A Study of the Hydration and Dehydration of Vanadyl Arsenate by X-ray Diffraction Analysis, Infrared and Raman Spectroscopy

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The course of the intercalation and deintercalation of water molecules in vanadyl arsenate has been studied by X-ray diffraction analysis and by infrared and Raman spectroscopies. The formation of $VOAsO_4$ hydrates at ambient temperature has been found to depend on relative humidity (r.h.): $VOAsO_4 \cdot 5\,H_2O$ (basal spacing $c = 10.48$ Å) is formed at r.h. above 76%, $VOAsO_4 \cdot 3\,H_2O$ ($c = 8.03$ Å) at 43–76% r.h., $VOAsO_4 \cdot 2\,H_2O$ ($c = 7.33$ Å) at 11–43% r.h.; dehydrated $VOAsO_4$ ($c = 4.18$ Å) exists near 0% r.h. Like the thermal dehydration of $VOPO_4 \cdot 2\,H_2O$, the thermal dehydration of $VOAsO_4 \cdot 3\,H_2O$ proceeds in a stepwise manner so that the dihydrate and monohydrate are formed en route to the anhydrous compound. The arsenate monohydrate is gradually dehydrated over a broad temperature range. The broad diffraction lines observed can be explained in terms of the existence of a disordered phase containing monohydrated and anhydrous forms of vanadyl arsenate. A similar phenomenon has been observed during the dehydration of $VOAsO_4 \cdot 3\,H_2O$ over phosphorus pentoxide at ambient temperature. The hydration of $VOAsO_4$ is different from that of $VOPO_4$. The first step, i.e. the insertion of water that coordinates to the vanadium atoms, is very slow. On the contrary, the uptake of further water molecules with the formation of higher hydrates is fast. It thus seems likely that the filling of one interlayer space with water facilitates the intercalation of further water into neighboring interlayer spaces. Therefore, only higher hydrates together with the original anhydrous phase are observed. Impedance spectral measurements indicate that the conductivity of the trihydrate has a mixed ionic/electronic character.

Introduction

Compounds of the general formula $MOXO_4$ (M = V, Nb, Ta; X = P, As) constitute an isomorphic series. X-ray diffraction studies have established the structures of tetragonal forms of $MOPO_4$[1–3] and $MOAsO_4$,[4,5] which consist of chains of corner-sharing MO_6 octahedra running parallel to the *c* axis. In the *xy* plane, each MO_6 octahedron shares corners with four XO_4 tetrahedra, which link the octahedral chains to produce an $(MOXO_4)_\infty$ layer. These layers are linked along the *c* axis by the *trans*-oxygen vertices of the octahedra to form a three-dimensional lattice.

Hydrates of some of these compounds are known and their formation may be rationalized in terms of cleavage of the long M–O bonds of the respective anhydrous forms and subsequent insertion of a water molecule at the sixth coordination site of the metal in the adjacent layer. Another molecule of water, as in $VOPO_4 \cdot 2\,H_2O$, spans two layers, being simultaneously hydrogen-bonded to each. The crystal structure of this hydrate was studied by neutron powder diffraction techniques on $VOPO_4 \cdot 2\,D_2O$.[6] It confirmed the apical position of the oxygen of the first water molecule in the VO_6 octahedron. The second water molecule was found to lie between two PO_4 tetrahedra of two different $(VOPO_4)_\infty$ layers. Due to the disorder of the second water molecule, its position could not be fully determined. Isostructural hydrates of this kind have been reported for $VOPO_4$,[7,8] $VOAsO_4$,[4] $NbOPO_4$,[9] and $NbOAsO_4$.[5] Molecules other than water can also penetrate between the layers of the anhydrous hosts and can even displace water from $MOXO_4$ hydrates.[10,11]

Vanadyl arsenate forms several hydrates.[4] Vanadyl arsenate trihydrate ($a = 6.39$ Å, $c = 8.08$ Å) can be prepared by refluxing vanadium pentoxide in an excess of arsenic acid (H_3AsO_4). It was found by thermogravimetric analysis that one molecule of water is released at 50 °C forming the dihydrate ($a = 6.37$ Å, $c = 7.39$ Å). The monohydrate is formed at 80 °C and complete dehydration occurs at 105 °C resulting in anhydrous $VOAsO_4$ ($a = 6.33$ Å, $c = 4.18$ Å).

