Effects of the crystal phase and microstructure of pottery bodies on the transmission characteristics of terahertz waves

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ABSTRACT

We recently reported that the terahertz (THz)-wave characteristics of pottery bodies varied significantly with firing temperature. This suggested the feasibility of conducting nondestructive inspection of the sinterability and manufacturing-process management of ceramics by THz-wave analysis. However, it is not clear why the THz-wave characteristics of ceramics change with firing temperature. In this study, we evaluated the THz-wave transmission properties of low-temperature-sintered porcelain bodies fired at various temperatures using THz time-domain spectroscopy and investigated the relationship between the crystal phase and microstructure. We found that the THz-wave transmittance increased with the dehydration of kaolinite and decreased with the formation of Mullite and glass phases in the body. Also, as the firing temperature increased, the THz-wave transmittance of these bodies was affected by scattering due to the formation of pores. Additionally, the refractive index in the THz range showed a good correlation with the bulk density. We established that the firing-temperature dependence of the refractive index in the THz range was related to the crystal phase and microstructure.

1. Introduction

Terahertz (THz) waves are electromagnetic waves in the frequency range of 0.3–10 THz (wavelength: 1 mm–30 μm). With the recent development of light source and detection technologies for application in the THz range and measurement techniques such as THz time-domain spectroscopy (THz-TDS), THz-wave analysis is poised to become a new nondestructive, noncontact inspection technique [1–7].

THz waves lie between light waves and radio waves and contain properties of both. Like light waves, THz waves can be freely manipulated by lenses and mirrors. At the same time, like radio waves, THz waves can partially penetrate various materials, such as plastics, paper, wood, ceramics, and semiconductors. THz waves also exhibit appropriate spatial resolution due to their shorter wavelengths compared with radio waves. Terahertz waves are also safer than ionizing radiation, such as X-rays and ultraviolet light, due to their low photon energy. Additionally, various materials with a unique absorption spectrum (fingerprint spectrum) in the THz range, including sugar, amino acids, and pharmaceuticals, have been reported [8–10].

We reported that the THz-wave transmission and reflection properties of potteries and ceramic tiles vary significantly with firing temperature [11,12]. The refractive index and reflectivity in the THz range, in particular, are closely related to the bulk density of the ceramics, a characteristic suggesting the possibility of applying THz-wave analysis for nondestructive inspection of sinterability and firing-process management. The reason why the THz-wave characteristics of ceramics change with firing temperature remains unclear, however. It is necessary that the relationship between the changes in ceramics caused by firing and the THz-wave characteristics be understood before applying this technology to nondestructive inspection. In this study, we evaluated the THz-wave transmission properties of pottery bodies fired at various temperatures using THz-TDS and investigated the relationship between the crystal phase and the microstructure.

2. Experimental procedures

2.1. Sample preparation

The low-temperature sintering porcelain bodies we developed used as the pottery bodies in this study can be sintered from 1100°C, which is about 200°C lower than the sintering temperature of conventional porcelain [13]. The raw material composition of this porcelain is 50% clay 50% a mixture of equal amounts of Indiana feldspar, nepheline syenite, and petalite. Table 1 lists the chemical compositions of the bodies before and after firing. The low-temperature sintering
2.2. Characterization

The sinterability of the low-temperature sintering porcelain bodies was evaluated in terms of apparent porosity and bulk density according to the Archimedes’ method. Kerosene was used as the immersion liquid for the samples fired at 100–600°C due to its solubility in water. For samples fired at 700–1400°C, distilled water was used as the immersion liquid. After immersion in the liquid, the open pores of the samples were forcibly saturated with the immersion liquid by decompressing them in a vacuum dryer and then restoring them to atmospheric pressure. The mass of the dried samples, \(W_1\), the mass of the samples saturated in the immersion liquid, \(W_2\), and the mass of the saturated samples, \(W_3\), at 20°C were then measured, and the apparent porosity, \(P_a\) (%), and bulk density, \(D_b\) (g-cm\(^{-3}\)), were calculated using Equations (1) and (2).

\[
P_a = \frac{W_3 - W_1}{W_3 - W_2} \times 100
\]

\[
D_b = \frac{W_1}{W_3 - W_2} \times S
\]

An X-ray diffractometer (RINT-2500, Rigaku Corp.) was used to identify the crystal phases of the low-temperature sintering porcelain bodies fired at different temperatures. The cross-sectional microstructures of the samples were investigated by scanning electron microscope (JSM-IT200, JEOL Ltd).

