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„ >- U*T VB— ¥ " uA] ¬ [(THz-TDS) % ØF¤J8 ¸!` 4'• ¢ • ö ¢ ]!` Ô Ç ’E =x ò-š 3@Ü ì"w ÊO¸3ÿ È=” : U• Ð#U 7 ØF¤J8 ¸!` 4'• 5 2 V : j+° d b U• , V g T 1.91 THzU• , V M T 1.77 THz K»,I#U Ò sP U• ØF¤J8 ¸!` 4'• d b g f Ò 9 Ù û = U•, 7 "´] e š ØF¤J8 ¸!` 4'• T 1.91 THz 0+°'¥ - d b LŽ/ T 9 8#U Ò 9 8 Ì& "K +° B Ÿ2' U• U*TKk R h x Û å/7 Ã \ ØF¤J8 ¸!` 4'•D˜ < !` 4'•+°&? f 381.13 J/g(232.6 kJ/mol)U• : L4 .f — ûFû& " (DSC),$! "wFûA f 4.2% E Ç3ÿ È=” : U•THz-TDS ü Ç ,.ù EK 5 t+°3ÿ ¢!` 4'•&? ì"w å"

ŸJZ@ù VB— ¥ uA]Už ØF¤J8 ¸!` 4'• Už]!` Ô Ç ’ Užd b Už&?

Y * 21§ # O657.61 ³(Z 3 -- A **doi** 10.11805/TKYDA2022205

Terahertz spectroscopy detection of zinc citrate dihydrate and its dehydration kinetics

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Abstract Terahertz Time Domain Spectroscopy(THz-TDS) is employed to detect the Zinc Citrate (ZC) dihydrate and its dehydration kinetics. Results show that there are two prominent absorption peaks: one at 1.91 THz, the other at 1.77 THz for the ZC dihydrate, while there is no featuring absorption peak for ZC anhydrate at room temperature. When the temperature increases, the absorption peak of ZC dihydrate at 1.91 THz decreases and gradually disappears. According to the variation of the absorption peak area of ZC dihydrate at 1.91 THz under different temperatures and heating time, the enthalpy change of ZC dihydrate transforming to anhydrate is 381.13 J/g(232.6 kJ/mol) by using the Arrhenius equation, and the error is 4.2% compared with the traditional Differential Scanning Calorimetry(DSC) measurement. These results indicate that THz-TDS can be used as an efficient and fast technique for the detection of ZC dihydrate and its dehydration kinetics.

Keywords Terahertz spectroscopyUžZinc Citrate dihydrateUždehydration kineticsUžabsorption peakUženthalpy change

[1]

[2]

[3]

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[4]

(dihydrate) 334 ℃ (
) (anhydrate)

[5] - [6] [7] [8-9] X-
[10-11]

-

X-

(THz) (Far Infrared FIR) 0.1~10 THz

[12-13]

[14] [15]

(THz-TDS)

(DSC)

1 ÊO¸@ê 3 ö c í b 3

1.1 THz-TDS 2'4

(Advantest TAS7500SU) 0.5~7.0 THz
2 2
1
132 ps
7.6 GHz 200 ms (TAS1030)
300 ℃ 1.0 ℃

