

# Microwave and Terahertz dielectric properties of MgTiO<sub>3</sub>-CaTiO<sub>3</sub> ceramics

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## Abstract.

The THz dielectric properties of MgTiO<sub>3</sub>-CaTiO<sub>3</sub> ceramics are reported. The ceramics were prepared via a solid-state reaction route and the sintering conditions were optimized to obtain ceramics with high permittivity and low loss in the terahertz frequency domain. The amount of impurities (MgTi<sub>2</sub>O<sub>5</sub>) and grain size increased with increasing sintering temperature. The dielectric properties improved with increasing density, and the best terahertz dielectric performance was obtained at 1260 °C, with a permittivity of 17.73 and loss of 3.07×10<sup>-3</sup>. Ceramics sintered above 1260 °C showed a sharp increase in loss, which is ascribed to an increase in the impurity content.

*Key words: Microwave, Terahertz, Dielectrics, MgTiO<sub>3</sub>-CaTiO<sub>3</sub>*

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## 1. Introduction

Terahertz (THz) technology has demonstrated extraordinary prospects in the past ten years due to its attractive applications in material, chemical, communication and life sciences [1-5]. Researchers are exploiting it to develop new portable, low loss and light weighted THz devices, for example sensors [6], resonators [7] and filters [8] to boost applications of THz technologies. However, the lack of advanced materials in the THz band is a major constraining factor. Although significant progress has

been made in the development of reliable measurement systems to extract materials' dielectric properties in the THz band [9, 10], systematic research on the development of materials with appropriate dielectric properties has barely started.  $\text{MgTiO}_3$ , exhibiting a rhombohedral structure with space group  $R3c$  [11], is a widely studied microwave material which shows a relatively low permittivity ( $\epsilon_r \sim 17$ ), high quality factor ( $Q \times f \sim 160000$  at 7 GHz) and negative temperature coefficient of resonant frequency ( $\tau_f \sim -50$  ppm/°C) [12]. In addition to a high permittivity and quality factor, a near-zero temperature coefficient of resonant frequency is also required for commercial applications. It is found that with a small addition of 5 mol%  $\text{CaTiO}_3$  (orthorhombic structure with space group  $Pbnm$ ) to ceramics produces improved permittivity (21), quality factor ( $Q \times f \sim 56000$  at 7 GHz) and near zero  $\tau_f$  [12]. It is reported that  $\text{MgTiO}_3$  and  $\text{CaTiO}_3$  do not form solid solutions but separate phases due to the different crystal structures [13]. In this paper,  $0.95\text{MgTiO}_3$ - $0.05\text{CaTiO}_3$  ceramics were prepared under different sintering conditions. The effects of density, phase purity and microstructure on the dielectric properties in the THz spectral domain were investigated.

## 2. Experimental

Ceramics of  $0.95\text{MgTiO}_3$ - $0.05\text{CaTiO}_3$  were prepared using a conventional solid-state reaction route, with raw chemicals of MgO (CP, 99%),  $\text{CaCO}_3$  (CP, 99%) and  $\text{TiO}_2$  (CP, 99%). The reagents were weighed based on the stoichiometry of  $0.95\text{MgTiO}_3$ - $0.05\text{CaTiO}_3$ . The mixed powder was calcined at 1150 °C for 2h with 1 wt% of ZnO added as a sintering aid. Green bodies were prepared and sintered at different temperatures, namely, 1240 °C, 1260 °C, 1280 °C and 1300 °C for 3 hours in air.

The crystal structures of the samples were identified with X-ray diffraction (XRD) using Cu  $K\alpha$  radiation (X'pert PRO, Panalytical, Holand). The microstructure of the specimens was observed using a

scanning electron microscope (SEM, TM-3000, Hitachi, Japan). Element analysis was carried out with Energy-Dispersive X-ray spectroscopy (EDX, Oxford instrument). Densities were obtained using the Archimedes' method. Microwave dielectric properties of the ceramics, including  $\epsilon_r$ ,  $Q \times f$  and  $\tau_f$ , were measured using the parallel plate resonator method coupled to a vector network analyzer (VNA)<sup>1</sup> at 8.2 GHz. The THz dielectric behavior of the samples between 0.22 THz and 0.32 THz were measured using a VNA<sup>2</sup>-driven quasi-optical transmissionmeter [14].

