Preparation and Properties of MCT Ceramics for RF and THz Applications

Zhaoxian Xiong*, Zhangzhao Weng*, Jinbao Huang*, Bin Yang#, R. Donnan#, Haixue Yan and M.J. Reece*
*Department of Materials Science and Engineering, Xiamen University, Xiamen 361005, China
#School of Electronic Engineering, Queen Mary University of London, London E14NS, UK
School of Engineering and Material Sciences, Queen Mary University of London, London E1 4NS, UK
*Email: zxxiong@xmu.edu.cn

Abstract — Dielectric ceramics of 0.95MgTiO₃-0.05CaTiO₃ 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 °C, which is attributable to their high density and high purity. However, the dielectric properties of the ceramics deteriorated when sintered above 1260 °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. MgTiO₃, chemically a rhombohedral structure with space group R3c [11], is a popular microwave material which displays a relatively low permittivity ($\varepsilon_r=17$), high quality factor ($Q_f=160,000$ at 7GHz) and negative temperature coefficient of resonant frequency ($\tau_f=50$ ppm/°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% CaTiO₃ (orthorhombic structure with space group Pbnm) to the samples produces improved permittivity (21), quality factor ($Q_f=56,000$ at 7GHz) and near zero $\tau_f$ [12]. It is reported that MgTiO₃ and CaTiO₃ do not react into solid solutions but separate phases due to the different crystal structures [13]. In this paper, 0.95MgTiO₃-0.05CaTiO₃ 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 PROCEDURE

Ceramics of 0.95MgTiO₃-0.05CaTiO₃ were prepared via a conventional solid-state reaction route, with chemical reagents of MgO (CP, 99%), CaCO₃ (CP, 99%) and TiO₂ (CP, 99%). The reagents were firstly weighed based on the stoichiometry of 0.95MgTiO₃-0.05CaTiO₃. The mixed powder was then calcined at 1150 °C for 2h with 1wt% of ZnO added as a sintering aid. Green bodies were pressed and sintered at different temperatures, 1240 °C, 1260 °C, 1280 °C and 1300 °C for 3h in air, respectively.

The crystal structures of the samples were identified with X-ray diffraction (XRD) using CuKα radiation (X’pert PRO, Panalytical, Holand). The microstructure of the specimens was observed by a scanning electron microscope (SEM, TM-3000, Hitachi, Japan). Energy-Dispersive X-ray spectroscopy (EDX, Oxford instrument) was used to perform the element analysis. Densities were obtained using the Archimedes’ method. Microwave dielectric properties of the ceramics, including $\varepsilon_r$, $Q_f$ and $\tau_f$, 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 °C, 1260 °C, 1280 °C and 1300 °C were determined to be 3.778g/cm³, 3.790g/cm³, 3.790g/cm³ and 3.790g/cm³, respectively. The apparent density increased with increasing sintering temperature and a near constant density was achieved for samples sintered above 1260 °C. The XRD patterns of dense ceramics 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 MgTiO₃ (JCPDS#79-0831), and minor ones of CaTiO₃ (JCPDS#22-0153) and MgTi₂O₅ (JCPDS#76-2673). In Fig. 1, MgTiO₃ is indexed in the XRD for 1300 °C, MgTi₂O₅ is indexed for 1280 °C and CaTiO₃ is indexed for 1260 °C. The formation of the impurity phase MgTi₂O₅ is
possibly resulted from the decomposition of MgTiO₃ [15]. With increasing sintering temperature, MgO maybe partially dissolved in the near region of grain boundary [15]. Therefore, the XRD peak intensity of MgTi₂O₅ increased with increasing sintering temperature. It is reported that MgTi₂O₅ 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, MgTi₃O₇ is indexed for 1300 °C, MgTiO₃ is for 1280 °C, and CaTiO₃ 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 MgTiO₃ due to a Mg/Ti ratio (0.97) of about 1:1. The small square block-shaped grains(2) were identified as CaTiO₃ due to a Ca/Ti ratio (0.96) of about 1:1. Moreover, the small bar-shaped grains(3) were identified as a MgTi₂O₅ due to Mg/Ti ratio (0.52) of about 1:2.

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 εᵣ=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 band 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 MgTi₂O₅ 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. 2 SEM image of ceramic sintered at 1280 °C for 3h.

Fig. 3 Dielectric properties at 8.2GHz of ceramics sintered at 1240 °C, 1260 °C, 1280 °C and 1300 °C for 3h.
Dielectric ceramics of $0.95\text{MgTi}_3\text{O}_7-0.05\text{CaTi}_3\text{O}_7$ were prepared via a solid-state reaction method. Best dielectric properties were achieved for samples sintered at $1260^\circ\text{C}$ for $3\text{h}$ in the frequency range $0.22\text{THz}$ to $0.32\text{THz}$.

IV. CONCLUSION

Dielectric ceramics of $0.95\text{MgTi}_3\text{O}_7-0.05\text{CaTi}_3\text{O}_7$ were prepared via a solid-state reaction method. Best dielectric properties were achieved for samples sintered at $1260^\circ\text{C}$ for $3\text{h}$, which is attributable to their high density and high purity. However, the dielectric properties of the samples deteriorated when sintered above $1260^\circ\text{C}$. 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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