Structural analysis of the microporous semiconductor K-SBC-1 during its reversible sorption of water

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ARTICLE INFO

ABSTRACT

The reversible sorption of water molecules in the crystalline microporous semiconductor K-SBC-1 was investigated using temperature-resolved single-crystal XRD analysis. Three crystallographic sites of adsorbed water molecules, differing in adsorption strength, were discovered in the pores of K-SBC-1. The least tightly bound is located at the centre of the $\{Sb_{12}O_{18}\}$ tube and begins to desorb around 50 °C. Above 200 °C the more strongly bound water molecules rearrange from their potassium-coordinating positions to the centre of the tube, thus obtaining the characteristics of the loosely bound water, and desorb thereafter. At 240 °C approximately 10% of the water has desorbed, leaving the host framework of K-SBC-1 intact. Upon re-adsorption of water at room temperature the molecules preferentially adsorb at sites in the centre of the $\{Sb_{12}O_{18}\}$ tube. This shows that a heat treatment of 240–300 °C activates K-SBC-1 for sorption and explains the observed facile desorption of water from activated samples.

1. Introduction

The structure of the crystalline microporous semiconductor K-SBC-1 [1] with the reduced crystal chemical formula $|(|K_6(H_2O)_6|[Sb_{12}O_{18}])_3|[Te_{36}]$ features a 24-ring tellurium 1-D tubular unit in which an $\{Sb_{12}O_{18}\}$ 1-D tubular unit resides as a guest. Potassium ions and water molecules are in turn hosted in the $\{Sb_{12}O_{18}\}$ tube, making the material the first example of a second-order zeoate according to the most recent suggestion for nomenclature [2]. In the first single crystal X-ray analysis of the K-SBC-1 structure only one crystallographic site was found for adsorbed water molecules [1]. However, the ability of the material to demonstrate reversible sorption of water molecules has since then been demonstrated by using a combination of DRIFT, TGA/DSC analysis and powder XRD and these results suggested that more than one adsorption site of molecular water exist inside the 1-D channels of K-SBC-1 [3]. It was also shown that water re-adsorbed in K-SBC-1 following a heat treatment at 300 °C can be much more readily removed from the structure than the water present prior to such a heat treatment [3]. For the structurally related cetineite family [4–6], it was recently reported that two different crystallographic positions of water guest molecules are present in the $\{Sb_{12}O_{18}\}$ tubular unit [7]. The K;Se version of the cetineite exhibits sorption properties that can be exploited for

detecting noble gases but requires evacuation at 10^{-5} mbar to desorb water and to make accessible the porosity of the $\{Sb_{12}O_{18}\}$ tube [7]. The facile reversible sorption found for K-SBC-1 is expected to make this structure even more useful for such similar applications.

In this study we report on the results of a temperature-resolved single-crystal X-ray diffraction analysis of K-SBC-1, which shed more light upon the intriguing reversible sorption of water molecules in this structure.

2. Experimental methods

The crystal structure of K-SBC-1 was determined during its exposure to different environmental conditions using a Siemens SMART CCD single-crystal X-ray diffractometer (MoKα radiation, $\lambda = 0.71073$ Å). The different conditions were employed in the following sequence: room temperature in dry N_2 flow, 50, 100, and 150 °C in dry N_2 flow, room temperature in ambient atmosphere with a Petri dish filled with water underneath the crystal, 200 °C in dry N_2 flow, 240 °C in dry N_2 flow, room temperature in ambient atmosphere after 1 month in ambient environment. Data collection and integration were carried out using the SMART and SAINT software [8]. Averaging and absorption correction were done using SADABS [9]. Structure solution and refinement were performed using the WinGX v1.70.01 program package [10]. During the structure refinement the site occupancy factors (s.o.f.'s) of the atoms in the framework, and of the potassium ions, were constrained to unity. The site occupancy factors of the

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oxygen atoms in guest water molecules were refined freely. In cases where the s.o.f.'s of these oxygen atoms refined to values above or within the standard deviation value from unity, these sites were assumed to be fully occupied and the s.o.f. of 1 was used for calculating the corresponding number of atoms in the unit cell. The isotropic/anisotropic displacement parameters for all atoms were refined freely. No attempts were made to locate hydrogen atoms due to the large number of heavy atoms in the structure.

