic symmetry, or the crystallinity is completely lost at high temperatures.

In Fig. 3 the effect of heat treatment on crystallinity is shown with X-ray powder diffraction. Ordered microporous materials such as, for instance, zeolites, demonstrate pronounced Bragg peaks at low angles in powder X-ray diffractograms. A calculated powder X-ray diffractogram of Rb-CTH-1 shown in Fig. 3a exhibits such a peak at 4.65° arising from the (100) reflection and corresponding to a *d*-spacing of 18.97 Å. Experimental diffractograms of a pure Rb-CTH-1 sample and a sample heat-treated in nitrogen at 150 °C are shown in Fig. 3b and c, respectively. Both diffractograms feature the same low-angle peak at 4.65°, which indicates that Rb-CTH-1 maintains its crystallinity at 150 °C. However, the peak at 9.35°, assigned to the (200) reflection nearly disappears for the sample heat-treated at 150 °C. Instead, two new peaks emerge; the peak at 38.4°, may be assigned to Sb₂Te₃, and/or Sb₂O₃ and the peak at 51.8°, which could not be assigned to any related material, but is perhaps a result of formation of an intermediate product during the heat treatment. The appearance of these peaks and the disappearance of the (200) peak possibly indicate that Rb-CTH-1 may begin to collapse at temperatures around 150 °C. However, it is well-known that the intensity of Bragg peaks in powder X-ray diffractograms of microporous solids, especially for small sample amounts and for crystals with needle-shaped morphology, may vary significantly [6]. The

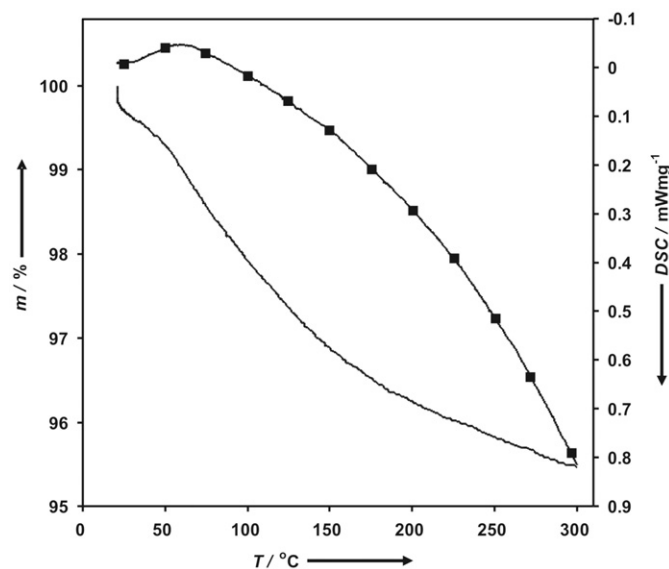


Fig. 2. TGA/DSC data of a Rb-CTH-1 sample heated in nitrogen to 300 °C. Solid line represents sample mass normalized to starting mass and line marked with squares represents calorimetric signal.

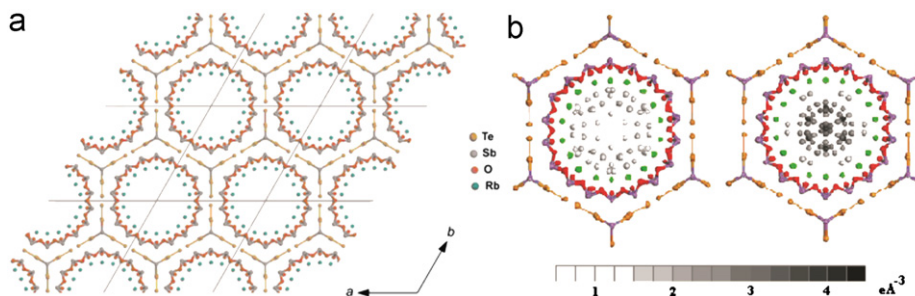


Fig. 1. (a) Structure of Rb-CTH-1 as projected onto the (001) plane and (b) residual electron density inside a 1-D channel represented for two different single crystals of Rb-CTH-1 with density values of residuals scaled to color scale.

