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Temperature stability, low loss and defect relaxation of MgO-TiO_2 microwave dielectric ceramics modified by $Ca_{0.8}Sr_{0.2}TiO_3$

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ABSTRACT

Temperature-stable and low-loss microwave dielectrics based on the MgO-TiO_2 system with nominal formation $Mg_{n+1}Ti_nO_{3n+1}$ (n = 5, MT) were prepared via the conventional solid-state reaction method. $Ca_{0.8}Sr_{0.2}TiO_3$ (CST) was chosen as a τ_f compensator for matrix MT to form the composite ceramics (1-x)$Mg_6Ti_5O_{16}$-$x$$Ca_{0.8}Sr_{0.2}TiO_3$ (0.10 ≤ x ≤ 0.26, MT-CST). The effects of CST additions on the phase composition, defect relaxation behavior, and microwave dielectric properties of MT were investigated. It revealed that undoped MT was basically consisted of $MgTiO_3$ as a major phase and Mg_2TiO_4 as a minor phase, and such two phases co-existed well with CST additions. Interestingly, τ_f could be tuned close to zero (−1.28 ppm/°C) for the MT-CST ceramics at x = 0.22, accompanied with a high $Q\times f$ value ~ 74,200 GHz and a proper ε_r ~ 20.25 (9.90 GHz). These materials possessed a good potential for applications in microwave components and devices. Meanwhile, significant relaxation phenomena were observed in all the MT-CST samples using dielectric spectroscopy and thermally stimulated depolarization current (TSDC) techniques. The oxygen-vacancy-related defects, shown as (Ti'_{Ti})-($V_O^{\bullet\bullet}$) dipoles and $V_O^{\bullet\bullet}$, were the main types of defects in MT-CST, which was responsible for the relaxation behavior; meanwhile, the defect concentrations increased with the increase of CST content, thus resulting in the increase of dielectric loss at low and high frequencies.

1. Introduction

Microwave dielectric ceramic (MWDC) materials play a key role in global wireless communication systems and devices including resonators, filters, Global Positioning System (GPS), *etc*. [1–3]. With the advances of information technology, the Tactile Internet (5th generation wireless communication systems) and Internet of Things require high-performance and low-cost MWDCs for commercial applications at high frequencies [4,5]. Generally, such MWDCs are desired to have a near-zero temperature coefficient of resonant frequency (τ_f) to enable good temperature stability, a low dielectric loss (or a high $Q\times f$ value; Q = 1/tanδ) to improve frequency selectivity and a relatively high dielectric constant ($\varepsilon_r > 15$) to allow device miniaturization [6–8]. However, along with the research and development of MWDCs, it leaves behind many counterparts with large τ_f values [2]. Therefore, many approaches have been considered to design temperature-stable (near-zero τ_f) MWDCs [9–18], including: 1) to form composite ceramics ($MgTiO_3$-$CaTiO_3$, Li_2MoO_4-TiO_2) [9,15] or solid solutions ($NdAlO_3$-$CaTiO_3$) [16] from those materials with opposite signatures of τ_f values; 2) to change the titling of oxygen octahedra in the materials such as $Ba_2Ca_{1-x}Sr_xWO_6$ [18]. Meanwhile, environmentally friendly non-toxic, low-cost and high-performance MWDCs are essentially needed for modern commercial usages.

Among the MgO-TiO_2 system, $MgTiO_3$ and Mg_2TiO_4 have been investigated intensively because of their excellent microwave dielectric properties [2]. The former has ε_r ~ 17, $Q\times f$ ~ 160,000 GHz and τ_f ~ −51 ppm/°C, while ε_r ~ 14, $Q\times f$ ~ 150,000 GHz and τ_f ~ −50 ppm/°C for the latter [9,19]. Recently, Chen et al. reported a new species with nominal formation of $Mg_{n+1}Ti_nO_{3n+1}$ (n ≥ 2) in the MgO-TiO_2 family which had higher $Q\times f$ values (> 300,000 GHz) than $MgTiO_3$ and Mg_2TiO_4 [20,21]. And yet, unlike typical Ruddlesden-Popper (R-P) layered dioxides, such as $Sr_{n+1}Ti_nO_{3n+1}$ and $Ca_{n+1}Ti_nO_{3n+1}$ [22–24], single-phase layered $Mg_{n+1}Ti_nO_{3n+1}$ cannot be obtained even at a low n value (n = 2). It is more likely a multi-phase material consisting of $MgTiO_3$ as a major phase and Mg_2TiO_4 as a minor phase [20,21]. Generally, the MgO-TiO_2 MWDCs besides $MgTiO_3$ and Mg_2TiO_4 basically exhibit negative τ_f ~ −50 ppm/°C [9–11]. $CaTiO_3$ and its derived counterparts possess large positive τ_f, such as a τ_f ~ 991 ppm/°C for $Ca_{0.8}Sr_{0.2}TiO_3$ (CST) together with a high ε_r ~ 181. More importantly, they have been demonstrated to well coexist with MgO-TiO_2 ceramics, which is beneficial for tuning τ_f close to zero [9–14]. As is reported, the ceramics with nominal formation $Mg_6Ti_5O_{16}$ (n = 5) possess a superior