3. Results and discussion

The K-SBC-1 structure was solved in the trigonal space group R-3 (no. 148) as reported earlier [1]. Table 1 presents unit cell dimensions and volume, R values and GooF parameters of the eight crystal structure analyses performed on K-SBC-1 at different conditions.

The crystal structure of K-SBC-1 obtained from the first data set at room temperature is presented in Fig. 1 and confirms the previously published structure of the framework [1]. However, the guests of the structure differ somewhat from the ones published earlier in that besides the previously reported water molecules coordinated to potassium ions, we find two additional residual electron density peaks at fractional coordinates (0,0,0) and (0,0,0.5), corresponding to Wyckoff positions 3a and 3b, and with a magnitude of 3.81 and 2.93 e$\mathring{A}^{-3}$, respectively. In some of the cetineites the octahedral voids at Wyckoff positions 2b at (0,0,0) and (0,0,0.5) were shown to be partially occupied by Sb^{3+} ions or water molecules [4,7]. The alterations in the site occupancy factors of the species confined to these fractional coordinates in K-SBC-1 at various conditions employed in this study imply temperature-induced reversible sorption of these guests. Additionally, due to the relatively small magnitudes of the residual electron density peaks at 3a and 3b Wyckoff positions in K-SBC-1 at room temperature it is unlikely that these sites are occupied by Sb^{3+} ions. Therefore these peaks are assigned to oxygen atoms belonging to two separate water molecules. These oxygen atoms are denoted O_{wc1} and O_{wc2}, respectively.

The distance between O_{wc1} and O_{wc2} atoms varies with the data collection temperature and is between 2.829(1) and 2.852(1) Å, which is typical for the O–O separation between hydrogen bonded water molecules. This distance is too large for the atoms to be part of the same molecule such as N_2, O_2 or a C–C chain, which also confirms the assignment to water. Noteworthy is the fact that the distance from the O_{wc1} and O_{wc2} atoms to the O_w atom ranges from 2.26(1) to 2.32(1) Å. This distance is hence somewhat shorter than a standard intermolecular distance of 2.8 Å between oxygen atoms of two neighbouring water molecules (r(O) = 1.4 Å). However, a number of structures have been

reported to show O–O distances between neighbouring water molecules in the range of 2.0–2.4 Å [11–13].

The site occupancy factors and the total number of the different oxygen atoms representing adsorbed water molecules at various temperatures and conditions are presented in Table 2. The results reveal the general trend for the water molecules to desorb from the channels of K-SBC-1 with rising temperature and to re-adsorb when exposed to ambient environment. Apparently the water molecules represented by O_{wc1} and O_{wc2} are loosely bound and start to desorb at a low temperature of 50 °C. This is consistent with the results of the previous TGA/DSC study of K-SBC-1 [3], where the first endothermic desorption peak appears between 35 and 70 °C. At 150 °C the O_w position is still fully occupied, while the total occupancy of the O_{wc} positions has decreased from 2.43 (at room temperature) to 1.37 atoms in the unit cell. Upon lowering the temperature to room temperature and placing a water-filled Petri dish beneath the crystal it re-adsorbs some of the O_{wc} water and attains 1.60 atoms per unit cell. At temperatures of 200 °C and above the more strongly bound water molecule represented by O_w appears to depart from its crystallographic position and to both relocate to the positions in the centre of the channels and to desorb from the structure. This is in agreement with the TGA/DSC study, which also showed a second endothermic peak. However, this peak appeared at somewhat lower temperature (105 °C) in the TGA study [3]. Overall, close to 8% of the total amount of water present initially desorbs from the channels of K-SBC-1 as the crystal is heated up to 240 °C, whereas the framework of the material remains intact. This desorption of water corresponds to a decrease by 0.3 wt% of the total crystal weight, which is lower than 1.4 wt% loss found at the same temperature for the sample studied with TGA [3]. One possible explanation for the differences in desorbed amount of water and in desorption temperature is that some of the diffusion paths are likely plugged by the epoxy glue used for mounting the
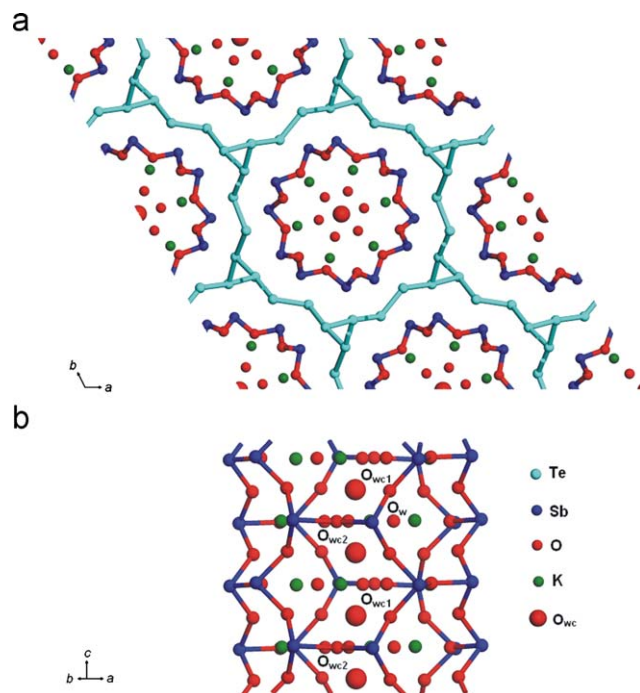

