Characterization of Inclusions in Evolution of Sodium Sulfate Using Terahertz Time-domain Spectroscopy

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The study of fluid inclusion is one of the important means to understanding the evolution of mineral crystals, and can therefore provide original information of mineral evolution. In the process of evolution, outside factors such as temperature and pressure, directly affect the number and size of inclusions, and thus are related to the properties of crystals. In this paper, terahertz time-domain spectroscopy (THz-TDS) was used to detect sodium sulfate crystals with different growth temperatures, and absorption coefficient spectra of the samples were obtained. It is suggested that the evolution of sodium sulfate could be divided into two stages, and 80°C was the turning point. X-ray diffraction (XRD) and polarizing microscopy were used to support this conclusion. The research showed that THz-TDS could characterize the evolution of mineral crystals, and it had a unique advantage in terms of crystal evolution.

Keywords Inclusions, crystal growth, sodium sulfate, THz-TDS

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Introduction

Making an important contribution to the study of the evolution of mineral crystals, research on and applications of fluid inclusions have progressed tremendously over the last three decades.^{1,2} Fluid inclusions are small volumes of ancient fluid trapped in minerals that provide indispensable information about geological processes, from high temperatures at depth towards low temperatures near the Earth's surface.^{3,4} The formation of inclusions is closely related to the mineral crystallization process, which exists throughout all geological processes. Fluid inclusions reveal geologically important information such as temperature, pressure, salinity, density and depth of trapping; and thereby provide direct information about the conditions at which given minerals and rocks are formed. So the study of the inclusions has great significance for clarifying the evolution of crystals.

The study of fluid inclusions has come a long way since their initial description by Sorby (1857). In recent decades, the research of inclusions has made great progress, and many methods have been applied to the study of inclusions, such as homogenization method, burst method and quenching method for measuring temperature;⁵ freezing method for the determination of salinity; laser Raman probes, chromatography, mass spectrometry, ultraviolet fluorescence spectroscopy for the determination of gas and liquid phase composition,⁶⁻⁸ and so on. These methods play an important role in the study of inclusions, and promote the development of research on inclusions.

However, these methods have their shortcomings, for example, invasion to samples, poor accuracy, poor reproducibility. Looking for new methods to study the inclusions is still important.

As a recently arisen spectroscopic method, terahertz time-domain spectroscopy (THz-TDS) uses terahertz waves that range from 0.1 to 10 THz, and bridges the gap between infrared and microwave as a light source.⁹ Terahertz waves can penetrate many nonpolar materials, but they do not damage the sample because of the lower photon energy.¹⁰ In addition, the waves can induce low frequency bond vibrations, crystal phonon vibration, hydrogen-bonding stretches, and torsion vibrations in materials.¹¹ In recent decades, because of these unique properties, THz-TDS has attracted more attention and has been employed in various fields, such as biochemistry, safety, medicine quality control, food, petroleum and geological evolution.¹²⁻¹⁶

In this paper, THz-TDS was applied to measure sodium sulfate crystals with different growth temperatures. The change of fluid inclusion and its influence on the evolution of sodium sulfate were characterized by terahertz optical parameters, which was verified by XRD and polarizing microscopy. This paper indicated that THz-TDS could be used to characterize the fluid inclusions in the crystal growth process and provided a new method to characterize crystal evolution.

Experimental

Crystals of Na₂SO₄ were grown by evaporation crystallization. First, a saturated solution of Na₂SO₄ was prepared at room temperature. After filtering, it was placed in the drying oven

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Fig. 1 Terahertz three-dimensional time-domain spectrum of samples.

that had been set to a temperature. Waiting for the solution to dry, sodium sulfate crystals were obtained. In order to get different samples, evaporation temperature was set at 20 to 150°C at temperature intervals of 10°C. In order to eliminate the effect of the particle size, obtained crystals were ground and shifted, which made particle size within 120 μm . Secondly, samples were made by tableting with 25 MPa pressure for 2 min. This operation did not destroy the structure of the crystal so that it had no effect on the inclusions. Each sample weighed 2 g, and had an average thickness of 1.352 mm. Finally, the samples were detected by THz-TDS.

In THz-TDS system, terahertz wave was produced by a femtosecond laser triggered photoconductive antenna. Femtosecond laser with center wavelength of 800 nm, repetition frequency of 80 MHz, and pulse width of 100 fs was produced by titanium sapphire femtosecond mode-locked pulse laser. Laser pulse could be divided into two beams by a beam splitter, a beam as a pump, to motivate GaAs photoconductive antenna generate THz pulse, and the other as a probe light, to measure THz signal by detector. Finally, THz signal was gathered by phase-locked amplifier controlled by the chopper, and transmitted to the computer for processing. In order to reduce the absorption of water vapor in the air to the THz wave, dry air was used in the terahertz optical path, with humidity of less 1% and temperature of 298 K. The dry air in the system was measured by THz-TDS, and the results were taken as reference spectra. The absorption coefficient spectra were calculated automatically according to the samples and the reference spectra by the system.