In this paper, we report on a study of these $VOAsO_4$ hydrates. The intercalation and deintercalation of water molecules has been studied by X-ray diffraction analysis and by infrared and Raman spectroscopies. The character of the hydrates has been also studied by alternating current (AC) conductivity.

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Results and Discussion

In order to study the formation of various hydrates, $VOAsO_4 \cdot 3\ H_2O$ was kept in an atmosphere of controlled relative humidity (r.h.) at ambient temperature. The dependence of basal spacing and water content on relative humidity is illustrated in Figure 1. Vanadyl arsenate trihydrate was found to be stable in the r.h. range from 43% to 76%. At higher r.h., vanadyl arsenate pentahydrate with a basal spacing of 10.48 Å is formed. Vanadyl arsenate dihydrate is observed in the r.h. range from 11% to 43%. In contrast to vanadyl phosphate dihydrate, $VOAsO_4 \cdot 2\ H_2O$ loses its remaining water molecules when the r.h. is close to 0%.

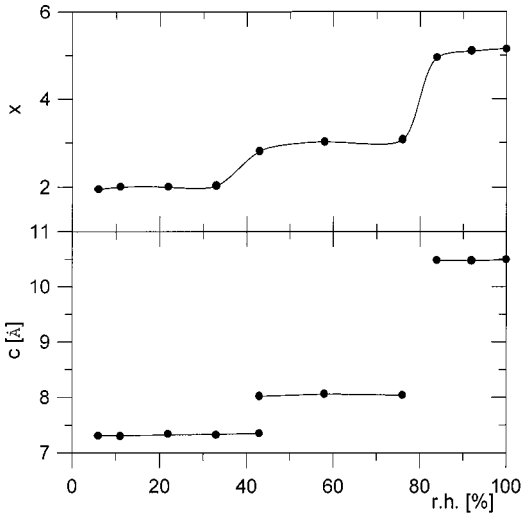

Figure 1. The dependence of the lattice parameter c and water content x of $VOAsO_4 \cdot x\ H_2O$ on relative humidity

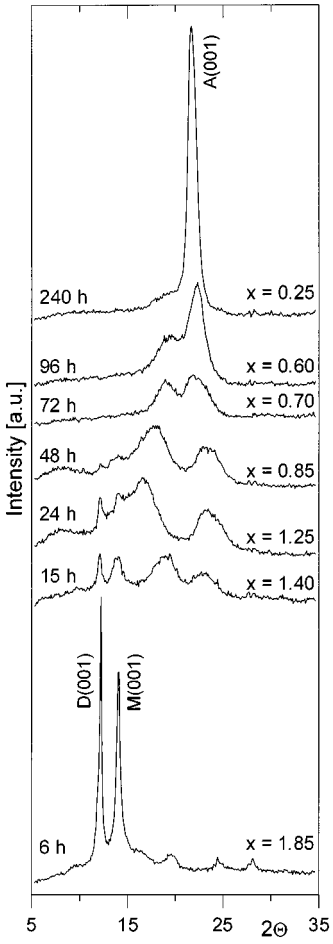

Figure 2. Diffractograms and water content x of $VOAsO_4 \cdot 3\ H_2O$ kept over P_2O_5 as a function of time; the (001) reflections of the dihydrate, monohydrate, and anhydrous compound are denoted as D, M, and A, respectively

The progressive dehydration of $VOAsO_4 \cdot 2\ H_2O$ on storage over phosphorus pentoxide at ambient temperature could be followed by XRD and TG (see Figure 2). After six hours, both the monohydrate and dihydrate were observed. Their (001) diffraction lines were sharp and the water content x became less than two. On continued dehydration, the intensities of these lines decreased, although they remained sharp. In addition, some very broad diffraction lines were seen, the positions and linewidths of which changed during the course of the dehydration. After ten days, the relatively sharp (001) line of anhydrous vanadyl arsenate had appeared. The broadening of the (00l) lines can be explained in terms of a fragmentation of the microcrystals during the dehydration, but the shift in the line positions remains unexplained. The described behavior is similar to that found for a Hendricks–Teller disordered layered lattice,[12] where layers of different types alternate randomly. However, the positions and linewidths calculated from the Hendricks–Teller functions do not correspond to those found experimentally, hence the formation of such a lattice can be excluded. As the diffractogram still shows the line due to the dihydrate after 24 h of dehydration, we presume that there is a random variation of the layers involving dihydrated, monohydrated, and anhydrous $VOAsO_4$.

