Far-infrared and Terahertz Spectroscopic study on Ancient Chinese Papers

Shan Tu[1], Jun Zhou[1], Xiujuan Zhang[2], Linzhi Xiao[2] and Yanbing Luo[2]
[1] Terahertz Research Center, University of Electronic Science and Technology of China, Chengdu 610054, China
[2] Department of Archaeology, School of History & Culture (Tourism), Sichuan University, Chengdu 610054, China

***Abstract*—In this study we discuss the transmittance, the refractive index of seven ancient paper sheets and five modern paper sheets made in ancient technology in the interval 5-85cm-1 and 300–1000cm-1, with terahertz time-domain spectroscopy in transmission mode and Fourier-transform infrared spectroscopy in transmission mode. By analyzing the optical characteristics of these twelve paper sheets, we discuss the link between the ancient and modern paper.**

I. Introduction

Chinese ancient calligraphy and painting art has a long history, the ancients left us a lot of cultural heritage. Because of not easy to preserve, many ancient works need to be repaired and maintained, so the research of material characteristics of ancient paper has important significance. In the paper making, bark, reed or bamboo was used usually. In order to recover some of the ancient paper, modern people use these materials to make paper based on the ancient papermaking technology. Because of these molecular motions such as rotational and vibrational ones lies in the THz frequency and far infrared waveband, detecting optical properties of ancient paper is an effective way to finding out its type. Terahertz time-domain spectroscopy (THz-TDS) is mainly used to study the properties and physical phenomena of materials in the THz frequency band. Fourier transform spectrometer (FTS) is used for identifying and analyzing far-infrared spectroscopy.

II. Materials and Methods

In this paper, seven ancient paper sheets were sampled from shedding sheets of documents dating from Ming Dynasty China to the Republic of China, and five modern paper sheets of approximately 2cm*2cm were manufactured by the ancient papermaking technology. The thickness of each sample was known. Each paper sample was analyzed in transmission mode using a TPS spectra 3000 (TeraView Ltd, Cambridge) with the range 5-85cm^{-1} and a SPS spectra 300 (Sciencetech, Canada) with the range 300-1000cm^{-1} at room temperature.

Sample pulse signal $E_{\text{sample}}(t)$ and reference pulse signal $E_{\text{reference}}(t)$ can be obtained directly in the THz-TDS system, and then be Fourier transformed to the frequency spectrum $\tilde{E}_{\text{sample}}(\omega)$ and $\tilde{E}_{reference}(\omega)$, respectively. According to the THz optical parameters extraction model proposed by Dorney, the transmittance $\tilde{T}(\omega)$ and refractive index $n(\omega)$ of measured samples can be written as

$$\tilde{T}(\omega)=\frac{\tilde{E}_{\text{sample}}(\omega)}{\tilde{E}_{reference}(\omega)}=T(\omega)e^{-j\varphi(\omega)} \qquad (1)$$

$$n(\omega)=\frac{\varphi(\omega)c}{\omega d}+1 \qquad (2)$$

where d is the thickness of the sample, c is the light speed, and $\varphi(\omega)$ is the phase difference between sample and reference signals.

With the FTS, the transmission spectra can be measured and the refractive index of the samples can be calculated based on Bouguer–Lambert–Beer law and Kramers-Kroning relation. The Formulas are written as

$$k(\omega)=\frac{\ln 1/\tilde{T}(\omega)}{4\pi\omega d} \qquad (3)$$

$$n(\omega)-1=\frac{2}{\pi}P\int_0^{\infty}\frac{\omega' k(\omega')}{\omega'^2-\omega^2}d\omega' \qquad (4)$$

where $k(\omega)$ is the imaginary part of the complex refractive index.

III. Results

The THz and far-infrared transmittance spectra of seven ancient paper sheets are shown in Fig.1. Ignoring the noise that may be caused by the environment, we can see some obvious absorption peaks of these paper sheets. In the range 5-85cm^{-1}, the absorption peaks of ancient paper sheets are approximately located at 13cm^{-1}, 24cm^{-1}, 38cm^{-1}, 66cm^{-1}, 70cm^{-1}, 81cm^{-1} except for ancient paper 004677. In the range 300-1000cm^{-1}, the absorption peaks of ancient paper sheets are approximately located at 360cm^{-1}, 440cm^{-1}, 540cm^{-1},720cm^{-1}, 810cm^{-1}, 860cm^{-1}, 960cm^{-1}.