Results and Discussion

Growth conditions, such as temperature, pressure, humidity and so on, play a critical role for crystal growth, and are a major cause of different results in crystal growth. This experiment mainly studied the effect of temperature on crystal growth in the temperature range of 20–150°C. Sodium sulfate crystals obtained by evaporating saturated solution at different temperatures were measured by the THz-TDS system to obtain the terahertz time-domain spectra of samples. Figure 1 shows the three-dimensional time-domain waveforms of samples.

Fig. 2 The relationship curve between the square of the THz e-field (P_s) and growth temperatures.

Fig. 3 Absorbance coefficients of samples grown in temperatures of 20, 50, 80, 120 and 150°C.

As shown in Fig. 1, there are different terahertz time-domain spectra of sodium sulfate crystals with different temperatures, especially the curve peak. The change of the peak value can be clearly seen from the figure. In order to show the phenomenon more clearly, we plotted a graph between square of the THz e-field (P_s) and growth temperatures, as shown in Fig. 2. When the temperature rises from 20 to 80°C, P_s decreases linearly from 0.0091 to 0.0004 V^2 . However, the change of P_s is various when the temperature continues to rise. As the temperature changes from 80 to 150°C, P_s linearly increases from 0.0004 to 0.0084 V^2 . The change can be divided into two parts, and 80°C is noted as a turning point.

The energy loss of the THz waves has a one-to-one correspondence with the absorption coefficient. Figure 3 shows a sample's absorption coefficient spectra within 0.2–1.0 THz. There are absorption coefficient curves at growth temperatures of 20, 50, 80, 120 and 150°C, respectively. The absorption coefficients increase with the increase of frequency. In addition, samples with different growth temperatures have disparate absorption coefficients. When the growth temperature is increased from 20 to 80°C, the absorption coefficients increase with grown a rise in temperature. On the contrary, absorption coefficients begin to decline when the growth temperature is

greater than 80°C.

To exhibit more clearly, Fig. 4 shows discontinuous absorption coefficients at 0.4, 0.5, 0.6, 0.7 and 0.8 THz, is used to indicate these objective law. At the same growth temperature, the higher the frequency, the greater the absorption coefficients, which can be seen in Fig. 4. Within the temperature range of 20 – 80°C, absorption coefficients increase when the growth temperature increases. But when the temperature is greater than 80°C, it is just the opposite, absorption coefficients decrease with the increase of temperature, which is anastomotic with the P_s . However, there is a special case that the absorption coefficient has reached the maximum at 70°C rather than at 80°C at 0.8 THz. The reason for this phenomenon may be the error, and it also may be because the temperature is not divided carefully enough, leading to deviation of the extremum.

In Fig. 5, the X-ray diffractometer is used in order to explore the causes of this phenomenon, whose scanned range is from 5 to 90 degrees. Five samples whose growth temperatures are respectively 20, 50, 80, 120 and 150°C are selected to draw XRD profiles, and XRD curves are positioned perpendicularly

in order to show a clear comparison. The result is that XRD peaks of samples are identical to the characteristic peaks of pure sodium sulfate, which shows that there is no crystal water inside sodium sulfate crystals. In other words, samples are Na_2SO_4 instead of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, and the above phenomenon is not caused by crystal water.

The cause of this phenomenon may be fluid inclusions inside crystals. Microscope photos of inclusions inside sodium sulfate crystals are as shown in Fig. 6. Most of inclusions are gas-liquid inclusions. The number and size of them are disparate because of the different growth temperatures, but the size of them is within 50 μm . The number of inclusions is less when the growth temperature is below 80°C, but when the growth temperature is higher than 80°C, it becomes more and more. This is due to growth temperature. As growth temperature increases, the crystallization rate becomes faster, and the possibility of crystal defect increases. So the number of inclusions becomes more and more. According to microscope photos, the number of inclusions' pixels is divided by the total number of pixels to get the proportion of the inclusions' area. It was measured in order to show more accurately differences of inclusions, and the result is shown in the following Table 1.

Fig. 4 Absorbance coefficients of samples with different growth temperature in 0.4, 0.5, 0.6, 0.7 and 0.8 THz.

