Terahertz Dielectric Properties of MgO-TiO_2-ZnO Based Ceramics

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Abstract—We investigated terahertz dielectric properties of MgO-TiO_2-ZnO based ceramics using a THz-TDS system. Doped with Ca^{2+}, the decrease in tetragonality (*c/a*) of pervoskite structure and porisity lead to an increase in refractive index, meanwhile, power absorption is enhanced due to the $CaTiO_3$ phase and small grains microstructure, which result in an increase in both the real and imaginary parts of dielectric constant.

I. INTRODUCTION

Microwave dielectric, MgO-TiO_2-ZnO(MTZ) based ceramics have been widely investigated due to their high dielectric constant ($\varepsilon \geq 40$), high Q ($Q \geq 10000$) and positive temperature coefficient in microwave range. Usually, $CaTiO_3$ was added for obtaining zero temperature coefficient ceramics (MTZC), and the sintering temperature was dramatically decreased [1].

However, the dielectric properties of MTZ based ceramics in terahertz range have not yet been measured. This paper reports an experimental investigation of the terahertz dielectric properties of MTZ based ceramics, which depend on the lattice parameters and microstructure of ceramics.

II. EXPERIMENT/RESULTS

Calcined $CaTiO_3$ was fabricated with reagent-grade $CaCO_3$ and TiO_2. The powders were ball milled in deionized water for 4.5h, dried and synthesized at 1290 ºC for 6h.

Reagent-grade $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, TiO_2, ZnO were used as the starting materials. Calcined MgO-TiO_2-ZnO were prepared according to (5~7mol%) $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ +(50~70mol%)TiO_2 + (25~35mol%) ZnO. The powders were ball milled in deionized water for 4.5h, dried and synthesized at 1290 ºC for 6h.

The MTZ and MTZC samples were fabricated by a conventional ceramic processing technique with powders of calcined MgO-TiO_2-ZnO and (0 or 0.5mol%) calcined $CaTiO_3$. The mixed powders were ball milled in deionized water for 4.5h, and dried, sieved, then pressed into disks with 15mm diameter, then sintered at 1350 ºC and 1290 ºC, respectively.

The phases existed in ceramics were examined using an X-ray diffractometer (XRD, Rigaku 2038X) with Cu Ka radiation (λ=0.15406nm) at a step width of 0.02˚ and a scan rate of 2˚/min. The surface microstructure of sintered samples was observed with Scanning Electron Microscopy (SEM, Philips XL 30). The THz properties of MTZ based ceramics were characterized by a broadband, photoconductive switch based THz-TDS system with 8-F confocal optical geometry.

Fig. 1 shows X-ray analysis of MTZ and MTZC. $MgTiO_3$, $ZnTiO_3$, $Zn_2Ti_3O_8$ and TiO_2 were formed in both samples, and $CaTiO_3$ is observed in MTZC. Pervoskite structure composite $MgTiO_3$, $ZnTiO_3$, $CaTiO_3$ can form partial solid solution. The radius of Ca^{2+}(100pm) is much larger than that of Mg^{2+}(72pm) and Zn^{2+}(74pm). Ca^{2+} ion is substituted for A-site in ABO_3 structure. Thus, Ca^{2+} doping decreases tetragonality (*c/a*) by increasing *a* and decreasing *c*.

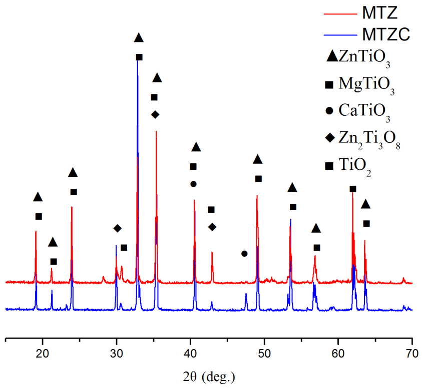

Fig. 1. XRD patterns of MTZ and MTZC ceramics.

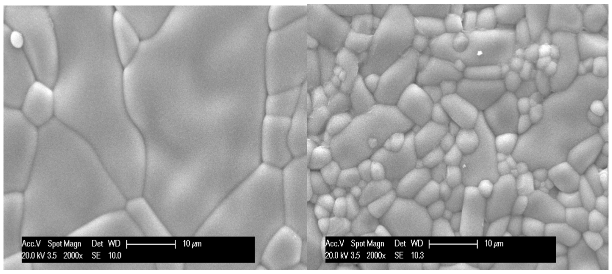

Fig. 2. SEM images of MTZ and MTZC ceramics (2000×).

Fig.2(a), (b) show SEM images of MTZ and MTZC ceramics respectively, the grains of MTZ and MTZC were well crystallized with smooth surface and clear boundaries. The grain size of MTZC was much smaller than that of MTZ. The reduction in grain size could be explained by that $CaTiO_3$ can form the grain-growth-inhibiting phases at the grain boundaries during the sintering process.

During the sintering process, $CaTiO_3$ were formed liquid phase due to the high sintering temperature above 1290ºC. The liquid phase enhances the ion diffusion via dissolution and reprecipitation process, and the densification of ceramics was accelerated, so the ceramics become quite dense and almost no air pore could be found. Compared with MTZ, the porosity of MTZC is decreased. The sintering ability of ceramics was enhanced, the sintering temperature of MgO-TiO_2-ZnO-based ceramics was significantly reduced from 1350 ºC to 1290 ºC.

