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ScienceDirect
Ceramics International 38S (2012) S61–S64
CERAMICS INTERNATIONAL
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The structure and properties of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics co-doped with ZnO–ZrO_2

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Available online 30 April 2011

Abstract

The $(Mg_{0.93}Ca_{0.05}Zn_{0.02})(Ti_{1-x}Zr_x)O_3$ ceramics were prepared by conventional solid-state route. The dielectric properties and structure of $(Mg_{0.93}Ca_{0.05}Zn_{0.02})(Ti_{1-x}Zr_x)O_3$ ceramics were investigated. It has been found that $MgTiO_3$ and $CaTiO_3$ are the main phases and a second phase $CaZrTi_2O_7$ appeared in 95MCT ceramics co-doped with Zn–Zr. With Zn–Zr additive, the sintering temperature of 95MCT ceramics can be reduced to 1300 °C, and adjust the temperature coefficient of dielectric constant. With the increasing of Zr content, dielectric constant ε_r decrease from 22.6 to 19.91 and the temperature coefficient of dielectric constant α_c from 5.93 to 2.52 ppm/°C when $x = 0.01$, 0.02, 0.03 and 0.04 mol respectively. The 95MCT ceramics with $x = 0.02$ has a dielectric constant ε_r of 22.02, a dielectric loss of 2.78×10^{-4} and a temperature coefficient of dielectric constant α_c value of 2.98 ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; Magnesium titanates; C. Temperature coefficient

1. Introduction

$MgTiO_3$–$CaTiO_3$ based ceramics (hereafter referred to as MCT) finds wide variety applications in temperature compensating type capacitor, dielectric resonator and patch antenna. The materials are made of a mixture of $MgTiO_3$ ($\varepsilon_r \sim 17$ and $\tau_f \sim -50$ ppm/°C) and $CaTiO_3$ ($\varepsilon_r \sim 170$ and $\tau_f \sim 800$ ppm/°C) [1,2]. With a ratio of Mg:Ca = 95:5 (denoted as 95MCT), it exhibits the dielectric properties of $\varepsilon_r \sim 20$–21 and $\tau_f \sim 0$ ppm/°C. However, 95MCT ceramics required sintering temperatures as high as 1400–1500 °C. Many researchers made efforts to study the microstructures and the dielectric properties of the 95MCT (Mg:Ca = 95:5) ceramics with various additives. Such as the substitution of Zn^{+2} ions for Mg^{+2} ion of MCT ceramics could effectively lower the sintering temperature of ceramics and improve dielectric properties [3–6]. Some sintering aids with low melting point such as B_2O_3, V_2O_5, CuO and Bi_2O_3 lower the sintering temperature of ceramics due to the liquid phase effect [7–10].

The structure and dielectric properties of MCT ceramics co-doped with ZnO and ZrO_2, Zn^{2+} and Zr^{2+} ions substituting for Mg^{2+} and Ti^{2+} respectively, were investigated in this paper at low frequency because the relationships of dielectric properties vs. temperature and frequency could be conveniently investigated at low frequency.

2. Experimental procedures

$(Mg_{0.93}Ca_{0.05}Zn_{0.02})(Ti_{1-x}Zr_x)O_3$ ceramics were prepared by the conventional mixed oxides route (where $x = 0.01$, 0.02, 0.03 and 0.04 mol respectively). The starting reagents were pure $MgCO_3$, $CaCO_3$, TiO_2, ZrO_2 and ZnO (>99.5%). The weighed batches were wet mixed in distilled water for 8 h. After drying, the powders were calcined at 1000 °C for 150 min. The calcined powders were mixed again, dried, and the disks were pressed uniaxially at 300 MPa with 5 wt% PVA solution added as binder. The pellets were sintered at 1200–1350 °C for 150 min.

Disk densities were evaluated using Archimedes principle. Crystal structure was characterized by powder X-ray diffraction (XRD, D/MAX-1200, Cu Kα radiation ($\lambda = 1.5406$ Å), $20 \leq 2\theta \leq 80°$, 0.03°/s). Microstructure studies were performed by scanning electron microscopy (SEM)

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0272-8842/$36.00 © 2011 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2011.04.050

(JSM-5900LV). The dielectric constant and loss of the ceramics were measured using an Agilent4284A.

3. Results and discussion

The X-ray diffraction (XRD) patterns of MCT ceramics with different contents of ZrO_2 are shown in Fig. 1. It gives mixed phases of $MgTiO_3$ as the main phase associated with $CaTiO_3$. Second phase $MgTi_2O_5$, usually formed as an intermediate phase during the growth, was identified in 95MCT ceramics without any additives. Second phase $MgTi_2O_5$ decrease dramatically when ZnO–ZrO_2 doped in 95MCT ceramics. These results suggested that ZnO–ZrO_2 addition effectively inhibits the formation of second phase. However the amount of ZrO_2 increase, another phase $CaZrTi_2O_7$ was detected. The d-spacing of (1 0 4) lattice plane was found to slowly increase as a function of composition from 2.7112 to 2.84411 as x = from 0.01 to 0.04. It suggests that it would increase in lattice parameters due to the larger ion radius of Zr^{4+} (0.072 nm) in place of Ti^{4+} (0.0605 nm).

