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

Alexander Shulman [a], Vratislav Langer [b], Anders E.C. Palmqvist [a,*]

[a] Department of Chemical and Biological Engineering, Applied Surface Chemistry, Chalmers University of Technology, 412 96 Göteborg, Sweden
[b] Department of Chemical and Biological Engineering, Environmental Inorganic Chemistry, Chalmers University of Technology, 412 96 Göteborg, Sweden

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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 (Mo*K*α 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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* Corresponding author. Fax: +46 31 160 062.
E-mail addresses: shulman@chalmers.se (A. Shulman), langer@chalmers.se (V. Langer), adde@chalmers.se (A.E. Palmqvist).

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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 3*a* and 3*b*, and with a magnitude of 3.81 and 2.93 e Å^{-3}, respectively. In some of the cetineites the octahedral voids at Wyckoff positions 2*b* 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 3*a* and 3*b* 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].

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 (Å^3)	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

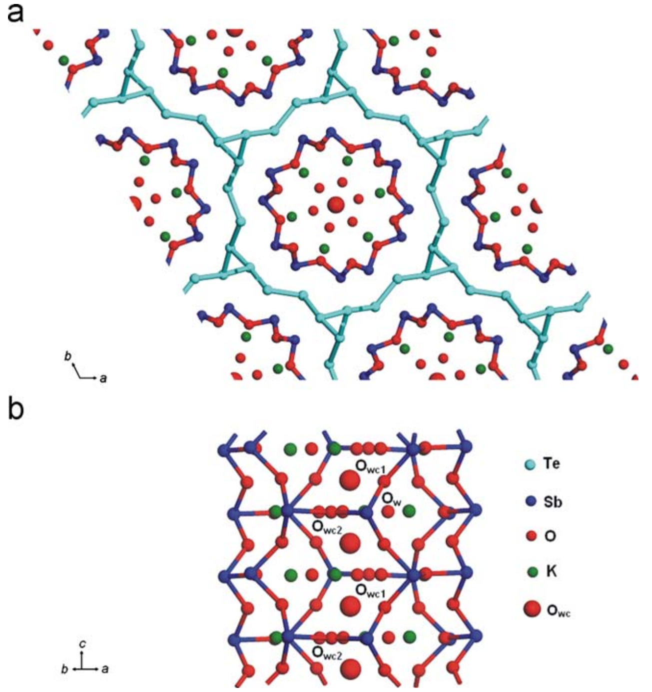

Fig. 1. Structure of K-SBC-1: (a) projection onto the (001) plane; (b) side front view of a $\{Sb_{12}O_{18}\}$ tubular unit, highlighting oxygen atoms that correspond to molecular water. The tellurium 24-ring tubular unit surrounding the $\{Sb_{12}O_{18}\}$ tube has been removed for clarity.

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