Evaluation of the sintering properties of pottery bodies using terahertz time-domain spectroscopy

Seiji Niijima\textsuperscript{a}, Masashi Shoyama\textsuperscript{a}, Kazumi Murakami\textsuperscript{b} and Kodo Kawase\textsuperscript{b}

\textsuperscript{a}Ceramic Science Branch, Mie Prefecture Industrial Research Institute, Mie, Japan; \textsuperscript{b}Department of Electronics, Nagoya University, Nagoya, Japan

ABSTRACT
Terahertz (THz) time-domain spectroscopy was applied to evaluate the sintering properties of pottery bodies. The transmittance, absorption coefficient, and refractive index of pottery bodies fired at various temperatures were evaluated over the THz frequency range of 0.3–1.3 THz, and the relationships between these properties and their sintering properties were examined. The absorption coefficient and refractive index at 0.5 THz were sensitive under sintering conditions. In particular, the sintering-temperature dependence of the refractive index in the THz region showed a similar trend to that shown by the bulk density. THz-wave two-dimensional imaging was used to visualize inhomogeneities inside the bodies. Our study demonstrated that THz-wave analysis can be used to manage the firing process of pottery and ceramics and to conduct nondestructive testing of products.

1. Introduction
Terahertz (THz) waves have frequencies ranging from 0.3 to 10 THz (wavelengths: 1 mm–30 μm), which lie between those of radio waves and far-infrared light. They exhibit the properties of both radio and far-infrared light waves. Like light waves, THz waves can be readily manipulated by lenses and mirrors; however, these waves can also be transmitted through various materials such as paper, woods, plastics, and ceramics like radio waves. THz waves have many unique features. For example, they have higher spatial resolution than radio waves due to their shorter wavelength; their photon energy is lower than that of light waves such as visible light, ultraviolet light, and X-rays. Furthermore, many chemicals, pharmaceutical products, and pesticides absorb in the THz-wave regime.

The THz-wave region was, until recently, a little-explored field due to the lack of efficient THz-wave oscillators and detectors. However, recent technological innovations have driven new applications of THz waves. One of the innovations is the advances provided by femtosecond-laser technology, which has led to the development of techniques for the generation and detection of broadband THz-wave pulses. THz time-domain spectroscopy (THz-TDS) based on this technology provides a direct measurement of both the amplitude and phase of transmitted or reflected THz-wave pulses. This enables the determination of the complex dielectric function and optical constants such as the absorption coefficient, refractive index, and extinction coefficient of a material. THz-TDS is expected to be applied as a nondestructive and noncontact inspection technique in diverse fields such as industry, pharmaceuticals, food, agriculture, cultural heritage, and security [1–11].

Management of the firing process is extremely important in the manufacturing of pottery and ceramics. Various conventional sensors such as thermocouples are currently used to monitor the process; however, the position of a thermocouple and the temperature distribution inhomogeneity inside a furnace can lead to insufficient sintering or excessive sintering. Such firing defects affect the quality of ceramic products [12–14]. Firing defects are currently evaluated as part of the physical property evaluation of ceramic products after firing. A system that allows for real-time measurement of the firing process is desired to maintain ceramic quality and establish a more efficient manufacturing process. Recently, Miao et al. examined the THz-wave characteristics of Chinese pottery bodies fired at different sintering temperatures and reported the possibility of firing-process management for pottery using THz waves [15]. However, detailed relationships between THz-wave characteristics and the sintering properties such as the water absorption rate, bulk density, and linear shrinkage of the pottery bodies have not been reported.

In this study, the relationships between the THz-wave characteristics and the sintering properties of three types of pottery bodies were examined to consider potential technologies for firing-process management using THz-TDS. Additionally, THz-wave two-dimensional (2D) imaging was performed.
2. Experimental

2.1. Sample preparation

The semi-porcelain body (usually fired at 1150–1200°C) classified as pottery, the Banko-Kyusu body (usually fired at 1150–1200°C) classified as stoneware, and the low-temperature-sintering porcelain (usually fired at 1100–1200°C) classified as porcelain, which are all commercially available, were used as pottery bodies in this study. Table 1 shows the chemical compositions of these pottery bodies. Powders of each pottery body were placed in a steel die and uniaxially pressed at 30 MPa into a disc having a diameter of 25 mm and a thickness of 3 mm. The resulting green compacts were fired at 800–1400°C in an electric furnace in an air atmosphere. The samples were heated to the target temperature at a heating rate of 1 °C/min and maintained at the target temperature for 1 h, followed by natural cooling to room temperature within the electric furnace. The obtained samples were shaped into plates having dimensions of 10 × 10 × 2 mm$^3$ for measurement.