Fig. 1. Structure of K-SBC-1: (a) projection onto the (001) plane; (b) side front view of a {$Sb_{12}O_{18}$} tubular unit, highlighting oxygen atoms that correspond to molecular water. The tellurium 24-ring tubular unit surrounding the {$Sb_{12}O_{18}$} tube has been removed for clarity.

Table 1
Lattice parameters, unit cell volumes, R values ($I > 2\sigma(I)$) and GooF parameters for a single crystal of K-SBC-1 at various conditions.

	$a = b$ (Å)	c (Å)	V (Å³)	R_1	wR_2	GooF
RT	27.412(6)	5.694(2)	3705.3(16)	0.036	0.082	1.010
50 °C	27.428(6)	5.698(2)	3712.6(15)	0.043	0.104	1.035
100 °C	27.434(5)	5.697(1)	3713.4(13)	0.033	0.078	1.033
150 °C	27.501(5)	5.704(2)	3735.7(14)	0.034	0.076	1.032
RT+H_2O	27.390(5)	5.694(2)	3699.6(13)	0.034	0.079	1.045
200 °C	27.556(1)	5.628(4)	3736.6(17)	0.041	0.095	1.033
240 °C	27.540(1)	5.658(4)	3717(3)	0.061	0.133	1.052
RT, after one month	27.582(8)	5.670(2)	3736(2)	0.047	0.086	1.072

Table 2
The refined site occupancy factors and the average number of water molecules per unit cell at various conditions.

	s.o.f. O_w	s.o.f. O_{wc1}	s.o.f. O_{wc2}	O_w (atoms/unit cell)	O_{wc} (atoms/unit cell)	O_{water} total (atoms/unit cell)
RT	1.09(3)	0.051(6)	0.084(11)	18.00	2.4(2)	20.4(2)
50 °C	1.00(4)	0.037(8)	0.047(8)	18.00	1.5(2)	19.5(2)
100 °C	0.98(3)	0.028(6)	0.038(5)	18.00	1.1(1)	19.1(1)
150 °C	1.02(3)	0.041(5)	0.035(5)	18.00	1.3(1)	19.3(1)
RT+H_2O	1.04(2)	0.060(6)	0.029(4)	18.00	1.6(1)	19.6(1)
200 °C	0.73(4)	0.18(1)	0.17(1)	13.1(7)	6.2(2)	19.3(8)
240 °C	0.53(6)	0.26(2)	0.25(2)	10(1)	9.1(5)	19(1)
RT, after 1 month	0.47(4)	0.36(1)	0.35(1)	8.4(3)	12.8(2)	21.2(8)

crystal, thus creating a slower desorption from the crystal studied with single crystal XRD. Additionally, desorption from a relatively large single crystal is expected to be much slower compared to desorption from microcrystalline material employed in the TGA/DSC analysis.