The density of MCT ceramics with various amounts of ZrO_2 vs. the sintering temperature are shown in Fig. 2. The density of 95MCT ceramics without any additive is 3.7 g.cm^{-3}, 95.8% of theoretical density at sintering temperature above 1400 °C. The density of the MCT ceramics doped with Zn/Zr increased with increasing sintering temperature and a maximum density of 3.8 g cm^{-3} (98.4% of theoretical density) was obtained sintered at 1300 °C for x = 0.02. The increase in the density compared with 95MCT ceramics without any additive was due to the elimination of pores. However, it slightly decreased with the increasing of x due to abnormal grain growth observed in Fig. 3. ZnO–ZrO_2 as additives could effectively promote the densification of the MCT ceramics due to the forming of liquid phase. The liquid phase effect had been observed in MCT ceramics doped with ZnO by Huang et al. who claimed the pores were almost eliminated for MCT ceramics with ZnO addition due to the effect of liquid phase [4,5]. ZrO_2 could enhance the liquid phase effect in MCT ceramics doped with ZnO showed in Fig. 3(d).

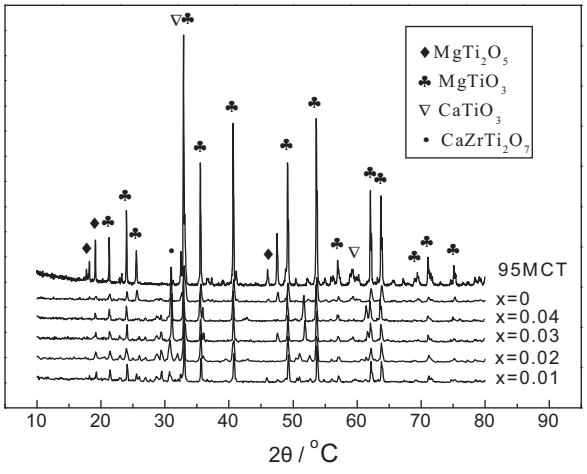

Fig. 1. X-ray diffraction (XRD) patterns of MCT ceramics with different amount of ZrO_2.

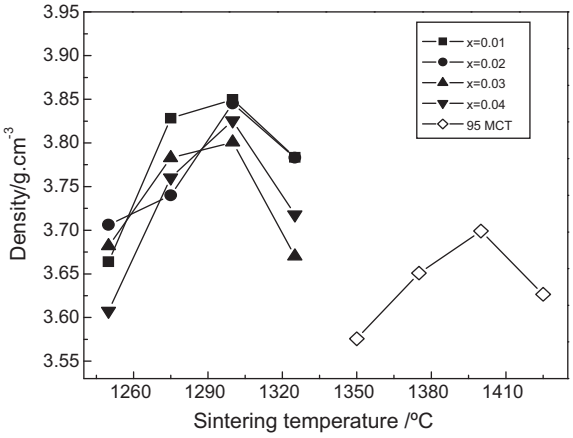

Fig. 2. Density sintering dependence of temperature for MCT ceramics.

The SEM photographs of MCT ceramics doped with various amounts of ZrO_2 (ZnO = 0.02 mol) addition at sintering temperature 1300 °C are illustrated in Fig. 3 (a)–(d). The pores in the ceramics were almost eliminated for specimen sintered at 1300 °C and the grain growth increased with the increasing of x. However, inhomogeneous grain growth can be clearly observed at the sintering temperature of 1300 °C as x = 0.04 mol, which might degrade the density. This is in accordance with the density. When x = 0.02 mol, no pore and inhomogeneous grain growth exist. Liquid phase clearly appeared in MCT ceramics as x = 0.04 mol, which results in the grain growth shown in Fig. 3(d). The SEM photographs of MCT ceramics co-doped with ZnO and ZrO_2 (both 0.02 mol) sintering at different sintering temperature are shown in Fig. 3(e)–(f). It can be seen some pores exist in ceramics as sintering temperature at 1250 °C and 1325 °C compared with 1300 °C and the compact ceramic could be obtained at the sintering temperature of 1300 °C in Fig. 3(b).

