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Microwave dielectric properties of the $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-x(Ca_{0.8}Sm_{0.4/3})TiO_3$ temperature stable ceramics

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ABSTRACT

The ceramic system of $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-x(Ca_{0.8}Sm_{0.4/3})TiO_3$ prepared by mixed oxide route has been found to possess excellent dielectric properties. $(Mg_{0.95}Zn_{0.05})TiO_3$ was combined with $(Ca_{0.8}Sm_{0.4/3})TiO_3$ to obtain a two-phase ceramic system and to achieve a temperature-stable material. As x value varied from 0.10 to 0.14, the temperature coefficient (indexed as TCF or τ_f) ranged from +16.96 ppm/°C to −8.80 ppm/°C. At $x=0.12$, the $0.88(Mg_{0.95}Zn_{0.05})TiO_3$–$0.12(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramic sintered at 1300 °C showed excellent microwave dielectric properties with a relative dielectric constant (ε_r) ~23, a quality factor ($Q\times f$) value ~60,000 GHz (at 7.7 GHz), and a τ_f~4.38 ppm/°C. X-ray diffraction and scanning electron microscopy were also included in our work to help identify and analyze the microstructure of the ceramics.

1. Introduction

Wireless communication systems witnessed unprecedented prosperity in recent decades, leading to an increasing demand for new integrated components suitable for operating in GHz frequencies [1–3]. A high-dielectric constant to reduce the size of the components, a high quality factor to increase the frequency selectivity, and a near zero τ_f to ensure temperature stability are considered to be three of the major characteristics of a good material adopted in resonators, filters or antennas [4,5]. However, as the carrier frequency of the communication systems is extended to GHz frequencies, it is a high quality factor ($Q\times f$) value that becomes the primary factor to consider, while materials with high dielectric constant tend to be less attractive. Meanwhile, a near zero temperature coefficient of frequency (TCF or τ_f) still plays an important role in dielectric materials. Conventionally, combining two compounds with negative and positive τ_f values to form a solid solution or mixed phases is considered as the most feasible way to obtain a zero τ_f [6].

$MgTiO_3$ has the ilmenite type structure, belonging to the trigonal space group $R\bar{3}$. $MgTiO_3$ ceramic shows nice dielectric properties: ε_r~17, $Q\times f$ value ~160,000 GHz (at 7 GHz) and the temperature coefficient at resonant frequency ~−51 ppm/°C [7,8]. With partial replacement of Mg^{2+} by Zn^{2+}, $(Mg_{0.95}Zn_{0.05})TiO_3$ ceramic systems were found to possess excellent dielectric properties of an ε_r value ~16.21, a $Q\times f$ value ~240,000 GHz (at 9 GHz) and a τ_f value ~−60 ppm/°C [9,10]. The $Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic

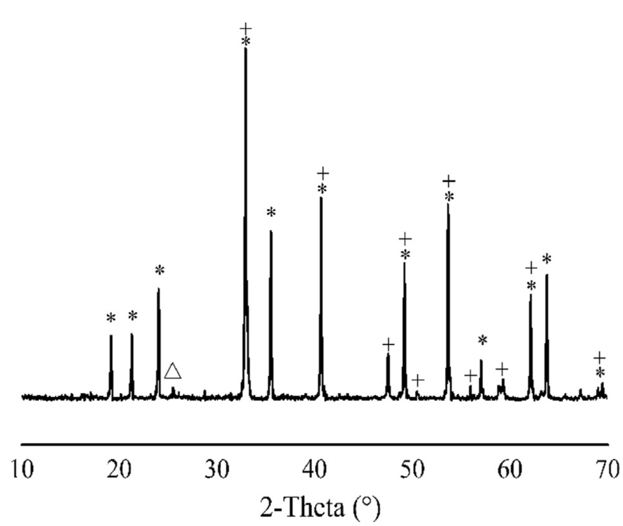

Fig. 1. X-ray diffraction patterns of 0.88 $(Mg_{0.95}Zn_{0.05})TiO_3$–$0.12(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramics sintered at 1300 °C for 4 h (*~$(Mg_{0.95}Zn_{0.05})TiO_3$,+$(Ca_{0.8}Sm_{0.4/3})TiO_3$, ▲~$(Mg_{0.95}Zn_{0.05})Ti_2O_5$).