Both in THz and far infrared region, the transmittance of ancient paper 9 is the biggest of the seven samples. Ancient paper 6 absorbs a lot light in the range 5-85cm^{-1}, but not in the range 300-1000cm^{-1}. On the other hand, ancient paper 7 absorbs much more light in the range 300-1000cm^{-1} than in the range 5-85cm^{-1}.

The refractive indices of seven ancient paper sheets in the range 5-85cm^{-1} and 300-1000cm^{-1} are shown in Fig.2. In the interval 300-1000cm^{-1}, the refractive index of ancient paper 4, ancient paper 6, ancient paper 7, ancient paper 8, ancient paper 9, ancient paper 17, and ancient paper 004677 is 1.27, 1.37, 1.42, 1.52, 1.41, 1.54, and 1.48, respectively. In the THz region, the refractive index of ancient paper 4, ancient paper 6, ancient paper 7, ancient paper 8, ancient paper 9, ancient paper 17, and ancient paper 004677 is 1.14, 1.30, 1.21, 1.24, 1.20, 1.28, and 1.18, respectively. Both in the interval 300-1000cm^{-1} and the interval 5-85cm^{-1}, ancient paper 7 and ancient paper 9 have the very similar properties, so they are likely to be made of the similar materials.

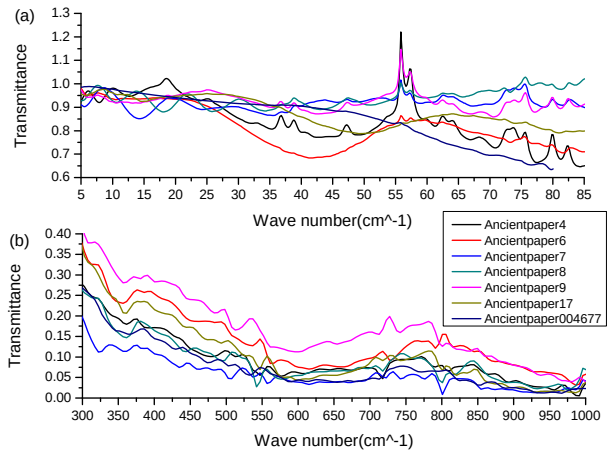

Fig.1. (a) The transmittance spectrum of seven ancient paper sheets within the spectral range 5-85cm^{-1} from THz-TDS measurements in transmission mode. (b) The transmittance spectrum of seven ancient paper sheets within the spectral range 300-1000cm^{-1} from FTS measurements in transmission mode.

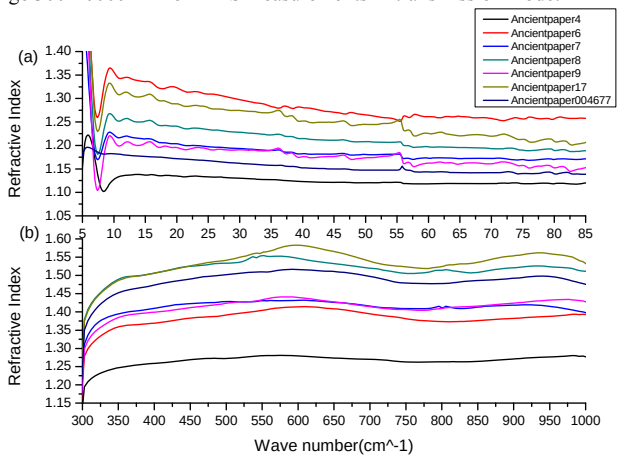

Fig.2. (a) The refractive indices of seven ancient paper sheets within the spectral range 5-85cm^{-1} from THz-TDS measurements in transmission mode. (b) The refractive indices of seven ancient paper sheets within the spectral range 300-1000cm^{-1} from FTS measurements in transmission mode.

Bamboo pulp paper, bitter bamboo paper, willow broussonetia paper, bark paper and mulberry paper are five modern paper sheets manufactured by the ancient papermaking technology. Comparing the spectrum of these five modern paper sheets and seven ancient paper sheets, the relationships between the three kinds of ancient paper (ancient paper 7, ancient paper 9, ancient paper 004677) and two kinds of modern paper (bitter bamboo paper and mulberry paper) are shown in Fig.3 and Fig.4.