Fig. 5 X-ray diffraction patterns of samples with different growth temperatures.

Fig. 6 Microscope photos of fluid inclusions inside samples.

Table 1 The proportion of inclusions' areas inside samples

Growth temperature/°C	The proportion of inclusions' areas, %
40	0.355
50	0.582
60	0.281
70	1.286
80	1.970
90	2.671
100	3.449
110	4.490
120	1.532
130	2.555
140	13.787

Table 2 Weights of samples before and after drying for 24 h in 300°C

Growth $\pm$ temperature/ °C	Before/g	After/g	Change/g
20	1.0112 $\pm$ 0.0001	1.0109 $\pm$ 0.0001	0.0003 $\pm$ 0.0002
30	1.0016 $\pm$ 0.0001	1.0011 $\pm$ 0.0001	0.0005 $\pm$ 0.0002
40	1.0139 $\pm$ 0.0001	1.0112 $\pm$ 0.0001	0.0027 $\pm$ 0.0002
50	1.0041 $\pm$ 0.0001	1.0018 $\pm$ 0.0001	0.0023 $\pm$ 0.0002
60	1.0262 $\pm$ 0.0001	1.0236 $\pm$ 0.0001	0.0026 $\pm$ 0.0002
70	1.0121 $\pm$ 0.0001	1.0098 $\pm$ 0.0001	0.0023 $\pm$ 0.0002
80	1.0116 $\pm$ 0.0001	1.0101 $\pm$ 0.0001	0.0015 $\pm$ 0.0002
90	1.0204 $\pm$ 0.0001	1.0190 $\pm$ 0.0001	0.0014 $\pm$ 0.0002
100	1.0096 $\pm$ 0.0001	1.0083 $\pm$ 0.0001	0.0013 $\pm$ 0.0002
110	1.0195 $\pm$ 0.0001	1.0182 $\pm$ 0.0001	0.0013 $\pm$ 0.0002
120	0.9944 $\pm$ 0.0001	0.9929 $\pm$ 0.0001	0.0015 $\pm$ 0.0002
130	0.9837 $\pm$ 0.0001	0.9821 $\pm$ 0.0001	0.0016 $\pm$ 0.0002
140	1.0144 $\pm$ 0.0001	1.0124 $\pm$ 0.0001	0.0020 $\pm$ 0.0002
150	0.9884 $\pm$ 0.0001	0.9861 $\pm$ 0.0001	0.0023 $\pm$ 0.0002

It can be seen that proportions of inclusions' area are mainly increased with the increase of growth temperature. When the growth temperature is below 80°C, the proportions of inclusions' area are minor, but when the growth temperature is higher than 80°C, they become more. So the growth temperature of the crystal has a great influence on inclusions.

Fluid inclusions contain water, and water has a strong absorption for terahertz waves. In order to measure the quantity of water in inclusions, 1 g was extracted from every sample and dried for 24 h in the drying oven whose temperature was set at 300°C, which ensured that inclusions were completely broken and water inside them was completely evaporated. Electronic balance was used to weigh the samples after drying, and the results are shown in Table 2. The quantity of water inside inclusions increased with the rise of growth temperature when the growth temperature was below 80°C. But at temperatures higher than 80°C, the quantity of water basically remained unchanged, which also indicated the content of the gas inside inclusions grew.

In summary, the number and size of inclusions were small when the growth temperature was below 80°C, and the quantity of water inside inclusions increased with the rise of growth temperature. So absorption coefficients of samples had an increasing trend because of the absorption of water for terahertz. On the contrary, with growth temperatures above 80°C, the number of inclusions inside samples multiplied, and the

proportions of inclusions' area were greater. But the quantity of water inside inclusions basically remained unchanged, which indicated the content of the gas grew with the increase of growth temperatures. When samples were irradiated by THz wave, the path that terahertz wave went through the gas gets longer. Therefore, the absorption coefficient showed a trend of decline. This study showed that growth temperature had a larger influence on crystal growth, especially inclusions, and it also illustrated that THz-TDS could accurately and rapidly detect the change of the inclusions inside crystals.

Conclusions

Fluid inclusion is one of the important parameters for studying the evolution process of mineral crystal. In this paper, THz-TDS was used to study sodium sulfate crystals with different growth temperatures. The results showed that terahertz absorption coefficients of sodium sulfate crystals exhibit the tendency of increasing first and then decrease with the increase of growth temperature, and the turning point was 80°C, which was closely related with fluid inclusions inside sodium sulfate crystals. It also showed that terahertz had a unique advantage in studying crystal growth and geological diagenetic and metallogenic evolution, and it will thus likely see greater applications in this area.

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