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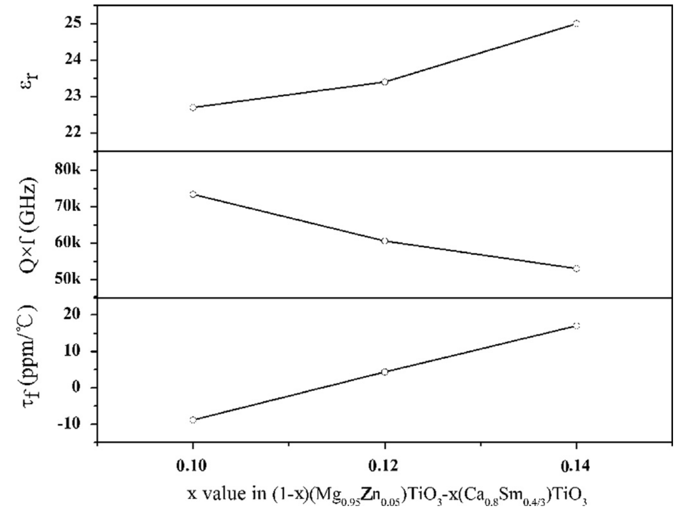

Fig. 2. Dielectric constant, $Q \times f$ and τ_f values of $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-x(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramic system as a function of x value.

has the perovskite structure, and it was reported to possess brilliant dielectric characteristics with a high ε_r of $\sim$119.3, a $Q \times f$ value $\sim$12,000 GHz and a τ_f value $\sim$400 ppm/°C [11]. In order to achieve a near-zero τ_f value, $Ca_{0.8}Sm_{0.4/3}TiO_3$ was added to $(Mg_{0.95}Zn_{0.05})TiO_3$ to form a ceramic system of $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-xCa_{0.8}Sm_{0.4/3}TiO_3$. In our present work, the characteristics of $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-xCa_{0.8}Sm_{0.4/3}TiO_3$ ceramic system were analyzed based upon the X-ray diffraction (XRD) patterns; the microwave dielectric properties were measured with a network analyzer; and the microstructure of the ceramics was observed by scanning electron microscopy (SEM).

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of $CaCO_3$ (> 99%, Guo-Yao Co. Ltd., Shanghai, China), MgO (Guo-Yao Co. Ltd., Shanghai, China), TiO_2 (> 98%, Guo-Yao Co. Ltd., Shanghai, China), ZnO(> 99%, Guo-Yao Co. Ltd., Shanghai, China) and Sm_2O_3(> 99.95%, Guo-Yao Co. Ltd., Shanghai, China) were mixed