The dielectric constant of ceramics decreases from 22.6 to 19.91 as x increases from 0.01 mol to 0.04 mol and the dielectric loss is 2.78 × 10^{-4} when x = 0.02 mol at 1 MHz. The ion radius of Zr^{4+} (0.072 nm) is larger than Ti^{4+} (0.0605 nm), which will result in the distortion of oxygen octahedra. Small ion will move easily in oxygen octahedra at the presence of an external electrical field. The reduction of the mobility of the larger ion corresponds to the decrease of polarizability and dielectric constant. The frequency temperature coefficient of materials for microwave devices mainly attributes to the temperature coefficient of dielectric constant which can be defined as α_c:

$$\alpha_c = \frac{\varepsilon_2 - \varepsilon_1}{(T_2 - T_1)\varepsilon_1} \quad (1)$$

where ε_1 and ε_2 represent the dielectric constant at T_1 and T_2 respectively and T_1 = −20 °C, T_2 = 120 °C. α_c values are 4.69, 2.98, 2.65 and 2.52 ppm/°C when x = 0.01, 0.02, 0.03 and 0.04 mol respectively. It showed that α_c value decreases with the increasing of x, which suggested ZrO_2 could adjust the temperature coefficient of dielectric constant. This could be considered as the distortion of oxygen octahedral and the change of polarizability [11].

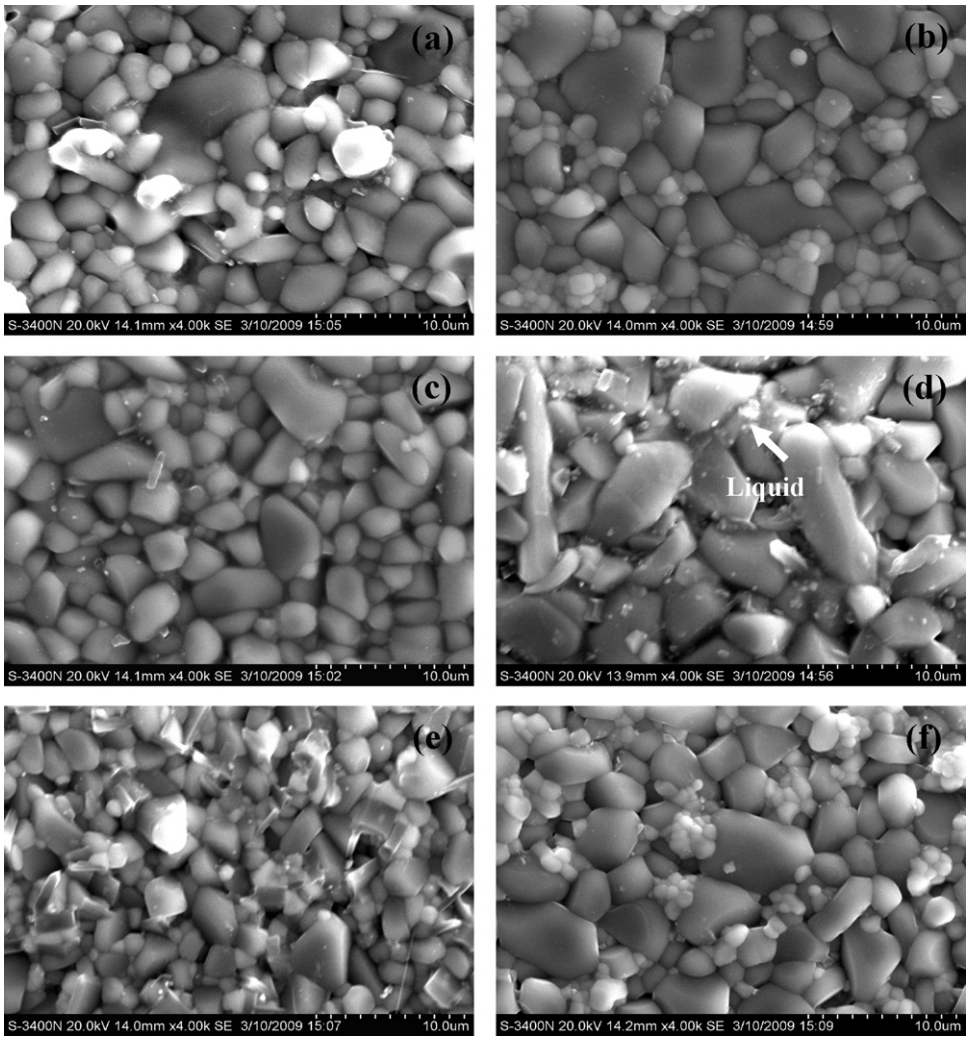

Fig. 3. SEM photographs of MCT ceramics (a) $x = 0.01$ mol, (b) $x = 0.02$ mol, (c) $x = 0.03$ mol, (d) $x = 0.04$ mol at sintering temperature 1300 °C, (e) $x = 0.02$ mol at sintering temperature 1250 °C, (f) $x = 0.02$ mol at sintering temperature 1325 °C.