2.2. Characterization

The sintering properties of the pottery bodies were evaluated by the water absorption rate and bulk density according to the Archimedes method. The water absorption rate, $W_a$ (%), and bulk density, $B_d$ (g/cm$^3$), of a sample were measured after boiling in distilled water for 3 h and soaking for an additional 24 h at ambient temperature, and then using the following equations:

$$W_a = \frac{W_2 - W_1}{W_1} \times 100$$

$$B_d = \frac{W_1}{W_2 - W_3}$$

where $W_1$ and $W_2$ are the masses of the dried and water-saturated sample in air, respectively, and $W_3$ is the mass of the water-saturated sample in water. Also, X-ray transmission images of the sample were obtained using X-ray computed tomography (SMX-225CT, Shimadzu Corp.) at 160 kV and 70 μA.

2.3. THz-TDS measurement and analysis

The THz-wave characteristics of the pottery bodies were measured using a THz spectroscopic imaging system (TAS-7400TS, Advantest Corp.). Figure 1 shows a schematic diagram of the THz-TDS setup in the transmission mode. Two fiber lasers (wavelength: 1550 nm) with a pulse width of 50 fs at a 50-MHz repetition rate were used as the pump and probe beams. The pump beam was guided to a fiber-coupled photovoltaic antenna (PCA) for THz-wave pulse generation. The PCA had a dipole antenna patterned on a low-temperature-grown GaAs layer. The probe beam was guided to another PCA of the same structure. The THz-wave pulse detection was given a time delay using a computerized controller, and the waveform of the THz-wave pulses transmitted through the sample was obtained in the time domain. The THz time-domain waveform of the sample was measured at the frequency resolution of 7.6 GHz, and 1024 waveforms were accumulated. The THz time-domain signal in the absence of a sample was also measured as the reference. The THz 2D-images were obtained by raster scanning with a step width of 1 mm. The imaging area of the XY-stage was 10 × 90 mm$^2$, over which nine samples that had been sintered at different temperatures were aligned. Each pixel based on the THz time-domain waveform was measured at the frequency resolution of 7.6 GHz, and 64 were accumulated.

In the present study, the samples were dried for 24 h at 100°C and cooled in a desiccator before evaluation. This was done to minimize the influence of surface-

| Composition     | Semi-porcelain | Banko-Kyusu | Low-temperature sintering porcelain |
|-----------------|----------------|-------------|-----------------------------------|
| SiO$_2$         | 69.96          | 64.55       | 58.32                             |
| Al$_2$O$_3$     | 20.90          | 18.37       | 27.58                             |
| Fe$_2$O$_3$     | 0.51           | 3.87        | 0.42                              |
| TiO$_2$         | 0.36           | 0.75        | 0.24                              |
| CaO             | 0.16           | 0.36        | 0.17                              |
| MgO             | 0.09           | 0.64        | 0.09                              |
| K$_2$O          | 1.81           | 2.36        | 2.91                              |
| Na$_2$O         | 0.37           | 0.68        | 2.35                              |
| Li$_2$O         | –              | –           | 0.60                              |
| Ig. Loss        | 6.67           | 8.56        | 7.56                              |
| Total           | 99.83          | 100.14      | 100.14                            |

Figure 1. Schematic diagram of the THz-TDS system in the transmission mode.
adsorbed water. Additionally, the measurement chamber was purged with dry air throughout the measurement to eliminate the influence of moisture in the THz beam path. All of the THz-TDS measurements were carried out at room temperature.

A fast Fourier transformation of the obtained time-domain waveform yielded the amplitude and phase in the frequency domain. By comparing the amplitude spectrum (power spectrum) of a sample to that of the reference, the transmittance, \( T(\omega) \), of the sample was calculated as follows:

\[
T(\omega) = \frac{P_{\text{sample}}(\omega)}{P_{\text{ref}}(\omega)} \times 100 \tag{3}
\]

where \( P_{\text{sample}} \) is the power spectrum of the sample, \( P_{\text{ref}} \) is the power spectrum of a reference, and \( \omega \) is the frequency. The absorption coefficient, \( \alpha(\omega) \), and refractive index, \( n(\omega) \), of the sample were calculated using the following equations [4–6]:

\[
\alpha(\omega) = \frac{2\omega\kappa(\omega)}{c} \tag{4}
\]

\[
n(\omega) = 1 + \frac{c(\phi_{\text{ref}} - \phi_{\text{sample}})}{\omega d} \tag{5}
\]

where \( c \) is the velocity of light, \( \phi_{\text{sample}} \) is the phase of the sample, \( \phi_{\text{ref}} \) is the phase of a reference, \( d \) is the sample thickness, and \( \kappa(\omega) \) is the extinction coefficient expressed as

\[
\kappa(\omega) = \frac{c}{\omega d} \ln \left[ \frac{4n(\omega)}{(n(\omega) + 1)^2} \frac{P_{\text{ref}}(\omega)}{P_{\text{sample}}(\omega)} \right] \tag{6}
\]