Ancient paper 7, ancient paper 9 and mulberry paper have nearly the same refractive indices and transmittance characteristics in the 5-85cm^{-1} region. And the refractive indices and transmittance characteristics of ancient paper 7, ancient paper 9 and mulberry paper in the 300-1000cm^{-1} waveband are very similar. It illustrates that ancient paper 7 and ancient paper 9 are mulberry paper.

Ancient paper 4 and bitter bamboo paper have the same transmittance characteristics in the range 300-1000cm^{-1} and the same refractive indices in both the 5-85cm^{-1} and the 300-1000cm^{-1} wavebands. It illustrates that ancient paper 004677 is bitter bamboo paper.

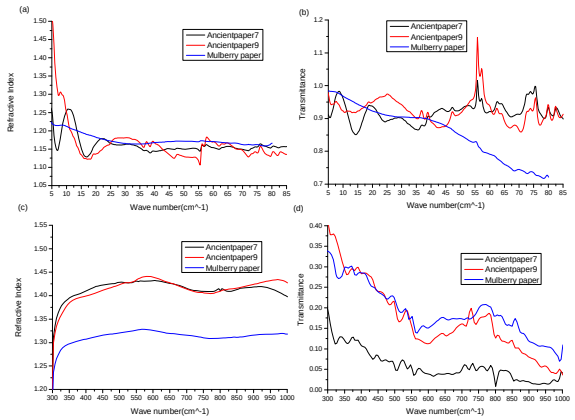

Fig.3. (a) The refractive indices of ancient paper 7, ancient paper 9 and mulberry paper within the spectral range 5-85cm^{-1}. (b) The transmittance spectrum of ancient paper 7, ancient paper 9 and mulberry paper within the spectral range 5-85cm^{-1}. (c) The refractive indices of ancient paper 7, ancient paper 9 and mulberry paper within the spectral range 300-1000cm^{-1}. (d) The transmittance spectrum of ancient paper 7, ancient paper 9 and mulberry paper within the spectral range 300-1000cm^{-1}.

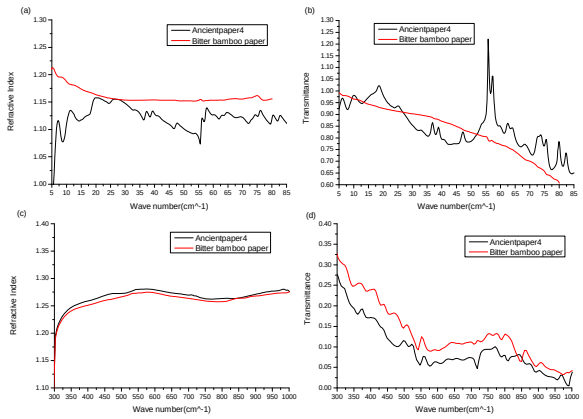

Fig.4. (a) The refractive indices of ancient paper 4 and bitter bamboo paper within the spectral range 5-85cm^{-1}. (b) The transmittance spectrum of ancient paper 4 and bitter bamboo paper within the spectral range 5-85cm^{-1}. (c) The refractive indices of ancient paper 4 and bitter bamboo paper within the spectral range 300-1000cm^{-1}. (d) The transmittance spectrum of ancient paper 4 and bitter bamboo paper within the spectral range 300-1000cm^{-1}.

IV. Summary

The study of seven ancient paper sheets with THz-TDS and FTS reveals their optical properties and types. Although the analysis work is very challenging, the results in this paper can provide a way for identifying ancient papers.

References

[1] A. V. Borodin, N. N. Brandt, and A. Yu. Chikishev, "Terahertz time-domain and FTIR spectroscopy of tris and its complexes with crown ether," *37th IRMMW-THz*, pp. 1-3, Wollongong, Australia, Sep. 23-28, 2012.

[2] Renbo Song, "Fingerprinting biological materials based on Fourier transform infrared spectroscopy," 3373088 Ph.D, Lehigh University, Ann Arbor, 2009

[3] T. R. Globus, D. L. Woolard, and A. C. Samuels, "Submillimeter-wave Fourier transform spectroscopy of biological macromolecules," *Journal of Applied Physics*, vol. 91, pp. 6105-6113, 2002.

[4] Tiphaine Bardon, R. K. May, P. F. Taday and Matija Strlič, "Material characterization of historical parchment using terahertz time-domain spectroscopy," *39th IRMMW-THz*, pp. 1-2, Tucson, Arizona, USA, Sep. 14-19, 2014.