In situ X-ray diffraction analysis was also employed to follow the dehydration of vanadyl arsenate trihydrate. The sample went through four diffracting phases during heating (see Figure 3). The basal spacings of these phases corresponded to the values found for $VOAsO_4 \cdot 3\ H_2O$ (c = 8.03 Å), $VOAsO_4 \cdot 2\ H_2O$ (c = 7.33 Å), $VOAsO_4 \cdot H_2O$ (c = 6.40 Å), and $VOAsO_4$ (c = 4.18 Å). The transformation of trihydrate to dihydrate was complete at 33 °C. Formation of the monohydrate was found to commence at 51 °C and this species was present up to 57 °C together with the dihydrate. In the temperature range from 63 to 111 °C, only very broad lines were observed. A Hendricks–Teller disordered structure is probably formed in this region. The temperatures of dehydration observed by XRD were lower than those determined by the thermogravimetric method. This difference can be ascribed to the fact that TG measures weight loss caused by evaporation of water released from the interlayer space of the sample.[15]

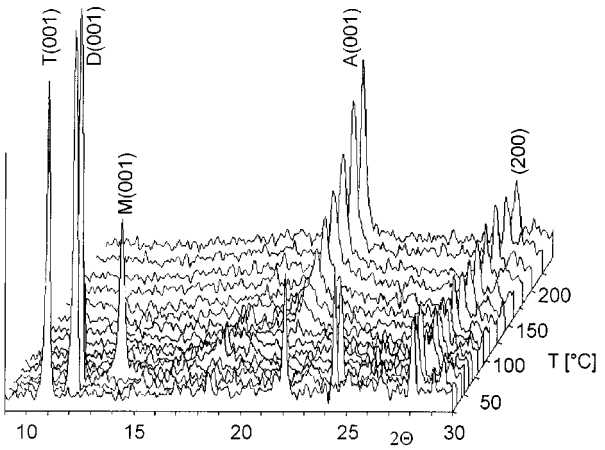

Figure 3. Temperature dependence of the X-ray diffractograms of $VOAsO_4 \cdot 3\ H_2O$

The progressive hydration of anhydrous vanadyl arsenate was studied by XRD at several relative humidities (r.h.). Even at an r.h. as high as 92%, the hydration was found to be very slow in comparison with that of $VOPO_4$.[14,16] After six hours, the intensity of the (001) diffraction line of anhydrous $VOAsO_4$ had decreased to 60% of its original value and the (001) lines of the pentahydrate and dihydrate had appeared. After one day, the intensity of the (001) line of $VOAsO_4$ had decreased to 10% and the prevailing phase was the pentahydrate. After four days, the lines due to anhydrous vanadyl arsenate had disappeared and both the pentahydrate and dihydrate were present. At an r.h. of 76%, the hydration occurred only on the surface of the crystallites of anhydrous $VOAsO_4$. The (001) reflection of the dihydrate appeared at very low intensity after one day and the diffractogram remained the same during a further five days.

Infrared Spectra

The ATR infrared spectrum of anhydrous vanadyl arsenate and the spectra of its dihydrate, trihydrate, and pentahydrate in the range 650 to 2000 cm^{-1} are shown in Figure 4. The observed bands can be fully assigned on the basis of previous studies of the $MOXO_4$ compounds.[17] The spectra have been interpreted in terms of the vibrations of the AsO_4^{3-} tetrahedron by analogy with the fundamental frequencies of the PO_4^{3-} ion in anhydrous $VOPO_4$.[16] The positions of all these bands are shifted to lower wavenumbers due to the mass effect of the As atom compared to P. Table 1 lists the spectra in the terms of the fundamental modes of AsO_4^{3-} ion, the vanadyl V=O vibration, and the O–H stretching and bending modes.