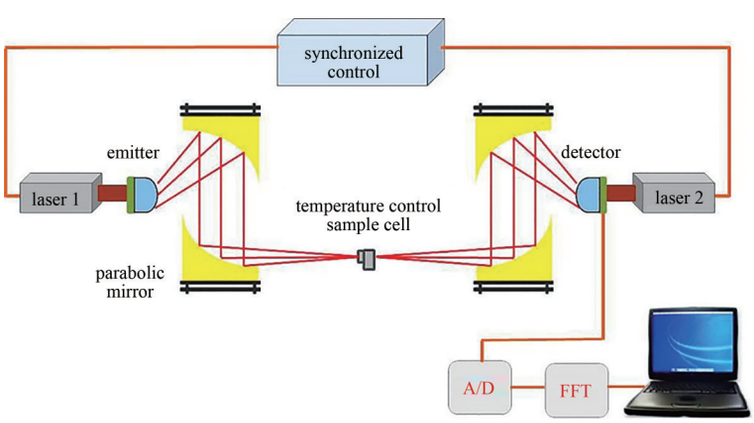


Fig.1 Schematic diagram of the Terahertz spectrometer
1

$E_{ref}(t)$

$\tilde{E}_{sam}(t)$ $\tilde{E}_{ref}(\omega)$

$\tilde{E}_{sam}(\omega)$ $n(\omega)$ $\alpha(\omega)$

$$n(\omega)=\varphi(\omega)\frac{c}{\omega d}+1 \tag{1}$$

$$\alpha(\omega)=\frac{2\kappa(\omega)\omega}{c}=\frac{2}{d}\ln\left[\frac{4n(\omega)}{\rho(\omega)\ (n(\omega)+1)^2}\right] \tag{2}$$

d c $\varphi(\omega)$ $\kappa(\omega)$ $\rho(\omega)$ $\tilde{E}_{\mathrm{sam}}(\omega)$ $\tilde{E}_{\mathrm{ref}}(\omega)$

1.2 c í b 3

≥98% aladdin( ) Macklin( )

80 mg

( ) 10 MPa 13 mm 0.55 mm

5%

2 3ÿ È :@Ô@æ

2.1 ØF¤J8 ¸!` 4'• ¸ !` 4'•+° VB— ¥ uA]

XRD(Rigaku MiniFlex600)

2 XRD 2(a)

XRD 300 ℃

XRD

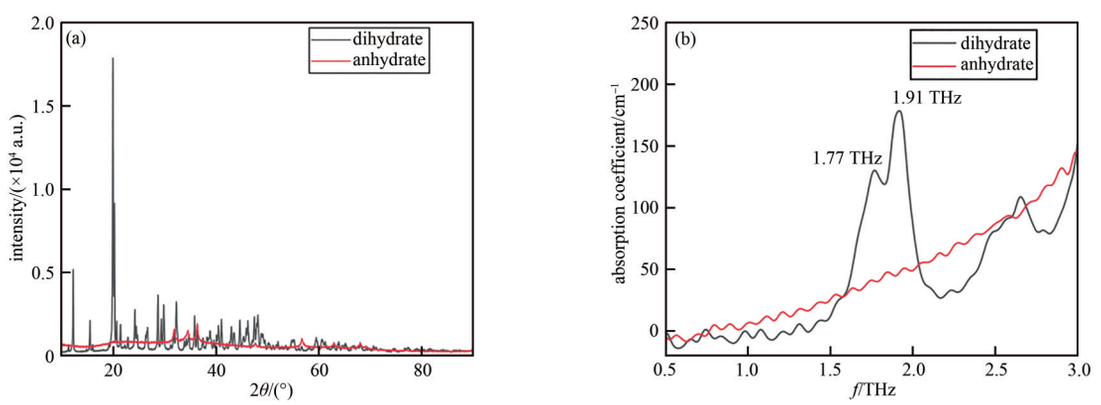


Fig.2 XRD patterns (a) and THz spectra (b) of ZC dihydrate and anhydrate

2 (a)XRD (b)THz

2(b) 1.77 THz

1.91 THz

[16] [17]

2.2 ØF¤J8 ¸!` 4'• 2 | °A•D˜ #U Ò

30 ℃ 300 ℃ 1 ℃/min 3(a) 3(b)

0.5~3.0 THz 30~300 ℃

300 ℃ 2 1.91 THz

1.77 THz 1.91 THz

1.91 THz

30 ℃ 300 ℃ 3(b)

[18-20]