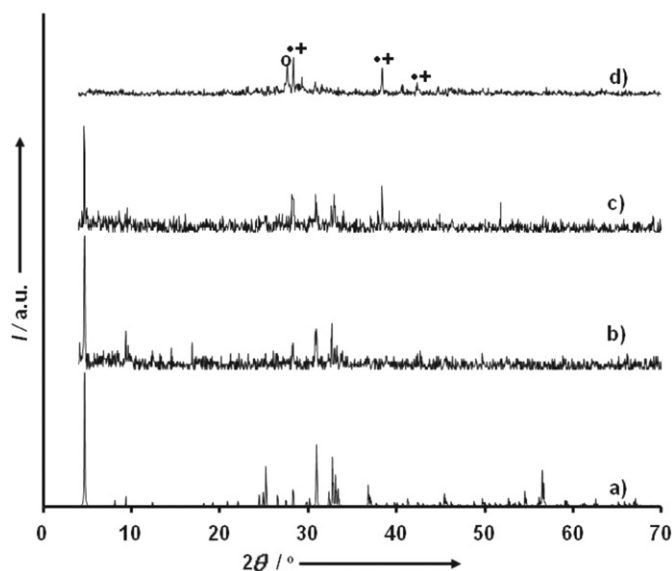


Fig. 3. (a) The theoretically calculated powder X-ray diffractogram of Rb-CTH-1 compared to experimental diffractograms of (b) purified fresh sample of Rb-CTH-1; (c) Rb-CTH-1 after heating in nitrogen at 150 °C; and (d) product formed after heating Rb-CTH-1 in nitrogen at 300 °C. Peaks marked by “•” represent Sb_2Te_3 ; peaks marked by “+” represent Sb_2O_3 ; and peaks marked by “o” represent TeO_2 .

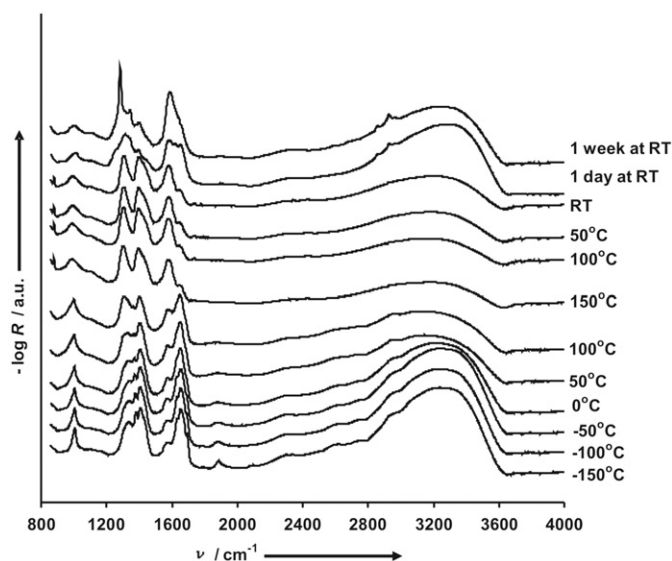


Fig. 4. Diffuse reflectance spectra of a Rb-CTH-1 sample grinded with KCl showing the logarithm of the inverse reflectance as a function of photon energy in the interval between 850 and 4000 cm^{-1} . Data collected in order starting from the spectra at the bottom.

low-angle peak is missing for a Rb-CTH-1 sample heat-treated at 300 °C (see Fig. 3d), indicating that Rb-CTH-1 decomposes completely upon heating to this temperature. Instead peaks that can be attributed to Sb_2Te_3 , TeO_2 and Sb_2O_3 appear.