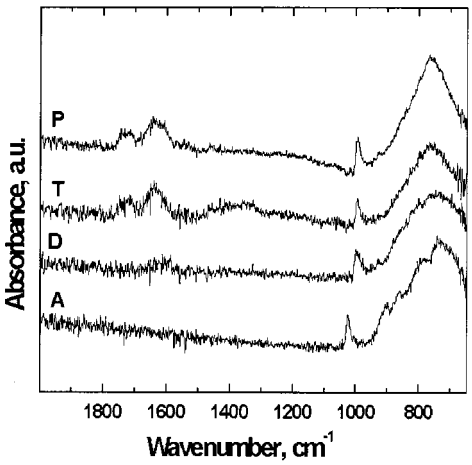

Figure 4. ATR infrared spectra of $VOAsO_4$ (A) and its dihydrate (D), trihydrate (T), and pentahydrate (P)

In the infrared spectrum of anhydrous $VOAsO_4$, the band corresponding to the degenerate antisymmetric $\nu_3(AsO_4^{3-})$ vibration is split into two bands at 905 cm^{-1} and 865 cm^{-1}. The symmetric $\nu_1(AsO_4^{3-})$ vibration at 737 cm^{-1}, which is very strong in the Raman spectrum, also appears in the infrared spectrum provided that the symmetry of the arsenate ion is perturbed from tetrahedral. It is also split in the infrared spectrum, the second band appearing at 793 cm^{-1}. The well-resolved isolated band at 1026 cm^{-1} can reasonably be attributed to the vibration of the vanadyl group V=O.

Vanadyl arsenate trihydrate is stable under ambient conditions. In the infrared spectrum of $VOAsO_4 \cdot 3\ H_2O$, in contrast to that of anhydrous $VOAsO_4$, the two bands due to the degenerate antisymmetric $\nu_3(AsO_4^{3-})$ vibration at 905 and 865 cm^{-1} are not distinguishable. They overlap with the bands of the symmetric $\nu_1(AsO_4^{3-})$ vibration in a broad maximum centred at about 740 cm^{-1}. This can be explained by the fact that there is no longer any internal stress causing

Table 1. Assignments of the observed vibration bands of $VOAsO_4$, $VOAsO_4 \cdot 2\ H_2O$, $VOAsO_4 \cdot 3\ H_2O$, and $VOAsO_4 \cdot 5\ H_2O$

Vibration	V=O	$\nu_3(AsO_4)$ + H_2O vibn.	$\nu_1(AsO_4)$ + H_2O vibn.	$\nu_2(H_2O)$ (C=O)	$\nu_1(H_2O)$	$\nu_3(H_2O)$
$VOAsO_4$	1026 cm^{-1}	905 cm^{-1} 865 cm^{-1}	793 cm^{-1} 737 cm^{-1}	not present	not present	not present
$VOAsO_4 \cdot 2\ H_2O$	1026 cm^{-1} 998 cm^{-1}	n[a]	740 cm^{-1}	1640 cm^{-1}	3500 cm^{-1}	
$VOAsO_4 \cdot 3\ H_2O$	1026 cm^{-1} 998 cm^{-1}	n[a]	740 cm^{-1}	1640 cm^{-1} (1728 cm^{-1})	3400 cm^{-1}	3580 cm^{-1}
$VOAsO_4 \cdot 5\ H_2O$	1026 cm^{-1} 997 cm^{-1}	n[a]	740 cm^{-1}	1635 cm^{-1} (1736 cm^{-1})	3400 cm^{-1}	3600 cm^{-1}

[a] Bands are overlapped or merged with the ν_1 band and cannot be distinguished.