The THz-wave transmission properties of the low-temperature sintering porcelain bodies were measured using a THz spectroscopic imaging system (TAS-7400TS, Advantest Corp.). The measurement frequency range was 0.3–1.5 THz, the frequency resolution was 1.9 GHz, and the cumulated number was 2048. Measurements were performed in a chamber purged with dry air to eliminate the effects of atmospheric moisture on the THz-wave characteristics. Five samples were prepared for each firing temperature, and the THz-wave transmission characteristics were measured for each sample. The mean values and standard error of the absorption coefficient and the refractive index in the THz range were determined. It should be noted that the THz-wave measurements were performed on samples fired in an electric furnace independent of the THz spectroscopic imaging system, and thus were not in-situ measurements. The THz wave transmission properties of quartz single crystals (\(\gamma\)-cut \(SiO_2\), 2-mm thick), mullite ceramics (\(3Al_2O_3 \cdot 2SiO_2\), 2-mm thick), and aluminosilicate glass (\(Na_2O\cdotAl_2O_3\cdot2SiO_2\), 2-mm thick) were also measured for use as reference samples. The measurement principle and analysis method applied to THz-TDS were as described in the previous report [11].

3. Results and discussion

3.1. Sinterability, crystal phase, and microstructure

Figure 1 shows the firing-temperature dependence of the apparent porosity and bulk density of the low-temperature sintering porcelain bodies. The apparent
porosity (○) increased slightly at temperatures up to 700°C, and then decreased significantly at above 1000°C. Subsequently, the apparent porosity became almost 0% at 1100–1350°C and increased slightly at 1400°C. On the other hand, the bulk density (●) decreased gradually with firing temperature, and then increased rapidly from 1000 to 1100 °C. The bulk density then remained almost constant up to 1250°C, and finally decreased significantly at above 1300°C.

Figure 2 shows the X-ray diffraction (XRD) patterns of low-temperature sintering porcelain bodies fired at various temperatures. The XRD patterns of the samples fired at 100–400°C (Figure 2(a)) displayed peaks attributed to kaolinite (Al₂O₃ · 2SiO₂ · 2H₂O), quartz (SiO₂), orthoclase (K₂O-Al₂O₃ · 6SiO), nepheline syenite (K₂O·3Na₂O·4Al₂O₃ · 8SiO₂), and petalite (Li₂O-Al₂O₃ · 8SiO₂). Kaolinite is a typical clay mineral that dehydrates and decomposes into amorphous metakaolin at above 500°C [14–16]. Therefore, the XRD peaks corresponding to kaolinite were absent in the sample fired at 500°C. The XRD peaks in the crystal phases, except for kaolinite, hardly changed up to 900°C, which suggested that liquid-phase sintering due to the melting of feldspar (orthoclase, nepheline syenite, and petalite) had not progressed. The XRD patterns of the sample fired at 1000°C (Figure 2(b)), however, showed much lower intensities for peaks corresponding to feldspar, resulting in a halo peak (a broad peak at around 2θ = 15–30°) attributed to the glass phase and peaks attributed to mullite. This indicates that densification began at 1000°C, which coincides with the temperature at which the bulk density began to increase (Figure 1). As the firing temperature increased further, the XRD peaks corresponding to feldspar and quartz disappeared so that only those corresponding to mullite and the glass phase were observed at above 1300°C. Also, the intensity of the halo peak corresponding to the glass phase hardly changed at above 1100°C. Therefore, mullite crystal growth occurred once the firing temperature was sufficiently high to enable liquid-phase sintering via the melting of the feldspar.