To identify the species desorbing from Rb-CTH-1 upon heat treatment to 150 °C and evaluate the effect of desorption on remaining guest species and on the electronic transitions DRIFT spectra were collected as a function of temperature. The temperature resolved diffuse reflectance mid-IR spectra of a Rb-CTH-1 sample mixed with KCl are presented in Figs. 4 and 5. Since the nature of the sample does not allow for collection of the real absorption spectrum, the logarithm of the inverse reflection is used

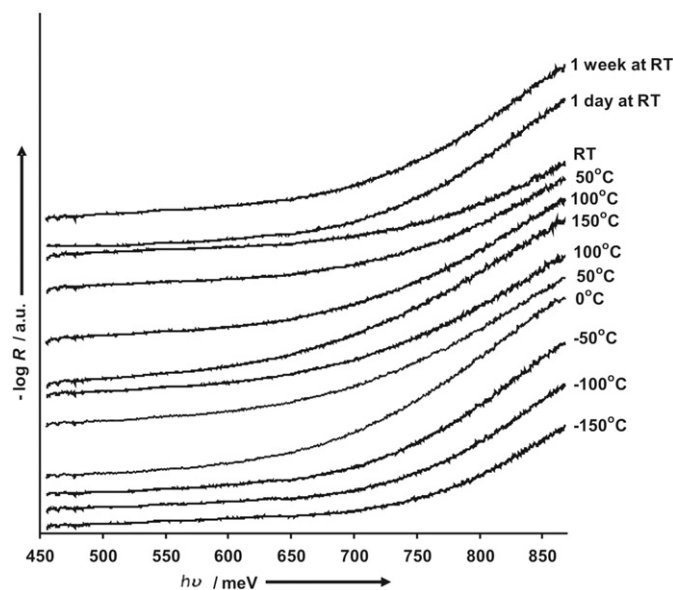


Fig. 5. Diffuse reflectance spectra of a Rb-CTH-1 sample grinded with KCl showing the logarithm of the inverse reflectance as a function of photon energy in the interval between 450 and 870 meV. Data collected in order starting from the spectra at the bottom.

as an estimate of the real absorption spectrum. The spectra feature two pronounced regions of photon absorption, namely a broad band in the region 2800–3660 cm^{-1} , and a series of peaks below 2000 cm^{-1} , as shown in Fig. 4. The distinct broad band centered around 3200 cm^{-1} shown in Fig. 4 is assigned primarily to –OH stretching modes due to disordered molecular water in the channels of Rb-CTH-1 [1]. Being synthesized in the presence of *n*-propylamine as a structure directing agent [1] Rb-CTH-1 may contain disordered molecules of the SDA or other amines produced during the synthesis within the channels. Some photon absorption in the region between 3200 and 3400 cm^{-1} may hence also be attributed to asymmetric and symmetric –NH stretching vibrations due to the presence of adsorbed amines [7,8]. However, the shape of the absorption band extending from 3000 to approximately 3600 cm^{-1} does not allow for unambiguous identification of amine species. The band remains practically unaltered between –150 and 0 °C, followed by a gradual decrease upon raising the temperature to 150 °C. After subjecting the sample to ambient environment this band attains a more pronounced profile anew.

A shoulder between 2830 and 3010 cm^{-1} , and centered around 2950 cm^{-1} , is observed at temperatures from –150 to 100 °C and is attributed to –CH stretching of disordered hydrocarbons in the $\{\text{Sb}_{18}\text{O}_{27}\}$ tubular unit [9]. This shoulder decreases at further heat treatment and is thereafter completely missing for the measurements at temperatures from 150 °C to room temperature. As the sample is subjected to ambient atmosphere three distinct peaks emerge in this region, at 2877, 2940 and 2983 cm^{-1} , respectively. These peaks are also assigned to –CH stretching of hydrocarbons [9].

The spectra in Fig. 4 show also a series of absorption bands between 1000 and 2000 cm^{-1} . These bands are associated with the optical vibration modes of the crystal structure [1] and with vibrations of guest species in the channels of Rb-CTH-1. The presence of bands or overtones of bands related to vibration frequencies of the framework below 2000 cm^{-1} is typical for zeolite type materials and renders complications in correct assignment of the peaks arising from the vibrations of guest species [10,11].