3. Results and discussion

3.1. Relation between the sintering properties and THz-wave characteristics

Figure 2 shows the sintering-temperature dependence of the water absorption rate and bulk density for each type of pottery body. The water absorption rate of the semi-porcelain and low-temperature-sintering porcelain bodies decreased with increasing sintering temperature, reaching almost 0% at 1300°C and 1100°C, respectively. The water absorption rate of the Banko-Kyusu bodies decreased with increasing sintering temperature, reaching almost 0% at 1200°C. Then, it gradually increased from 1300°C. Bulk density increased with increasing sintering temperature for all of the pottery bodies, reaching a maximum at the temperature at which the water absorption rate reached almost 0%, and then decreased. The low-temperature-sintering porcelain body was different from other pottery bodies; its bulk density became almost constant at 1100–1250°C.

Generally, densification increases in pottery and ceramics as the sintering temperature increases, and the water absorption rate simultaneously decreases. Normally, the optimal sintering temperature is below the temperature at which densification is maximized. Therefore, when the temperature exceeds the optimal sintering temperature range, it reaches what is called an “excess-sintering” state in which pores form on the surface and inside the pottery bodies. As a result, the bulk density decreases and the water absorption rate increases [12]. In Figure 2, the bulk density decreased at 1350°C for the semi-porcelain body, at 1250°C for the Banko-Kyusu body, and at 1300°C for the low-temperature-sintering porcelain body, which indicated an excess-sintering state.
Figure 3 shows the THz-wave transmission spectra at 0.3–1.3 THz for each type of pottery body fired at temperatures ranging from 1100 to 1400 °C. There were no characteristic peaks in the THz-wave transmission spectra. However, for all pottery bodies, as the sintering temperature increased, the transmittance in the THz region decreased considerably. In the sintering temperature range of 800–1000°C, there was no notable difference in the transmission spectrum. It is well-known that THz waves are sensitive to water [10]. In this study, to remove the effects of water, samples were dried at 100°C for 24 h and the measurements were performed in a chamber purged with dry air. Therefore, the notable decrease in THz transmittance was not due to moisture. Consequently, the THz-wave transmission spectrum of the pottery bodies was dependent upon the sintering temperature. However, changes in the THz-wave transmission spectra could not provide information concerning excess-sintering. Therefore, the absorption coefficients and refractive indices of the pottery bodies in the THz region were calculated using Eqs. (4) and (5), and their relationships with the sintering properties of the pottery bodies were examined.

Figures 4 and 5 show the sintering-temperature dependences of the absorption coefficient and refractive index, respectively, at 0.5 THz for each pottery type fired at 800–1400°C. The frequency of 0.5 THz was selected due to the improved signal-to-noise ratio. Figure 4 shows that the absorption coefficient increased with increasing sintering temperature and continued to increase even past the optimal sintering temperature range of each type of pottery. Therefore, although there was a relationship between the absorption coefficient in the THz region and the sintering properties of the pottery bodies, the information did not provide any information concerning excess sintering. In contrast, as shown in Figure 5, the refractive index at 0.5 THz for

![Figure 3](image1.png)

**Figure 3.** THz-wave transmission spectra of (a) semi-porcelain, (b) Banko-Kyusu, and (c) low-temperature sintering porcelain bodies fired at various temperatures.

![Figure 4](image2.png)

**Figure 4.** Relationship between the absorption coefficient at 0.5 THz and the sintering temperature of the pottery bodies.
which the refractive index decreased was 1350°C for the semi-porcelain body, 1250°C for the Banko-Kyusu case, and 1300°C for the low-temperature-sintering porcelain case. These temperatures are consistent with those at which the bulk density of each pottery body decreased (Figure 2). In other words, the refractive index in the THz region was closely related to the bulk density. This result suggests that by examining the sintering-temperature dependence of the refractive index in the THz region, the density of pottery bodies and information on firing defects such as insufficient sintering or excess sintering can be obtained.

