

Preparation and Properties of MCT Ceramics for RF and THz Applications

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Abstract — Dielectric ceramics of $0.95\text{MgTiO}_3\text{-}0.05\text{CaTiO}_3$ were prepared via a solid-state reaction method. It is evident that high permittivity and low loss are correlated to high density and high purity in the THz frequency domain. Best dielectric properties were obtained for samples sintered at $1260\text{ }^\circ\text{C}$, which is attributable to their high density and high purity. However, the dielectric properties of the ceramics deteriorated when sintered above $1260\text{ }^\circ\text{C}$, which is attributed to the significantly increased content of second phase produced by ‘over’ sintering.

Index Terms — Dielectric ceramics, THz application, resonators, filters.

I. INTRODUCTION

In the past ten years, Terahertz (THz) technology has demonstrated extraordinary prospects due to its attractive applications in material, chemical, communication and life sciences [1–5]. Portable, low loss and light weighted THz devices are developed, for example sensors [6], resonators [7] and filters [8], to accelerate applications of THz technologies. However, the lack of advanced materials in the THz band is a major limited factor. Although obvious progress has been achieved in the reliable measurement systems to test dielectric properties of materials in the THz band [9,10], systematic study on the materials with suitable dielectric properties was rarely reported. MgTiO_3 , chemically a rhombohedral structure with space group $R\bar{3}c$ [11], is a popular microwave material which displays a relatively low permittivity ($\epsilon_r=17$), high quality factor ($Q_f=160,000$ at 7GHz) and negative temperature coefficient of resonant frequency ($\tau_f=50\text{ ppm}/^\circ\text{C}$) [12]. Beside a high permittivity and quality factor, a near-zero temperature coefficient of resonant frequency is also demanded for commercial applications. It is found that with a small addition of 5mol% CaTiO_3 (orthorhombic structure with space group $Pbnm$) to the samples produces improved permittivity (21), quality factor ($Q_f=56,000$ at 7GHz) and near zero τ_f [12]. It is reported that MgTiO_3 and CaTiO_3 do not react into solid solutions but separate phases due to the different crystal structures [13]. In this paper, $0.95\text{MgTiO}_3\text{-}0.05\text{CaTiO}_3$ ceramics, i.e., MCT, were prepared under different sintering conditions. The effects of density, phase purity and microstructure on the dielectric properties of the samples were investigated in the THz spectral domain.

II. EXPERIMENTAL PROCEDURES

Ceramics of $0.95\text{MgTiO}_3\text{-}0.05\text{CaTiO}_3$ were prepared via a conventional solid-state reaction route, with chemical reagents of MgO (CP, 99%), CaCO_3 (CP, 99%) and TiO_2 (CP, 99%). The reagents were firstly weighed based on the stoichiometry of $0.95\text{MgTiO}_3\text{-}0.05\text{CaTiO}_3$. The mixed powder was then calcined at $1150\text{ }^\circ\text{C}$ for 2h with 1wt% of ZnO added as a sintering aid. Green bodies were pressed and sintered at different temperatures, $1240\text{ }^\circ\text{C}$, $1260\text{ }^\circ\text{C}$, $1280\text{ }^\circ\text{C}$ and $1300\text{ }^\circ\text{C}$ for 3h in air, respectively.

The crystal structures of the samples were identified with X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation (X’pert PRO, Panalytical, Holand). The microstructure of the specimens was observed by 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 ϵ_r , Q_f and τ_f , were measured with the parallel plate resonator method connected with a vector network analyzer (VNA) at 8.2GHz. The THz dielectric behavior of the samples between 0.22THz and 0.32THz were measured using a VNA2-driven quasi-optical transmission meter [14].

