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Investigation of copper sulfate pentahydrate dehydration by terahertz time-domain spectroscopy*

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Copper sulfate pentahydrate is investigated by terahertz time-domain spectroscopy. It is shown that the terahertz absorption coefficients are correlated with the particle size of the samples, as well as the heating rates of the ambient temperature. Furthermore, the water molecules of copper sulfate pentahydrate can be quantitatively characterized due to the high sensitivity of the terahertz wave to water molecules. Based on such results, the status of water incorporated in mineral opal is also characterized using terahertz time-domain spectroscopy. It indicates that terahertz technology can be considered as an efficient method to detect the dehydration of minerals.

Keywords: copper sulfate pentahydrate, water status, terahertz time-domain spectroscopy

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1. Introduction

Copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), which is commonly well-known as chalcanthite or blue vitriol, is a naturally occurring or synthetic crystal of sulfate mineral. The chemical formula of $CuSO_4{\cdot}5H_2O$ with five water molecules indicates that there is a rich concentration of hydrogen bonds and hydroxyls in $CuSO_4{\cdot}5H_2O$. The water status will have important impacts on the physical and chemical properties of $CuSO_4{\cdot}5H_2O$.[1–3] These features of $CuSO_4{\cdot}5H_2O$ are similar to nominally anhydrous minerals (NAMs).[4] NAMs, with tens to hundreds of parts per million (ppm) water entering the structure of minerals, have widely raised the interests of scientists for the considerable geological significances.[5] Despite the trace amounts of hydrous component of NAMs, it can possess a disproportionately large influence on the physical and chemical properties of mantle minerals. In particular, water content can affect the elastic properties of pyroxene and garnet,[6] change the thermal structure and rheological properties of minerals,[7] and impact the electrical properties (conductivity and dielectric constant).[8] Thus, the water content and status in hydrous minerals play a key role in the interpretation of the geological environment during the formation of the minerals.

The water content and status of this mineral have been widely investigated by Fourier transform infrared spectrometer (FTIR). Infrared spectra are easily obtained but are still not rigorously self-calibrating.[9] In the last few decades, terahertz technology in the communications, imaging, and spectroscopy area has attracted lots of attention.[10–13] Compared to FTIR, terahertz time-domain spectroscopy (THz-TDS) has a better signal-to-noise ratio (SNR). It can be applied for the optical characterization in a further longwave band.[14–16] Meanwhile, due to the high sensitivity and the strong absorption by the water molecules, terahertz measurement is generally performed in a nitrogen ambient.[17–20] Until now, there have been a few studies carried out based on such water sensitivity. In this paper, the number of water molecules of $CuSO_4{\cdot}5H_2O$ is quantitatively identified using THz-TDS. Meanwhile, based on the studies of copper sulfate pentahydrate, the water content of mineral opal ($SiO_2{\cdot}nH_2O$) is characterized. These results encouragingly show that THz-TDS is an available tool to analyze water content and the status of hydrous minerals. This work is a promising indication to analyze the hydrous minerals by the water content and status.

2. Experiments

$CuSO_4{\cdot}5H_2O$ crystal and opal were crushed into powders. Different particle sizes were determined by different mesh sieves. To get a trihydrate, monohydrate, and anhydrate, the $CuSO_4{\cdot}5H_2O$ powders were heated to 60 °C and 260 °C with a heating rate of 5 °C/min, and heated to 90 °C with heating rates of 5 °C/min, 8 °C/min, and 11 °C/min. While the mineral opal was heated to 120 °C, 300 °C, 600 °C, 900 °C, and 1200 °C, all heating treatments were kept for 30 min to

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complete the phase transition. After the dehydration process, one part of the $CuSO_4{\cdot}5H_2O$ powders was identified by the powder x-ray diffractometer (PXRD) (40 kV) with Cu Kα_1 radiation ($\lambda = 1.5406$ Å) and Cu Kα_2 radiation ($\lambda = 1.5444$ Å). The scanning range of the diffraction angle is $10°$–$70°/2\theta$ with the step size of $0.02°$. The other part of $CuSO_4{\cdot}5H_2O$ and mineral opal powders were pressed into pellets to be measured by THz-TDS.

The THz-TDS experiments were performed with a transmission configuration under room temperature. A single point measurement without moving the target was conducted using the THz-TDS system in the experiment. The instrument was employed to realize the time delay scanning with the step size of 0.005 mm. Totally, 600 points were recorded to obtain the time-domain waveform, controlled by Newport time-delay stage. Further detailed principle of the THz-TDS system has been reported previously.[21] The spectrometer was continuously purged with nitrogen to minimize the absorption from atmospheric water. The reference and the sample signals were then collected.