The band at 1650 cm^{-1} in the absorption spectra of Rb-CTH-1 is likely due to water molecules that are hydrogen bonded to the

framework. Zeolites feature a similar band centered at 1630 cm^{-1} [12]. This band is pronounced for spectra collected between -150 and $100\text{ }^{\circ}\text{C}$, whereupon it decreases and remains small at $150\text{ }^{\circ}\text{C}$ and after cooling the sample to room temperature. However, spectra collected after further exposing the sample to ambient environment demonstrate an increase of this band. The band at 1590 cm^{-1} is assigned to bending of molecular water [9] that is less strongly bound to the framework. The band is small at $-150\text{ }^{\circ}\text{C}$ and maintains a low intensity at temperatures up to $100\text{ }^{\circ}\text{C}$ but becomes more pronounced at further heat treatment of the sample at $150\text{ }^{\circ}\text{C}$ and during the subsequent cooling to room temperature and exposure to air. The peak at 1380 cm^{-1} , attributed to $-\text{CH}$ deformation in adsorbed hydrocarbons is observed at temperatures up to $100\text{ }^{\circ}\text{C}$. This peak shifts to slightly lower wavenumbers and disappears upon further heat treatment to $150\text{ }^{\circ}\text{C}$ and during subsequent cooling to room temperature. As the sample is then subjected to ambient environment the peak at 1350 cm^{-1} can be observed instead, also assigned to vibrations of hydrocarbons [9]. Peaks at 1010 , 1415 cm^{-1} and a band in the region $1260\text{--}1340\text{ cm}^{-1}$ with a centre shifting from 1330 to 1280 cm^{-1} in the progress of the study could not be assigned to any specific guest species, and are tentatively attributed to vibrational modes of the framework.

In general, the spectra in Fig. 4 reveal that molecular water and hydrocarbons are desorbed upon heating of the sample to $150\text{ }^{\circ}\text{C}$ and re-adsorbed by the sample upon cooling to room temperature and exposing the sample to ambient atmosphere. The shapes of the peaks suggest that the guests are re-adsorbed at positions different from the original. Such behavior of re-adsorbed guests has been observed in structurally related antimony(III) oxide telluride K-SBC-1 [13,14]. These reversible sorption properties of Rb-CTH-1 are accompanied by shifts of some vibrational modes of the structure upon heating to $150\text{ }^{\circ}\text{C}$. The irreversible nature of these shifts suggests desorption-induced rearrangements of the remaining guest species that give rise to changes in guest–guest and guest–host interactions. It is however unclear whether water molecules, hydrocarbons, or both relocate since the exact nature and positions of the guest species are hard to locate by means of single-crystal X-ray diffraction due to high degree of disorder of the guests.

Fig. 5 shows the corresponding spectra for higher photon energies, which demonstrate a rise in the absorption characteristic for valence band to conduction band transitions. The spectra indicate that Rb-CTH-1 maintains semiconductive properties in the temperature range from -150 to $150\text{ }^{\circ}\text{C}$. Clearly the desorption and the rearrangement of the guest species influence the onset energy for the valence band to conduction band transitions, since the spectrum collected at $50\text{ }^{\circ}\text{C}$ during cooling of the sample does not precisely match the spectrum collected at $50\text{ }^{\circ}\text{C}$ during heating. A distinct difference between the spectrum of the sample at room temperature and the spectra of the sample subjected during 1 day, respectively, 1 week to ambient atmosphere suggests that guest species re-adsorbed from air influence the electronic structure of Rb-CTH-1.