III. RESULTS AND DISCUSSION

The density of ceramics sintered at $1240\text{ }^\circ\text{C}$, $1260\text{ }^\circ\text{C}$, $1280\text{ }^\circ\text{C}$ and $1300\text{ }^\circ\text{C}$ were determined to be $3.778\text{g}/\text{cm}^3$, $3.790\text{g}/\text{cm}^3$, $3.790\text{g}/\text{cm}^3$ and $3.790\text{g}/\text{cm}^3$, respectively. The apparent density increased with increasing sintering temperature and a near constant density was achieved for samples sintered above $1260\text{ }^\circ\text{C}$. The XRD patterns of dense ceramics sintered at $1260\text{ }^\circ\text{C}$, $1280\text{ }^\circ\text{C}$ and $1300\text{ }^\circ\text{C}$ are shown in Fig. 1. The samples are multi-phase, with a main crystal phase of MgTiO_3 (JCPDS#79-0831), and minor ones of CaTiO_3 (JCPDS#22-0153) and MgTi_2O_5 (JCPDS#76-2673). In Fig. 1, MgTi_2O_5 is indexed in the XRD for $1300\text{ }^\circ\text{C}$, MgTiO_3 is indexed for $1280\text{ }^\circ\text{C}$ and CaTiO_3 is indexed for $1260\text{ }^\circ\text{C}$. The formation of the impurity phase MgTi_2O_5 is

possibly resulted from the decomposition of $MgTiO_3$ [15]. With increasing sintering temperature, MgO maybe partially dissolved in the near region of grain boundary [15]. Therefore, the XRD peak intensity of $MgTi_2O_5$ increased with increasing sintering temperature. It is reported that $MgTi_2O_5$ could not be fully eliminated when ceramics were prepared using conventional sintering [16]. Here, the amount of ZnO and MgO is too small to be detected by XRD.

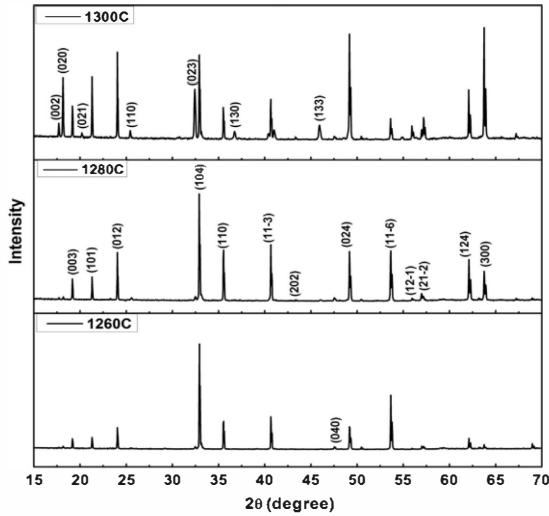


Fig. 1 XRD patterns of ceramics sintered at 1260 °C, 1280 °C and 1300 °C for 3h. Here, $MgTi_2O_5$ is indexed for 1300 °C, $MgTiO_3$ is for 1280 °C, and $CaTiO_3$ is only for 1260 °C.

Three different shapes of grains were observed in the ceramics sintered from 1260 °C to 1300 °C for 3h. An SEM image in addition to EDX analysis, of the ceramic sintered at 1280 °C is demonstrated in Fig. 2. According to the semi-quantitative molar ratio of Mg/Ti and Ca/Ti , the big block-shaped grains(1) were identified as $MgTiO_3$ due to a Mg/Ti ratio (0.97) of about 1:1. The small square block- shape grains(2) were identified as $CaTiO_3$ due to a Ca/Ti ratio (0.96) of about 1:1. Moreover, the small bar-shaped grains(3) were identified as a $MgTi_2O_5$ due to Mg/Ti ratio (0.52) of about 1:2.

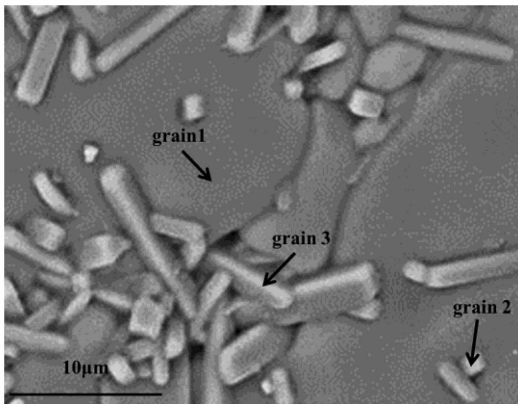


Fig. 2 SEM image of ceramic sintered at 1280 °C for 3h.