Figure 3 shows cross-sectional SEM images of low-temperature sintering porcelain bodies fired at various temperatures. Little change in the cross-sectional microstructures was observed in samples fired at 100–500°C. The SEM image at 600°C reveals that the metakaolin produced by the decomposition of kaolin adhered to the particles. The SEM image of the sample fired at 1000°C also shows melted particles, which indicates that liquid-phase sintering had started. Sintering advanced further with increases in the firing temperature, and few large pores were observed at up to 1200°C. However, pores 10–20 µm in size were observed at 1250°C, and those pores connected and grew at temperatures above 1300°C. Eventually, the connected pore size exceeded 200 µm. Under these extreme firing conditions, swelling of the internal pores, or “bloating”, occurred and the apparent volume increased, which resulted in a decrease in bulk density [17]. This is consistent with the results shown in Figure 1.

![Figure 2](image-url) **Figure 2.** X-ray diffraction patterns of the low-temperature sintering porcelain bodies fired at various temperatures: (a)100–900°C, (b)1000–1400 °C: k: kaolinite, q: quartz, o: orthoclase, n: nepheline syenite, p: petalite, m: mullite.
Figure 4 shows cross-sectional SEM images of a low-temperature fired porcelain substrate with the observation surface etched for 30 seconds using a 5 mass% HF solution. At 1100°C, quartz particles several micrometers in size and fine needlelike mullite crystals precipitated in the glass matrix were observed. At 1300°C and 1400°C, an increase in the precipitation and growth of needlelike mullite crystals and a felt-like structure were observed where they intertwined.

### 3.2. Relationship among the THz transmission properties, crystal phase, and microstructure

Figure 5 shows the THz-transmittance spectra of the low-temperature sintering porcelain bodies fired at 100–1400°C. There were no characteristic (fingerprint) peaks in the THz-transmission spectra of the low-temperature sintering porcelain bodies, but the THz transmittance increased with increases in the firing temperature (Figure 5(a)). On the other hand, Figure 5(b) and (c) show decreased THz transmittance with increases in the firing temperature. Also, the transmittance of the samples fired at above 1100°C decreased by more than four orders of magnitude up to 0.9 THz. Since water is easily absorbed in the THz range [18], the samples were thoroughly dried to remove water from the surface and pores. Additionally, measurements were taken in an acrylic sample chamber purged of water vapor by dry air. The observed changes in THz transmittance were therefore likely not due to moisture.

Figure 6 shows the firing-temperature dependence of the absorption coefficient of the low-temperature sintering porcelain bodies at 0.3, 0.5, and 0.7 THz. The

![Figure 3](image-url). Scanning electron microscopic images of cross-sections of the low-temperature sintering porcelain bodies fired at various temperatures.
higher the frequency, the greater the change in the absorption coefficient with firing temperature. Hence, it would be more appropriate to use the absorption coefficient in the high-frequency range for nondestructive inspection and firing-process management of ceramics.

At each frequency, the absorption coefficient decreased to 500°C and then remained almost constant up to 900°C. The absorption coefficient increased subsequently at above 1000°C and remained almost constant from 1100 to 1250°C. At 1300–1400°C, the absorption coefficient increased slowly with the firing temperature. The THz-wave transmission characteristics of the low-temperature sintering porcelain bodies were divided into four categories, i.e. 100–500°C, 600–900°C, 1000–1250°C, and 1300–1400°C. Thus, we examined the relationship between the observed THz-wave transmission properties and the changes in the crystal phase and microstructure caused by firing.

The decrease in the absorption coefficient at temperatures above the 100–500°C range was likely due to decomposition and dehydration of the kaolinite present in the raw material. The water contained in kaolinite, a layered silicate mineral, is in the form of adsorbed, interlayer, and constitutional water. Adsorbed water is that adsorbed on the surface of the clay particles. In this study, the effect of absorbed water on the THz-wave characteristics was considered to be negligible because the samples were dried at 100°C for 24 h. Interlayer water is found between
crystal layers, and constitutional water is present in the crystals in the form of hydroxyl (–OH) groups. Both these types of water are removed during the heating and decomposition of kaolinite. The interlayer and constitutional water contents in kaolinite typically undergo dehydration in the ranges of 100–300°C and 400–600°C, respectively [14–16]. As shown in Figure 2(a), the disappearance of the XRD peak corresponding to kaolinite at 500°C suggests that little interlayer or constitutional water was present at this temperature. Therefore, the decrease in the absorption coefficient observed in the range of 100–500°C was likely due to a decrease in the interlayer and constitutional water, since the structure of kaolinite changed with heating.