The near-IR diffuse reflectance spectra of Rb-CTH-1 presented in Fig. 6 demonstrate that the bandgap shifts to lower energy with rising temperature, as would be predicted for a semiconductor. The bandgap energy in Rb-CTH-1 was estimated from the derivative spectrum of inverse logarithmic reflectance with respect to the photon energy. This particular sample of Rb-CTH-1 has the bandgap of 0.95 eV at room temperature, compared to 0.85 eV as previously reported [1], possibly due to differences in the nature of guest species. The bandgap at $-150\text{ }^{\circ}\text{C}$ was determined to be 1.08 eV . The bandgap at $150\text{ }^{\circ}\text{C}$, however, was calculated to be 1.0 eV . The bandgap energy at $30\text{ }^{\circ}\text{C}$ is 0.96 eV during heating cycle and 0.98 eV during cooling cycle, respectively.

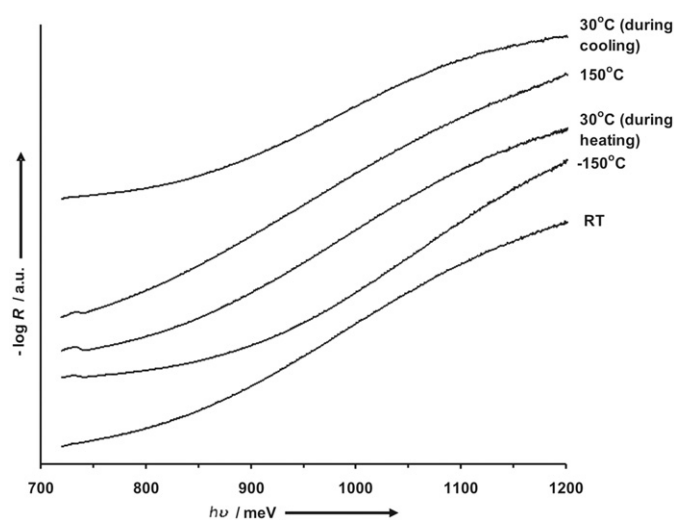


Fig. 6. Diffuse reflectance spectra of a Rb-CTH-1 sample grinded with KCl showing the logarithm of the inverse reflectance as a function of photon energy in the interval between 720 and 1200 meV. Data collected in order starting from the bottom.

In general, the bandgap is expected to decrease with rising temperature. Rb-CTH-1 demonstrates the opposite behavior in the temperature interval between room temperature and $150\text{ }^{\circ}\text{C}$. Recently Sendor et al. have shown that in structurally related cetineites the increase in optical bandgap is attributed to the decrease of the lattice constant [15]. Plausibly the desorption and the rearrangement of guest species influence the electronic structure of Rb-CTH-1 or affect alterations of the lattice constant of the material. The spectra also confirm the results of the investigation in the mid-IR region and it is clear that an irreversible process occurs when the sample is kept at $150\text{ }^{\circ}\text{C}$. As a consequence the final measurement at $30\text{ }^{\circ}\text{C}$ taken when the sample was cooled down does not reproduce the previous measurement at similar temperature, which was collected prior to heating the sample.

4. Conclusions

The results of this study demonstrate that Rb-CTH-1 exhibits heat-induced reversible sorption of disordered guest species (mainly water and perhaps some hydrocarbons) in the 1D channels. This is accompanied by desorption-induced irreversible rearrangements of the remaining guest species. The desorption of the guest species initiates at $35\text{ }^{\circ}\text{C}$ and continues with rising temperature, reaching 3 wt% of the total mass at $150\text{ }^{\circ}\text{C}$. Rb-CTH-1 maintains crystallinity and semiconductive properties at temperatures up to $150\text{ }^{\circ}\text{C}$. The structure, however, appears to collapse and transform into Sb_2Te_3 , TeO_2 and Sb_2O_3 when heated to $300\text{ }^{\circ}\text{C}$. The energy bandgap of Rb-CTH-1 was found to increase with rising temperature in the interval between room temperature and $150\text{ }^{\circ}\text{C}$. This observation suggests that the semiconductive properties of Rb-CTH-1 are affected by the desorption and the rearrangement of guest species inside the 1-D channels. Rb-CTH-1 shows thus great potential for application within the field of gas sensors.

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