deformation of the AsO_4^{3-} tetrahedron that leads to IR activity of this symmetric vibration. Moreover, these bands also overlap with vibration bands of H_2O molecules, which are usually observed at around 800 cm^{-1}.[16] The vanadyl group vibration band is shifted to 998 cm^{-1} in all hydrates of vanadyl arsenate. As in $VOPO_4$, this effect is caused by the coordination of a water molecule to the vanadium atom, which influences the stretching vibration of the V=O double bond. A band due to the As–O–V lattice vibrations is probably present below 400 cm^{-1}. Besides the position of the vanadyl group absorption, the spectra of all the hydrates differ from that of anhydrous vanadyl arsenate in that H_2O vibration bands are of course present. The deformation vibration of the O–H group is seen at 1640 cm^{-1}. A broad asymmetric band is observed in the region of the valence vibration of the O–H group at 3400 cm^{-1}, together with a maximum at 3580 cm^{-1} (see Table 1). The IR spectrum of the pentahydrate $VOAsO_4 \cdot 5\ H_2O$ is practically identical to that of the trihydrate $VOAsO_4 \cdot 3\ H_2O$. The spectra of these two compounds differ from that of the dihydrate in the presence of a band at about 1728 cm^{-1}, which corresponds to a small degree of contamination by the carbonyl group C=O.

Water molecules penetrated into the sample when pure, completely characterized samples of anhydrous vanadyl arsenate were briefly exposed to atmospheric moisture. The ATR infrared spectra of anhydrous $VOAsO_4$ and its progressive intercalates with water molecules under ambient conditions in the range 650 to 1150 cm^{-1} are presented in Figure 5.

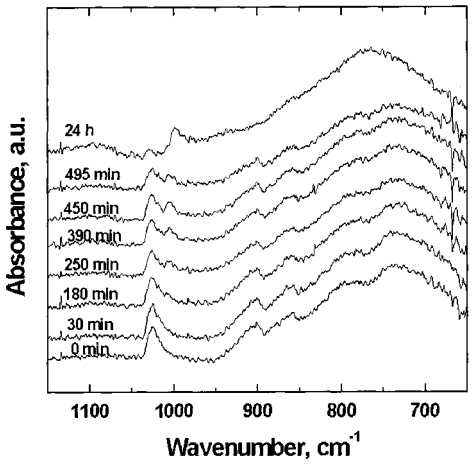

Figure 5. ATR infrared spectrum of anhydrous $VOAsO_4$ and its progressive intercalates with water molecules under ambient conditions

Analysis of these spectra led to the following conclusions:

(i) During the intercalation of water molecules, the intensity of the band at 1026 cm^{-1} due to the vanadyl V=O stretching vibration in the anhydrous form decreases, while a new band appears at 998 cm^{-1}, characteristic of the dihydrate, trihydrate, or pentahydrate.

(ii) Bands due to the symmetric stretching vibration $\nu_1(AsO_4^{3-})$ and the degenerate antisymmetric stretching vibration $\nu_3(AsO_4^{3-})$ change their profile upon hydration and become overlapped with H_2O vibration modes.

(iii) Bands due to deformation and stretching vibrations of water molecules appear at about 1640 cm^{-1} and 3400 cm^{-1} upon hydration.

(iv) The spectrum after 24 hours (Figure 5) is very similar to that of vanadyl arsenate trihydrate (or pentahydrate).

The fact that vanadyl stretching bands are present in both of the aforementioned positions in the initial stages of the intercalation indicates the simultaneous presence of anhydrous and hydrated forms. The changes in the profile of the $\nu_3(AsO_4)$ vibration bands indicate that the system of hydrogen bonds between water molecules and the oxygen of the AsO_4 tetrahedron affects its stretching and bending modes, as was observed for the hydrates of $VOPO_4$.[16]

Raman Spectroscopy

The Raman spectra strongly support the assignments of the bands observed in the infrared spectra of all the studied compounds. Unfortunately, it was not possible to study the kinetics of the hydration process by Raman spectroscopy since the laser irradiation caused a partial escape of water molecules during the measurements. The spectra corresponding to the different hydrated states of the samples between the anhydrous and hydrated forms (spectra 1, 2, and 3 in Figure 6) were obtained by regulation of the incident beam power and of the number of scans.