There was no significant change in the THz absorption coefficient in the 600–900°C range. Figure 2(a) and 3 also reveal that no significant changes occurred in the crystal phase or microstructure. In this firing temperature range, the expansion of quartz via the α-β transition at 573°C, thermal decomposition of the carbonate, and solid-phase sintering between the particles may have occurred. However, these changes appear to have had little impact on the THz-wave transmission characteristics.

Figure 2(b) shows that the halo peak attributed to the glass phase and peaks corresponding to mullite appeared in the XRD pattern of low-temperature sintering porcelain bodies at above 1000°C. With the accompanying densification resulting from liquid-phase sintering, the absorption coefficient in the THz range increased significantly from 1000 to 1100°C, and then remained almost constant up to 1250°C.

Figure 7 shows the THz wave absorption spectra of y-cut quartz, mullite, and aluminosilicate glass. The chemical composition of the formed glass phase was thought to be aluminosilicate glass based on the chemical composition in Table 1. While quartz exhibits a relatively low degree of absorption in the THz range, mullite and aluminosilicate glass exhibits high degree of THz absorption. Therefore, the sharp increase in absorption coefficients observed in the 1000–1100°C range was likely due to the formation of mullite and the glass phase via densification. Additionally, the XRD peak intensities showed little change in the amounts of mullite and the glass phase in the 1100–1250°C range (Figure 2(b)), which accounts for the near-constant absorption coefficients in the THz range with firing at 1100–1250°C.

At 1300–1400°C, the absorption coefficient in the THz range increased slightly. Figure 2(b) shows that the halo peak intensity did not change significantly in this firing temperature range, while the XRD peak intensity of mullite increased. This increased mullite formation was probably responsible for the observed increase in the absorption coefficient in the THz range. In addition to this change in the crystal phase, a significant change in the microstructure of the low-temperature sintering porcelain was observed at 1300–1400°C. Figure 3 shows that bloating occurred in this firing temperature range, and that connected pores with sizes ranging from 200 to 400 µm were observed. The THz waves used in this study were in the range of 0.3–1.5 THz, corresponding to wavelengths of 1 mm–200 µm. Generally, pores with similar or larger sizes than the irradiating wavelength cause Mie scattering. THz wave attenuation caused by such scattering sources has been reported for resin and pharmaceutical tablets [19,20]. Therefore, large pores formed in pottery bodies would likely attenuate THz waves, resulting in
3.3. Relationship between the THz refractive index and bulk density

Figure 8 presents the THz-wave refractive index spectra over the range of 0.3–0.7 THz for the low-temperature sintering porcelain bodies fired at various temperatures. The refractive indices in the THz range varied with firing temperature. Figure 9 shows the firing-temperature dependence of the refractive index at 0.5 THz of the low-temperature sintering porcelain bodies. Herein, the refractive index at 0.5 THz is used as an example, since the refractive index in the THz range had little frequency dependence. The refractive index at 0.5 THz decreased significantly at 500°C, remaining almost constant until 900°C and then rapidly increasing from 1000°C. Subsequently, the refractive index at 0.5 THz remained almost constant from 1100 to 1250°C and decreased significantly at above 1300°C. The firing-temperature dependence of the refractive index in the THz range of the low-temperature sintering porcelain bodies was divided into four categories, i.e. 100–500°C, 600–900°C, 1000–1250°C, and 1300–1400°C.