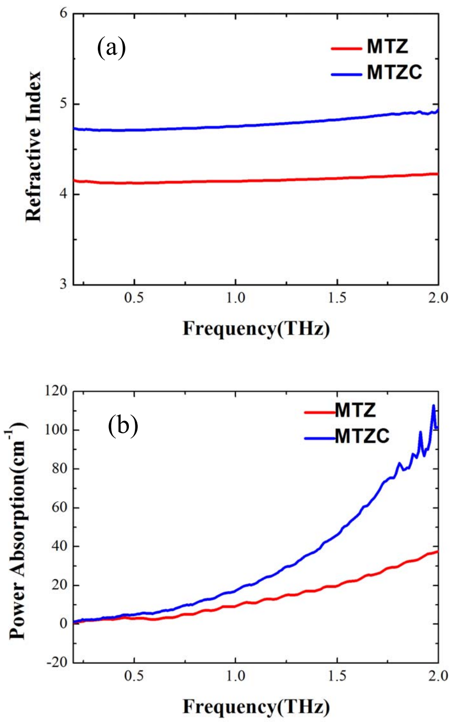

Fig. 3.Comparison of the measured results of (a) refractive index, *n*(ω), and (b) power absorption, *α*(ω).

The measured refractive index, $n(\omega)$, and power absorption coefficient, $\alpha(\omega)$, of two samples, were obtained from the Fourier-transformed spectra of the measured THz time domain pulses. $n(\omega)$ of MTZ is ~4.2, while $n(\omega)$ of MTZC is ~4.7, and $n(\omega)$ of both ceramics show a comparatively smooth feature below 2 THz. Doped with Ca^{2+}, the reason of the increase in $n(\omega)$ could be explained as follows: Ca^{2+} doping change the crystal lattice of ceramics, that is the increase of *a* and decrease of *c*, and result in the decrease of tetragonality (*c/a*). So polarisability of the ceramics is altered, the refractive index is changed accordingly. As shown in Fig.2, the porosity of MTZC is decreased, which also result in enhancement of $n(\omega)$, because porosity introduces an effective average refractive index which is lower than that of fully dense material[2].

In Fig. 3(b) plots the $\alpha(\omega)$ of MTZ and MTZC, and large differences in total loss are observed. This suggests that the loss mechanism is related to absorption of $CaTiO_3$. The increase $\alpha(\omega)$ of MTZC could also attribute to the small grain size. The $\alpha(\omega)$ of the MTZ is extremely low and less than $10cm^{-1}$ in magnitude below 1THz. It is evident that the MZT exhibits a good transparency to terahertz radiation below 1THz, which makes it a good choice as a transparent material for terahertz application.

Through the relations, $\varepsilon_r = n^2-(\alpha\lambda_0/(4\pi))^2$ and $\varepsilon_i = \alpha n\lambda_0/(2\pi)$, the complex dielectric functions were obtained with the real and imaginary parts presented in Figs. 4(a) and 4(b), respectively[3]. Doped with Ca^{2+}, both the real and imaginary parts of dielectric constant are increased according to the equation of ε_r and ε_i equation.

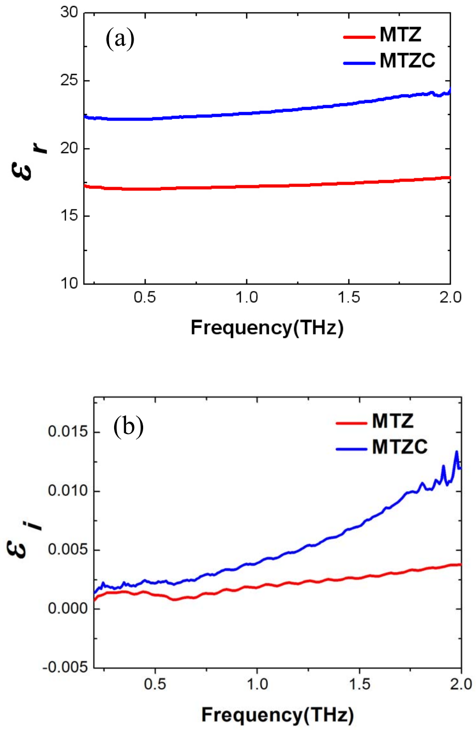

Fig. 4. Complex dielectric function of MTZ and MTZC ceramics: (a)measured real part, $\varepsilon_r(\omega)$, and (b) imaginary part, $\varepsilon_i(\omega)$.

III. SUMMARY

Doped with Ca^{2+}, the decrease in tetragonality (*c/a*) of pervoskite structure and porosity lead to the increase in $n(\omega)$. And microstructure of ceramics has great influence on the $\alpha(\omega)$. The terahertz dielectric properties of ceramics can be modified by the variation of the lattice parameters and microstructure. Terahertz dielectric properties of ceramics in the range from 0.2 to 2 THz are as following: ε_r of MTZ is ~16.5, ε_i of MTZ is less than 0.005; while ε_r of MTZC is ~ 22.5, ε_i of MTZC is less than 0.015.

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