### 3. Results and discussion

The density of ceramics sintered at 1240 °C, 1260 °C, 1280 °C and 1300 °C were determined to be 3.778 g/cm<sup>3</sup>, 3.790 g/cm<sup>3</sup>, 3.790 g/cm<sup>3</sup> and 3.790 g/cm<sup>3</sup> respectively. The apparent density increased with increasing sintering temperature and a near-constant density was obtained for samples sintered above 1260 °C. The XRD patterns of dense samples sintered at 1260 °C, 1280 °C and 1300 °C are shown in Fig. 1. The samples are multi-phase, with a main crystal phase of MgTiO<sub>3</sub> (JCPDS#79-0831), and minor ones of CaTiO<sub>3</sub> (JCPDS#22-0153) and MgTi<sub>2</sub>O<sub>5</sub> (JCPDS#76-2673). In Fig.1, MgTi<sub>2</sub>O<sub>5</sub> is indexed in the XRD for 1300 °C, MgTiO<sub>3</sub> is indexed for 1280 °C and CaTiO<sub>3</sub> is indexed for 1260 °C. The formation of the impurity phase MgTi<sub>2</sub>O<sub>5</sub> is probably produced by the decomposition of MgTiO<sub>3</sub> [15],



With increasing sintering temperature, MgO may be partially dissolved in the near grain boundary region [15]. As a result, the XRD peak intensity of MgTi<sub>2</sub>O<sub>5</sub> increased with increasing sintering temperature. It is reported that MgTi<sub>2</sub>O<sub>5</sub> could not be fully eliminated when samples were prepared

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<sup>1</sup> model E8362B, Agilent, USA

<sup>2</sup> model N5250C, Agilent, USA

using conventional sintering [16]. The amount of ZnO and MgO is too small to be detected by XRD.

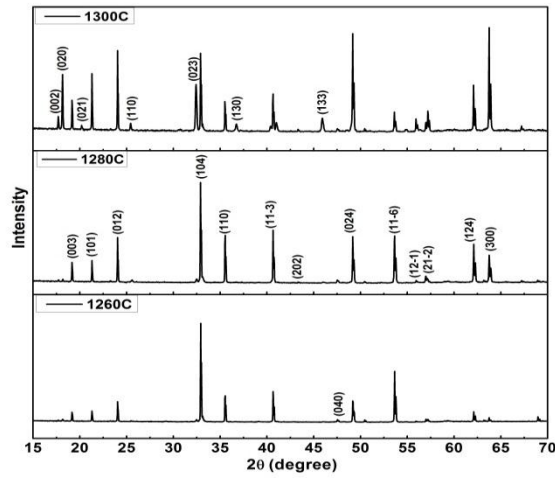


Fig. 1. XRD patterns of ceramics sintered at 1260 °C, 1280 °C and 1300 °C.  $\text{MgTi}_2\text{O}_5$  is indexed for 1300 °C;  $\text{MgTiO}_3$  is indexed for 1280 °C;  $\text{CaTiO}_3$  is indexed for 1260 °C.

Three different types of grains were observed in the ceramics sintered from 1260 °C to 1300 °C. An SEM micrograph and EDX analysis of the ceramic sintered at 1280 °C are shown in Fig. 2 and Table 1 respectively. According to the semi-quantitative molar ratio of Mg/Ti, the big block-shaped grains (1) were identified as  $\text{MgTiO}_3$  due to a Mg/Ti ratio of about 1:1. The small square block-shape grains (2) were identified as  $\text{CaTiO}_3$  due to a Ca/Ti ratio of about 1:1. Moreover, the small bar-shaped grains (3) were identified as  $\text{MgTi}_2\text{O}_5$  due to a Mg/Ti ratio of about 1:2.

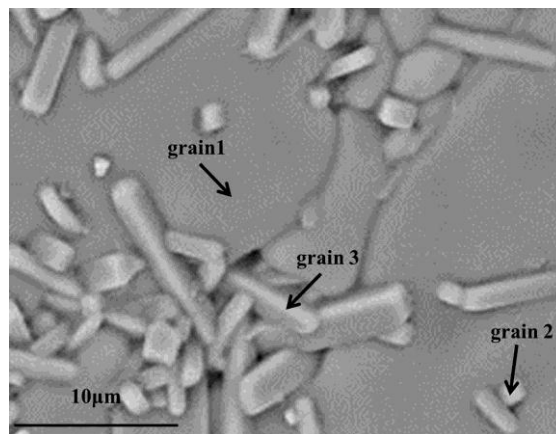


Fig. 2. SEM micrograph of ceramic sintered at 1280 °C.