As previously reported [11], the changes in the refractive index in the THz range were similar to the change in bulk density (● in Figure 1). Therefore, we investigated the relationship between the refractive index in the THz range and bulk density. In general, the refractive index, $n$, of a material depends on the electronic polarizability, $\alpha$, and density, $\rho$, and is given by the Lorentz-Lorenz formula [21] shown in Equation (3):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N_A}{3M} \alpha \rho$$

where $N_A$ is Avogadro’s number and $M$ is the molar mass. By solving Equation (3) for $n$, we can express the refractive index as a function of density, as shown in Equation (4):

$$n = \sqrt{1 + \frac{2K\rho}{1-K\rho}}$$

where $K$ is a constant given by Equation (5):

$$K = \frac{4\pi N_A\alpha}{3M}$$

Figure 10 shows the correlation between the bulk density and refractive index of the low-temperature sintering porcelain bodies at 0.5 THz. The regression curve is that of Equation (4) with $K = 0.06 \text{ cm}^3 \text{ g}^{-1}$, where the coefficient of determination $R^2$ is 0.97. From Table 1, the molar mass of a low-temperature sintering porcelain body fired at 1200°C, $M_{\text{fired}}$, was 69.15 g·mol$^{-1}$. Then, substituting $M_{\text{fired}} = 69.15 \text{ g·mol}^{-1}$,
$K = 0.06 \text{ cm}^3\text{g}^{-1}$, and $N_k = 6.02 \times 10^{23} \text{ mol}^{-1}$, the electronic polarizability, $\alpha_{\text{free}}$, is $1.63 \times 10^{-24} \text{ cm}^3$. Before firing, the molar mass, $M_{\text{raw}}$, and electronic polarizability, $\alpha_{\text{raw}}$, were 69.37 g mol$^{-1}$ and $1.65 \times 10^{-24} \text{ cm}^3$, respectively. The electronic polarizability did not significantly change with firing. It should be noted, however, that the molar mass, $M$, is affected by the microstructure (porosity). Assuming that the pores of a sample are filled with air ($N_k$: 80%, $O_2$: 20%, the molar mass: 28.80 g mol$^{-1}$), the molar mass of the sample is expected to decrease as the porosity increases. When $K$ is constant in Equation (5), as the molar mass, $M$, decreases, the electronic polarizability, $\alpha$, also decreases. Therefore, the microstructure of a low-temperature sintering porcelain body affects the bulk density and the electronic polarizability, which in turn affects the refractive index in the THz range. Pores caused in porcelain bodies by the removal of the interlayer and constitutional water from kaolinite, thermal decomposition of carbonate, and bloating all reduced the density and, thus, the refractive index in the THz range. Meanwhile, the refractive index in the THz range increased as the pores disappeared and densification increased due to solid– and liquid-phase sintering. These trends indicate that the changes in the refractive index in the THz range with firing temperature were caused by changes in the crystal phase and microstructure.

4. Conclusions

THz-TDS was used to investigate the THz-wave transmission properties of low-temperature sintering porcelain bodies fired at various temperatures, and to establish the relationship between the crystal phase and the microstructure. The absorption coefficient of low-temperature sintering porcelain bodies in the THz range was significantly affected by water (interlayer and constitutional water), mullite, and the glass phase, which are all absorbed significantly in the THz range. The absorption coefficient in the THz range decreased with the dehydration of kaolinite during firing and increased with the formation of mullite and glass, accompanied by densification. Mie scattering caused by pores formed by bloating also increased the absorption coefficient. Changes in the crystal phase and microstructure also affected the refractive index in the THz range, which decreased with the formation of pores due to the thermal decomposition of kaolinite and carbonate and the accompanying bloating. Meanwhile, the refractive index in the THz range increased with the disappearance of pores and densification due to solid–liquid-phase sintering. A clear correlation was identified between the bulk density and the refractive index.

Firing enables ceramics to achieve the crystal phase and microstructure necessary for their desired functions and characteristics. The results of this study will provide important foundational data for nondestructive inspection and firing-process management of ceramic products by THz-wave analysis. Nondestructive inspection of ceramics solely by THz-wave analysis will be possible once the correlation between parameters such as the crystal phase and microstructure of ceramics and the THz-wave characteristics are organized as reference data.

Disclosure statement

No potential conflict of interest was reported by the authors.

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