The frequency dependencies of dielectric loss for MCT ceramics at the frequency of 100 Hz to 1 MHz are illustrated in Fig. 4. The results showed that the dielectric loss is higher for $x = 0.01$ and 0.04 mol than for $x = 0.02$ and 0.03 mol due to the porosity in the ceramics. As can be seen, the dielectric loss of ceramics at $x = 0.01$ and 0.04 mol increases at low frequency. The increase of dielectric loss is most likely due to conductive loss at low frequency. The pores, inhomogeneous grain growth or low density could lead to conductive loss, which corresponds to the dielectric loss at low frequency [12]. The temperature

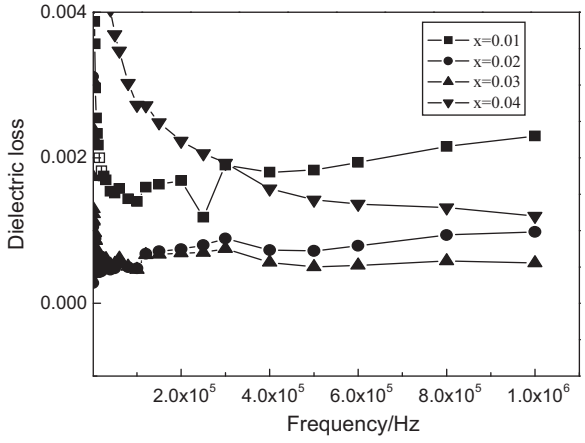

Fig. 4. Frequency dependence of dielectric loss for MCT ceramics.

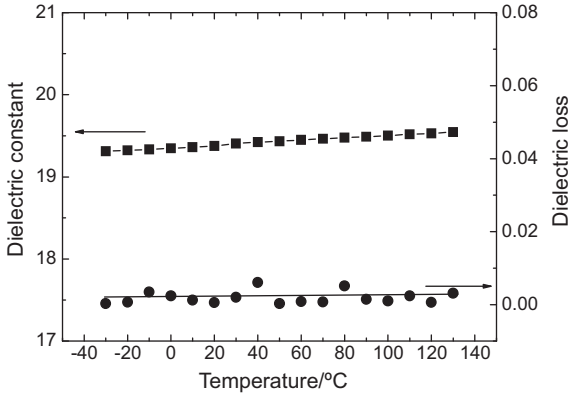

Fig. 5. The dielectric constant and loss vs. temperature for MCT ceramics as $x = 0.02$ mol (at 1 MHz).

dependencies of dielectric constant and loss for MCT ceramics as $x = 0.02$ mol at 1 MHz are illustrated in Fig. 5. It can be seen that the dielectric constant and loss are stable, especially the dielectric loss is almost independent of temperature in the temperature range of −30 to 130 °C. So it can be considered that the conductive loss results from electronic conduction, not due to ionic conduction [12]. The electronic conduction may be linked to the second phase $CaZrTi_2O_7$ [13] or the space charge in the pores.

4. Conclusions

The structure and dielectric properties of MCT ceramics co-doped with ZnO and ZrO_2 have been examined. Second phase $MgTi_2O_5$ could be effectively inhibited by doping with ZnO–ZrO_2, but another phase $CaZrTi_2O_7$ would form when the amount of ZrO_2 (ZnO = 0.02 mol) increase. The density of MCT ceramics with various amounts of ZrO_2 is at a maximum density of 3.8 g cm^{-3} (98.4% of theoretical density) at 1300 °C for $x = 0.02$ mol. ZnO–ZrO_2 as additives could effectively promote the densification and lower the sintering temperature of the MCT ceramics. The grain size increased as the amount of ZrO_2 increases, inhomogeneous grain growth can be observed as $x = 0.04$ mol due to liquid phase.

The dielectric constant of ceramics decreases as x increases at 1 MHz. The distortion of oxygen octahedral that result from larger Zr^{4+} ionic radius of 0.072 nm than Ti^{4+} (0.0605 nm) leads to the reduction of mobility of the larger ions, corresponding to the decrease of polarizability and dielectric constant. The temperature coefficient of dielectric constant can be adjusted by dopants ZrO_2. The increase of dielectric loss for MCT ceramics at low frequency suggested that the conductive loss existed. The electronic conduction could be considered as the mechanism of conductive loss that may be related with the second phase $CaZrTi_2O_7$ or the space charge in the pores.

Acknowledgements

The work was supported by National Natural Science foundation of China under Grant No. 11074203, Key Disciplinary of Materials Science and Fluid Machine of Sichuan Province under Grant No. XZD0814-09-1, SZD0412-08 and the talents foundation of Xihua University under Grant No. R0620109.

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