Table 1 EDX analysis of ceramic sintered at 1280 °C

	grain 1	grain 2	grain 3
Molar ratio of Mg/Ti	0.97	0.96	0.52
composition	MgTiO <sub>3</sub>	CaTiO <sub>3</sub>	MgTi <sub>2</sub> O <sub>5</sub>

The microwave dielectric properties at 8.2 GHz for ceramics sintered at different temperatures are shown in Fig. 3. The improvement of microwave dielectric properties for samples sintered from 1240 °C to 1260 °C is attributed to the increase of the density. The maximum value of  $Q \times f = 91238$  GHz (8.2 GHz) and  $\epsilon = 20.5$  were obtained for the ceramic sintered at 1260 °C. The grain size increases with increasing sintering temperature so that the total area of the grain boundary is reduced, leading to an increase of the quality factor. However, the permittivity and  $Q \times f$  for samples sintered above 1260 °C both decreased. The reason for this is probably because of the increasing second phase content, as identified by XRD and SEM analysis rather than a grain size effect in the dense samples.

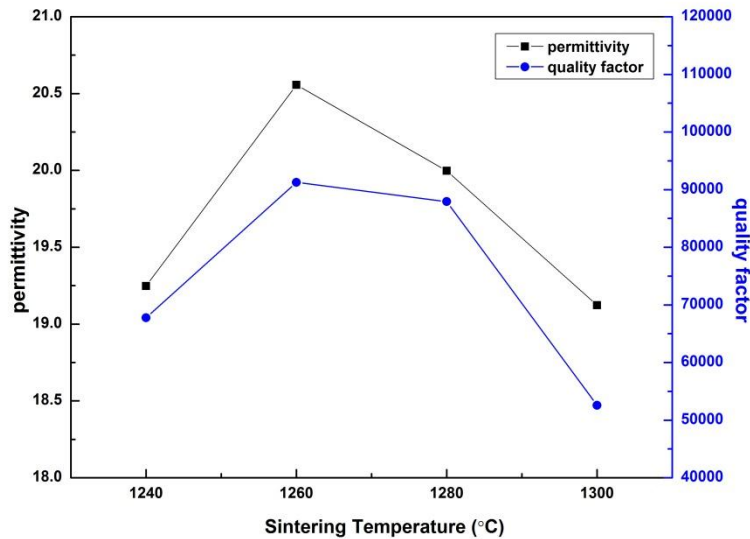


Fig. 3. Dielectric properties at 8.2 GHz of ceramics sintered at 1240 °C, 1260 °C, 1280 °C and 1300 °C.

The sample sintered at 1240 °C was eliminated from the THz investigation because of its low density

and low permittivity. According to the algorithm in the work of Yang et al [9], dielectric properties (permittivity and loss tangent) can be obtained through complex transmission spectra of ceramics measured over a broadband frequency domain, i.e. 0.22 to 0.32 THz. The permittivity of samples sintered at 1260 °C, 1280 °C and 1300 °C was around 18, exhibiting minimal dispersion. The dielectric losses of the samples varied significantly from 0.0019 (sintered at 1260 °C) to 0.0072 (sintered at 1300 °C) at 0.22 THz as shown in Fig. 4. This indicates that the MgTi<sub>2</sub>O<sub>5</sub> second phase had a strong influence on the increase of loss not only in the microwave frequency domain [17] but also in the THz frequency domain (Fig. 4).

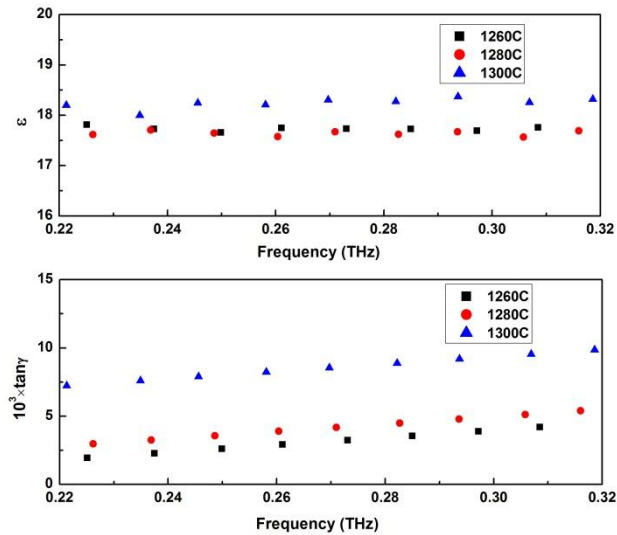


Fig.4. Calculated permittivity (top) and loss tangent (bottom) of ceramics sintered at 1260 °C, 1280 °C and 1300 °C in the frequency range 0.22 to 0.32 THz.