At experimental conditions for which the O_w positions are fully occupied, the unit cell volume evidently correlates with temperature. The crystal expands due to thermal expansion when the temperature is raised from RT to 150 °C, and contracts at lowering the temperature back to RT (see Tables 1 and 2). Desorption and re-adsorption of O_{wc} water molecules may also influence the unit cell volume. Some microporous zeolite-type materials have demonstrated a connection between the unit cell volume and the degree of hydration, where a smaller degree of hydration causes the unit cell to expand [14]. Following the temperature increase to 200 °C the framework expands (see Table 1). The cell volume then decreases when heated to 240 °C. Upon cooling to RT the volume becomes considerably larger than what it was in the original crystal at RT. These observations are consistent with a lattice expansion caused by increased temperature up to 200 °C and desorption of water at the O_w position and relocation to the O_{wc} positions at higher temperatures. Upon cooling, water is re-adsorbed in a larger amount than present in the unheated sample and preferentially at the O_{wc} positions, which provides an explanation for the difference to the original RT measurement.

After one month in ambient environment water is re-adsorbed by the material in an amount that is slightly higher compared to the initial water content. Most interestingly, the occupancy of the oxygen atoms corresponding to loosely bound molecular water increases, whereas the amount of the more strongly bound water remains virtually unchanged from that at 240 °C. This shows that despite losing about 50% of the strongly bound water the crystallinity of the framework of K-SBC-1 remains intact. It further shows that the reversible sorption of water of K-SBC-1 is specific to the loosely bound water located in the centre of the $\{Sb_{12}O_{18}\}$ channels. There appears to be an even distribution of water molecules between the two O_{wc} sites for all of the conditions studied, suggesting that the two O_{wc} sites have similar properties.

The results explain in addition the surprising DRIFT results that water re-adsorbed after heat treatment at 300 °C can be removed by exposure to nitrogen at room temperature [3]. Following a heat treatment to 240 °C roughly 50% of the water present in K-SBC-1 is located in the O_w position and the rest in the centre of the channels at the weaker bound O_{wc} positions. Upon lowering the temperature and exposing the sample to humid air the amount of loosely bound water increases (as observed with DRIFT [3]). This implies that a K-SBC-1 sample activated by heat treatment between 200 and 300 °C will be responsive to changes in composition of the gas it is being exposed to. We hope to perform a study of this topic in the future.

4. Conclusions

The results of this study confirm and explain the previous observations [3] obtained using a combination of infrared techniques, TGA/DSC analysis and powder XRD that demonstrated heat-induced reversible sorption of water in the 1-D channels of K-SBC-1. In addition to the potassium-coordinating water molecules previously known, we have found two additional adsorption sites for water in K-SBC-1, both located at the centre of the $\{Sb_{12}O_{18}\}$ tubular unit and with lower adsorption strength. The less tightly bound water molecules begin to desorb at temperatures around 50 °C, whereas at more elevated temperatures of 200 °C and higher the water molecules that are bound tighter relocate to the centre of the tube and desorb from the structure. At 240 °C, 8% of the total water content in the channels has desorbed, while the framework of K-SBC-1 maintains its integrity. Lowering the temperature enables re-adsorption of water at the weak adsorption sites but apparently not at the strong adsorption sites. These re-adsorbed water molecules can subsequently be readily desorbed by exposure to a flow of dry N_2 at room temperature and ambient pressure. This feature has not previously been found in any semiconducting material to our knowledge and opens new possibilities for applications of microporous semiconductors.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2009.05.028.

Crystallographic information files (CIF) K-SBC-1-RT.cif, K-SBC-1-50C-cif, K-SBC-1-100C.cif, K-SBC-1-150C.cif, K-SBC-1-RT+Water.cif, K-SBC-1-200C.cif, K-SBC-1-240C.cif, K-SBC-1-RTfinal.cif.

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