3. Results and discussions

To explore the effect of the size of the particle constituting the copper sulfate pentahydrate on the absorption, figure 1 displays the time-domain spectra and frequency-domain spectra with different particle sizes. In the case of a specific thickness, the amplitude of the terahertz time-domain spectrum decreases as the particle size increases. The results show that the particle size dominates the increase of absorption coefficients as shown in Fig. 2. In addition, in the frequency range from 0.4 THz to 1.4 THz, the absorption coefficient increases with the frequency increasing due to the scattering effect.

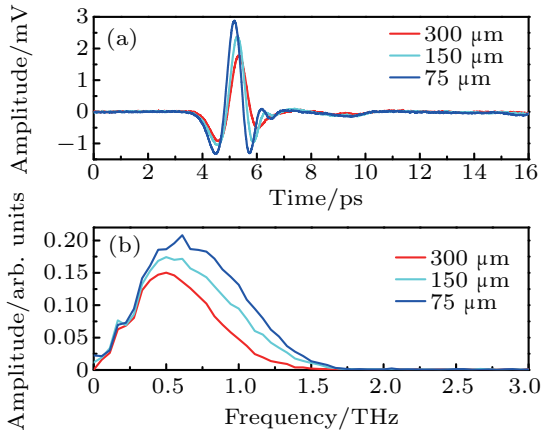


Fig. 1. The (a) time-domain spectra and (b) frequency-domain spectra of $CuSO_4{\cdot}5H_2O$ with different sizes of the particles

The absorption coefficients of samples $A(\omega)$ within different particle sizes consist of two parts: the absorption of the sample itself $Aa(\omega)$ and the scattering absorption $As(\omega)$

$$A(\omega) = Aa(\omega) + As(\omega). \tag{1}$$

Under the same absorption of the sample itself, scattering absorption mainly arises from the particle size of the samples. Generally, the larger the particle size, the more intense the scattering effect. Scattering can be divided into elastic scattering and inelastic scattering.[22] When the terahertz wave is incident on a substance, it will be scattered by atoms or molecules. Most of the photons are elastically scattered. Elastic scattering is divided into Rayleigh scattering and Mie scattering.[23] The one with the particle size much smaller than the incident wavelength is called Rayleigh scattering, while the one with the incident wavelength close to or greater than the particle size is called Mie scattering. Because the detection bands range from 0.1 THz to 3.0 THz (3000 μm–100 μm), the current particle size causes Rayleigh scattering. The Rayleigh scattering formula is as follows:

$$I_s = \frac{8\pi^4\alpha^6}{r^2\lambda^4}\left(\frac{n^2-1}{n^2+2}\right) I_0\left(1+\cos^2\theta\right) \tag{2}$$

where I_s is the scattering light intensity, I_0 is the incident light intensity, λ is the wavelength of incident light, α is the particle size parameter, r is the distance from the scattering particle to the observation point, and n is the refractive index of the medium. The intensity of the scattered light is proportional to the sixth power of the particle size. Scattering effects can cause baseline shifts in the absorption coefficient spectrum, especially at higher frequencies. Therefore, the particle size is supposed to be kept as small as possible to alleviate the scattering effect. In this THz-TDS experiments, the selected particle size of the sample is approximately 75 μm.

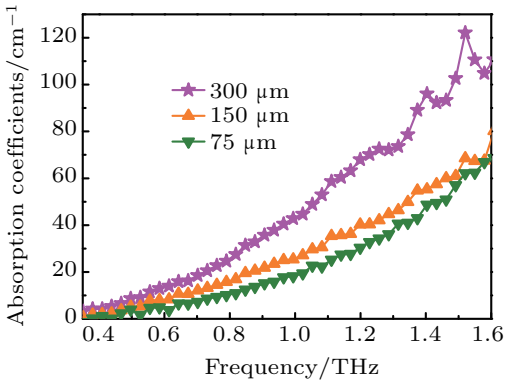


Fig. 2. Frequency-dependent absorption coefficients of $CuSO_4{\cdot}5H_2O$ with different sizes of the particles.

In addition to the size of the particle composed the samples, the effect of the heating rate of the ambient temperature is tested in Fig. 3. The heating rates are 5 °C/min, 8 °C/min, and 11 °C/min, respectively. Figure 3 demonstrates that the

absorption curves of different heating rates are basically the same from 0.4 THz to 0.9 THz. After 0.9 THz, the absorption curves begin to separate at around 1.1 THz. The reason is that the heating rate varies upon the efficiency of dehydration, which results in the differences in the particle size. The separating point of the absorption curve corresponds to the terahertz wavelength that is similar to the particle size. These results are quite related to the scattering effect as mentioned earlier.