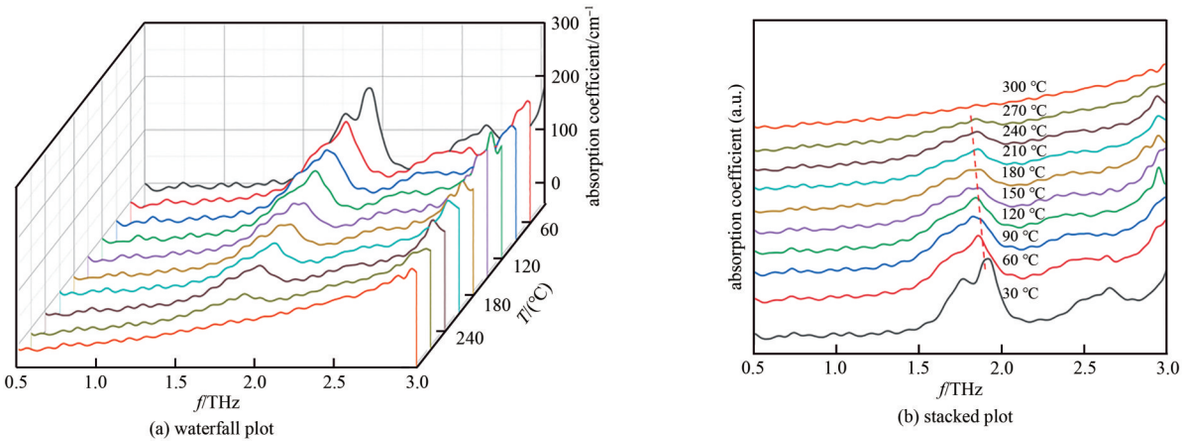
1.91 THz

4 30~100 ℃ 100~200 ℃

200~300 ℃

275 ℃

[21]



(a) waterfall plot (b) stacked plot

Fig.3 THz absorption spectra of ZC dihydrate at 30~300 ℃

3 30~300 ℃

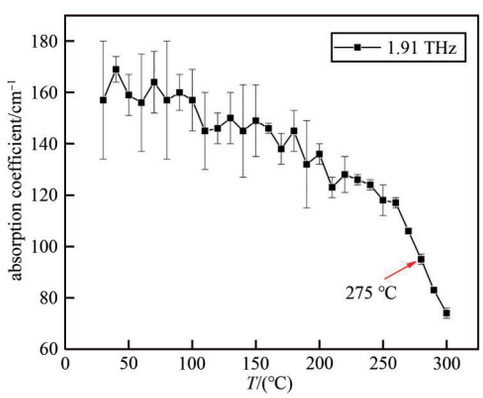


Fig.4 Variation of absorption coefficient of Zinc citrate dihydrate with temperature at 1.91 THz,30~300 ℃

4 30~300 ℃ (1.91 THz)

2.3 ØF¤J8 ¸!` 4'• ]!` Ô Ç ’

2.2 6 6

260 ℃,265 ℃,270 ℃,275 ℃,280 ℃,285 ℃

5(a)~(f) 0.9~2.8 THz

6

6(a)

[18]

$$1-(1-A)^{\frac{1}{2}}=kt \tag{3}$$

k t A t 0

6(b) (3)