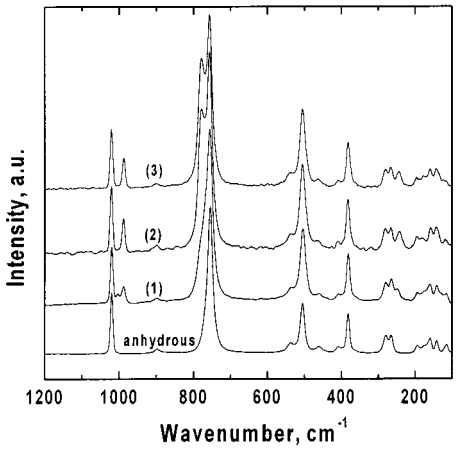

Figure 6. Raman spectra of $VOAsO_4$ and its intermediate hydrate states

The Raman spectrum of anhydrous $VOAsO_4$ (measured in a sealed ampoule) in the range 100 to 1200 cm^{-1} is shown in Figure 6. A strong symmetric $\nu_1(AsO_4^{3-})$ vibration is observed only at 756 cm^{-1}. A very small band due to the degenerate antisymmetric $\nu_3(AsO_4^{3-})$ vibration is observed only at 899 cm^{-1}. The position of the well-resolved isolated band at 1020 cm^{-1} corresponds to the vibration of the vanadyl group V=O in anhydrous vanadyl arsenate. In addition to these features, bands due to symmetric bending vibrations $\nu_4(AsO_4^{3-})$ at 535 cm^{-1} and 506 cm^{-1} and antisymmetric bending vibrations $\nu_2(AsO_4^{3-})$ at 408 and 382 cm^{-1} are also observed in the Raman spectra. The bands at about

270 cm^{-1} can probably be attributed to δ(O–As–O) deformation vibrations.

The effect of water on the spectra of vanadyl arsenate can thus be summarized as follows (see also Figure 6):

(i) In addition to the well-resolved isolated band at 1020 cm^{-1}, attributed to the vibration of the vanadyl group V=O in the anhydrous form of $VOAsO_4$, another peak at 989 cm^{-1} is observed in the Raman spectra of the hydrated forms of $VOAsO_4$.

(ii) A strong symmetric $\nu_1(AsO_4^{3-})$ vibration at 756 cm^{-1} with a strong overlapping shoulder at 780 cm^{-1} is observed.

(iii) A band due to the degenerate antisymmetric $\nu_3(AsO_4^{3-})$ vibration is observed at 899 cm^{-1} and a small shoulder is seen at 920 cm^{-1} in accordance with the infrared results.

AC Conductivity

In order to compare the electrical properties of $VOAsO_4$ with those of the previously studied $VOPO_4$,[20] its AC conductivity was determined by impedance spectroscopy. The impedance data show an arc-shaped dependence of the imaginary versus the real component, which passes through the origin in the complex impedance plot. A resistance connected in parallel with a constant phase element (CPE) was chosen as an equivalent circuit.[18] The dependence of impedance Z (where $Z = Z' - jZ''$) on frequency f for this circuit is given by Equation 1.

$$Z = \frac{R}{1 + \left(j\omega\tau_0\right)^{1-\alpha}} \quad (1)$$

Here, $\omega = 2\pi f$ is the angular frequency, R is the resistance, τ_0 is the relaxation time, and α is a parameter describing a distribution of relaxation times in frequency space. Parameters R, τ_0, and α were estimated from the experimental values by a complex nonlinear least-squares fitting.[19] The conductivity σ_m was then calculated from the estimated resistance R and the dimensions of the sample. The AC impedance curve measured at room temperature and 58% relative humidity was similar to that found for $VOPO_4 2H_2O$[20] indicating similar conductivity behavior. Indeed, the conductivities of $VOPO_4 \cdot 2\,H_2O$ and $VOAsO_4 \cdot 3\,H_2O$ are roughly the same, $\sigma_m = 1.3 \cdot 10^{-5}$ S cm^{-1}. These facts suggest that the electrical properties of $VOXO_4$ materials are not influenced by the atom X. According to these preliminary measurements, the M atom in $MOXO_4$ plays a more important role in the conductivity mechanisms. A more detailed study of the conductivities of these materials is currently underway.