#### 4. Conclusion

Dielectric ceramics of 0.95MgTiO<sub>3</sub>-0.05CaTiO<sub>3</sub> were prepared via a solid-state reaction route. Optimized dielectric properties were obtained for samples sintered at 1260 °C, which is attributable to their high density and high purity. However, the dielectric properties of the ceramics deteriorated when

sintered above 1260 °C. This is attributed to the significantly increased content of second phase produced by ‘over’ sintering. It is evident that high permittivity and low loss are correlated to high density and high purity in the THz frequency domain.

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## References

- [1] Ferguson B, Zhang XC. Materials for terahertz science and technology. *Nat Mater* 2002;1:26-33.
- [2] McIntosh AI, Yang B, Goldup SM, Watkinson M, Donnan RS. Terahertz spectroscopy: a powerful new tool for the chemical sciences? *Chem Soc Rev*. 2012;41:2072-82.
- [3] Son J-H. Terahertz electromagnetic interactions with biological matter and their applications. *J Appl Phys*. 2009;105:102033.
- [4] Weightman P. Prospects for the study of biological systems with high power sources of terahertz radiation. *Phys Biol*. 2012;9:053001.
- [5] Koenig S, Lopez-Diaz D, Antes J, Boes F, Henneberger R, Leuther A, et al. Wireless sub-THz communication system with high data rate. *Nat Photonics*. 2013;7:977-81.
- [6] Nagel M, Först M, Kurz H. THz biosensing devices: fundamentals and technology. *J Phys: Condens Matter*. 2006;18:S601.
- [7] Al-Naib IAI, Jansen C, Koch M. Thin-film sensing with planar asymmetric metamaterial resonators. *Appl Phys Lett*. 2008;93:083507.
- [8] Zhu Y, Vegesna S, Kuryatkov V, Holtz M, Saed M, Bernussi AA. Terahertz bandpass filters using double-stacked metamaterial layers. *Opt Lett*. 2012;37:296-8.
- [9] Yang B, Wylde RJ, Martin DH, Goy P, Donnan RS, Carroopen S. Determination of the gyrotropic characteristics of hexaferrite ceramics from 75 to 600 GHz. *IEEE Trans Microwave Theory Tech*. 2010;58:3587-97.
- [10] Tomasino A, Parisi A, Stivala S, Livreri P, Cino A, Busacca A, et al. Wideband THz time domain spectroscopy based on optical rectification and electro-optic sampling. *Scientific reports*. 2013;3.
- [11] Wechsler BA, Von Dreele R. Structure refinements of Mg<sub>2</sub>TiO<sub>4</sub>, MgTiO<sub>3</sub> and MgTi<sub>2</sub>O<sub>5</sub> by time-of-flight neutron powder diffraction. *Acta Crystallogr Sect B: Struct Sci*. 1989;45:542-9.
- [12] Ferreira V, Azough F, Freer R, Baptista J. The effect of Cr and La on MgTiO<sub>3</sub> and MgTiO<sub>3</sub>-CaTiO<sub>3</sub> microwave dielectric ceramics. *J Mater Res*. 1997;12:3293-9.
- [13] Liou YC, Tsai WC, Yang SL. Synthesis of 0.95MgTiO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics by reaction-sintering. the proceedings of the 16th International conference on composite materials.
- [14] Wang Y, Yang B, Tian Y, Donnan RS, Lancaster MJ. Micromachined thick mesh filters for millimeter-wave and terahertz applications. *IEEE Trans on Terahertz Sci and Tech*. 2014;4:247-53.
- [15] Shin HK, Shin H, Cho SY, Hong KS. Phase Evolution and Dielectric Properties of MgTiO<sub>3</sub>-CaTiO<sub>3</sub>-Based Ceramic Sintered with Lithium Borosilicate Glass for Application to Low Temperature Co-Fired Ceramics. *J Am Ceram Soc*. 2005;88:2461-5.
- [16] Zhou X, Yuan Y, Xiang L, Huang Y. Synthesis of MgTiO<sub>3</sub> by solid state reaction and

characteristics with addition. *J Mater Sci.* 2007;42:6628-32.

[17] Huang CL, Pan CL, Shium SJ. Liquid phase sintering of MgTiO<sub>3</sub>-CaTiO<sub>3</sub> microwave dielectric ceramics. *Mater Chem Phys.* 2003;78:111-5.

### Figure caption

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