1

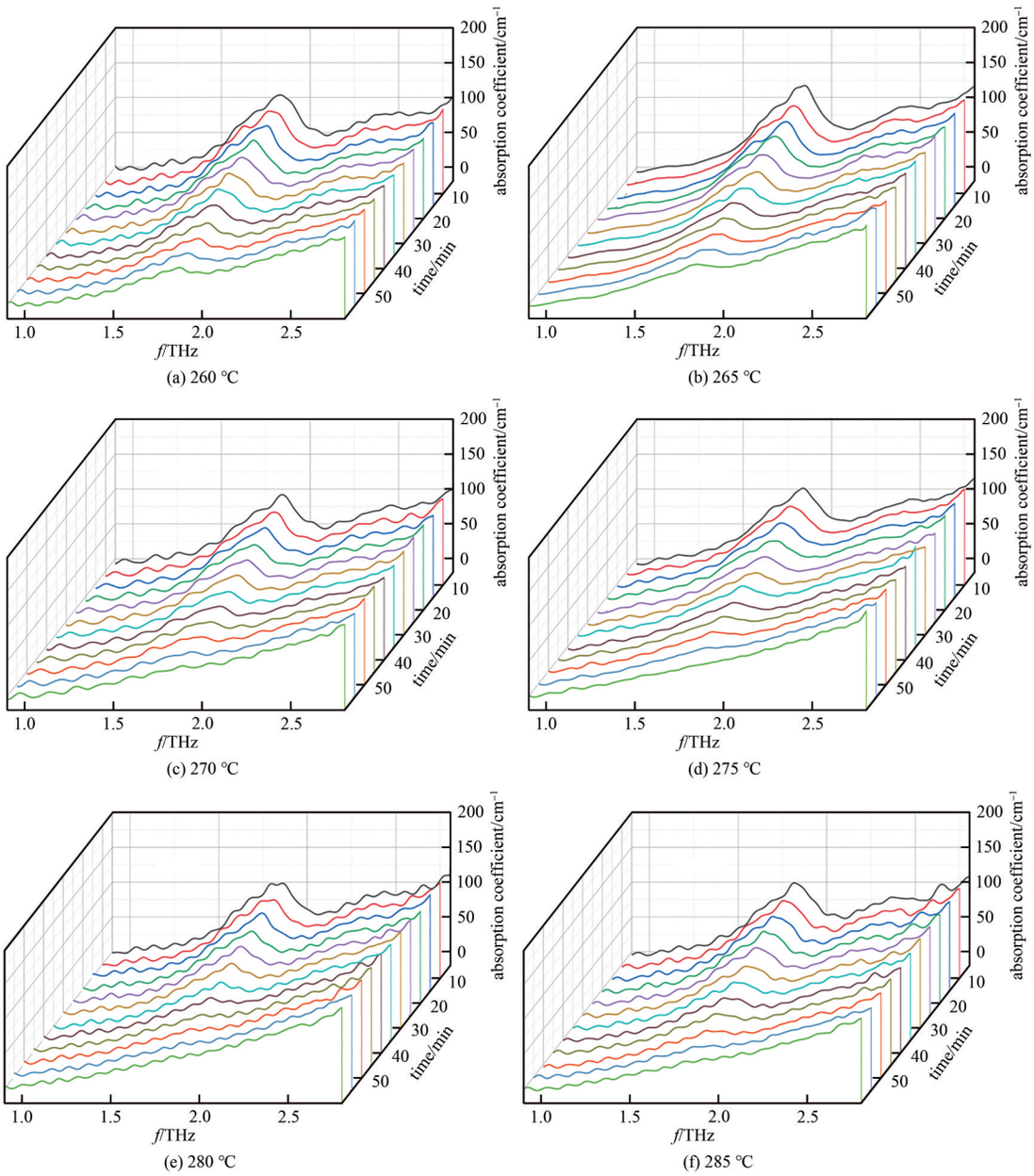


Fig.5 THz absorption spectra of ZC dihydrate at 0.9~2.8 THz under different temperatures and different heating time

5 (0.9~2.8 THz)

$$k = B\exp\left(-\frac{E_{\mathrm{A}}}{RT}\right) \tag{4}$$

B E_{A} k R (8.314 J·mol^{-1}·K^{-1}) T (4)

$$\ln k = \ln B - \frac{E_A}{R} \times \frac{1}{T} \tag{5}$$

(5) 1 381.13 J/g (≈232.6 kJ/mol) 7(a)