The microwave dielectric properties at 8.2GHz for ceramics sintered at different temperatures are revealed in Fig. 3. The improvement of microwave dielectric properties for samples sintered from 1240 °C to 1260 °C for 3h is attributed to the increase of the density. The maximum value of $Qf=91,238GHz$ (at 8.2GHz) and $\epsilon_r=20.5$ 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 Qf for samples sintered above 1260 °C both decreased. The reason for this is probably due to the increasing second phase content, as identified by XRD and SEM analysis, rather than a grain size effect in the dense samples. 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 broad frequency domain, i.e. 0.22THz to 0.32THz. The permittivity of ceramics sintered at 1260 °C, 1280 °C and 1300 °C for 3h were 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 0.22THz as displayed in Fig. 4. This indicates that the $MgTi_2O_5$ second phase had a obvious influence on the increase of loss not only in the microwave frequency domain [17] but also in the THz frequency domain (Fig. 4).

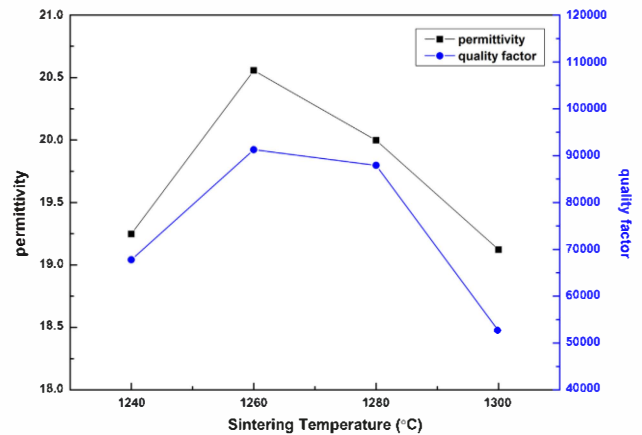


Fig. 3 Dielectric properties at 8.2GHz of ceramics sintered at 1240 °C, 1260 °C, 1280 °C and 1300 °C for 3h.

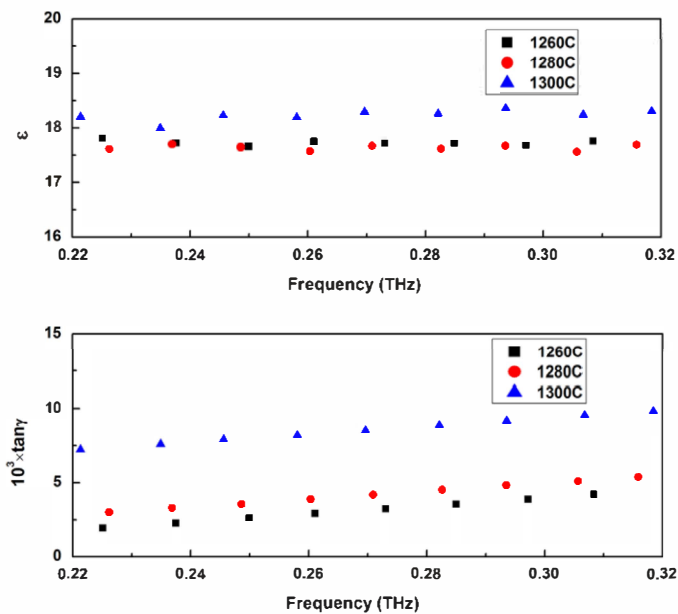


Fig. 4 Calculated permittivity (top) and loss tangent (bottom) of ceramics sintered at 1260 °C, 1280 °C and 1300 °C for 3h in the frequency range 0.22THz to 0.32THz.

IV. CONCLUSION

Dielectric ceramics of $0.95\text{MgTiO}_3\text{-}0.05\text{CaTiO}_3$ were prepared via a solid-state reaction method. Best dielectric properties were achieved for samples sintered at 1260 °C for 3h, which is attributable to their high density and high purity. However, the dielectric properties of the samples deteriorated when sintered above 1260 °C. This is attributed to the significantly increased content of second phase due to ‘over’ sintering of samples. 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] B. Ferguson, X.C. Zhang, “Materials for Terahertz Science and Technology,” *Nat. Mater.*, vol.1, pp.26-33, 2002.
- [2] Al McIntosh, B. Yang, S.M. Goldup, M. Watkinson, R.S. Donnan, “Terahertz Spectroscopy: a Powerful New Tool for the Chemical Sciences? ”, *Chem. Soc. Rev.*, vol.41, pp. 2072–2082, 2012.
- [3] J.H. Son, “Terahertz electromagnetic interactions with biological matter and their applications,” *J. Appl. Phys.*, vol.105, pp:102033, 2009.