Experimental Section

Materials: Vanadyl arsenate trihydrate was prepared by prolonged boiling of a mixture of vanadium pentoxide and arsenic acid (H_3AsO_4) in water[4] and was stored over a saturated aq. solution of NaBr (r.h. 58%). The samples of $VOAsO_4 \cdot 2\,H_2O$ and $VOAsO_4 \cdot 5\,H_2O$ for IR measurements were obtained by prolonged storage of the trihydrate over saturated solutions of LiCl (r.h. 11%) and KNO_3 (r.h. 92%), respectively. Anhydrous $VOAsO_4$ was prepared by dehydration of the trihydrate at about 300 °C in vacuo for 4 h. The water contents of samples were determined thermogravimetrically. The TG analyses were performed using a Derivatograph C (MOM, Budapest, Hungary). The measurements were performed in air between 20 and 500 °C at a heating rate of 5 K min^{-1}.

X-ray Diffraction: Powder data were obtained with an HZG-4 X-ray diffractometer (Freiberger Präzisionsmechanik, Germany) using Cu-K_α radiation with elimination of Cu-K_β radiation by means of an Ni filter. Diffraction angles were measured in the 2θ range 5–50°. Variable-temperature measurements in the range 20–250 °C were carried out on a thermocouple-controlled heated corundum plate.[21]

Infrared Spectroscopy: IR measurements were made with a Nicolet Impact 400 Fourier transform infrared (FTIR) spectrophotometer in an H_2O-purged environment. An ambient-temperature deuterated triglycine sulfate (DTGS) detector was used for the range from 400 to 4000 cm^{-1}. A Happ–Genzel apodization function was used in all regions and the spectral resolution was 2 cm^{-1}. Approximately 300 scans were accumulated to achieve the signal-to-noise ratio shown. The Baseline Horizontal Attenuated Total Reflection (ATR) accessory with a ZnSe crystal (n = 2.4 at 1000 cm^{-1}) was used in measuring the infrared spectra of the samples. The effective pathlength was approximately a few μm (incident angle 60°, number of reflections 7). The ATR correction was made to eliminate the dependence of the effective pathlength on the wavelength. After some trials, it was found that the best results were obtained when the sample was exposed to the external conditions for a definite time without being removed from the crystal between the subsequent spectral measurements. In this way, the water molecules are deposited on the surface of the ZnSe crystal from the volume and the adsorption of water onto the surface of the sample under investigation is avoided. The vibrational spectrum of each compound was recorded five times using five different samples of the same material. No variation of the studied spectral features was observed between the samples.

Raman Spectroscopy: FT Raman spectra were recorded using an Equinox 55/S Fourier-transform near-infrared (FT-NIR) spectrometer (Bruker) equipped with an FT Raman module FRA 106/S (Bruker). The samples were irradiated with a focused laser beam with a power of 100 mW (Nd-YAG laser, 1064 nm, coherent). The scattered light was collected in a back-scattering geometry. A quartz beamsplitter and a Ge detector (liquid N_2 cooled) were used to obtain interferograms. 128 interferograms were accumulated and subsequently Fourier-transformed using Blackman–Harris 4-term apodization and a zero-filling factor of 8 to obtain final FT Raman spectra in the range 4000–1000 cm^{-1} with 4 cm^{-1} resolution. The FT Raman spectra of pure, well-defined species ($VOAsO_4$, $VOAsO_4 \cdot 3\,H_2O$, $VOAsO_4 \cdot 5\,H_2O$) were recorded from samples in sealed glass ampoules. The ampoules were placed in the sample holder and aligned by the motorized x-y-z sample stage to achieve the optimal optical conditions for sample irradiation and the collection of the scattered light. The FT Raman spectra collected during the intercalation of water were obtained from samples placed in an aluminium cup. The aluminium cup was optically pre-aligned using sulfur as a sample and then the sulfur was replaced by the sample under investigation.

AC Conductivity: Rectangular pellets of dimensions 8 × 3 × 2 mm were prepared by compressing 15 mg of the sample at 2.5 MPa. As

a result of the applied pressure, the layers were preferentially oriented in a plane perpendicular to the direction of the pressure. The opposite sides of the pellets were coated with graphite paste, which served as electrodes, and the AC conductivity was measured along the layers. A Tesla BM 653 impedance meter working in the frequency range 20 Hz to 500 kHz was used for the measurements.

Acknowledgments

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