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$Q\times f$ value of 382,500 GHz among the $Mg_{n+1}Ti_nO_{3n+1}$ materials [20,21], which would be a promising candidate for temperature-stable and high-Q MWDCs with the cooperation of τ_f compensators.

Herein, $Mg_6Ti_5O_{16}$ (n = 5, MT) was chosen as the matrix ceramics, and CST was employed as a τ_f compensator for MT [22]. The effects of CST additions on the phase composition, microstructure, microwave dielectric properties and defect relaxation behavior of MT were investigated systematically.

2. Experimental procedure

MgO (99.9%), TiO_2 (99.99%), $CaCO_3$ (99.99%), and $SrCO_3$ (99.99%) powders were used as the raw materials. Firstly, MT and CST were separately synthesized from corresponding oxides and carbonates. For instance, MgO and TiO_2 powders were weighed based on the nominal formation of $Mg_6Ti_5O_{16}$, and then ball-mixed in ethanol for 4 h with zirconia balls. The slurry was dried and calcined at 1100 °C for 4 h. According to the nominal formation of MT-CST (x = 0.10, 0.14, 0.18, 0.22 and 0.26), the as-prepared CST powders were added into MT powders and they were re-milled for 4 h. The composite powders were uniaxially pressed with 5 wt% solution of polyvinyl alcohol into cylinders and pellets with appropriate size. The samples were sintered at 1250–1400 °C for 4 h under a heating rate of 5 °C/min.

The bulk densities were measured by the Archimedes method. The crystal phases of the samples were identified by X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany). The microstructures were observed by scanning electron microscopy (SEM, MERLIN VP Compact, Carl Zeiss, Germany). The microwave dielectric properties were characterized by a network analyzer (HP8720ES, Hewlett-Packard, Santa, Rosa, CA) and a temperature chamber (MC-811T, Espec, Osaka, Japan). The τ_f values were obtained from 25 °C to 80 °C. The pellets were applied with silver electrodes on both sides, and then delivered to low-frequency dielectric spectroscopy and thermally stimulated depolarization current (TSDC) measurements. Temperature-dependent dielectric properties were performed from 100 Hz to 1 MHz using an Alpha-A High performance Frequency Analyzer (Novocontrol, Montabaur, Germany). TSDC was performed using a pA meter (6517B, Keithley, Cleveland, Ohio, USA). The temperature during the dielectric spectroscopy and TSDC characterizations was controlled by a Novocontrol Quatro controller.

3. Results and discussion

The XRD patterns of the MT-CST specimens are depicted in Fig. 1. The MT and CST powders calcined at 1100 °C were shown in Figs. 1a and 1f as comparison, respectively. For the MT calcined powders, the detectable reflections can be identified as $MgTiO_3$ (JCPDS 06-0494) being a major phase and Mg_2TiO_4 (JCPDS 25-1157) being a minor phase, while orthorhombic $CaTiO_3$ structure (JCPDS 70-0584) for the CST calcined powders. With CST additions, all the samples are consisted of multi-phases of $MgTiO_3$, Mg_2TiO_4 and $CaTiO_3$. For a certain composition as shown in Figs. 1b-c (or 1d-e), there seems no apparent change in the intensities of each phase for the samples sintered from 1250 °C to 1400 °C. With increasing CST content from 0.10 to 0.26 as shown in Figs. 1b and 1d (or 1c and 1e), the CST reflections show an increase in the intensities for the samples sintered at the same temperature. The results indicate CST additions can coexist well with matrix MT ceramics.