DSC(TA DSC Q2000 50 mL/min
6.100 mg 25~400 ℃ 5 ℃/min)
7(b) DSC 397.90 J/g
4.2%

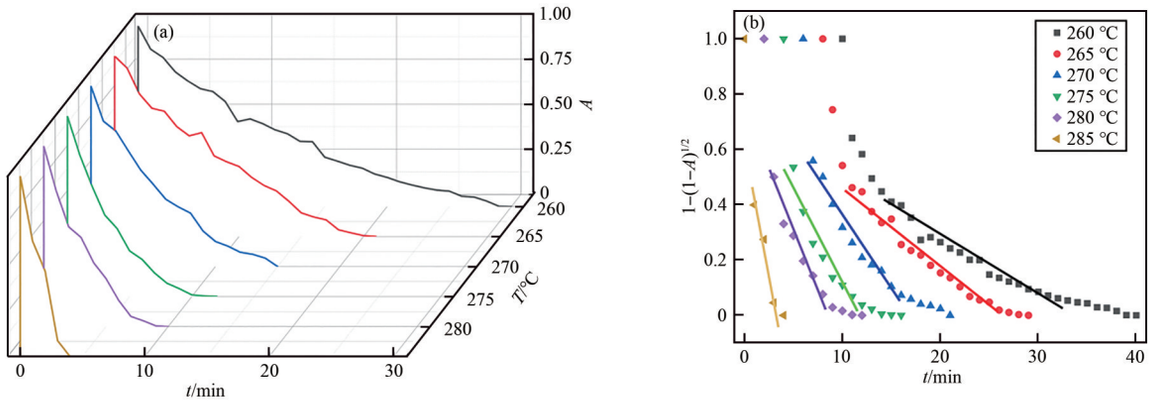


Fig.6 (a) variation of the normalized THz absorption peak area with the heating time at different temperatures; (b) fitting curves according to the contraction area equation
6 (a) (b)

1

Table1 Correlation coefficients and dehydration rate constants at different heating temperatures obtained by fitting the contraction area equation

T/℃	correlation coefficient	dehydration rate constant *k*/min^{-1}
260	0.957	0.013
265	0.959	0.028
270	0.918	0.031
275	0.940	0.059
280	0.952	0.074
285	0.943	0.177

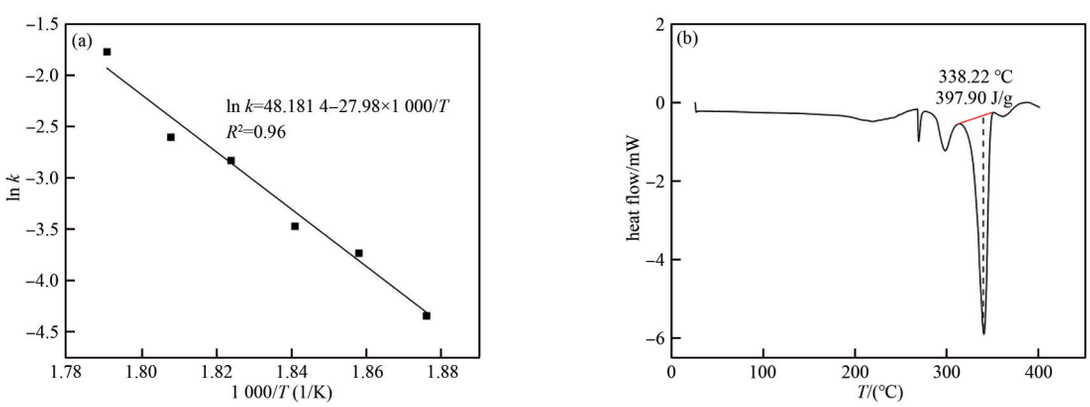


Fig.7 (a) semi-logarithm plot of *k* vs. 1 000/*T* and the linear fitting result; (b) the enthalpy change of ZC dihydrate transforming to anhydrate with DSC measurement
7 (a) *k* 1 000/*T* (b) (DSC)

3 3ÿ@æ

1.77 THz 1.91 THz

381.13 J/g DSC 4.2%

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