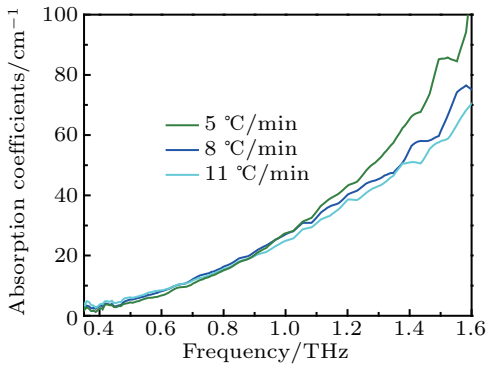


Fig. 3. Frequency-dependent absorption coefficients of $CuSO_4{\cdot}5H_2O$ at different heating rates of the ambient temperature.

Figure 4 shows the XRD patterns of dehydration of copper sulfate pentahydrate at different temperatures. The pattern shows many sharp peaks at room temperature. This can be interpreted by the fact that the copper sulfate pentahydrate forms triclinic single crystals and has the most stable configuration at room temperature. As the temperature rises to 60 °C, two water molecules coordinating with copper ions begin to loss forming $CuSO_4{\cdot}3H_2O$. The crystal structure changes with the loss of crystal water. At 100 °C, the remaining two water molecules coordinating with copper ions are lost. The molecular formula has changed to $CuSO_4{\cdot}H_2O$. The position of the characteristic peak shifts as the strength decreases.[24] The two water molecules that are hydrogen bonded to an external water molecule require higher energy for the dehydration. For the last crystal water molecule coordinating with sulfate ion, it is released at 260 °C to form $CuSO_4$. The intensity of the characteristic peak of 260 °C is the weakest.

The transmission terahertz temporal signals and frequency-domain spectra of $CuSO_4{\cdot}5H_2O$ from 23 °C to 260 °C are shown in Fig. 5. It can be clearly seen from Fig. 5(a) that the amplitudes of transmission terahertz-domain signals at different temperatures are well-resolved. The frequency-domain spectra in Fig. 5(b) are obtained through fast Fourier transform (FFT) of terahertz time-domain spectrums. The amplitudes of the frequency-domain spectra increase upon the dehydration of the crystal water. Various cutoff frequencies of different temperatures represent the confidence interval of the measured data. The cutoff frequency of 23 °C and 60 °C is about 2.2 THz, and at 100 °C and 260 °C, it drops to around 2.6 THz. This phenomenon can be ascribed to the sensitivity of the terahertz wave to water molecules. The content of water molecules has an influence on the signal-to-noise ratio of THz-TDS, which will cause the deviation of the cutoff frequency.

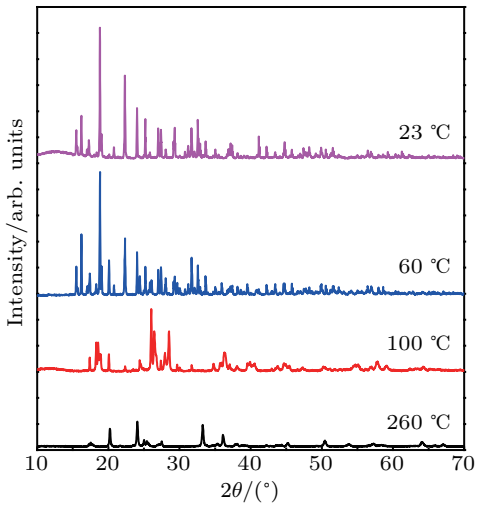


Fig. 4. The XRD patterns of $CuSO_4{\cdot}5H_2O$ at different heating temperatures.

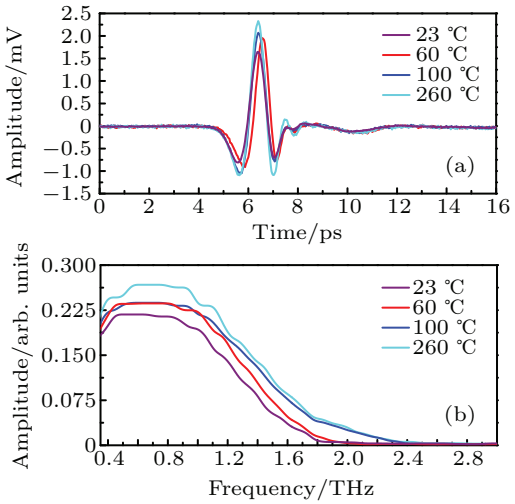


Fig. 5. Diagrams of (a) THz-TDS and (b) THz-FDS of $CuSO_4{\cdot}5H_2O$ heated to different temperatures.