The backscattered electron (BSE) micrograph in SEM analysis can be a valid method to monitor the grain distributions (with different grey-levels) for multi-phase materials at a microscopic level [25]. Fig. 2 displays the typical BSE images of the surfaces of MT-CST (x = 0.10, 0.18 and 0.26) ceramics sintered at 1300 °C. In each BSE image, obviously, there are two types of grains with distinctive grey-levels distributing uniformly in a dense microstructure of the specimen. Fig. 2d gives the results of EDS analysis for the grains labeled as A, B and C in Fig. 2b. It indicates that the light grains (A) belong to CST, and the dark grains (B and C) are MgO-TiO_2. More specifically, large-grain-size B and small-grain-size C pertain to $MgTiO_3$ and Mg_2TiO_4, respectively. When x is increased from 0.10 to 0.26, it is obvious that the numbers of light grains A (CST) increase apparently, suggesting that the amounts of CST increase in the composite ceramics. The observations are consistent with the results of XRD characterizations.

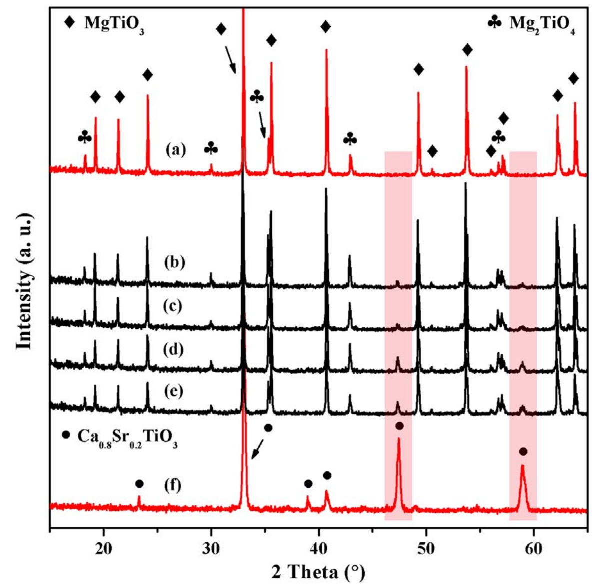

Fig. 1. XRD patterns of MT-CST specimens: (a) MT powder calcined at 1100 °C; (b) x = 0.1, 1250 °C; (c) x = 0.1, 1400 °C; (d) x = 0.26, 1250 °C; (e) x = 0.26, 1400 °C; (f) CST powder calcined at 1100 °C.

The bulk densities and microwave dielectric properties of the MT-CST ceramics are shown in Fig. 3 and Table I. With increasing sintering temperature (Fig. 3a), the buck densities of each composition show a typical increase-then-decrease trend and reach their maximum values at 1300 °C. As shown in Fig. 3b, the dependence of ε_r upon sintering temperature almost shares a similar trend to that of bulk densities, because ε_r is mainly dominated by densification for MWDCs with a certain composition [2,13]. When the sintering temperature is increased, $Q\times f$ values similarly show an increase-then-decrease trend at x = 0.10. And yet, when $x > 0.10$, $Q\times f$ values initially show a decrease, probably because some other factors become much more important than densification, which results in the degradation of $Q\times f$ values.

As x is increased from 0.10 to 0.26 shown in Table 1 and Fig. 3, both ε_r and τ_f show an increase for the well sintered MT-CST ceramics, while $Q\times f$ values decrease. To better obtain the effects of CST additions on the microwave dielectric properties of matrix materials, the undoped MT ceramics were also prepared, which have $\varepsilon_r \sim 17.40$ (10.33 GHz), $Q\times f \sim 221{,}600$ GHz and $\tau_f \sim -45.31$ ppm/°C. From the above XRD and SEM observations, it demonstrates that CST additions coexist well with MT. As is reported, CST possesses a large positive $\tau_f \sim 991$ ppm/°C, a high $\varepsilon_r \sim 181$ and a $Q\times f \sim 8300$ GHz [22]. According to the well-known Lichtenecker empirical rule [26], the relationship between microwave dielectric properties and CST content in the multi-phase MT-CST ceramics varies as expected. It is worth noting that τ_f can be tuned close to zero (−1.28 ppm/°C) for the composite ceramics, accompanied with a high $Q\times f$ value ∼ 74,200 GHz and a proper $\varepsilon_r \sim 20.25$ (9.90 GHz). In consideration of many merits such as environmentally friendly, low cost, easy to process and good microwave dielectric performance, these materials are promising candidates for applications in microwave components and devices.

In general, microwave dielectric loss (or Q) is the least understood among the key parameters (ε_r, $Q\times f$ and τ_f) of MWDCs, and it is