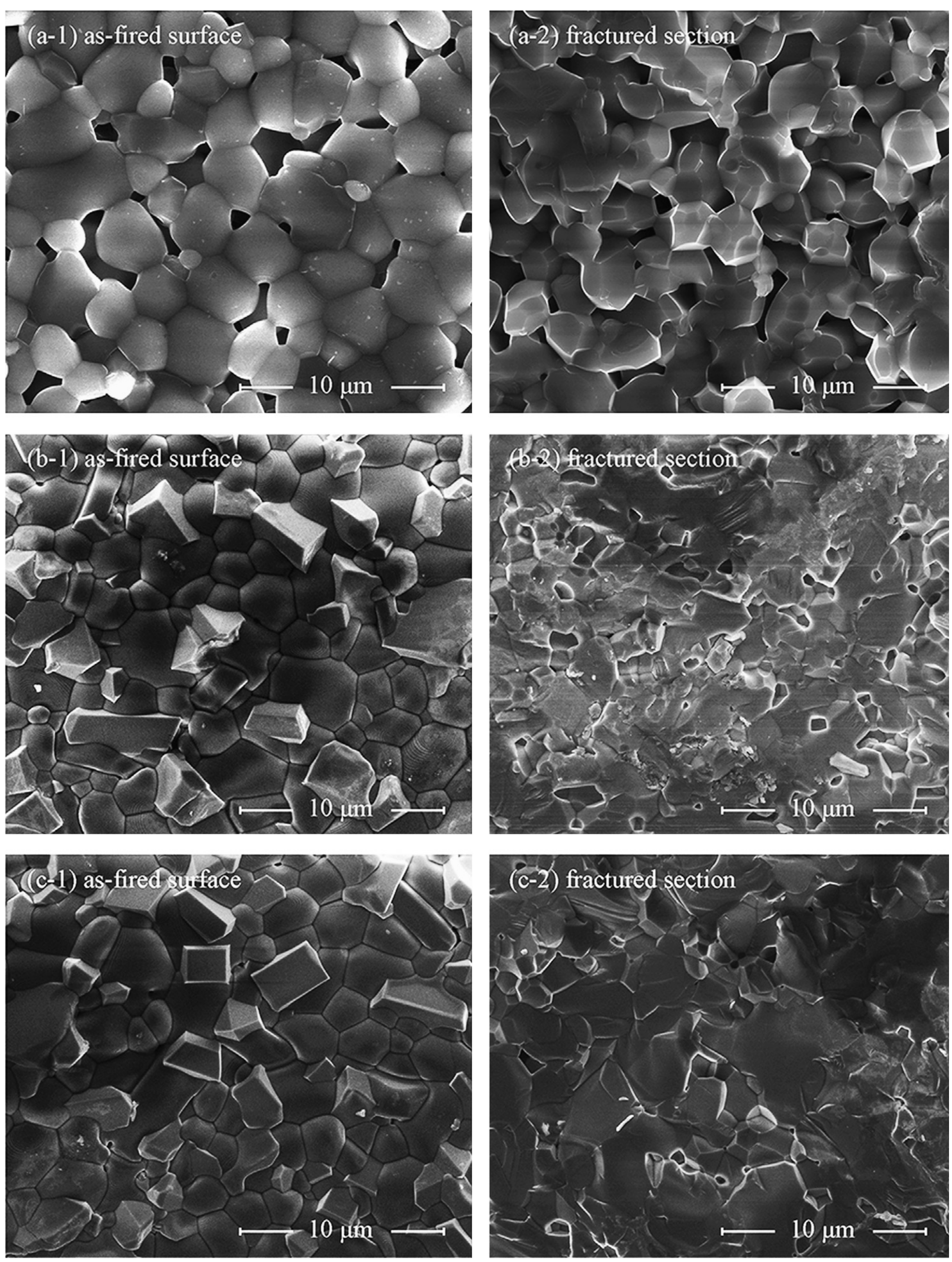

Fig. 3. SEM graphs of $0.88(Mg_{0.95}Zn_{0.05})TiO_3$–$0.12(Ca_{0.8}Sm_{0.4/3})TiO_3$ sintered at (a) 1225 °C, (b) 1275 °C, and (c) 1325 °C for 4 h.

and milled in absolute ethyl alcohol for 4 h by using a planetary mill (Nanjing Machine Factory, Nanjing, China) operating at a running speed of 450 rpm with the Zirconia balls (2 mm in diameter) used as milling media. The dried powders were calcined at 1000 °C for 4 h and then were re-milled in distilled water for 4 h to increase reactivity and better homogeneity. The fine powders were mixed with PVA binder and granulated, and then these powders were pressed into cylinders (10 mm in diameter and 4–6 mm in height) in a steel die under an uniaxial pressure of 100 MPa. Samples were sintered at the temperature range from 1200 °C to 1325 °C for 4 h in air.

The crystalline structures of samples were identified by X-ray diffraction (XRD) with Cu-Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surfacesand fractured sections with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The apparent densities of sintered ceramics were measured by the Archimedes method. Microwave dielectric properties were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of 25–85 °C. The temperature coefficient of resonant frequency (τ_f) value was calculated with the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85-25)} \times 10^6 \ \mathrm{ppm/^\circ C} \qquad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

3. Results and discussions

Fig. 1 illustrates the XRD pattern of 0.88 $(Mg_{0.95}Zn_{0.05})TiO_3$–0.12 $(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramics sintered at 1275 °C for 4 h. The pattern was identified to be a two-phase ceramic system. The system contains a main crystalline phase $(Mg_{0.95}Zn_{0.05})TiO_3$ and a minor phase $(Ca_{0.8}Sm_{0.4/3})TiO_3$. It is known that the structures of $MgTiO_3$ and $CaTiO_3$ are rhombohedral (ICDD-PDF #00-006-0494) and orthorhombic (ICDD-PDF #00-022-0153), respectively. $MgTi_2O_5$ also has the orthorhombic structure (ICDD-PDF #00–035-0792), and it always forms as an intermediate phase in $MgTiO_3$ samples prepared by the mixed oxide route. In our specimen, a second phase of $(Mg_{0.95}Zn_{0.05})Ti_2O_5$ was also detected.