- [4] P.Weightman, “Prospects for the study of biological systems with high power sources of terahertz radiation,” *Phys. Biol.*, vol. 9, pp:053001, 2012.
- [5] S. Koenig, D. Lopez-Diaz, J. Antes, F. Boes, R. Henneberger, A. Leuther, et al, “Wireless sub-THz communication system with high data rate,” *Nat. Photonics*, vol. 7, pp: 977–981, 2013.
- [6] M. Nagel, M. Först, H. Kurz, “THz biosensing devices: fundamentals and technology,” *J. Phys. Condens. Matter.*, vol.18, pp: S601, 2006.
- [7] I. Al-Naib, C. Jansen, M. Koch, “Thin-film sensing with planar asymmetric metamaterial resonators,” *Appl. Phys. Lett.*, vol. 93, pp: 083507, 2008.
- [8] Y. Zhu, S.Vegesna, V. Kuryatkov, M. Holtz, M. Saed, A.A. Bernussi, “Terahertz bandpass filters using double-stacked metamaterial layers,” *Opt. Lett.*, vol. 37, pp:296–298, 2012.
- [9] B. Yang, R.J. Wylde, D.H. Martin, P. Goy, R.S. Donnan, S. Caroopen, “Determination of the gyrotropic characteristics of hexaferrite ceramics from 75 to 600GHz,” *IEEE Trans. Microwave Theory Tech.*, vol.58, pp:3587–3597, 2010.
- [10] A. Tomasino, A. Parisi, S. Stivala, P. Liveri, A. Cino, A. Busacca, et al., “Wide band THz time domain spectroscopy based on optical rectification and electro-optic sampling,” *Sci. Rep.*, pp:3, 2013.
- [11] B.A. Wechsler, R. VonDreele, “Structure refinements of Mg_2TiO_4 , MgTiO_3 and MgTi_2O_5 by time-of-flight neutron powder diffraction,” *Acta. Crystallogr., Sect B: Struct. Sci.*, vol.45, pp:542–549, 1989.
- [12] V. Ferreira, F. Azough, R. Freer, J. Baptista, “The effect of Cr and La on MgTiO_3 and $\text{MgTiO}_3\text{-CaTiO}_3$ microwave dielectric ceramics”, *J. Mater. Res.*; vol.12, pp:3293–3299, 1997.
- [13] Y.C. Liou, W.C. Tsai, S.L. Yang, “Synthesis of $0.95\text{MgTiO}_3\text{-}0.05\text{CaTiO}_3$ ceramics by reaction-sintering,” *The proceedings of the 16th international conference on composite materials*.
- [14] Y. Wang, B. Yang, Y. Tian, R.S. Donnan, M.J. Lancaster, “Micromachined thick mesh filters for millimeter-wave and terahertz applications”, *IEEE Trans. Terahertz Sci. Tech.*, vol.4, pp:247–253, 2014.
- [15] H.K. Shin, H. Shin, S.Y. Cho, K.S. Hong, “Phase evolution and dielectric properties of $\text{MgTiO}_3\text{-CaTiO}_3$ - based ceramic sintered with lithium borosilicate glass for application to low temperature co - fired ceramics”, *J. Am. Ceram. Soc.*, vol.88, pp:2461–2465, 2005.
- [16] X. Zhou, Y. Yuan, L. Xiang, Y. Huang, “Synthesis of MgTiO_3 by solid state reaction and characteristics with addition”, *J. Mater. Sci.*, vol.42, pp:6628–6632, 2007.
- [17] C.L. Huang, C.L. Pan, S.J. Shium, “Liquid phase sintering of $\text{MgTiO}_3\text{-CaTiO}_3$ microwave dielectric ceramics”, *Mater. Chem. Phys.*, vol.78, pp:111–115, 2003.