Figure 6 shows the refractive index and absorption coefficient distributions of $CuSO_4{\cdot}5H_2O$ heated to different temperatures at 0.6 THz, 0.8 THz, 1.0 THz, and 1.2 THz, respectively. The optical constants of absorption coefficients and refractive index present the same tendency as the temperature increases. The refractive indexes of different frequencies are basically invariable at the same temperature. The absorption coefficients of the sample under four temperatures increase rapidly towards higher frequencies, especially below 23 °C and 60 °C. This phenomenon illustrates that the water molecules are more sensitive to the higher terahertz frequency. In addition to the intrinsic absorption of $CuSO_4$, the sensitivity of the terahertz wave to water molecules causes the main

absorption. Furthermore, the dehydration of the crystal water at different temperatures will cause a variety of lattice sizes. Thus, vibrations of the lattice are also a part of deviations in the absorption.

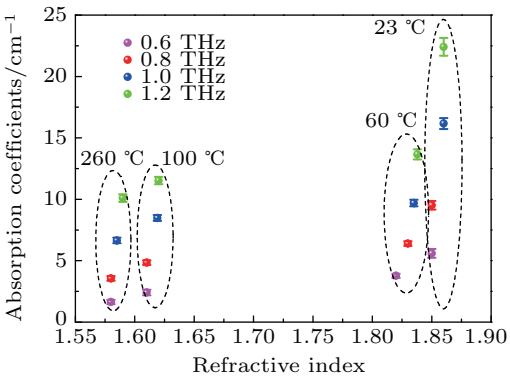


Fig. 6. The refractive index and absorption coefficient distributions of $CuSO_4{\cdot}5H_2O$ samples under different temperatures at 0.6 THz, 0.8 THz, 1.0 THz, and 1.2 THz, respectively.

To further determine the water content and status of the hydrous mineral, a mineral opal is adopted. According to the relationship between water and the crystal structure of its host minerals, water mainly exists in three status, free hydrogen-bonded water, crystal-water, and structural-water. The dehydration temperature is determined by water status. The dehydration temperature is about 120 °C for free hydrogen-bonded water, about 200 °C to 500 °C for crystal-water, and about 600 °C to 1000 °C or even higher for structural-water.[25] In experiments, the temperatures of 120 °C, 300 °C, 600 °C, 900 °C, and 1200 °C are selected. It is shown in Fig. 7 that the absorption curves under different temperatures are distinguishable. The decreasing absorption coefficient indicates that the water content of the opal decreases as the temperature increases. The absorption curve is flattened from 0.2 THz to 1.8 THz and the absorption curve gradually approaches zero. This is due to the mineral opal after losing the water to transform to the SiO_2 phase, which is highly transparent to the terahertz wave.

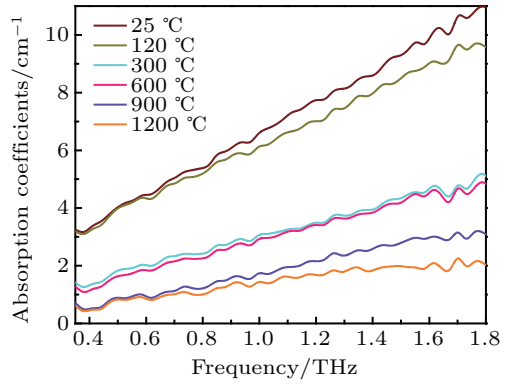


Fig. 7. Frequency-dependent absorption coefficients of mineral opal heated to different temperatures.

4. Conclusions

In summary, this work reports the evidence in support of the theory suggesting that THz-TDS is an effective method to examine $CuSO_4{\cdot}5H_2O$ and mineral opal. On the one hand, for $CuSO_4{\cdot}5H_2O$, the heating rate does not influence the absorption at terahertz frequencies while the particle size mainly decides the terahertz responses. The dehydration of crystal water molecules and the transformation of its hydrates can be identified by THz-TDS. For opal, the clear differences of absorption coefficients at different temperatures can be used to distinguish the water content and status of opal. These experimental results confirm that it is feasible to use THz-TDS to assess the water content and status of hydrous minerals. However, other geoscience technologies are required to further investigate the mineral's characteristics.

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