3.2. THz-wave 2D imaging

Figure 6 shows 2D representations of the THz-wave transmission, refractive index, and X-ray transmission of a semi-porcelain body fired at 900–1400°C. There was no apparent difference in the X-ray transmission image with changing sintering temperature. Conversely, notable differences were observed in the THz-wave transmission and refractive index images. Figures 3 and 5 show that these differences were due to the sintering temperature dependence of the THz-waves. The THz-wave 2D refractive index images clearly correspond with changes in the sintering properties. Notably, the uneven contrast in the THz-wave imaging suggests inhomogeneous density within the

![Figure 5. Relationship between the refractive index at 0.5 THz and the sintering temperature of the pottery bodies.](image)

![Figure 6. THz transmission, THz refractive index and X-ray transmission images of semi-porcelain bodies fired at various temperatures.](image)

![Figure 6.](image)

Each type of pottery body increased initially with the sintering temperature, reaching a maximum and then decreasing at a certain temperature. The temperature at
fired samples. Therefore, THz-wave imaging can visualize not only the sintering properties of a sample but also inhomogeneity within. THz-TDS imaging would be a novel nondestructive and noncontact inspection technology for pottery and ceramics.

4. Conclusions

The characteristics of three types of pottery bodies fired at various temperatures were measured by THz-TDS, and the relationships between these characteristics and their sintering properties were examined. The THz-wave characteristics of the pottery bodies depended on the sintering temperature, and the refractive index in the THz region for pottery bodies was closely related to the bulk density. Additionally, THz-wave 2D images mapped closely with certain sintering properties and also revealed inhomogeneities within samples. It is therefore expected that THz-wave technology will be useful for managing the firing of pottery and ceramics and also to provide a nondestructive and noncontact inspection technology for products. Future research will further develop in situ THz measurement techniques related to the firing of pottery and ceramics.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

1. Tonouchi M. Cutting-edge terahertz technology. Nat Photonics. 2007;1(2):97–105.
2. Naftaly M, Robert R. Terahertz Time-Domain Spectroscopy for Material Characterization. Proc IEEE. 2007;95(8):1658–1665.
3. Fujii T, Ando A, Sakabe Y. Characterization of dielectric properties of oxide materials in frequency range from GHz to THz. J Eur Ceram Soc. 2006;26(10–11):1857–1860.
4. Stoik CD, Bohn MJ, Blackshire JL. Nondestructive evaluation of aircraft composites using transmissive terahertz time domain spectroscopy. Opt Express. 2008;16(21):17039–17051.
5. Rajab KZ, Naftaly M, Linfield EH, et al. Broadband dielectric characterization of Aluminum Oxide (Al2O3). J Micro And Elect Pack. 2008;5:101–106.
6. Xing L, Cui HL, Shi C, et al. Nondestructive examination of polyethylene and oxide composite structures with terahertz time-domain spectroscopy. Polym Test. 2017;57:141–148.
7. Kawase K, Ogawa Y, Watanabe Y, et al. Non-destructive terahertz imaging of illicit drugs using spectral fingerprints. Opt Express. 2003;11(20):2549–2554.
8. Takeuchi I, Tomoda K, Nakajima T, et al. Estimation of crystallinity of trehalose dihydrate microspheres by usage of terahertz time-domain spectroscopy. J Pharm Sci. 2012;101(9):3465–3472.
9. Jepsen PU, Møller U, Merbold H. Investigation of aqueous alcohol and sugar solutions with reflection terahertz time-domain spectroscopy. Opt Express. 2007;15(22):14717–14737.
10. Castro-Camus E, Falomir M, Covarrubias AA. Leaf water dynamics of Arabidopsis thaliana monitored in vivo using terahertz time-domain spectroscopy. Sci Rep. 2013;3:2910.
11. Fukunaga K, Picollo M. Terahertz spectroscopy applied to the analysis of artists’ materials. Appl Phys A. 2010;100:591–597.
12. Kohayashi Y, Ohira O, Ohashi Y, et al. Effect of firing temperature on bending strength of porcelains for tableware. J Am Ceram Soc. 1992;75(7):1801–1806.
13. Ananta S, Thomas NW. Relationships between sintering conditions, microstructure and dielectric properties of lead iron niobate. J Eur Ceram Soc. 1999;19(10):1873–1881.
14. Vats G, Vaish R. Selection of optimal sintering temperature of K0.5Na0.5NbO3 ceramics for electromechanical applications. J Asian Ceram Soc. 2014;2:5–10.
15. Miao XY, Yang QN, Feng CJ, et al. Optical properties of traditional ceramic with different sintering temperatures in terahertz range. Proc SPIE. 2015;9795:321–326.