The microwave dielectric properties of $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-x(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramic systems sintered at 1275 °C for 4 h as a function of x value are shown in Fig. 2. According to the mixing rule, the addition of $(Ca_{0.8}Sm_{0.4/3})TiO_3$ into the $(Mg_{0.95}Zn_{0.05})TiO_3$ system would increase the dielectric constant and adjust the temperature coefficient at resonant frequency (TCF) to zero. As x value increased from 0.10 to 0.14, the temperature coefficients of the ceramic systems varied from −8.8 ppm/°C to +17.0 ppm/°C. The specimen 0.88 $(Mg_{0.95}Zn_{0.05})TiO_3$–0.12$(Ca_{0.8}Sm_{0.4/3})TiO_3$ possessing an optimal temperature stability with $\tau_f = 4.4$ ppm/°C, a more detailed investigation of the dielectric properties based on this specimen will be introduced below.

Fig. 3 demonstrates the SEM graphs of 0.88 $(Mg_{0.95}Zn_{0.05})TiO_3$–0.12$(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramics sintered at different temperatures. As the temperature increases, the size of the grain grew, and the pores in the specimen were gradually eliminated. The ceramic sample can be well densified at around 1325 °C.

The dielectric constant, $Q \times f$ value, and apparent density of 0.88 $(Mg_{0.95}Zn_{0.05})TiO_3$–0.12$(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramics as a function of temperature are presented in Fig. 4. The dielectric constant and $Q \times f$ value first increased with the sintering temperature, and both the dielectric constant and apparent density reached peak values at 1300 °C (23.53 and 3.92 g/cm^3, respectively), while the maximum $Q \times f$ value (60,615 GHz) was achieved at 1275 °C. The deterioration of the microwave dielectric properties at a high temperature above 1300 °C may be caused by the abnormal growth of the grains. In addition, the evaporation of zinc could attribute to the decrease of density and $Q \times f$ value[5].

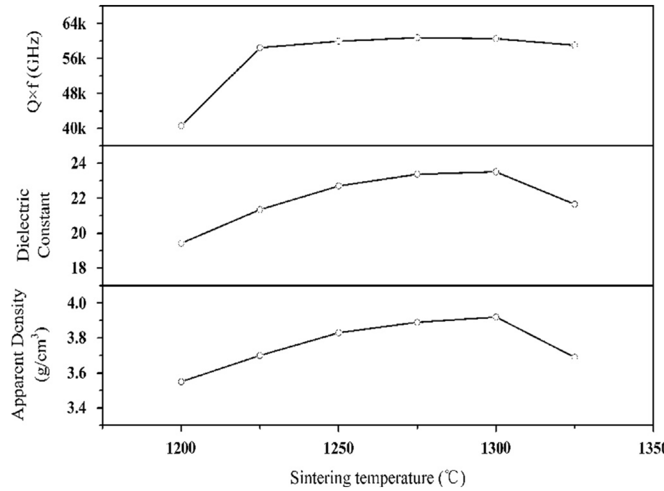

Fig. 4. The variation of $Q \times f$ value, dielectric constant and apparent density of 0.88 $(Mg_{0.95}Zn_{0.05})TiO_3$–0.12$(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramics following sintering temperature.

4. Conclusion

The ceramic system of $(1-x)(Mg_{0.95}Zn_{0.05})TiO_3-x(Ca_{0.8}Sm_{0.4/3})TiO_3$ was found to be a two-phase material with a major phase of $(Mg_{0.95}Zn_{0.05})TiO_3$, a minor phase of $(Ca_{0.8}Sm_{0.4/3})TiO_3$ and a second phase of $(Mg_{0.95}Zn_{0.05})Ti_2O_5$. High performance of microwave dielectric properties with a dielectric constant of 23.53, a $Q \times f \sim 60{,}147$ GHz (at 7.7 GHz) and a τ_f of −4.38 ppm/°C were obtained from 0.88$(Mg_{0.95}Zn_{0.05})TiO_3$–0.12$(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramics sintered at 1300 °C for 4 h. Therefore, the 0.88$(Mg_{0.95}Zn_{0.05})TiO_3$–0.12$(Ca_{0.8}Sm_{0.4/3})TiO_3$ ceramic is a promising microwave dielectric material and can be employed in wireless communication systems.

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